Pentamethyl- and 1,2,4-tri(tert-butyl)cyclopentadienyl containing p-block complexes – differences and similarities

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NMR SPECTRA

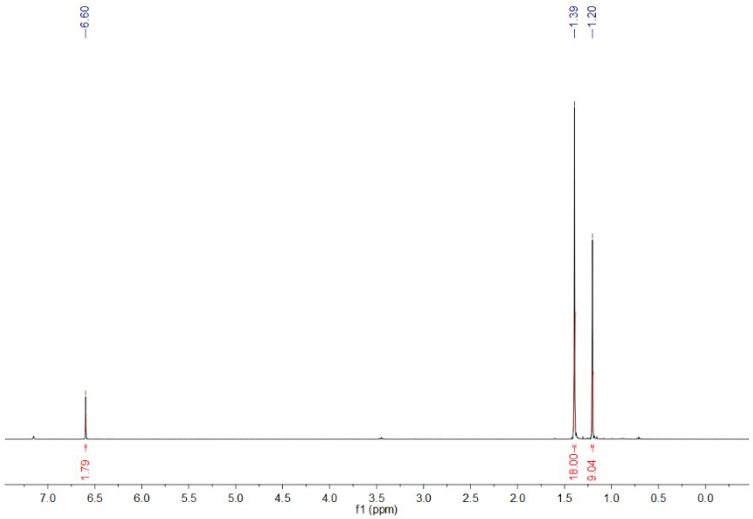

Figure S1.1 ^{1}H NMR of compound **1**

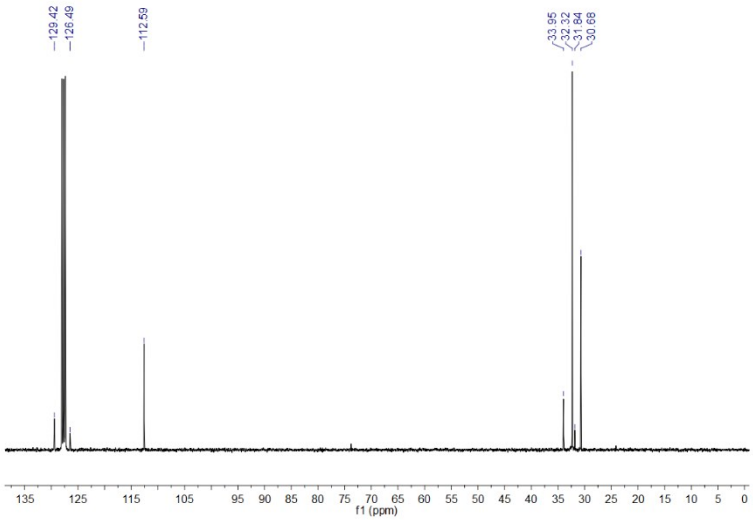

Figure S1.2 ^{13}C NMR of compound **1**

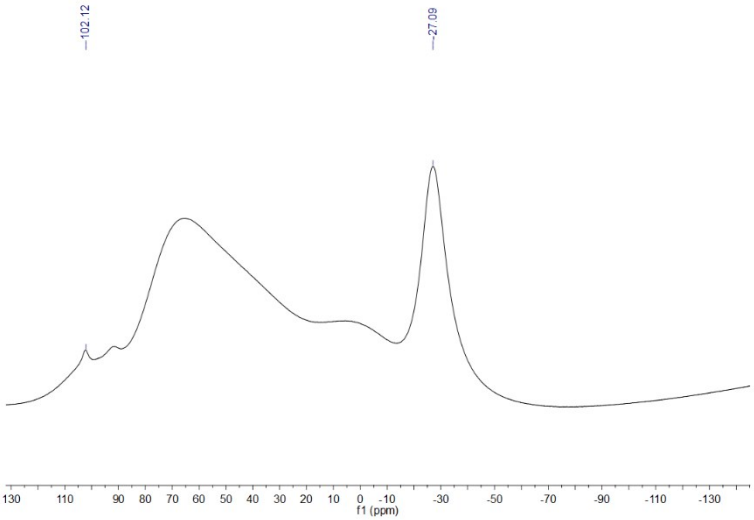

Figure S1.3 ^{27}Al NMR of compound **1** ($AlCl_3$ peak at 102.12 ppm).

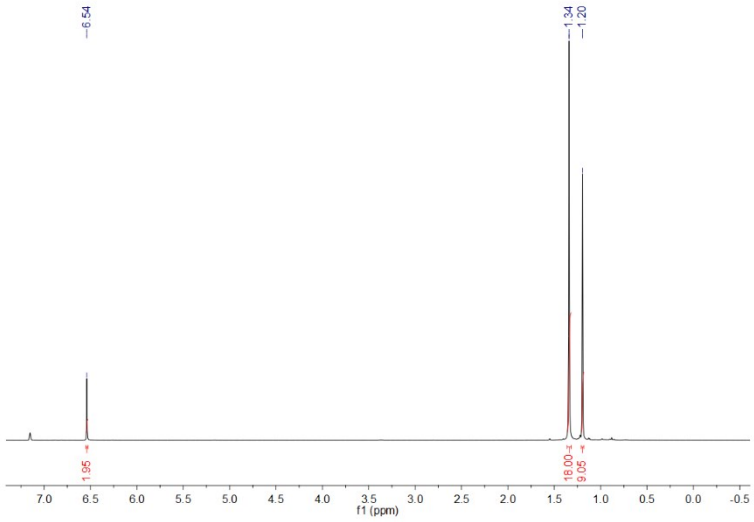

Figure S2.1 ^{1}H NMR of compound **2**

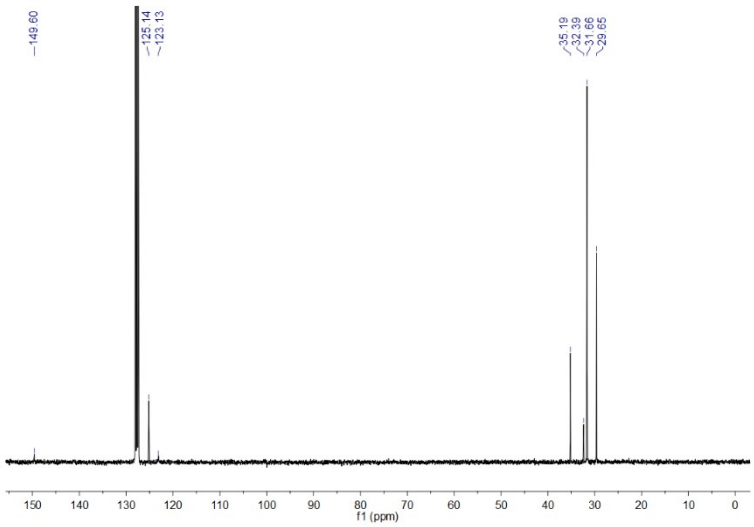

Figure S2.2 ^{13}C NMR of compound **2**

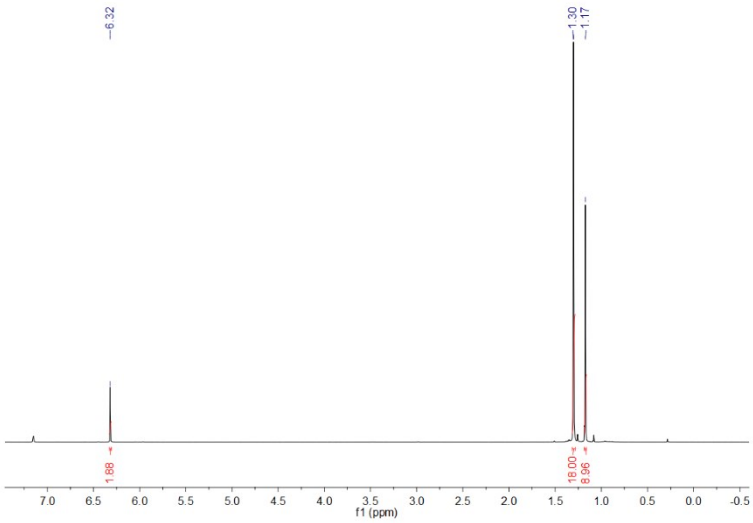

Figure S3.1 ^{1}H NMR of compound **3**

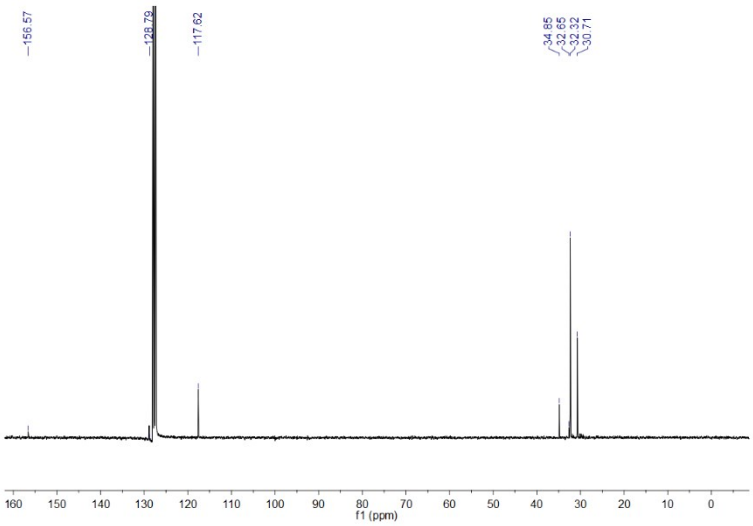

Figure S3.2 ^{13}C NMR of compound **3**

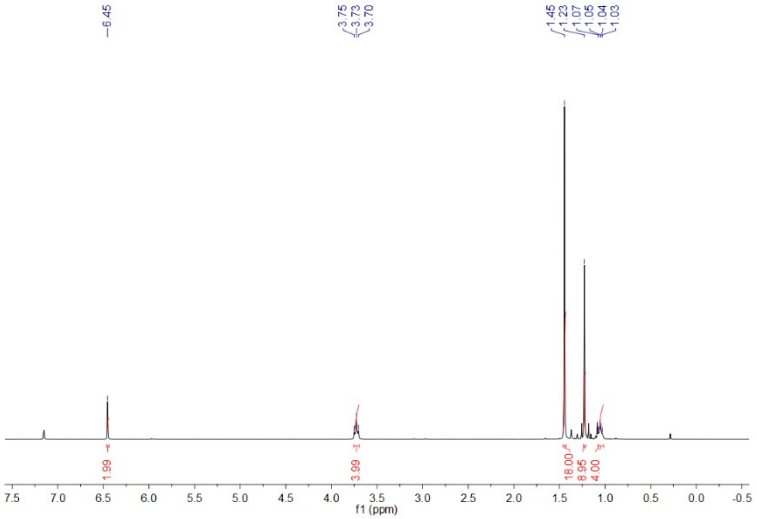

Figure S4.1 ^{1}H NMR of compound **4**

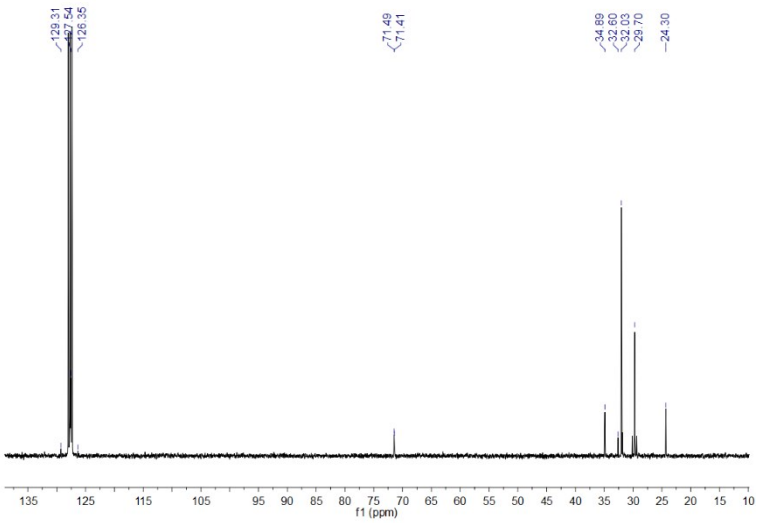

Figure S4.2 ^{13}C NMR of compound **4**

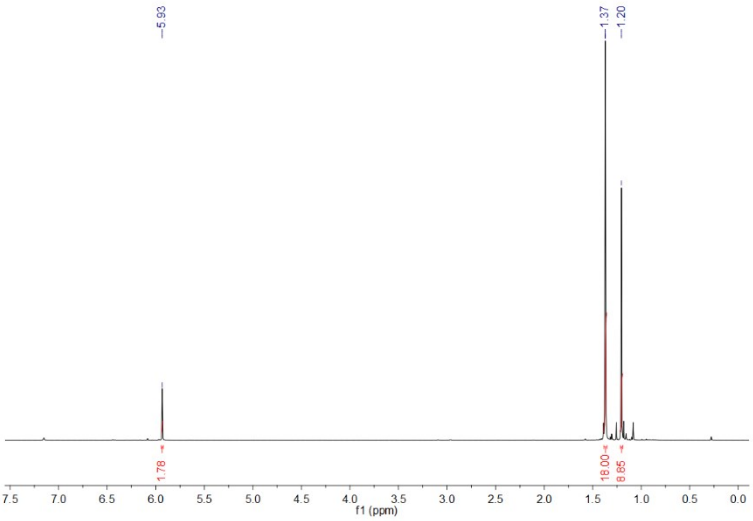

Figure S5.1 ^{1}H NMR of compound **5**

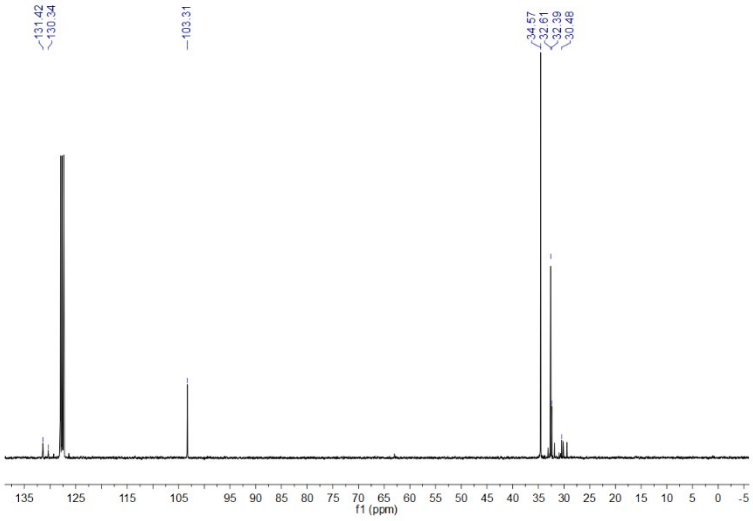

Figure S5.2 ^{13}C NMR of compound **5**

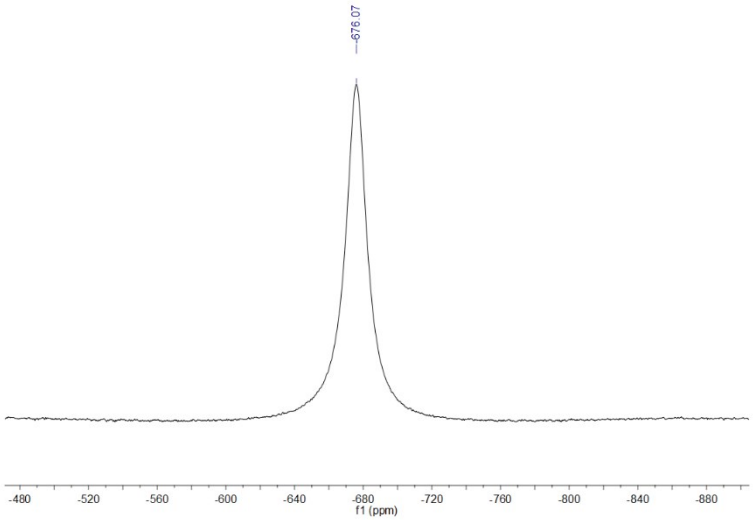

Figure S5.3 ^{71}Ga NMR of compound **5**

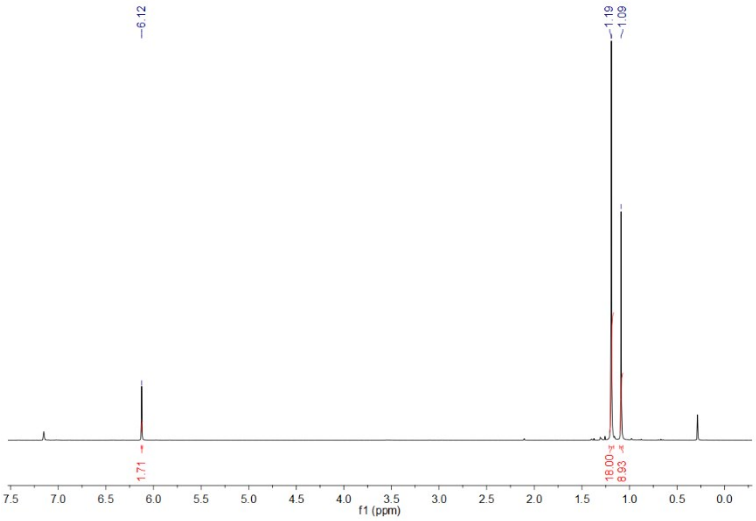

Figure S6.1 ^{1}H NMR of compound **6**

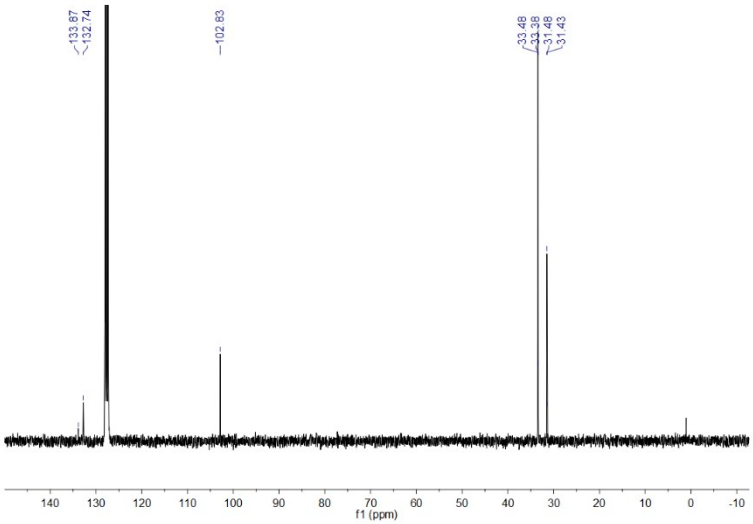

Figure S6.2 ^{13}C NMR of compound **6**

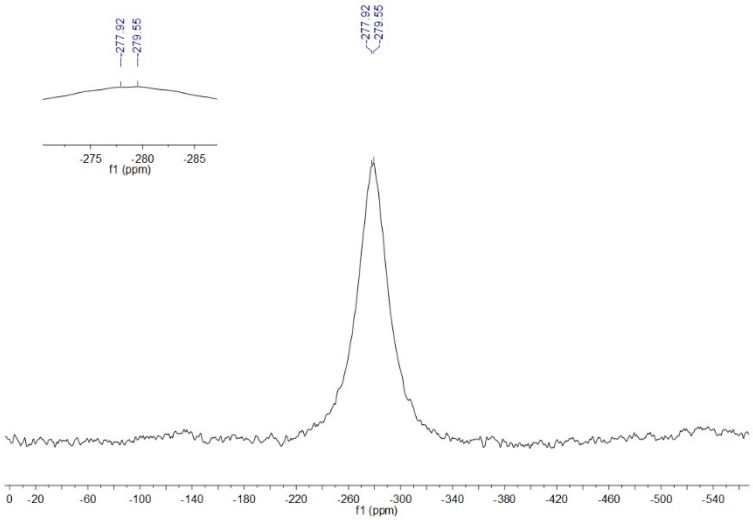

Figure S6.3 ^{71}Ga NMR of compound **6**

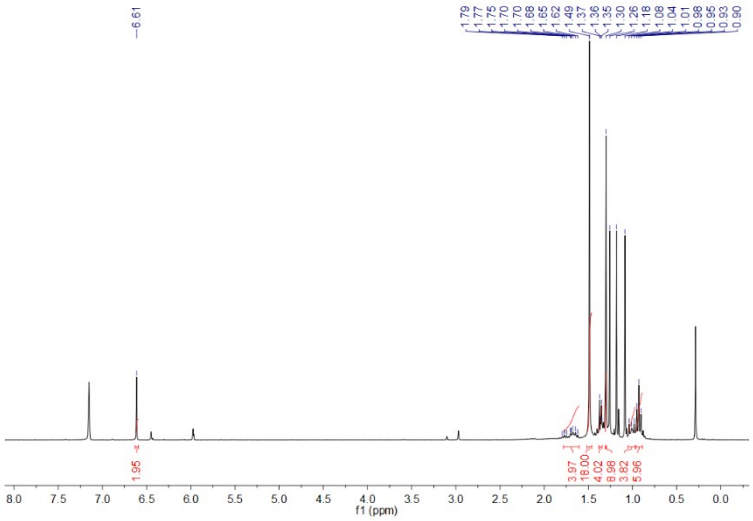

Figure S7.1 ^{1}H NMR of compound **7**

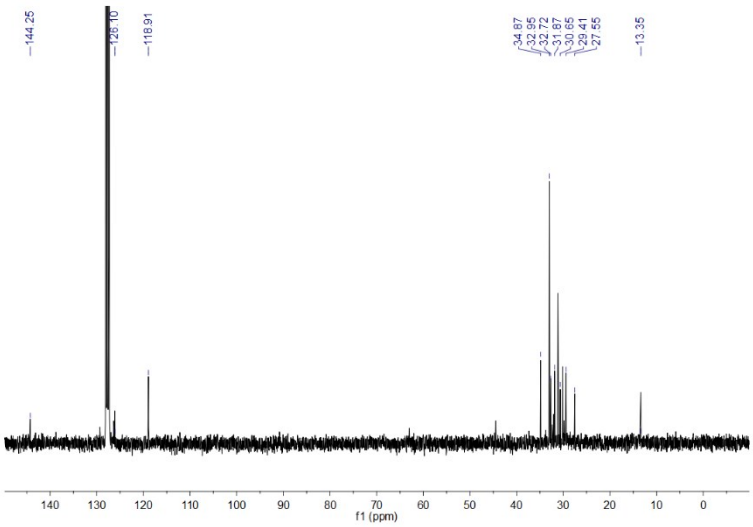

Figure S7.2 ^{13}C NMR of compound **7**

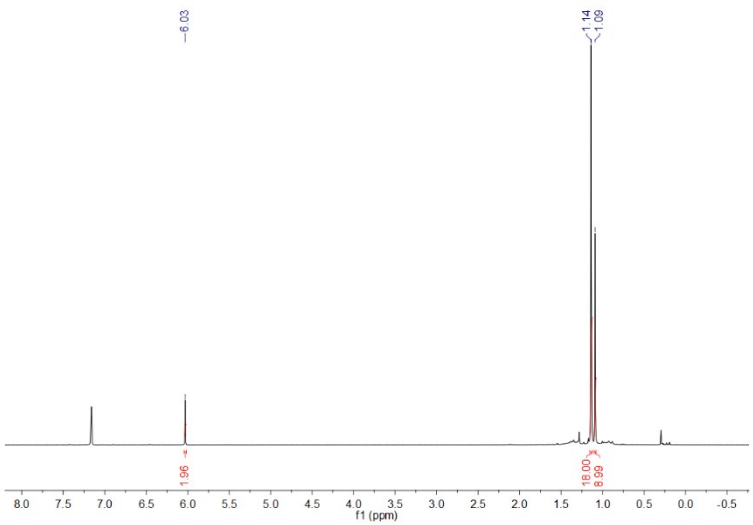

Figure S8.1 ^{1}H NMR of compound **8**

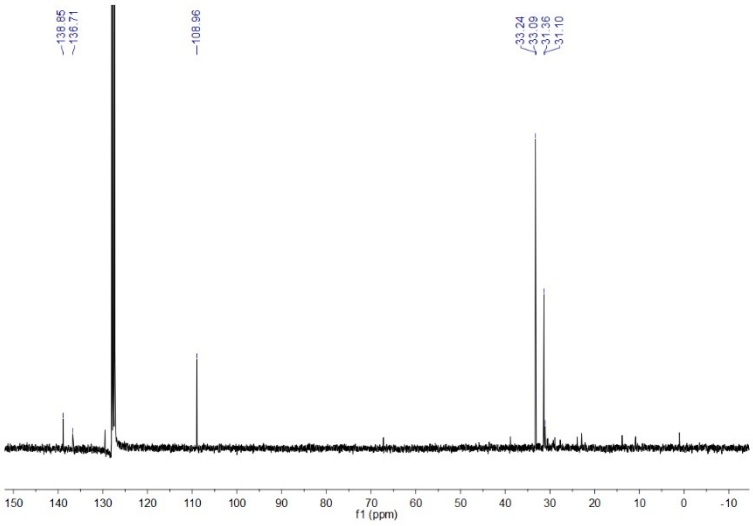

Figure S8.2 ^{13}C NMR of compound **8**

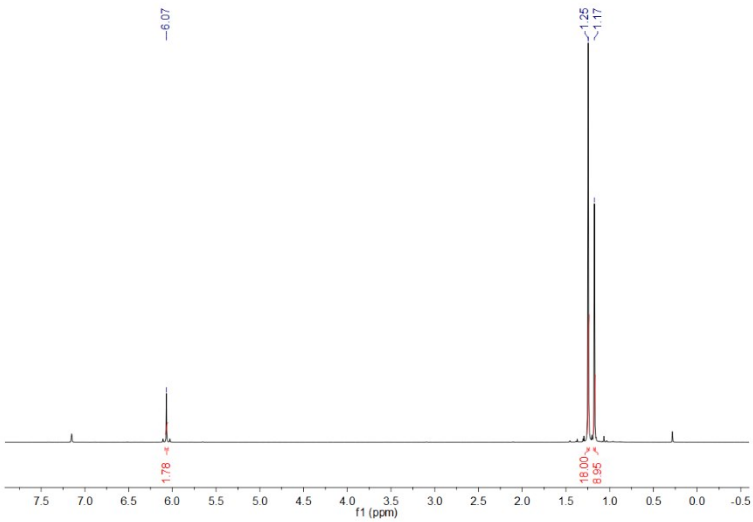

Figure S9.1 ^{1}H NMR of compound **9**

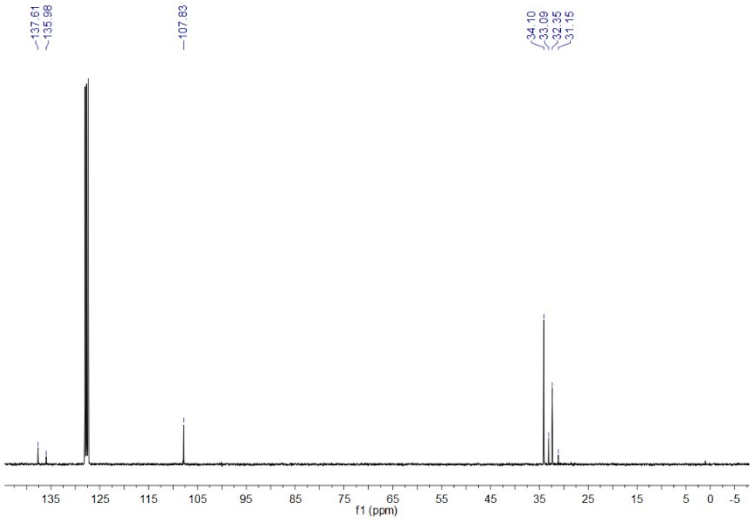

Figure S9.2 ^{13}C NMR of compound **9**

Single Crystal X-ray Structure Determination and Refinement

All crystals were selected under cooling, using a X-Temp2 device.[1] The diffraction data of **2** and **6** – **8** were collected using an Incoatec Mo Microsource, whereas the data **3** and **4** were collected using a Bruker Mo Rotating Anode. All measurements used a Bruker Apex II detector. The data was integrated with SAINT.[2] A multi-scan absorption correction and a was applied using SADABS[3] and TWINABS[4], respectively. The structures were solved by SHELXT[5] and refined on F^2 using SHELXL[6] in the graphical user interface ShelXle.[7] All the crystallographic details are provided in Table S1 and Table S2.

Table S1. Crystal data and structure refinement for compounds **2-4**.

Compound	**2**	**3**	**4**
CCDC	2049785	2049786	2049787
Empirical formula	$C_{34}H_{58}Cl_4Ga_2$	$C_{34}H_{58}Ga_2I_4$	$C_{21}H_{37}Cl_2GaO$
Formula weight	748.04	1113.84	446.12
Temperature (K)	100(2)	100(2)	100(2)
Crystal system	triclinic	monoclinic	orthorhombic
Space group	$P\bar{1}$	$P2_1/n$	$P2_12_12$
a (Å)	11.601(2)	9.984(2)	15.744(2)
b (Å)	12.454(2)	23.624(3)	24.553(4)
c (Å)	13.378 (3)	17.260(2)	11.926(2)
α (deg)	91.96(2)	90	90
β (deg)	101.72(3)	99.89(2)	90
γ (deg)	90.14(2)	90	90
V (Å^3)	1891.3(6)	4010.5(11)	4610.1(12)
Z	2	4	8
μ/mm^{-1}	1.728	4.443	1.432

Crystal size(mm)	0.247×0.118×0.101	0.195×0.136×0.097	0.13×0.12×0.11
Θ max (deg)	27.638	27.570	27.544
Reflections collected	74912	91909	96451
Independent reflections $R_{(int)}$	0.0532	0.0696	0.0493
Data/restraints/parameters	8777 / 0/ 380	9246 / 0 / 379	10598 / 0 /470
Absolute structure parameter	-	-	0.441(9)
$R1^a$ ($I>2\sigma(I)$)	0.0385	0.0292	0.0293
$wR2^b$(all data)	0.1036	0.0617	0.0724
$\Delta\rho_{max}/\Delta\rho_{min}$(e Å^{-3})	1.190/-0.983	1.686/-0.602	0.603/-0.437

$^aR1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. $^bwR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma(F_0^2)]^{1/2}$

Table S2. Crystal data and structure refinement for compounds **6-9**.

Compound	**6**	**7**	**8**	**9**
CCDC	2049788	2049789	2049790	2049791
Empirical formula	$C_{17}H_{29}Ga_2I_3$	$C_{42}H_{76}Br_2In_2$	$C_{17}H_{29}Ge,Cl_3Ge$	$C_{17}H_{29}Br_{0.31}Cl_{2.69}Sn_2$
Formula weight	753.54	970.48	484.93	590.89
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Crystal system	triclinic	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	*Pbca*	*C2/c*
a (Å)	10.845(2)	9.494(2)	17.206(2)	27.222(3)
b (Å)	11.250(3)	10.197(2)	9.715(2)	8.752(2)
c (Å)	11.306(3)	12.616(3)	25.399(3)	19.398(2)
α (deg)	82.69(2)	71.33(2)	90	90
β (deg)	61.37(2)	73.77(2)	90	106.84(2)
γ (deg)	74.03(3)	77.36(3)	90	90
V (Å^3)	1164.0(6)	1099.7(5)	4245.6(11)	4423.3(13)
Z	2	1	8	8
μ/mm^{-1}	6.343	2.891	3.205	3.138
Crystal size(mm)	0.244×0.205×0.098	0.149×0.148×0.05	0.272×0.223×0.169	0.346×0.249×0.138
Θ max (deg)	27.883	27.509	30.583	28.308
Reflections collected	20363	22845	86549	33569

Independent reflections $R_{(int)}$	0.0385	0.0733	0.0294	0.0205
Data/restraints/parameters	5543 / 0 / 208	5060 / 0 / 218/	6504 / 89 / 224	5495 / 6 / 220
$R1^a$ ($I > 2\sigma(I)$)	0.0238	0.0350	0.0271	0.0140
$wR2^b$(all data)	0.0581	0.0748	0.0622	0.0329
$\Delta\rho_{max}/\Delta\rho_{min}$(e Å^{-3})	0.995/-0.961	0.712/-0.525	0.481/-0.523	0.426/-0.214

$^aR1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. $^bwR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma(F_0^2)]^{1/2}$.

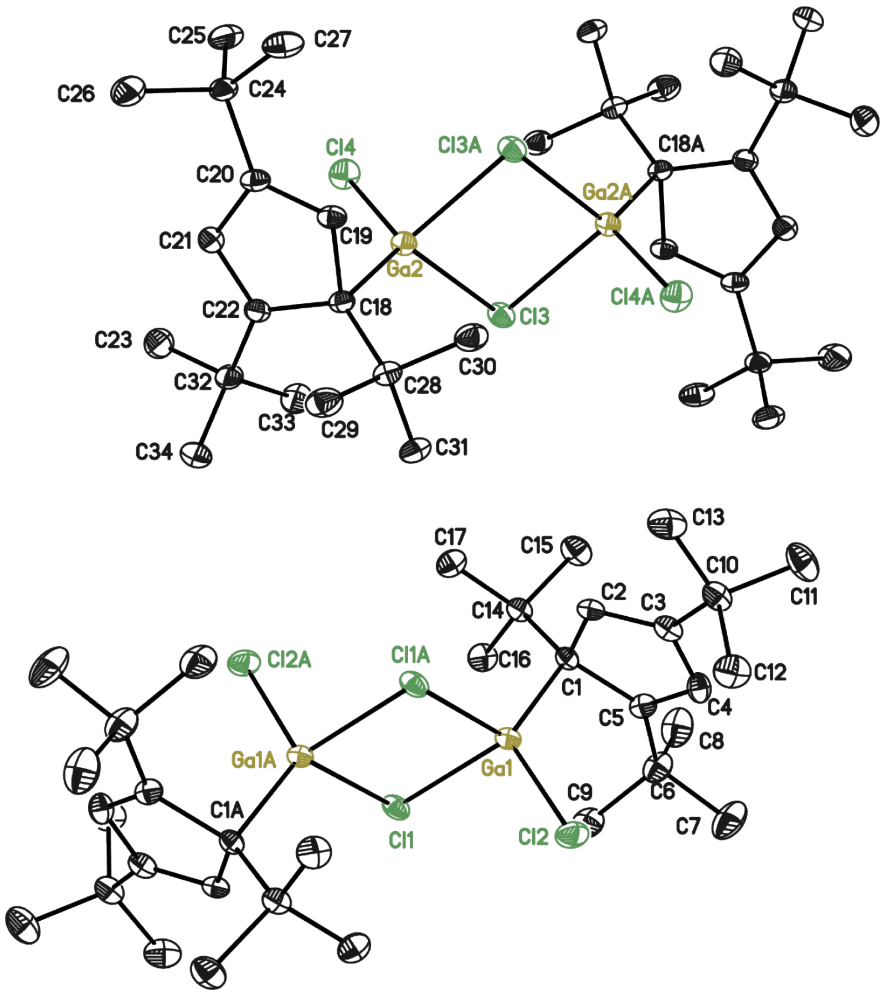

Figure S10. Symmetry completed molecules from the asymmetric unit for compound **2**. Hydrogen atoms are omitted for clarity ADPs are depicted at 50% probability level. Unlabelled atoms, as well as Ga1A and Ga2A, are symmetry generated. The data were collected on a non-merohedral twin with the twin law 1 0 0 0 -1 0 -0.47 0 -1. The fractional contribution of the minor component refined to 0.1204(15).

Table S3. Bond lengths [Å] and angles [°] for **2**.

Ga(1)-C(1)	2.005(2)	C(4)-C(5)	1.368(4)
Ga(1)-Cl(2)	2.1520(8)	C(5)-C(6)	1.531(3)
Ga(1)-Cl(1)	2.3497(10)	C(6)-C(7)	1.538(4)
Ga(1)-Cl(1)#1	2.3817(9)	C(6)-C(8)	1.540(4)
Ga(1)-C(2)	2.495(2)	C(6)-C(9)	1.541(4)
C(1)-C(2)	1.505(3)	C(10)-C(13)	1.526(4)
C(1)-C(5)	1.525(3)	C(10)-C(11)	1.528(4)
C(1)-C(14)	1.566(3)	C(10)-C(12)	1.535(3)
C(2)-C(3)	1.344(3)	C(14)-C(16)	1.527(3)
C(3)-C(4)	1.439(4)	C(14)-C(17)	1.537(4)
C(3)-C(10)	1.519(3)	C(14)-C(15)	1.538(3)

Ga(2)-C(18)	2.003(2)	C(5)-C(1)-Ga(1)	99.87(15)
Ga(2)-Cl(4)	2.1518(8)	C(14)-C(1)-Ga(1)	119.43(16)
Ga(2)-Cl(3)	2.3486(9)	C(3)-C(2)-C(1)	111.3(2)
Ga(2)-Cl(3)#2	2.3753(10)	C(3)-C(2)-Ga(1)	108.07(17)
Ga(2)-C(19)	2.497(2)	C(1)-C(2)-Ga(1)	53.50(11)
C(18)-C(19)	1.509(3)	C(2)-C(3)-C(4)	107.5(2)
C(18)-C(22)	1.525(3)	C(2)-C(3)-C(10)	127.9(2)
C(18)-C(28)	1.564(3)	C(4)-C(3)-C(10)	124.6(2)
C(19)-C(20)	1.350(3)	C(5)-C(4)-C(3)	112.2(2)
C(20)-C(21)	1.451(3)	C(4)-C(5)-C(1)	106.7(2)
C(20)-C(24)	1.517(3)	C(4)-C(5)-C(6)	123.1(2)
C(21)-C(22)	1.362(3)	C(1)-C(5)-C(6)	129.9(2)
C(22)-C(32)	1.537(3)	C(5)-C(6)-C(7)	109.9(2)
C(23)-C(32)	1.544(4)	C(5)-C(6)-C(8)	111.0(2)
C(24)-C(27)	1.523(4)	C(7)-C(6)-C(8)	106.7(2)
C(24)-C(26)	1.533(4)	C(5)-C(6)-C(9)	112.0(2)
C(24)-C(25)	1.533(3)	C(7)-C(6)-C(9)	106.3(2)
C(28)-C(29)	1.528(3)	C(8)-C(6)-C(9)	110.8(2)
C(28)-C(31)	1.530(3)	C(3)-C(10)-C(13)	110.4(2)
C(28)-C(30)	1.541(4)	C(3)-C(10)-C(11)	109.5(2)
C(32)-C(33)	1.532(4)	C(13)-C(10)-C(11)	109.0(2)
C(32)-C(34)	1.538(4)	C(3)-C(10)-C(12)	108.8(2)
		C(13)-C(10)-C(12)	109.4(2)
C(1)-Ga(1)-Cl(2)	122.38(7)	C(11)-C(10)-C(12)	109.7(2)
C(1)-Ga(1)-Cl(1)	119.90(7)	C(16)-C(14)-C(17)	106.0(2)
Cl(2)-Ga(1)-Cl(1)	103.26(3)	C(16)-C(14)-C(15)	109.9(2)
C(1)-Ga(1)-Cl(1)#1	117.33(7)	C(17)-C(14)-C(15)	107.9(2)
Cl(2)-Ga(1)-Cl(1)#1	100.08(3)	C(16)-C(14)-C(1)	115.7(2)
Cl(1)-Ga(1)-Cl(1)#1	86.94(3)	C(17)-C(14)-C(1)	110.2(2)
C(1)-Ga(1)-C(2)	37.11(9)	C(15)-C(14)-C(1)	106.97(19)
Cl(2)-Ga(1)-C(2)	108.19(6)	C(18)-Ga(2)-Cl(4)	123.09(7)
Cl(1)-Ga(1)-C(2)	148.44(6)	C(18)-Ga(2)-Cl(3)	119.28(7)
Cl(1)#1-Ga(1)-C(2)	90.10(6)	Cl(4)-Ga(2)-Cl(3)	102.99(3)
Ga(1)-Cl(1)-Ga(1)#1	93.06(3)	C(18)-Ga(2)-Cl(3)#2	116.88(8)
C(2)-C(1)-C(5)	102.2(2)	Cl(4)-Ga(2)-Cl(3)#2	100.43(3)
C(2)-C(1)-C(14)	113.7(2)	Cl(3)-Ga(2)-Cl(3)#2	87.18(3)
C(5)-C(1)-C(14)	125.4(2)	C(18)-Ga(2)-C(19)	37.17(9)
C(2)-C(1)-Ga(1)	89.39(14)	Cl(4)-Ga(2)-C(19)	109.30(6)

Cl(3)-Ga(2)-C(19)	147.61(6)	C(20)-C(24)-C(27)	110.9(2)
Cl(3)#2-Ga(2)-C(19)	89.54(6)	C(20)-C(24)-C(26)	110.6(2)
Ga(2)-Cl(3)-Ga(2)#2	92.82(3)	C(27)-C(24)-C(26)	109.3(2)
C(19)-C(18)-C(22)	102.48(19)	C(20)-C(24)-C(25)	107.9(2)
C(19)-C(18)-C(28)	113.3(2)	C(27)-C(24)-C(25)	109.1(2)
C(22)-C(18)-C(28)	125.6(2)	C(26)-C(24)-C(25)	109.0(2)
C(19)-C(18)-Ga(2)	89.53(14)	C(29)-C(28)-C(31)	109.8(2)
C(22)-C(18)-Ga(2)	99.10(15)	C(29)-C(28)-C(30)	108.2(2)
C(28)-C(18)-Ga(2)	119.94(16)	C(31)-C(28)-C(30)	106.0(2)
C(20)-C(19)-C(18)	111.0(2)	C(29)-C(28)-C(18)	107.2(2)
C(20)-C(19)-Ga(2)	107.10(17)	C(31)-C(28)-C(18)	115.3(2)
C(18)-C(19)-Ga(2)	53.31(12)	C(30)-C(28)-C(18)	110.3(2)
C(19)-C(20)-C(21)	107.3(2)	C(33)-C(32)-C(22)	112.0(2)
C(19)-C(20)-C(24)	127.1(2)	C(33)-C(32)-C(34)	110.9(2)
C(21)-C(20)-C(24)	125.5(2)	C(22)-C(32)-C(34)	111.0(2)
C(22)-C(21)-C(20)	112.2(2)	C(33)-C(32)-C(23)	106.0(2)
C(21)-C(22)-C(18)	107.0(2)	C(22)-C(32)-C(23)	109.9(2)
C(21)-C(22)-C(32)	123.1(2)	C(34)-C(32)-C(23)	106.7(2
C(18)-C(22)-C(32)	129.7(2)		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1 #2 -x+1,-y,-z+1

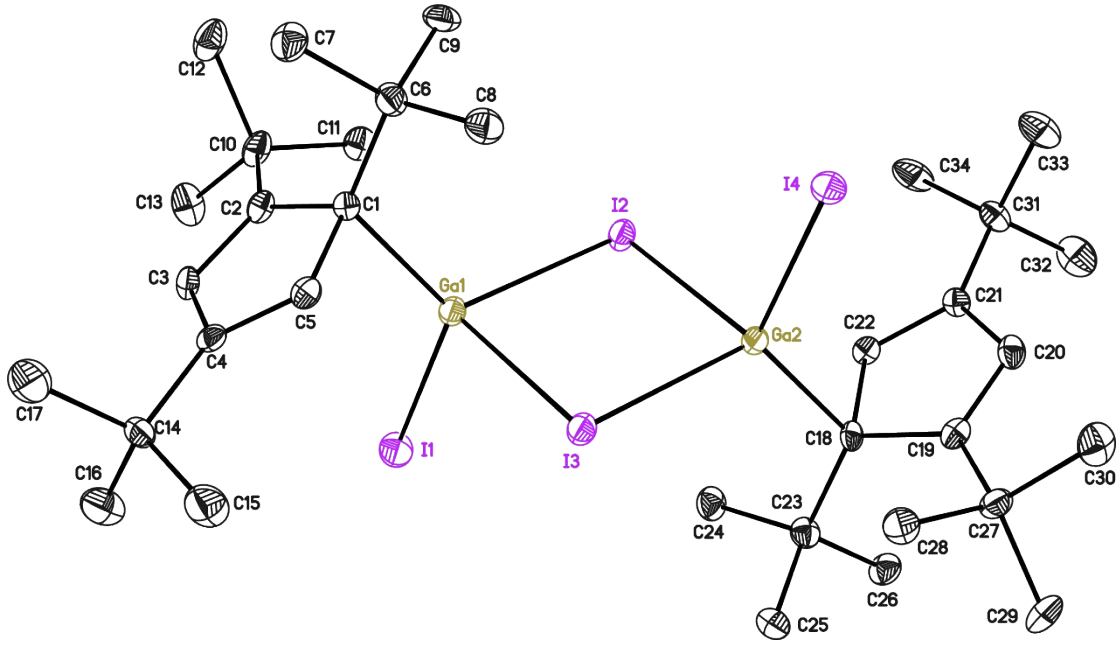

Figure S11. Full asymmetric unit for compound **3**. Hydrogen atoms are omitted for clarity ADPs are depicted at 50% probability level.

Table S4. Bond lengths [Å] and angles [°] for **3**.

I(1)-Ga(1)	2.5197(6)	C(23)-C(24)	1.536(5)
I(2)-Ga(1)	2.7039(6)	C(23)-C(26)	1.540(5)
I(2)-Ga(2)	2.7610(5)	C(27)-C(28)	1.532(5)
I(3)-Ga(2)	2.7103(6)	C(27)-C(30)	1.541(5)
I(3)-Ga(1)	2.7736(5)	C(27)-C(29)	1.546(5)
I(4)-Ga(2)	2.5186(6)	C(31)-C(34)	1.520(5)
Ga(1)-C(1)	2.034(3)	C(31)-C(32)	1.537(5)
Ga(1)-C(5)	2.525(4)	C(31)-C(33)	1.543(5)
Ga(2)-C(18)	2.030(3)		
Ga(2)-C(22)	2.516(3)	Ga(1)-I(2)-Ga(2)	90.081(17)
C(1)-C(5)	1.498(5)	Ga(2)-I(3)-Ga(1)	89.684(16)
C(1)-C(2)	1.526(5)	C(1)-Ga(1)-I(1)	122.50(10)
C(1)-C(6)	1.558(5)	C(1)-Ga(1)-C(5)	36.39(12)
C(2)-C(3)	1.364(5)	I(1)-Ga(1)-C(5)	107.25(8)
C(2)-C(10)	1.528(5)	C(1)-Ga(1)-I(2)	118.24(10)
C(3)-C(4)	1.446(5)	I(1)-Ga(1)-I(2)	104.99(2)
C(4)-C(5)	1.344(5)	C(5)-Ga(1)-I(2)	147.45(8)
C(4)-C(14)	1.511(5)	C(1)-Ga(1)-I(3)	114.15(10)
C(6)-C(9)	1.528(5)	I(1)-Ga(1)-I(3)	101.07(2)
C(6)-C(8)	1.539(5)	C(5)-Ga(1)-I(3)	88.18(8)
C(6)-C(7)	1.540(5)	I(2)-Ga(1)-I(3)	90.042(17)
C(10)-C(11)	1.537(5)	C(18)-Ga(2)-C(22)	36.76(12)
C(10)-C(13)	1.546(5)	C(18)-Ga(2)-I(4)	121.59(10)
C(10)-C(12)	1.548(5)	C(22)-Ga(2)-I(4)	108.22(8)
C(14)-C(15)	1.524(5)	C(18)-Ga(2)-I(3)	119.34(10)
C(14)-C(17)	1.533(5)	C(22)-Ga(2)-I(3)	146.97(8)
C(14)-C(16)	1.534(5)	I(4)-Ga(2)-I(3)	104.68(2)
C(18)-C(22)	1.506(5)	C(18)-Ga(2)-I(2)	113.69(10)
C(18)-C(19)	1.521(5)	C(22)-Ga(2)-I(2)	85.94(8)
C(18)-C(23)	1.568(5)	I(4)-Ga(2)-I(2)	101.78(2)
C(19)-C(20)	1.358(5)	I(3)-Ga(2)-I(2)	90.176(16)
C(19)-C(27)	1.532(5)	C(5)-C(1)-C(2)	102.4(3)
C(20)-C(21)	1.425(5)	C(5)-C(1)-C(6)	113.5(3)
C(21)-C(22)	1.357(5)	C(2)-C(1)-C(6)	124.4(3)
C(21)-C(31)	1.508(5)	C(5)-C(1)-Ga(1)	90.0(2)
C(23)-C(25)	1.533(5)	C(2)-C(1)-Ga(1)	101.6(2)

C(6)-C(1)-Ga(1)	118.6(2)	C(22)-C(18)-Ga(2)	89.5(2)
C(3)-C(2)-C(1)	106.9(3)	C(19)-C(18)-Ga(2)	101.8(2)
C(3)-C(2)-C(10)	122.7(3)	C(23)-C(18)-Ga(2)	118.8(2)
C(1)-C(2)-C(10)	130.2(3)	C(20)-C(19)-C(18)	106.7(3)
C(2)-C(3)-C(4)	111.8(3)	C(20)-C(19)-C(27)	123.2(3)
C(5)-C(4)-C(3)	107.5(3)	C(18)-C(19)-C(27)	129.9(3)
C(5)-C(4)-C(14)	127.9(3)	C(19)-C(20)-C(21)	113.0(3)
C(3)-C(4)-C(14)	124.6(3)	C(22)-C(21)-C(20)	107.2(3)
C(4)-C(5)-C(1)	111.4(3)	C(22)-C(21)-C(31)	127.0(3)
C(4)-C(5)-Ga(1)	110.6(2)	C(20)-C(21)-C(31)	125.8(3)
C(1)-C(5)-Ga(1)	53.65(17)	C(21)-C(22)-C(18)	110.7(3)
C(9)-C(6)-C(8)	105.6(3)	C(21)-C(22)-Ga(2)	109.8(2)
C(9)-C(6)-C(7)	109.1(3)	C(18)-C(22)-Ga(2)	53.78(17)
C(8)-C(6)-C(7)	108.2(3)	C(25)-C(23)-C(24)	105.6(3)
C(9)-C(6)-C(1)	116.6(3)	C(25)-C(23)-C(26)	109.4(3)
C(8)-C(6)-C(1)	110.9(3)	C(24)-C(23)-C(26)	109.1(3)
C(7)-C(6)-C(1)	106.2(3)	C(25)-C(23)-C(18)	115.3(3)
C(2)-C(10)-C(11)	112.6(3)	C(24)-C(23)-C(18)	110.8(3)
C(2)-C(10)-C(13)	109.8(3)	C(26)-C(23)-C(18)	106.5(3)
C(11)-C(10)-C(13)	106.5(3)	C(19)-C(27)-C(28)	112.0(3)
C(2)-C(10)-C(12)	111.2(3)	C(19)-C(27)-C(30)	110.0(3)
C(11)-C(10)-C(12)	110.3(3)	C(28)-C(27)-C(30)	107.6(3)
C(13)-C(10)-C(12)	106.2(3)	C(19)-C(27)-C(29)	111.1(3)
C(4)-C(14)-C(15)	111.4(3)	C(28)-C(27)-C(29)	110.1(3)
C(4)-C(14)-C(17)	108.4(3)	C(30)-C(27)-C(29)	105.7(3)
C(15)-C(14)-C(17)	109.4(3)	C(21)-C(31)-C(34)	111.1(3)
C(4)-C(14)-C(16)	110.3(3)	C(21)-C(31)-C(32)	108.1(3)
C(15)-C(14)-C(16)	108.8(3)	C(34)-C(31)-C(32)	109.9(3)
C(17)-C(14)-C(16)	108.6(3)	C(21)-C(31)-C(33)	109.9(3)
C(22)-C(18)-C(19)	102.3(3)	C(34)-C(31)-C(33)	108.5(3)
C(22)-C(18)-C(23)	112.6(3)	C(32)-C(31)-C(33)	109.3(3)
C(19)-C(18)-C(23)	125.3(3)		

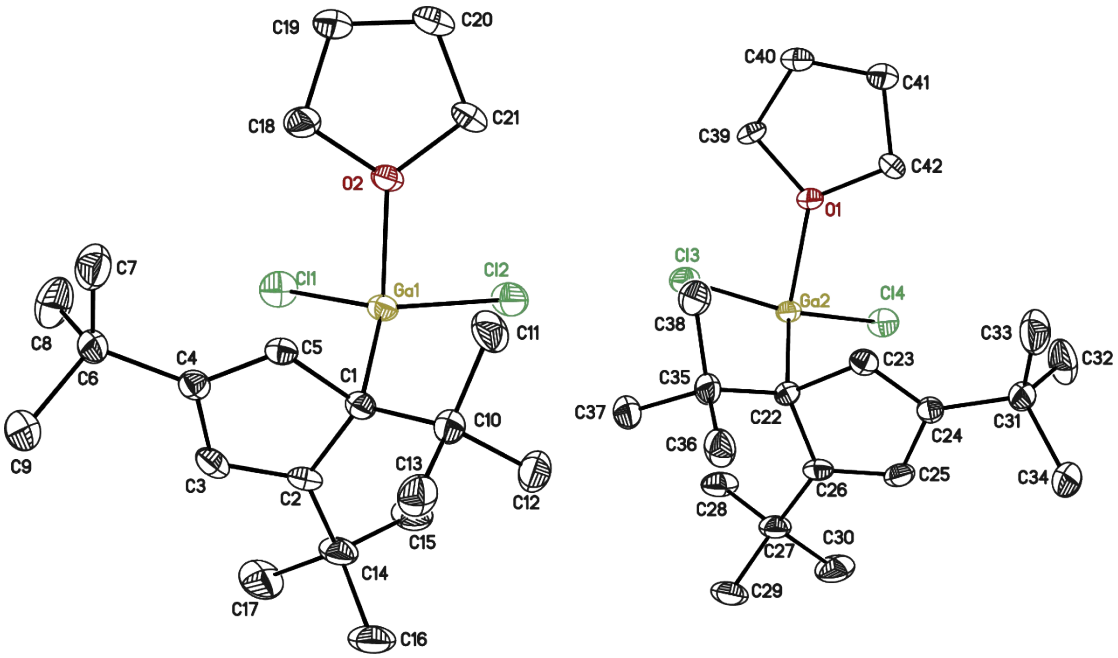

Figure S12. Full asymmetric unit for compound **4**. Hydrogen atoms are omitted for clarity

ADPs are depicted at 50% probability level. The structure was refined as an inversion twin.

Table S5. Bond lengths [Å] and angles [°] for **4**.

Ga(1)-O(2)	2.017(2)	C(23)-C(24)	1.347(4)
Ga(1)-C(1)	2.021(3)	C(24)-C(25)	1.450(5)
Ga(1)-Cl(1)	2.1869(9)	C(24)-C(31)	1.511(4)
Ga(1)-Cl(2)	2.1886(9)	C(25)-C(26)	1.355(5)
C(1)-C(5)	1.508(4)	C(26)-C(27)	1.533(4)
C(1)-C(2)	1.524(4)	C(27)-C(30)	1.531(5)
C(1)-C(10)	1.565(4)	C(27)-C(28)	1.537(5)
C(2)-C(3)	1.352(5)	C(27)-C(29)	1.547(5)
C(2)-C(14)	1.538(4)	C(31)-C(33)	1.527(5)
C(3)-C(4)	1.443(5)	C(31)-C(32)	1.530(5)
C(4)-C(5)	1.346(4)	C(31)-C(34)	1.535(5)
C(4)-C(6)	1.520(4)	C(35)-C(36)	1.533(5)
C(6)-C(7)	1.517(5)	C(35)-C(37)	1.534(5)
C(6)-C(9)	1.531(5)	C(35)-C(38)	1.535(5)
C(6)-C(8)	1.533(5)	C(39)-C(40)	1.497(4)
C(10)-C(11)	1.534(5)	C(40)-C(41)	1.512(5)
C(10)-C(13)	1.538(5)	C(41)-C(42)	1.507(4)
C(10)-C(12)	1.543(5)		
C(14)-C(15)	1.537(5)	O(2)-Ga(1)-C(1)	112.12(10)
C(14)-C(16)	1.538(5)	O(2)-Ga(1)-Cl(1)	99.01(7)
C(14)-C(17)	1.539(5)	C(1)-Ga(1)-Cl(1)	117.50(10)
O(1)-C(42)	1.469(4)	O(2)-Ga(1)-Cl(2)	95.22(7)
O(1)-C(39)	1.469(4)	C(1)-Ga(1)-Cl(2)	121.11(10)
O(1)-Ga(2)	2.021(2)	Cl(1)-Ga(1)-Cl(2)	107.46(4)
C(18)-O(2)	1.468(4)	C(5)-C(1)-C(2)	101.6(3)
C(18)-C(19)	1.511(5)	C(5)-C(1)-C(10)	112.8(3)
C(19)-C(20)	1.509(5)	C(2)-C(1)-C(10)	124.9(3)
C(20)-C(21)	1.507(5)	C(5)-C(1)-Ga(1)	95.04(18)
C(21)-O(2)	1.478(4)	C(2)-C(1)-Ga(1)	103.6(2)
Ga(2)-C(22)	2.021(3)	C(10)-C(1)-Ga(1)	114.3(2)
Ga(2)-Cl(4)	2.1863(9)	C(3)-C(2)-C(1)	107.3(3)
Ga(2)-Cl(3)	2.1891(9)	C(3)-C(2)-C(14)	122.3(3)
C(22)-C(23)	1.501(4)	C(1)-C(2)-C(14)	130.1(3)
C(22)-C(26)	1.527(4)	C(2)-C(3)-C(4)	112.5(3)
C(22)-C(35)	1.571(4)	C(5)-C(4)-C(3)	106.8(3)

C(5)-C(4)-C(6)	129.0(3)	C(23)-C(22)-Ga(2)	95.45(19)
C(3)-C(4)-C(6)	124.1(3)	C(26)-C(22)-Ga(2)	103.7(2)
C(4)-C(5)-C(1)	111.6(3)	C(35)-C(22)-Ga(2)	113.9(2)
C(7)-C(6)-C(4)	111.5(3)	C(24)-C(23)-C(22)	111.7(3)
C(7)-C(6)-C(9)	109.0(3)	C(23)-C(24)-C(25)	106.7(3)
C(4)-C(6)-C(9)	110.2(3)	C(23)-C(24)-C(31)	128.3(3)
C(7)-C(6)-C(8)	108.4(3)	C(25)-C(24)-C(31)	124.8(3)
C(4)-C(6)-C(8)	108.9(3)	C(26)-C(25)-C(24)	112.4(3)
C(9)-C(6)-C(8)	108.7(3)	C(25)-C(26)-C(22)	107.1(3)
C(11)-C(10)-C(13)	108.5(3)	C(25)-C(26)-C(27)	122.3(3)
C(11)-C(10)-C(12)	104.6(3)	C(22)-C(26)-C(27)	130.4(3)
C(13)-C(10)-C(12)	109.0(3)	C(30)-C(27)-C(26)	109.9(3)
C(11)-C(10)-C(1)	110.1(3)	C(30)-C(27)-C(28)	106.2(3)
C(13)-C(10)-C(1)	108.1(3)	C(26)-C(27)-C(28)	112.9(3)
C(12)-C(10)-C(1)	116.4(3)	C(30)-C(27)-C(29)	106.6(3)
C(15)-C(14)-C(16)	109.9(3)	C(26)-C(27)-C(29)	110.9(3)
C(15)-C(14)-C(2)	112.4(3)	C(28)-C(27)-C(29)	110.1(3)
C(16)-C(14)-C(2)	110.8(3)	C(24)-C(31)-C(33)	111.3(3)
C(15)-C(14)-C(17)	106.7(3)	C(24)-C(31)-C(32)	108.6(3)
C(16)-C(14)-C(17)	106.5(3)	C(33)-C(31)-C(32)	108.3(3)
C(2)-C(14)-C(17)	110.3(3)	C(24)-C(31)-C(34)	111.1(3)
C(42)-O(1)-C(39)	109.5(2)	C(33)-C(31)-C(34)	108.6(3)
C(42)-O(1)-Ga(2)	123.24(18)	C(32)-C(31)-C(34)	108.9(3)
C(39)-O(1)-Ga(2)	125.92(18)	C(36)-C(35)-C(37)	108.3(3)
O(2)-C(18)-C(19)	103.7(3)	C(36)-C(35)-C(38)	109.6(3)
C(20)-C(19)-C(18)	103.3(3)	C(37)-C(35)-C(38)	105.1(3)
C(21)-C(20)-C(19)	103.5(3)	C(36)-C(35)-C(22)	108.1(3)
O(2)-C(21)-C(20)	104.5(3)	C(37)-C(35)-C(22)	116.4(3)
C(22)-Ga(2)-O(1)	111.91(10)	C(38)-C(35)-C(22)	109.2(3)
C(22)-Ga(2)-Cl(4)	116.30(9)	C(18)-O(2)-C(21)	110.0(2)
O(1)-Ga(2)-Cl(4)	99.49(7)	C(18)-O(2)-Ga(1)	122.17(19)
C(22)-Ga(2)-Cl(3)	122.35(10)	C(21)-O(2)-Ga(1)	125.8(2)
O(1)-Ga(2)-Cl(3)	94.41(7)	O(1)-C(39)-C(40)	104.8(3)
Cl(4)-Ga(2)-Cl(3)	107.89(4)	C(39)-C(40)-C(41)	103.2(3)
C(23)-C(22)-C(26)	102.0(3)	C(42)-C(41)-C(40)	103.1(3)
C(23)-C(22)-C(35)	112.5(2)	O(1)-C(42)-C(41)	104.5(3)
C(26)-C(22)-C(35)	124.9(3)		

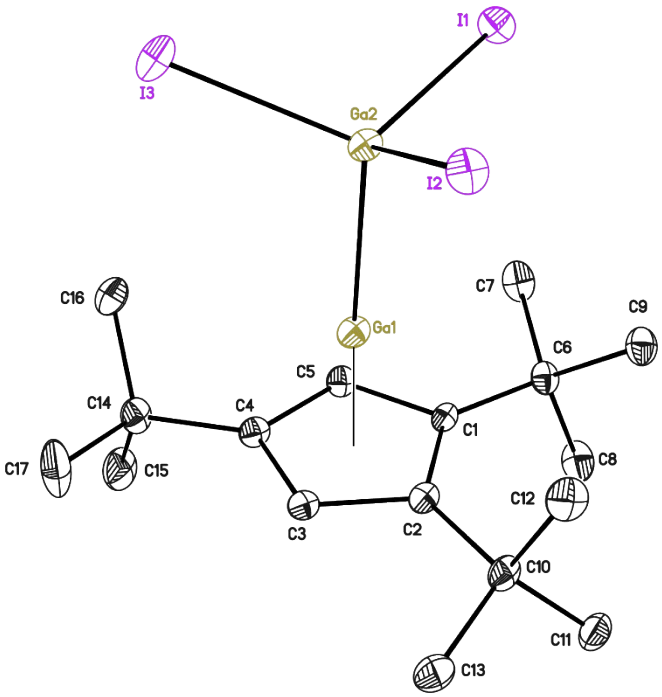

Figure S13. Full asymmetric unit for compound **6**. Hydrogen atoms are omitted for clarity ADPs are depicted at 50% probability level.

Table S6. Bond lengths [Å] and angles [°] for **6**.

I(1)-Ga(2)	2.5391(11)	C(4)-C(14)	1.517(4)
I(2)-Ga(2)	2.5371(8)	C(6)-C(9)	1.529(4)
I(3)-Ga(2)	2.5169(8)	C(6)-C(7)	1.535(5)
Ga(1)-C(3)	2.182(3)	C(6)-C(8)	1.538(5)
Ga(1)-C(2)	2.210(3)	C(10)-C(13)	1.533(5)
Ga(1)-C(4)	2.235(3)	C(10)-C(11)	1.538(5)
Ga(1)-C(5)	2.236(3)	C(10)-C(12)	1.542(5)
Ga(1)-C(1)	2.249(3)	C(14)-C(16)	1.520(5)
Ga(1)-Ga(2)	2.4563(9)	C(14)-C(17)	1.531(5)
C(1)-C(5)	1.444(4)	C(14)-C(15)	1.540(5)
C(1)-C(2)	1.460(5)		
C(1)-C(6)	1.531(4)	C(3)-Ga(1)-C(2)	38.24(11)
C(2)-C(3)	1.439(4)	C(3)-Ga(1)-C(4)	37.51(12)
C(2)-C(10)	1.538(4)	C(2)-Ga(1)-C(4)	63.95(12)
C(3)-C(4)	1.421(4)	C(3)-Ga(1)-C(5)	61.71(12)
C(4)-C(5)	1.418(4)	C(2)-Ga(1)-C(5)	62.91(12)

C(4)-Ga(1)-C(5)	36.99(12)	C(2)-C(3)-Ga(1)	71.93(17)
C(3)-Ga(1)-C(1)	63.18(12)	C(5)-C(4)-C(3)	105.9(3)
C(2)-Ga(1)-C(1)	38.22(12)	C(5)-C(4)-C(14)	125.1(3)
C(4)-Ga(1)-C(1)	63.42(12)	C(3)-C(4)-C(14)	129.0(3)
C(5)-Ga(1)-C(1)	37.56(11)	C(5)-C(4)-Ga(1)	71.52(18)
C(3)-Ga(1)-Ga(2)	156.75(9)	C(3)-C(4)-Ga(1)	69.21(18)
C(2)-Ga(1)-Ga(2)	149.95(8)	C(14)-C(4)-Ga(1)	125.5(2)
C(4)-Ga(1)-Ga(2)	146.03(8)	C(4)-C(5)-C(1)	110.9(3)
C(5)-Ga(1)-Ga(2)	138.10(9)	C(4)-C(5)-Ga(1)	71.49(19)
C(1)-Ga(1)-Ga(2)	138.98(8)	C(1)-C(5)-Ga(1)	71.73(18)
Ga(1)-Ga(2)-I(3)	107.37(3)	C(9)-C(6)-C(1)	113.9(3)
Ga(1)-Ga(2)-I(2)	110.40(3)	C(9)-C(6)-C(7)	106.1(3)
I(3)-Ga(2)-I(2)	113.19(2)	C(1)-C(6)-C(7)	110.4(3)
Ga(1)-Ga(2)-I(1)	104.77(3)	C(9)-C(6)-C(8)	110.4(3)
I(3)-Ga(2)-I(1)	111.31(3)	C(1)-C(6)-C(8)	109.1(3)
I(2)-Ga(2)-I(1)	109.44(3)	C(7)-C(6)-C(8)	106.8(3)
C(5)-C(1)-C(2)	106.0(3)	C(13)-C(10)-C(11)	106.7(3)
C(5)-C(1)-C(6)	120.0(3)	C(13)-C(10)-C(2)	110.2(3)
C(2)-C(1)-C(6)	133.9(3)	C(11)-C(10)-C(2)	112.6(3)
C(5)-C(1)-Ga(1)	70.72(18)	C(13)-C(10)-C(12)	107.1(3)
C(2)-C(1)-Ga(1)	69.44(17)	C(11)-C(10)-C(12)	109.1(3)
C(6)-C(1)-Ga(1)	126.8(2)	C(2)-C(10)-C(12)	110.8(3)
C(3)-C(2)-C(1)	106.4(3)	C(4)-C(14)-C(16)	110.3(3)
C(3)-C(2)-C(10)	120.5(3)	C(4)-C(14)-C(17)	110.7(3)
C(1)-C(2)-C(10)	133.1(3)	C(16)-C(14)-C(17)	109.6(3)
C(3)-C(2)-Ga(1)	69.82(17)	C(4)-C(14)-C(15)	108.0(3)
C(1)-C(2)-Ga(1)	72.34(17)	C(16)-C(14)-C(15)	109.2(3)
C(10)-C(2)-Ga(1)	122.2(2)	C(17)-C(14)-C(15)	109.0(3)
C(4)-C(3)-C(2)	110.8(3)		
C(4)-C(3)-Ga(1)	73.28(19)		

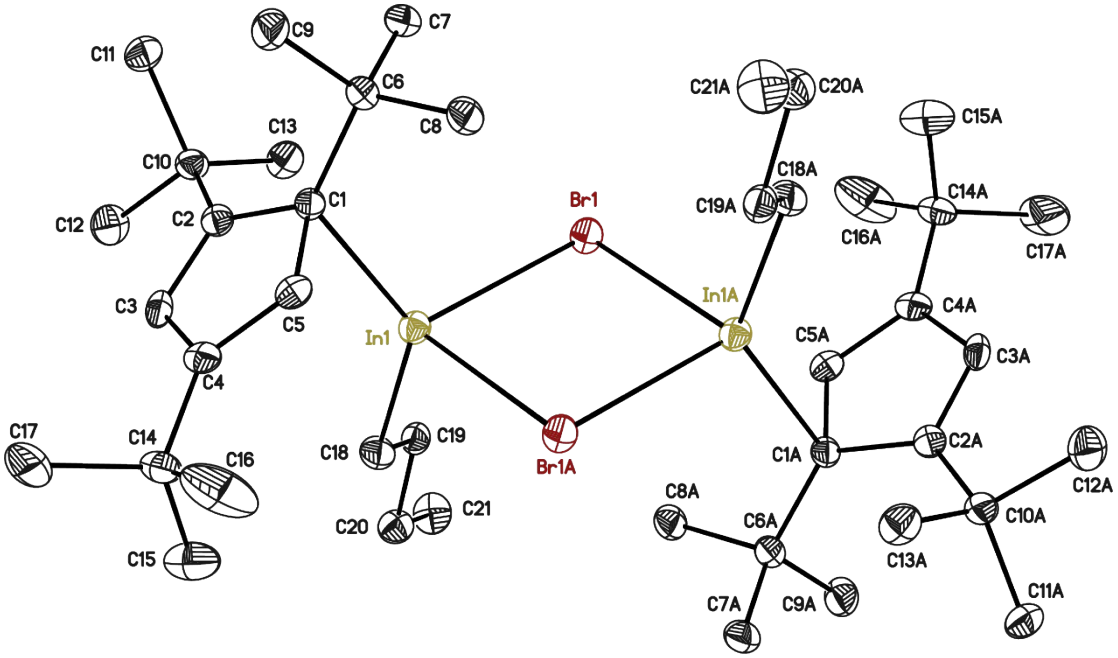

Figure S14. Symmetry completed full asymmetric unit for compound **7**. Hydrogen atoms are omitted for clarity ADPs are depicted at 50% probability level. Atoms labelled with the index "A" are symmetry generated.

Table S7. Bond lengths [Å] and angles [°] for **7**.

In(1)-C(18)	2.158(3)	C(10)-C(13)	1.533(4)
In(1)-C(1)	2.257(3)	C(10)-C(12)	1.541(4)
In(1)-C(5)	2.566(3)	C(10)-C(11)	1.550(4)
In(1)-Br(1)	2.7019(9)	C(14)-C(16)	1.509(5)
In(1)-Br(1)#1	2.7935(8)	C(14)-C(15)	1.517(5)
C(1)-C(5)	1.477(4)	C(14)-C(17)	1.527(5)
C(1)-C(2)	1.499(4)	C(18)-C(19)	1.533(4)
C(1)-C(6)	1.557(4)	C(19)-C(20)	1.516(4)
C(2)-C(3)	1.378(4)	C(20)-C(21)	1.529(5)
C(2)-C(10)	1.527(4)		
C(3)-C(4)	1.436(4)	C(18)-In(1)-C(1)	132.49(12)
C(4)-C(5)	1.376(4)	C(18)-In(1)-C(5)	120.00(11)
C(4)-C(14)	1.513(4)	C(1)-In(1)-C(5)	34.92(10)
C(6)-C(7)	1.523(4)	C(18)-In(1)-Br(1)	107.17(9)
C(6)-C(8)	1.526(4)	C(1)-In(1)-Br(1)	110.23(8)
C(6)-C(9)	1.540(4)	C(5)-In(1)-Br(1)	132.81(7)

C(18)-In(1)-Br(1)#1	100.78(9)	C(7)-C(6)-C(8)	106.2(2)
C(1)-In(1)-Br(1)#1	110.49(8)	C(7)-C(6)-C(9)	109.8(3)
C(5)-In(1)-Br(1)#1	84.76(7)	C(8)-C(6)-C(9)	108.6(3)
Br(1)-In(1)-Br(1)#1	85.14(2)	C(7)-C(6)-C(1)	116.0(3)
In(1)-Br(1)-In(1)#1	94.86(2)	C(8)-C(6)-C(1)	110.1(3)
C(5)-C(1)-C(2)	103.8(2)	C(9)-C(6)-C(1)	106.0(2)
C(5)-C(1)-C(6)	115.7(3)	C(2)-C(10)-C(13)	112.2(3)
C(2)-C(1)-C(6)	129.0(3)	C(2)-C(10)-C(12)	110.0(3)
C(5)-C(1)-In(1)	84.05(18)	C(13)-C(10)-C(12)	106.1(3)
C(2)-C(1)-In(1)	94.56(19)	C(2)-C(10)-C(11)	112.0(3)
C(6)-C(1)-In(1)	119.4(2)	C(13)-C(10)-C(11)	110.9(3)
C(3)-C(2)-C(1)	106.6(3)	C(12)-C(10)-C(11)	105.3(3)
C(3)-C(2)-C(10)	122.5(3)	C(16)-C(14)-C(4)	111.0(3)
C(1)-C(2)-C(10)	130.7(3)	C(16)-C(14)-C(15)	108.3(3)
C(2)-C(3)-C(4)	112.2(3)	C(4)-C(14)-C(15)	108.5(3)
C(5)-C(4)-C(3)	106.2(3)	C(16)-C(14)-C(17)	109.9(3)
C(5)-C(4)-C(14)	127.6(3)	C(4)-C(14)-C(17)	110.0(3)
C(3)-C(4)-C(14)	126.1(3)	C(15)-C(14)-C(17)	109.1(3)
C(4)-C(5)-C(1)	111.0(3)	C(19)-C(18)-In(1)	116.4(2)
C(4)-C(5)-In(1)	100.3(2)	C(20)-C(19)-C(18)	112.4(3)
C(1)-C(5)-In(1)	61.03(16)	C(19)-C(20)-C(21)	113.5(3)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z

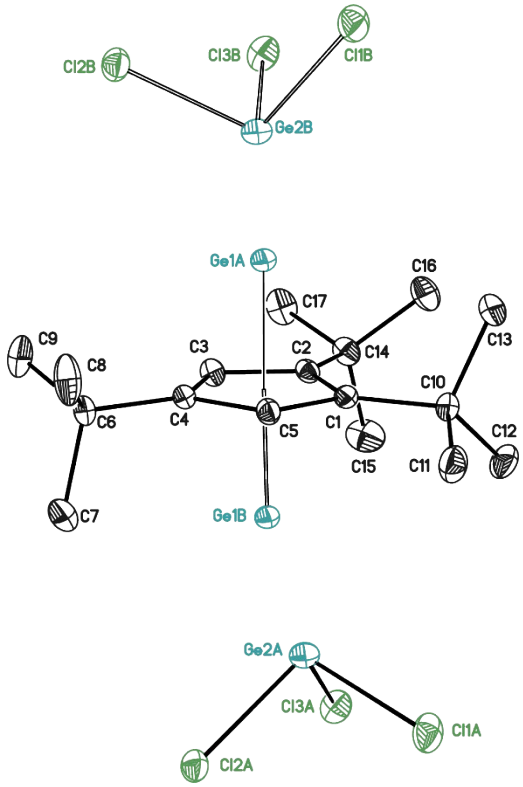

Figure S15. Full asymmetric unit for compound **8**. Hydrogen atoms are omitted for clarity ADPs are depicted at 50% probability level. Atoms labelled with the indexes "A" and "B" belong to mutually exclusive disordered groups. There atoms belonging to the disorder were refined with restraints for the distances and ADPs. The ADPs of the chlorine atoms were fixed to identical values with their nearest neighbour. The occupancy of the minor component refined to 0.0161(4).

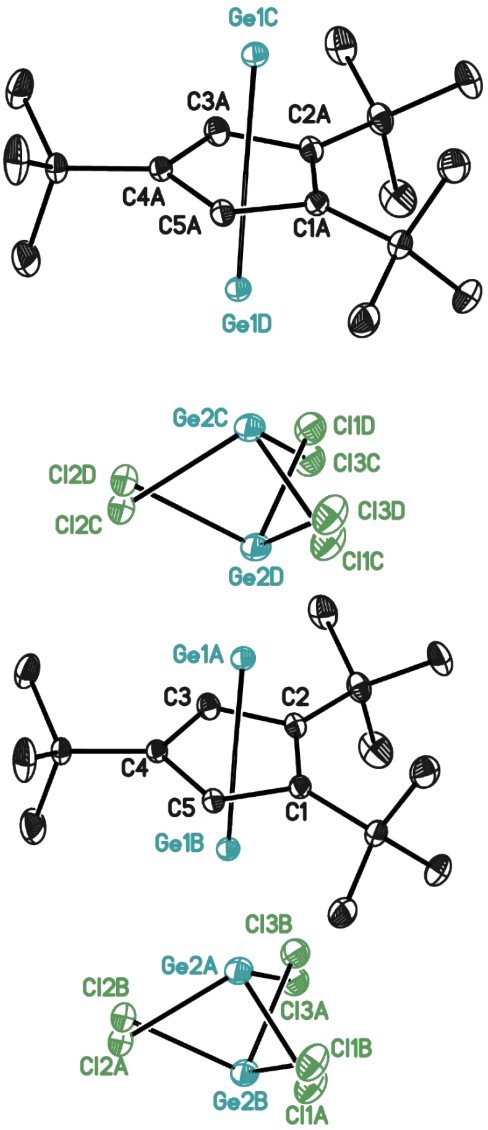

Figure S16. Excerpt of the one-dimensional chain of **8**. Hydrogen atoms are omitted for clarity ADPs are depicted at 50% probability level. Chlorine and germanium atoms labelled A and B belong to the major disorder faction; chlorine and germanium atoms labelled B and D belong to the minor disorder faction.

Table S8. Bond lengths [Å] and angles [°] for **8**.

Ge(1A)-C(3)	2.2529(16)	Ge(1B)-C(4)	2.324(8)
Ge(1A)-C(5)	2.2819(16)	Ge(1B)-C(2)	2.334(8)
Ge(1A)-C(2)	2.2860(16)	Ge(1B)-C(3)	2.348(8)
Ge(1A)-C(4)	2.2869(16)	C(1)-C(5)	1.435(2)
Ge(1A)-C(1)	2.3233(16)	C(1)-C(2)	1.454(2)
Ge(1B)-C(5)	2.238(8)	C(1)-C(10)	1.539(2)
Ge(1B)-C(1)	2.246(8)	C(2)-C(3)	1.439(2)

C(2)-C(14)	1.533(2)	C(4)-Ge(1B)-C(3)	35.30(13)
C(3)-C(4)	1.417(2)	C(2)-Ge(1B)-C(3)	35.80(13)
C(4)-C(5)	1.422(2)	C(5)-C(1)-C(2)	106.35(13)
C(4)-C(6)	1.511(2)	C(5)-C(1)-C(10)	120.58(14)
C(6)-C(9)	1.527(2)	C(2)-C(1)-C(10)	133.01(14)
C(6)-C(8)	1.529(2)	C(5)-C(1)-Ge(1B)	71.0(3)
C(6)-C(7)	1.535(3)	C(2)-C(1)-Ge(1B)	74.8(3)
C(10)-C(13)	1.535(2)	C(10)-C(1)-Ge(1B)	121.0(3)
C(10)-C(12)	1.536(2)	C(5)-C(1)-Ge(1A)	70.28(9)
C(10)-C(11)	1.541(2)	C(2)-C(1)-Ge(1A)	70.22(8)
C(14)-C(16)	1.533(2)	C(10)-C(1)-Ge(1A)	121.98(11)
C(14)-C(17)	1.538(3)	C(3)-C(2)-C(1)	106.41(13)
C(14)-C(15)	1.540(3)	C(3)-C(2)-C(14)	119.59(14)
Ge(2A)-Cl(1A)	2.3076(6)	C(1)-C(2)-C(14)	133.90(14)
Ge(2A)-Cl(3A)	2.3128(5)	C(3)-C(2)-Ge(1A)	70.27(9)
Ge(2A)-Cl(2A)	2.3163(6)	C(1)-C(2)-Ge(1A)	73.02(9)
Ge(2B)-Cl(2B)	2.312(14)	C(14)-C(2)-Ge(1A)	123.88(11)
Ge(2B)-Cl(1B)	2.314(15)	C(3)-C(2)-Ge(1B)	72.7(3)
Ge(2B)-Cl(3B)	2.321(14)	C(1)-C(2)-Ge(1B)	68.2(3)
		C(14)-C(2)-Ge(1B)	121.3(3)
C(3)-Ge(1A)-C(5)	59.92(6)	C(4)-C(3)-C(2)	110.66(14)
C(3)-Ge(1A)-C(2)	36.96(6)	C(4)-C(3)-Ge(1A)	73.12(9)
C(5)-Ge(1A)-C(2)	60.84(6)	C(2)-C(3)-Ge(1A)	72.77(9)
C(3)-Ge(1A)-C(4)	36.37(5)	C(4)-C(3)-Ge(1B)	71.4(3)
C(5)-Ge(1A)-C(4)	36.26(5)	C(2)-C(3)-Ge(1B)	71.5(3)
C(2)-Ge(1A)-C(4)	61.81(6)	C(3)-C(4)-C(5)	105.84(13)
C(3)-Ge(1A)-C(1)	60.80(6)	C(3)-C(4)-C(6)	126.94(14)
C(5)-Ge(1A)-C(1)	36.31(5)	C(5)-C(4)-C(6)	127.15(14)
C(2)-Ge(1A)-C(1)	36.76(6)	C(3)-C(4)-Ge(1A)	70.51(9)
C(4)-Ge(1A)-C(1)	61.31(6)	C(5)-C(4)-Ge(1A)	71.68(9)
C(5)-Ge(1B)-C(1)	37.34(14)	C(6)-C(4)-Ge(1A)	124.67(11)
C(5)-Ge(1B)-C(4)	36.25(14)	C(3)-C(4)-Ge(1B)	73.3(3)
C(1)-Ge(1B)-C(4)	61.9(2)	C(5)-C(4)-Ge(1B)	68.6(3)
C(5)-Ge(1B)-C(2)	60.7(2)	C(6)-C(4)-Ge(1B)	120.6(3)
C(1)-Ge(1B)-C(2)	36.96(14)	C(4)-C(5)-C(1)	110.72(14)
C(4)-Ge(1B)-C(2)	60.6(2)	C(4)-C(5)-Ge(1B)	75.2(3)
C(5)-Ge(1B)-C(3)	59.1(2)	C(1)-C(5)-Ge(1B)	71.6(3)
C(1)-Ge(1B)-C(3)	60.5(2)	C(4)-C(5)-Ge(1A)	72.06(9)

C(1)-C(5)-Ge(1A)	73.42(9)	C(1)-C(10)-C(11)	109.60(13)
C(4)-C(6)-C(9)	111.00(14)	C(2)-C(14)-C(16)	114.40(14)
C(4)-C(6)-C(8)	111.24(13)	C(2)-C(14)-C(17)	110.22(14)
C(9)-C(6)-C(8)	109.15(15)	C(16)-C(14)-C(17)	105.97(15)
C(4)-C(6)-C(7)	106.97(14)	C(2)-C(14)-C(15)	107.67(14)
C(9)-C(6)-C(7)	108.89(16)	C(16)-C(14)-C(15)	111.22(15)
C(8)-C(6)-C(7)	109.53(16)	C(17)-C(14)-C(15)	107.15(16)
		Cl(1A)-Ge(2A)-Cl(3A)	93.71(2)
C(13)-C(10)-C(12)	110.53(15)	Cl(1A)-Ge(2A)-Cl(2A)	95.84(2)
C(13)-C(10)-C(1)	110.81(14)	Cl(3A)-Ge(2A)-Cl(2A)	96.24(2)
C(12)-C(10)-C(1)	112.48(14)	Cl(2B)-Ge(2B)-Cl(1B)	94.8(10)
C(13)-C(10)-C(11)	107.43(15)	Cl(2B)-Ge(2B)-Cl(3B)	95.4(10)
C(12)-C(10)-C(11)	105.75(14)	Cl(1B)-Ge(2B)-Cl(3B)	94.2(10)

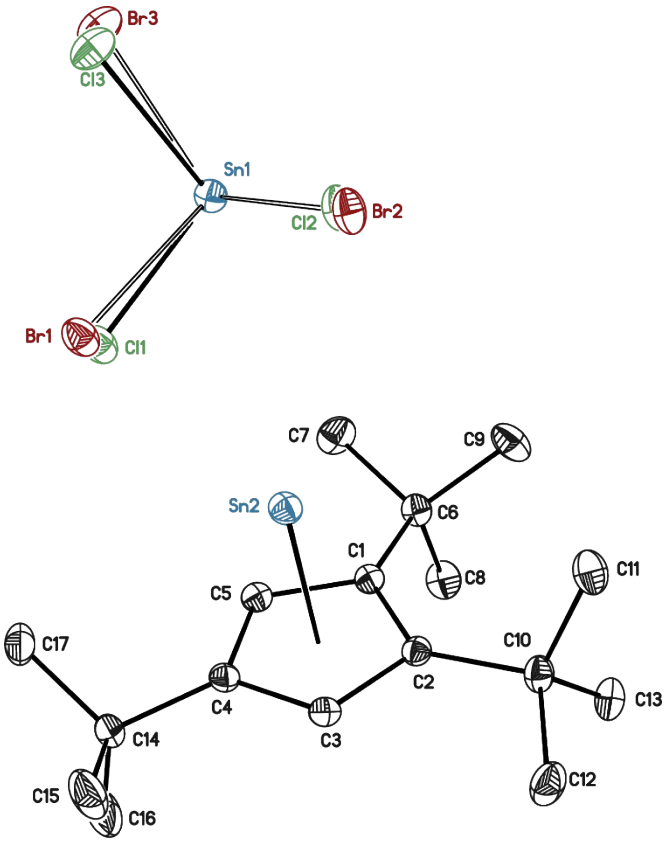

Figure S17. Full asymmetric unit for compound **9**. Hydrogen atoms are omitted for clarity ADPs are depicted at 50% probability level. Each chlorine atom is disordered with a small amount of bromine, the bromine from the impurities $SnBr_2$ or $SnBr_3Cl$ in the starting material $SnCl_2$. The Sn-Cl and the Sn-Br distances were refined with distance restraint, while the ADPs were fixed to equal values. The occupancies of the bromine atoms refined to 0.1014(14),

0.1634(14) and 0.0445(14).

Table S9. Bond lengths [Å] and angles [°] for **9**.

Sn(1)-Cl(3)	2.4747(12)	C(4)-Sn(2)-C(5)	33.35(4)
Sn(1)-Cl(1)	2.5200(19)	C(4)-Sn(2)-C(3)	33.12(4)
Sn(1)-Cl(2)	2.554(5)	C(5)-Sn(2)-C(3)	54.00(4)
Sn(1)-Br(3)	2.599(11)	C(4)-Sn(2)-C(1)	55.50(5)
Sn(1)-Br(1)	2.627(7)	C(5)-Sn(2)-C(1)	32.90(4)
Sn(1)-Br(2)	2.653(10)	C(3)-Sn(2)-C(1)	54.24(5)
Sn(2)-C(4)	2.4759(14)	C(4)-Sn(2)-C(2)	55.21(4)
Sn(2)-C(5)	2.4793(14)	C(5)-Sn(2)-C(2)	54.29(4)
Sn(2)-C(3)	2.5080(14)	C(3)-Sn(2)-C(2)	32.56(4)
Sn(2)-C(1)	2.5606(14)	C(1)-Sn(2)-C(2)	32.91(4)
Sn(2)-C(2)	2.5856(14)	C(5)-C(1)-C(2)	106.46(12)
C(1)-C(5)	1.4293(19)	C(5)-C(1)-C(6)	119.47(12)
C(1)-C(2)	1.4580(19)	C(2)-C(1)-C(6)	133.57(12)
C(1)-C(6)	1.5395(19)	C(5)-C(1)-Sn(2)	70.42(8)
C(2)-C(3)	1.4300(19)	C(2)-C(1)-Sn(2)	74.49(8)
C(2)-C(10)	1.5457(19)	C(6)-C(1)-Sn(2)	125.64(9)
C(3)-C(4)	1.4207(19)	C(3)-C(2)-C(1)	106.30(12)
C(4)-C(5)	1.4218(19)	C(3)-C(2)-C(10)	120.49(12)
C(4)-C(14)	1.5191(19)	C(1)-C(2)-C(10)	133.20(12)
C(6)-C(9)	1.538(2)	C(3)-C(2)-Sn(2)	70.73(8)
C(6)-C(7)	1.539(2)	C(1)-C(2)-Sn(2)	72.60(7)
C(6)-C(8)	1.539(2)	C(10)-C(2)-Sn(2)	121.54(9)
C(10)-C(13)	1.540(2)	C(4)-C(3)-C(2)	110.85(12)
C(10)-C(12)	1.540(2)	C(4)-C(3)-Sn(2)	72.20(8)
C(10)-C(11)	1.542(2)	C(2)-C(3)-Sn(2)	76.70(8)
C(14)-C(17)	1.527(2)	C(3)-C(4)-C(5)	105.63(12)
C(14)-C(15)	1.528(2)	C(3)-C(4)-C(14)	127.25(12)
C(14)-C(16)	1.538(2)	C(5)-C(4)-C(14)	126.57(12)
		C(3)-C(4)-Sn(2)	74.68(8)
Cl(3)-Sn(1)-Cl(1)	91.48(4)	C(5)-C(4)-Sn(2)	73.46(8)
Cl(3)-Sn(1)-Cl(2)	93.44(16)	C(14)-C(4)-Sn(2)	123.47(9)
Cl(1)-Sn(1)-Cl(2)	85.83(15)	C(4)-C(5)-C(1)	110.75(12)
Br(3)-Sn(1)-Br(1)	91.9(3)	C(4)-C(5)-Sn(2)	73.19(8)
Br(3)-Sn(1)-Br(2)	95.4(5)	C(1)-C(5)-Sn(2)	76.68(8)
Br(1)-Sn(1)-Br(2)	88.0(4)	C(9)-C(6)-C(7)	105.57(13)

C(9)-C(6)-C(8)	110.64(12)	C(12)-C(10)-C(2)	110.08(12)
C(7)-C(6)-C(8)	106.84(12)	C(11)-C(10)-C(2)	111.36(12)
C(9)-C(6)-C(1)	115.34(12)	C(4)-C(14)-C(17)	111.12(12)
C(7)-C(6)-C(1)	110.24(12)	C(4)-C(14)-C(15)	111.04(12)
C(8)-C(6)-C(1)	107.90(12)	C(17)-C(14)-C(15)	109.26(13)
C(13)-C(10)-C(12)	105.73(12)	C(4)-C(14)-C(16)	107.41(12)
C(13)-C(10)-C(11)	110.49(12)	C(17)-C(14)-C(16)	108.11(13)
C(12)-C(10)-C(11)	107.03(12)	C(15)-C(14)-C(16)	109.84(14)
C(13)-C(10)-C(2)	111.89(12)		

MASS SPECTRA

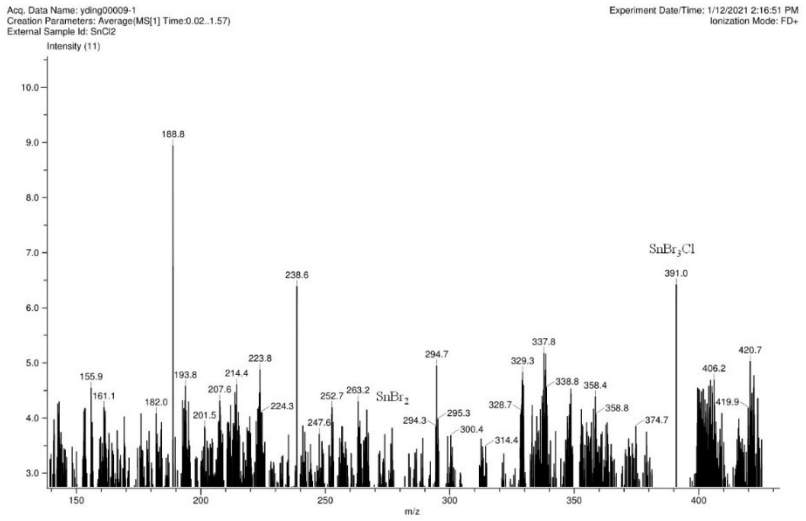

Figure S18. Mass spectra of the starting material $SnCl_2$.

References

(1). a) D. Stalke, Chem. *Soc. Rev*. 1998, ***27***, 171-178; b) T. Kottke, D. Stalke, *J. Appl. Crystallogr*. 1993, ***26***, 615-619.

(2). T. Schulz, K. Meindl, D. Leusser, D. Stern, J. Graf, C. Michaelsen, M. Ruf, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr.* 2009, **42**, 885-891.

(3). Bruker AXS Inc., in *Bruker Apex CCD, SAINT v8.30C* (Ed.: Bruker AXS Inst. Inc.), WI, USA, Madison, 2013.

(4). L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, *J. Appl. Crystallogr*. 2015, ***48***, 3-10.

(5). M. Sevvana, M. Ruf, I. Usón, G. M. Sheldrick, R. Herbst-Irmer, *Acta Crystallogr.*, 2019, ***D75***, 1040-1050.

(6). G. M. Sheldrick, *Acta Crystallogr.* 2015, ***C71***, 3-8.

(7). C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* 2011, ***44***, 1281-1284.