Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Geminal C–Cl and Si–Cl Bond Activation of Chloromethanes and Chlorosilanes by Gallanediyl LGa

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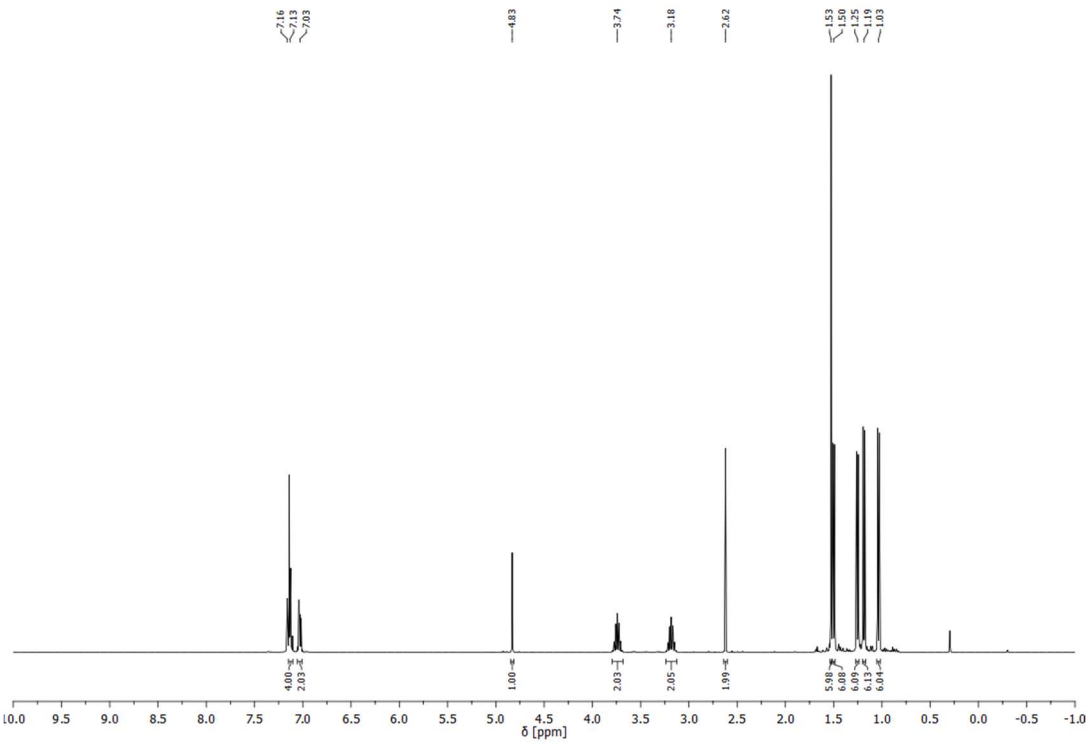


Figure S1. ^{1}H NMR spectrum (400.1 MHz, C_6D_6) of L(Cl)GaCH$_2$Cl (**1**).

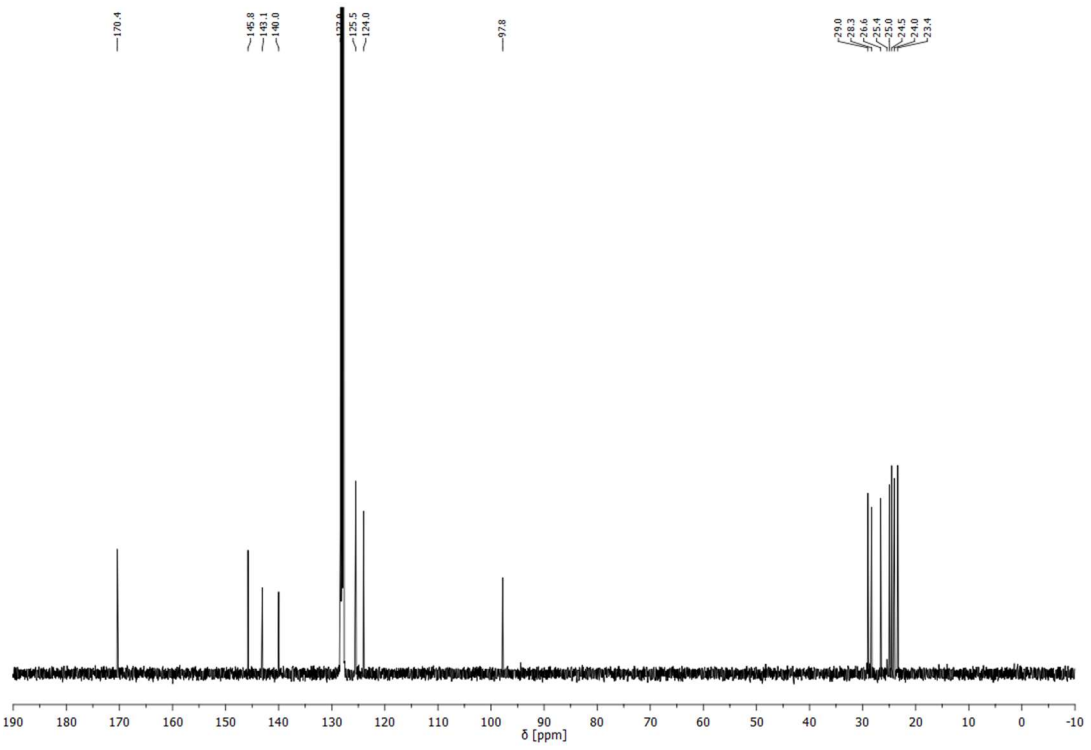


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6) of L(Cl)GaCH$_2$Cl (**1**).

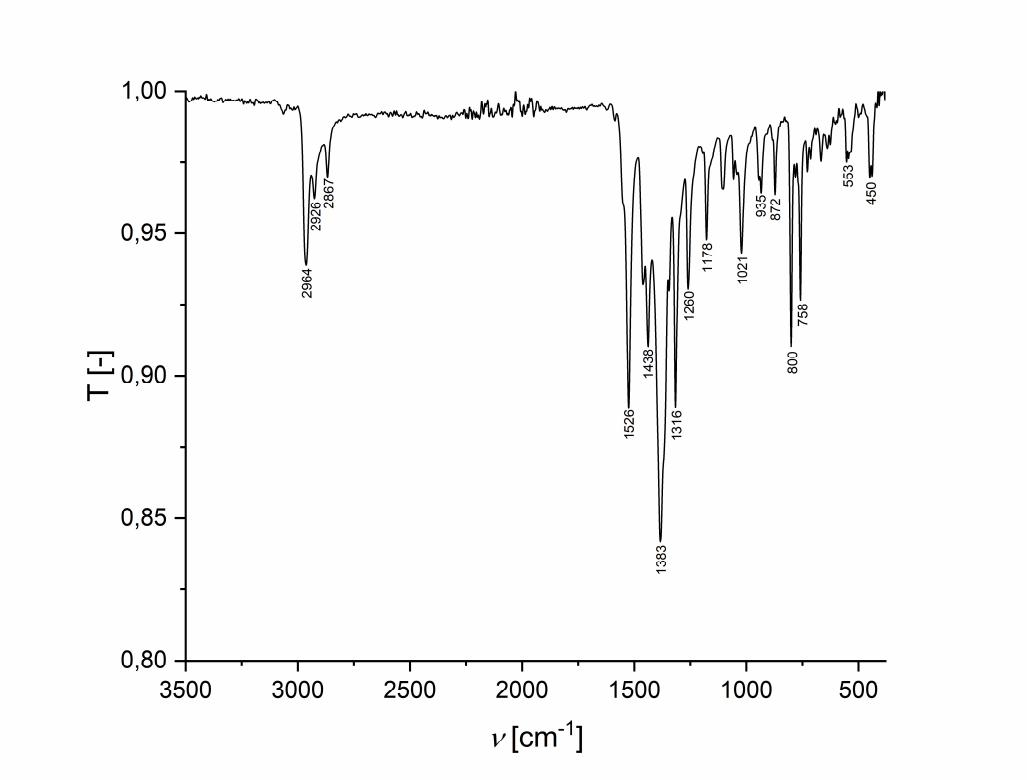


Figure S3. IR spectrum of L(Cl)GaCH$_2$Cl (**1**).

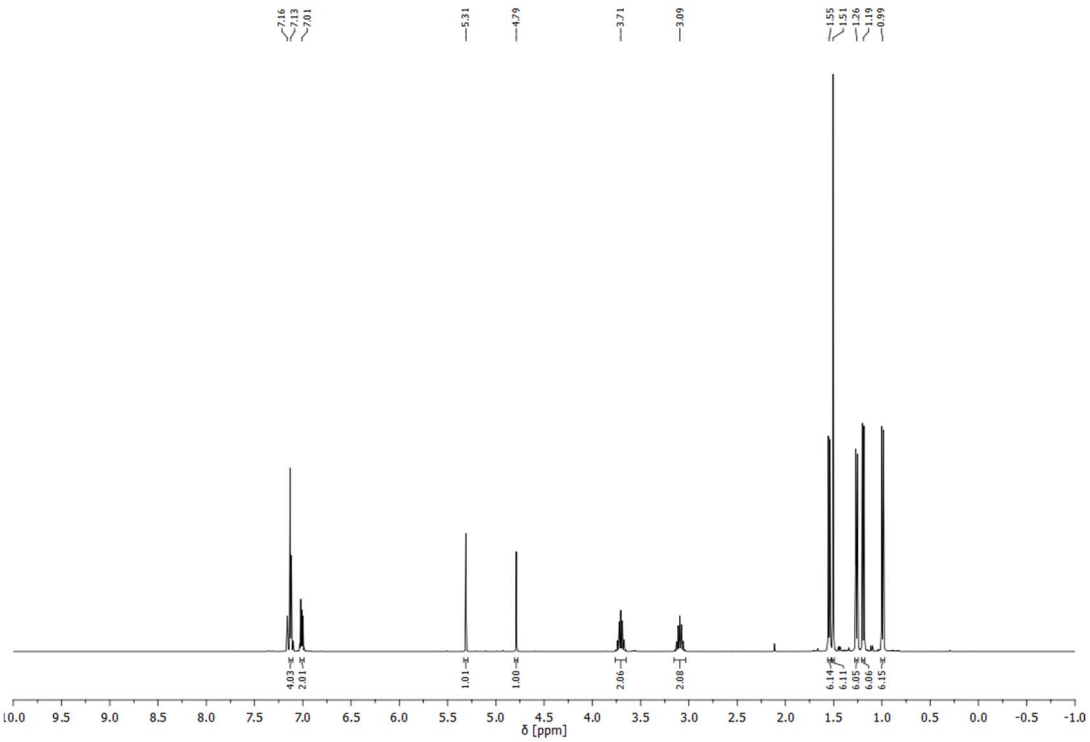


Figure S4. ^{1}H NMR spectrum (400.1 MHz, C_6D_6) of L(Cl)GaCHCl$_2$ (**2**).

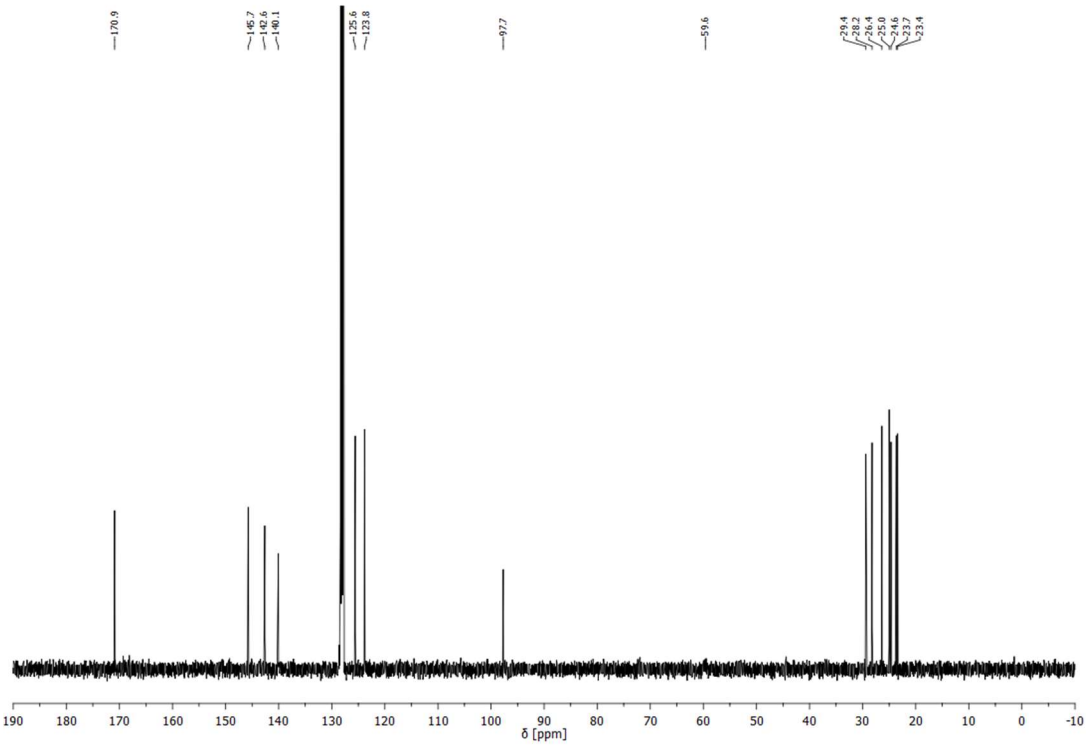


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6) of L(Cl)GaCHCl$_2$ (**2**).

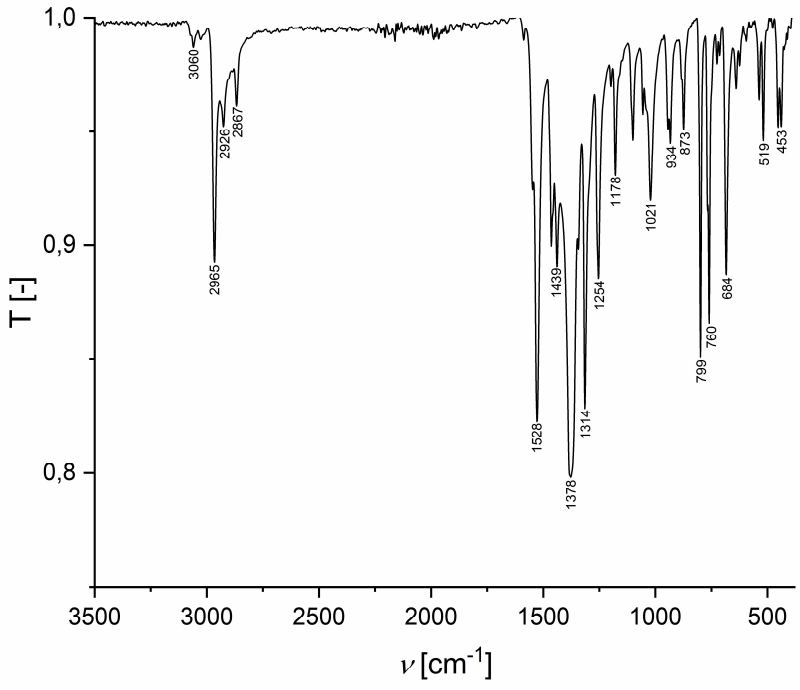


Figure S6. IR spectrum of L(Cl)GaCHCl$_2$ (**2**).

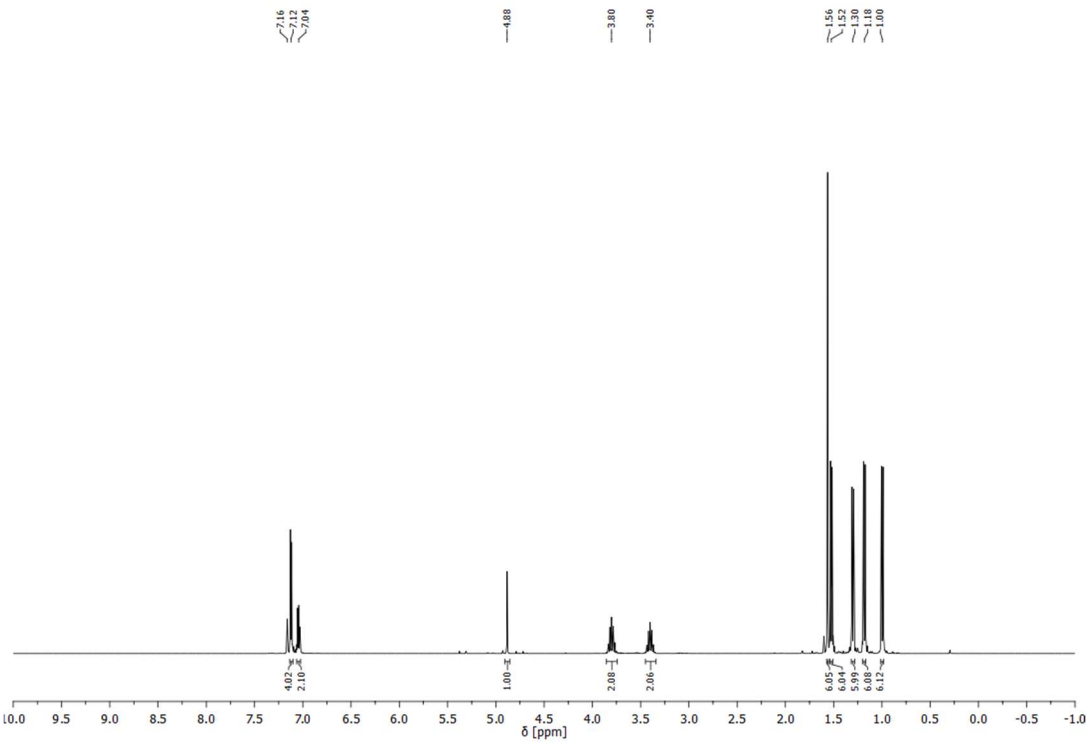


Figure S7. ^{1}H NMR spectrum (400.1 MHz, C_6D_6) of L(Cl)GaCCl$_3$ (**3**).

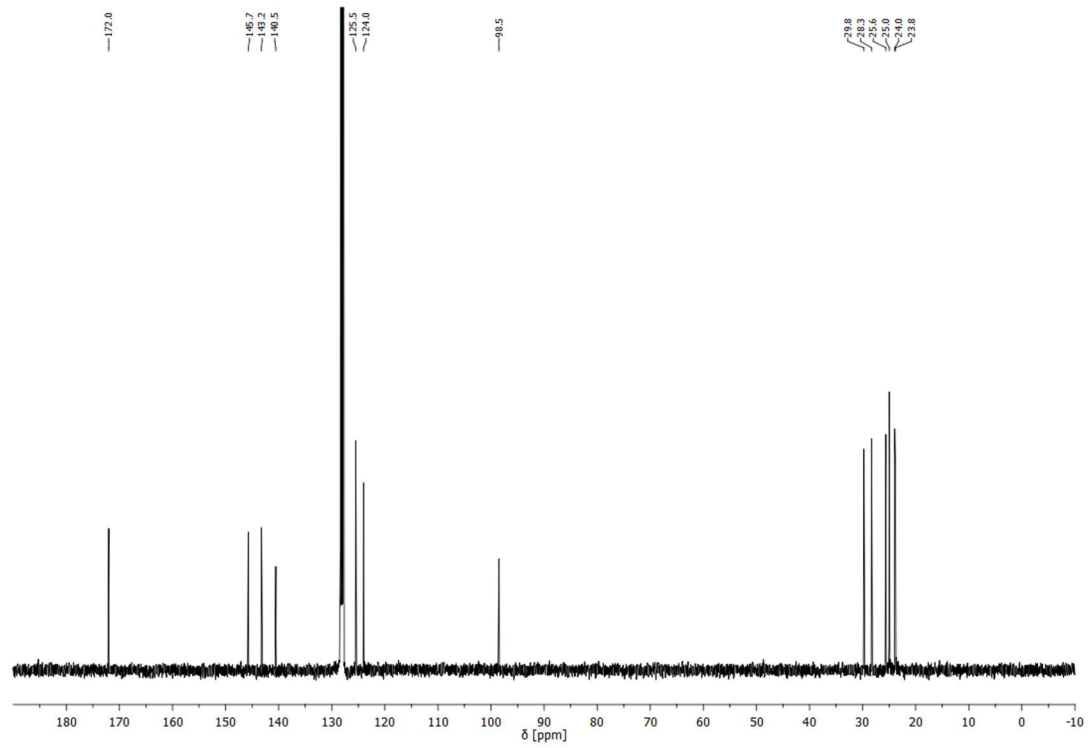


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6) of L(Cl)GaCCl$_3$ (**3**).

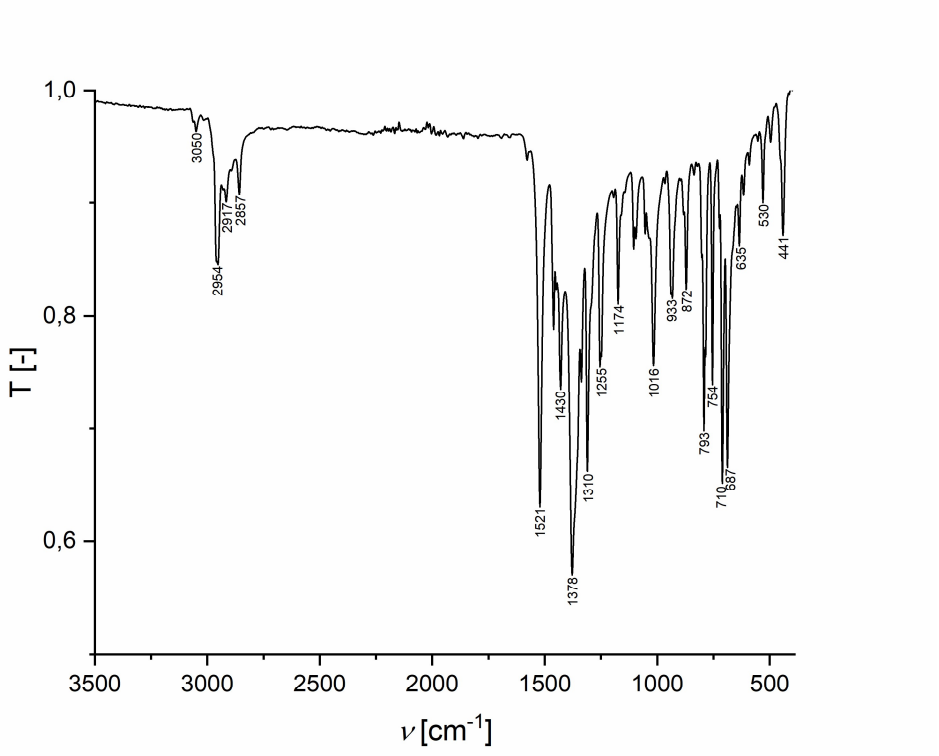


Figure S9. IR spectrum of L(Cl)GaCCl$_3$ (**3**).

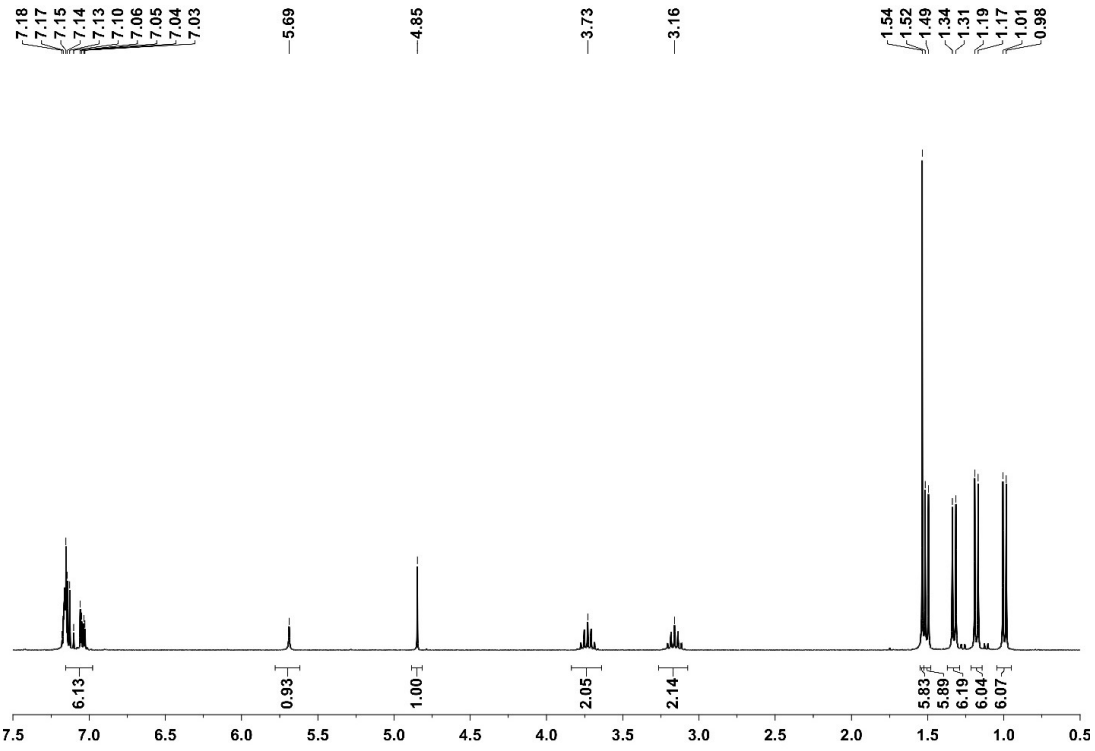


Figure S10. ^{1}H NMR spectrum (300.1 MHz, C_6D_6) of L(Cl)GaSiHCl$_2$ (**4**).

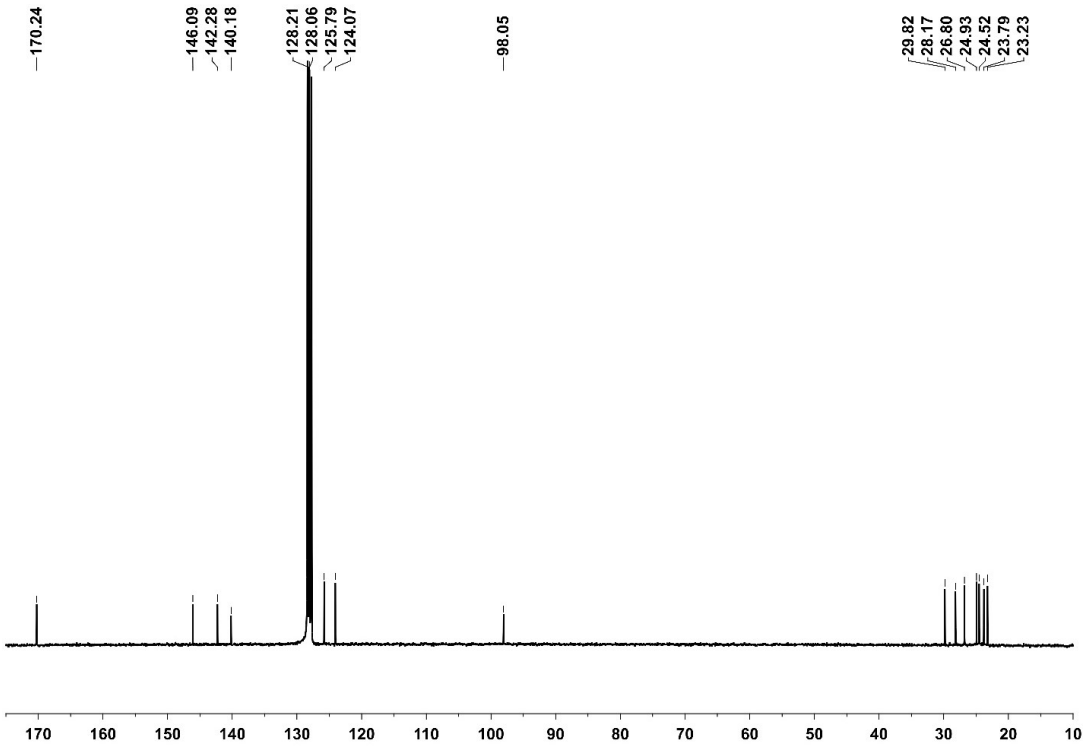
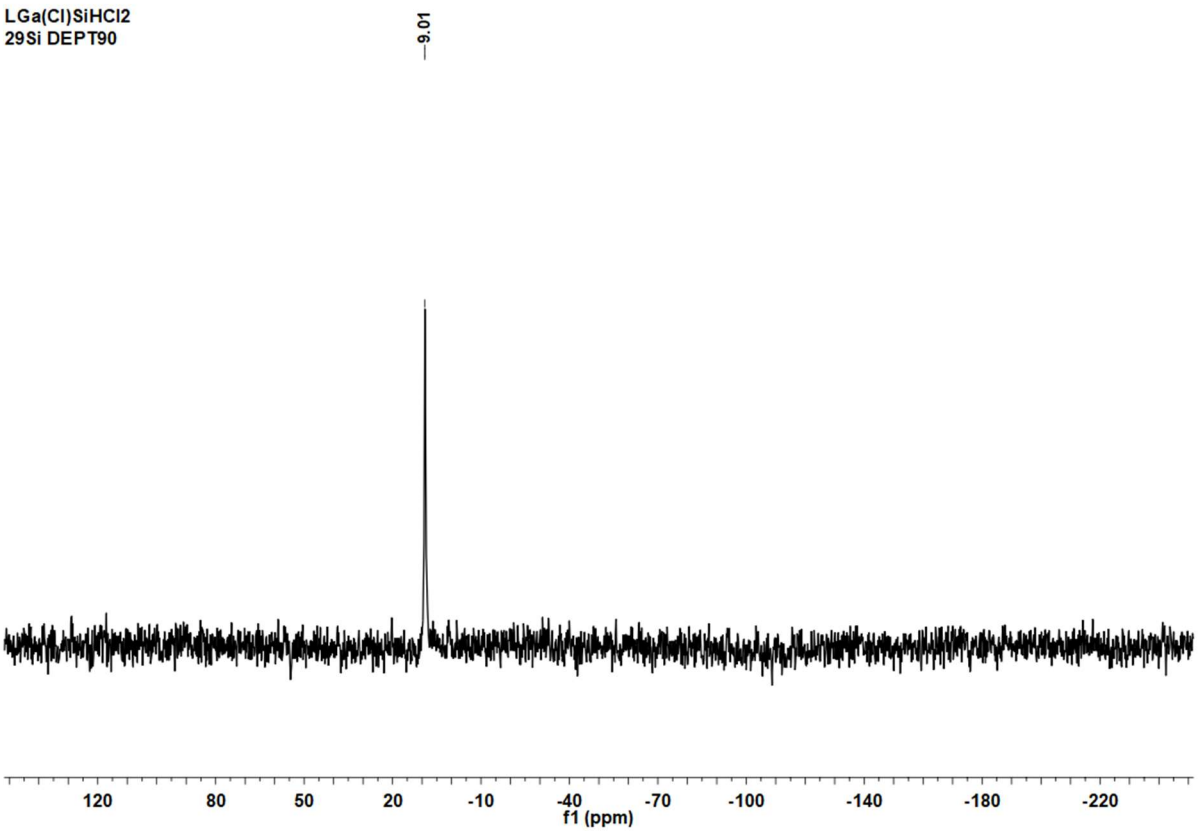
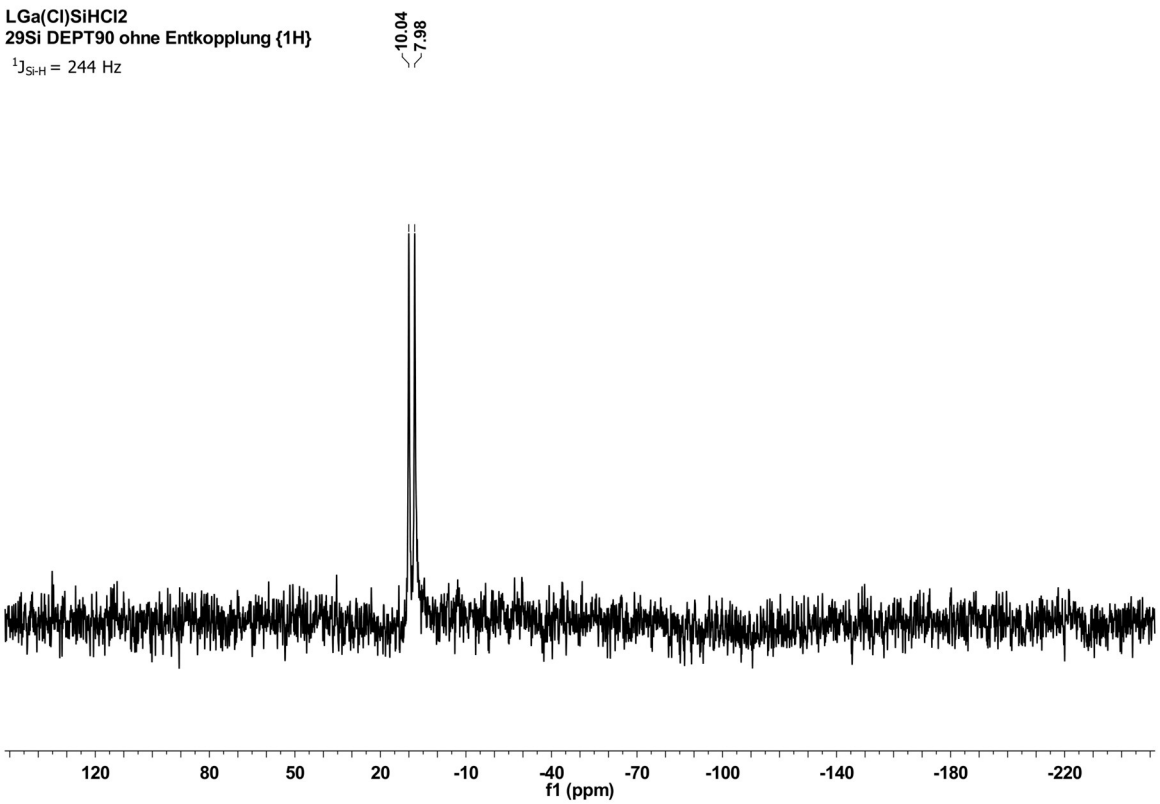


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (75.5 MHz, C_6D_6) of L(Cl)GaSiHCl$_2$ (**4**).



Figures S12. ^{29}Si NMR spectrum (119 MHz, C_6D_6) of (**4**).



Figures S13. $^{29}Si\{^1H\}$ NMR spectrum (119 MHz, C_6D_6) of (**4**).

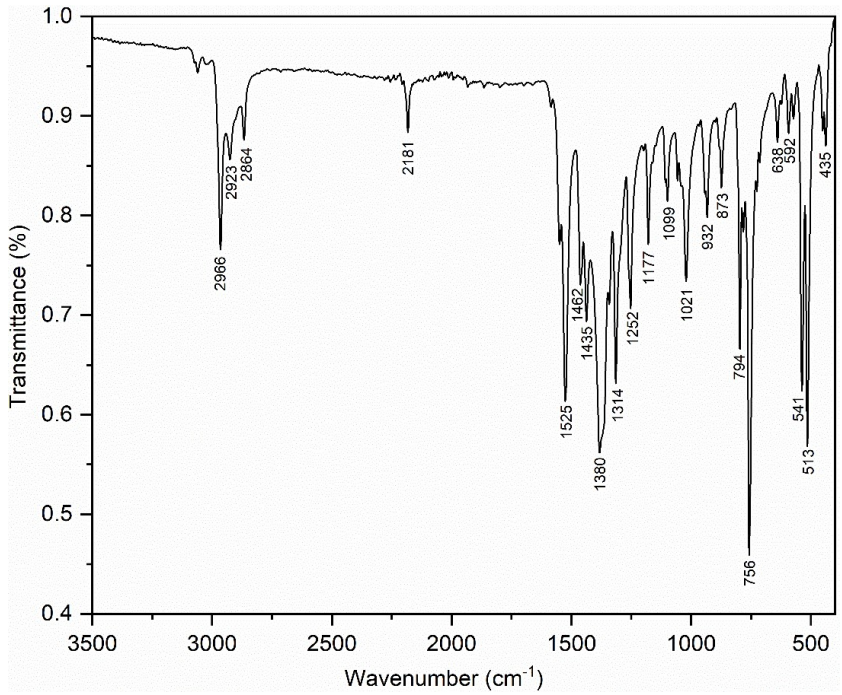


Figure S14. IR spectrum of $L(Cl)GaSiHCl_2$ (**4**).

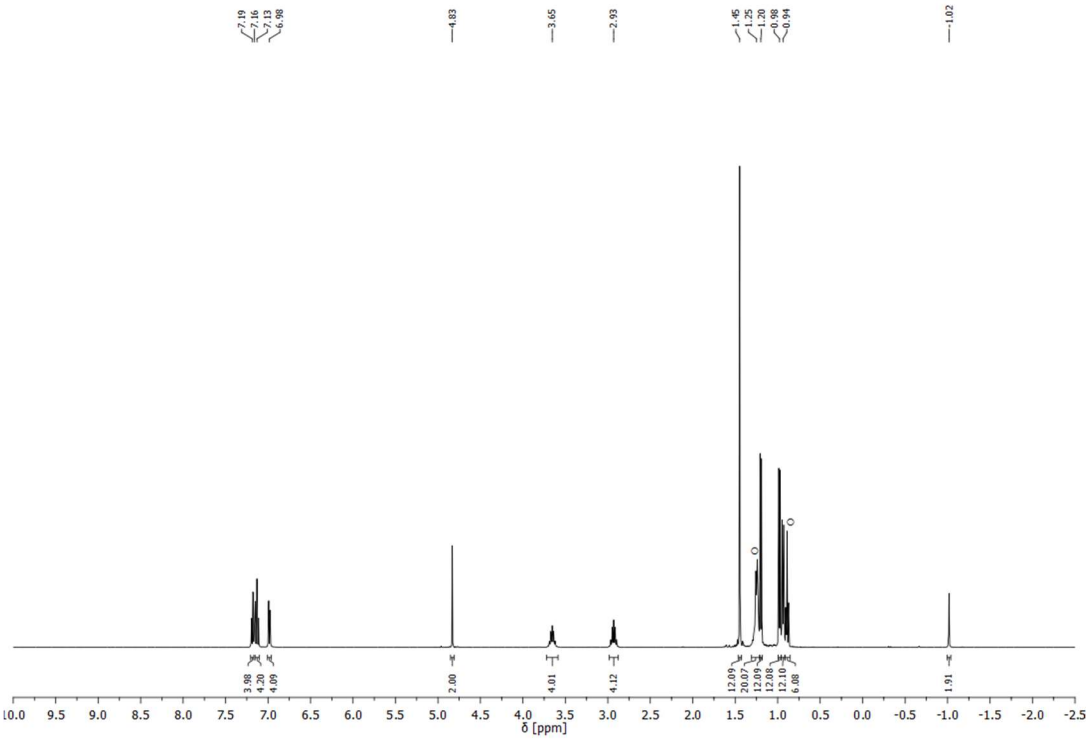


Figure S15. ^{1}H NMR spectrum (400.1 MHz, C_6D_6) of $[L(Cl)Ga]_2CH_2$ (**5**) (○ = *n*-hexane from crystal lattice).

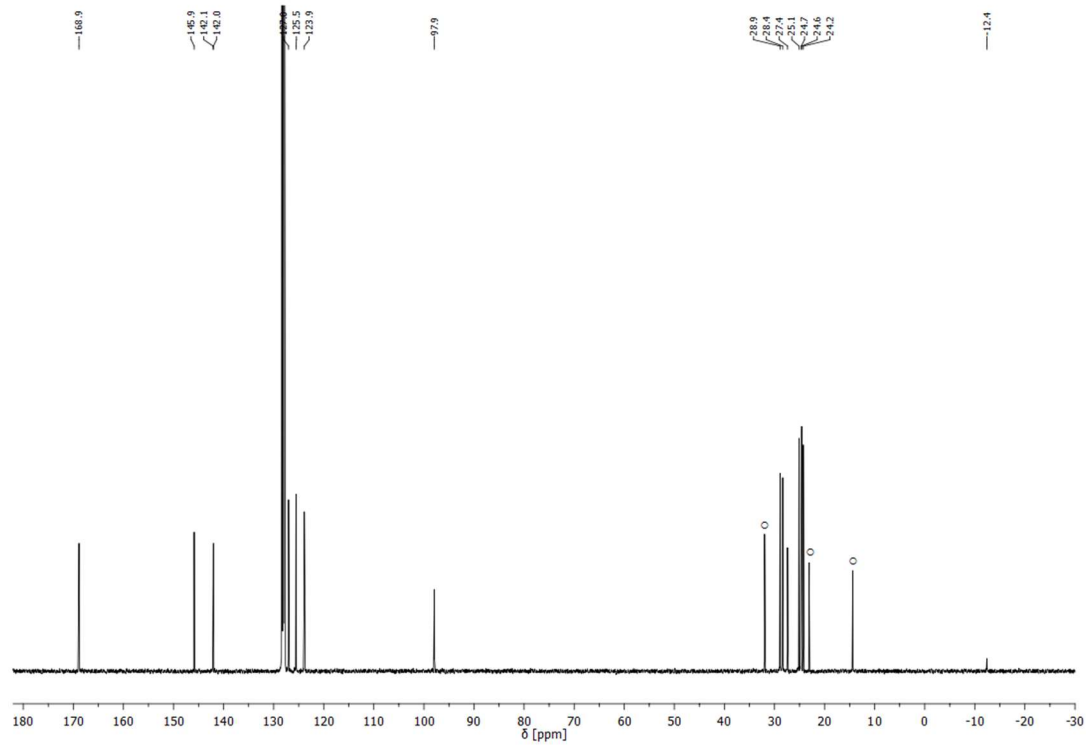


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6) of $[L(Cl)Ga]_2CH_2$ (**5**) (○ = *n*-hexane from crystal lattice).

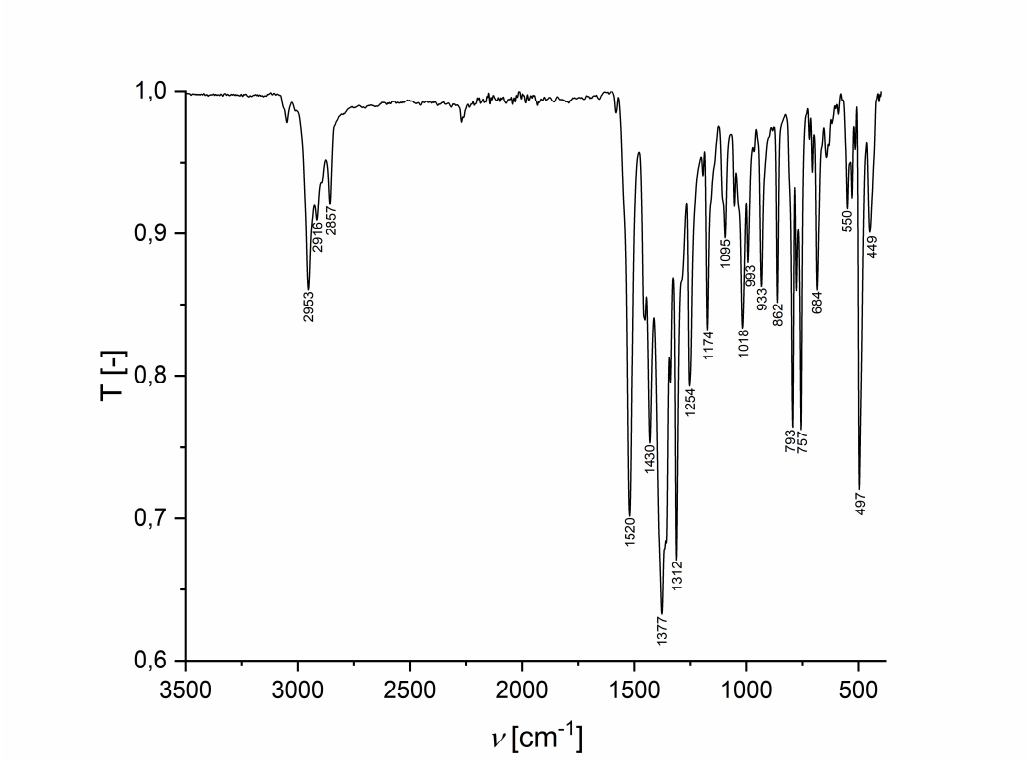


Figure S17. IR spectrum of $[L(Cl)Ga]_2CH_2$ (**5**).

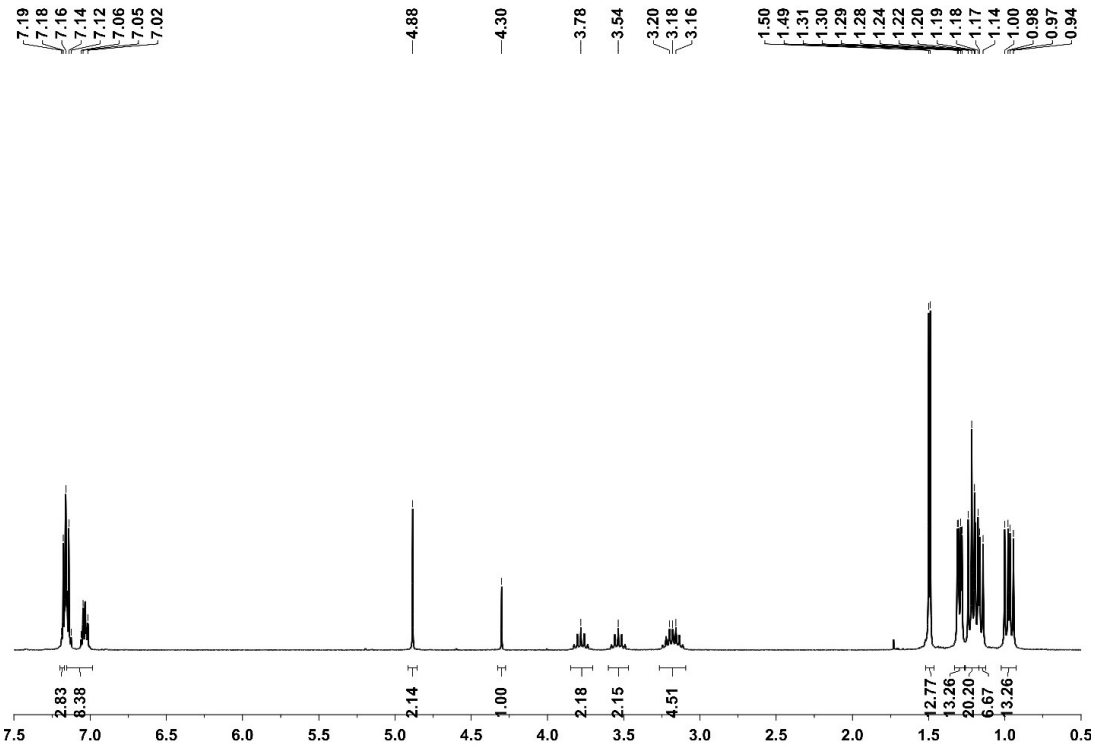


Figure S18. ^1H NMR spectrum (300.1 MHz, C_6D_6) of $[L(Cl)Ga]_2SiHCl$ (**6**).

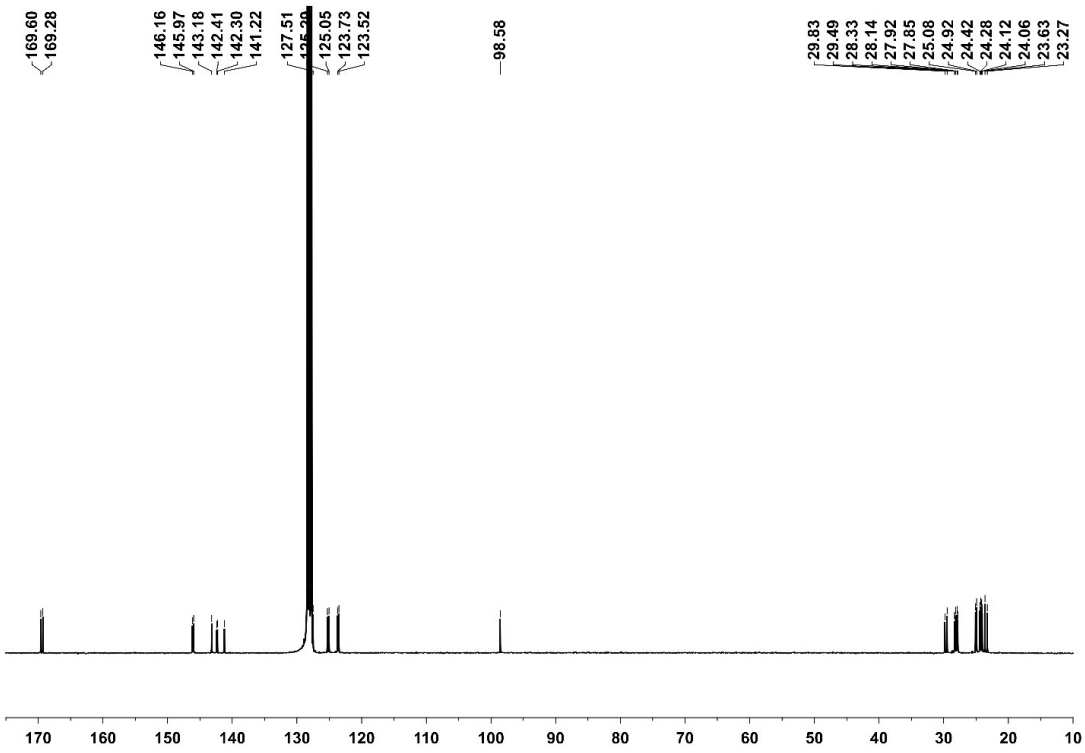
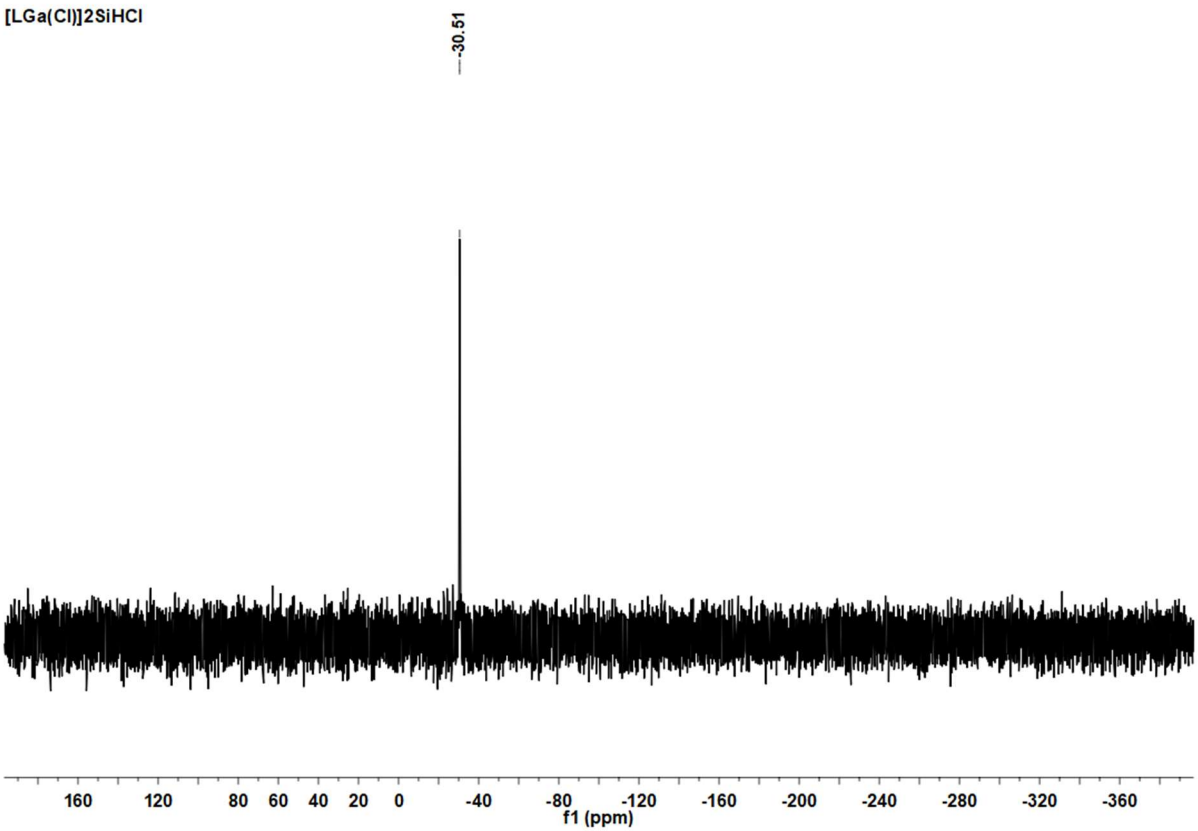
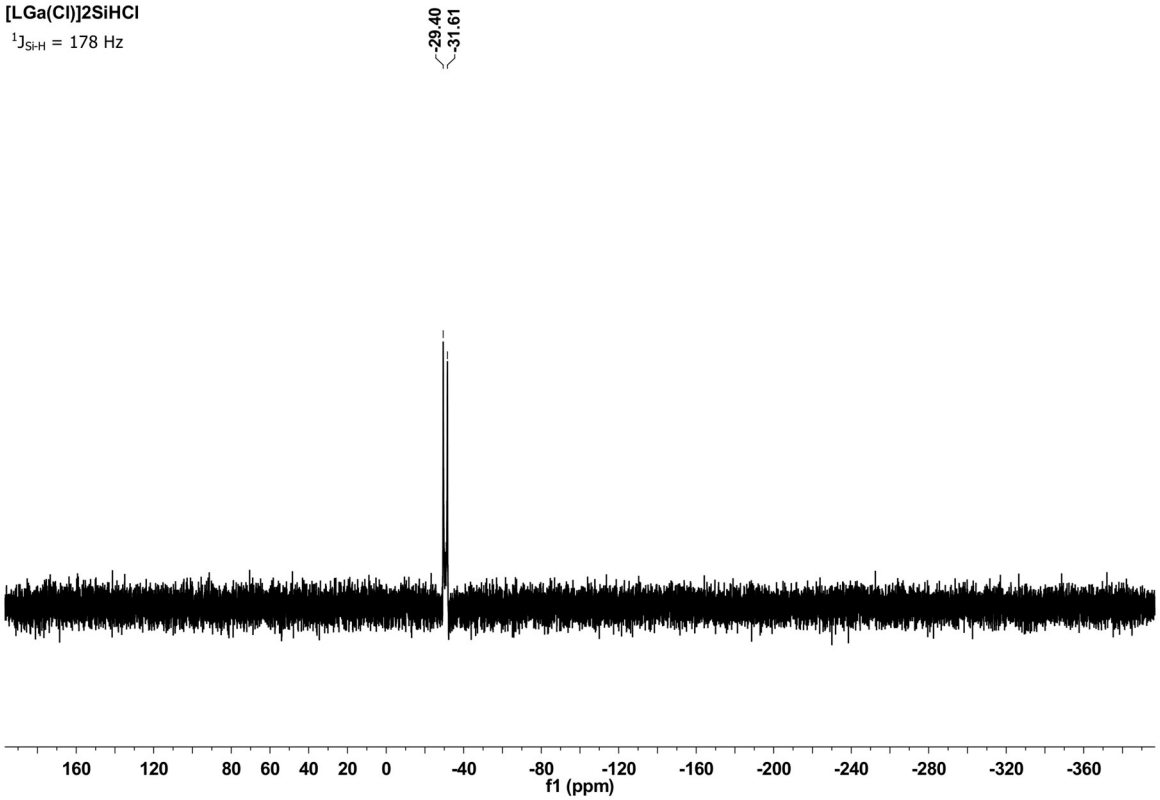


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum (75.5 MHz, C_6D_6) of $[L(Cl)Ga]_2SiHCl$ (**6**).



Figures S20. ^{29}Si NMR spectrum (119 MHz, C_6D_6) of (**6**).



Figures S21. $^{29}Si\{^{1}H\}$ NMR spectrum (119 MHz, C_6D_6) of (**6**).

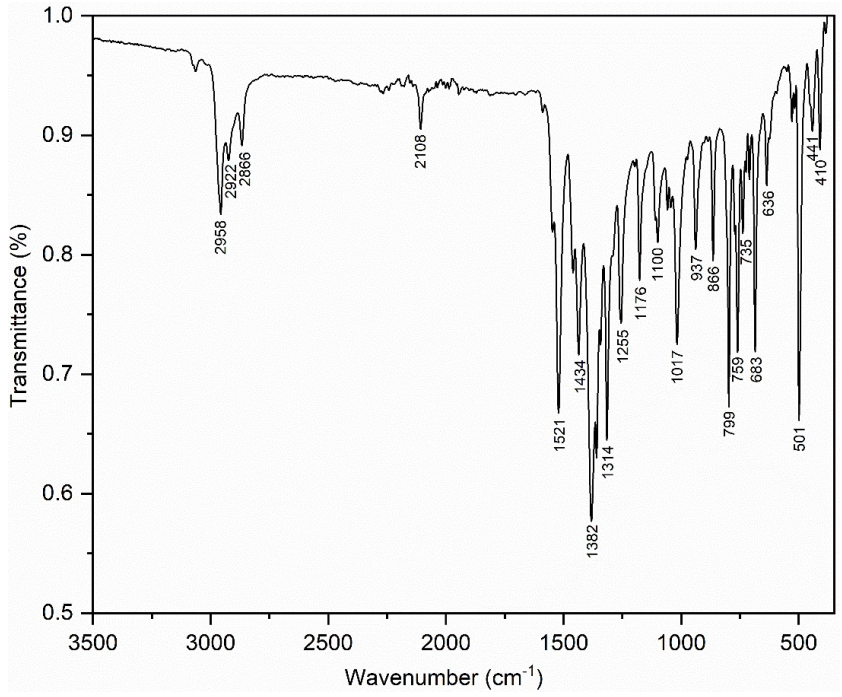


Figure S22. IR spectrum of $[L(Cl)Ga]_2SiHCl$ (**6**).

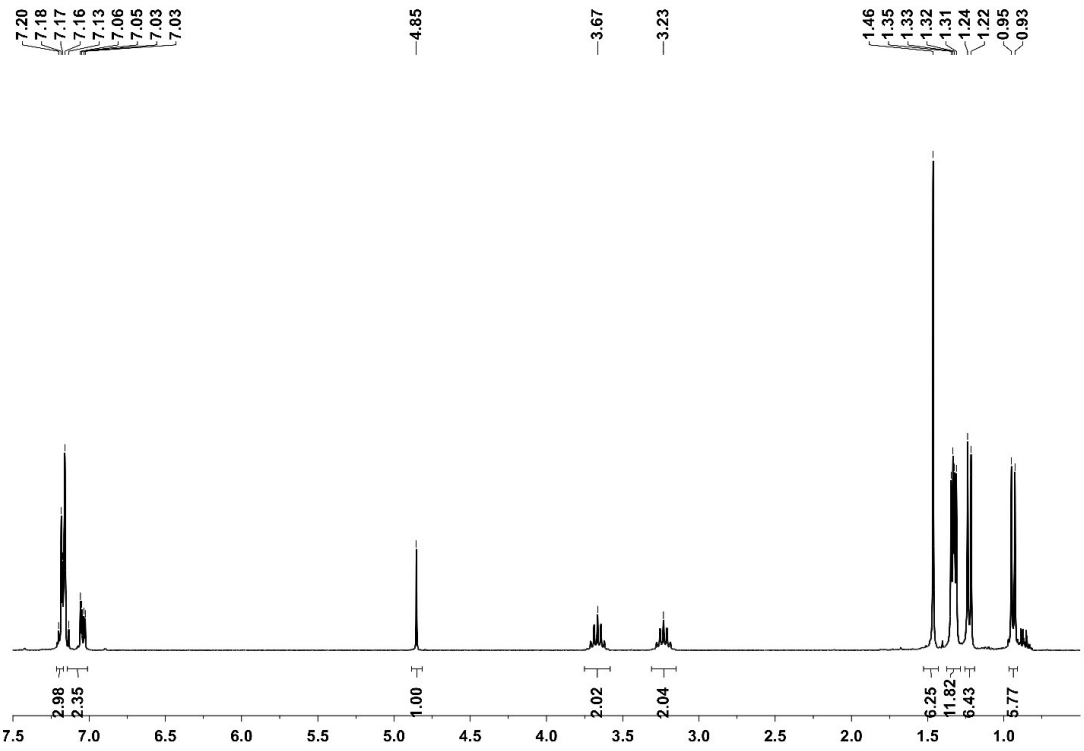


Figure S23. ^{1}H NMR spectrum (300.1 MHz, C_6D_6) of $[L(Cl)Ga]_2SiCl_2$ (**7**).

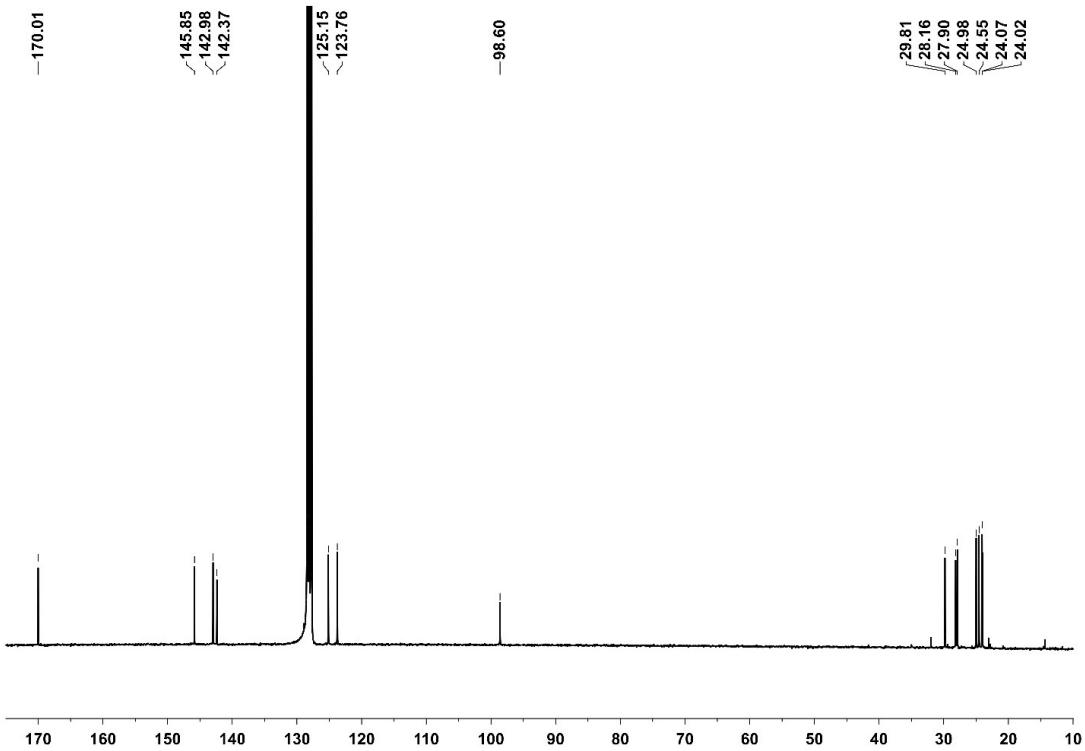


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum (75.5 MHz, C_6D_6) of $[L(Cl)Ga]_2SiCl_2$ (**7**).

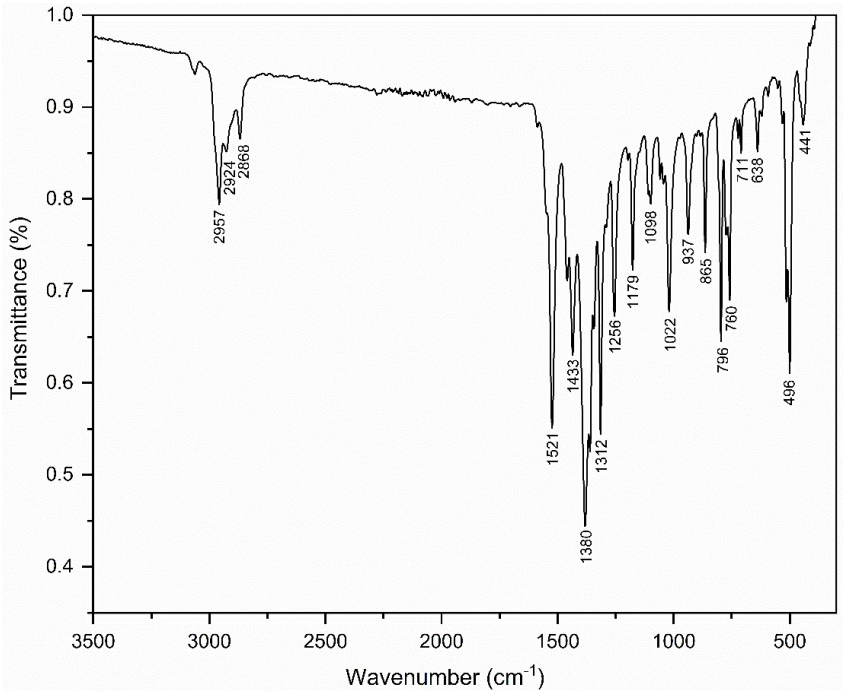


Figure S25. IR spectrum of $[L(Cl)Ga]_2SiCl_2$ (**7**).

Table S1. Crystallographic details of **1**–**3**.

	1	**2**	**3**
Empirical formula	$C_{30}H_{43}Cl_2GaN_2$	$C_{30}H_{42}Cl_3GaN_2$	$C_{30}H_{41}Cl_4GaN_2$
M [g mol^{-1}]	572.28	606.72	641.17
Crystal size [mm]	0.261 x 0.211 x 0.051	0.251 x 0.214 x 0.134	0.404 x 0.199 x 0.070
T [K]	102(2)	100(2)	100(2)
Crystal system	monoclinic	orthorhombic	Monoclinic
Space group	$P2_1/n$	$Pnma$	$P2_1/m$
a [Å]	14.9053(13)	14.7721(12)	9.0298(8)
b [Å]	10.0058(9)	21.3548(19)	20.455(2)
c [Å]	40.988(4)	9.6684(8)	9.5707(9)
α [°]	90	90	90
β [°]	96.581(3)	90	117.700(5)
γ [°]	90	90	90
V [Å^3]	6072.6(9)	3051.4(4)	1565.1(3)
Z	8	4	2
D_{calcd} [g cm^{-3}]	1.252	1.321	1.360
μ(K_α [mm^{-1}])	2.996 (Cu)	1.186 (Mo)	1.242 (Mo)
Transmissions	0.75/0.58	0.75/0.61	0.75/0.64
F(000)	2416	1272	668
Index ranges	$-19 \le h \le 17$	$0 \le h \le 25$	$-13 \le h \le 13$
	$-12 \le k \le 12$	$0 \le k \le 37$	$-31 \le k \le 31$
	$-52 \le l \le 52$	$0 \le l \le 16$	$-14 \le l \le 14$
ϑ_{max} [°]	80.446	38.763	33.213
Reflections collected	238009	262220	57935
Independent reflections	13192	8677	6121
R_{int}	0.0561	0.0512	0.0429
Refined parameters	703	174	180
R_1 [$I > 2\sigma(I)$]	0.0449	0.0461	0.0305
wR_2 [all data]	0.1258	0.1100	0.0795
GooF	1.017	1.080	1.046
$\Delta\rho_{final}$ (max/min) [e·Å^{-3}]	1.552/-0.702	1.732/-0.790	1.169/-0.850

Table S2. Crystallographic details of **4**–**7**.

	4	**5**	**6**	**7**
Empirical formula	$C_{29}H_{42}Cl_3GaN_2Si$	$C_{65}H_{98}Cl_2Ga_2N_4$	$C_{64}H_{89}Cl_3Ga_2N_4Si$	$C_{85}H_{109}Cl_4Ga_2N_4Si$
M [g mol^{-1}]	622.80	1145.81	1188.27	1496.09
Crystal size [mm]	0.242 x 0.232 x 0.216	0.232 x 0.148 x 0.054	0.213 × 0.174 × 0.169	0.607 x 0.156 x 0.151
T [K]	100(2)	100(2)	100(2)	100(2)
Crystal system	orthorhombic	monoclinic	monoclinic	Triclinic
Space group	*Pnma*	*C*2/*c*	$P2_1/c$	*P*−1
a [Å]	15.7276(13)	21.398(3)	13.931(2)	12.8721(12)
b [Å]	21.0688(17)	12.3770(15)	24.762(4)	15.8286(15)
c [Å]	9.4846(8)	24.247(3)	18.434(3)	20.983(2)
α [°]	90	90	90	92.951(5)
β [°]	90	106.591(2)	92.869(7)	91.421(5)
γ [°]	90	90	90	109.252(4)
V [Å^3]	3142.8(4)	6154.1(13)	6350.8(16)	4026.9(7)
Z	4	4	4	2
D_{calcd} [g cm^{-3}]	1.316	1.237	1.243	1.234
$\mu(K_\alpha$ [mm^{-1}])	1.189	1.004 (Mo)	1.034 (Mo)	0.861 (Mo)
Transmissions	0.75/0.64	0.75/0.69	0.75/0.62	0.75/0.64
F(000)	1304	2448	2512	1582
Index ranges	$-18 \le h \le 23$	$-32 \le h \le 31$	$-21 \le h \le 21$	$-19 \le h \le 19$
	$-30 \le k \le 32$	$-19 \le k \le 19$	$-38 \le k \le 38$	$-23 \le k \le 24$
	$-14 \le l \le 14$	$-37 \le l \le 37$	$-26 \le l \le 28$	$-31 \le l \le 32$
ϑ_{max} [°]	33.221	33.318	33.249	33.345
Reflections collected	100125	121649	239951	199445
Independent reflections	6080	11793	24298	29948
R_{int}	0.0261	0.0644	0.0664	0.0305
Refined parameters	207	368	714	940
R_1 [$I > 2\sigma(I)$]	0.0309	0.0334	0.0371	0.0319
wR_2 [all data]	0.0823	0.0812	0.0971	0.0892
GooF	1.089	1.055	1.017	1.069
$\Delta\rho_{final}$ (max/min) [e·Å^{-3}]	1.182/-1.015	0.704/-0.421	0.968/-0.600	1.022/-0.645

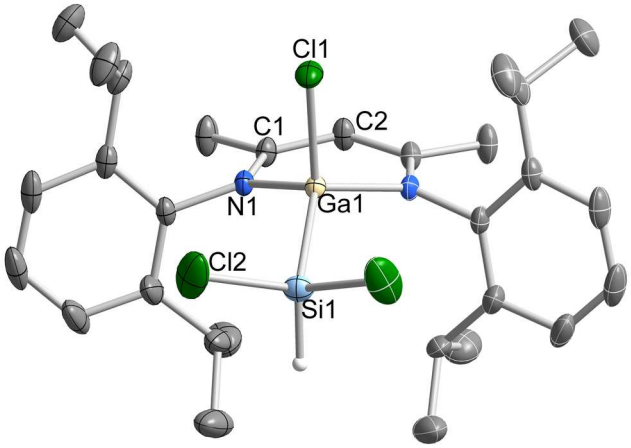


Figure S26. Molecular structure of **4** in the solid-state. Hydrogen atoms (except $SiHCl_2$) and the minor component of the disordered *i*-Pr group were omitted for clarity. Displacement ellipsoids are drawn at 50 % probability level, whereas hydrogen atoms are displayed as spheres of arbitrary radius. The symmetry generated parts is depicted with pale inner lines.

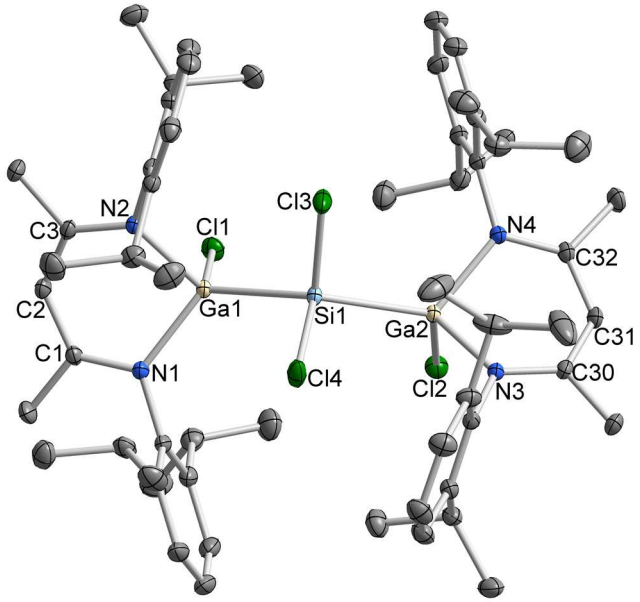


Figure S27. Molecular structure of **7** in the solid-state. Hydrogen atoms and the co-crystallized benzene molecules were omitted for clarity. Displacement ellipsoids are drawn at 50 % probability level.