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SUPPLEMENTARY INFORMATION

Synthesis and Structural Investigation of R_2Si (R = Me, Ph) Bridged Di-N-Heterocyclic Carbenes

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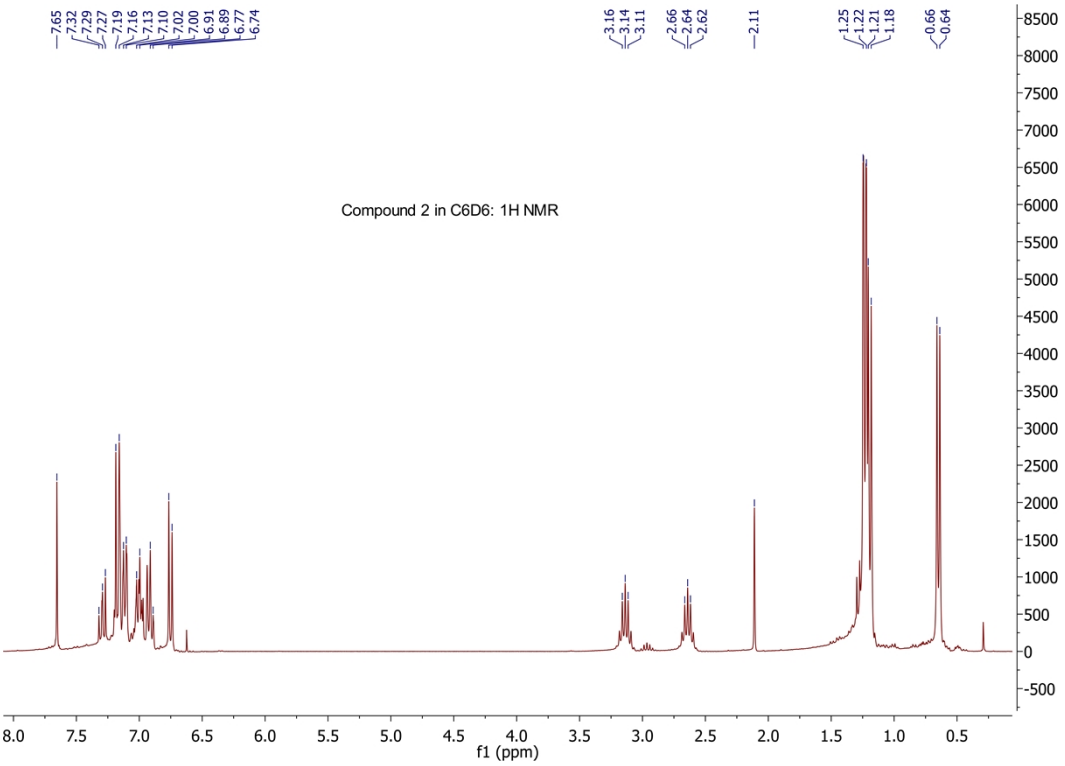
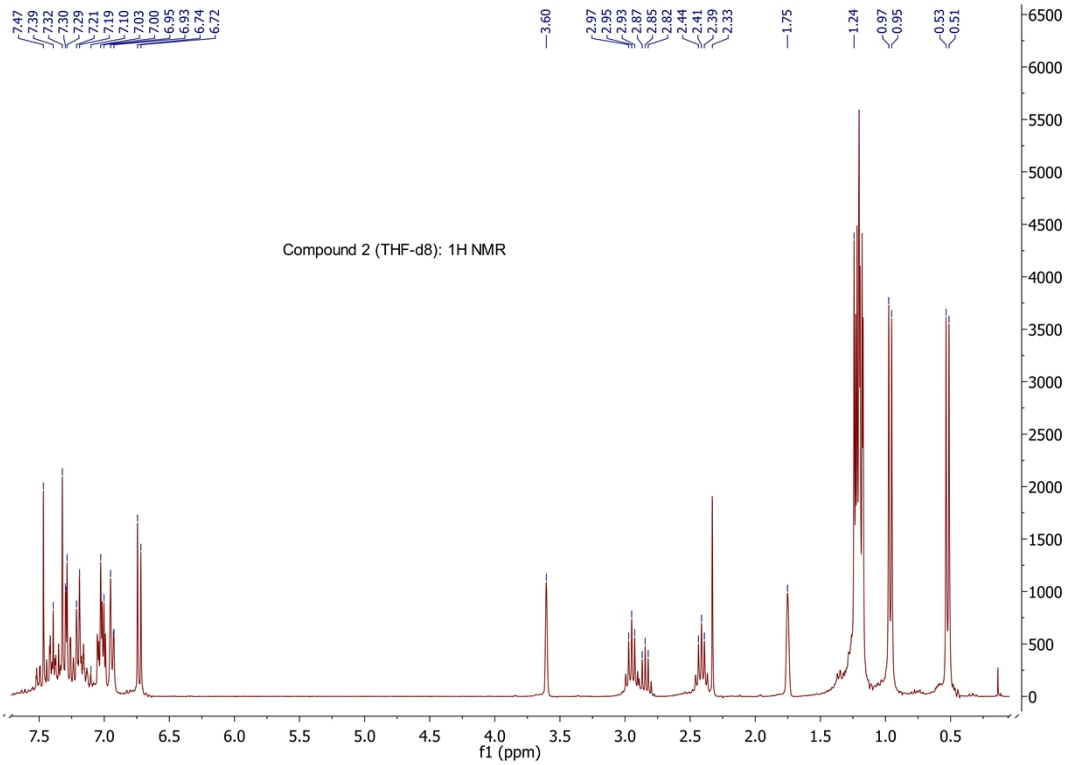
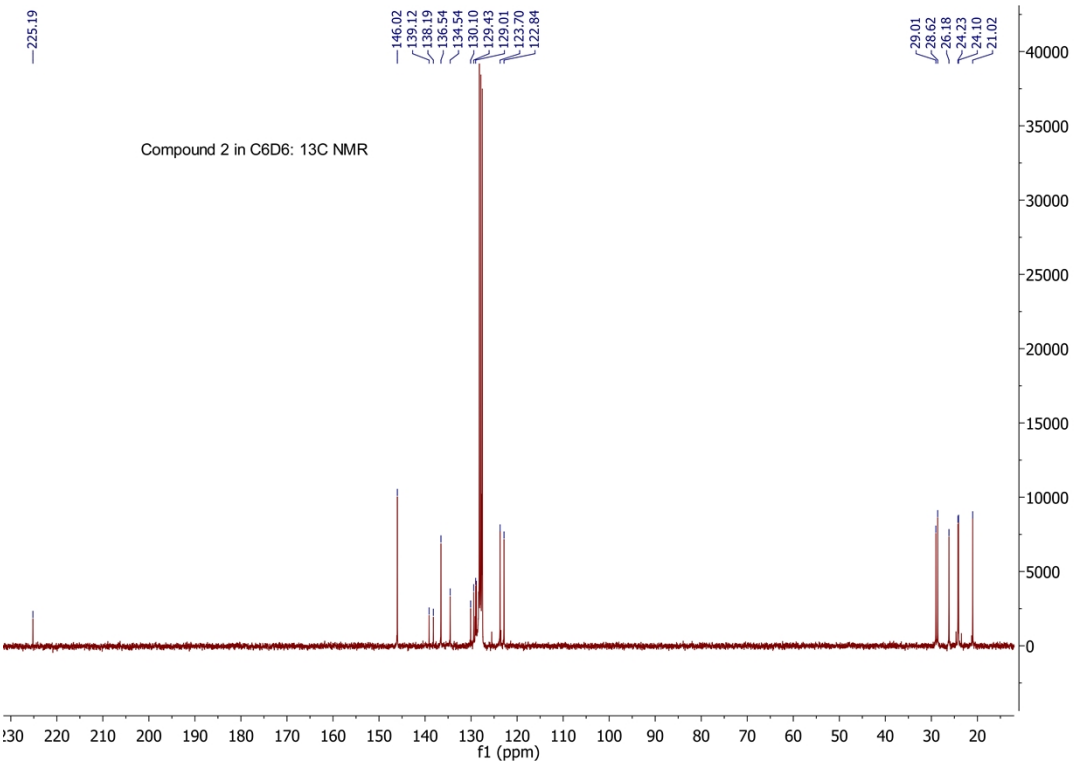
NMR Plots for Compounds 2-6:



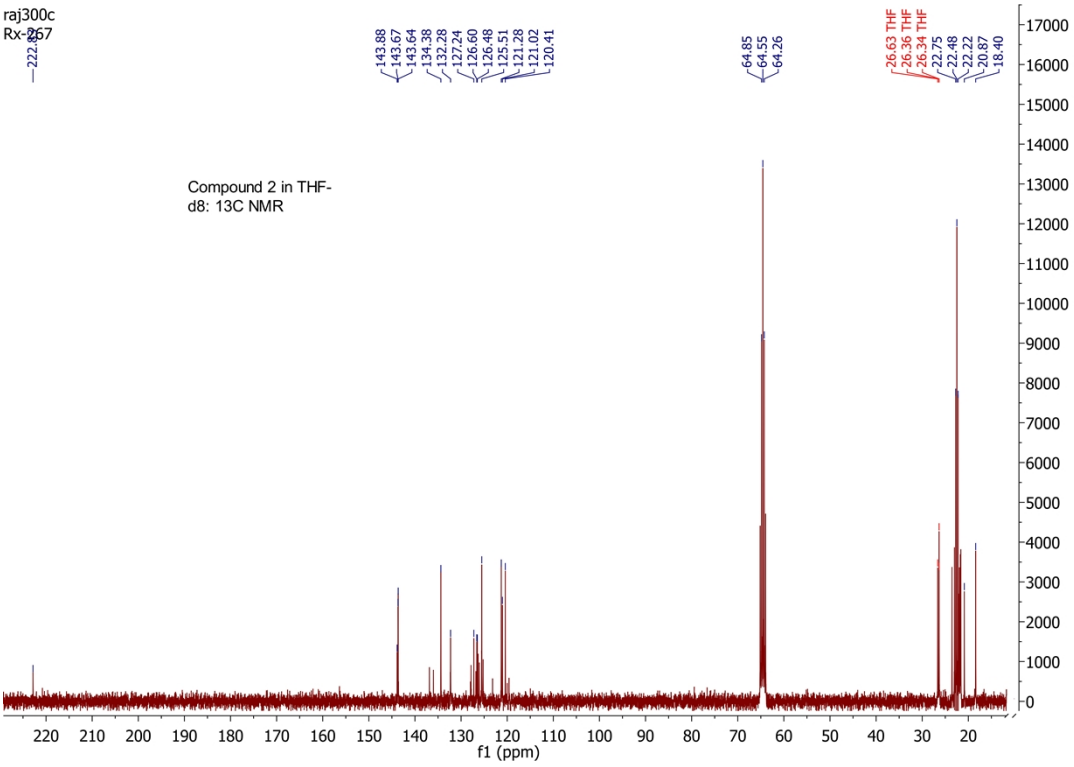
Plot 1. ^{1}H NMR (in C_6D_6) spectrum of compound **2**.



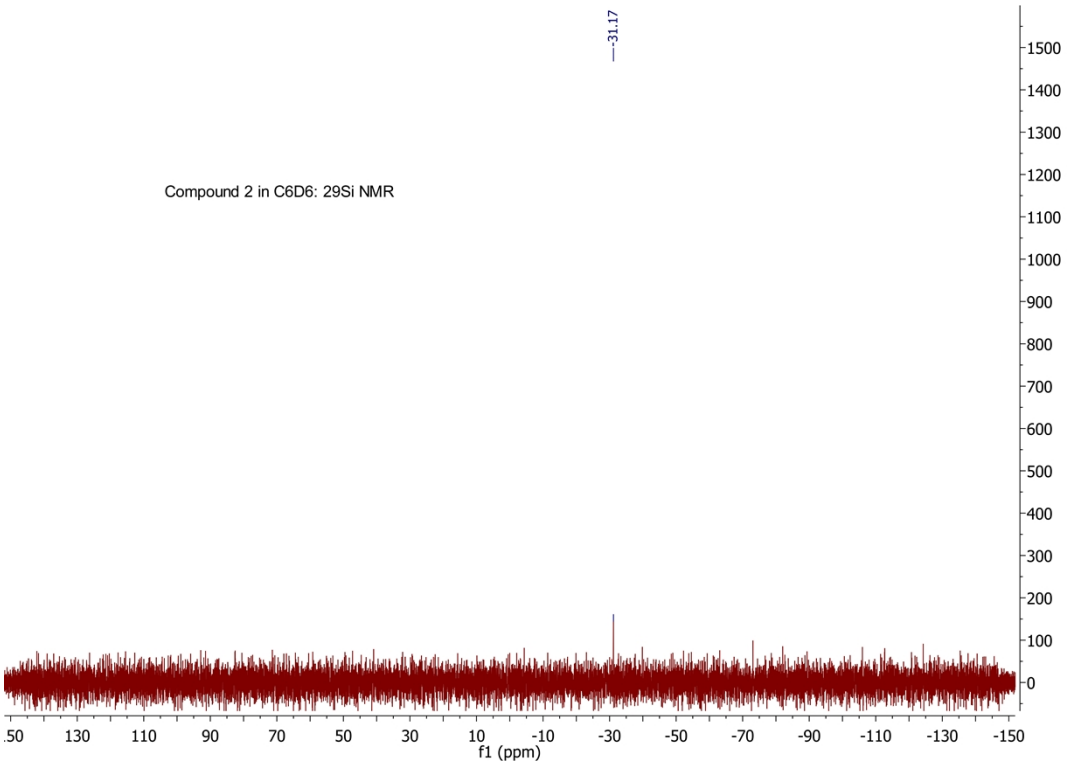
Plot 2. ^{1}H NMR (in $[D_8]THF$) spectrum of compound **2**.



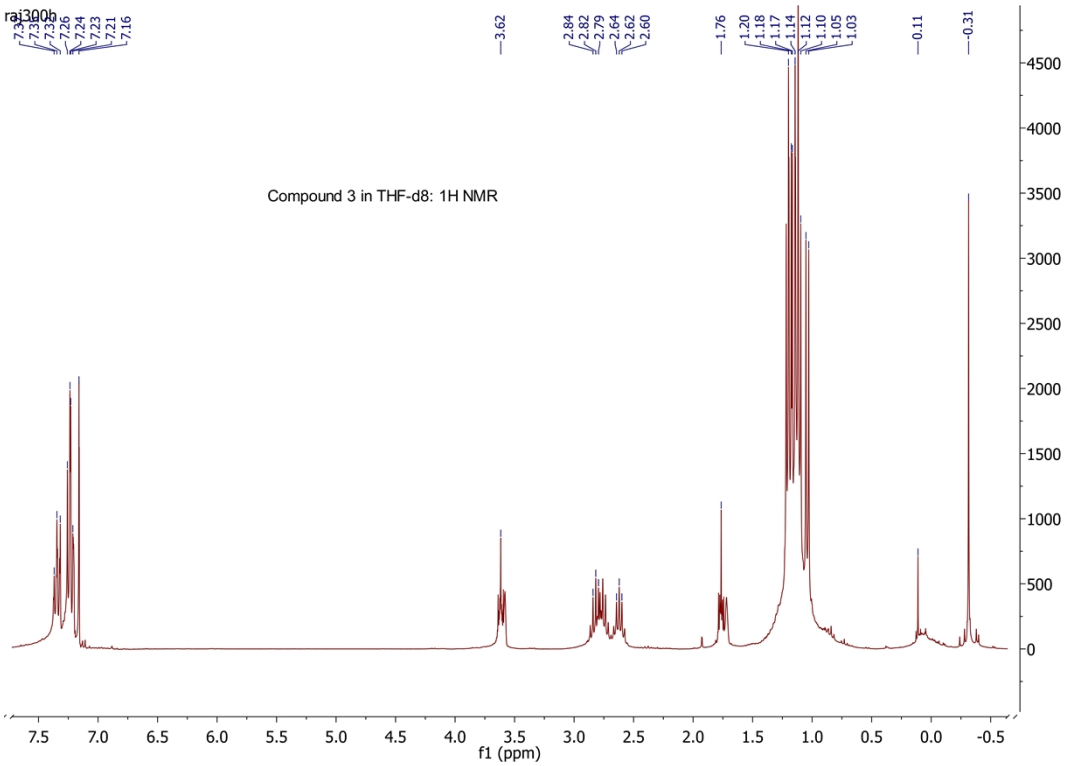
Plot 3. ^{13}C NMR (in C_6D_6) spectrum of compound **2**.



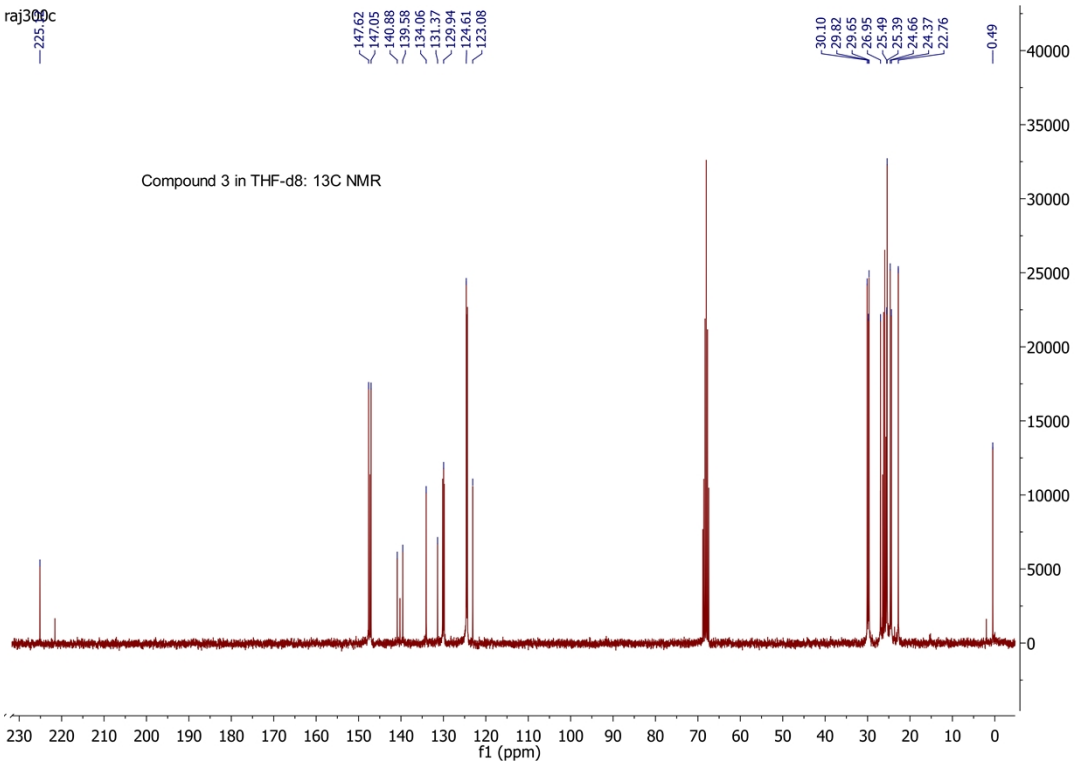
Plot 4. ^{13}C NMR (in $[D_8]$THF) spectrum of compound **2**.



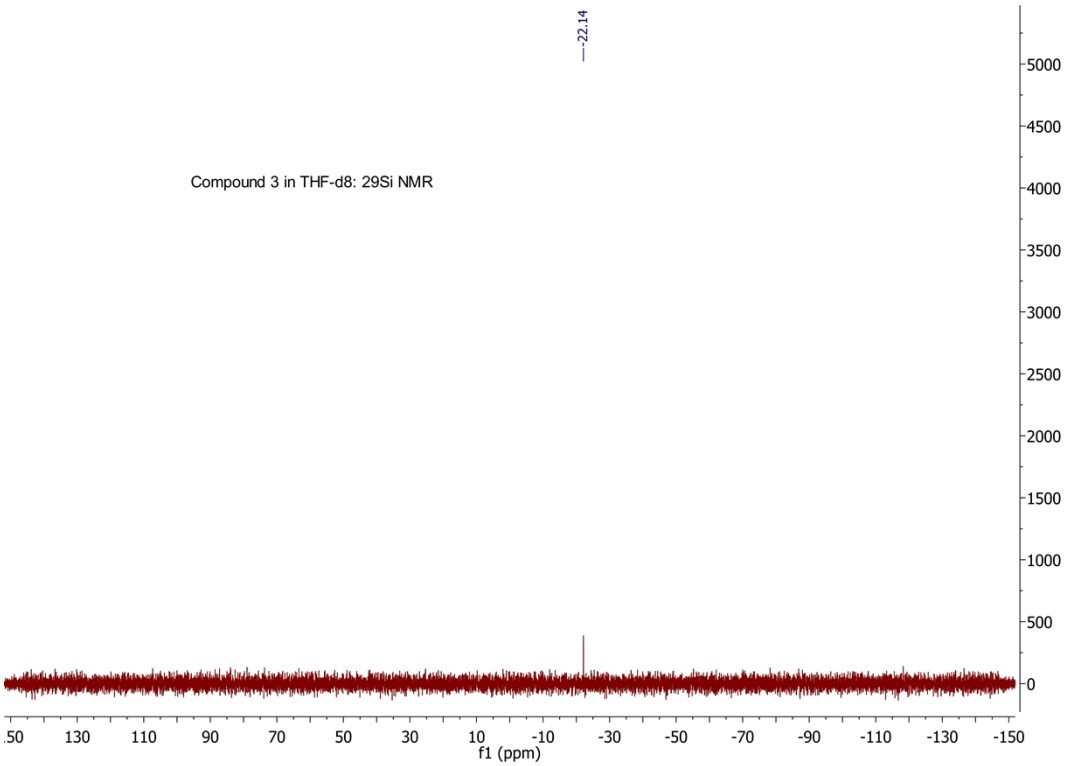
Plot 5. ^{29}Si NMR (in C_6D_6) spectrum of compound **2**.



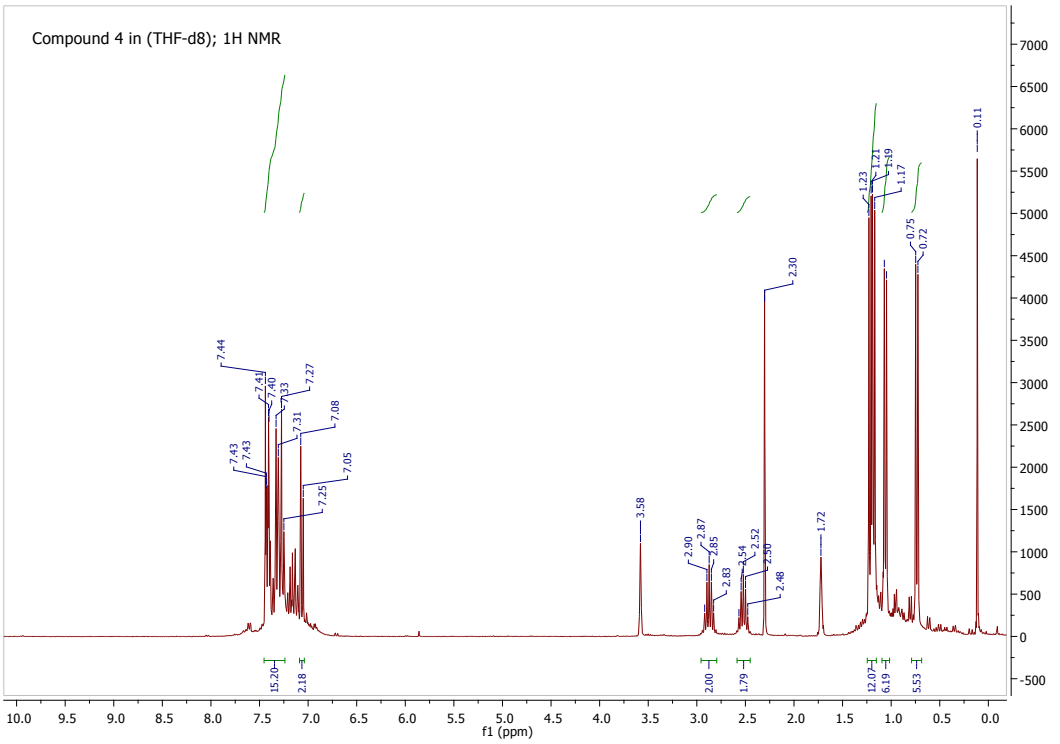
Plot 6. ^{1}H NMR (in $[D_8]THF$) spectrum of compound **3**.



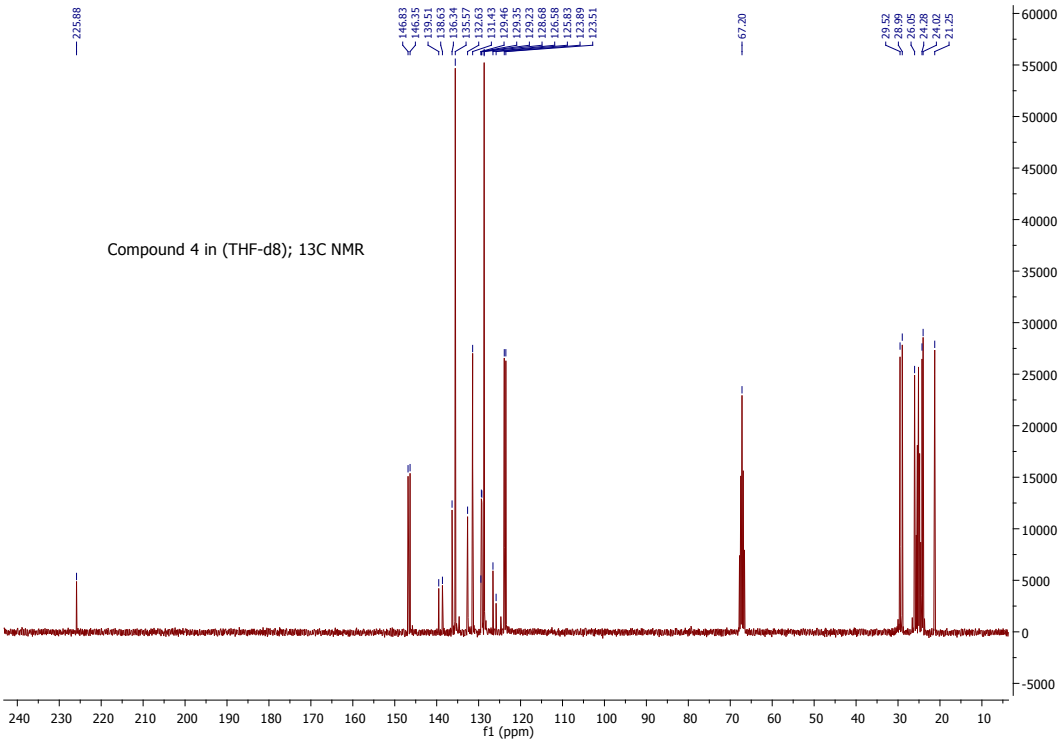
Plot 7. ^{13}C NMR (in $[D_8]THF$) spectrum of compound **3**.



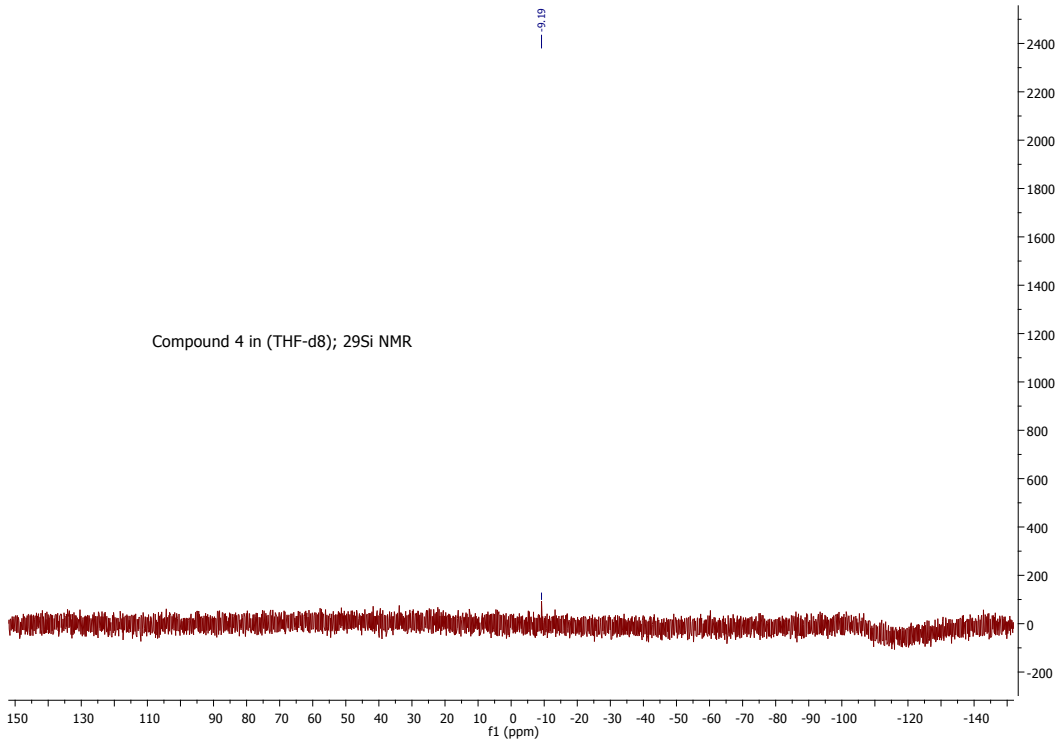
Plot 8. ^{29}Si NMR (in $[D_8]THF$) spectrum of compound **3**.



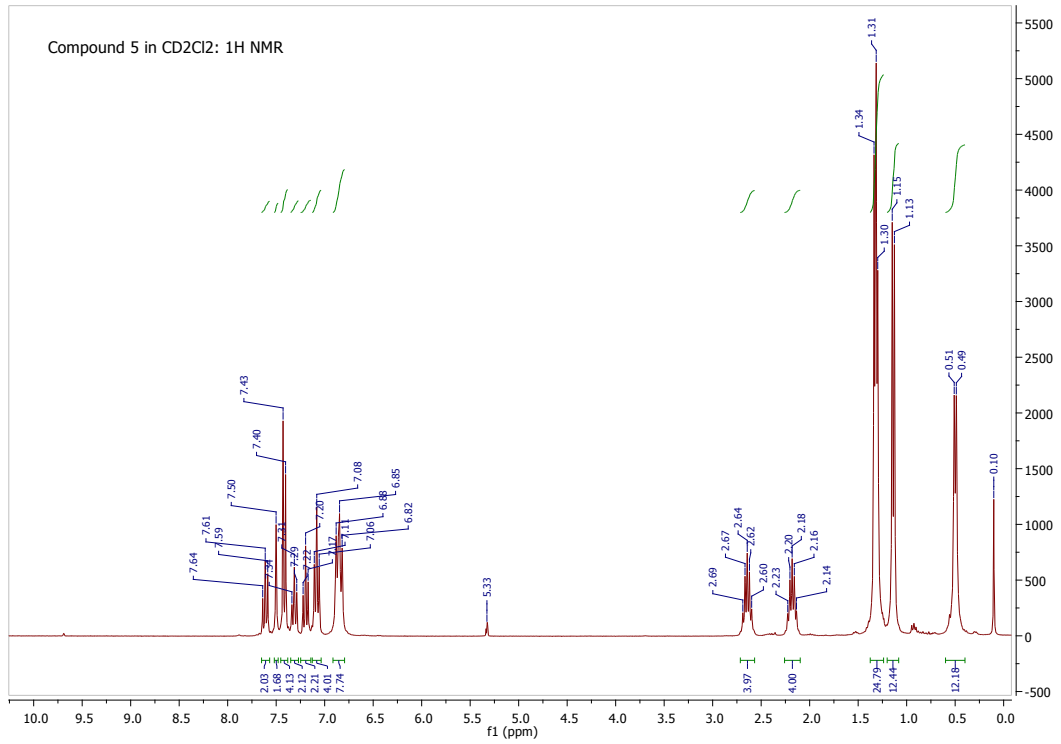
Plot 9: ^{1}H NMR (in $[D_8]THF$) spectrum of compound **4**.



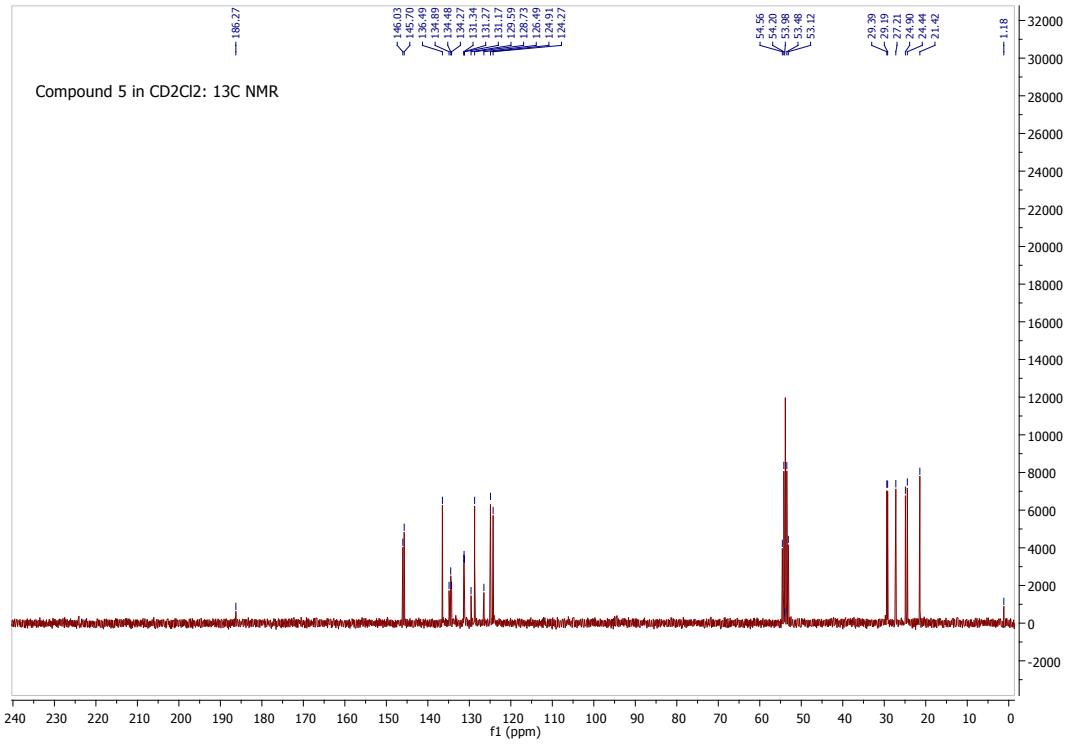
Plot 10: ^{13}C NMR (in $[D_8]THF$) spectrum of compound **4**.



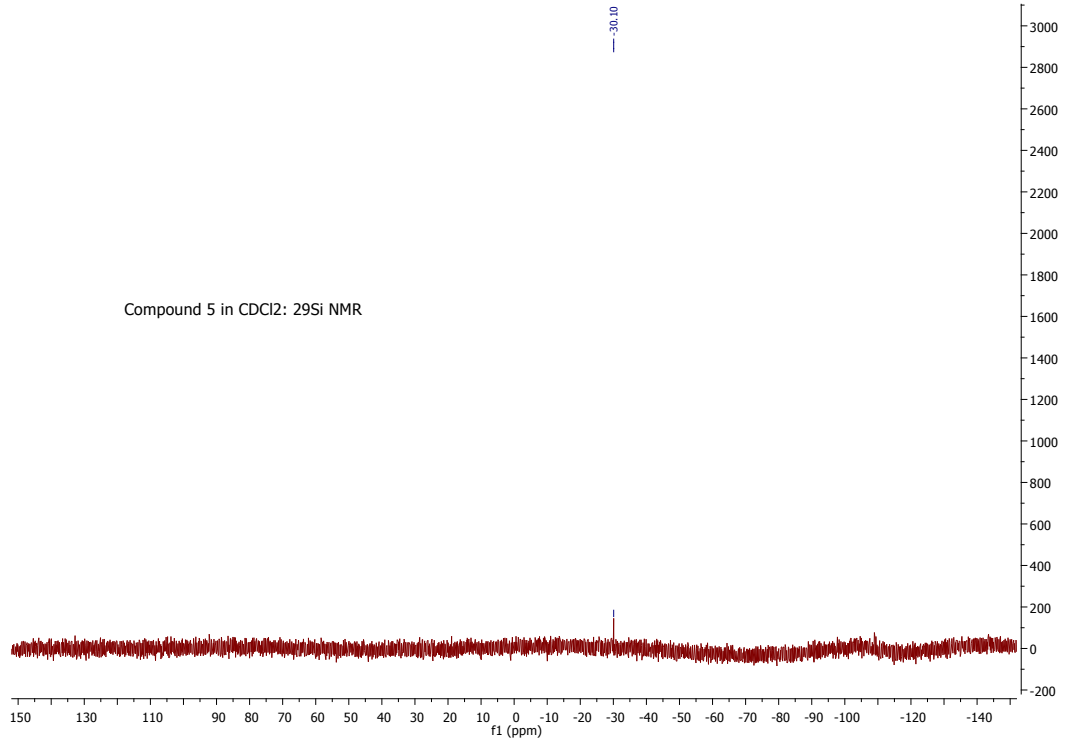
Plot 11: ^{29}Si NMR (in $[D_8]THF$) spectrum of compound **4**.



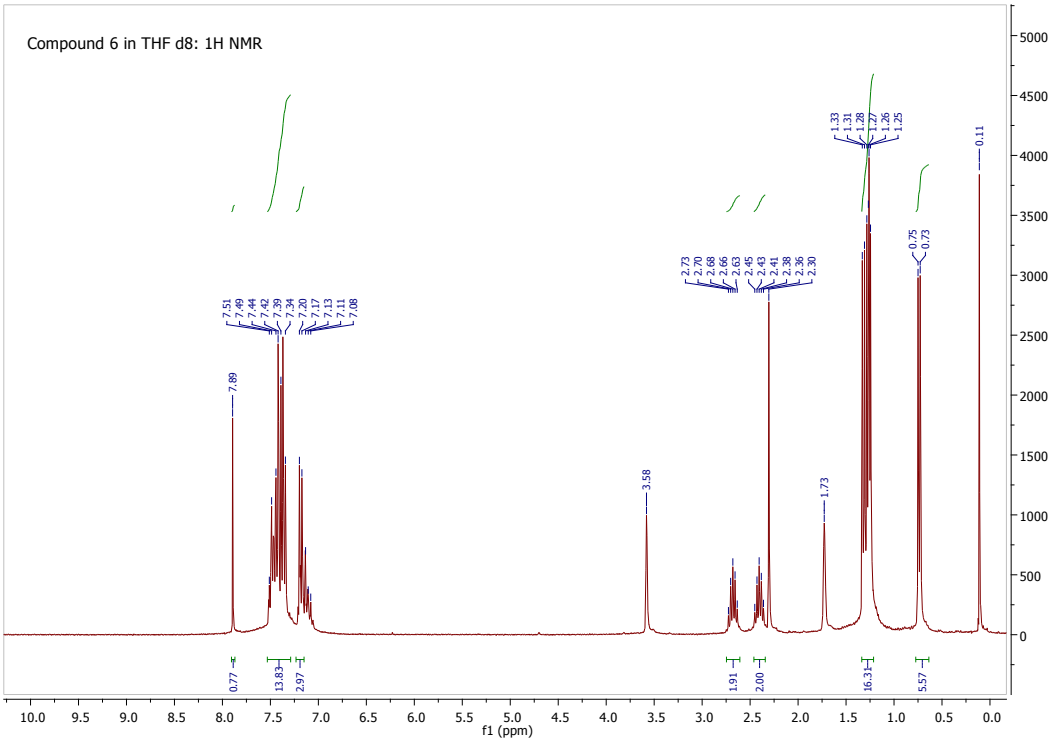
Plot 12: ^{1}H NMR (in CD_2Cl_2) spectrum of compound **5**.



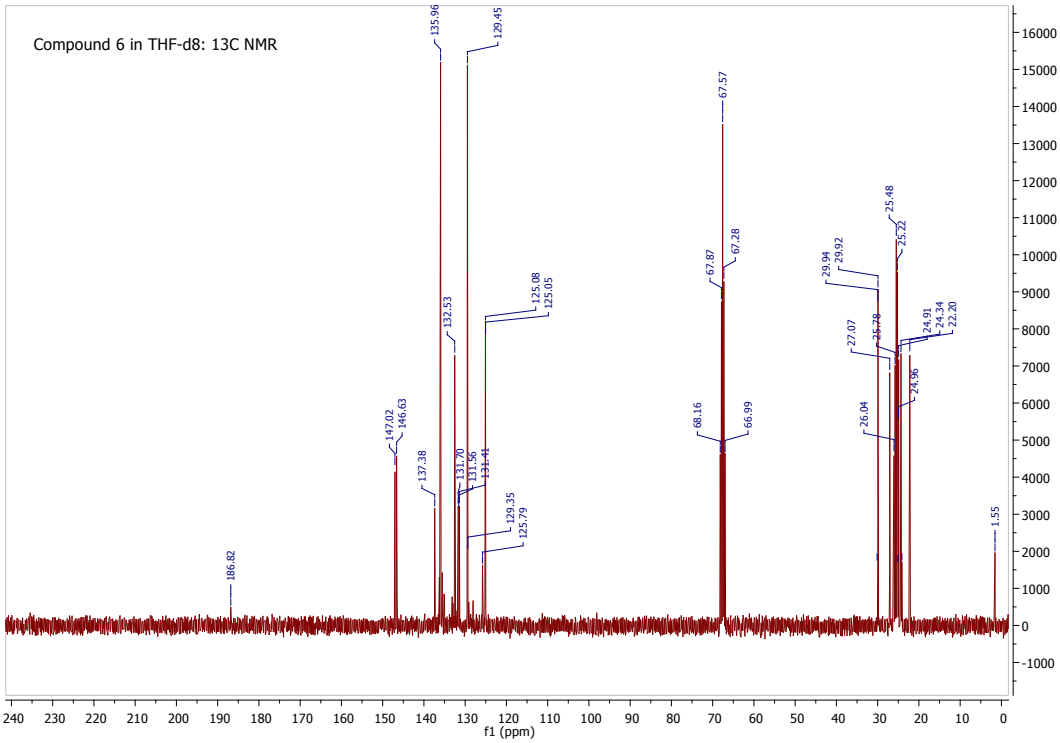
Plot 13: ^{13}C NMR (in CD_2Cl_2) spectrum of compound **5**.



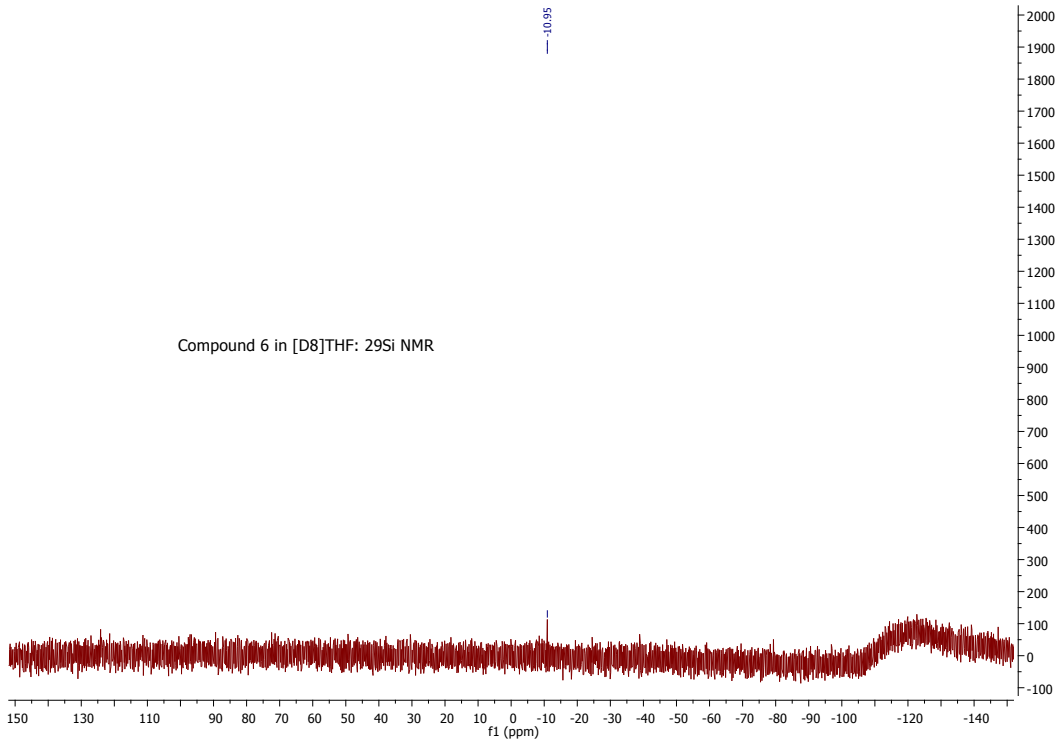
Plot 14: ^{29}Si NMR (in CD_2Cl_2) spectrum of compound **5**.



Plot 15: ^{1}H NMR (in $[D_8]THF$) spectrum of compound **6**.



Plot 16: ^{13}C NMR (in $[D_8]THF$) spectrum of compound **6**.



Plot 17: ^{29}Si NMR (in [D_8]THF) spectrum of compound **6**.

X-ray crystallography

Table S1 Crystallographic detail for compounds **2**, **4**, **5** and **6**.

Compound	**2** (PhMe)	**4** (PhMe)	**5** (3 CH_2Cl_2)	**6** (PhMe)
Empirical formula	$C_{72.44}H_{87.36}N_4Si$	$C_{46}H_{53}ClN_2$ Si	$C_{69}H_{86}Cl_8Cu_2N_4Si$	$C_{46}H_{53}Cl_2CuN_2Si$
CCDC no.	982101	982103	982104	982102
Molecular weight	1042.19	697.44	1410.18	796.43
Crystal size [mm]	0.1 x 0.1 x 0.07	0.19 x 0.134 x 0.09	0.368 x 0.190 x 0.964	0.235 x 0.196 x 0.150
Crystal system	monoclinic	triclinic	orthorhombic	monoclinic
Space group	$P\,2_1/c$	$P\bar{1}$	$Pna2_1$	$P2_1/c$
a [Å]	13.646(2)	10.900(2)	24.735(3)	11.380(2)
b [Å]	20.372(2)	11.162(2)	11.999(2)	15.471(2)
c [Å]	22.809(2)	18.612(3)	23.789(2)	24.575(3)
α [°]	90	78.13(2)	90	90
β [°]	95.89(2)	79.30(3)	90	98.03(2)
γ [°]	90	65.94(2)	90	90
V [Å ^{3}]	6307.3(13)	2010.3(7)	7060.5(16)	4301.9(11)
Z	4	2	4	4
Temperature [K]	101(2)	100(2)	100(2)	100(2)
ρ [gcm^{-3}]	1.098	1.152	1.327	1.230
μ [mm^{-1}]	0.081	0.158	0.964	0.692
F (000)	2256	748	2944	1680
θ-area [°]	1.343 to 26.029	1.125 to 27.483	1.647 to 26.347	1.558 to 26.378
Reflections collected.	102837	55303	226192	97304
Independent reflections	12433 [R(int) = 0.0485]	9200 [R(int) = 0.0418]	14390 [R(int) = 0.0340]	8799 [R(int) = 0.0519]
Number of restraints	840	459	2847	0
Parameters	850	523	1003	478
$R1$ [$I>2\sigma(I)$]	0.0449	0.0410	0.0352	0.0288
$wR2$ [$I>2\sigma(I)$]	0.1072	0.0965	0.0955	0.0697
$R1$ [all data]	0.0608	0.0541	0.0373	0.0368
$wR2$ [all data]	0.1170	0.1034	0.0968	0.0740
GooF	1.029	1.049	1.075	1.036
Largest diff. peak / hole [e· Å^{-3}]	0.343 and -0.259	0.354 and -0.346	0.824 and -0.561	0.367 and -0.272

Refinement of compound 5: The molecular structure of compound **5** shows pseudo-symmetry. It can also be refined in space group *Pccn*, but then the results are much poorer (Table S2). To identify the correct space group we had a closer look at the weak reflection.[1] A good figure of merit is the K value calculated as $K = |[F_O^2]|/|[F_C^2]|$ for reflections with low intensity (Table S2).[2] In this case the K value for *P*na2$_{(1)}$ does not deviate much from unity compared to the *P*ccn model. Furthermore the R1 (%) value drops from 7.94 (in *Pccn*) down to 3.62 (in *Pna*2$_{(1)}$), indicating that the space group *Pna*2$_{(1)}$ fits best. Additionally the systematic absences of space group *Pccn* are not fulfilled (Table S3).

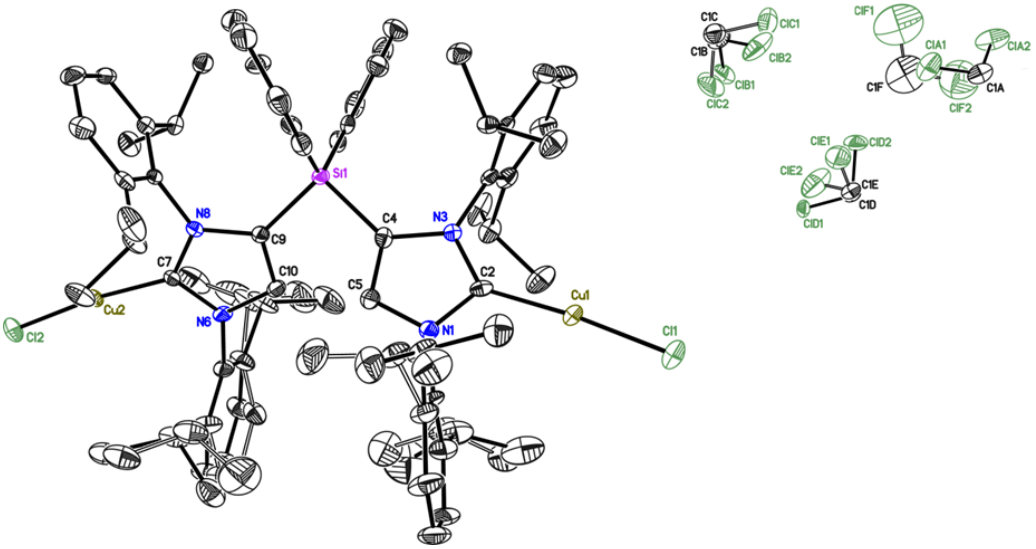


Figure F1: Molecular structure of $Ph_2Si\{(IPr^H)CuCl\}_2$ (**5**) with three dichloromethane molecules in the asymmetric unit. Anisotropic displacement parameters are depicted at the 50% probability level. All hydrogen atoms are omitted for clarity. The dichloromethane molecules are disordered on the two positions each. The site occupation factor refine to 0,691(8), 0.717(5), 0.683(6)).

Table S2. K-value for the reflections with weakest intensity and R1 for all data for the two space groups *P*ccn and *P*na2$_{(1)}$

	Pccn	***Pna*2$_{(1)}$**
K for the reflections with weakest intensity	8.842	1.291
R1 all data [%]	8.19	3.73

Table S3. Abstract of the program XPREP –Reciprocal space exploration- Version 2013/2 for Windows

Systematic absence exceptions:

	b--	**c--**	**n--**	**21--**	**-c-**	**-a-**	**-n-**	**-21-**	**--a**	**--b**	**--n**	**--21**
N	6535	6554	6487	72	3155	3196	3197	121	3149	3158	3165	127
N I>3s	2925	26	2941	9	1472	2166	2176	37	1466	1492	48	20
<I>	29.8	0.1	30.0	0.2	1.9	31.6	31.7	0.6	23.1	23.0	0.2	0.4
<I/s>	10.9	0.5	11.0	1.1	4.9	12.9	13.0	2.2	11.0	11.0	0.6	1.8

Identical indices and Friedel opposites combined before calculating R(sym)

Option	**Space Group**	**No.**	**Type**	**Axes**	**CSD**	**R(sym)**	**N(eq)**	**Syst.**	**Abs.**	**CFOM**
[A]	*Pna*2$_{(1)}$	#33	Non-cen	5	903	0.014	20848	2.2	4.9	5.73
[B]	*Pnma*	#62	centro	4	894	0.014	20848	2.2	4.9	2.64

In space group $Pna2_{(1)}$ the structure crystallizes as a twin by inversion. The fractional contribution of the minor domain refines to 0.19(2). All solvent molecules are severely disordered (Fig. F1). Although we tried to resolve the disorder, the results are not quit satisfying leading to still relatively high residual density. Trials with the SQUEEZE routine of the PLATON program package did not improve the model.[3] The large non-solvent Ueq(max)/Ueq(min) ratio of 6.6 is caused by disorder of the isopropyl groups.

References:

1 (a) M. Walker, E. Pohl, R. Herbst-Irmer, M. Gerlitz, J. Rohr and G. M. Sheldrick, *Acta Cryst. B,* 1999, **55**, 607-616; (b) R. Marsh, *Acta Cryst. B,* 1986, **42**, 193-198; (c) R. Marsh, *Acta Cryst. B,* 1981, **37**, 1985-1988; (d) V. Schomaker and R. E. Marsh, *Acta Cryst. B,* 1979, **35**, 1933-1934.

2 H. Flack, *Acta Cryst. A,* 1983, 876−881.

3 (a) A. L. Spek*, J. Appl. Cryst.,* 2003, **36**, 7-13; (b) P. van der Sluis and A. L. Spek, *Acta Cryst., A* 1990, **46**, 194−201.