SUPPLEMENTARY INFORMATION

for

Silanetriols as powerful starting materials for the selective condensation to bulky POSS cages

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a) Crystallographic Data

b) Spectroscopic Data

Crystallographic Data

Table S1: Crystal data and structure refinement for **2b**, **2d**, **2g** and **4a-d**.

	2b	**2d**	**2g**	**4a**	**4b**	**4c**	**4d**
Formula	$C_{10}H_{26}O_5Si_2$	$C_{14}H_{34}O_5Si_2$	$C_{20}H_{46}O_5Si_2$	$C_{32}H_{72}O_{12}Si_8$	$C_{40}H_{88}O_{12}Si_8$	$C_{48}H_{104}O_{12}Si_8$	$C_{56}H_{120}O_{12}Si_8$
Formular weight	282.49	338.59	422.75	873.62	985.81	1098.03	1210.24
Temperature [K]	100	100	100	100	100	100	173(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	monoclinic	triclinic	trigonal	triclinic	monoclinic
Space group	*C 2/m*	*C222$_1$*	*C 2/c*	*P-1*	*R-3c*	*P-1*	*P 2$_1$/n*
Unit cell dimensions:							
***a* [Å]**	7.2163(4)	10.1695(11)	7.2195(4)	10.7426(14)	13.2192(4)	10.8944(4)	14.1192(9)
***b* [Å]**	10.1628(5)	7.2991(8)	10.0508(5)	11.0102(13)	13.2192(4)	12.6042(4)	12.8237(5)
***c* [Å]**	10.6832(5)	27.408(4)	35.0554(17)	11.8640(14)	53.3347(18)	13.4936(5)	20.1991(12)
***α* [°]**	90	90	90	111.291(9)	90	68.8952(11)	90
***β* [°]**	98.452(1)	90	92.856(2)	72.229(9)	90	87.8745(12)	97.065(5)
***γ* [°]**	90	90	90	94.686(10)	120	66.4831(11)	90
Volume [Å^3]	774.97(7)	2034.5(4)	2540.5(2)	1244.4(3)	8071.4(5)	1572.7(1)	3629.5(3)
Z	2	4	4	1	6	1	2
Calcd. density [mg/m^3]	1.211	1.105	1.105	1.166	1.217	1.159	1.107
***μ* [mm^{-1}]**	0.236	0.190	0.164	0.264	0.252	0.222	0.198
***Θ*-range for data collected [°]**	3.49-30.00	1.49-24.99	2.33-26.00	1.93-24.84	2.34-30.00	1.98-30.00	1.67 - 25.00
Goodness-of-fit on F^2	1.082	1.089	1.169	1.013	1.064	1.055	1.003
***R*$_1$ (obsd. data)**	0.0348	0.0685	0.0745	0.0454	0.0416	0.0264	0.0745
***wR*$_2$ (all data)**	0.0967	0.1752	0.1649	0.1334	0.1280	0.0783	0.2028
***R*$_{int}$**	0.0167	0.1641	0.0232	0.0537	0.0238	0.0168	0.1663
r.e.d. min/max [e Å^{-3}]	-0.280/0.627	-0.319/1.049	-0.736/0.654	-0.458/0.349	-0.408/0.744	-0.365/0.519	-0.547/0.515

X-ray diffraction data of 2b. All the measurements were performed using graphite-monochromatized Mo K_α radiation at 100K: $C_{10}H_{26}O_5Si_2$, M_r 282.49, monoclinic, space group C 2/m, a = 7.2163(4) Å, b = 10.1628(5) Å, c = 10.6832(5) Å, β = 98.4520(10)°, V = 774.97(7) $Å^3$, Z = 2, d_{calc} = 1.211 g cm^{-3} μ = 0.236 mm^{-1}. A total of 2799 reflections were collected (Θ_{max} = 30.0°), from which 1164 were unique (R_{int} = 0.0167), with 1095 having I > 2σ(I). The structure was solved by direct methods (SHELXS-97)[2] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97)[2]. The H atoms of the OH group are disordered over two sites. They were refined with a common isotropic displacement parameter and with site occupation factors of 0.5. Only the bond length was fixed to be 0.84 Å, no angular or conformational constraints were applied. The 2-methyl-2-butyl group is disordered over two sites: the central C atom and one methyl group lie on the crystallographic mirror plane, the methyl group on one side and the ethyl group on the other side of that plane are disordered through the plane and were refined with site occupation factors of 0.5. The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the disordered CH_2 group were included at calculated positions at C–H distances of 0.99 Å with their isotropic displacement parameters fixed to 1.2 times U_{eq} of the C atom they are bonded to. The H atoms of the ordered methyl group were refined with a common isotropic displacement parameter and idealized geometry with tetrahedral angles, staggered conformation, and C-H distances of 0.98 Å. The H atoms of the disordered methyl group were included at calculated positions with their isotropic displacement parameters fixed to 1.3 times U_{eq} of the C atom they are bonded to. For 67 parameters final *R* indices of R_1 = 0.0348 and wR_2 = 0.0967 (GOF = 1.082) were obtained. The largest peak in a difference Fourier map was 0.627 $eÅ^{-3}$.

X-ray Crystal Structure. The crystal structure analysis of **2b** confirmed the compound as 1,3-di(2-methyl-2-butyl)-1,1,3,3-tetrahydroxydisiloxane. The molecules lie with the central O atom O1 on a crystallographic symmetry element 2/m (= C_{2h} symmetry) and is therefore disordered around the mirror plane. The Si–O–Si angle is restricted by symmetry to 180° as also observed in 1,3-di(*tert*-butyl)-1,1,3,3-tetrahydroxydisiloxane[3] (inversion center). In the other modification of the latter compound[4] and in the 1,3-di(phenyl) derivative[5] Si–O–Si angles of 165.57° and 153.75°, resp., were observed. In the packing the molecules aggregate to sheets normal to the c-axis. The molecules are held together by strong hydrogen bonds. The same hydrogen bonding scheme is also identifiable in all the other 1,1,3,3-tetrahydroxydisiloxanes with known crystal structure[3, 4, 5].

References

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(2) G. M. Sheldrick, Acta Cryst. A 64, 112-122 (2008).

(3) P. D. Lickiss, S. A. Litster, A. D. Redhouse, C. J. Wisener (1991) Chem. Commun. 173.

(4) S. Spirk, M. Nieger, F. Belaj, R. Pietschnig (2009) Dalton Trans. 163.

(5) K. Suyama, T. Nakatuka, T. Gunji, Y. Abe (2007) J. Organomet. Chem. 692, 2028.

Table S2. Crystal data and structure refinement for **2b**.

Crystal data		
Identification code		NH156
Empirical formula		$C_{10}H_{26}O_5Si_2$
Formula weight		282.49
Crystal description		plate, colourless
Crystal size		0.40 x 0.38 x 0.18mm
Crystal system, space group		monoclinic, C 2/m
Unit cell dimensions:	a	7.2163(4)Å
	b	10.1628(5)Å
	c	10.6832(5)Å
	ß	98.4520(10)°
Volume		774.97(7)Å³
Z		2
Calculated density		1.211Mg/m³
F(000)		308
Linear absorption coefficient µ		$0.236mm^{-1}$
Absorption correction		semi-empirical from equivalents
Max. and min. transmission		1.000 and 0.827
Unit cell determination		3.49 <Θ< 30.48°
		2261 reflections used at 100K
Data collection		
Temperature		100K
Diffractometer		Bruker APEX-II CCD
Radiation source		fine-focus sealed tube
Radiation and wavelength		MoK_α, 0.71073Å
Monochromator		graphite
Scan type		ϕ and ω scans
Θ range for data collection		3.49 to 30.00°
Index ranges		$-10 \le h \le 7$, $-14 \le k \le 12$, $-15 \le l \le 15$
Reflections collected / unique		2799 / 1164
Significant unique reflections		1095 with $I > 2\sigma(I)$
R(int), R(sigma)		0.0167, 0.0160
Completeness to Θ = 30.0°		98.1%
Refinement		
Refinement method		Full-matrix least-squares on F²
Data / parameters / restraints		1164 / 67 / 2
Goodness-of-fit on F²		1.082
Final R indices [I > 2σ(I)]		$R_1 = 0.0348$, $wR_2 = 0.0940$
R indices (all data)		$R_1 = 0.0369$, $wR_2 = 0.0967$
Extinction expression		none
Weighting scheme		$w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P=(F_o^2+2F_c^2)/3$
Weighting scheme parameters a, b		0.0563, 0.5737
Largest Δ/σ in last cycle		0.001
Largest difference peak and hole		0.627 and -0.280e/Å³
Structure Solution Program		SHELXS-97 (Sheldrick, 2008)
Structure Refinement Program		SHELXL-97 (Sheldrick, 2008)

Table S3. Hydrogen bonds for **2b** [Å, °].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(2)-H(1)···O(2)[i)]	0.84	1.820(3)	2.6585(15)	176(3)
O(2)-H(2)···O(2)[ii)]	0.84	1.824(2)	2.6626(16)	177(3)

Symmetry transformations used to generate equivalent atoms:
[i)] 1-x, y, 2-z ;[ii)] 3/2-x, 3/2-y, 2-z

Table S4. Atomic coordinates, site occupation factors, and equivalent isotropic displacement parameters (Å²) for **2b**. U_{eq} is defined as one third of the trace of the orthogonalizedU_{ij} tensor.

	x	y	z	s.o.f.	U_{eq}
O(1)	1	0.5	1	1	0.0240(3)
Si(1)	0.78370(5)	0.5	0.93746(4)	1	0.01463(14)
O(2)	0.68097(11)	0.62840(8)	0.98862(9)	1	0.0233(2)
C(1)	0.7648(3)	0.5	0.76238(17)	1	0.0315(4)
C(2)	0.5493(4)	0.5	0.7087(2)	1	0.0509(6)
C(3)	0.8487(9)	0.3751(9)	0.7187(9)	0.5	0.0338(16)
C(4)	0.8741(16)	0.6251(10)	0.7245(10)	0.5	0.064(3)
C(5)	0.8441(9)	0.6504(5)	0.5799(4)	0.5	0.0766(16)

Table S5. Hydrogen coordinates, site occupation factors, and isotropic displacement parameters (Å²) for **2b**.

	x	y	z	s.o.f.	U_{iso}
H(1)	0.5655(9)	0.627(3)	0.992(3)	0.5	0.023(5)
H(2)	0.728(4)	0.7041(13)	0.998(3)	0.5	0.023(5)
H(21)	0.5329	0.5	0.6160	1	0.077(6)
H(22)	0.4905	0.5787	0.7384	1	0.077(6)
H(31)	0.8487	0.3790	0.6270	0.5	0.044
H(32)	0.7742	0.2995	0.7390	0.5	0.044
H(33)	0.9776	0.3656	0.7617	0.5	0.044
H(41)	0.8319	0.7032	0.7679	0.5	0.077
H(42)	1.0096	0.6131	0.7542	0.5	0.077
H(51)	0.9146	0.7287	0.5616	0.5	0.100
H(52)	0.7105	0.6643	0.5503	0.5	0.100
H(53)	0.8882	0.5742	0.5365	0.5	0.100

Table S6. Anisotropic displacement parameters (Å²) for **2b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O(1)	0.0086(6)	0.0247(8)	0.0382(9)	0	0.0022(6)	0
Si(1)	0.0094(2)	0.0093(2)	0.0250(2)	0	0.00191(14)	0
O(2)	0.0158(4)	0.0121(4)	0.0429(5)	-0.0035(3)	0.0074(3)	0.0013(3)
C(1)	0.0481(11)	0.0195(8)	0.0257(8)	0	0.0015(7)	0
C(2)	0.0601(16)	0.0451(13)	0.0412(12)	0	-0.0132(11)	0
C(3)	0.0316(16)	0.033(3)	0.039(3)	-0.011(2)	0.0117(15)	-0.0030(17)
C(4)	0.126(7)	0.038(4)	0.031(3)	0.003(3)	0.019(4)	-0.036(4)
C(5)	0.133(5)	0.058(3)	0.0436(19)	0.0101(18)	0.027(2)	-0.019(3)

Table S7. Full list of bond lengths [Å] and angles [°] for **2b**.

O(1)-Si(1)	1.6050(4)
Si(1)-O(2)	1.6340(8)
Si(1)-C(1)	1.8553(19)
O(2)-H(1)	0.84
O(2)-H(2)	0.84
C(1)-C(3)	1.510(9)
C(1)-C(2)	1.577(3)
C(1)-C(4)	1.580(11)
C(2)-H(21)	0.98
C(2)-H(22)	0.98
C(3)-H(31)	0.98
C(3)-H(32)	0.98
C(3)-H(33)	0.98
C(4)-C(5)	1.549(11)
C(4)-H(41)	0.99
C(4)-H(42)	0.99
C(5)-H(51)	0.98
C(5)-H(52)	0.98
C(5)-H(53)	0.98

O(1)-Si(1)-O(2)	108.79(3)
O(2)-Si(1)-O(2)$^{i)}$	105.99(6)
Si(1)-O(1)-Si(1)$^{ii)}$	180.0
O(1)-Si(1)-C(1)	110.03(7)
O(2)-Si(1)-C(1)	111.56(5)
Si(1)-O(2)-H(1)	121(2)
Si(1)-O(2)-H(2)	125(2)
H(1)-O(2)-H(2)	113(3)
C(3)-C(1)-C(3)$^{i)}$	114.5(6)
C(3)-C(1)-C(2)	107.8(3)
C(3)-C(1)-C(4)	111.1(3)
C(2)-C(1)-C(4)	114.2(4)
C(4)-C(1)-C(4)$^{i)}$	107.2(8)
C(3)-C(1)-Si(1)	109.8(4)
C(2)-C(1)-Si(1)	106.81(16)
C(4)-C(1)-Si(1)	107.0(4)
C(5)-C(4)-C(1)	112.8(7)
C(1)-C(2)-H(21)	109.5
C(1)-C(2)-H(22)	109.5
H(21)-C(2)-H(22)	109.5
H(22)-C(2)-H(22)$^{i)}$	109.5
C(1)-C(3)-H(31)	109.5
C(1)-C(3)-H(32)	109.5
H(31)-C(3)-H(32)	109.5
C(1)-C(3)-H(33)	109.5
H(31)-C(3)-H(33)	109.5
H(32)-C(3)-H(33)	109.5
C(5)-C(4)-H(41)	109.0
C(1)-C(4)-H(41)	109.0
C(5)-C(4)-H(42)	109.0
C(1)-C(4)-H(42)	109.0
H(41)-C(4)-H(42)	107.8
C(4)-C(5)-H(51)	109.5
C(4)-C(5)-H(52)	109.5
H(51)-C(5)-H(52)	109.5
C(4)-C(5)-H(53)	109.5
H(51)-C(5)-H(53)	109.5
H(52)-C(5)-H(53)	109.5

O(1)-Si(1)-C(1)-C(3)	63.3(2)
O(2)$^{i)}$-Si(1)-C(1)-C(3)	-57.5(3)
O(2)-Si(1)-C(1)-C(3)	-175.8(2)
O(1)-Si(1)-C(1)-C(3)$^{i)}$	-63.3(2)
O(2)$^{i)}$-Si(1)-C(1)-C(3)$^{i)}$	175.8(2)
O(2)-Si(1)-C(1)-C(3)$^{i)}$	57.5(3)
O(1)-Si(1)-C(1)-C(2)	180.0
O(2)$^{i)}$-Si(1)-C(1)-C(2)	59.16(4)
O(2)-Si(1)-C(1)-C(2)	-59.16(4)
O(1)-Si(1)-C(1)-C(4)$^{i)}$	57.3(4)
O(2)$^{i)}$-Si(1)-C(1)-C(4)$^{i)}$	-63.5(4)
O(2)-Si(1)-C(1)-C(4)$^{i)}$	178.1(4)
O(1)-Si(1)-C(1)-C(4)	-57.3(4)
O(2)$^{i)}$-Si(1)-C(1)-C(4)	-178.1(4)
O(2)-Si(1)-C(1)-C(4)	63.5(4)
C(3)-C(1)-C(4)-C(5)	69.3(8)
C(3)$^{i)}$-C(1)-C(4)-C(5)	-54(6)
C(2)-C(1)-C(4)-C(5)	-52.9(7)
C(4)$^{i)}$-C(1)-C(4)-C(5)	74.6(9)
Si(1)-C(1)-C(4)-C(5)	-170.9(5)

Symmetry transformations used to generate equivalent atoms:
$^{i)}$ x, 1-y, z $^{ii)}$ 2-x, 1-y, 2-z

X-ray diffraction data of 2d.

Table S8. Crystal data and structure refinement for **2d**.

Crystal data		
Identification code		i1044
Empirical formula		$C_{14}H_{34}O_5Si_2$
Formula weight		338.59
Crystal description		plate, colourless
Crystal size		0.58 x 0.31 x 0.01 mm
Crystal system, space group		orthorhombic, C 2 2 21
Unit cell dimensions:	a	10.1695(11) Å
	b	7.2991(8) Å
	c	27.408(4) Å
	α	90 °
Volume		2034.5(4) Å³
Z		4
Calculated density		1.105 Mg/m³
F(000)		744
Linear absorption coefficient μ		0.190 mm^{-1}
Absorption correction		integration
Max. and min. transmission		0.9972 and 0.9012
Data collection		
Temperature		100(2) K
Diffractometer		STOE IPDS
Radiation source		sealed X-ray tube, 12 x 0.4 mm long-fine focus
Radiation and wavelength		MoK_α, 0.71073 Å
Monochromator		graphite
θ range for data collection		1.49 to 24.99°
Index ranges		$-12 \le h \le 12$, $-7 \le k \le 8$, $-32 \le l \le 32$
Reflections collected		6611
Independent reflections		1051
R(int)		0.1641
Refinement		
Refinement method		Full-matrix least-squares on F^2
Data / parameters / restraints		1051 / 4 / 111
Goodness-of-fit on F^2		1.089
Final R indices [$I > 2\sigma(I)$]		$R_1 = 0.0686$, $wR_2 = 0.1714$
R indices (all data)		$R_1 = 0.0711$, $wR_2 = 0.1732$
Extinction expression		none
Largest difference peak and hole		1.038 and -0.314 e/Å³
Structure Solution Program		SHELXS-97 (Sheldrick, 2008)
Structure Refinement Program		SHELXL-97 (Sheldrick, 2008)

Table S9. Hydrogen bonds for **2d** [Å, °].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(2)-H(22A)···O(3)[i)]	0,892	1,817	2,658	156,10
O(2)-H(22B)···O(2)[ii)]	0,899	1,917	2,706	145,57
O(3)-H(33A)···O(3)[ii)]	0,902	1,806	2,677	161,74
O(3)-H(33B)···O(2)[iii)]	0,895	1,898	2,658	141,67

Symmetry transformations used to generate equivalent atoms:
[i)]x-1/2, -y-1/2, -z ; [ii)]x, -y-1, -z ; [iii)] x+1/2, -y-1/2,-z

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å² x 10^3) for **2d**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	-6193(1)	-1934(2)	-914(1)	33(1)
C(2)	-6198(2)	-3942(2)	-1105(1)	38(1)
C(3)	-6506(2)	-4248(3)	-1643(1)	46(1)
C(4)	-6355(2)	-6251(3)	-1796(1)	54(1)
C(5)	-6785(2)	-6639(4)	-2314(1)	72(1)
C(6)	-7496(2)	-958(2)	-1045(1)	39(1)
C(7)	-5021(2)	-838(3)	-1124(1)	45(1)
O(1)	-5975(2)	0	0	37(1)
O(2)	-7296(1)	-3147(2)	12(1)	35(1)
O(3)	-4726(1)	-3181(2)	-62(1)	34(1)
Si(1)	-6045(1)	-2046(1)	-230(1)	29(1)

Table S11. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å²x 10^3) for **2d**.

	x	y	z	U(eq)
H(2A)	-5322	-4479	-1037	45
H(2B)	-6847	-4642	-911	45
H(3A)	-5909	-3483	-1843	55
H(3B)	-7418	-3846	-1709	55
H(4B)	-5421	-6609	-1760	65
H(4A)	-6878	-7024	-1571	65
H(5A)	-7735	-6440	-2342	86
H(5B)	-6579	-7913	-2397	86
H(5C)	-6321	-5815	-2537	86
H(6A)	-7563	-833	-1400	46
H(6B)	-7512	259	-894	46
H(6C)	-8239	-1683	-923	46
H(7A)	-5107	-756	-1479	54
H(7B)	-4197	-1460	-1041	54
H(7C)	-5018	398	-984	54
H(22A)	-7998(8)	-2454(16)	75(9)	42
H(22B)	-7180(30)	-4264(10)	-119(5)	42
H(33A)	-4760(30)	-4346(9)	47(7)	41
H(33B)	-4127(9)	-2286(12)	-79(12)	41

Table S12. Anisotropic displacement parameters (Å² x 10^3) for **2d**. The anisotropic displacement factor exponent takes the form: $2\pi^2[h^2 a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U11	U22	U33	U23	U13	U12
C(1)	23(1)	26(1)	51(1)	-1(1)	0(1)	2(1)
C(2)	32(1)	32(1)	50(1)	2(1)	3(1)	7(1)
C(3)	42(1)	38(1)	56(1)	-1(1)	-2(1)	1(1)
C(4)	60(1)	45(1)	57(1)	-6(1)	-1(1)	6(1)
C(5)	81(2)	62(1)	74(1)	-23(1)	-14(1)	12(1)
C(6)	33(1)	24(1)	58(1)	3(1)	-6(1)	4(1)
C(7)	38(1)	40(1)	58(1)	5(1)	5(1)	-6(1)
O(1)	32(1)	21(1)	58(1)	-4(1)	0	0
O(2)	21(1)	30(1)	55(1)	0(1)	4(1)	-3(1)
O(3)	21(1)	20(1)	61(1)	2(1)	-3(1)	1(1)
Si(1)	20(1)	18(1)	49(1)	-1(1)	0(1)	1(1)

Table S13. Bond lengths [Å] and angles [°] for **2d**.

C(1)-C(7)	1.547(2)	C(3)-C(2)-H(2B)	107.9
C(1)-C(6)	1.547(2)	C(1)-C(2)-H(2B)	107.9
C(1)-C(2)	1.557(2)	H(2A)-C(2)-H(2B)	107.2
C(1)-Si(1)	1.8801(16)	C(2)-C(3)-C(4)	112.58(15)
C(2)-C(3)	1.525(3)	C(2)-C(3)-H(3A)	109.1
C(2)-H(2A)	0.9900	C(4)-C(3)-H(3A)	109.1
C(2)-H(2B)	0.9900	C(2)-C(3)-H(3B)	109.1
C(3)-C(4)	1.529(3)	C(4)-C(3)-H(3B)	109.1
C(3)-H(3A)	0.9900	H(3A)-C(3)-H(3B)	107.8
C(3)-H(3B)	0.9900	C(5)-C(4)-C(3)	114.01(18)
C(4)-C(5)	1.512(3)	C(5)-C(4)-H(4B)	108.8
C(4)-H(4B)	0.9900	C(3)-C(4)-H(4B)	108.8
C(4)-H(4A)	0.9900	C(5)-C(4)-H(4A)	108.8
C(5)-H(5A)	0.9800	C(3)-C(4)-H(4A)	108.8
C(5)-H(5B)	0.9800	H(4B)-C(4)-H(4A)	107.6
C(5)-H(5C)	0.9800	C(4)-C(5)-H(5A)	109.5
C(6)-H(6A)	0.9800	C(4)-C(5)-H(5B)	109.5
C(6)-H(6B)	0.9800	H(5A)-C(5)-H(5B)	109.5
C(6)-H(6C)	0.9800	C(4)-C(5)-H(5C)	109.5
C(7)-H(7A)	0.9800	H(5A)-C(5)-H(5C)	109.5
C(7)-H(7B)	0.9800	H(5B)-C(5)-H(5C)	109.5
C(7)-H(7C)	0.9800	C(1)-C(6)-H(6A)	109.5
O(1)-Si(1)#1	1.6232(4)	C(1)-C(6)-H(6B)	109.5
O(1)-Si(1)	1.6233(4)	H(6A)-C(6)-H(6B)	109.5
O(2)-Si(1)	1.6440(11)	C(1)-C(6)-H(6C)	109.5
O(2)-H(22A)	0.892(9)	H(6A)-C(6)-H(6C)	109.5
O(2)-H(22B)	0.899(9)	H(6B)-C(6)-H(6C)	109.5
O(3)-Si(1)	1.6427(11)	C(1)-C(7)-H(7A)	109.5
O(3)-H(33A)	0.902(8)	C(1)-C(7)-H(7B)	109.5
O(3)-H(33B)	0.895(9)	H(7A)-C(7)-H(7B)	109.5
C(7)-C(1)-C(6)	109.59(14)	C(1)-C(7)-H(7C)	109.5
C(7)-C(1)-C(2)	111.37(13)	H(7A)-C(7)-H(7C)	109.5
C(6)-C(1)-C(2)	110.66(13)	H(7B)-C(7)-H(7C)	109.5
C(7)-C(1)-Si(1)	109.38(11)	Si(1)#1-O(1)-Si(1)	174.98(12)
C(6)-C(1)-Si(1)	108.66(11)	Si(1)-O(2)-H(22A)	114.9(9)
C(2)-C(1)-Si(1)	107.10(11)	Si(1)-O(2)-H(22B)	100.3(15)
C(3)-C(2)-C(1)	117.63(14)	H(22A)-O(2)-H(22B)	134.5(19)
C(3)-C(2)-H(2A)	107.9	Si(1)-O(3)-H(33A)	122.5(19)
C(1)-C(2)-H(2A)	107.9	Si(1)-O(3)-H(33B)	100.0(8)

H(33A)-O(3)-H(33B)	137(2)	O(1)-Si(1)-C(1)	110.54(5)
O(1)-Si(1)-O(3)	108.60(7)	O(3)-Si(1)-C(1)	111.52(6)
O(1)-Si(1)-O(2)	109.05(7)	O(2)-Si(1)-C(1)	111.16(6)
O(3)-Si(1)-O(2)	105.81(6)		

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

X-ray diffraction data of 2g. All the measurements were performed using graphite-monochromatized Mo K_α radiation at 100 K: $C_{20}H_{46}O_5Si_2$, M_r 422.75, monoclinic, space group C 2/c, a = 7.2195(4) Å, b = 10.0508(5) Å, c = 35.0554(17) Å, β = 92.856(2)°, V = 2540.5(2) $Å^3$, Z = 4, d_{calc} = 1.105g cm^{-3}, μ = 0.164 mm^{-1}. A total of 7769 reflections were collected (Θ_{max} = 26.0°), from which 2471 were unique (R_{int} = 0.0232), with 2417 having I > 2σ(I). The structure was solved by direct methods (SHELXS-97)[2] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97)[2]. The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. Since twinning was detected a twin matrix (-1 0 0 / 0 1 0 / 1 0 -1) was applied and a scale factor was refined [0.0123(9)] between the two unequal components. The H atoms of the OH groups are disordered over two sites. They were refined with site occupation factors of 0.5 and with common isotropic displacement parameters for the H atoms bonded to the same O atom. Only the bond lengths were fixed to be 0.88 Å, no angular or conformational constraints were applied. The H atoms of the CH_2 groups were included at calculated positions with their isotropic displacement parameters fixed to 1.2 times U_{eq} of the C atom they are bonded to. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98 Å. For 144 parameters final *R* indices of R_1 = 0.0745 and wR_2 = 0.1649 (GOF = 1.169) were obtained. The largest peak in a difference Fourier map was 0.654 $eÅ^{-3}$.

Results and Discussion

X-ray Crystal Structure. The crystal structure analysis of **2g** confirmed the compound as 1,3-bis(1,1-dimethyloctyl)-1,1,3,3-tetrahydroxydisiloxane. The molecule is located with the central O atom O1 at a two-fold rotation axis and shows an unfolded conformation. The packing consists of two-dimensional sheets where the central parts of the molecules are held together by presumably strong [O···O 2.645(3)-2.663(4)Å, O–H···O > 167(7)°] hydrogen bonds. The H atoms of the OH groups are disordered over two sites and were refined with site occupation factors of 0.5. Each molecule is connected by 8 hydrogen bonds to its 6 neighbours.

References

(1) C. K. Johnson, ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA (1965).

(2) G. M. Sheldrick, Acta Cryst. A 64, 112-122 (2008).

Table S14. Crystal data and structure refinement for **2g**.

Crystal data		
Identification code		NH231A
Empirical formula		$C_{20}H_{46}O_5Si_2$
Formula weight		422.75
Crystal description		needles, colourless
Crystal size		0.38 x 0.32 x 0.20mm
Crystal system, space group		monoclinic, C 2/c
Unit cell dimensions:	a	7.2195(4)Å
	b	10.0508(5)Å
	c	35.0554(17)Å
	β	92.856(2)°
Volume		2540.5(2)Å^3
Z		4
Calculated density		1.105Mg/m^3
F(000)		936
Linear absorption coefficient μ		0.164mm^{-1}
Absorption correction		semi-empirical from equivalents
Max. and min. transmission		0.7462 and 0.6163
Unit cell determination		3.48° <Θ< 31.18°
		8860 reflections used at 100K
Data collection		
Temperature		100K
Diffractometer		Bruker APEX-II CCD
Radiation source		fine-focus sealed tube
Radiation and wavelength		MoK_α, 0.71073Å
Monochromator		graphite
Scan type		ϕ and ω scans
Θ range for data collection		2.33 to 26.00°
Index ranges		$-8 \le h \le 8$, $-12 \le k \le 12$, $-43 \le l \le 43$
Reflections collected / unique		7769 / 2471
Significant unique reflections		2417 with $I > 2\sigma(I)$
R(int), R(sigma)		0.0232, 0.0281
Completeness to Θ = 26.0°		98.6%
Refinement		
Refinement method		Full-matrix least-squares on F^2
Data / parameters / restraints		2471 / 144 / 4
Goodness-of-fit on F^2		1.169
Final R indices [$I > 2\sigma(I)$]		$R_1 = 0.0745$, $wR_2 = 0.1643$
R indices (all data)		$R_1 = 0.0755$, $wR_2 = 0.1649$
Extinction expression		none
Weighting scheme		$w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P = (F_o^2+2F_c^2)/3$
Weighting scheme parameters a, b		0.0187, 18.366
Largest Δ/σ in last cycle		0.001
Largest difference peak and hole		0.654 and -0.736e/Å^3
Structure Solution Program		SHELXS-97 (Sheldrick, 2008)
Structure Refinement Program		SHELXL-97 (Sheldrick, 2008)

Table S15. Hydrogen bonds for **2g** [Å, °].

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(DHA)
O(2)-H(21)···O(2)[i)]	0.88	1.780(12)	2.654(4)	172(8)
O(2)-H(22)···O(3)[ii)]	0.88	1.765(3)	2.645(3)	179(8)
O(3)-H(31)···O(2)[iii)]	0.88	1.781(17)	2.645(3)	167(7)
O(3)-H(32)···O(3)[i)]	0.88	1.784(7)	2.663(4)	176(8)

Symmetry transformations used to generate equivalent atoms:

[i)] 1-x, y, 3/2-z [ii)] 3/2-x, y-1/2, 3/2-z [iii)] 3/2-x, y+1/2, 3/2-z

Table S16. Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for **2g**. U_{eq} is defined as one third of the trace of the orthogonalizedU_{ij} tensor.

	x	y	z	U_{eq}
Si(1)	0.80222(11)	0.48508(7)	0.76917(2)	0.0113(2)
O(1)	1	0.4764(3)	0.75	0.0176(7)
O(2)	0.6818(3)	0.35256(19)	0.75777(7)	0.0179(5)
O(3)	0.6845(3)	0.60970(19)	0.75024(7)	0.0182(5)
C(11)	0.8381(5)	0.5027(4)	0.82184(10)	0.0227(7)
C(12)	0.6447(5)	0.5089(4)	0.83911(10)	0.0260(8)
C(13)	0.6429(5)	0.5416(4)	0.88187(10)	0.0308(9)
C(14)	0.4489(5)	0.5378(4)	0.89735(11)	0.0323(9)
C(15)	0.4510(6)	0.5670(5)	0.94017(12)	0.0428(11)
C(16)	0.2594(6)	0.5680(5)	0.95734(12)	0.0444(11)
C(17)	0.1429(6)	0.6883(6)	0.94687(13)	0.0455(12)
C(18)	-0.0424(6)	0.6886(6)	0.96671(14)	0.0525(13)
C(19)	0.9529(6)	0.3875(4)	0.83853(11)	0.0334(9)
C(20)	0.9442(5)	0.6353(4)	0.82942(10)	0.0292(8)

Table S17. Hydrogen coordinates, site occupation factors, and isotropic displacement parameters ($Å^2$) for **2g**.

	x	y	z	s.o.f.	U_{iso}
H(21)	0.5600(8)	0.350(7)	0.755(2)	0.50	0.021(14)
H(22)	0.725(10)	0.272(3)	0.755(2)	0.50	0.021(14)
H(31)	0.731(9)	0.687(3)	0.744(2)	0.50	0.021(14)
H(32)	0.5629(11)	0.608(7)	0.751(2)	0.50	0.021(14)
H(121)	0.5696	0.5767	0.8249	1	0.031
H(122)	0.5828	0.4220	0.8348	1	0.031
H(131)	0.7229	0.4770	0.8963	1	0.037
H(132)	0.6964	0.6313	0.8863	1	0.037
H(141)	0.3940	0.4488	0.8925	1	0.039
H(142)	0.3696	0.6041	0.8835	1	0.039
H(151)	0.5101	0.6548	0.9449	1	0.051
H(152)	0.5291	0.4994	0.9538	1	0.051
H(161)	0.1911	0.4871	0.9487	1	0.053
H(162)	0.2766	0.5634	0.9855	1	0.053
H(171)	0.1178	0.6900	0.9189	1	0.055
H(172)	0.2132	0.7697	0.9541	1	0.055
H(181)	-0.1162	0.7657	0.9581	1	0.077(11)
H(182)	-0.0183	0.6936	0.9944	1	0.077(11)
H(183)	-0.1107	0.6067	0.9603	1	0.077(11)
H(191)	1.0745	0.3866	0.8273	1	0.037(7)

H(192)	0.8887	0.3034	0.8328	1	0.037(7)
H(193)	0.9693	0.3983	0.8663	1	0.037(7)
H(201)	0.8677	0.7099	0.8199	1	0.032(6)
H(202)	1.0607	0.6338	0.8162	1	0.032(6)
H(203)	0.9711	0.6458	0.8569	1	0.032(6)

Table S18. Anisotropic displacement parameters ($Å^2$) for **2g**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si(1)	0.0053(4)	0.0041(4)	0.0245(4)	-0.0002(3)	0.0012(3)	0.0004(3)
O(1)	0.0067(14)	0.0174(15)	0.0291(17)	0	0.0034(12)	0
O(2)	0.0077(11)	0.0072(10)	0.0390(14)	-0.0046(9)	0.0021(9)	-0.0028(8)
O(3)	0.0079(11)	0.0129(11)	0.0337(13)	0.0023(9)	0.0011(9)	0.0008(8)
C(11)	0.0140(16)	0.0274(18)	0.0266(17)	0.0005(14)	-0.0002(12)	-0.0024(14)
C(12)	0.0170(17)	0.033(2)	0.0280(18)	-0.0003(15)	0.0033(13)	-0.0014(15)
C(13)	0.0197(19)	0.044(2)	0.0293(19)	-0.0028(17)	0.0039(14)	-0.0005(16)
C(14)	0.022(2)	0.044(2)	0.031(2)	0.0018(17)	0.0066(15)	0.0000(17)
C(15)	0.027(2)	0.071(3)	0.031(2)	-0.001(2)	0.0079(17)	0.005(2)
C(16)	0.031(2)	0.072(3)	0.030(2)	0.001(2)	0.0090(17)	0.002(2)
C(17)	0.026(2)	0.075(3)	0.035(2)	-0.005(2)	0.0050(17)	0.000(2)
C(18)	0.025(2)	0.080(4)	0.053(3)	-0.014(3)	0.008(2)	-0.001(2)
C(19)	0.024(2)	0.048(2)	0.0284(19)	0.0090(17)	-0.0008(15)	0.0113(18)
C(20)	0.0193(18)	0.046(2)	0.0222(17)	-0.0089(16)	-0.0013(13)	-0.0099(16)

Table S19. Full list of bond lengths [Å] and angles [°] for **2g**.

Si(1)-O(1)	1.6104(8)	C(18)-H(181)	0.98
Si(1)-O(2)	1.630(2)	C(18)-H(182)	0.98
Si(1)-O(3)	1.636(2)	C(18)-H(183)	0.98
Si(1)-C(11)	1.860(3)	C(19)-H(191)	0.98
O(2)-H(21)	0.88	C(19)-H(192)	0.98
O(2)-H(22)	0.88	C(19)-H(193)	0.98
O(3)-H(31)	0.88	C(20)-H(201)	0.98
O(3)-H(32)	0.88	C(20)-H(202)	0.98
C(11)-C(19)	1.524(5)	C(20)-H(203)	0.98
C(11)-C(12)	1.551(5)		
C(11)-C(20)	1.553(5)	O(1)-Si(1)-O(2)	109.07(13)
C(12)-C(13)	1.535(5)	O(1)-Si(1)-O(3)	109.03(12)
C(12)-H(121)	0.99	O(2)-Si(1)-O(3)	105.44(11)
C(12)-H(122)	0.99	O(1)-Si(1)-C(11)	109.67(11)
C(13)-C(14)	1.528(5)	O(2)-Si(1)-C(11)	111.56(15)
C(13)-H(131)	0.99	O(3)-Si(1)-C(11)	111.94(15)
C(13)-H(132)	0.99	Si(1)-O(1)-Si(1)$^{i)}$	173.8(2)
C(14)-C(15)	1.529(5)	Si(1)-O(2)-H(21)	125(5)
C(14)-H(141)	0.99	Si(1)-O(2)-H(22)	127(5)
C(14)-H(142)	0.99	H(21)-O(2)-H(22)	109(7)
C(15)-C(16)	1.536(6)	Si(1)-O(3)-H(31)	126(5)
C(15)-H(151)	0.99	Si(1)-O(3)-H(32)	118(5)
C(15)-H(152)	0.99	H(31)-O(3)-H(32)	115(7)
C(16)-C(17)	1.508(7)	C(19)-C(11)-C(12)	111.3(3)
C(16)-H(161)	0.99	C(19)-C(11)-C(20)	109.4(3)
C(16)-H(162)	0.99	C(12)-C(11)-C(20)	110.2(3)
C(17)-C(18)	1.538(6)	C(19)-C(11)-Si(1)	110.8(3)
C(17)-H(171)	0.99	C(12)-C(11)-Si(1)	107.9(2)
C(17)-H(172)	0.99	C(20)-C(11)-Si(1)	107.1(2)

C(13)-C(12)-C(11)	116.2(3)	C(17)-C(18)-H(181)	109.5
C(13)-C(12)-H(121)	108.2	C(17)-C(18)-H(182)	109.5
C(11)-C(12)-H(121)	108.2	H(181)-C(18)-H(182)	109.5
C(13)-C(12)-H(122)	108.2	C(17)-C(18)-H(183)	109.5
C(11)-C(12)-H(122)	108.2	H(181)-C(18)-H(183)	109.5
H(121)-C(12)-H(122)	107.4	H(182)-C(18)-H(183)	109.5
C(14)-C(13)-C(12)	113.2(3)	C(11)-C(19)-H(191)	109.5
C(14)-C(13)-H(131)	108.9	C(11)-C(19)-H(192)	109.5
C(12)-C(13)-H(131)	108.9	H(191)-C(19)-H(192)	109.5
C(14)-C(13)-H(132)	108.9	C(11)-C(19)-H(193)	109.5
C(12)-C(13)-H(132)	108.9	H(191)-C(19)-H(193)	109.5
H(131)-C(13)-H(132)	107.8	H(192)-C(19)-H(193)	109.5
C(13)-C(14)-C(15)	112.3(3)	C(11)-C(20)-H(201)	109.5
C(13)-C(14)-H(141)	109.1	C(11)-C(20)-H(202)	109.5
C(15)-C(14)-H(141)	109.1	H(201)-C(20)-H(202)	109.5
C(13)-C(14)-H(142)	109.1	C(11)-C(20)-H(203)	109.5
C(15)-C(14)-H(142)	109.1	H(201)-C(20)-H(203)	109.5
H(141)-C(14)-H(142)	107.9	H(202)-C(20)-H(203)	109.5
C(14)-C(15)-C(16)	114.9(4)	O(1)-Si(1)-C(11)-C(19)	-57.2(3)
C(14)-C(15)-H(151)	108.5	O(2)-Si(1)-C(11)-C(19)	63.8(3)
C(16)-C(15)-H(151)	108.5	O(3)-Si(1)-C(11)-C(19)	-178.3(2)
C(14)-C(15)-H(152)	108.5	O(1)-Si(1)-C(11)-C(12)	-179.3(2)
C(16)-C(15)-H(152)	108.5	O(2)-Si(1)-C(11)-C(12)	-58.3(3)
H(151)-C(15)-H(152)	107.5	O(3)-Si(1)-C(11)-C(12)	59.5(3)
C(17)-C(16)-C(15)	114.3(4)	O(1)-Si(1)-C(11)-C(20)	62.1(3)
C(17)-C(16)-H(161)	108.7	O(2)-Si(1)-C(11)-C(20)	-176.9(2)
C(15)-C(16)-H(161)	108.7	O(3)-Si(1)-C(11)-C(20)	-59.1(3)
C(17)-C(16)-H(162)	108.7	C(19)-C(11)-C(12)-C(13)	65.8(4)
C(15)-C(16)-H(162)	108.7	C(20)-C(11)-C(12)-C(13)	-55.7(4)
H(161)-C(16)-H(162)	107.6	Si(1)-C(11)-C(12)-C(13)	-172.4(3)
C(16)-C(17)-C(18)	112.3(4)	C(11)-C(12)-C(13)-C(14)	-176.6(3)
C(16)-C(17)-H(171)	109.2	C(12)-C(13)-C(14)-C(15)	178.5(4)
C(18)-C(17)-H(171)	109.2	C(13)-C(14)-C(15)-C(16)	178.6(4)
C(16)-C(17)-H(172)	109.2	C(14)-C(15)-C(16)-C(17)	-73.4(6)
C(18)-C(17)-H(172)	109.2	C(15)-C(16)-C(17)-C(18)	-176.5(4)
H(171)-C(17)-H(172)	107.9		

Symmetry transformations used to generate equivalent atoms:

[i)]2-x, y, 3/2-z

X-ray diffraction data of 4a.

Table S20. Crystal data and structure refinement for **4a**.

Crystal data		
Identification code		i1154
Empirical formula		$C_{32}H_{72}O_{12}Si_8$
Formula weight		873.62
Crystal description		plates, colourless
Crystal size		0.52 x 0.33 x 0.07 mm
Crystal system, space group		triclinic, P-1
Unit cell dimensions:	a	10.7426(14)Å
	b	11.0102(13)Å
	c	11.8640(14) Å
	α	111.291(9)°
	β	72.229(9)°
	γ	94.686(10)°
Volume		1244.4(3)Å^3
Z		1
Calculated density		1.166Mg/m^3
F(000)		472
Linear absorption coefficient μ		0.264mm^{-1}
Absorption correction		Integration
Max. and min. transmission		0.9812 and 0.8894
Data collection		
Temperature		100(2)K
Diffractometer		STOE IPDS
Radiation source		fine-focus sealed tube
Radiation and wavelength		MoK_α, 0.71073Å
Monochromator		graphite
Θ range for data collection		1.93 to 24.84°
Index ranges		$-12 \le h \le 12$, $-13 \le k \le 11$, $-13 \le l \le 13$
Reflections collected		8177
Significant unique reflections		4199 with $I > 2\sigma(I)$
R(int), R(sigma)		0.0537
Refinement		
Refinement method		Full-matrix least-squares on F^2
Data / parameters / restraints		4199 / 247 / 0
Goodness-of-fit on F^2		1.013
Final R indices [$I > 2\sigma(I)$]		R_1 = 0.0454, $wR_2$0.1293
R indices (all data)		R_1 = 0.0534, wR_2 = 0.1334
Extinction expression		none
Largest difference peak and hole		0.349 and -0.458 /Å^3
Structure Solution Program		SHELXS-97 (Sheldrick, 2008)
Structure Refinement Program		SHELXL-97 (Sheldrick, 2008)

Table S30. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å² x 10^3) for **4a**. U(eq) is defined as one third of the trace of the orthogonalizedUij tensor.

x	y	z	U(eq)	
C(1)	1763(2)	2379(2)	3513(2)	48(1)
C(2)	419(3	786(3)	3504(3)	70(1)
C(3)	1720(3)	3793(3)	3554(3)	70(1)
C(4)	2096(3)	2391(3)	4690(2)	71(1)
C(5)	6734(2)	3423(2)	2583(2)	48(1)
C(6)	6030(3)	4686(3)	2814(3)	69(1)
C(7)	8207(3)	3516(3)	1976(3)	70(1)
C(8)	6529(3)	3223(3)	3846(2)	72(1)
C(9)	7909(2)	-1593(2)	1303(2)	49(1)
C(10)	7419(4)	-1195(4)	2756(3)	86(1)
C(11)	9261(3)	-1036(3)	924(3)	65(1)
C(12)	8030(3)	-3088(3)	677(3)	75(1)
C(13)	2956(2)	-2656(2)	2182(2)	51(1)
C(14)	3082(4)	-2100(4)	3533(3)	81(1)
C(15)	3659(3	3996(3)	1473(3)	77(1)
C(16)	1502(3)	-2795(3)	2253(3)	72(1)
O(1)	4481(2)	1998(2)	2100(1)	46(1)
O(2)	6709(2)	650(2)	1340(1)	46(1)
O(3)	5294(2)	-1452(2)	1208(1)	47(1)
O(4)	3056(2)	-105(2)	2004(1)	47(1)
O(5)	2765(2)	1414(2)	793(1)	47(1)
O(6)	6391(2)	2156(2)	129(1)	47(1)
Si(1)	3054(1)	1395(1)	2058(1)	39(1)
Si(2)	6060(1)	2016(1)	1511(1)	38(1)
Si(3)	6752(1)	-937(1)	749(1)	39(1)
Si(4)	3745(1)	-1556(1)	1296(1)	39(1)

Table S31. Hydrogen coordinates (x10^4) and isotropic displacement parameters (Å^2 x 10^3) for **4a**.

	x	y	z	U(eq)
H(2A)	226	1756	2739	84
H(2B)	-254	2324	4255	84
H(2C)	429	900	3512	84
H(3A)	1085	4319	4344	84
H(3B)	1461	3796	2831	84
H(3C)	2588	4161	3512	84
H(4C)	2978	2717	4661	85
H(4B)	2060	1504	4703	85
H(4A)	1463	2961	5456	85
H(6A)	6184	4813	2007	83
H(6B)	6367	5425	3391	83
H(6C)	5089	4628	3192	83
H(7A)	8554	4241	2558	84
H(7B)	8349	3666	1182	84
H(7C)	8658	2700	1802	84
H(8C)	7019	2437	3692	87
H(8B)	5596	3123	4224	87
H(8A)	6840	3980	4427	87
H(10A)	7305	-244	3147	103
H(10B)	8060	-1491	3045	103
H(10C)	6580	-1598	3000	103
H(11A)	9874	-1393	1199	78
H(11B)	9202	-84	1329	78
H(11C)	9571	-1276	2	78
H(12C)	8399	-3333	-242	90

H(12B)	7162	-3456	872	90
H(12A)	8604	-3429	1003	90
H(14A)	4009	-2052	3491	97
H(14B)	2646	-2669	3997	97
H(14C)	2670	-1224	3970	97
H(15A)	3262	-4589	1921	92
H(15B)	4586	-3908	1431	92
H(15C)	3579	-4348	612	92
H(16C)	1418	-3120	1394	87
H(16B)	1047	-1944	2732	87
H(16A)	1116	-3412	2677	87

Table S32. Anisotropic displacement parameters ($Å^2$x10*3) for **4a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U11	U22	U33	U23	U13	U12
C(1)	51(1)	51(1)	34(1)	9(1)	-8(1)	4(1)
C(2)	53(2)	82(2)	56(2)	8(1)	-6(1)	2(1)
C(3)	72(2)	56(2)	62(2)	10(1)	-2(1)	20(1)
C(4)	76(2)	91(2)	31(1)	11(1)	-8(1)	12(2)
C(5)	54(1)	47(1)	39(1)	8(1)	-17(1)	3(1)
C(6)	82(2)	42(1)	76(2)	1(1)	-35(2)	4(1)
C(7)	59(2)	65(2)	72(2)	6(1)	-25(1)	-7(1)
C(8)	99(2)	77(2)	42(1)	11(1)	-38(1)	-12(2)
C(9)	54(1)	53(1)	48(1)	21(1)	-20(1)	3(1)
C(10)	91(2)	131(3)	57(2)	48(2)	-28(2)	19(2)
C(11)	60(2)	68(2)	81(2)	31(2)	-34(1)	-3(1)
C(12)	79(2)	62(2)	107(2)	41(2)	-44(2)	3(1)
C(13)	55(1)	58(2)	49(1)	30(1)	-14(1)	1(1)
C(14)	95(2)	111(3)	53(2)	52(2)	-21(2)	-19(2)
C(15)	81(2)	61(2)	98(2)	51(2)	-11(2)	1(2)
C(16)	59(2)	90(2)	82(2)	55(2)	-15(1)	-9(2)
O(1)	45(1)	51(1)	38(1)	11(1)	-11(1)	3(1)
O(2)	57(1)	41(1)	42(1)	9(1)	-20(1)	7(1)
O(3)	46(1)	56(1)	45(1)	23(1)	-14(1)	-1(1)
O(4)	56(1)	45(1)	38(1)	15(1)	-8(1)	6(1)
O(5)	54(1)	54(1)	31(1)	12(1)	-12(1)	12(1)
O(6)	61(1)	48(1)	34(1)	15(1)	-17(1)	-4(1)
Si(1)	46(1)	41(1)	29(1)	9(1)	-10(1)	6(1)
Si(2)	47(1)	38(1)	30(1)	9(1)	-13(1)	3(1)
Si(3)	47(1)	41(1)	31(1)	13(1)	-14(1)	4(1)
Si(4)	47(1)	40(1)	31(1)	15(1)	-12(1)	2(1)

Table S33. Full list of bond lengths [Å] and angles [°] for **4a**.

C(1)-C(2)	1.537(4)	O(6)-Si(4)#1	1.6248(15)
C(1)-C(4)	1.539(3)	O(6)-Si(2)	1.6296(15)
C(1)-C(3)	1.543(4)	Si(3)-O(5)#1	1.6308(15)
C(1)-Si(1)	1.871(2)	Si(4)-O(6)#1	1.6248(15)
C(2)-H(2A)	0.9800	C(2)-C(1)-C(4)	109.9(2)
C(2)-H(2B)	0.9800	C(2)-C(1)-C(3)	109.0(2)
C(2)-H(2C)	0.9800	C(4)-C(1)-C(3)	109.1(2)
C(3)-H(3A)	0.9800	C(2)-C(1)-Si(1)	110.05(17)
C(3)-H(3B)	0.9800	C(4)-C(1)-Si(1)	109.02(18)
C(3)-H(3C)	0.9800	C(3)-C(1)-Si(1)	109.74(17)
C(4)-H(4C)	0.9800	C(1)-C(2)-H(2A)	109.5
C(4)-H(4B)	0.9800	C(1)-C(2)-H(2B)	109.5
C(4)-H(4A)	0.9800	H(2A)-C(2)-H(2B)	109.5
C(5)-C(6)	1.532(4)	C(1)-C(2)-H(2C)	109.5
C(5)-C(7)	1.538(4)	H(2A)-C(2)-H(2C)	109.5
C(5)-C(8)	1.541(3)	H(2B)-C(2)-H(2C)	109.5
C(5)-Si(2)	1.868(2)	C(1)-C(3)-H(3A)	109.5
C(6)-H(6A)	0.9800	C(1)-C(3)-H(3B)	109.5
C(6)-H(6B)	0.9800	H(3A)-C(3)-H(3B)	109.5
C(6)-H(6C)	0.9800	C(1)-C(3)-H(3C)	109.5
C(7)-H(7A)	0.9800	H(3A)-C(3)-H(3C)	109.5
C(7)-H(7B)	0.9800	H(3B)-C(3)-H(3C)	109.5
C(7)-H(7C)	0.9800	C(1)-C(4)-H(4C)	109.5
C(8)-H(8C)	0.9800	C(1)-C(4)-H(4B)	109.5
C(8)-H(8B)	0.9800	H(4C)-C(4)-H(4B)	109.5
C(8)-H(8A)	0.9800	C(1)-C(4)-H(4A)	109.5
C(9)-C(11)	1.530(4)	H(4C)-C(4)-H(4A)	109.5
C(9)-C(12)	1.539(4)	H(4B)-C(4)-H(4A)	109.5
C(9)-C(10)	1.541(4)	C(6)-C(5)-C(7)	109.2(2)
C(9)-Si(3)	1.868(2)	C(6)-C(5)-C(8)	110.2(2)
C(10)-H(10A)	0.9800	C(7)-C(5)-C(8)	108.7(2)
C(10)-H(10B)	0.9800	C(6)-C(5)-Si(2)	109.17(17)
C(10)-H(10C)	0.9800	C(7)-C(5)-Si(2)	110.26(16)
C(11)-H(11A)	0.9800	C(8)-C(5)-Si(2)	109.28(18)
C(11)-H(11B)	0.9800	C(5)-C(6)-H(6A)	109.5
C(11)-H(11C)	0.9800	C(5)-C(6)-H(6B)	109.5
C(12)-H(12C)	0.9800	H(6A)-C(6)-H(6B)	109.5
C(12)-H(12B)	0.9800	C(5)-C(6)-H(6C)	109.5
C(12)-H(12A)	0.9800	H(6A)-C(6)-H(6C)	109.5
C(13)-C(15)	1.532(4)	H(6B)-C(6)-H(6C)	109.5
C(13)-C(16)	1.535(4)	C(5)-C(7)-H(7A)	109.5
C(13)-C(14)	1.539(4)	C(5)-C(7)-H(7B)	109.5
C(13)-Si(4)	1.872(2)	H(7A)-C(7)-H(7B)	109.5
C(14)-H(14A)	0.9800	C(5)-C(7)-H(7C)	109.5
C(14)-H(14B)	0.9800	H(7A)-C(7)-H(7C)	109.5
C(14)-H(14C)	0.9800	H(7B)-C(7)-H(7C)	109.5
C(15)-H(15A)	0.9800	C(5)-C(8)-H(8C)	109.5
C(15)-H(15B)	0.9800	C(5)-C(8)-H(8B)	109.5
C(15)-H(15C)	0.9800	H(8C)-C(8)-H(8B)	109.5
C(16)-H(16C)	0.9800	C(5)-C(8)-H(8A)	109.5
C(16)-H(16B)	0.9800	H(8C)-C(8)-H(8A)	109.5
C(16)-H(16A)	0.9800	H(8B)-C(8)-H(8A)	109.5
O(1)-Si(2)	1.6272(16)	C(11)-C(9)-C(12)	108.5(2)
O(1)-Si(1)	1.6283(17)	C(11)-C(9)-C(10)	109.1(2)
O(2)-Si(3)	1.6277(16)	C(12)-C(9)-C(10)	109.9(2)
O(2)-Si(2)	1.6286(16)	C(11)-C(9)-Si(3)	109.33(17)
O(3)-Si(3)	1.6217(16)	C(12)-C(9)-Si(3)	109.92(17)
O(3)-Si(4)	1.6318(16)	C(10)-C(9)-Si(3)	109.95(18)
O(4)-Si(4)	1.6262(16)	C(9)-C(10)-H(10A)	109.5
O(4)-Si(1)	1.6293(17)	C(9)-C(10)-H(10B)	109.5
O(5)-Si(1)	1.6297(15)	H(10A)-C(10)-H(10B)	109.5
O(5)-Si(3)#1	1.6308(15)	C(9)-C(10)-H(10C)	109.5

H(10A)-C(10)-H(10C)	109.5	H(16C)-C(16)-H(16B)	109.5
H(10B)-C(10)-H(10C)	109.5	C(13)-C(16)-H(16A)	109.5
C(9)-C(11)-H(11A)	109.5	H(16C)-C(16)-H(16A)	109.5
C(9)-C(11)-H(11B)	109.5	H(16B)-C(16)-H(16A)	109.5
H(11A)-C(11)-H(11B)	109.5	Si(2)-O(1)-Si(1)	152.59(11)
C(9)-C(11)-H(11C)	109.5	Si(3)-O(2)-Si(2)	147.83(11)
H(11A)-C(11)-H(11C)	109.5	Si(3)-O(3)-Si(4)	152.81(11)
H(11B)-C(11)-H(11C)	109.5	Si(4)-O(4)-Si(1)	147.61(11)
C(9)-C(12)-H(12C)	109.5	Si(1)-O(5)-Si(3)#1	146.76(11)
C(9)-C(12)-H(12B)	109.5	Si(4)#1-O(6)-Si(2)	147.33(11)
H(12C)-C(12)-H(12B)	109.5	O(1)-Si(1)-O(4)	109.24(9)
C(9)-C(12)-H(12A)	109.5	O(1)-Si(1)-O(5)	109.08(9)
H(12C)-C(12)-H(12A)	109.5	O(4)-Si(1)-O(5)	109.23(9)
H(12B)-C(12)-H(12A)	109.5	O(1)-Si(1)-C(1)	109.75(10)
C(15)-C(13)-C(16)	109.5(2)	O(4)-Si(1)-C(1)	109.19(10)
C(15)-C(13)-C(14)	109.6(2)	O(5)-Si(1)-C(1)	110.33(10)
C(16)-C(13)-C(14)	109.3(2)	O(1)-Si(2)-O(2)	109.11(9)
C(15)-C(13)-Si(4)	108.04(17)	O(1)-Si(2)-O(6)	108.83(9)
C(16)-C(13)-Si(4)	110.48(17)	O(2)-Si(2)-O(6)	109.18(8)
C(14)-C(13)-Si(4)	109.95(19)	O(1)-Si(2)-C(5)	110.03(10)
C(13)-C(14)-H(14A)	109.5	O(2)-Si(2)-C(5)	110.17(10)
C(13)-C(14)-H(14B)	109.5	O(6)-Si(2)-C(5)	109.50(10)
H(14A)-C(14)-H(14B)	109.5	O(3)-Si(3)-O(2)	108.99(9)
C(13)-C(14)-H(14C)	109.5	O(3)-Si(3)-O(5)#1	109.12(9)
H(14A)-C(14)-H(14C)	109.5	O(2)-Si(3)-O(5)#1	109.09(8)
H(14B)-C(14)-H(14C)	109.5	O(3)-Si(3)-C(9)	110.18(10)
C(13)-C(15)-H(15A)	109.5	O(2)-Si(3)-C(9)	109.50(10)
C(13)-C(15)-H(15B)	109.5	O(5)#1-Si(3)-C(9)	109.94(10)
H(15A)-C(15)-H(15B)	109.5	O(6)#1-Si(4)-O(4)	109.07(9)
C(13)-C(15)-H(15C)	109.5	O(6)#1-Si(4)-O(3)	108.91(8)
H(15A)-C(15)-H(15C)	109.5	O(4)-Si(4)-O(3)	109.16(9)
H(15B)-C(15)-H(15C)	109.5	O(6)#1-Si(4)-C(13)	109.44(10)
C(13)-C(16)-H(16C)	109.5	O(4)-Si(4)-C(13)	110.83(10)
C(13)-C(16)-H(16B)	109.5	O(3)-Si(4)-C(13)	109.41(10)

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

X-ray diffraction data of 4b. All the measurements were performed using graphite-monochromatized Mo K_α radiation at 100 K: $C_{40}H_{88}O_{12}Si_8$, M_r 985.81, trigonal, space group R -3 c, a = 13.2192(4) Å, c = 53.3347(18) Å, V = 8071.4(5) $Å^3$, Z = 6, d_{calc} = 1.217g cm^{-3}, μ = 0.252mm^{-1}. A total of 14563 reflections were collected (Θ_{max} = 30.0°), from which 2623 were unique (R_{int} = 0.0238), with 2265 having I > 2σ(I). The structure was solved by direct methods (SHELXS-97)[2] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97)[2]. The tert. pentyl group bonded to the atom Si1, which lies on a three-fold rotation axis, is disordered over three orientations and was refined with site occupation factors of 1/3 and 2/3, respectively. The tert. pentyl group bonded to the atom Si2, which lies on a general position, is also disordered over three orientations and was refined with site occupation factors adding to unity. The ordered non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. Due to disorder the C–C distances were fixed to be equal in length but this C–C bond length was enabled to refine resulting in a value of 1.538(2) Å. The bonds within the tert. pentyl groups were subjected to a rigid bond restraint. The H atoms of the CH_2 groups were refined with one common isotropic displacement parameter for these H atoms and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99 Å. The H atoms of the methyl groups were refined with one common isotropic displacement parameter for these H atoms and idealized geometry with tetrahedral angles, staggered conformation, and C–H distances of 0.98 Å. For 157 parameters final *R* indices of R_1 = 0.0416 and wR_2 = 0.1280 (GOF = 1.064) were obtained. The largest peak in a difference Fourier map was 0.744 $eÅ^{-3}$.

Results and Discussion

X-ray Crystal Structure. The crystal structure analysis of **4b** confirmed the compound as octakis(1,1-dimethylpentyl)octasilsesquioxane. The tert. pentyl groups are disordered. The almost spherical molecules pack in a slightly distorted cubic closed packing.

References

(1) C. K. Johnson, ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA (1965).

(2) G. M. Sheldrick, Acta Cryst. A 64, 112-122 (2008).

Table S34. Crystal data and structure refinement for **4b**.

Crystal data	
Identification code	NH235B
Empirical formula	$C_{40}H_{88}O_{12}Si_8$
Formula weight	985.81
Crystal description	block, colourless
Crystal size	0.30 x 0.26 x 0.25mm
Crystal system, space group	trigonal, R -3 c
Unit cell dimensions: a	13.2192(4)Å
c	53.3347(18)Å
Volume	8071.4(5)Å^3
Z	6
Calculated density	1.217Mg/m^3
F(000)	3216
Linear absorption coefficient μ	0.252mm^{-1}
Absorption correction	semi-empirical from equivalents
Max. and min. transmission	0.7462 and 0.5440
Unit cell determination	2.34° <Θ< 31.03°
	9715 reflections used at 100K
Data collection	
Temperature	100K
Diffractometer	Bruker APEX-II CCD
Radiation source	fine-focus sealed tube
Radiation and wavelength	MoK_α, 0.71073Å
Monochromator	graphite
Scan type	ϕ and ω scans
Θ range for data collection	2.34 to 30.00°
Index ranges	$-17 \le h \le 13$, $-14 \le k \le 18$, $-75 \le l \le 54$
Reflections collected / unique	14563 / 2623
Significant unique reflections	2265 with $I > 2\sigma(I)$
R(int), R(sigma)	0.0238, 0.0172
Completeness to Θ = 30.0°	99.7%
Refinement	
Refinement method	Full-matrix least-squares on F^2
Data / parameters / restraints	2623 / 157 / 125
Goodness-of-fit on F^2	1.064
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0416$, $wR_2 = 0.1200$
R indices (all data)	$R_1 = 0.0482$, $wR_2 = 0.1280$
Extinction expression	none
Weighting scheme	$w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P = (F_o^2+2F_c^2)/3$
Weighting scheme parameters a, b	0.0725, 12.290
Largest Δ/σ in last cycle	0.001
Largest difference peak and hole	0.744 and -0.408e/Å^3
Structure Solution Program	SHELXS-97 (Sheldrick, 2008)
Structure Refinement Program	SHELXL-97 (Sheldrick, 2008)

Table S35. Atomic coordinates, site occupation factors, and equivalent isotropic displacement parameters ($Å^2$) for **4b**. U_{eq} is defined as one third of the trace of the orthogonalizedU_{ij} tensor.

	x	y	z	s.o.f.	U_{eq}
Si(1)	0.6667	0.3333	0.282618(15)	1	0.02474(18)
Si(2)	0.74593(3)	0.55322(3)	0.316449(8)	1	0.02359(15)
O(1)	0.71725(11)	0.46502(10)	0.29307(2)	1	0.0311(3)
O(2)	0.62762(10)	0.51057(10)	0.33262(2)	1	0.0296(3)
C(11)	0.6667	0.3333	0.24764(6)	1	0.0405(6)
C(12)	0.6153(5)	0.4089(6)	0.23836(15)	0.66667	0.0608(14)
C(13)	0.6433(8)	0.4278(8)	0.2371(3)	0.33333	0.0468(18)
C(14)	0.5159(7)	0.3934(8)	0.24245(16)	0.33333	0.0576(18)
C(21)	0.79990(15)	0.70412(14)	0.30437(4)	1	0.0364(3)
C(22)	0.6984(2)	0.70702(19)	0.29107(5)	1	0.0532(6)
C(23)	0.8303(6)	0.7850(4)	0.32772(10)	0.575(4)	0.0549(15)
C(24)	0.8647(5)	0.8033(6)	0.32282(13)	0.425(4)	0.0436(12)
C(25)	0.7827(5)	0.7919(5)	0.34380(12)	0.425(4)	0.0565(13)
C(26)	0.8979(5)	0.7331(7)	0.28477(12)	0.425(4)	0.0391(10)
C(27)	0.9231(6)	0.7598(9)	0.2932(2)	0.274(6)	0.0503(18)
C(28)	0.9413(7)	0.8585(6)	0.27481(14)	0.274(6)	0.0426(17)
C(29)	0.8785(9)	0.7248(16)	0.28109(14)	0.301(5)	0.050(2)
C(30)	0.9891(7)	0.7198(9)	0.2869(2)	0.301(5)	0.068(3)

Table S36. Hydrogen coordinates, site occupation factors, and isotropic displacement parameters ($Å^2$) for **4b**.

	x	y	z	s.o.f.	U_{iso}
H(121)	0.5346	0.3751	0.2443	0.66667	0.078(4)
H(122)	0.6166	0.4111	0.2200	0.66667	0.078(4)
H(123)	0.6621	0.4884	0.2449	0.66667	0.078(4)
H(131)	0.6578	0.4358	0.2188	0.33333	0.060(9)
H(132)	0.6966	0.5039	0.2451	0.33333	0.060(9)
H(141)	0.5006	0.4536	0.2358	0.33333	0.078(4)
H(142)	0.5022	0.3862	0.2606	0.33333	0.078(4)
H(143)	0.4636	0.3185	0.2344	0.33333	0.078(4)
H(221)	0.7252	0.7858	0.2846	1	0.078(4)
H(222)	0.6345	0.6860	0.3030	1	0.078(4)
H(223)	0.6706	0.6511	0.2772	1	0.078(4)
H(231)	0.8953	0.7862	0.3369	0.575(4)	0.078(4)
H(232)	0.7620	0.7552	0.3387	0.575(4)	0.078(4)
H(233)	0.8530	0.8643	0.3223	0.575(4)	0.078(4)
H(241)	0.9327	0.8004	0.3297	0.425(4)	0.060(9)
H(242)	0.8936	0.8792	0.3142	0.425(4)	0.060(9)
H(251)	0.8240	0.8562	0.3557	0.425(4)	0.078(4)
H(252)	0.7553	0.7172	0.3524	0.425(4)	0.078(4)
H(253)	0.7156	0.7950	0.3368	0.425(4)	0.078(4)
H(261)	0.8677	0.6741	0.2715	0.425(4)	0.078(4)
H(262)	0.9642	0.7333	0.2930	0.425(4)	0.078(4)
H(263)	0.9234	0.8103	0.2775	0.425(4)	0.078(4)
H(271)	0.9332	0.6999	0.2842	0.274(6)	0.060(9)
H(272)	0.9819	0.7925	0.3068	0.274(6)	0.060(9)
H(281)	1.0213	0.8970	0.2683	0.274(6)	0.078(4)
H(282)	0.9279	0.9158	0.2836	0.274(6)	0.078(4)
H(283)	0.8860	0.8249	0.2608	0.274(6)	0.078(4)
H(291)	0.8326	0.6650	0.2683	0.301(5)	0.060(9)
H(292)	0.9010	0.8022	0.2739	0.301(5)	0.060(9)
H(301)	1.0357	0.7361	0.2715	0.301(5)	0.078(4)

H(302)	0.9676	0.6419	0.2931	0.301(5)	0.078(4)
H(303)	1.0349	0.7784	0.2996	0.301(5)	0.078(4)

Table S37. Anisotropic displacement parameters ($Å^2$) for **4b**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si(1)	0.0194(2)	0.0194(2)	0.0354(4)	0	0	0.00971(11)
Si(2)	0.0157(2)	0.0130(2)	0.0416(3)	0.00275(15)	0.00193(15)	0.00684(15)
O(1)	0.0294(6)	0.0197(5)	0.0428(6)	0.0020(4)	0.0044(5)	0.0112(4)
O(2)	0.0193(5)	0.0196(5)	0.0502(7)	0.0007(5)	0.0057(5)	0.0101(4)
C(11)	0.0418(9)	0.0418(9)	0.0380(14)	0	0	0.0209(4)
C(12)	0.058(3)	0.064(3)	0.058(3)	0.028(2)	-0.007(2)	0.029(2)
C(13)	0.048(3)	0.040(3)	0.053(4)	0.006(2)	0.007(3)	0.022(3)
C(14)	0.055(3)	0.065(4)	0.064(4)	0.023(3)	0.014(3)	0.038(3)
C(21)	0.0286(7)	0.0174(6)	0.0605(9)	0.0069(6)	-0.0063(6)	0.0096(6)
C(22)	0.0454(10)	0.0316(9)	0.0830(16)	0.0070(9)	-0.0218(9)	0.0195(8)
C(23)	0.068(4)	0.0115(16)	0.073(3)	-0.0009(18)	-0.021(2)	0.011(2)
C(24)	0.028(2)	0.019(2)	0.074(2)	0.002(2)	-0.0074(14)	0.0053(18)
C(25)	0.057(3)	0.038(2)	0.066(3)	-0.003(2)	-0.002(2)	0.017(2)
C(26)	0.0241(17)	0.021(2)	0.045(2)	0.0140(18)	-0.0105(15)	-0.0099(19)
C(27)	0.0385(17)	0.036(3)	0.068(4)	0.016(3)	0.007(2)	0.012(3)
C(28)	0.039(3)	0.030(3)	0.048(3)	0.004(2)	-0.002(2)	0.009(2)
C(29)	0.046(3)	0.043(4)	0.051(3)	0.014(3)	-0.003(2)	0.013(3)
C(30)	0.054(3)	0.061(5)	0.096(6)	0.035(4)	0.030(3)	0.034(4)

Table S38. Full list of bond lengths [Å] and angles [°] for **4b**.

Si(1)-O(1)	1.6199(12)
Si(1)-C(11)	1.865(4)
Si(2)-O(1)	1.6175(13)
Si(2)-O(2)$^{i)}$	1.6194(12)
Si(2)-O(2)	1.6203(12)
Si(2)-C(21)	1.8655(17)
C(11)-C(13)	1.535(5)
C(11)-C(12)	1.544(3)
C(12)-H(121)	0.98
C(12)-H(122)	0.98
C(12)-H(123)	0.98
C(13)-C(14)	1.535(5)
C(13)-H(131)	0.99
C(13)-H(132)	0.99
C(14)-H(141)	0.98
C(14)-H(142)	0.98
C(14)-H(143)	0.98
C(21)-C(24)	1.516(4)
C(21)-C(27)	1.532(4)
C(21)-C(22)	1.535(2)
C(21)-C(29)	1.553(5)
C(21)-C(26)	1.556(4)
C(21)-C(23)	1.557(4)
C(22)-H(221)	0.98
C(22)-H(222)	0.98
C(22)-H(223)	0.98
C(23)-H(231)	0.98
C(23)-H(232)	0.98
C(23)-H(233)	0.98
C(24)-C(25)	1.512(4)
C(24)-H(241)	0.99
C(24)-H(242)	0.99
C(25)-H(251)	0.98
C(25)-H(252)	0.98
C(25)-H(253)	0.98
C(26)-H(261)	0.98
C(26)-H(262)	0.98
C(26)-H(263)	0.98
C(27)-C(28)	1.553(5)
C(27)-H(271)	0.99
C(27)-H(272)	0.99
C(28)-H(281)	0.98
C(28)-H(282)	0.98
C(28)-H(283)	0.98
C(29)-C(30)	1.527(5)
C(29)-H(291)	0.99
C(29)-H(292)	0.99
C(30)-H(301)	0.98
C(30)-H(302)	0.98
C(30)-H(303)	0.98

O(1)$^{ii)}$-Si(1)-O(1)	108.82(5)
O(1)-Si(1)-C(11)	110.12(5)
O(1)-Si(2)-O(2)$^{i)}$	109.17(7)
O(1)-Si(2)-O(2)	108.78(7)
O(2)$^{i)}$-Si(2)-O(2)	109.17(5)
O(1)-Si(2)-C(21)	109.33(8)
O(2)$^{i)}$-Si(2)-C(21)	110.35(7)
O(2)-Si(2)-C(21)	110.02(7)
Si(2)-O(1)-Si(1)	149.53(9)
Si(2)$^{iii)}$-O(2)-Si(2)	148.96(8)
C(13)$^{ii)}$-C(11)-C(13)	107.4(6)
C(13)$^{ii)}$-C(11)-C(12)$^{iv)}$	118.9(5)
C(13)-C(11)-C(12)$^{iv)}$	98.1(4)
C(13)$^{iv)}$-C(11)-C(12)$^{ii)}$	98.1(4)
C(13)-C(11)-C(12)$^{ii)}$	118.9(5)
C(12)$^{iv)}$-C(11)-C(12)$^{ii)}$	110.2(3)
C(13)$^{iv)}$-C(11)-C(12)	118.9(5)
C(13)$^{ii)}$-C(11)-C(12)	98.1(4)
C(12)$^{iv)}$-C(11)-C(12)	110.2(3)
C(12)$^{ii)}$-C(11)-C(12)	110.2(3)
C(13)-C(11)-Si(1)	111.4(6)
C(12)-C(11)-Si(1)	108.7(3)
C(11)-C(12)-H(121)	109.5
C(11)-C(12)-H(122)	109.5
H(121)-C(12)-H(122)	109.5
C(11)-C(12)-H(123)	109.5
H(121)-C(12)-H(123)	109.5
H(122)-C(12)-H(123)	109.5
C(11)-C(13)-C(14)	109.2(5)
C(11)-C(13)-H(131)	109.8
C(14)-C(13)-H(131)	109.8
C(11)-C(13)-H(132)	109.8
C(14)-C(13)-H(132)	109.8
H(131)-C(13)-H(132)	108.3
C(13)-C(14)-H(141)	109.5
C(13)-C(14)-H(142)	109.5
H(141)-C(14)-H(142)	109.5
C(13)-C(14)-H(143)	109.5
H(141)-C(14)-H(143)	109.5
H(142)-C(14)-H(143)	109.5
C(24)-C(21)-C(27)	80.3(6)
C(24)-C(21)-C(22)	113.6(4)
C(27)-C(21)-C(22)	122.8(4)
C(24)-C(21)-C(29)	109.1(7)
C(22)-C(21)-C(29)	98.2(4)
C(24)-C(21)-C(26)	100.5(4)
C(22)-C(21)-C(26)	108.3(3)
C(27)-C(21)-C(23)	97.6(6)
C(22)-C(21)-C(23)	106.3(3)
C(29)-C(21)-C(23)	126.7(7)
C(26)-C(21)-C(23)	118.1(4)
C(24)-C(21)-Si(2)	116.7(4)
C(27)-C(21)-Si(2)	113.2(3)
C(22)-C(21)-Si(2)	108.33(12)
C(29)-C(21)-Si(2)	109.2(7)
C(26)-C(21)-Si(2)	108.8(3)
C(23)-C(21)-Si(2)	106.7(3)
C(21)-C(22)-H(221)	109.5
C(21)-C(22)-H(222)	109.5
H(221)-C(22)-H(222)	109.5
C(21)-C(22)-H(223)	109.5
H(221)-C(22)-H(223)	109.5
H(222)-C(22)-H(223)	109.5
C(21)-C(23)-H(231)	109.5
C(21)-C(23)-H(232)	109.5
H(231)-C(23)-H(232)	109.5
C(21)-C(23)-H(233)	109.5
H(231)-C(23)-H(233)	109.5
H(232)-C(23)-H(233)	109.5
C(25)-C(24)-C(21)	109.1(4)
C(25)-C(24)-H(241)	109.9
C(21)-C(24)-H(241)	109.9
C(25)-C(24)-H(242)	109.9

C(21)-C(24)-H(242)	109.9
H(241)-C(24)-H(242)	108.3
C(24)-C(25)-H(251)	109.5
C(24)-C(25)-H(252)	109.5
H(251)-C(25)-H(252)	109.5
C(24)-C(25)-H(253)	109.5
H(251)-C(25)-H(253)	109.5
H(252)-C(25)-H(253)	109.5
C(21)-C(26)-H(261)	109.5
C(21)-C(26)-H(262)	109.5
H(261)-C(26)-H(262)	109.5
C(21)-C(26)-H(263)	109.5
H(261)-C(26)-H(263)	109.5
H(262)-C(26)-H(263)	109.5
C(21)-C(27)-C(28)	109.3(5)
C(21)-C(27)-H(271)	109.8
C(28)-C(27)-H(271)	109.8
C(21)-C(27)-H(272)	109.8
C(28)-C(27)-H(272)	109.8
H(271)-C(27)-H(272)	108.3
C(27)-C(28)-H(281)	109.5
C(27)-C(28)-H(282)	109.5
H(281)-C(28)-H(282)	109.5
C(27)-C(28)-H(283)	109.5
H(281)-C(28)-H(283)	109.5
H(282)-C(28)-H(283)	109.5
C(30)-C(29)-C(21)	113.7(6)
C(30)-C(29)-H(291)	108.8
C(21)-C(29)-H(291)	108.8
C(30)-C(29)-H(292)	108.8
C(21)-C(29)-H(292)	108.8
H(291)-C(29)-H(292)	107.7
C(29)-C(30)-H(301)	109.5
C(29)-C(30)-H(302)	109.5
H(301)-C(30)-H(302)	109.5
C(29)-C(30)-H(303)	109.5
H(301)-C(30)-H(303)	109.5
H(302)-C(30)-H(303)	109.5

$O(2)^{i)}$-Si(2)-O(1)-Si(1)	64.16(18)
O(2)-Si(2)-O(1)-Si(1)	-54.87(18)
C(21)-Si(2)-O(1)-Si(1)	-175.03(16)
$O(1)^{iv)}$-Si(1)-O(1)-Si(2)	-63.98(16)
$O(1)^{ii)}$-Si(1)-O(1)-Si(2)	54.45(17)
C(11)-Si(1)-O(1)-Si(2)	175.24(15)
O(1)-Si(2)-O(2)-$Si(2)^{iii)}$	64.90(18)
$O(2)^{i)}$-Si(2)-O(2)-$Si(2)^{iii)}$	-54.14(16)
C(21)-Si(2)-O(2)-$Si(2)^{iii)}$	-175.37(16)
$O(1)^{iv)}$-Si(1)-C(11)-$C(13)^{iv)}$	-33.2(4)
$O(1)^{ii)}$-Si(1)-C(11)-$C(13)^{iv)}$	-153.2(4)
O(1)-Si(1)-C(11)-$C(13)^{iv)}$	86.8(4)
$O(1)^{iv)}$-Si(1)-C(11)-$C(13)^{ii)}$	86.8(4)
$O(1)^{ii)}$-Si(1)-C(11)-$C(13)^{ii)}$	-33.2(4)
O(1)-Si(1)-C(11)-$C(13)^{ii)}$	-153.2(4)
$O(1)^{iv)}$-Si(1)-C(11)-C(13)	-153.2(4)
$O(1)^{ii)}$-Si(1)-C(11)-C(13)	86.8(4)
O(1)-Si(1)-C(11)-C(13)	-33.2(4)
$O(1)^{iv)}$-Si(1)-C(11)-$C(12)^{iv)}$	-46.1(3)
$O(1)^{ii)}$-Si(1)-C(11)-$C(12)^{iv)}$	-166.1(3)
O(1)-Si(1)-C(11)-$C(12)^{iv)}$	73.9(3)
$O(1)^{iv)}$-Si(1)-C(11)-$C(12)^{ii)}$	73.9(3)
$O(1)^{ii)}$-Si(1)-C(11)-$C(12)^{ii)}$	-46.1(3)
O(1)-Si(1)-C(11)-$C(12)^{ii)}$	-166.1(3)
$O(1)^{iv)}$-Si(1)-C(11)-C(12)	-166.1(3)
$O(1)^{ii)}$-Si(1)-C(11)-C(12)	73.9(3)
O(1)-Si(1)-C(11)-C(12)	-46.1(3)
$C(13)^{iv)}$-C(11)-C(13)-C(14)	168.0(5)
$C(13)^{ii)}$-C(11)-C(13)-C(14)	52.6(16)
$C(12)^{iv)}$-C(11)-C(13)-C(14)	176.5(10)
$C(12)^{ii)}$-C(11)-C(13)-C(14)	57.9(9)
C(12)-C(11)-C(13)-C(14)	10(3)
Si(1)-C(11)-C(13)-C(14)	-69.7(10)
O(1)-Si(2)-C(21)-C(24)	-162.2(3)
$O(2)^{i)}$-Si(2)-C(21)-C(24)	-42.1(3)
O(2)-Si(2)-C(21)-C(24)	78.4(3)
O(1)-Si(2)-C(21)-C(27)	-71.6(6)
$O(2)^{i)}$-Si(2)-C(21)-C(27)	48.4(6)
O(2)-Si(2)-C(21)-C(27)	169.0(6)
O(1)-Si(2)-C(21)-C(22)	68.03(17)
$O(2)^{i)}$-Si(2)-C(21)-C(22)	-171.89(15)
O(2)-Si(2)-C(21)-C(22)	-51.37(17)
O(1)-Si(2)-C(21)-C(29)	-37.9(4)
$O(2)^{i)}$-Si(2)-C(21)-C(29)	82.2(4)
O(2)-Si(2)-C(21)-C(29)	-157.3(4)
O(1)-Si(2)-C(21)-C(26)	-49.5(3)
$O(2)^{i)}$-Si(2)-C(21)-C(26)	70.6(3)
O(2)-Si(2)-C(21)-C(26)	-168.9(3)
O(1)-Si(2)-C(21)-C(23)	-177.8(3)
$O(2)^{i)}$-Si(2)-C(21)-C(23)	-57.7(3)
O(2)-Si(2)-C(21)-C(23)	62.8(3)
C(27)-C(21)-C(24)-C(25)	-174.3(7)
C(22)-C(21)-C(24)-C(25)	64.0(7)
C(29)-C(21)-C(24)-C(25)	172.5(7)
C(26)-C(21)-C(24)-C(25)	179.5(7)
C(23)-C(21)-C(24)-C(25)	-4.6(16)
Si(2)-C(21)-C(24)-C(25)	-63.2(7)
C(24)-C(21)-C(27)-C(28)	-87.3(9)
C(22)-C(21)-C(27)-C(28)	24.6(11)
C(29)-C(21)-C(27)-C(28)	68.4(14)
C(26)-C(21)-C(27)-C(28)	75.6(12)
C(23)-C(21)-C(27)-C(28)	-90.5(9)
Si(2)-C(21)-C(27)-C(28)	157.7(6)
C(24)-C(21)-C(29)-C(30)	65.1(13)
C(27)-C(21)-C(29)-C(30)	39.7(9)
C(22)-C(21)-C(29)-C(30)	-176.3(11)
C(26)-C(21)-C(29)-C(30)	26(4)
C(23)-C(21)-C(29)-C(30)	66.2(15)
Si(2)-C(21)-C(29)-C(30)	-63.6(13)

Symmetry transformations used to generate equivalent atoms:

$^{i)}$ y+1/3, y-x+2/3, 2/3-z $^{ii)}$ 1-y, x-y, z $^{iii)}$ x-y+1/3, x-1/3, 2/3-z $^{iv)}$ y-x+1, 1-x, z

X-ray diffraction data of 4c. All the measurements were performed using graphite-monochromatized Mo K_α radiation at 100K: $C_{48}H_{104}O_{12}Si_8$, M_r 1098.03, triclinic, space group P -1, a = 10.8944(4) Å, b = 12.6042(4) Å, c = 13.4936(5) Å, α = 68.8952(11)°, ß = 87.8745(12)°, γ = 66.4831(11)°, V = 1572.67(10) $Å^3$, Z = 1, d_{calc} = 1.159g cm^{-3}, μ = 0.222 mm^{-1}. A total of 26387 reflections were collected (Θ_{max} = 30.0°), from which 9065 were unique (R_{int} = 0.0168), with 8236 having I > 2σ(I). The structure was solved by direct methods (SHELXS-97)[2] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97)[2]. The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms of the CH_2 groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometry with approximately tetrahedral angles and C–H distances of 0.99Å. The H atoms of the methyl groups were refined with common isotropic displacement parameters for the H atoms of the same group and idealized geometries with tetrahedral angles, enabling rotation around the C–C bond, and C–H distances of 0.98 Å. For 339 parameters final *R* indices of R_1 = 0.0264 and wR_2 = 0.0783 (GOF = 1.055) were obtained. The largest peak in a difference Fourier map was 0.519 $eÅ^{-3}$.

X-ray Crystal Structure. The crystal structure analysis of **4c** confirmed the compound as octakis(1,1-dimethylbutyl)octasilsesquioxane and is the first one of a Si_8O_{12} cage having tertiary C atoms bonded to Si. All the atoms lie on general positions, but the molecules lie around inversion centres. Although the conformations of the four independent 1,1-dimethylbutyl substituents are quite different, the C atoms at the ends of the chains (C14, C24, C34, C44) lie in a plane that is almost co-planar with the best plane through the Si atoms Si1, Si2, Si3, and Si4 [angle of 2.78(1)° between the planes].

References

(1) C. K. Johnson, ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA (1965).

(2) G. M. Sheldrick, Acta Cryst. A 64, 112-122 (2008).

Table S39. Crystal data and structure refinement for **4c**.

Crystal data		
Identification code		NH260
Empirical formula		$C_{48}H_{104}O_{12}Si_8$
Formula weight		1098.03
Crystal description		block, colourless
Crystal size		0.38 x 0.36 x 0.36mm
Crystal system, space group		triclinic, P -1
Unit cell dimensions:	a	10.8944(4)Å
	b	12.6042(4)Å
	c	13.4936(5)Å
	α	68.8952(11)°
	ß	87.8745(12)°
	γ	66.4831(11)°
Volume		1572.67(10)Å^3
Z		1
Calculated density		1.159Mg/m^3
F(000)		600
Linear absorption coefficient μ		0.222mm^{-1}
Absorption correction		semi-empirical from equivalents
Max. and min. transmission		0.7462 and 0.6812
Unit cell determination		3.25° <Θ< 31.13°
		9989 reflections used at 100K
Data collection		
Temperature		100K
Diffractometer		Bruker APEX-II CCD
Radiation source		fine-focus sealed tube
Radiation and wavelength		MoK_α, 0.71073Å
Monochromator		graphite
Scan type		ϕ and ω scans
Θ range for data collection		1.98 to 30.00°
Index ranges		$-15 \le h \le 15$, $-17 \le k \le 17$, $-18 \le l \le 18$
Reflections collected / unique		26387 / 9065
Significant unique reflections		8236 with $I > 2\sigma(I)$
R(int), R(sigma)		0.0168, 0.0159
Completeness to Θ = 30.0°		98.7%
Refinement		
Refinement method		Full-matrixleast-squares on F^2
Data / parameters / restraints		9065 / 339 / 0
Goodness-of-fit on F^2		1.055
Final R indices [$I > 2\sigma(I)$]		R_1 = 0.0264, wR_2 = 0.0742
R indices (all data)		R_1 = 0.0300, wR_2 = 0.0783
Extinction expression		none
Weighting scheme		$w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$ where $P = (F_o^2+2F_c^2)/3$
Weighting scheme parameters a, b		0.0397, 0.5414
Largest Δ/σin last cycle		0.001
Largest difference peak and hole		0.519 and -0.365e/Å^3
Structure Solution Program		SHELXS-97 (Sheldrick, 2008)
Structure Refinement Program		SHELXL-97 (Sheldrick, 2008)

Table S40. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **4c**. U_{eq} is defined as one third of the trace of the orthogonalizedU_{ij} tensor.

	x	y	z	U_{eq}
Si(1)	0.59859(2)	0.61403(2)	0.326282(17)	0.00906(5)
O(1)	0.66028(6)	0.46547(6)	0.34929(5)	0.01360(12)
Si(2)	0.65442(2)	0.33197(2)	0.416723(17)	0.00933(5)
O(2)	0.70818(6)	0.28909(6)	0.54155(5)	0.01446(12)

Si(3)	0.70694(2)	0.31801(2)	0.649487(17)	0.00941(5)
O(3)	0.72229(6)	0.44856(6)	0.62050(5)	0.01388(12)
Si(4)	0.65101(2)	0.59944(2)	0.559612(17)	0.00952(5)
O(4)	0.63865(7)	0.63363(6)	0.43117(5)	0.01456(12)
O(5)	0.43537(6)	0.66959(6)	0.30345(5)	0.01391(12)
O(6)	0.49945(6)	0.34796(6)	0.40660(5)	0.01400(12)
C(11)	0.66943(9)	0.69300(8)	0.20812(7)	0.01384(15)
C(12)	0.66449(10)	0.81750(9)	0.20744(8)	0.01973(18)
C(13)	0.52677(12)	0.91780(10)	0.20423(10)	0.0267(2)
C(14)	0.53584(17)	1.03503(12)	0.20571(13)	0.0435(3)
C(15)	0.59280(11)	0.71448(10)	0.10411(7)	0.02115(18)
C(16)	0.81882(10)	0.60609(10)	0.21455(9)	0.0259(2)
C(21)	0.76195(8)	0.20693(8)	0.36880(7)	0.01274(15)
C(22)	0.70063(9)	0.22100(8)	0.26115(7)	0.01527(16)
C(23)	0.68024(11)	0.33846(10)	0.16340(7)	0.02262(19)
C(24)	0.62866(13)	0.33174(12)	0.06301(8)	0.0296(2)
C(25)	0.77104(11)	0.08116(8)	0.45257(8)	0.02085(18)
C(26)	0.90510(9)	0.20281(10)	0.36188(8)	0.02016(18)
C(31)	0.84943(8)	0.19016(8)	0.75177(7)	0.01355(15)
C(32)	0.83041(10)	0.06756(9)	0.78221(7)	0.01867(17)
C(33)	0.93555(12)	-0.04866(10)	0.86731(9)	0.0302(2)
C(34)	0.90337(15)	-0.16216(11)	0.89424(11)	0.0387(3)
C(35)	0.84658(13)	0.22631(11)	0.84955(8)	0.0301(2)
C(36)	0.98293(10)	0.17804(10)	0.70489(9)	0.0260(2)
C(41)	0.75495(9)	0.67077(9)	0.59507(7)	0.01619(16)
C(42)	0.81538(10)	0.60668(9)	0.71421(7)	0.01862(17)
C(43)	0.71836(10)	0.60692(10)	0.79850(8)	0.02079(18)
C(44)	0.79478(13)	0.54930(12)	0.91090(8)	0.0299(2)
C(45)	0.67058(14)	0.81176(10)	0.56577(9)	0.0300(2)
C(46)	0.87520(13)	0.65242(15)	0.52927(9)	0.0347(3)

Table S41. Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for **4c**.

	x	y	z	U_{iso}
H(121)	0.7217	0.7986	0.2722	0.026(2)
H(122)	0.7059	0.8527	0.1446	0.026(2)
H(131)	0.4837	0.8844	0.2667	0.038(3)
H(132)	0.4691	0.9401	0.1386	0.038(3)
H(141)	0.5887	1.0143	0.2725	0.060(3)
H(142)	0.4449	1.0984	0.2010	0.060(3)
H(143)	0.5797	1.0677	0.1447	0.060(3)
H(151)	0.6327	0.7522	0.0425	0.032(2)
H(152)	0.4978	0.7705	0.0987	0.032(2)
H(153)	0.5992	0.6343	0.1050	0.032(2)
H(161)	0.8251	0.5283	0.2098	0.036(2)
H(162)	0.8674	0.5872	0.2827	0.036(2)
H(163)	0.8590	0.6475	0.1552	0.036(2)
H(221)	0.7593	0.1478	0.2444	0.021(2)
H(222)	0.6119	0.2170	0.2712	0.021(2)
H(231)	0.7668	0.3469	0.1535	0.030(3)
H(232)	0.6145	0.4129	0.1751	0.030(3)
H(241)	0.6949	0.2592	0.0505	0.044(3)
H(242)	0.6152	0.4081	0.0013	0.044(3)
H(243)	0.5428	0.3236	0.0729	0.044(3)
H(251)	0.8256	0.0132	0.4292	0.029(2)
H(252)	0.6802	0.0836	0.4597	0.029(2)
H(253)	0.8130	0.0669	0.5218	0.029(2)
H(261)	0.9616	0.1351	0.3390	0.028(2)
H(262)	0.9442	0.1882	0.4323	0.028(2)
H(263)	0.9006	0.2826	0.3099	0.028(2)
H(321)	0.7408	0.0816	0.8074	0.033(3)
H(322)	0.8288	0.0501	0.7165	0.033(3)

H(331)	1.0251	-0.0671	0.8414	0.050(3)
H(332)	0.9402	-0.0320	0.9331	0.050(3)
H(341)	0.8152	-0.1448	0.9207	0.058(3)
H(342)	0.9729	-0.2342	0.9495	0.058(3)
H(343)	0.9013	-0.1805	0.8298	0.058(3)
H(351)	0.9240	0.1630	0.9029	0.044(3)
H(352)	0.7628	0.2313	0.8809	0.044(3)
H(353)	0.8511	0.3076	0.8271	0.044(3)
H(361)	0.9896	0.2585	0.6816	0.040(2)
H(362)	0.9856	0.1534	0.6435	0.040(2)
H(363)	1.0587	0.1145	0.7597	0.040(2)
H(421)	0.8761	0.5186	0.7277	0.024(2)
H(422)	0.8720	0.6472	0.7256	0.024(2)
H(431)	0.6672	0.5588	0.7940	0.030(3)
H(432)	0.6530	0.6938	0.7844	0.030(3)
H(441)	0.8566	0.4621	0.9261	0.035(2)
H(442)	0.7303	0.5526	0.9636	0.035(2)
H(443)	0.8463	0.5962	0.9151	0.035(2)
H(451)	0.7267	0.8489	0.5827	0.041(3)
H(452)	0.5936	0.8242	0.6069	0.041(3)
H(453)	0.6378	0.8519	0.4891	0.041(3)
H(461)	0.8416	0.6947	0.4527	0.046(3)
H(462)	0.9279	0.5630	0.5460	0.046(3)
H(463)	0.9325	0.6879	0.5472	0.046(3)

Table S42. Anisotropic displacement parameters ($Å^2$) for **4c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si(1)	0.00957(10)	0.00960(10)	0.00815(9)	-0.00293(7)	0.00107(7)	-0.00444(8)
O(1)	0.0156(3)	0.0104(3)	0.0140(3)	-0.0045(2)	0.0036(2)	-0.0049(2)
Si(2)	0.00992(10)	0.00906(10)	0.00854(10)	-0.00376(8)	0.00071(7)	-0.00304(8)
O(2)	0.0167(3)	0.0148(3)	0.0101(3)	-0.0052(2)	-0.0008(2)	-0.0040(2)
Si(3)	0.00879(10)	0.00988(10)	0.00796(9)	-0.00274(8)	-0.00038(7)	-0.00275(8)
O(3)	0.0131(3)	0.0114(3)	0.0156(3)	-0.0037(2)	-0.0015(2)	-0.0044(2)
Si(4)	0.00987(10)	0.01063(10)	0.00926(10)	-0.00391(8)	0.00055(7)	-0.00520(8)
O(4)	0.0190(3)	0.0175(3)	0.0104(3)	-0.0054(2)	0.0011(2)	-0.0104(2)
O(5)	0.0101(3)	0.0162(3)	0.0127(3)	-0.0034(2)	0.0010(2)	-0.0046(2)
O(6)	0.0113(3)	0.0156(3)	0.0169(3)	-0.0086(2)	0.0021(2)	-0.0052(2)
C(11)	0.0148(4)	0.0149(4)	0.0120(3)	-0.0037(3)	0.0031(3)	-0.0076(3)
C(12)	0.0248(4)	0.0191(4)	0.0180(4)	-0.0037(3)	0.0021(3)	-0.0147(4)
C(13)	0.0315(5)	0.0171(4)	0.0327(5)	-0.0094(4)	0.0030(4)	-0.0111(4)
C(14)	0.0648(9)	0.0220(5)	0.0486(8)	-0.0141(5)	0.0046(7)	-0.0218(6)
C(15)	0.0312(5)	0.0243(4)	0.0112(4)	-0.0060(3)	0.0036(3)	-0.0153(4)
C(16)	0.0176(4)	0.0259(5)	0.0283(5)	-0.0053(4)	0.0104(4)	-0.0084(4)
C(21)	0.0129(3)	0.0118(3)	0.0120(3)	-0.0052(3)	0.0011(3)	-0.0031(3)
C(22)	0.0175(4)	0.0158(4)	0.0144(4)	-0.0085(3)	0.0022(3)	-0.0061(3)
C(23)	0.0328(5)	0.0241(5)	0.0133(4)	-0.0054(3)	-0.0002(3)	-0.0152(4)
C(24)	0.0413(6)	0.0346(6)	0.0142(4)	-0.0097(4)	-0.0003(4)	-0.0162(5)
C(25)	0.0277(5)	0.0108(4)	0.0186(4)	-0.0046(3)	0.0022(3)	-0.0035(3)
C(26)	0.0126(4)	0.0246(4)	0.0230(4)	-0.0132(4)	0.0019(3)	-0.0037(3)
C(31)	0.0121(3)	0.0132(4)	0.0113(3)	-0.0030(3)	-0.0021(3)	-0.0025(3)
C(32)	0.0183(4)	0.0139(4)	0.0163(4)	0.0003(3)	-0.0023(3)	-0.0044(3)
C(33)	0.0322(6)	0.0163(4)	0.0264(5)	0.0022(4)	-0.0086(4)	-0.0029(4)
C(34)	0.0473(7)	0.0174(5)	0.0349(6)	0.0033(4)	0.0033(5)	-0.0088(5)
C(35)	0.0401(6)	0.0234(5)	0.0169(4)	-0.0079(4)	-0.0123(4)	-0.0021(4)
C(36)	0.0115(4)	0.0227(5)	0.0320(5)	-0.0008(4)	0.0002(4)	-0.0041(3)
C(41)	0.0198(4)	0.0217(4)	0.0134(4)	-0.0068(3)	0.0019(3)	-0.0146(3)
C(42)	0.0191(4)	0.0248(4)	0.0158(4)	-0.0090(3)	0.0001(3)	-0.0114(4)
C(43)	0.0230(4)	0.0233(4)	0.0161(4)	-0.0087(3)	0.0027(3)	-0.0086(4)

C(44)	0.0396(6)	0.0360(6)	0.0159(4)	-0.0101(4)	0.0011(4)	-0.0170(5)
C(45)	0.0492(7)	0.0189(5)	0.0253(5)	-0.0029(4)	-0.0071(5)	-0.0213(5)
C(46)	0.0317(6)	0.0700(9)	0.0247(5)	-0.0228(6)	0.0125(4)	-0.0389(6)

Table S43. Full list of bond lengths [Å] and angles [°] for **4c**.

Si(1)-O(4)	1.6243(7)	C(32)-H(321)	0.99
Si(1)-O(5)	1.6244(6)	C(32)-H(322)	0.99
Si(1)-O(1)	1.6269(7)	C(33)-C(34)	1.5225(18)
Si(1)-C(11)	1.8727(8)	C(33)-H(331)	0.99
O(1)-Si(2)	1.6255(6)	C(33)-H(332)	0.99
Si(2)-O(6)	1.6234(7)	C(34)-H(341)	0.98
Si(2)-O(2)	1.6239(6)	C(34)-H(342)	0.98
Si(2)-C(21)	1.8651(9)	C(34)-H(343)	0.98
O(2)-Si(3)	1.6222(7)	C(35)-H(351)	0.98
Si(3)-O(5)$^{i)}$	1.6237(6)	C(35)-H(352)	0.98
Si(3)-O(3)	1.6248(7)	C(35)-H(353)	0.98
Si(3)-C(31)	1.8634(8)	C(36)-H(361)	0.98
O(3)-Si(4)	1.6242(7)	C(36)-H(362)	0.98
Si(4)-O(6)$^{i)}$	1.6215(6)	C(36)-H(363)	0.98
Si(4)-O(4)	1.6250(6)	C(41)-C(45)	1.5417(15)
Si(4)-C(41)	1.8660(9)	C(41)-C(46)	1.5420(14)
O(5)-Si(3)$^{i)}$	1.6237(6)	C(41)-C(42)	1.5458(12)
O(6)-Si(4)$^{i)}$	1.6215(6)	C(42)-C(43)	1.5237(13)
C(11)-C(15)	1.5405(13)	C(42)-H(421)	0.99
C(11)-C(16)	1.5413(13)	C(42)-H(422)	0.99
C(11)-C(12)	1.5452(13)	C(43)-C(44)	1.5293(14)
C(12)-C(13)	1.5175(15)	C(43)-H(431)	0.99
C(12)-H(121)	0.99	C(43)-H(432)	0.99
C(12)-H(122)	0.99	C(44)-H(441)	0.98
C(13)-C(14)	1.5269(16)	C(44)-H(442)	0.98
C(13)-H(131)	0.99	C(44)-H(443)	0.98
C(13)-H(132)	0.99	C(45)-H(451)	0.98
C(14)-H(141)	0.98	C(45)-H(452)	0.98
C(14)-H(142)	0.98	C(45)-H(453)	0.98
C(14)-H(143)	0.98	C(46)-H(461)	0.98
C(15)-H(151)	0.98	C(46)-H(462)	0.98
C(15)-H(152)	0.98	C(46)-H(463)	0.98
C(15)-H(153)	0.98		
C(16)-H(161)	0.98	O(4)-Si(1)-O(5)	109.05(3)
C(16)-H(162)	0.98	O(4)-Si(1)-O(1)	109.36(3)
C(16)-H(163)	0.98	O(5)-Si(1)-O(1)	108.25(3)
C(21)-C(26)	1.5400(12)	O(4)-Si(1)-C(11)	110.08(4)
C(21)-C(22)	1.5426(12)	O(5)-Si(1)-C(11)	111.01(4)
C(21)-C(25)	1.5469(12)	O(1)-Si(1)-C(11)	109.05(4)
C(22)-C(23)	1.5277(13)	Si(2)-O(1)-Si(1)	146.58(4)
C(22)-H(221)	0.99	O(6)-Si(2)-O(2)	109.41(3)
C(22)-H(222)	0.99	O(6)-Si(2)-O(1)	109.14(3)
C(23)-C(24)	1.5282(14)	O(2)-Si(2)-O(1)	108.63(4)
C(23)-H(231)	0.99	O(6)-Si(2)-C(21)	109.00(4)
C(23)-H(232)	0.99	O(2)-Si(2)-C(21)	108.14(4)
C(24)-H(241)	0.98	O(1)-Si(2)-C(21)	112.48(4)
C(24)-H(242)	0.98	Si(3)-O(2)-Si(2)	151.04(4)
C(24)-H(243)	0.98	O(2)-Si(3)-O(5)$^{i)}$	109.01(4)
C(25)-H(251)	0.98	O(2)-Si(3)-O(3)	109.14(3)
C(25)-H(252)	0.98	O(5)$^{i)}$-Si(3)-O(3)	109.43(3)
C(25)-H(253)	0.98	O(2)-Si(3)-C(31)	110.44(4)
C(26)-H(261)	0.98	O(5)$^{i)}$-Si(3)-C(31)	109.74(4)
C(26)-H(262)	0.98	O(3)-Si(3)-C(31)	109.07(4)
C(26)-H(263)	0.98	Si(4)-O(3)-Si(3)	146.06(4)
C(31)-C(36)	1.5371(13)	O(6)$^{i)}$-Si(4)-O(3)	109.12(3)
C(31)-C(35)	1.5389(13)	O(6)$^{i)}$-Si(4)-O(4)	108.62(3)
C(31)-C(32)	1.5465(13)	O(3)-Si(4)-O(4)	108.83(3)
C(32)-C(33)	1.5243(13)	O(6)$^{i)}$-Si(4)-C(41)	110.88(4)

O(3)-Si(4)-C(41)	109.89(4)	C(21)-C(25)-H(251)	109.5
O(4)-Si(4)-C(41)	109.45(4)	C(21)-C(25)-H(252)	109.5
Si(1)-O(4)-Si(4)	151.20(4)	H(251)-C(25)-H(252)	109.5
Si(3)$^{i)}$-O(5)-Si(1)	148.34(4)	C(21)-C(25)-H(253)	109.5
Si(4)$^{i)}$-O(6)-Si(2)	148.33(4)	H(251)-C(25)-H(253)	109.5
C(15)-C(11)-C(16)	108.71(8)	H(252)-C(25)-H(253)	109.5
C(15)-C(11)-C(12)	110.58(7)	C(21)-C(26)-H(261)	109.5
C(16)-C(11)-C(12)	107.42(8)	C(21)-C(26)-H(262)	109.5
C(15)-C(11)-Si(1)	109.55(6)	H(261)-C(26)-H(262)	109.5
C(16)-C(11)-Si(1)	108.22(6)	C(21)-C(26)-H(263)	109.5
C(12)-C(11)-Si(1)	112.25(6)	H(261)-C(26)-H(263)	109.5
C(13)-C(12)-C(11)	117.16(8)	H(262)-C(26)-H(263)	109.5
C(13)-C(12)-H(121)	108.0	C(36)-C(31)-C(35)	109.44(9)
C(11)-C(12)-H(121)	108.0	C(36)-C(31)-C(32)	111.02(8)
C(13)-C(12)-H(122)	108.0	C(35)-C(31)-C(32)	110.97(8)
C(11)-C(12)-H(122)	108.0	C(36)-C(31)-Si(3)	108.95(6)
H(121)-C(12)-H(122)	107.3	C(35)-C(31)-Si(3)	107.79(6)
C(12)-C(13)-C(14)	112.03(10)	C(32)-C(31)-Si(3)	108.58(6)
C(12)-C(13)-H(131)	109.2	C(33)-C(32)-C(31)	116.88(8)
C(14)-C(13)-H(131)	109.2	C(33)-C(32)-H(321)	108.1
C(12)-C(13)-H(132)	109.2	C(31)-C(32)-H(321)	108.1
C(14)-C(13)-H(132)	109.2	C(33)-C(32)-H(322)	108.1
H(131)-C(13)-H(132)	107.9	C(31)-C(32)-H(322)	108.1
C(13)-C(14)-H(141)	109.5	H(321)-C(32)-H(322)	107.3
C(13)-C(14)-H(142)	109.5	C(34)-C(33)-C(32)	112.27(10)
H(141)-C(14)-H(142)	109.5	C(34)-C(33)-H(331)	109.1
C(13)-C(14)-H(143)	109.5	C(32)-C(33)-H(331)	109.1
H(141)-C(14)-H(143)	109.5	C(34)-C(33)-H(332)	109.1
H(142)-C(14)-H(143)	109.5	C(32)-C(33)-H(332)	109.1
C(11)-C(15)-H(151)	109.5	H(331)-C(33)-H(332)	107.9
C(11)-C(15)-H(152)	109.5	C(33)-C(34)-H(341)	109.5
H(151)-C(15)-H(152)	109.5	C(33)-C(34)-H(342)	109.5
C(11)-C(15)-H(153)	109.5	H(341)-C(34)-H(342)	109.5
H(151)-C(15)-H(153)	109.5	C(33)-C(34)-H(343)	109.5
H(152)-C(15)-H(153)	109.5	H(341)-C(34)-H(343)	109.5
C(11)-C(16)-H(161)	109.5	H(342)-C(34)-H(343)	109.5
C(11)-C(16)-H(162)	109.5	C(31)-C(35)-H(351)	109.5
H(161)-C(16)-H(162)	109.5	C(31)-C(35)-H(352)	109.5
C(11)-C(16)-H(163)	109.5	H(351)-C(35)-H(352)	109.5
H(161)-C(16)-H(163)	109.5	C(31)-C(35)-H(353)	109.5
H(162)-C(16)-H(163)	109.5	H(351)-C(35)-H(353)	109.5
C(26)-C(21)-C(22)	111.01(7)	H(352)-C(35)-H(353)	109.5
C(26)-C(21)-C(25)	108.61(7)	C(31)-C(36)-H(361)	109.5
C(22)-C(21)-C(25)	106.85(7)	C(31)-C(36)-H(362)	109.5
C(26)-C(21)-Si(2)	110.11(6)	H(361)-C(36)-H(362)	109.5
C(22)-C(21)-Si(2)	112.82(6)	C(31)-C(36)-H(363)	109.5
C(25)-C(21)-Si(2)	107.23(6)	H(361)-C(36)-H(363)	109.5
C(23)-C(22)-C(21)	117.90(8)	H(362)-C(36)-H(363)	109.5
C(23)-C(22)-H(221)	107.8	C(45)-C(41)-C(46)	109.02(9)
C(21)-C(22)-H(221)	107.8	C(45)-C(41)-C(42)	110.48(8)
C(23)-C(22)-H(222)	107.8	C(46)-C(41)-C(42)	106.58(8)
C(21)-C(22)-H(222)	107.8	C(45)-C(41)-Si(4)	110.05(7)
H(221)-C(22)-H(222)	107.2	C(46)-C(41)-Si(4)	107.70(7)
C(22)-C(23)-C(24)	110.52(9)	C(42)-C(41)-Si(4)	112.85(6)
C(22)-C(23)-H(231)	109.5	C(43)-C(42)-C(41)	118.05(8)
C(24)-C(23)-H(231)	109.5	C(43)-C(42)-H(421)	107.8
C(22)-C(23)-H(232)	109.5	C(41)-C(42)-H(421)	107.8
C(24)-C(23)-H(232)	109.5	C(43)-C(42)-H(422)	107.8
H(231)-C(23)-H(232)	108.1	C(41)-C(42)-H(422)	107.8
C(23)-C(24)-H(241)	109.5	H(421)-C(42)-H(422)	107.1
C(23)-C(24)-H(242)	109.5	C(42)-C(43)-C(44)	110.87(9)
H(241)-C(24)-H(242)	109.5	C(42)-C(43)-H(431)	109.5
C(23)-C(24)-H(243)	109.5	C(44)-C(43)-H(431)	109.5
H(241)-C(24)-H(243)	109.5	C(42)-C(43)-H(432)	109.5
H(242)-C(24)-H(243)	109.5	C(44)-C(43)-H(432)	109.5

H(431)-C(43)-H(432)	108.1
C(43)-C(44)-H(441)	109.5
C(43)-C(44)-H(442)	109.5
H(441)-C(44)-H(442)	109.5
C(43)-C(44)-H(443)	109.5
H(441)-C(44)-H(443)	109.5
H(442)-C(44)-H(443)	109.5
C(41)-C(45)-H(451)	109.5
C(41)-C(45)-H(452)	109.5
H(451)-C(45)-H(452)	109.5
C(41)-C(45)-H(453)	109.5
H(451)-C(45)-H(453)	109.5
H(452)-C(45)-H(453)	109.5
C(41)-C(46)-H(461)	109.5
C(41)-C(46)-H(462)	109.5
H(461)-C(46)-H(462)	109.5
C(41)-C(46)-H(463)	109.5
H(461)-C(46)-H(463)	109.5
H(462)-C(46)-H(463)	109.5

O(4)-Si(1)-O(1)-Si(2)	68.18(9)
O(5)-Si(1)-O(1)-Si(2)	-50.52(9)
C(11)-Si(1)-O(1)-Si(2)	-171.41(8)
Si(1)-O(1)-Si(2)-O(6)	50.74(9)
Si(1)-O(1)-Si(2)-O(2)	-68.49(9)
Si(1)-O(1)-Si(2)-C(21)	171.84(7)
O(6)-Si(2)-O(2)-Si(3)	-69.91(10)
O(1)-Si(2)-O(2)-Si(3)	49.14(10)
C(21)-Si(2)-O(2)-Si(3)	171.48(9)
Si(2)-O(2)-Si(3)-O(5)$^{i)}$	69.89(10)
Si(2)-O(2)-Si(3)-O(3)	-49.57(10)
Si(2)-O(2)-Si(3)-C(31)	-169.47(9)
O(2)-Si(3)-O(3)-Si(4)	69.59(8)
O(5)$^{i)}$-Si(3)-O(3)-Si(4)	-49.62(9)
C(31)-Si(3)-O(3)-Si(4)	-169.68(7)
Si(3)-O(3)-Si(4)-O(6)$^{i)}$	49.31(9)
Si(3)-O(3)-Si(4)-O(4)	-69.07(8)
Si(3)-O(3)-Si(4)-C(41)	171.09(7)
O(5)-Si(1)-O(4)-Si(4)	70.94(10)
O(1)-Si(1)-O(4)-Si(4)	-47.26(10)
C(11)-Si(1)-O(4)-Si(4)	-167.05(9)
O(6)$^{i)}$-Si(4)-O(4)-Si(1)	-71.10(10)
O(3)-Si(4)-O(4)-Si(1)	47.60(10)
C(41)-Si(4)-O(4)-Si(1)	167.71(9)
O(4)-Si(1)-O(5)-Si(3)$^{i)}$	-44.51(10)
O(1)-Si(1)-O(5)-Si(3)$^{i)}$	74.38(9)
C(11)-Si(1)-O(5)-Si(3)$^{i)}$	-165.96(8)
O(2)-Si(2)-O(6)-Si(4)$^{i)}$	44.88(9)
O(1)-Si(2)-O(6)-Si(4)$^{i)}$	-73.86(9)
C(21)-Si(2)-O(6)-Si(4)$^{i)}$	162.94(8)
O(4)-Si(1)-C(11)-C(15)	-160.30(6)
O(5)-Si(1)-C(11)-C(15)	-39.46(7)
O(1)-Si(1)-C(11)-C(15)	79.72(7)
O(4)-Si(1)-C(11)-C(16)	81.31(7)
O(5)-Si(1)-C(11)-C(16)	-157.84(7)
O(1)-Si(1)-C(11)-C(16)	-38.66(8)
O(4)-Si(1)-C(11)-C(12)	-37.05(7)
O(5)-Si(1)-C(11)-C(12)	83.79(7)
O(1)-Si(1)-C(11)-C(12)	-157.03(6)
C(15)-C(11)-C(12)-C(13)	63.01(11)
C(16)-C(11)-C(12)-C(13)	-178.51(9)
Si(1)-C(11)-C(12)-C(13)	-59.66(10)
C(11)-C(12)-C(13)-C(14)	179.06(10)
O(6)-Si(2)-C(21)-C(26)	171.74(6)
O(2)-Si(2)-C(21)-C(26)	-69.39(7)
O(1)-Si(2)-C(21)-C(26)	50.57(7)
O(6)-Si(2)-C(21)-C(22)	47.11(7)
O(2)-Si(2)-C(21)-C(22)	165.97(6)
O(1)-Si(2)-C(21)-C(22)	-74.07(7)
O(6)-Si(2)-C(21)-C(25)	-70.26(7)
O(2)-Si(2)-C(21)-C(25)	48.60(7)
O(1)-Si(2)-C(21)-C(25)	168.56(6)
C(26)-C(21)-C(22)-C(23)	-61.71(10)
C(25)-C(21)-C(22)-C(23)	-179.97(8)
Si(2)-C(21)-C(22)-C(23)	62.43(9)
C(21)-C(22)-C(23)-C(24)	175.81(8)
O(2)-Si(3)-C(31)-C(36)	58.60(8)
O(5)$^{i)}$-Si(3)-C(31)-C(36)	178.80(7)
O(3)-Si(3)-C(31)-C(36)	-61.34(7)
O(2)-Si(3)-C(31)-C(35)	177.28(7)
O(5)$^{i)}$-Si(3)-C(31)-C(35)	-62.53(8)
O(3)-Si(3)-C(31)-C(35)	57.34(8)
O(2)-Si(3)-C(31)-C(32)	-62.44(7)
O(5)$^{i)}$-Si(3)-C(31)-C(32)	57.76(7)
O(3)-Si(3)-C(31)-C(32)	177.62(6)
C(36)-C(31)-C(32)-C(33)	61.56(11)
C(35)-C(31)-C(32)-C(33)	-60.39(11)
Si(3)-C(31)-C(32)-C(33)	-178.69(8)
C(31)-C(32)-C(33)-C(34)	177.52(10)
O(6)$^{i)}$-Si(4)-C(41)-C(45)	-42.77(8)
O(3)-Si(4)-C(41)-C(45)	-163.50(7)
O(4)-Si(4)-C(41)-C(45)	77.04(7)
O(6)$^{i)}$-Si(4)-C(41)-C(46)	-161.50(7)
O(3)-Si(4)-C(41)-C(46)	77.77(8)
O(4)-Si(4)-C(41)-C(46)	-41.69(8)
O(6)$^{i)}$-Si(4)-C(41)-C(42)	81.14(7)
O(3)-Si(4)-C(41)-C(42)	-39.59(8)
O(4)-Si(4)-C(41)-C(42)	-159.05(6)
C(45)-C(41)-C(42)-C(43)	63.48(11)
C(46)-C(41)-C(42)-C(43)	-178.21(9)
Si(4)-C(41)-C(42)-C(43)	-60.19(10)
C(41)-C(42)-C(43)-C(44)	-175.37(9)

Symmetry transformations used to generate equivalent atoms:

$^{i)}$ 1-x, 1-y, 1-z

X-ray diffraction data of 4d.

Table S44. Crystal data and structure refinement for **4d**.

Crystal data		
Identification code		i1113
Empirical formula		$C_{56}H_{120}O_{12}Si_8$
Formula weight		1210.24
Crystal description		needle, colourless
Crystal size		0.60 x 0.60 x 0.07 mm
Crystal system, space group		monoclinic, P 21/n
Unit cell dimensions:	a	14.1192(9)Å
	b	12.8237(5)Å
	c	20.1991(12)Å
	α	90°
	ß	97.065(5)°
	γ	90°
Volume		3629.5(3)Å^3
Z		2
Calculated density		1.107 Mg/m^3
F(000)		1328
Linear absorption coefficient μ		0.198 mm^{-1}
Absorption correction		Integration
Data collection		
Temperature		173(2)K
Diffractometer		STOE IPDS
Radiation source		sealed X-ray tube, 12 x 0.4 mm long-fine focus
Radiation and wavelength		MoK_α, 0.71073Å
Monochromator		graphite
Θ range for data collection		1.67 to 25.00°
Index ranges		-16≤ h ≤ 16, -14≤ k ≤ 15, -24≤ l ≤24
Reflections collected		22786
Independent reflections		6395
R(int)		0.1663
Refinement		
Refinement method		Full-matrixleast-squares on F^2
Data / parameters / restraints		6395 / 0 / 355
Goodness-of-fit on F^2		1.025
Final R indices [I > 2σ(I)]		R_1 = 0.0834, wR_2 = 0.2197
R indices (all data)		R_1 = 0.1043, wR_2 = 0.2372
Largest difference peak and hole		0.562 and -0.543/Å^3
Structure Solution Program		SHELXS-97 (Sheldrick, 2008)
Structure Refinement Program		SHELXL-97 (Sheldrick, 2008)

Table S45. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å² x 10^3) for **4d**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U_{eq}
O(1)	830(2)	1170(2)	997(1)	48(1)
O(2)	-1010(2)	1418(2)	581(1)	48(1)
O(3)	-1792(2)	305(2)	-448(1)	49(1)
O(4)	-1348(2)	-591(2)	722(1)	50(1)
O(5)	276(2)	1974(2)	-194(1)	51(1)
O(6)	-462(2)	808(2)	-1204(1)	50(1)
Si(1)	1304(1)	20(1)	1105(1)	42(1)
Si(2)	-1744(1)	473(1)	-353(1)	43(1)
Si(3)	47(1)	1918(1)	574(1)	42(1)
Si(4)	484(1)	1424(1)	-882(1)	43(1)
C(1)	2213(3)	-16(3)	1854(2)	53(1)
C(2)	3177(3)	439(4)	1707(2)	65(1)
C(3)	3167(3)	1547(4)	1435(3)	66(1)
C(4)	4148(4)	1935(5)	1310(3)	90(2)
C(5)	4126(5)	3009(6)	1012(5)	124(3)
C(6)	1836(4)	551(5)	2441(2)	75(1)
C(7)	2382(4)	-1176(4)	2066(3)	77(1)
C(8)	-2959(3)	762(4)	589(2)	62(1)
C(9)	-3395(8)	1691(11	248(9)	285(11)
C(10)	-3188(5)	2423(6)	-104(4)	112(2)
C(11)	-3616(10)	3339(9)	-456(7)	207(6)
C(12)	-3588(17)	4035(10)	-697(8)	328(15)
C(13)	-2894(4)	939(7)	1324(3)	116(3)
C(14)	-3591(4)	-159(7)	414(4)	122(3)
C(15)	100(3)	3267(3)	926(2)	51(1)
C(16)	34(6)	3284(4)	1689(3)	96(2)
C(17)	-680(9)	2786(8)	1972(4)	170(5)
C(18)	-798(11)	2949(14)	2694(6)	254(10)
C(19)	-410(12)	3208(19)	3101(6)	326(15)
C(20)	-674(4)	3937(4)	539(3	84(2)
C(21)	1070(4)	3743(4)	847(3)	83(2)
C(22)	814(3)	2439(3)	-1474(2)	49(1)
C(23)	1729(3)	2996(3)	-1146(2)	60(1)
C(24)	2136(3)	3853(4)	-1552(2)	65(1)
C(25)	3001(4)	4359(5)	-1178(3)	90(2)
C(26)	3441(5)	5193(5)	-1591(4)	112(2)
C(27)	991(4)	1898(3)	-2128(2)	62(1)
C(28)	-18(3)	3218(3)	-1615(2)	62(1)

Table S46. Hydrogen coordinates ($Å^2x10^4$) and isotropic displacement parameters ($Å^2x10^3$) for **4d**.

	x	y	z	U(eq)
H(2A)	3624	418	2125	78
H(2B)	3439	-25	1383	78
H(3A)	2734	1575	1011	79
H(3B)	2909	2020	1756	79
H(4B)	4573	1940	1738	108
H(4A)	4420	1444	1006	108
H(5A)	3874	3504	1316	148
H(5B)	3715	3007	584	148
H(5C)	4774	3215	941	148
H(6A)	1757	1294	2336	90
H(6B)	2291	466	2844	90
H(6C)	1219	253	2516	90
H(7A)	2828	-1207	2478	92
H(7B)	2652	-1555	1712	92
H(7C)	1774	-1494	2142	92
H(9A)	-3959	1390	-25	342
H(9B)	-3657	2058	616	342
H(10A)	-2908	2055	-464	134
H(10B)	-2635	2734	176	134
H(11B)	-4051	2969	-800	248
H(11A)	-4037	3555	- 123	248
H(12A)	-3530	3909	-1169	394
H(12B)	-3035	4434	-494	394
H(12C)	-4173	4430	-659	394
H(13A)	-3528	1102	1445	139
H(13B)	- 2460	1522	1450	139
H(13C)	-2650	308	1560	139
H(14A)	-3654	-276	-69	146
H(14B)	-4223	-26	551	146
H(14C)	-3312	-778	646	146
H(16A)	646	3001	1909	115
H(16B)	13	4026	1820	115
H(17A)	-596	2028	1907	204
H(17B)	-1292	2981	1708	204
H(18A)	-1378	3389	2669	305
H(18B)	-1004	2253	2832	305
H(19A)	-440	3971	3112	392
H(19B)	254	2986	3100	392
H(19C)	-660	2924	3495	392
H(20A)	-642	4646	720	101
H(20B)	-1302	3636	580	101
H(20C)	- 575	3957	67	101
H(21A)	1571	3360	1125	100
H(21B)	1079	4476	986	100
H(21C)	1183	3701	378	100
H(23A)	1589	3303	-719	72
H(23B)	2231	2462	-1038	72
H(24A)	2309	3551	-1972	78
H(24B)	1639	4389	-1670	78
H(25B)	3485	3817	-1044	108
H(25A)	2820	4684	-767	108
H(26A)	2955	5713	-1746	134
H(26B)	3679	4865	-1976	134
H(26C)	3970	5535	-1314	134
H(27A)	1532	1418	-2041	74
H(27B)	1133	2424	-2454	74

H(27C)	420	1506	-	2306	74
H(28C)	-605	2839		-1774	74
H(28B)	126	3718		-1956	74
H(28A)	-105	3593		-1204	74

Table S47. Anisotropic displacement parameters ($Å^2$x10*3) for **4d**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U11	U22	U33	U23	U13	U12
C(1)	48(2)	68(2)	43(2)	0(2)	0(2)	0(2)
C(2)	50(2)	83(3)	59(3)	-9(2)	-3(2)	-2(2)
C(3)	50(2)	75(3)	72(3)	-12(2)	8(2)	-15(2)
C(4)	70(3)	112(4)	88(4)	-23(3)	11(3)	-35(3)
C(5)	98(5)	114(5)	165(8)	2(5)	43(5)	-46(4)
C(6)	74(3)	106(4)	44(2)	-9(2)	3(2)	-7(3)
C(7)	72(3)	86(3)	67(3)	21(2)	-16(2)	2(3)
C(8)	43(2)	78(3)	68(3)	-6(2)	11(2)	7(2)
C(9)	160(9)	284(14)	450(20)	263(16)	213(13)	170(10)
C(10)	99(5)	117(5)	120(6)	28(4)	19(4)	43(4)
C(11)	244(14)	170(9)	200(12)	51(9)	6(10)	147(10)
C(12)	570(40)	131(9)	227(16)	67(10)	-160(20)	43(15)
C(13)	55(3)	207(8)	91(4)	-67(5)	30(3)	-24(4)
C(14)	56(3)	182(7)	133(6)	-83(5)	38(3)	-40(4)
C(15)	56(2)	46(2)	50(2)	-2(2)	5(2)	-4(2)
C(16)	152(6)	73(3)	66(3)	-18(3)	31(3)	-9(4)
C(17)	279(13)	159(7)	91(5)	-55(5)	102(7)	-106(8)
C(18)	265(15)	420(20)	98(7)	-107(10)	88(8)	-224(16)
C(19)	250(17)	640(40)	98(8)	-125(15)	53(9)	-230(20)
C(20)	84(3)	53(2)	110(4)	-12(3)	-13(3)	15(2)
C(21)	70(3)	56(3)	124(5)	-19(3)	13(3)	-12(2)
C(22)	55(2)	48(2)	44(2)	0(2)	8(2)	-5(2)
C(23)	63(2)	65(2)	53(2)	4(2)	12(2)	-19(2)
C(24)	73(3)	63(2)	62(3)	5(2)	19(2)	-12(2)
C(25)	91(4)	98(4)	81(4)	4(3)	13(3)	-46(3)
C(26)	112(5)	100(4)	127(6)	16(4)	32(4)	-45(4)
C(27)	80(3)	63(2)	44(2)	-1(2)	16(2)	-5(2)
C(28)	71(3)	58(2)	56(2)	12(2)	9(2)	3(2)
O(1)	45(1)	49(1)	49(1)	-2(1)	1(1)	0(1)
O(2)	44(1)	51(1)	50(1)	-7(1)	6(1)	-2(1)
O(3)	43(1)	61(2)	42(1)	-4(1)	4(1)	4(1)
O(4)	43(1)	56(1)	52(2)	8(1)	12(1)	-1(1)
O(5)	58(2)	52(1)	44(2)	-2(1)	13(1)	-3(1)
O(6)	47(1)	53(1)	47(1)	3(1)	2(1)	-7(1)
Si(1)	38(1)	48(1)	39(1)	0(1)	2(1)	0(1)
Si(2)	35(1)	51(1)	44(1)	-2(1)	7(1)	1(1)
Si(3)	43(1)	43(1)	41(1)	-2(1)	7(1)	-1(1)
Si(4)	45(1)	46(1)	39(1)	2(1)	8(1)	-4(1)

Table S48. Full list of bond lengths [Å] and angles [°] for **4d**.

C(1)-C(6)	1.541(6)	C(19)-H(19C)	0.9800
C(1)-C(2)	1.543(6)	C(20)-H(20A)	0.9800
C(1)-C(7)	1.558(6)	C(20)-H(20B)	0.9800
C(1)-Si(1)	1.861(4)	C(20)-H(20C)	0.9800
C(2)-C(3)	1.523(7)	C(21)-H(21A)	0.9800
C(2)-H(2A)	0.9900	C(21)-H(21B)	0.9800
C(2)-H(2B)	0.9900	C(21)-H(21C)	0.9800
C(3)-C(4)	1.521(7)	C(22)-C(27)	1.539(5)
C(3)-H(3A)	0.9900	C(22)-C(28)	1.543(6)
C(3)-H(3B)	0.9900	C(22)-C(23)	1.552(6)
C(4)-C(5)	1.502(10)	C(22)-Si(4)	1.866(4)
C(4)-H(4B)	0.9900	C(23)-C(24)	1.525(6)
C(4)-H(4A)	0.9900	C(23)-H(23A)	0.9900
C(5)-H(5A)	0.9800	C(23)-H(23B)	0.9900
C(5)-H(5B)	0.9800	C(24)-C(25)	1.502(7)
C(5)-H(5C)	0.9800	C(24)-H(24A)	0.9900
C(6)-H(6A)	0.9800	C(24)-H(24B)	0.9900
C(6)-H(6B)	0.9800	C(25)-C(26)	1.534(7)
C(6)-H(6C)	0.9800	C(25)-H(25B)	0.9900
C(7)-H(7A)	0.9800	C(25)-H(25A)	0.9900
C(7)-H(7B)	0.9800	C(26)-H(26A)	0.9800
C(7)-H(7C)	0.9800	C(26)-H(26B)	0.9800
C(8)-C(9)	1.472(10)	C(26)-H(26C)	0.9800
C(8)-C(13)	1.494(7)	C(27)-H(27A)	0.9800
C(8)-C(14)	1.496(8)	C(27)-H(27B)	0.9800
C(8)-Si(2)	1.873(4)	C(27)-H(27C)	0.9800
C(9)-C(10)	1.234(10)	C(28)-H(28C)	0.9800
C(9)-H(9A)	0.9900	C(28)-H(28B)	0.9800
C(9)-H(9B)	0.9900	C(28)-H(28A)	0.9800
C(10)-C(11)	1.464(10)	O(1)-Si(1)	1.623(3)
C(10)-H(10A)	0.9900	O(1)-Si(3)	1.625(3)
C(10)-H(10B)	0.9900	O(2)-Si(2)	1.624(3)
C(11)-C(12)	1.020(15)	O(2)-Si(3)	1.626(3)
C(11)-H(11B)	0.9900	O(3)-Si(1)#1	1.622(3)
C(11)-H(11A)	0.9900	O(3)-Si(2)	1.626(3)
C(12)-H(12A)	0.9800	O(4)-Si(2)	1.622(3)
C(12)-H(12B)	0.9800	O(4)-Si(4)#1	1.623(3)
C(12)-H(12C)	0.9800	O(5)-Si(4)	1.616(3)
C(13)-H(13A)	0.9800	O(5)-Si(3)	1.626(3)
C(13)-H(13B)	0.9800	O(6)-Si(4)	1.618(3)
C(13)-H(13C)	0.9800	O(6)-Si(1)#1	1.625(3)
C(14)-H(14A)	0.9800	Si(1)-O(3)#1	1.622(3)
C(14)-H(14B)	0.9800	Si(1)-O(6)#1	1.625(3)
C(14)-H(14C)	0.9800	Si(4)-O(4)#1	1.623(3)
C(15)-C(21)	1.526(6)	C(6)-C(1)-C(2)	111.5(4)
C(15)-C(20)	1.527(6)	C(6)-C(1)-C(7)	107.1(4)
C(15)-C(16)	1.555(7)	C(2)-C(1)-C(7)	107.8(4)
C(15)-Si(3)	1.868(4)	C(6)-C(1)-Si(1)	110.1(3)
C(16)-C(17)	1.377(10)	C(2)-C(1)-Si(1)	111.8(3)
C(16)-H(16A)	0.9900	C(7)-C(1)-Si(1)	108.3(3)
C(16)-H(16B)	0.9900	C(3)-C(2)-C(1)	117.0(4)
C(17)-C(18)	1.502(11)	C(3)-C(2)-H(2A)	108.1
C(17)-H(17A)	0.9900	C(1)-C(2)-H(2A)	108.1
C(17)-H(17B)	0.9900	C(3)-C(2)-H(2B)	108.1
C(18)-C(19)	0.988(12)	C(1)-C(2)-H(2B)	108.1
C(18)-H(18A)	0.9900	H(2A)-C(2)-H(2B)	107.3
C(18)-H(18B)	0.9900	C(4)-C(3)-C(2)	113.4(4)
C(19)-H(19A)	0.9800	C(4)-C(3)-H(3A)	108.9
C(19)-H(19B)	0.9800	C(2)-C(3)-H(3A)	108.9

C(4)-C(3)-H(3B)	108.9	H(13B)-C(13)-H(13C)	109.5
C(2)-C(3)-H(3B)	108.9	C(8)-C(14)-H(14A)	109.5
H(3A)-C(3)-H(3B)	107.7	C(8)-C(14)-H(14B)	109.5
C(5)-C(4)-C(3)	113.1(5)	H(14A)-C(14)-H(14B)	109.5
C(5)-C(4)-H(4B)	109.0	C(8)-C(14)-H(14C)	109.5
C(3)-C(4)-H(4B)	109.0	H(14A)-C(14)-H(14C)	109.5
C(5)-C(4)-H(4A)	109.0	H(14B)-C(14)-H(14C)	109.5
C(3)-C(4)-H(4A)	109.0	C(21)-C(15)-C(20)	108.5(4)
H(4B)-C(4)-H(4A)	107.8	C(21)-C(15)-C(16)	105.2(4)
C(4)-C(5)-H(5A)	109.5	C(20)-C(15)-C(16)	111.9(4)
C(4)-C(5)-H(5B)	109.5	C(21)-C(15)-Si(3)	109.0(3)
H(5A)-C(5)-H(5B)	109.5	C(20)-C(15)-Si(3)	109.5(3)
C(4)-C(5)-H(5C)	109.5	C(16)-C(15)-Si(3)	112.6(3)
H(5A)-C(5)-H(5C)	109.5	C(17)-C(16)-C(15)	122.8(6)
H(5B)-C(5)-H(5C)	109.5	C(17)-C(16)-H(16A)	106.6
C(1)-C(6)-H(6A)	109.5	C(15)-C(16)-H(16A)	106.6
C(1)-C(6)-H(6B)	109.5	C(17)-C(16)-H(16B)	106.6
H(6A)-C(6)-H(6B)	109.5	C(15)-C(16)-H(16B)	106.6
C(1)-C(6)-H(6C)	109.5	H(16A)-C(16)-H(16B)	106.6
H(6A)-C(6)-H(6C)	109.5	C(16)-C(17)-C(18)	120.9(8)
H(6B)-C(6)-H(6C)	109.5	C(16)-C(17)-H(17A)	107.1
C(1)-C(7)-H(7A)	109.5	C(18)-C(17)-H(17A)	107.1
C(1)-C(7)-H(7B)	109.5	C(16)-C(17)-H(17B)	107.1
H(7A)-C(7)-H(7B)	109.5	C(18)-C(17)-H(17B)	107.1
C(1)-C(7)-H(7C)	109.5	H(17A)-C(17)-H(17B)	106.8
H(7A)-C(7)-H(7C)	109.5	C(19)-C(18)-C(17)	137.6(14)
H(7B)-C(7)-H(7C)	109.5	C(19)-C(18)-H(18A)	102.7
C(9)-C(8)-C(13)	108.3(9)	C(17)-C(18)-H(18A)	102.7
C(9)-C(8)-C(14)	109.0(8)	C(19)-C(18)-H(18B)	102.7
C(13)-C(8)-C(14)	108.4(5)	C(17)-C(18)-H(18B)	102.7
C(9)-C(8)-Si(2)	112.5(4)	H(18A)-C(18)-H(18B)	105.0
C(13)-C(8)-Si(2)	109.7(3)	C(18)-C(19)-H(19A)	109.5
C(14)-C(8)-Si(2)	108.8(3)	C(18)-C(19)-H(19B)	109.5
C(10)-C(9)-C(8)	140.4(7)	H(19A)-C(19)-H(19B)	109.5
C(10)-C(9)-H(9A)	101.9	C(18)-C(19)-H(19C)	109.5
C(8)-C(9)-H(9A)	101.9	H(19A)-C(19)-H(19C)	109.5
C(10)-C(9)-H(9B)	101.9	H(19B)-C(19)-H(19C)	109.5
C(8)-C(9)-H(9B)	101.9	C(15)-C(20)-H(20A)	109.5
H(9A)-C(9)-H(9B)	104.7	C(15)-C(20)-H(20B)	109.5
C(9)-C(10)-C(11)	141.1(9)	H(20A)-C(20)-H(20B)	109.5
C(9)-C(10)-H(10A)	101.8	C(15)-C(20)-H(20C)	109.5
C(11)-C(10)-H(10A)	101.8	H(20A)-C(20)-H(20C)	109.5
C(9)-C(10)-H(10B)	101.8	H(20B)-C(20)-H(20C)	109.5
C(11)-C(10)-H(10B)	101.8	C(15)-C(21)-H(21A)	109.5
H(10A)-C(10)-H(10B)	104.7	C(15)-C(21)-H(21B)	109.5
C(12)-C(11)-C(10)	154(2)	H(21A)-C(21)-H(21B)	109.5
C(12)-C(11)-H(11B)	98.1	C(15)-C(21)-H(21C)	109.5
C(10)-C(11)-H(11B)	98.1	H(21A)-C(21)-H(21C)	109.5
C(12)-C(11)-H(11A)	98.1	H(21B)-C(21)-H(21C)	109.5
C(10)-C(11)-H(11A)	98.1	C(27)-C(22)-C(28)	109.5(3)
H(11B)-C(11)-H(11A)	103.7	C(27)-C(22)-C(23)	111.1(3)
C(11)-C(12)-H(12A)	109.5	C(28)-C(22)-C(23)	110.8(3)
C(11)-C(12)-H(12B)	109.5	C(27)-C(22)-Si(4)	108.4(3)
H(12A)-C(12)-H(12B)	109.5	C(28)-C(22)-Si(4)	109.0(3)
C(11)-C(12)-H(12C)	109.5	C(23)-C(22)-Si(4)	107.9(3)
H(12A)-C(12)-H(12C)	109.5	C(24)-C(23)-C(22)	116.8(4)
H(12B)-C(12)-H(12C)	109.5	C(24)-C(23)-H(23A)	108.1
C(8)-C(13)-H(13A)	109.5	C(22)-C(23)-H(23A)	108.1
C(8)-C(13)-H(13B)	109.5	C(24)-C(23)-H(23B)	108.1
H(13A)-C(13)-H(13B)	109.5	C(22)-C(23)-H(23B)	108.1
C(8)-C(13)-H(13C)	109.5	H(23A)-C(23)-H(23B)	107.3
H(13A)-C(13)-H(13C)	109.5	C(25)-C(24)-C(23)	112.2(4)

C(25)-C(24)-H(24A)	109.2	Si(2)-O(2)-Si(3)	147.84(18)
C(23)-C(24)-H(24A)	109.2	Si(1)#1-O(3)-Si(2)	151.44(18)
C(25)-C(24)-H(24B)	109.2	Si(2)-O(4)-Si(4)#1	148.55(17)
C(23)-C(24)-H(24B)	109.2	Si(4)-O(5)-Si(3)	151.62(18)
H(24A)-C(24)-H(24B)	107.9	Si(4)-O(6)-Si(1)#1	148.27(18)
C(24)-C(25)-C(26)	112.8(5)	O(3)#1-Si(1)-O(1)	109.47(14)
C(24)-C(25)-H(25B)	109.0	O(3)#1-Si(1)-O(6)#1	108.81(14)
C(26)-C(25)-H(25B)	109.0	O(1)-Si(1)-O(6)#1	108.30(14)
C(24)-C(25)-H(25A)	109.0	O(3)#1-Si(1)-C(1)	109.81(16)
C(26)-C(25)-H(25A)	109.0	O(1)-Si(1)-C(1)	111.37(16)
H(25B)-C(25)-H(25A)	107.8	O(6)#1-Si(1)-C(1)	109.03(17)
C(25)-C(26)-H(26A)	109.5	O(4)-Si(2)-O(2)	108.99(14)
C(25)-C(26)-H(26B)	109.5	O(4)-Si(2)-O(3)	108.42(14)
H(26A)-C(26)-H(26B)	109.5	O(2)-Si(2)-O(3)	109.14(14)
C(25)-C(26)-H(26C)	109.5	O(4)-Si(2)-C(8)	108.91(18)
H(26A)-C(26)-H(26C)	109.5	O(2)-Si(2)-C(8)	110.66(18)
H(26B)-C(26)-H(26C)	109.5	O(3)-Si(2)-C(8)	110.67(18)
C(22)-C(27)-H(27A)	109.5	O(1)-Si(3)-O(5)	108.97(14)
C(22)-C(27)-H(27B)	109.5	O(1)-Si(3)-O(2)	109.19(14)
H(27A)-C(27)-H(27B)	109.5	O(5)-Si(3)-O(2)	108.40(14)
C(22)-C(27)-H(27C)	109.5	O(1)-Si(3)-C(15)	110.76(16)
H(27A)-C(27)-H(27C)	109.5	O(5)-Si(3)-C(15)	108.61(16)
H(27B)-C(27)-H(27C)	109.5	O(2)-Si(3)-C(15)	110.86(16)
C(22)-C(28)-H(28C)	109.5	O(5)-Si(4)-O(6)	109.23(14)
C(22)-C(28)-H(28B)	109.5	O(5)-Si(4)-O(4)#1	109.16(14)
H(28C)-C(28)-H(28B)	109.5	O(6)-Si(4)-O(4)#1	108.79(14)
C(22)-C(28)-H(28A)	109.5	O(5)-Si(4)-C(22)	109.42(15)
H(28C)-C(28)-H(28A)	109.5	O(6)-Si(4)-C(22)	109.99(16)
H(28B)-C(28)-H(28A)	109.5	O(4)#1-Si(4)-C(22)	110.22(16)
Si(1)-O(1)-Si(3)	148.23(17)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z

Spectroscopic data

NMR-Data

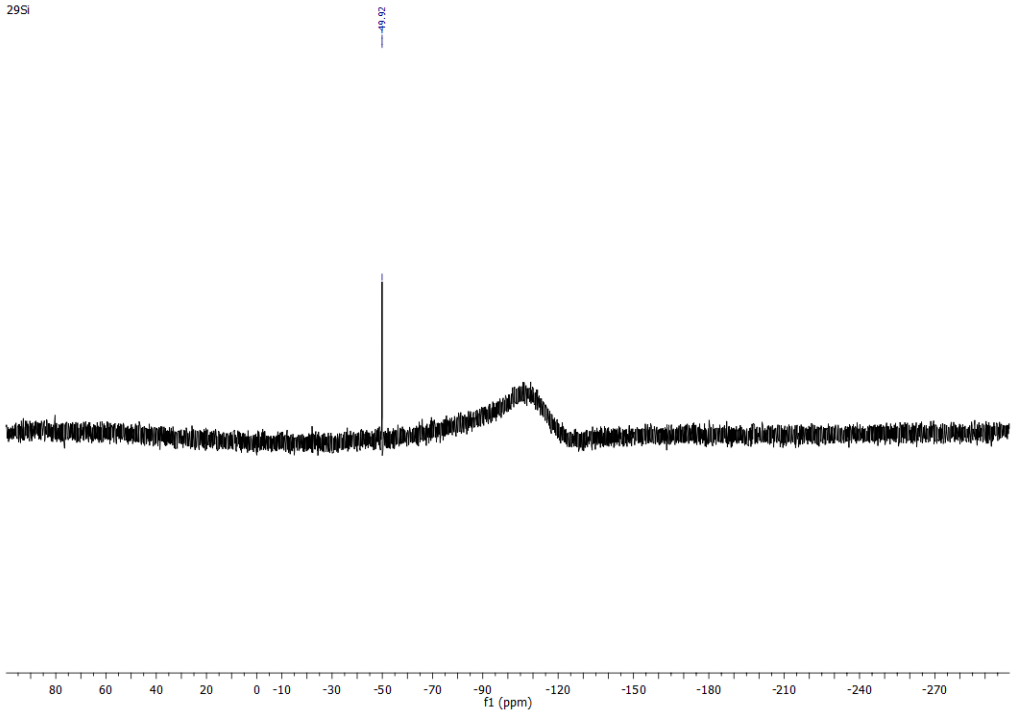

Figure S1: ^{29}Si-NMR spectrum of compound **2b** in THF-d_8

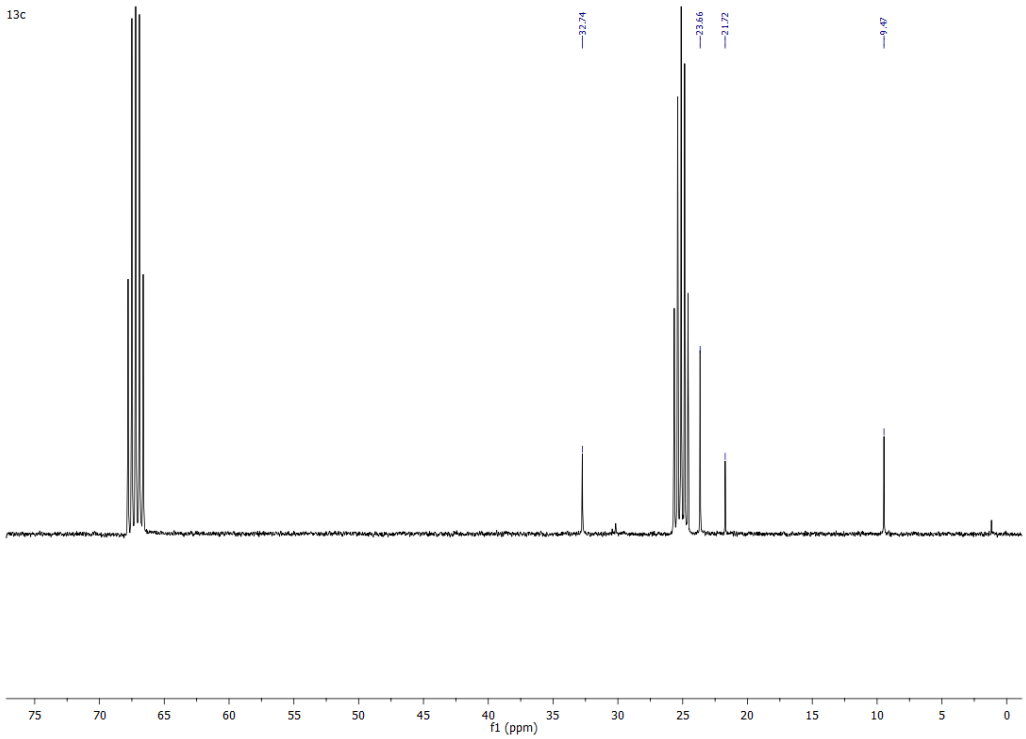

Figure S2: ^{13}C-NMR spectrum of compound **2b** in THF-d_8

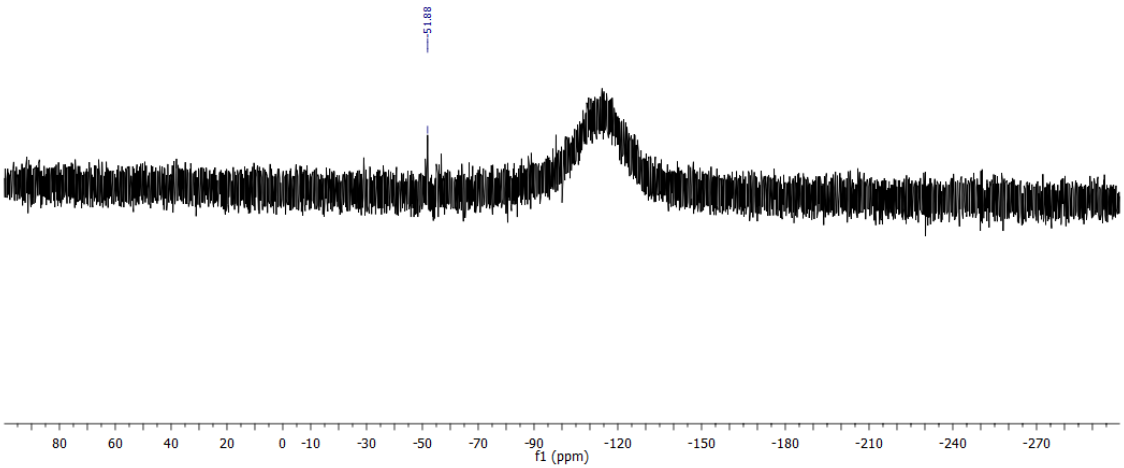

Figure S3: ^{29}Si-NMR spectrum of compound **2c** in THF-d_8

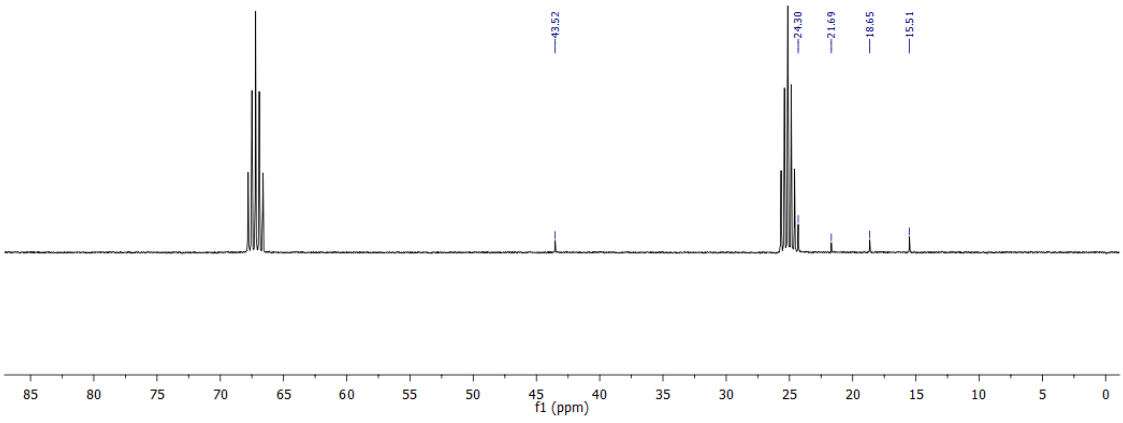

Figure S4: ^{13}C-NMR spectrum of compound **2c** in THF-d_8

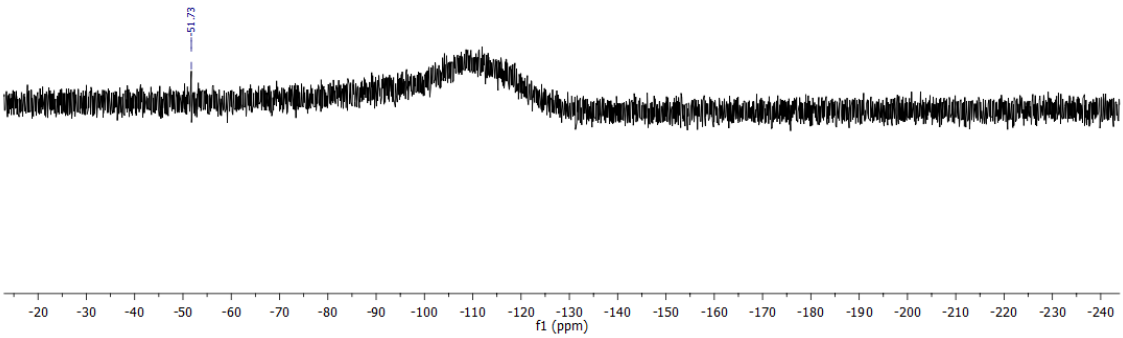

Figure S5: ^{29}Si-NMR spectrum of compound **2d** in THF-d_8

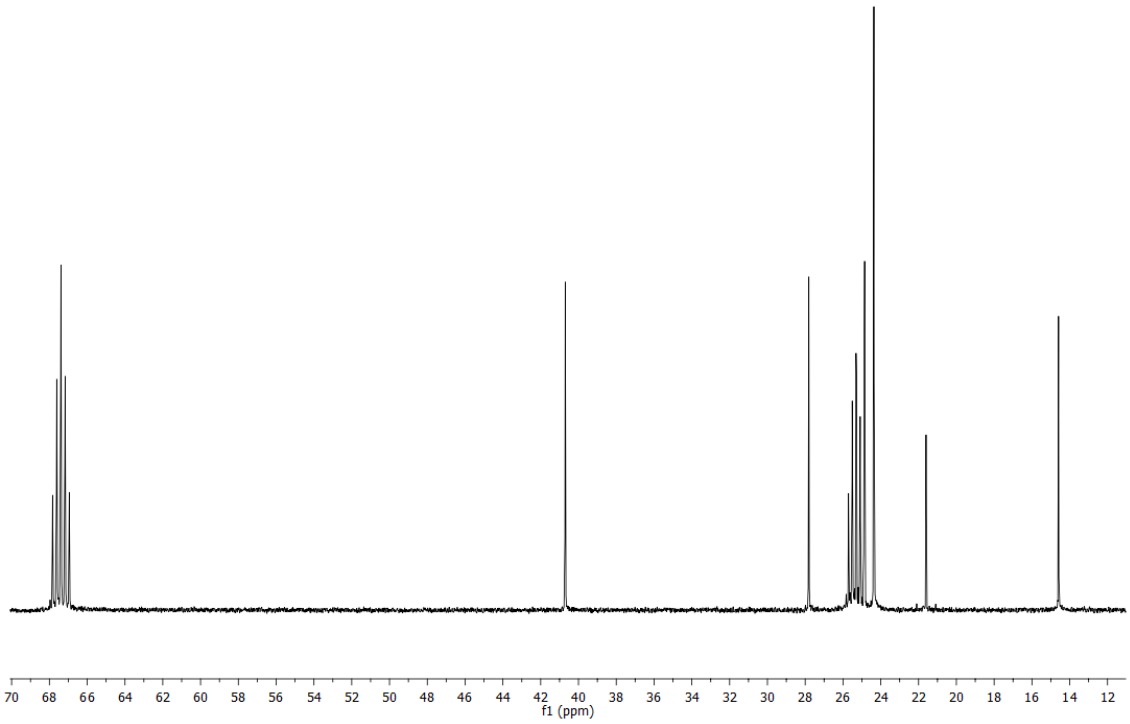

Figure S6: ^{13}C-NMR spectrum of compound **2d** in THF-d_8

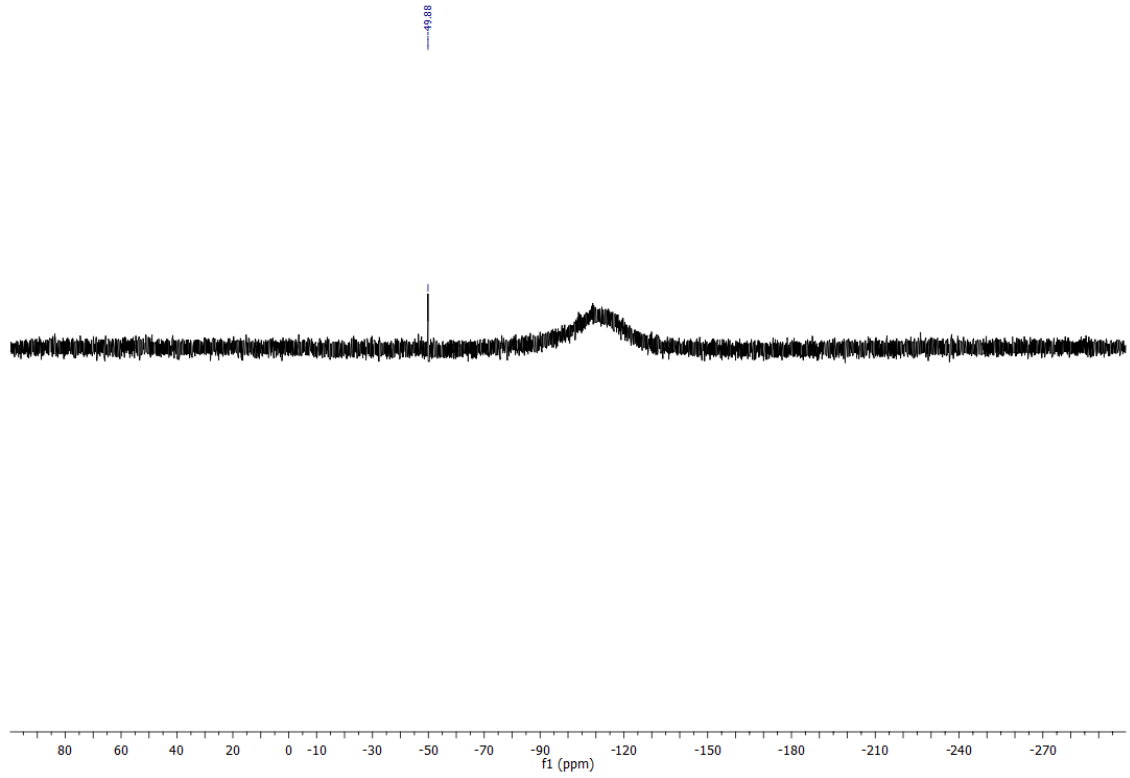

Figure S7: ^{29}Si-NMR spectrum of compound **2e** in THF-d_8

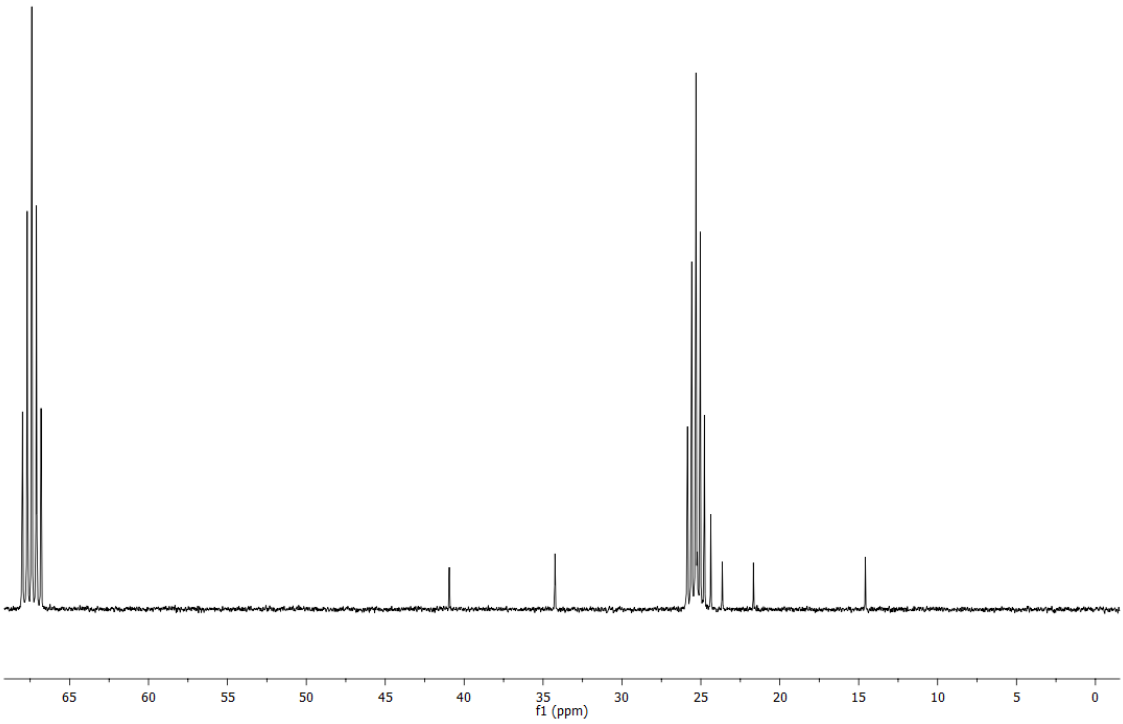

Figure S8: ^{13}C-NMR spectrum of compound **2e** in THF-d_8

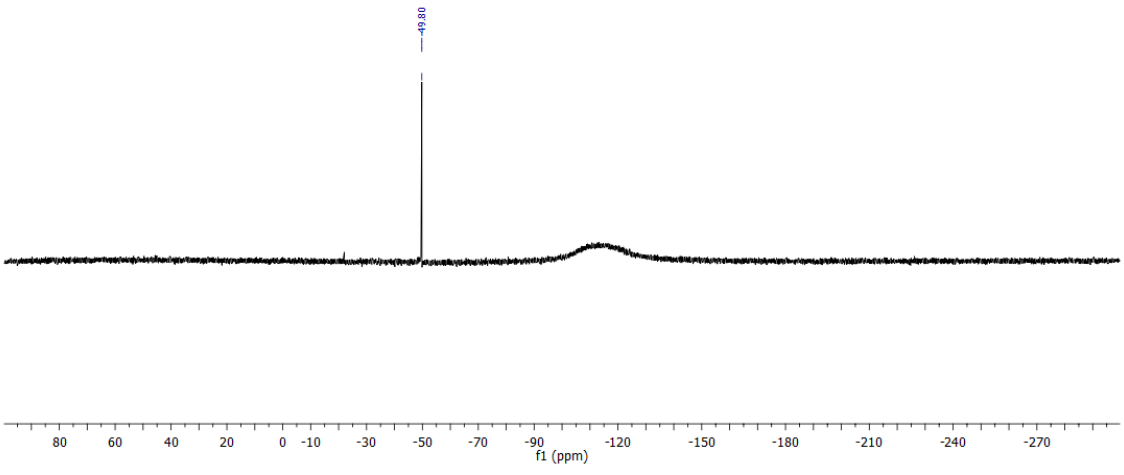

Figure S9: ^{29}Si-NMR spectrum of compound **2f** in THF-d_8

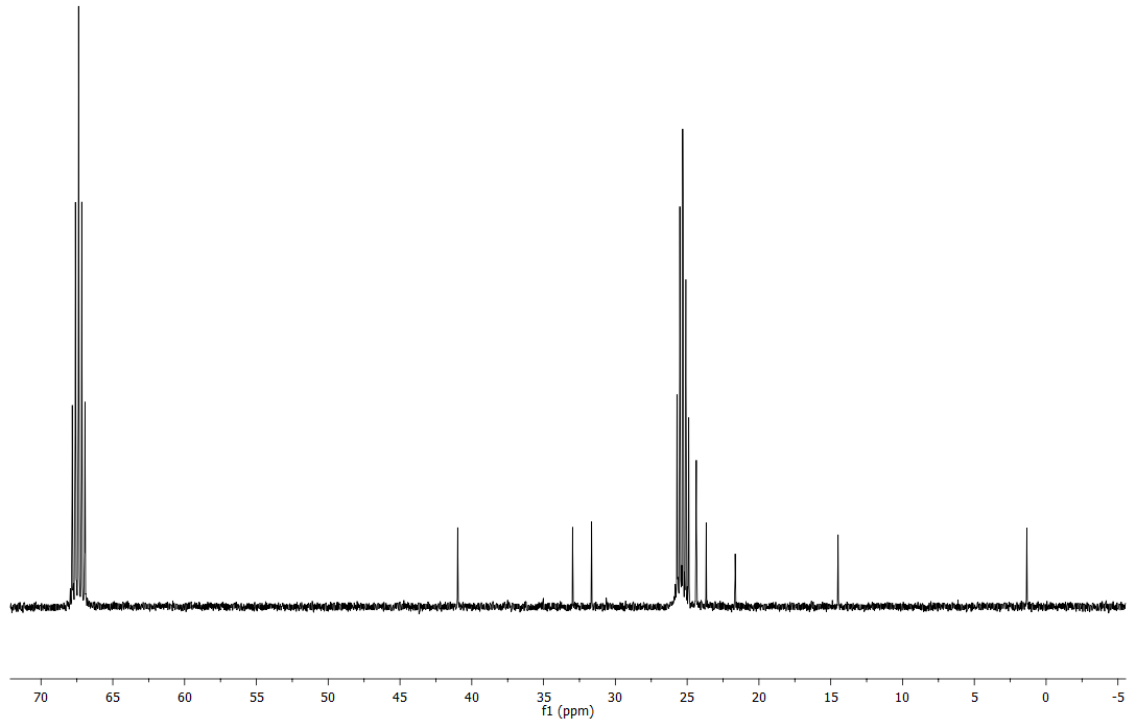

Figure S10: ^{13}C-NMR spectrum of compound **2f** in THF-d_8

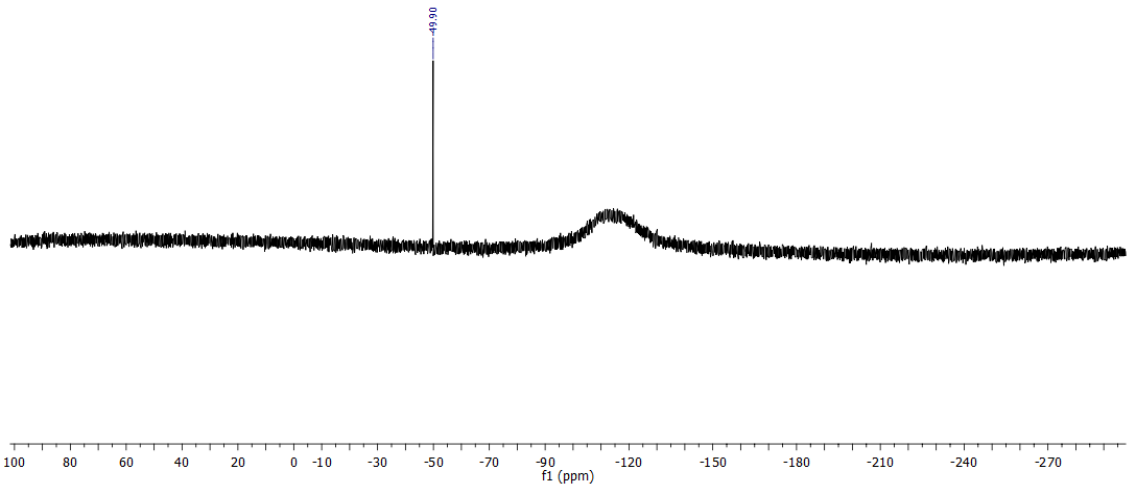

Figure S11: ^{13}C-NMR spectrum of compound **2g** in THF-d_8

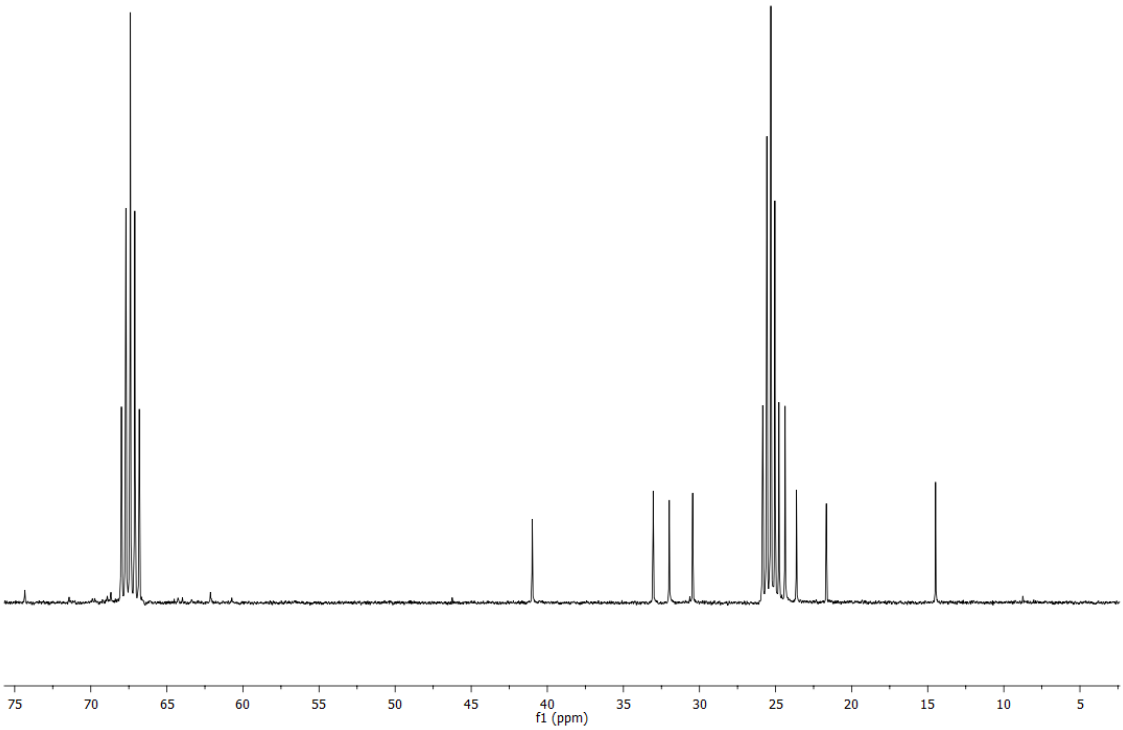

Figure S12: ^{13}C-NMR spectrum of compound **2g** in THF-d_8

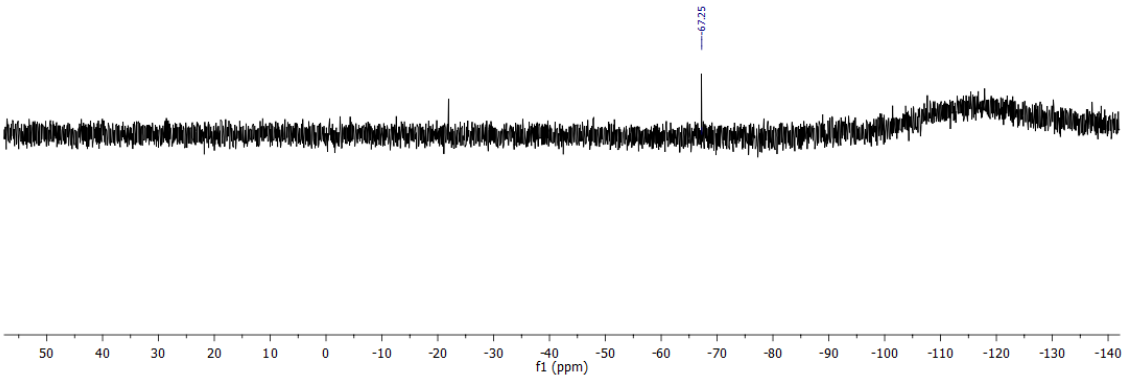

Figure S13: ^{29}Si-NMR spectrum of compound **4b** in $CDCl_3$.

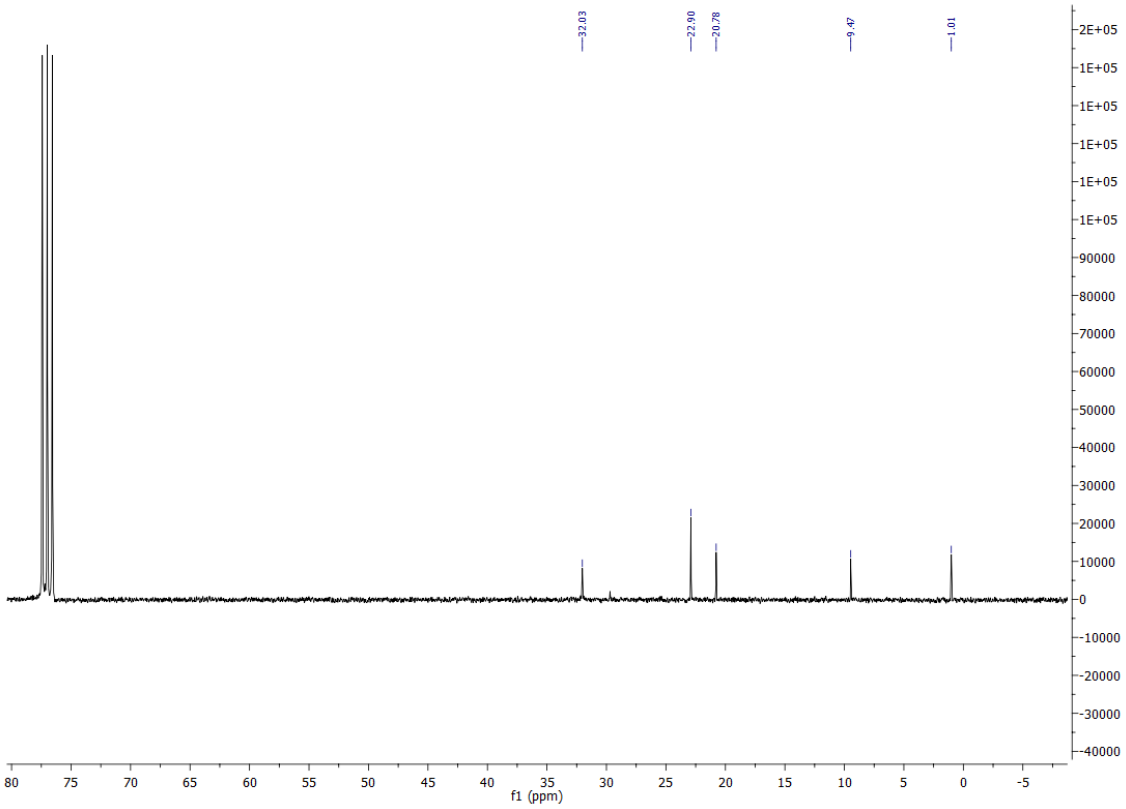

Figure S14: ^{13}C-NMR spectrum of compound **4b** in $CDCl_3$.

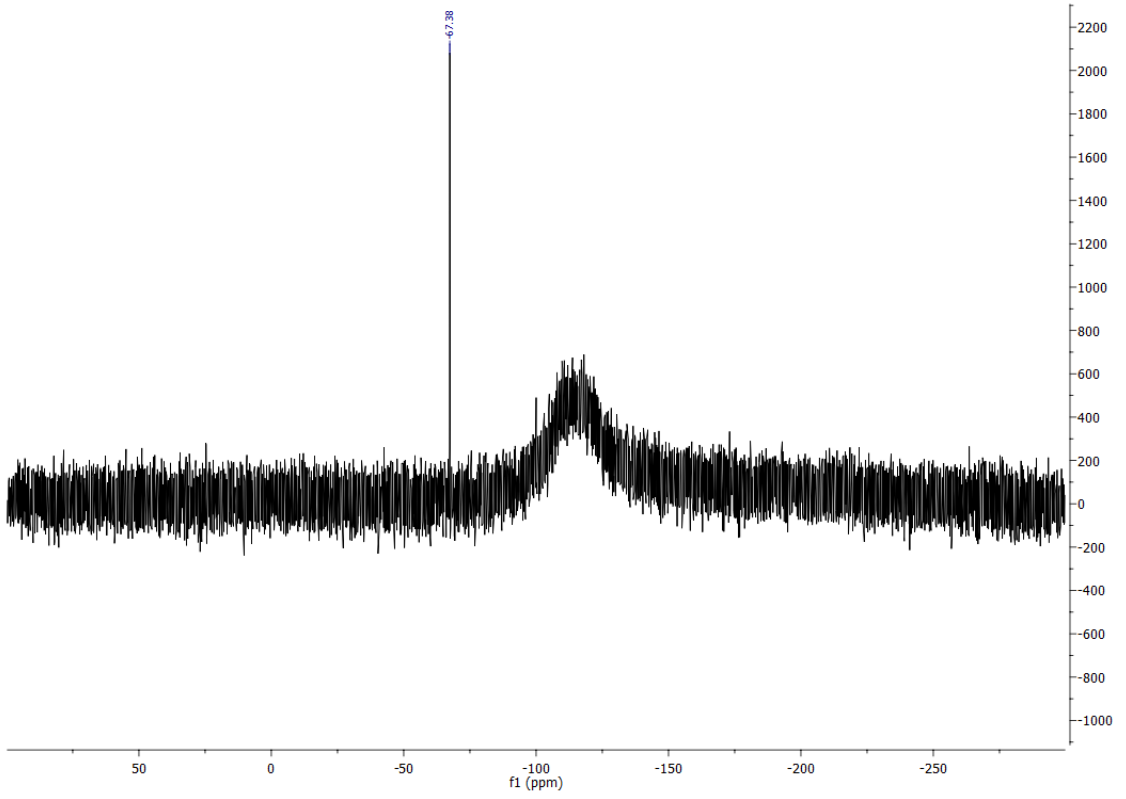

Figure S15: ^{29}Si-NMR spectrum of compound **4c** in $CDCl_3$.

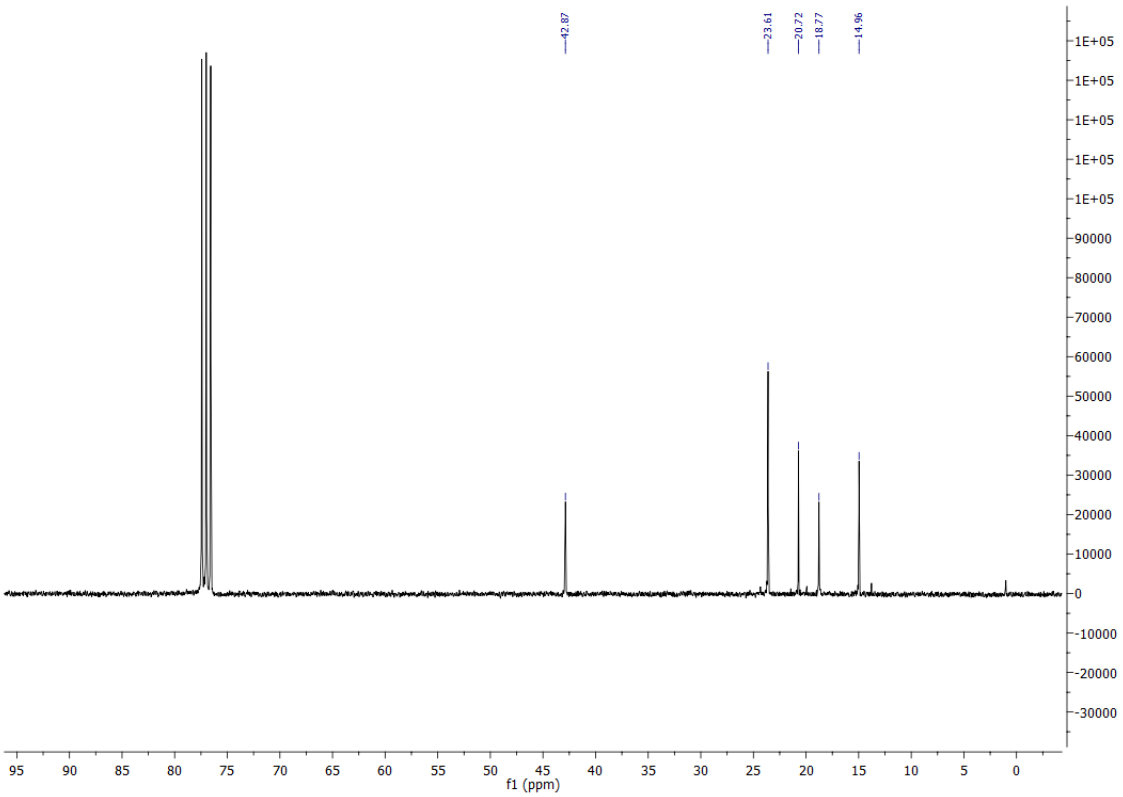

Figure S16: ^{13}C-NMR spectrum of compound **4c** in $CDCl_3$.

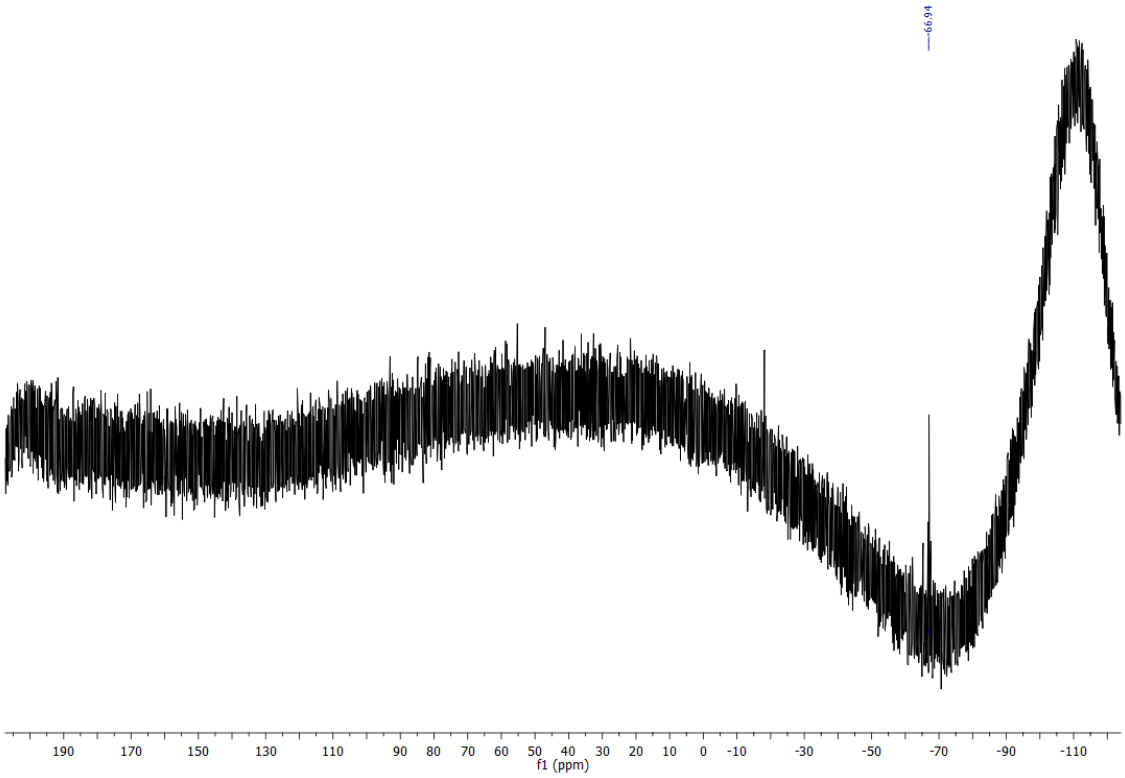

Figure S17: ^{29}Si-NMR spectrum of compound **4d** in $CDCl_3$.

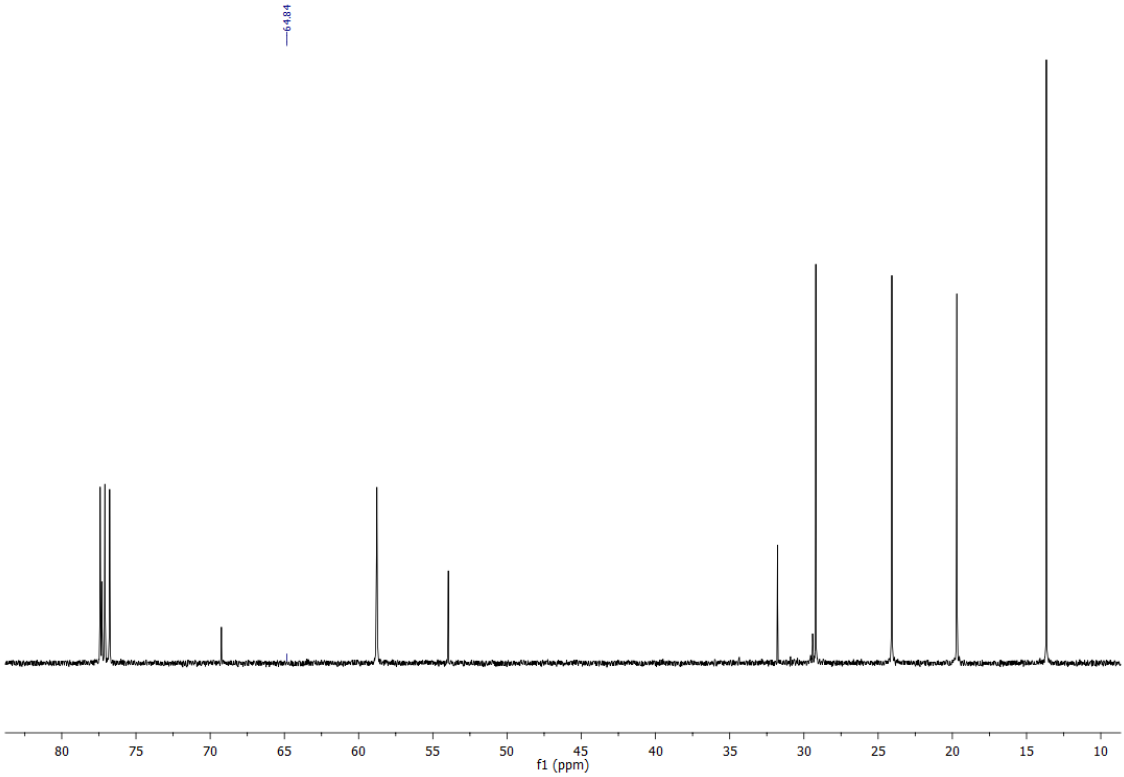

Figure S18: ^{13}C-NMR spectrum of compound **4d** in $CDCl_3$.

IR-Data

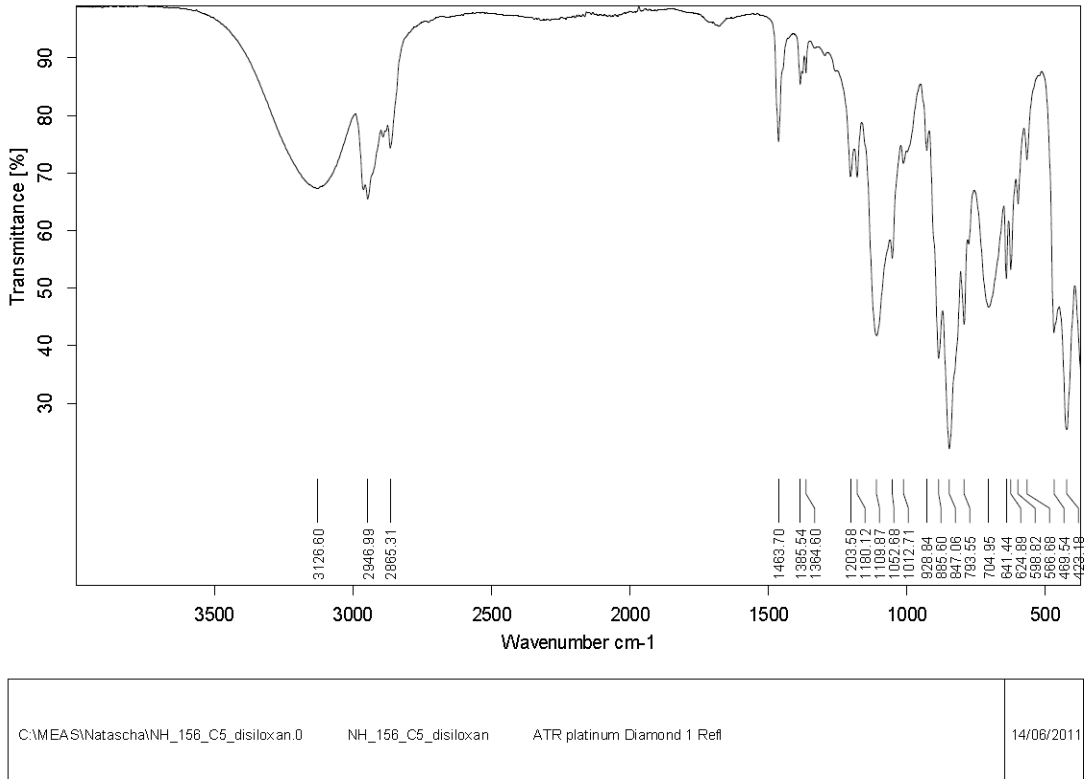

Figure S19: ATR-IR spectrum of compound **2b**.

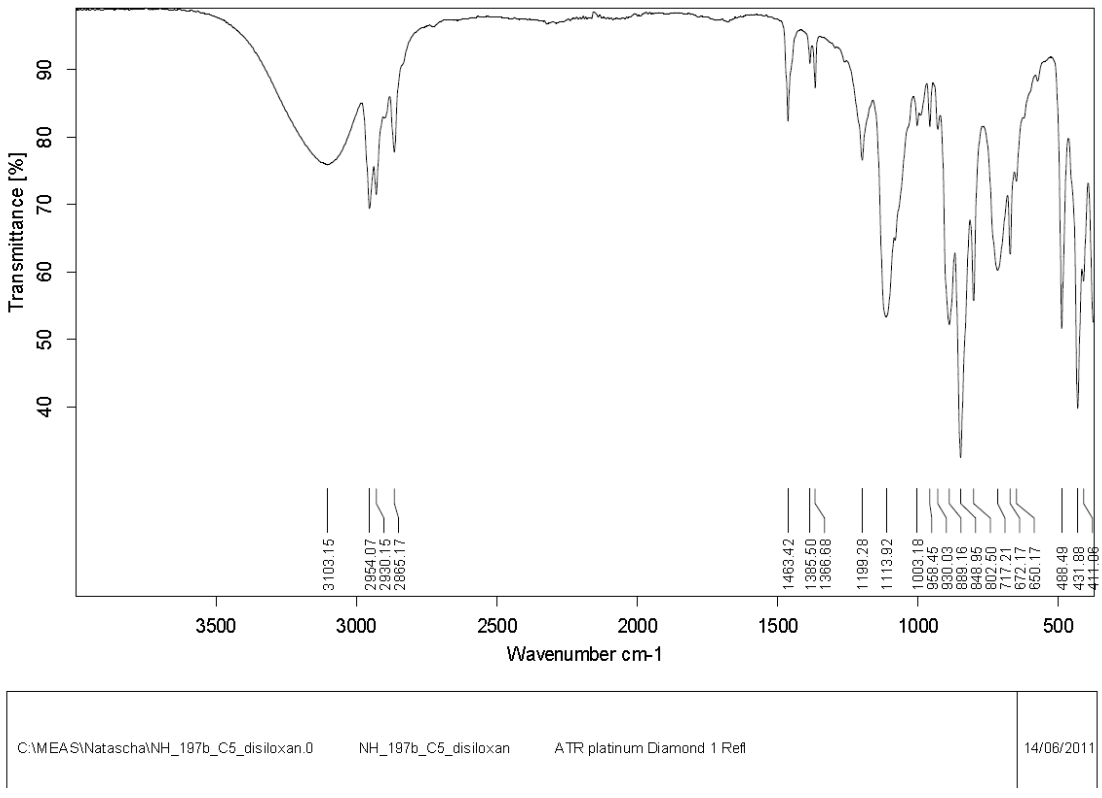

Figure S20: ATR-IR spectrum of compound **2c**.

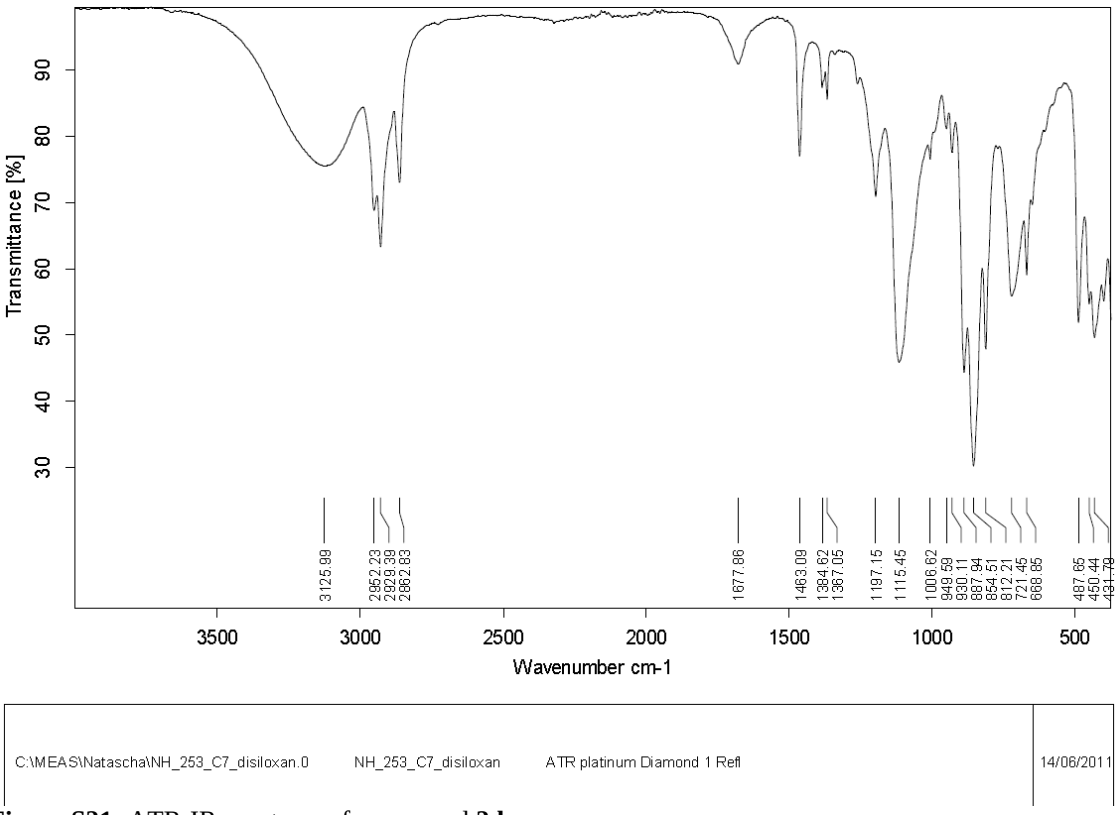

Figure S21: ATR-IR spectrum of compound **2d**.

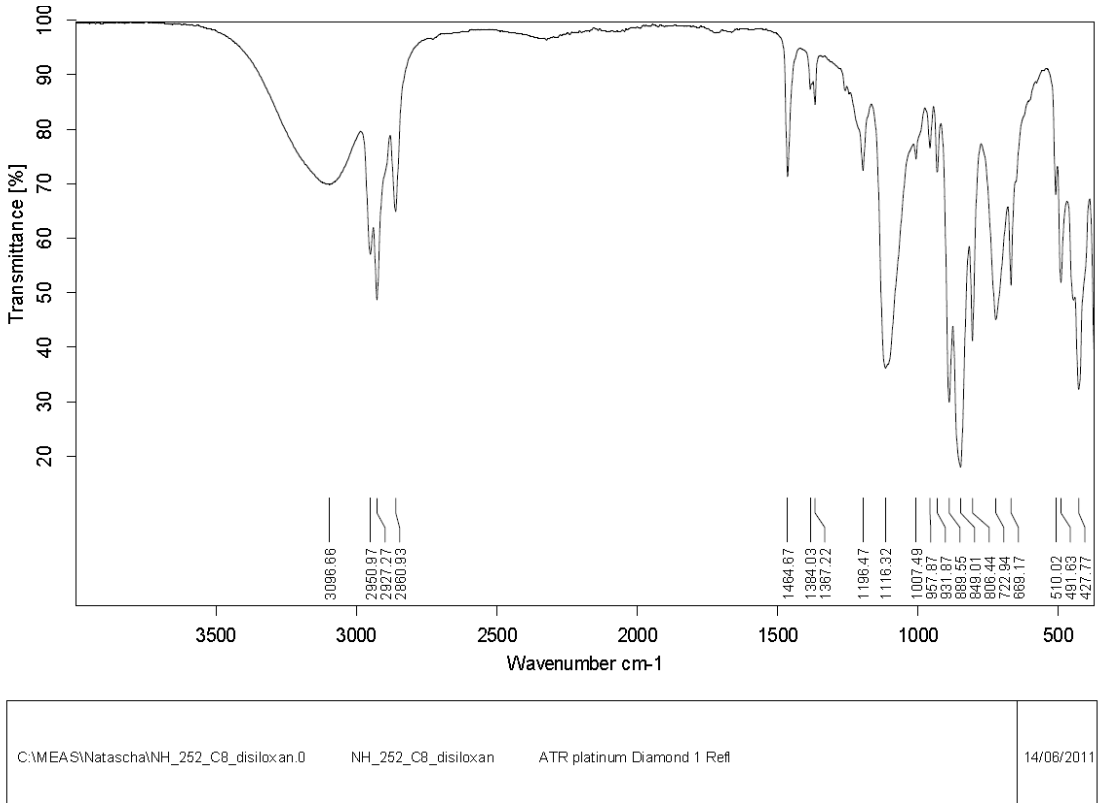

Figure S22: ATR-IR spectrum of compound **2e**.

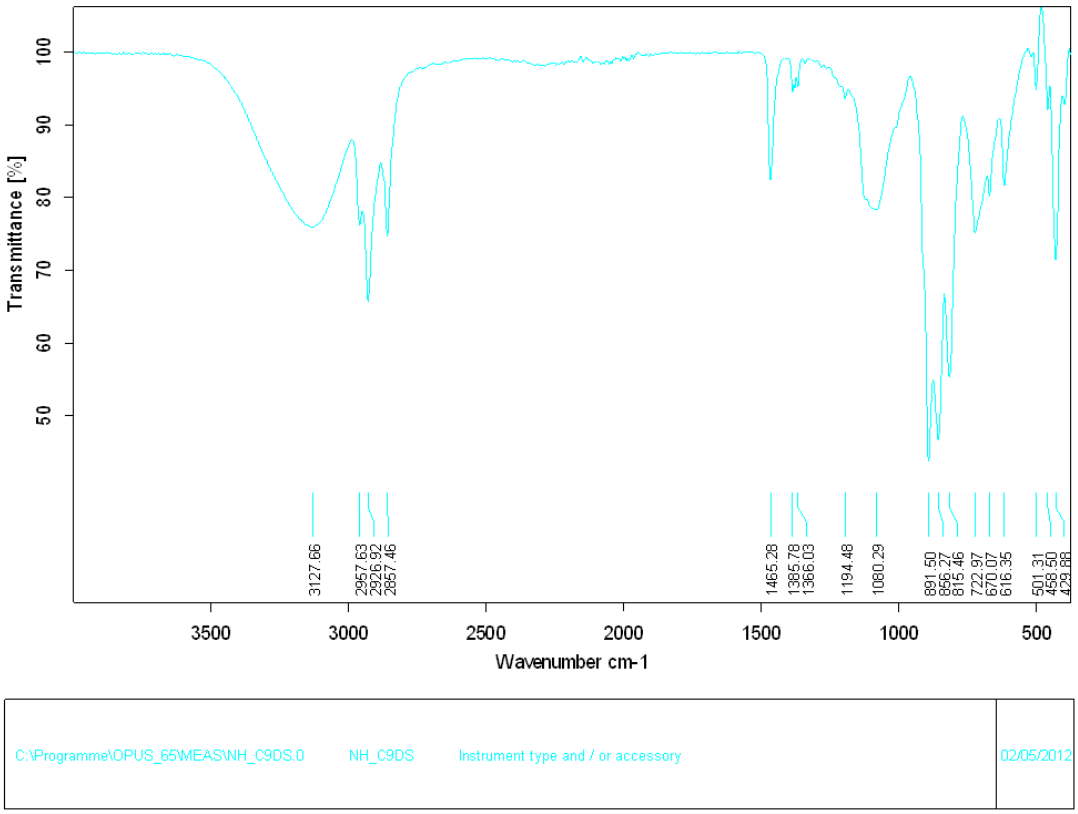

Figure S23: ATR-IR spectrum of compound **2f**.

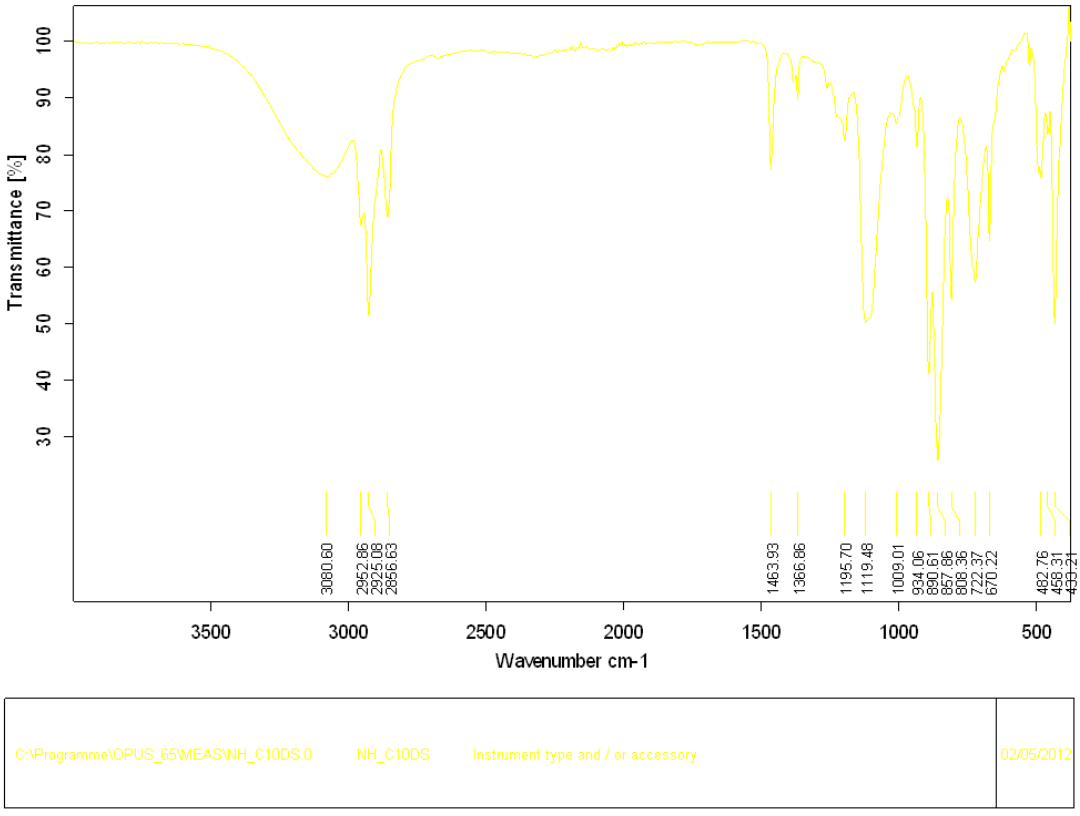

Figure S24: ATR-IR spectrum of compound **2g**.

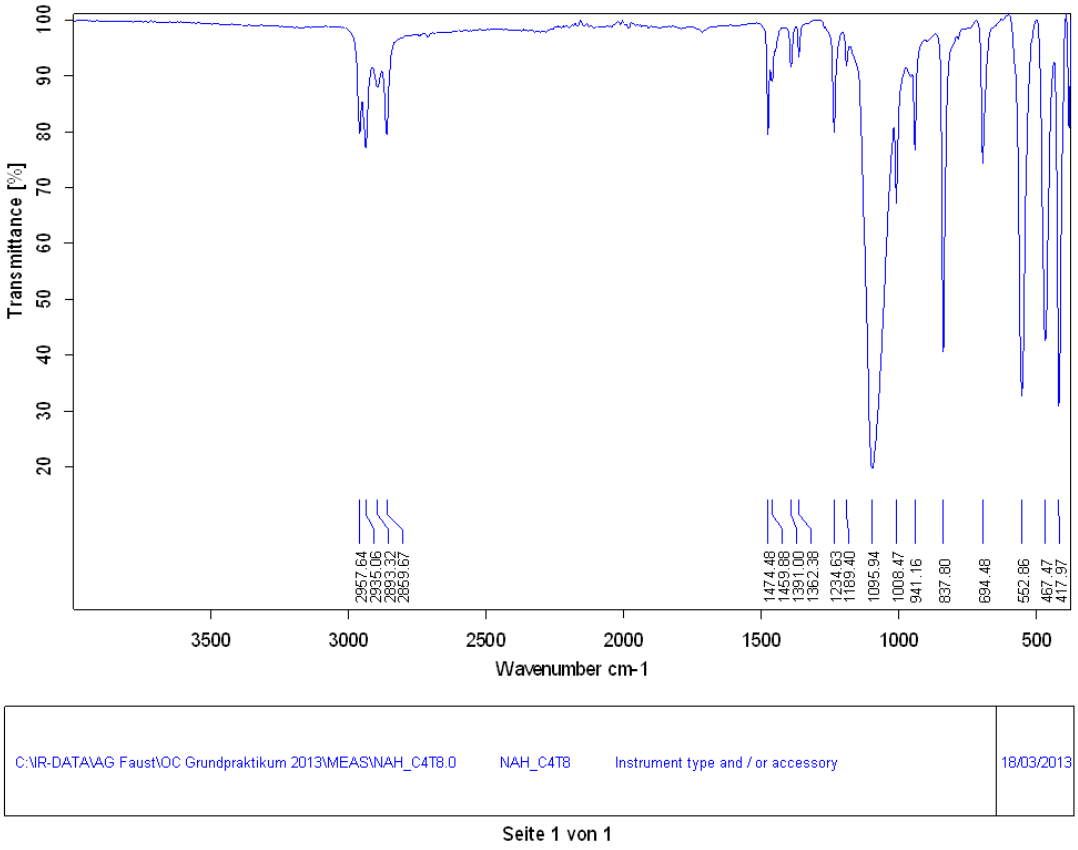

Figure S25: ATR-IR spectrum of compound **4a**.

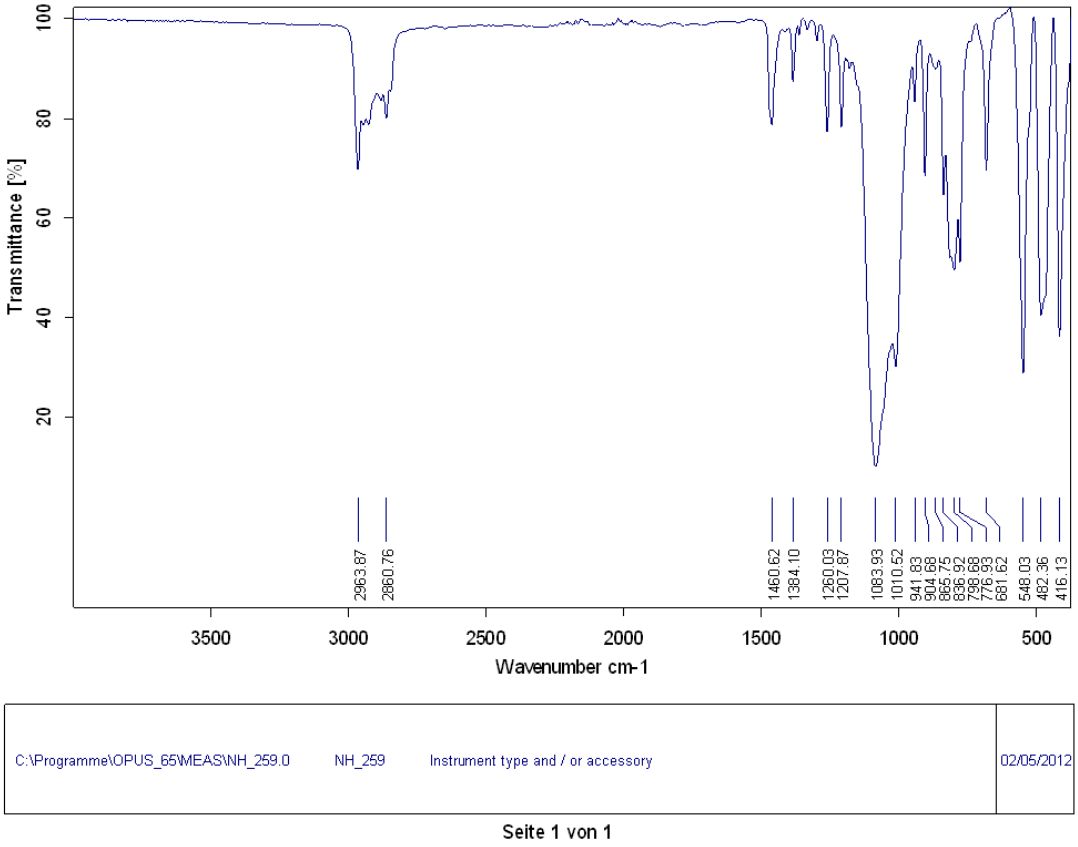

Figure S26: ATR-IR spectrum of compound **4b**.

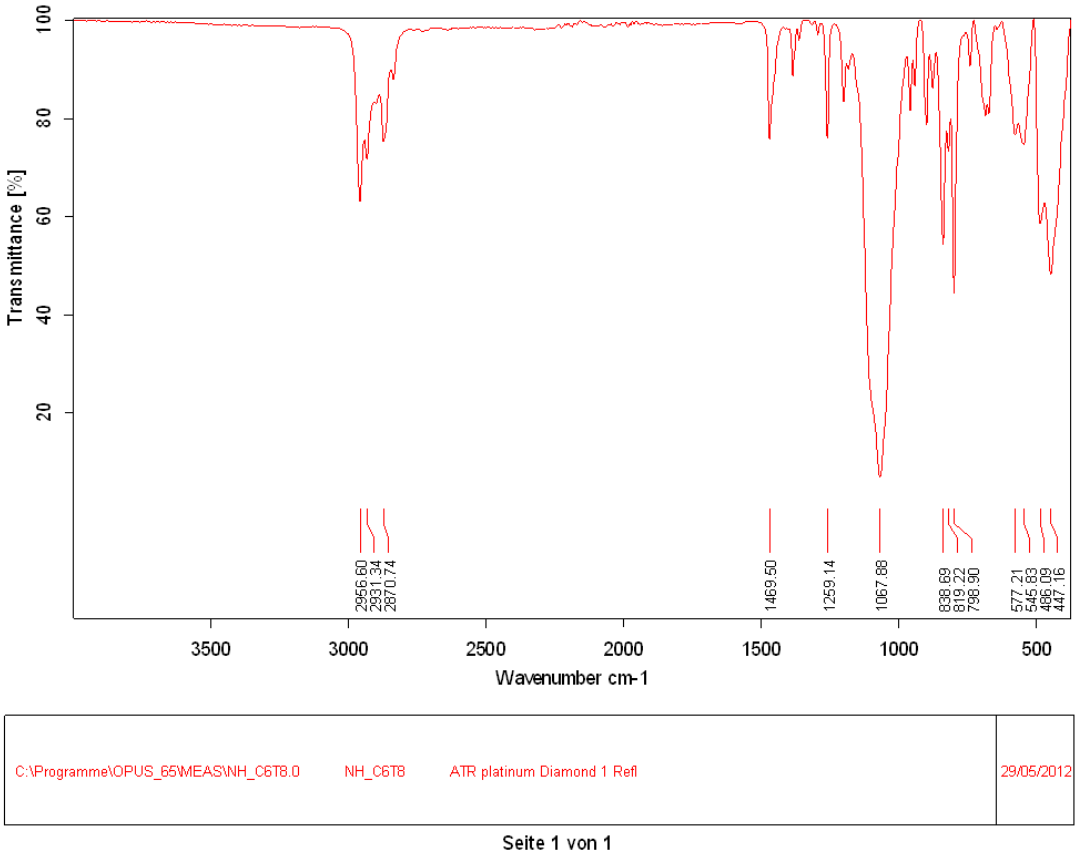

Figure S27: ATR-IR spectrum of compound **4c**.

MS-Data

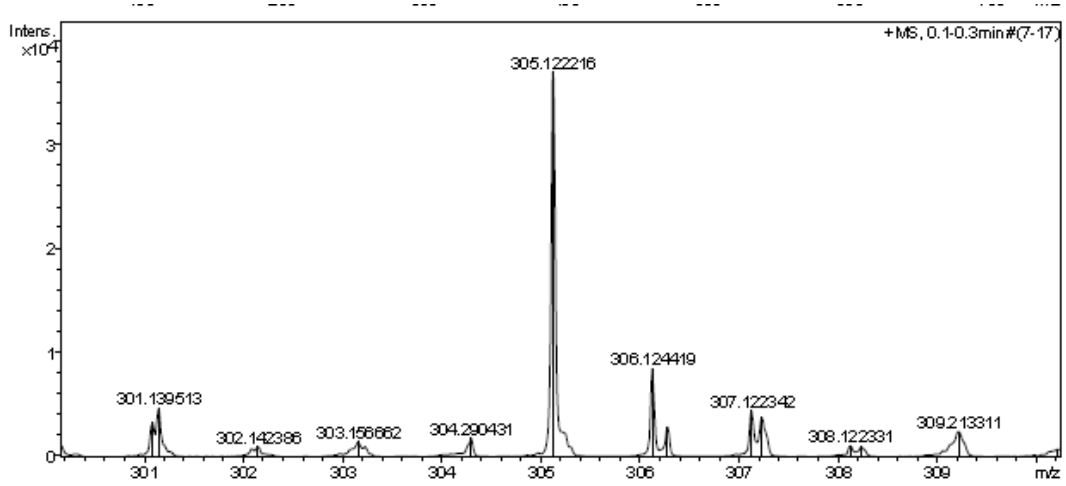

Figure S28: HR-ESI-MS spectrum of compound **2b**.

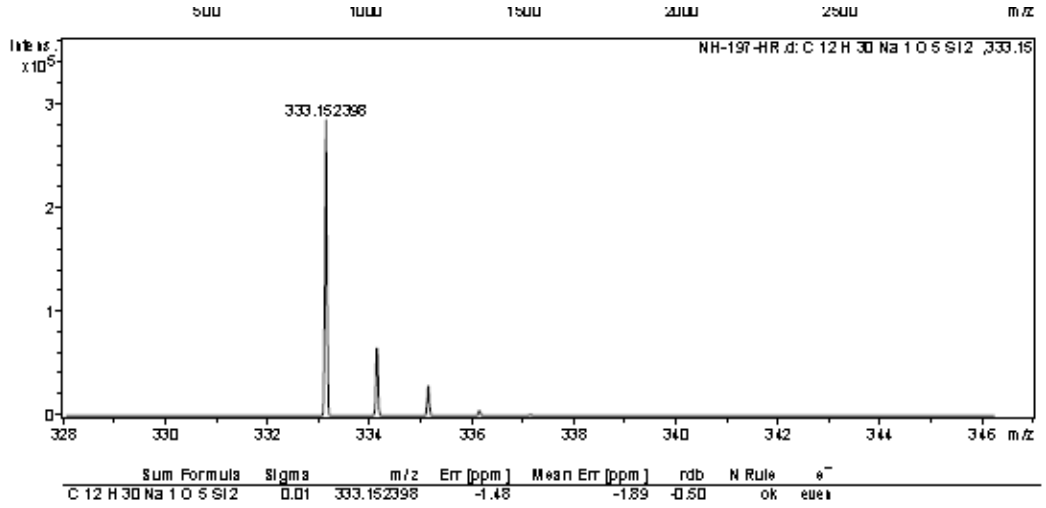

Figure S29: HR-ESI-MS spectrum of compound **2c**.

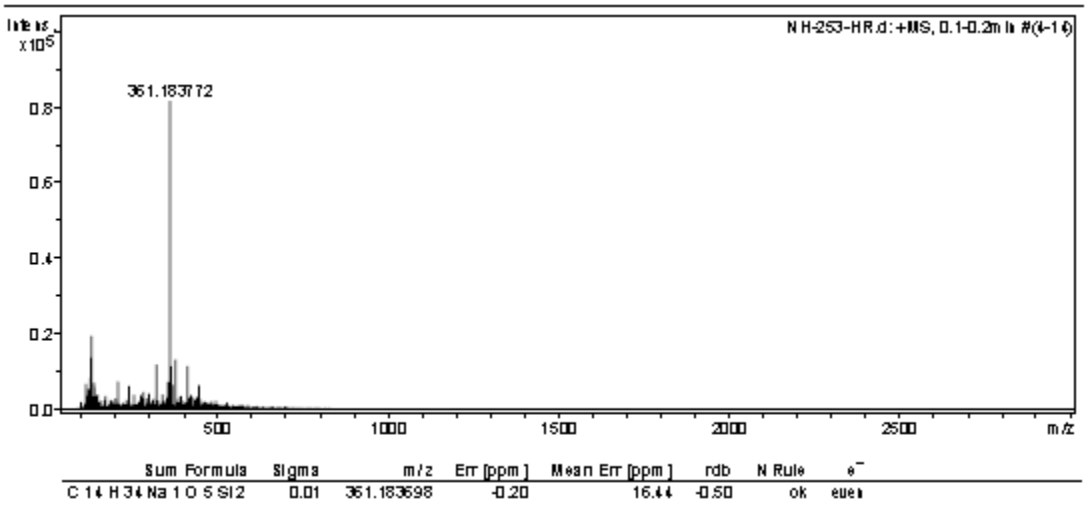

Figure S30: HR-ESI-MS spectrum of compound **2d**.

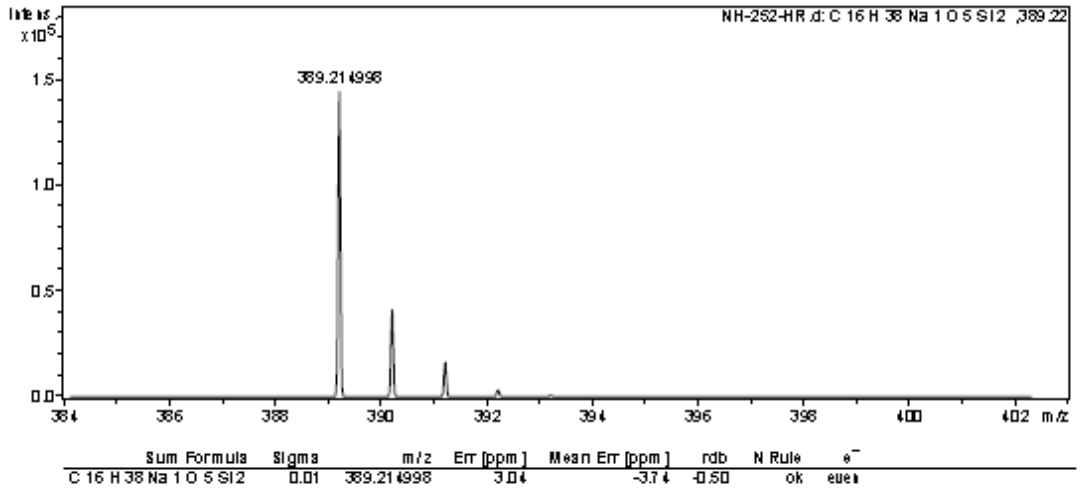

Figure S31: HR-ESI-MS spectrum of compound **2e**.

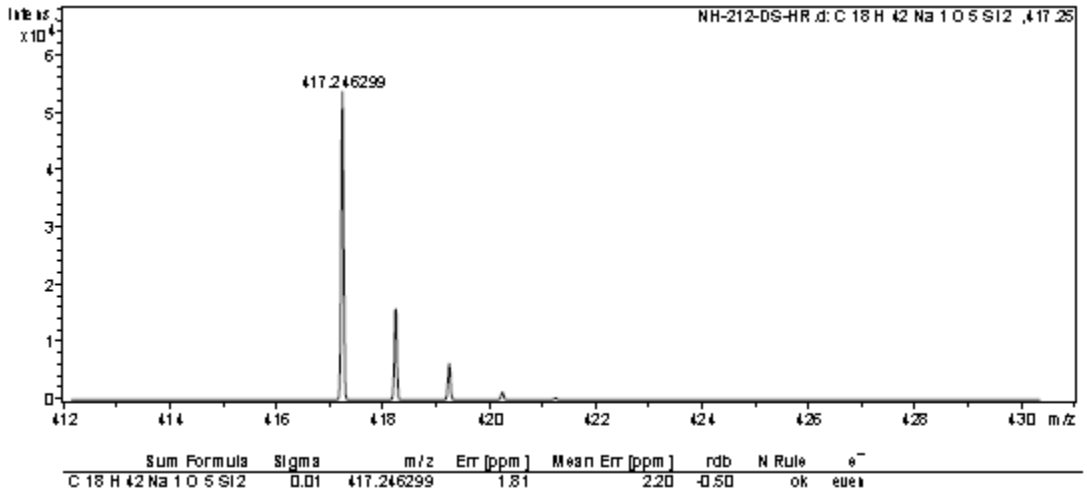

Figure S32: HR-ESI-MS spectrum of compound **2f**.

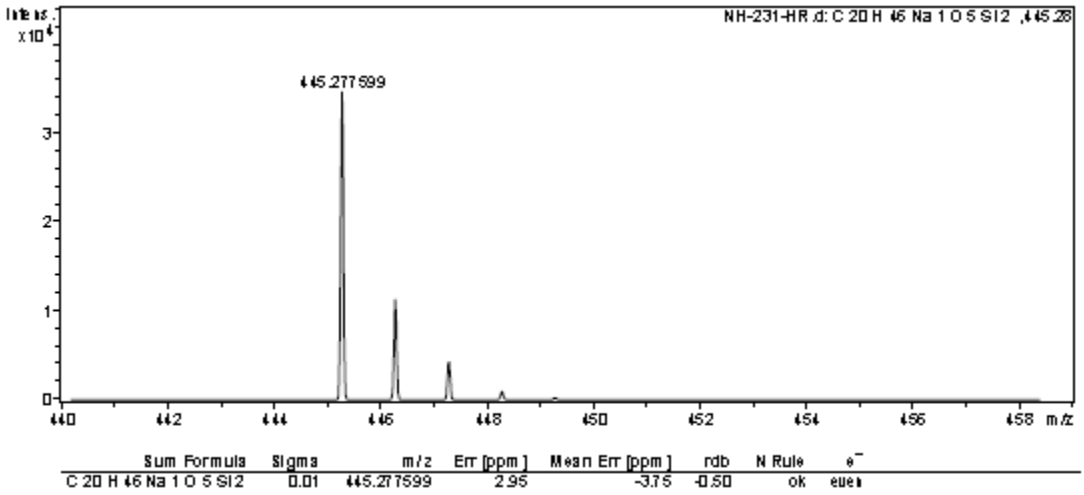

Figure S33: HR-ESI-MS spectrum of compound **2g**.

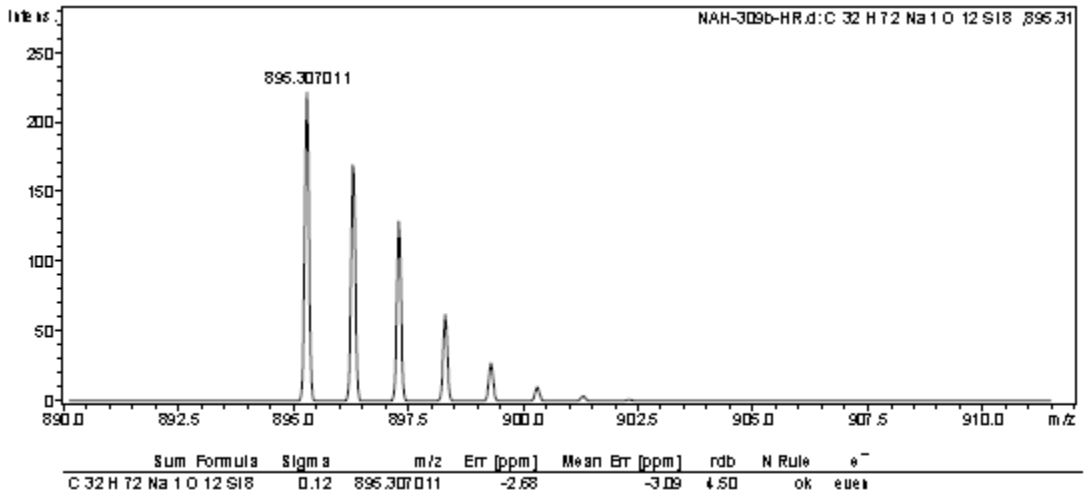

Figure S34: HR-ESI-MS spectrum of compound **4a**.

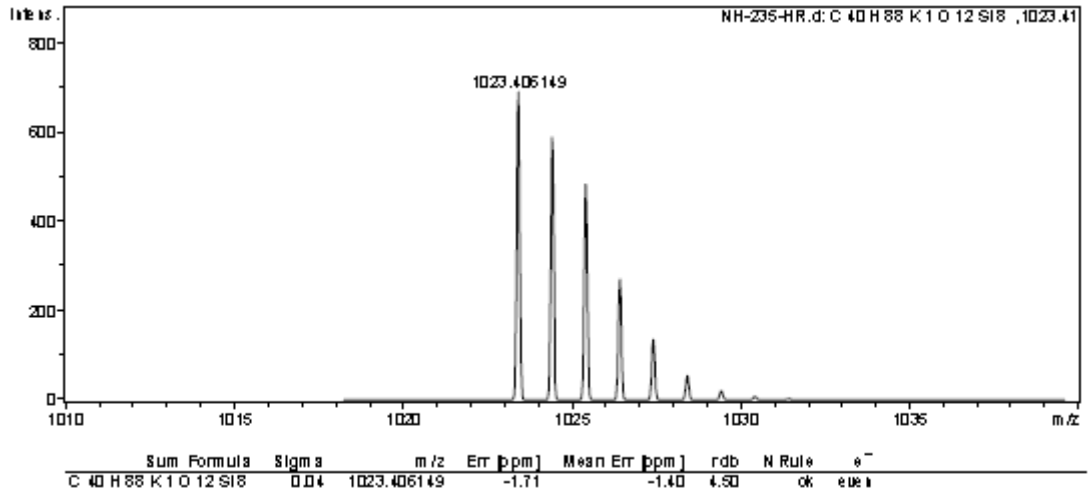

Figure S35: HR-ESI-MS spectrum of compound **4b**.

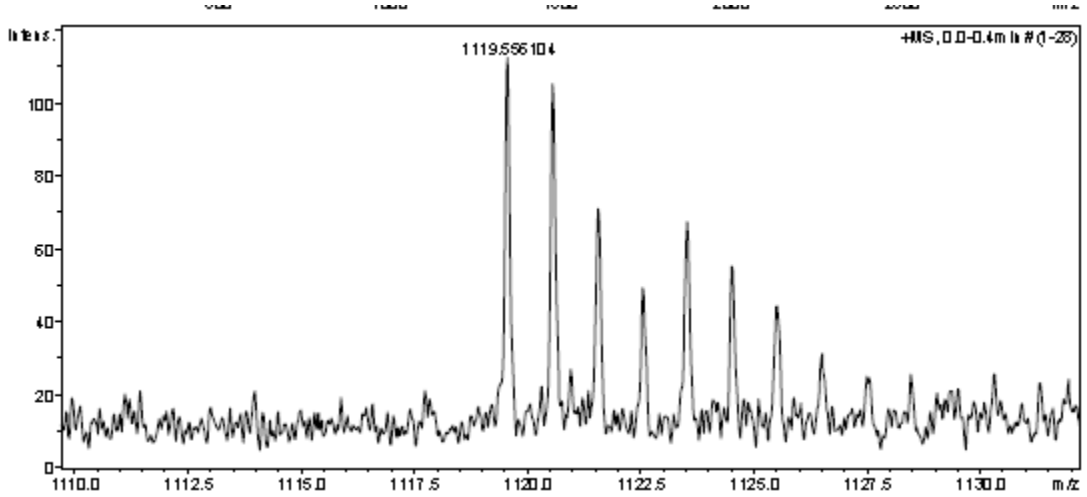

Figure S36: HR-ESI-MS spectrum of compound **4c**.

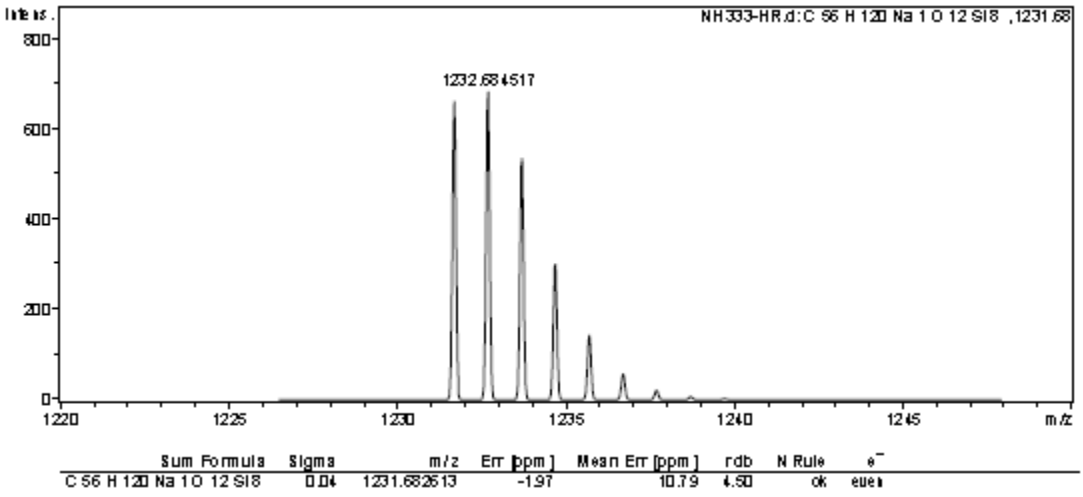

Figure S37: HR-ESI-MS spectrum of compound **4d**.