Supporting Information

Equilibrium Between Tetra-, Penta- and Hexacoordinate Imine- and Enamine Chelates of Silicon: Crystal Structure and Variable Temperature NMR

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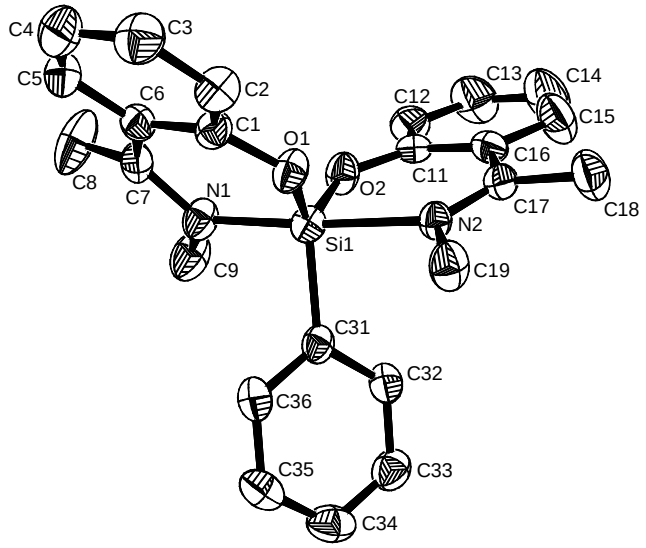


Figure SI1. Molecular structure of compound **2** (ORTEP plot with 50% prbability ellipsoids, hydrogen atoms omitted).

Table 1. Crystal data and structure refinement for **2**.

Identification code	compound **2**
Empirical formula	C24 H24 N2 O2 Si
Formula weight	400.54
Temperature	198(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 8.8530(10) A alpha = 90 deg.
	b = 17.0160(10) A beta = 100.385(10) deg.
	c = 14.010(2) A gamma = 90 deg.
Volume	2075.9(4) A^3
Z, Calculated density	4, 1.282 Mg/m^3
Absorption coefficient	0.136 mm^-1
F(000)	848
Crystal size	0.43 x 0.39 x 0.26 mm
Theta range for data collection	3.63 to 22.99 deg.
Limiting indices	-9<=h<=9, -18<=k<=18, -15<=l<=15
Reflections collected / unique	23039 / 2877 [R(int) = 0.0749]
Completeness to theta = 22.99	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9655 and 0.9439
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2877 / 0 / 262
Goodness-of-fit on F^2	1.016
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.0942
R indices (all data)	R1 = 0.0663, wR2 = 0.1033
Largest diff. peak and hole	0.235 and -0.231 e.A^-3

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

	x	y	z	U(eq)
Si(1)	1662(1)	6525(1)	1428(1)	33(1)
N(1)	2153(2)	6319(1)	2709(1)	38(1)
N(2)	1262(2)	6708(1)	-66(1)	31(1)
O(1)	2512(2)	5739(1)	1070(1)	37(1)
O(2)	2563(2)	7387(1)	1552(1)	39(1)
C(1)	3384(3)	5167(1)	1594(2)	33(1)
C(2)	3842(3)	4556(1)	1051(2)	39(1)
C(3)	4777(3)	3973(2)	1502(2)	49(1)
C(4)	5259(4)	3993(2)	2497(2)	52(1)
C(5)	4786(3)	4597(2)	3030(2)	43(1)
C(6)	3842(3)	5207(1)	2597(2)	33(1)
C(7)	3336(3)	5856(1)	3176(2)	36(1)
C(8)	4003(4)	5963(2)	4111(2)	70(1)
C(9)	1611(4)	6903(2)	3334(2)	53(1)
C(11)	2821(3)	7992(1)	980(2)	33(1)
C(12)	3429(3)	8670(2)	1451(2)	44(1)
C(13)	3739(4)	9315(2)	936(2)	64(1)
C(14)	3456(4)	9292(2)	-69(3)	76(1)
C(15)	2865(4)	8622(2)	-541(2)	62(1)
C(16)	2514(3)	7954(2)	-33(2)	37(1)
C(17)	1751(3)	7268(1)	-554(2)	34(1)
C(18)	1518(4)	7268(2)	-1639(2)	52(1)
C(19)	396(3)	6060(2)	-611(2)	43(1)
C(31)	-478(3)	6538(1)	1352(2)	31(1)
C(32)	-1403(3)	7150(1)	902(2)	37(1)
C(33)	-2971(3)	7156(2)	867(2)	43(1)
C(34)	-3671(3)	6545(2)	1257(2)	47(1)
C(35)	-2803(3)	5929(2)	1696(2)	44(1)
C(36)	-1220(3)	5935(1)	1757(2)	37(1)

Table 3. Bond lengths [A] and angles [deg] for **2**.

Si(1)-O(1)	1.6555(17)	C(11)-C(12)	1.388(3)
Si(1)-O(2)	1.6636(18)	C(13)-C(14)	1.385(5)
Si(1)-N(1)	1.804(2)	C(14)-C(15)	1.374(4)
Si(1)-C(31)	1.878(3)	C(15)-C(16)	1.404(4)
Si(1)-N(2)	2.081(2)	C(16)-C(17)	1.474(3)
N(1)-C(7)	1.378(3)	C(17)-C(18)	1.496(3)
N(1)-C(9)	1.462(3)	C(31)-C(36)	1.393(3)
N(2)-C(17)	1.293(3)	C(31)-C(32)	1.403(3)
N(2)-C(19)	1.476(3)	C(32)-C(33)	1.380(4)
O(1)-C(1)	1.370(3)	C(33)-C(34)	1.372(4)
O(2)-C(11)	1.350(3)	C(34)-C(35)	1.377(4)
C(1)-C(2)	1.391(3)	C(35)-C(36)	1.388(4)
C(1)-C(6)	1.393(3)	C(11)-C(16)	1.398(3)
C(2)-C(3)	1.371(4)	C(12)-C(13)	1.369(4)
C(3)-C(4)	1.383(4)	C(12)-C(13)	1.369(4)
C(4)-C(5)	1.379(4)	C(12)-C(13)	1.369(4)
C(5)-C(6)	1.401(3)	C(12)-C(13)	1.369(4)
C(6)-C(7)	1.486(3)	C(12)-C(13)	1.369(4)
C(7)-C(8)	1.348(4)	C(11)-C(16)	1.398(3)

O(1)-Si(1)-O(2)	120.51(10)	C(5)-C(6)-C(7)	121.9(2)
O(1)-Si(1)-N(1)	95.88(9)	C(8)-C(7)-N(1)	123.2(2)
O(2)-Si(1)-N(1)	92.40(9)	C(8)-C(7)-C(6)	120.5(2)
O(1)-Si(1)-C(31)	120.10(10)	N(1)-C(7)-C(6)	116.3(2)
O(2)-Si(1)-C(31)	117.11(10)	C(35)-C(36)-C(31)	121.7(2)
N(1)-Si(1)-C(31)	96.78(10)	O(2)-C(11)-C(12)	116.4(2)
O(1)-Si(1)-N(2)	79.71(8)	O(2)-C(11)-C(16)	123.0(2)
O(2)-Si(1)-N(2)	87.99(8)	C(12)-C(11)-C(16)	120.6(2)
N(1)-Si(1)-N(2)	175.07(10)	C(13)-C(12)-C(11)	120.9(3)
C(31)-Si(1)-N(2)	87.40(9)	C(12)-C(13)-C(14)	119.7(3)
C(7)-N(1)-C(9)	114.1(2)	C(15)-C(14)-C(13)	119.8(3)
C(7)-N(1)-Si(1)	127.61(17)	C(14)-C(15)-C(16)	121.8(3)
C(9)-N(1)-Si(1)	114.66(16)	C(11)-C(16)-C(15)	117.1(2)
C(17)-N(2)-C(19)	118.0(2)	C(11)-C(16)-C(17)	121.8(2)
C(17)-N(2)-Si(1)	129.06(16)	C(15)-C(16)-C(17)	120.9(2)
C(19)-N(2)-Si(1)	112.77(15)	N(2)-C(17)-C(16)	119.3(2)
C(1)-O(1)-Si(1)	130.94(16)	N(2)-C(17)-C(18)	122.6(2)
C(11)-O(2)-Si(1)	137.69(16)	C(16)-C(17)-C(18)	118.1(2)
O(1)-C(1)-C(2)	115.5(2)	C(36)-C(31)-C(32)	116.7(2)
O(1)-C(1)-C(6)	122.6(2)	C(36)-C(31)-Si(1)	120.91(18)
C(2)-C(1)-C(6)	121.9(2)	C(32)-C(31)-Si(1)	122.35(19)
C(3)-C(2)-C(1)	120.0(3)	C(33)-C(32)-C(31)	121.5(2)
C(2)-C(3)-C(4)	119.9(3)	C(34)-C(33)-C(32)	120.3(3)
C(5)-C(4)-C(3)	119.7(3)	C(33)-C(34)-C(35)	119.9(3)
C(4)-C(5)-C(6)	122.2(3	C(34)-C(35)-C(36)	119.8(3)
C(1)-C(6)-C(5)	116.3(2)	C(34)-C(35)-C(36)	119.8(3)
C(1)-C(6)-C(7)	121.7(2)		

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **2**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Si(1)	34(1)	32(1)	31(1)	-1(1)	3(1)	2(1)
N(1)	45(1)	42(1)	25(1)	-4(1)	3(1)	9(1)
N(2)	34(1)	34(1)	23(1)	-1(1)	3(1)	-1(1)
O(1)	44(1)	38(1)	27(1)	-1(1)	2(1)	10(1)
O(2)	47(1)	38(1)	29(1)	0(1)	-2(1)	-4(1)
C(1)	31(1)	28(1)	37(2)	4(1)	2(1)	-2(1)
C(2)	42(2)	36(1)	39(2)	-5(1)	4(1)	2(1)
C(3)	53(2)	37(2)	56(2)	-2(1)	11(2)	7(1)
C(4)	57(2)	39(2)	61(2)	13(2)	11(2)	13(1)
C(5)	45(2)	44(2)	41(2)	13(1)	5(1)	2(1)
C(6)	32(1)	32(1)	35(2)	5(1)	6(1)	-5(1)
C(7)	42(2)	34(1)	30(1)	6(1)	3(1)	-4(1)
C(8)	100(3)	60(2)	39(2)	-5(2)	-19(2)	28(2)
C(9)	64(2)	62(2)	32(2)	-7(1)	2(1)	19(2)
C(11)	23(1)	38(1)	37(2)	1(1)	6(1)	-1(1)
C(12)	39(2)	47(2)	43(2)	-5(1)	2(1)	-8(1)
C(13)	70(2)	58(2)	65(2)	-8(2)	12(2)	-31(2)
C(14)	93(3)	67(2)	68(2)	8(2)	20(2)	-46(2)
C(15)	74(2)	69(2)	43(2)	5(2)	15(2)	-29(2)
C(16)	30(1)	45(2)	37(2)	2(1)	9(1)	-6(1)
C(17)	32(1)	41(2)	28(1)	1(1)	6(1)	2(1)
C(18)	64(2)	64(2)	31(2)	3(1)	12(1)	-13(2)
C(19)	57(2)	41(2)	30(2)	-4(1)	1(1)	-12(1)
C(31)	37(1)	35(1)	22(1)	-2(1)	4(1)	3(1)
C(32)	43(2)	37(1)	31(1)	4(1)	9(1)	2(1)
C(33)	41(2)	49(2)	38(2)	0(1)	6(1)	10(1)
C(34)	36(2)	60(2)	48(2)	-13(2)	15(1)	-3(2)
C(35)	45(2)	47(2)	45(2)	-4(1)	19(1)	-10(1)
C(36)	49(2)	33(1)	29(1)	2(1)	10(1)	2(1)

Table 6. Torsion angles [deg] for **2**.

O(1)-Si(1)-N(1)-C(7)	22.4(2)	C(1)-C(6)-C(7)-N(1)	13.2(3)
O(2)-Si(1)-N(1)-C(7)	-98.6(2)	C(5)-C(6)-C(7)-N(1)	-166.0(2)
C(31)-Si(1)-N(1)-C(7)	143.7(2)	Si(1)-O(2)-C(11)-C(12)	168.6(2)
O(1)-Si(1)-N(1)-C(9)	179.3(2)	Si(1)-O(2)-C(11)-C(16)	-11.8(4)
O(2)-Si(1)-N(1)-C(9)	58.3(2)	O(2)-C(11)-C(12)-C(13)	179.7(3)
C(31)-Si(1)-N(1)-C(9)	-59.3(2)	C(16)-C(11)-C(12)-C(13)	0.1(4)
O(1)-Si(1)-N(2)-C(17)	-115.9(2)	C(11)-C(12)-C(13)-C(14)	-0.5(5)
O(2)-Si(1)-N(2)-C(17)	5.6(2)	C(12)-C(13)-C(14)-C(15)	0.0(6)
C(31)-Si(1)-N(2)-C(17)	122.9(2)	C(13)-C(14)-C(15)-C(16)	0.9(6)
O(1)-Si(1)-N(2)-C(19)	58.85(17)	O(2)-C(11)-C(16)-C(15)	-178.8(3)
O(2)-Si(1)-N(2)-C(19)	-179.64(18)	C(12)-C(11)-C(16)-C(15)	0.7(4)
C(31)-Si(1)-N(2)-C(19)	-62.38(18)	O(2)-C(11)-C(16)-C(17)	5.7(4)
O(2)-Si(1)-O(1)-C(1)	92.1(2)	C(12)-C(11)-C(16)-C(17)	-174.8(2)
N(1)-Si(1)-O(1)-C(1)	-4.2(2)	C(14)-C(15)-C(16)-C(11)	-1.3(5)
C(31)-Si(1)-O(1)-C(1)	-105.5(2)	C(14)-C(15)-C(16)-C(17)	174.4(3)
N(2)-Si(1)-O(1)-C(1)	173.6(2)	C(19)-N(2)-C(17)-C(16)	175.3(2)
O(1)-Si(1)-O(2)-C(11)	82.7(3)	Si(1)-N(2)-C(17)-C(16)	-10.2(3)
N(1)-Si(1)-O(2)-C(11)	-179.0(2)	C(19)-N(2)-C(17)-C(18)	-2.0(4)
C(31)-Si(1)-O(2)-C(11)	-80.1(3)	Si(1)-N(2)-C(17)-C(18)	172.46(19)
N(2)-Si(1)-O(2)-C(11)	5.9(2)	C(11)-C(16)-C(17)-N(2)	4.5(4)
Si(1)-O(1)-C(1)-C(2)	175.95(18)	C(15)-C(16)-C(17)-N(2)	-170.9(3)
Si(1)-O(1)-C(1)-C(6)	-6.7(3)	C(11)-C(16)-C(17)-C(18)	-178.0(2)
O(1)-C(1)-C(2)-C(3)	177.0(2)	C(15)-C(16)-C(17)-C(18)	6.6(4)
C(6)-C(1)-C(2)-C(3)	-0.4(4)	O(1)-Si(1)-C(31)-C(36)	52.1(2)
C(1)-C(2)-C(3)-C(4)	0.2(4)	O(2)-Si(1)-C(31)-C(36)	-144.95(18)
C(2)-C(3)-C(4)-C(5)	0.5(4)	N(1)-Si(1)-C(31)-C(36)	-48.7(2)
C(3)-C(4)-C(5)-C(6)	-1.1(4)	N(2)-Si(1)-C(31)-C(36)	128.64(19)
O(1)-C(1)-C(6)-C(5)	-177.3(2)	O(1)-Si(1)-C(31)-C(32)	-128.57(19)
C(2)-C(1)-C(6)-C(5)	-0.1(4)	O(2)-Si(1)-C(31)-C(32)	34.4(2)
O(1)-C(1)-C(6)-C(7)	3.5(4)	N(1)-Si(1)-C(31)-C(32)	130.58(19)
C(2)-C(1)-C(6)-C(7)	-179.3(2)	N(2)-Si(1)-C(31)-C(32)	-52.0(2)
C(4)-C(5)-C(6)-C(1)	0.8(4)	C(36)-C(31)-C(32)-C(33)	0.4(3)
C(4)-C(5)-C(6)-C(7)	-180.0(3)	Si(1)-C(31)-C(32)-C(33)	-178.93(19)
C(9)-N(1)-C(7)-C(8)	-3.9(4)	C(31)-C(32)-C(33)-C(34)	-1.7(4)
Si(1)-N(1)-C(7)-C(8)	153.2(3)	C(32)-C(33)-C(34)-C(35)	0.9(4)
C(9)-N(1)-C(7)-C(6)	174.9(2)	C(33)-C(34)-C(35)-C(36)	1.0(4)
Si(1)-N(1)-C(7)-C(6)	-28.1(3)	C(34)-C(35)-C(36)-C(31)	-2.3(4)
C(1)-C(6)-C(7)-C(8)	-168.0(3)	C(32)-C(31)-C(36)-C(35)	1.6(3)
C(5)-C(6)-C(7)-C(8)	12.8(4)	Si(1)-C(31)-C(36)-C(35)	-179.07(19)

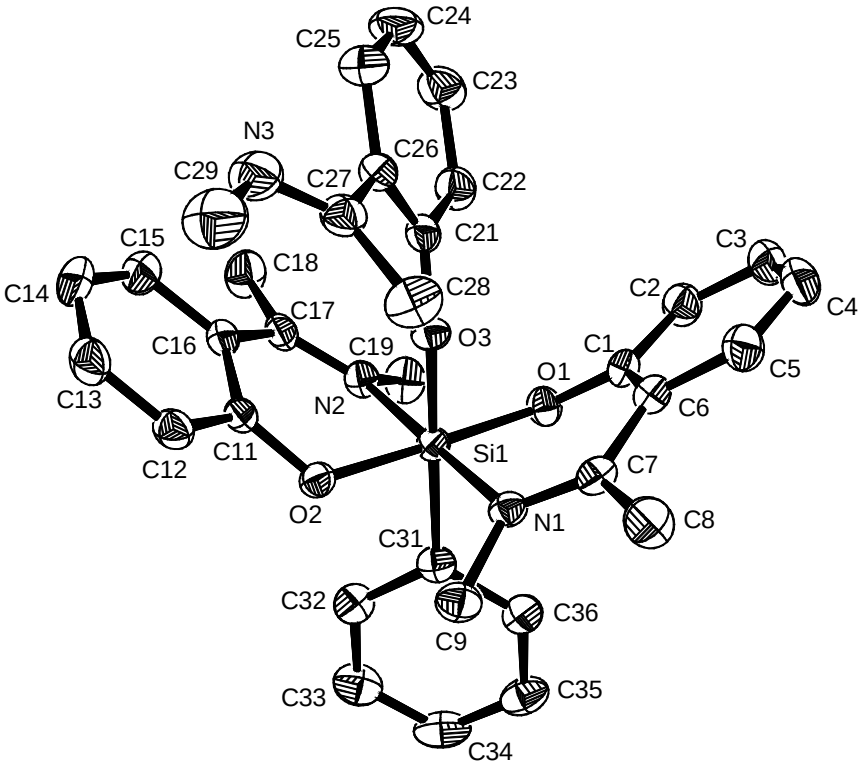


Figure SI2. Molecular structure of compound **3** (ORTEP plot with 50% probability ellipsoids, hydrogen atoms and p-xylene molecule omitted).

Table 1. Crystal data and structure refinement for **3**.

Identification code	**compound 3**
Empirical formula	C37 H40 N3 O3 Si
Formula weight	602.81
Temperature	198(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 11.889(2) A alpha = 90 deg.
	b = 21.871(4) A beta = 101.94(3) deg.
	c = 12.464(3) A gamma = 90 deg.
Volume	3170.8(11) A^3
Z, Calculated density	4, 1.263 Mg/m^3
Absorption coefficient	0.116 mm^-1
F(000)	1284
Crystal size	0.3 x 0.3 x 0.3 mm
Theta range for data collection	3.53 to 25.00 deg.
Limiting indices	-14<=h<=14, -26<=k<=26, -14<=l<=14
Reflections collected / unique	54176 / 5567 [R(int) = 0.0518]
Completeness to theta = 25.00	99.7 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5567 / 0 / 398
Goodness-of-fit on F^2	1.077
Final R indices [I>2sigma(I)]	R1 = 0.0475, wR2 = 0.1014
R indices (all data)	R1 = 0.0729, wR2 = 0.1110
Largest diff. peak and hole	0.309 and -0.239 e.A^-3

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

	x	y	z	U(eq)
Si(1)	712(1)	1066(1)	8220(1)	21(1)
N(1)	-341(2)	413(1)	7573(2)	23(1)
N(2)	1692(2)	1741(1)	8864(2)	24(1)
N(3)	-3149(2)	2324(1)	8621(2)	43(1)
O(1)	1177(1)	1154(1)	6978(1)	26(1)
O(2)	227(1)	998(1)	9455(1)	24(1)
O(3)	-457(1)	1567(1)	7749(1)	24(1)
C(1)	498(2)	1149(1)	5977(2)	26(1)
C(2)	850(2)	1479(1)	5145(2)	33(1)
C(3)	192(3)	1486(1)	4097(2)	41(1)
C(4)	-830(2)	1162(1)	3848(2)	43(1)
C(5)	-1179(2)	827(1)	4655(2)	37(1)
C(6)	-525(2)	804(1)	5736(2)	28(1)
C(7)	-858(2)	390(1)	6547(2)	26(1)
C(8)	-1792(2)	-69(1)	6143(2)	41(1)
C(9)	-604(2)	-60(1)	8330(2)	31(1)
C(11)	-137(2)	1471(1)	9962(2)	24(1)
C(12)	-1039(2)	1373(1)	10511(2)	29(1)
C(13)	-1454(2)	1848(1)	11042(2)	36(1)
C(14)	-981(2)	2427(1)	11050(2)	41(1)
C(15)	-79(2)	2525(1)	10540(2)	36(1)
C(16)	377(2)	2054(1)	9988(2)	25(1
C(17)	1398(2)	2147(1)	9518(2)	26(1)
C(18)	2114(2)	2713(1)	9818(2)	40(1)
C(19)	2809(2)	1816(1)	8536(2)	34(1)
C(21)	-643(2)	2156(1)	7472(2)	26(1)
C(22)	146(2)	2514(1)	7054(2)	34(1)
C(23)	-73(2)	3127(1)	6828(2)	41(1)
C(24)	-1069(3)	3394(1)	7007(2)	45(1)
C(25)	-1864(2)	3045(1)	7388(2)	41(1)
C(26)	-1684(2)	2418(1)	7615(2)	29(1)
C(27)	-2586(2)	2058(1)	7990(2)	32(1)
C(28)	-2814(2)	1411(1)	7571(2)	41(1)
C(29)	-4060(3)	1979(2)	8983(3)	55(1)
C(31)	1918(2)	475(1)	8736(2)	26(1)
C(32)	2508(2)	452(1)	9827(2)	31(1)
C(33)	3374(2)	29(1)	10195(2)	39(1)
C(34)	3676(2)	-392(1)	9476(2)	40(1)
C(35)	3098(2)	-390(1)	8395(2)	36(1)
C(36)	2242(2)	39(1)	8038(2)	31(1)
C(41)	4709(2)	591(1)	4672(3)	50(1)
C(42)	4526(2)	393(1)	5684(2)	46(1)
C(43)	4828(3)	-200(1)	6001(2)	50(1)
C(44)	4003(3)	811(2)	6413(3)	68(1)

Table 3. Bond lengths [A] and angles [deg] for **3**.

Si(1)-O(2)	1.7586(16)	C(11)-C(12)	1.402(3)
Si(1)-O(1)	1.7587(16)	C(11)-C(16)	1.411(3)
Si(1)-O(3)	1.7721(16)	C(12)-C(13)	1.377(3)
Si(1)-C(31)	1.939(2)	C(13)-C(14)	1.386(4)
Si(1)-N(2)	1.9483(19)	C(14)-C(15)	1.371(4)
Si(1)-N(1)	1.9593(19)	C(15)-C(16)	1.408(3)
N(1)-C(7)	1.300(3)	C(16)-C(17)	1.468(3)
N(1)-C(9)	1.477(3)	C(17)-C(18)	1.504(3)
N(2)-C(17)	1.301(3)	C(21)-C(22)	1.403(3)
N(2)-C(19)	1.477(3)	C(21)-C(26)	1.408(3)
N(3)-C(27)	1.274(3)	C(22)-C(23)	1.383(4)
N(3)-C(29)	1.466(4)	C(23)-C(24)	1.379(4)
O(1)-C(1)	1.338(3)	C(24)-C(25)	1.375(4)
O(2)-C(11)	1.331(3)	C(25)-C(26)	1.407(3)
O(3)-C(21)	1.340(3)	C(26)-C(27)	1.481(3)
C(1)-C(2)	1.397(3)	C(27)-C(28)	1.513(4)
C(1)-C(6)	1.410(3)	C(31)-C(32)	1.396(3)
C(2)-C(3)	1.377(4)	C(31)-C(36)	1.397(3)
C(3)-C(4)	1.385(4)	C(32)-C(33)	1.389(3)
C(4)-C(5)	1.376(4)	C(33)-C(34)	1.382(4)
C(5)-C(6)	1.410(3)	C(34)-C(35)	1.380(4)
C(6)-C(7)	1.471(3)	C(35)-C(36)	1.388(3)
C(7)-C(8)	1.504(3)		

O(2)-Si(1)-O(1)	178.40(8)	N(1)-C(7)-C(8)	121.5(2)
O(2)-Si(1)-O(3)	88.05(7)	C(6)-C(7)-C(8)	117.7(2)
O(1)-Si(1)-O(3)	90.47(8)	O(2)-C(11)-C(12)	117.9(2)
O(2)-Si(1)-C(31)	90.41(9)	O(2)-C(11)-C(16)	122.12(19)
O(1)-Si(1)-C(31)	91.11(9)	C(12)-C(11)-C(16)	119.9(2)
O(3)-Si(1)-C(31)	176.22(9)	C(13)-C(12)-C(11)	120.3(2)
O(2)-Si(1)-N(2)	88.89(8)	C(12)-C(13)-C(14)	120.5(2)
O(1)-Si(1)-N(2)	90.56(8)	C(15)-C(14)-C(13)	119.6(2)
O(3)-Si(1)-N(2)	91.68(8)	C(14)-C(15)-C(16)	122.0(2)
C(31)-Si(1)-N(2)	91.75(9)	C(15)-C(16)-C(11)	117.6(2)
O(2)-Si(1)-N(1)	90.06(8)	C(15)-C(16)-C(17)	121.8(2)
O(1)-Si(1)-N(1)	90.42(8)	C(11)-C(16)-C(17)	120.5(2)
O(3)-Si(1)-N(1)	85.61(8)	N(2)-C(17)-C(16)	120.4(2)
C(31)-Si(1)-N(1)	90.94(9)	N(2)-C(17)-C(18)	120.4(2)
N(2)-Si(1)-N(1)	177.12(8)	C(16)-C(17)-C(18)	119.2(2)
C(7)-N(1)-C(9)	118.76(19)	O(3)-C(21)-C(22)	123.0(2)
C(7)-N(1)-Si(1)	124.43(15)	O(3)-C(21)-C(26)	117.5(2)
C(9)-N(1)-Si(1)	116.71(14)	C(22)-C(21)-C(26)	119.5(2)
C(17)-N(2)-C(19)	118.15(19)	C(23)-C(22)-C(21)	120.3(2)
C(17)-N(2)-Si(1)	124.06(15	C(24)-C(23)-C(22)	120.6(2)
C(19)-N(2)-Si(1)	117.69(15)	C(25)-C(24)-C(23)	119.7(2)
C(27)-N(3)-C(29)	118.1(2)	C(24)-C(25)-C(26)	121.6(3)
C(1)-O(1)-Si(1)	125.54(14)	C(25)-C(26)-C(21)	118.2(2)
C(11)-O(2)-Si(1)	123.16(14)	C(25)-C(26)-C(27)	119.4(2)
C(21)-O(3)-Si(1)	139.13(14)	C(21)-C(26)-C(27)	122.4(2)
O(1)-C(1)-C(2)	118.2(2)	N(3)-C(27)-C(26)	117.4(2)
O(1)-C(1)-C(6)	122.0(2)	N(3)-C(27)-C(28)	124.1(2)
C(2)-C(1)-C(6)	119.7(2)	C(26)-C(27)-C(28)	118.5(2)
C(3)-C(2)-C(1)	120.7(2)	C(32)-C(31)-C(36)	115.7(2)
C(2)-C(3)-C(4)	120.4(2)	C(32)-C(31)-Si(1)	122.36(17)
C(5)-C(4)-C(3)	119.5(2)	C(36)-C(31)-Si(1)	121.89(18)
C(4)-C(5)-C(6)	121.8(2)	C(33)-C(32)-C(31)	122.3(2)
C(1)-C(6)-C(5)	117.8(2)	C(34)-C(33)-C(32)	120.2(2)
C(1)-C(6)-C(7)	121.7(2)	C(35)-C(34)-C(33)	119.2(2)
C(5)-C(6)-C(7)	120.3(2)	C(34)-C(35)-C(36)	119.9(2)
N(1)-C(7)-C(6)	120.8(2)	C(35)-C(36)-C(31)	122.6(2)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **3**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Si(1)	22(1)	21(1)	23(1)	-1(1)	7(1)	-1(1)
N(1)	23(1)	20(1)	28(1)	0(1)	8(1)	0(1)
N(2)	24(1)	26(1)	24(1)	0(1)	6(1)	-5(1)
N(3)	41(1)	43(1)	49(1)	6(1)	18(1)	9(1)
O(1)	25(1)	30(1)	24(1)	0(1)	7(1)	-3(1)
O(2)	28(1)	21(1)	26(1)	0(1)	11(1)	0(1)
O(3)	25(1)	19(1)	28(1)	2(1)	6(1)	-1(1)
C(1)	31(1)	25(1)	23(1)	-4(1)	8(1)	3(1)
C(2)	39(1)	32(1)	31(1)	-1(1)	12(1)	-5(1)
C(3)	61(2)	37(2)	26(1)	1(1)	12(1)	-3(1)
C(4)	58(2)	41(2)	24(1)	1(1)	-1(1)	-3(1)
C(5)	41(2)	35(1)	30(1)	-4(1)	0(1)	-4(1)
C(6)	32(1)	24(1)	27(1)	-4(1)	6(1)	1(1)
C(7)	24(1)	23(1)	31(1)	-3(1)	5(1)	1(1)
C(8)	45(2)	38(2)	38(2)	-1(1)	0(1)	-16(1)
C(9)	32(1)	26(1)	35(1)	3(1)	7(1)	-5(1)
C(11)	27(1)	26(1)	19(1)	2(1)	5(1)	4(1)
C(12)	30(1)	32(1)	29(1)	6(1)	11(1)	4(1)
C(13)	36(1)	45(2)	31(1)	5(1)	17(1)	6(1)
C(14)	53(2)	40(2)	36(1)	-8(1)	22(1)	8(1)
C(15)	48(2)	30(1)	32(1)	-5(1)	11(1)	-1(1)
C(16)	31(1)	26(1)	19(1)	0(1)	4(1)	0(1)
C(17)	33(1)	27(1)	18(1)	1(1)	3(1)	-4(1)
C(18)	47(2)	36(2)	38(2)	-8(1)	12(1)	-16(1)
C(19)	27(1)	40(2)	37(1)	-4(1)	12(1)	-11(1)
C(21)	32(1)	26(1)	20(1)	-1(1)	1(1)	-2(1)
C(22)	39(1)	32(1)	31(1)	0(1)	9(1)	-6(1)
C(23)	48(2)	34(2)	41(2)	7(1)	8(1)	-9(1)
C(24)	59(2)	24(1)	49(2)	8(1)	3(1)	-1(1)
C(25)	48(2)	32(2)	42(2)	4(1)	6(1)	9(1)
C(26)	33(1)	28(1)	24(1)	0(1)	1(1)	5(1)
C(27)	29(1)	35(1)	32(1)	4(1)	4(1)	6(1)
C(28)	33(2)	36(2)	55(2)	-2(1)	10(1)	-5(1)
C(29)	47(2)	56(2)	70(2)	7(2)	29(2)	6(2)
C(31)	22(1)	26(1)	30(1)	2(1)	8(1)	-4(1)
C(32)	27(1)	32(1)	33(1)	-2(1)	4(1)	-1(1)
C(33)	30(1)	41(2)	44(2)	6(1)	-1(1)	-1(1)
C(34)	22(1)	31(1)	67(2)	11(1)	10(1)	4(1)
C(35)	31(1)	27(1)	54(2)	-1(1)	17(1)	1(1)
C(36)	30(1)	29(1)	35(1)	-1(1)	11(1)	-1(1)
C(41)	42(2)	42(2)	68(2)	-1(2)	15(2)	-4(1)
C(42)	32(1)	47(2)	62(2)	-15(1)	18(1)	-14(1)
C(43)	49(2)	52(2)	52(2)	-3(1)	18(1)	-11(1)
C(44)	54(2)	58(2)	101(3)	-29(2)	39(2)	-16(2)

Table 6. Torsion angles [deg] for **3**.

O(2)-Si(1)-N(1)-C(7)	145.92(18)	C(14)-C(15)-C(16)-C(11)	0.8(4)
O(1)-Si(1)-N(1)-C(7)	-32.56(18)	C(14)-C(15)-C(16)-C(17)	-175.1(2)
O(3)-Si(1)-N(1)-C(7)	57.88(18)	O(2)-C(11)-C(16)-C(15)	179.5(2)
C(31)-Si(1)-N(1)-C(7)	-123.67(19)	C(12)-C(11)-C(16)-C(15)	-2.4(3)
O(2)-Si(1)-N(1)-C(9)	-30.44(16)	O(2)-C(11)-C(16)-C(17)	-4.5(3)
O(1)-Si(1)-N(1)-C(9)	151.08(15)	C(12)-C(11)-C(16)-C(17)	173.6(2)
O(3)-Si(1)-N(1)-C(9)	-118.48(16)	C(19)-N(2)-C(17)-C(16)	-171.7(2)
C(31)-Si(1)-N(1)-C(9)	59.97(16)	Si(1)-N(2)-C(17)-C(16)	12.0(3)
O(2)-Si(1)-N(2)-C(17)	-37.34(19)	C(19)-N(2)-C(17)-C(18)	7.1(3)
O(1)-Si(1)-N(2)-C(17)	141.16(19)	Si(1)-N(2)-C(17)-C(18)	-169.18(17)
O(3)-Si(1)-N(2)-C(17)	50.67(19)	C(15)-C(16)-C(17)-N(2)	-168.9(2)
C(31)-Si(1)-N(2)-C(17)	-127.72(19)	C(11)-C(16)-C(17)-N(2)	15.4(3)
O(2)-Si(1)-N(2)-C(19)	146.39(17)	C(15)-C(16)-C(17)-C(18)	12.3(3)
O(1)-Si(1)-N(2)-C(19)	-35.11(17)	C(11)-C(16)-C(17)-C(18)	-163.4(2)
O(3)-Si(1)-N(2)-C(19)	-125.59(17)	Si(1)-O(3)-C(21)-C(22)	28.4(3)
C(31)-Si(1)-N(2)-C(19)	56.02(17)	Si(1)-O(3)-C(21)-C(26)	-151.57(18
O(3)-Si(1)-O(1)-C(1)	-43.61(18)	O(3)-C(21)-C(22)-C(23)	-177.2(2)
C(31)-Si(1)-O(1)-C(1)	132.95(18)	C(26)-C(21)-C(22)-C(23)	2.8(4)
N(2)-Si(1)-O(1)-C(1)	-135.29(17)	C(21)-C(22)-C(23)-C(24)	-0.2(4)
N(1)-Si(1)-O(1)-C(1)	42.00(18)	C(22)-C(23)-C(24)-C(25)	-1.5(4)
O(3)-Si(1)-O(2)-C(11)	-42.73(17)	C(23)-C(24)-C(25)-C(26)	0.6(4)
C(31)-Si(1)-O(2)-C(11)	140.72(17)	C(24)-C(25)-C(26)-C(21)	2.0(4)
N(2)-Si(1)-O(2)-C(11)	48.98(17)	C(24)-C(25)-C(26)-C(27)	-178.0(2)
N(1)-Si(1)-O(2)-C(11)	-128.34(17	O(3)-C(21)-C(26)-C(25)	176.4(2)
O(2)-Si(1)-O(3)-C(21)	114.0(2)	C(22)-C(21)-C(26)-C(25)	-3.6(3)
O(1)-Si(1)-O(3)-C(21)	-65.4(2)	O(3)-C(21)-C(26)-C(27)	-3.7(3)
N(2)-Si(1)-O(3)-C(21)	25.2(2)	C(22)-C(21)-C(26)-C(27)	176.3(2)
N(1)-Si(1)-O(3)-C(21)	-155.8(2)	C(29)-N(3)-C(27)-C(26)	178.8(2)
Si(1)-O(1)-C(1)-C(2)	151.85(17)	C(29)-N(3)-C(27)-C(28)	1.3(4)
Si(1)-O(1)-C(1)-C(6)	-30.7(3)	C(25)-C(26)-C(27)-N(3)	-36.2(3)
O(1)-C(1)-C(2)-C(3)	179.4(2)	C(21)-C(26)-C(27)-N(3)	143.8(2)
C(6)-C(1)-C(2)-C(3)	1.9(4)	C(25)-C(26)-C(27)-C(28)	141.4(2)
C(1)-C(2)-C(3)-C(4)	-0.4(4)	C(21)-C(26)-C(27)-C(28)	-38.5(3)
C(2)-C(3)-C(4)-C(5)	-0.7(4)	O(2)-Si(1)-C(31)-C(32)	-37.53(19)
C(3)-C(4)-C(5)-C(6)	0.2(4)	O(1)-Si(1)-C(31)-C(32)	141.97(19)
O(1)-C(1)-C(6)-C(5)	-179.7(2)	N(2)-Si(1)-C(31)-C(32)	51.38(19)
C(2)-C(1)-C(6)-C(5)	-2.3(3)	N(1)-Si(1)-C(31)-C(32)	-127.59(19)
O(1)-C(1)-C(6)-C(7)	-5.1(3)	O(2)-Si(1)-C(31)-C(36)	141.68(19)
C(2)-C(1)-C(6)-C(7)	172.3(2)	O(1)-Si(1)-C(31)-C(36)	-38.83(19)
C(4)-C(5)-C(6)-C(1)	1.3(4)	N(2)-Si(1)-C(31)-C(36)	-129.42(19)
C(4)-C(5)-C(6)-C(7)	-173.4(2)	N(1)-Si(1)-C(31)-C(36)	51.61(19)
C(9)-N(1)-C(7)-C(6)	-172.5(2)	C(36)-C(31)-C(32)-C(33)	0.9(3)
Si(1)-N(1)-C(7)-C(6)	11.2(3)	Si(1)-C(31)-C(32)-C(33)	-179.83(18)
C(9)-N(1)-C(7)-C(8)	6.0(3)	C(31)-C(32)-C(33)-C(34)	-0.5(4)
Si(1)-N(1)-C(7)-C(8)	-170.28(18)	C(32)-C(33)-C(34)-C(35)	-0.7(4)
C(1)-C(6)-C(7)-N(1)	13.2(3)	C(33)-C(34)-C(35)-C(36)	1.3(4)
C(5)-C(6)-C(7)-N(1)	-172.3(2)	C(34)-C(35)-C(36)-C(31)	-0.8(4)
C(1)-C(6)-C(7)-C(8)	-165.4(2)	C(32)-C(31)-C(36)-C(35)	-0.3(3)
C(5)-C(6)-C(7)-C(8)	9.1(3)	Si(1)-C(31)-C(36)-C(35)	-179.53(18)
Si(1)-O(2)-C(11)-C(12)	145.01(17)		
Si(1)-O(2)-C(11)-C(16)	-36.9(3)		
O(2)-C(11)-C(12)-C(13)	-179.6(2)		
C(16)-C(11)-C(12)-C(13)	2.3(3)		
C(11)-C(12)-C(13)-C(14)	-0.5(4)		
C(12)-C(13)-C(14)-C(15)	-1.2(4)		
C(13)-C(14)-C(15)-C(16)	1.0(4)		

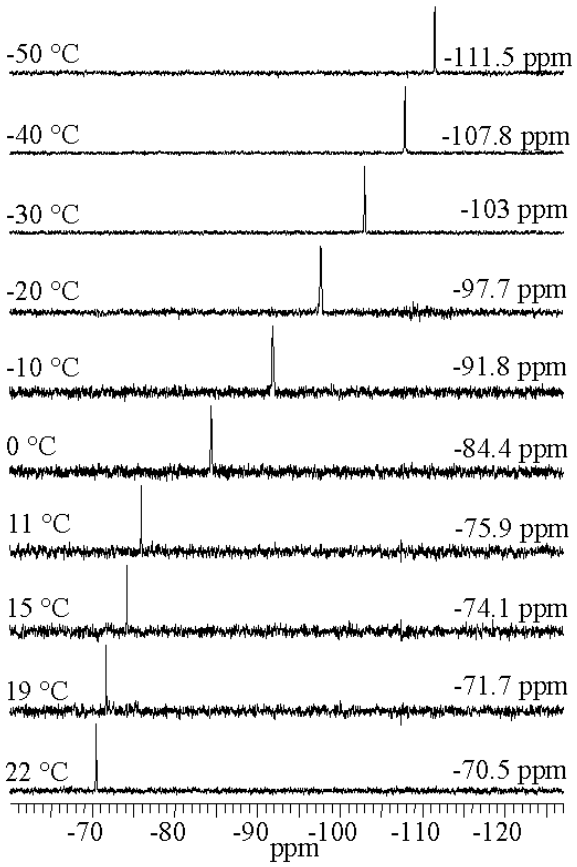


Figure SI3. Stack plot of the ^{29}Si NMR (79.49 MHz) spectra of **2** in CD_2Cl_2 at various temperatures.

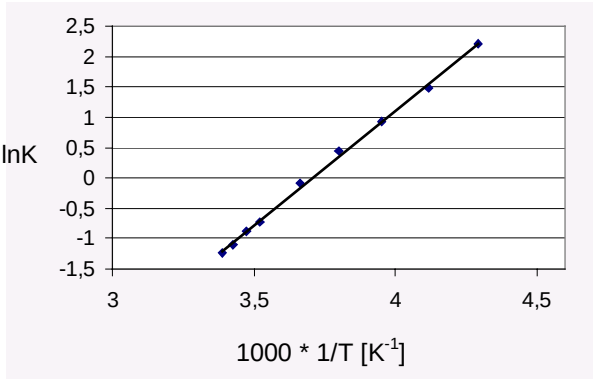


Figure SI4. Linearized plot of lnK vs 1/T for the equilibrium between tetra- and pentacoordinate **2** in CD_2Cl_2. lnK = 3785.1*1/T-14.033; R^2 = 0.9981.

Quantum chemical calculations

The ab initio calculations were carried out using the GAUSSIAN 98 series of programs.[1] Geometries were fully optimized at the density functional theory level (DFT), using Becke's three-parameter hybrid exchange function and the correlation function of Lee, Yang and Parr (B3LYP).[2, 3] Geometry optimizations, harmonic frequencies, and zero-point vibrational energies were calculated with the polarized 6-31G* basis set for all atoms.[4, 5] All structures were identified as true local minima by their Hessian matrices. Final energies were obtained with the optimized geometries from the B3LYP/6-31G* calculations with the methods B3LYP/6-31+G(d,p); B3LYP/6-311+G(2d,p); MP2/6-31+G(d,p) and MP2/6-311+G(2d,p). The chemical shielding tensors were calculated from the optimized molecules using the Gauge-Independent Atomic Orbital (GIAO) method at the Hartree-Fock level with an extended 6-311+G(2d,p) basis set.[6, 7] Theoretical shieldings σ were transformed to relative chemical shifts δ by subtracting from the calculated chemical shielding of TMS with $\sigma(^{29}Si)$ = 385.89 [B3LYP/6-31G(d)//HF/6-311+G(2d,p)].

To gain a more detailed insight into the various possible tetra- and pentacoordinate species of **2** in solution and to find out the reason for the differences in ^{29}Si chemical shifts between the solid state and solution NMR spectra, various inherent molecular geometries of this complex were optimized. Their relative energies were determined (Table SI1) and their isotropic ^{29}Si NMR chemical shift values were calculated as well (Fig. SI5). The optimized structures in Figure SI5 give quite a comprehensive image of the possible conformations and coordination modes of the molecule **2** in solution. The structure of molecule **2b** with a pentacoordinate silicon atom resembles the molecular structure of **2** in the solid state. According to the calculated energies, this also should be the favored pentacoordinate species in solution. The ^{29}Si NMR shift of **2** in the solid state has a deviation of +8.5 ppm referring to the shift value of the analogous optimized molecule **2b**.

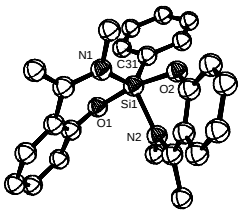
Referring to the calculated ^{29}Si NMR, chemical shift, values differ too greatly and any assessment of the measured value -113.3 ppm (at -55°C in solution) to one of these two pentacoordinate alternatives **2a**, **2b** is not possible. The ^{29}Si NMR shift values of the minimum energy geometries **2c**, **2d** and **2e** also differ from those experimentally observed (-58 ppm) by nearly +8 ppm. Assuming there is a systematic error which is also responsible for the deviation between the values of **2** in solid state and **2b**, the measured chemical shift of -113.3 ppm at a lower temperature should correspond to a geometry with a calculated chemical shift value of approximately -105 ppm. Species **2b** meets these preconditions more so than **2a**.

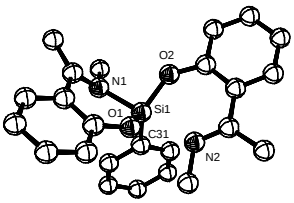
The final energies of the optimized geometries **2a** to **2e** have been calculated with B3LYP/6-311+G(2d,p); B3LYP/6-31+G(d,p); MP2/6-31+G(d,p); and MP2/6-311+G(2d,p). The energy differences at the B3LYP level of theory do not agree with the experimentally estimated values from the NMR experiment. Instead, the energetic order of the molecules is the reverse of the experimental data sequence! This suggests a weakness in the B3LYP

method, which should be further investigated. The energy values of the calculation at the MP2 level agree rather well with the experimental data.

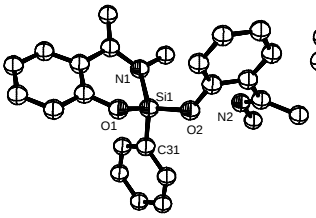
Table SI1. Calculated relative energies (kJ/mol) of **2a** to **2e** optimized with B3LYP/6-31G*.

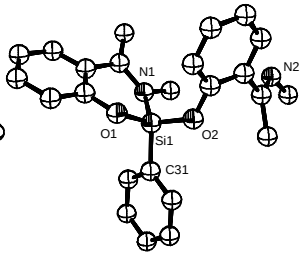
Method/	B3LYP/	B3LYP/	MP2/	MP2/
Basis set	6-31+G(d,p)	6-311+G(2d,p)	6-31+G(d,p)	6-311+G(2d,p)
2a	15.4	24.1	0.0	3.6
2b	6.9	13.5	0.6	0.0
2c	6.0	5.7	25.8	24.8
2d	0.0	0.0	14.9	17.1
2e	2.7	3.9	25.2	25.2



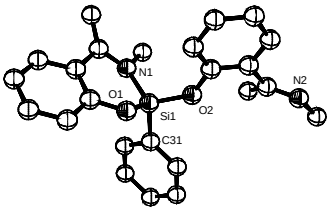


2a δ^{29}Si (calc.): -116.3 **2b** δ^{29}Si (calc.): -100.9





2c δ^{29}Si (calc.): -51.8 **2d** δ^{29}Si (calc.): -48.9



2e δ^{29}Si (calc.): -51.0

Figure SI5. Molecular geometries of **2**, optimized with B3LYP/6-31G*, and isotropic ^{29}Si chemical shift, calculated with HF/6-311+G(2d,p).

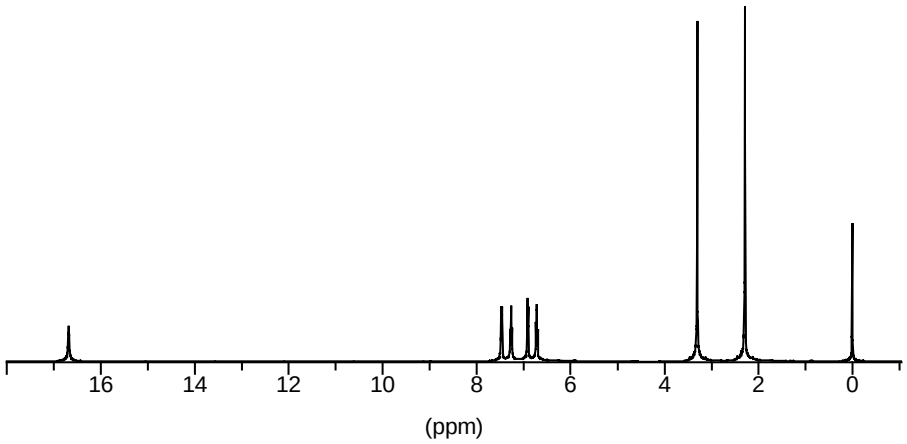


Figure SI6. ^{1}H NMR spectrum of **1** in $CDCl_3$ with TMS.

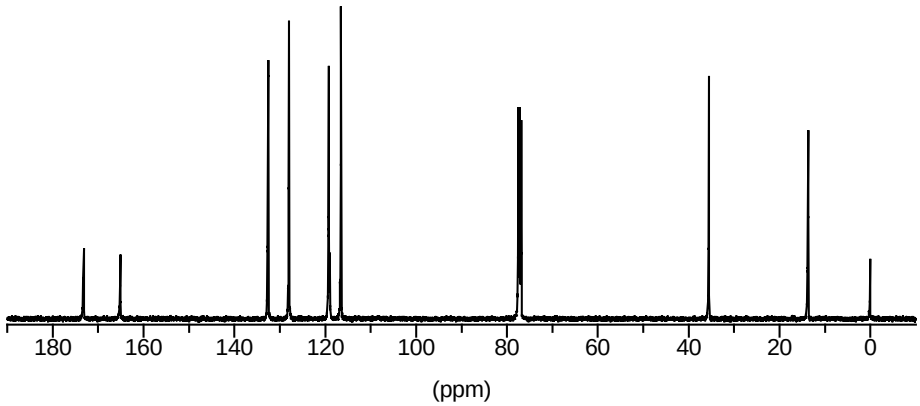


Figure SI7. ^{13}C NMR spectrum of **1** in $CDCl_3$ with TMS.

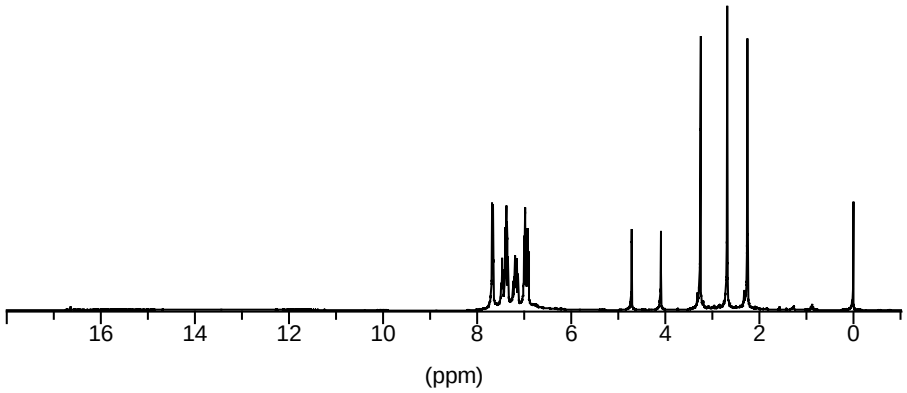


Figure SI8. ^{1}H NMR spectrum of **2** in $CDCl_3$ with TMS.

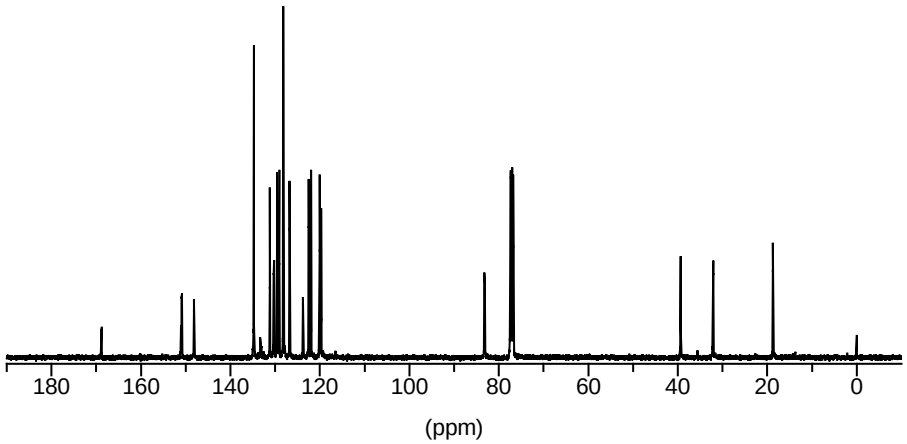


Figure SI9. ^{13}C NMR spectrum of **2** in $CDCl_3$ with TMS.

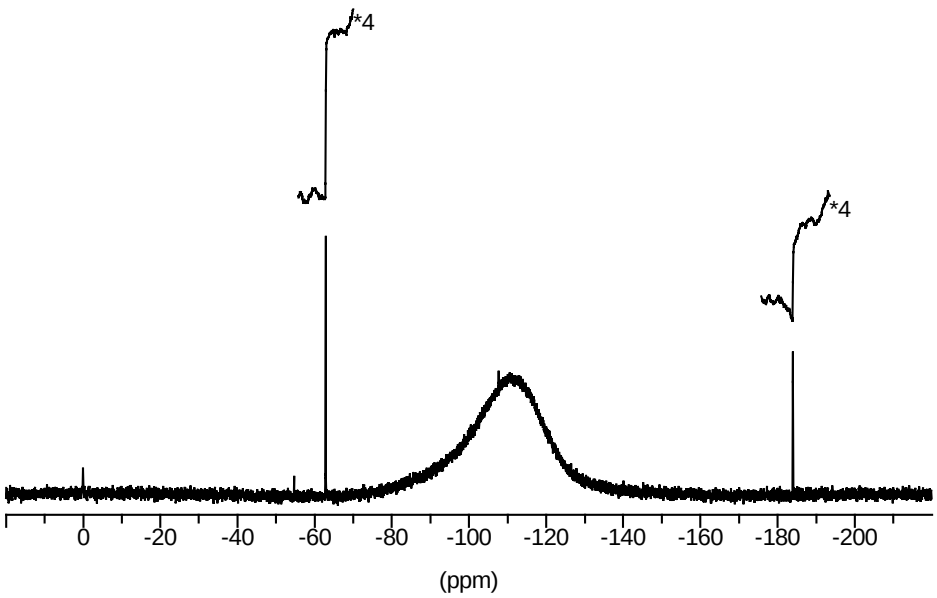


Figure SI10. ^{29}Si NMR spectrum of **3** in $CDCl_3$ (with TMS) with integral traces (δ -62.9 = **2**; -184.0 = undissociated **3**).

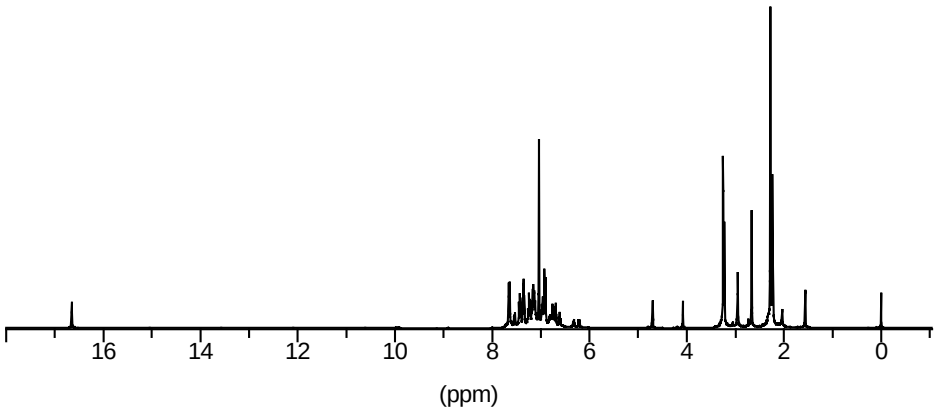


Figure SI11. ^{1}H NMR spectrum of **3** in $CDCl_3$ with TMS.

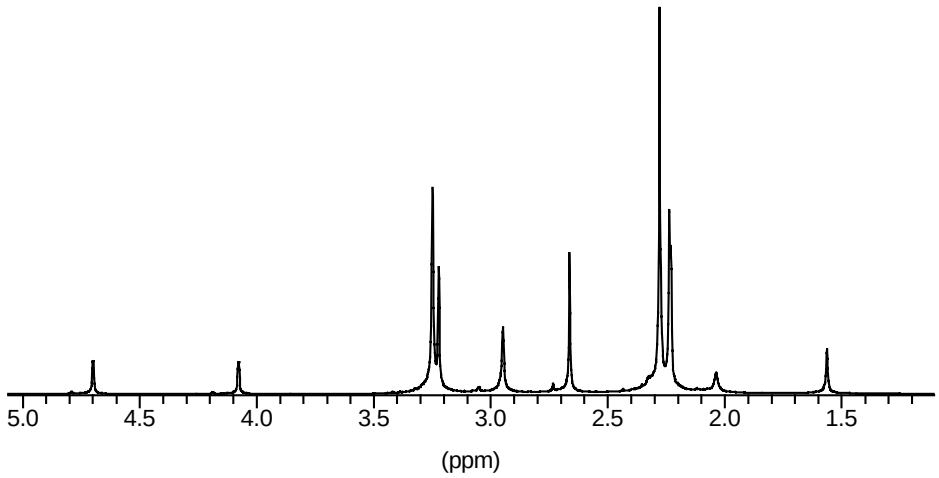


Figure SI12. Section of the ^{1}H NMR spectrum of **3** in $CDCl_3$ (δ 1.56; 2.04; 2.23; 2.24; 2.28; 2.66; 2.95; 3.22; 3.25; 4.08; 4.70). The peaks at 1.56; 2.24; 2.95 and part of 3.25 are assigned to the undissociated **3**, 2.28 originates from p-xylene; 2.23; 2.66; 3.22; 4.08 and 4.70 from **2** and 2.24; 3.25 from **1**.

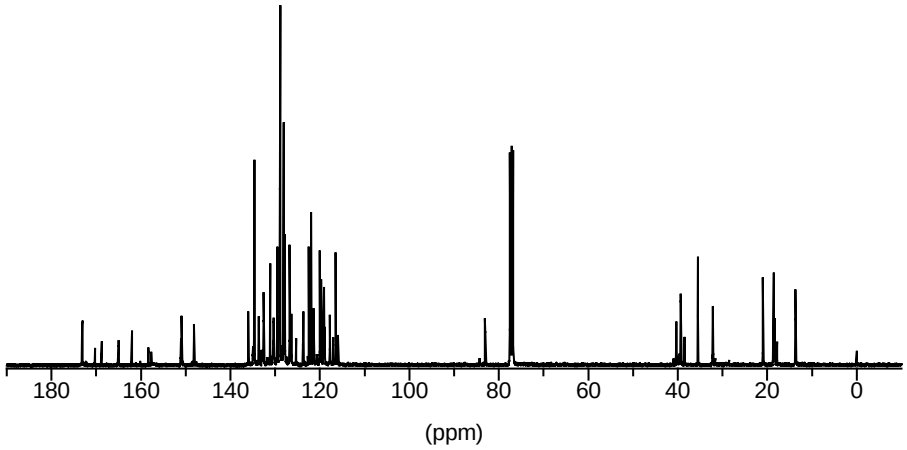


Figure SI13. ^{13}C NMR spectrum of **3** in $CDCl_3$ with TMS.

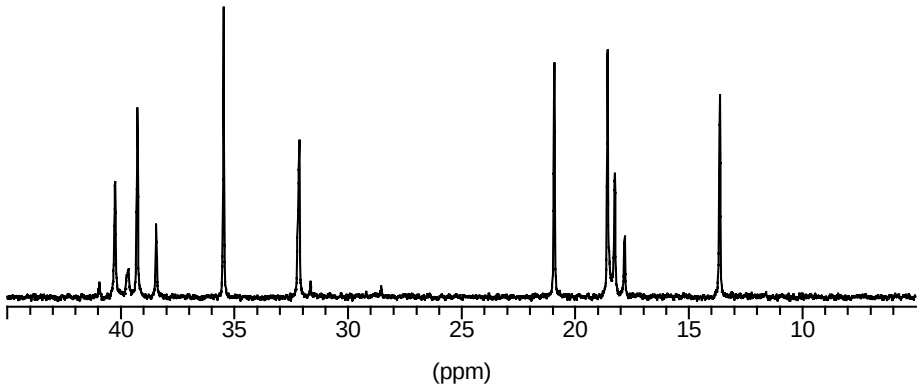


Figure SI14. Section of the ^{13}C NMR spectrum of **1** in $CDCl_3$ (δ 13.6; 17.8; 18.3; 18.6; 20.9; 32.2; 35.5; 38.4; 39.3; 40.3). The peaks at 17.8; 18.3; 38.4 and 40.3 are assigned to the undissociated **3**, 20.9 originates from p-xylene, 13.6 and 35.5 from **1** and 20.9; 32.2; 39.3 from **2**.

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