

**Table S1.** Crystal data and structure refinement for **9**.

**Table S2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **9**.

**Table S3.** Bond lengths ( $\text{\AA}$ ) and angles (degrees) for **9**.

**Table S4.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **9**.

**Table S5.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **9**.

**Table S6.** Selected torsion angles (deg) for **9**.

**Table S7.** Least-squares planes through the starred atoms for **9**.

**Figure S1.** ORTEP drawing of **9**.

**Figure S2.** Packing diagrams of **9**.

**Table S1.** Crystal data and structure refinement for 9.

Empirical formula	$C_{30}H_{36}NNbSi_2$
Formula weight	559.69
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	$a = 10.4150(10)$ Å $\alpha = 101.90$ deg. $b = 10.8580(10)$ Å $\beta = 97.95$ deg. $c = 13.6040(10)$ Å $\gamma = 94.85$ deg.
Volume	1480.7(2) Å <sup>3</sup>
Z, Calculated density	2, 1.255 Mg/m <sup>3</sup>
Absorption coefficient	0.505 mm <sup>-1</sup>
F(000)	584
Crystal size	0.2 x 0.3 x 0.3 mm
Theta range for data collection	2.19 to 28.00 deg.
Limiting indices	-13 ≤ h ≤ 13, -14 ≤ k ≤ 14, 0 ≤ l ≤ 17
Reflections collected / unique	7433 / 7137 [R(int) = 0.0638]
Completeness to theta = 27.82	99.7 %
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	7137 / 0 / 313
Goodness-of-fit on $F^2$	1.022
Final R indices [I > 2σ(I)]	R1 = 0.0642, wR2 = 0.1510
R indices (all data)	R1 = 0.2007, wR2 = 0.2188
Largest diff. peak and hole	0.612 and -0.672 e.Å <sup>-3</sup>

**Table S2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **9**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Nb(1)	7857(1)	9525(1)	6547(1)	40(1)
Si(1)	8649(2)	12265(3)	8984(2)	70(1)
Si(2)	8231(3)	6009(3)	6531(3)	99(1)
N(1)	6487(5)	8717(6)	6929(5)	55(2)
C(1)	7258(7)	8792(7)	4924(6)	54(2)
C(2)	6966(7)	8400(7)	4022(6)	53(2)
C(3)	8448(14)	10964(11)	9675(7)	129(5)
C(4)	10363(10)	13015(15)	9186(11)	177(8)
C(5)	7607(11)	13482(9)	9468(7)	90(3)
C(6)	7003(12)	5595(12)	5385(11)	143(5)
C(7)	9584(14)	4975(12)	6465(18)	243(13)
C(8)	7435(17)	5933(14)	7689(13)	185(8)
C(11)	8047(7)	11684(7)	7575(6)	53(2)
C(12)	8735(7)	11786(6)	6745(5)	53(2)
C(13)	7871(8)	11481(7)	5849(6)	63(2)
C(14)	6596(8)	11211(7)	6089(6)	61(2)
C(15)	6733(7)	11366(7)	7143(6)	56(2)
C(21)	9031(7)	7679(7)	6717(7)	60(2)
C(22)	9378(8)	8577(8)	7621(6)	65(2)
C(23)	10139(7)	9620(8)	7458(6)	63(2)
C(24)	10264(7)	9374(7)	6431(6)	58(2)
C(25)	9591(7)	8186(7)	5971(6)	57(2)
C(31)	6688(7)	7852(8)	2931(6)	55(2)
C(32)	6450(10)	6553(10)	2561(8)	89(3)
C(33)	6188(11)	6061(12)	1528(9)	113(4)
C(34)	6147(10)	6851(14)	852(7)	109(5)
C(35)	6344(8)	8152(12)	1196(7)	90(3)
C(36)	6620(7)	8651(9)	2241(6)	64(2)
C(41)	5327(7)	8334(7)	7212(6)	53(2)
C(42)	5231(8)	8490(11)	8232(7)	93(3)
C(43)	4052(10)	8118(12)	8527(8)	105(4)
C(44)	2983(10)	7604(11)	7820(9)	96(3)
C(45)	3089(8)	7429(9)	6809(9)	82(3)
C(46)	4261(8)	7791(8)	6504(7)	68(2)

**Table S3.** Bond lengths [Å] and angles [deg] for **9**.

Nb(1)-N(1)	1.804(5)
Nb(1)-C(1)	2.170(7)
Nb(1)-C(22)	2.441(7)
Nb(1)-C(11)	2.447(7)
Nb(1)-C(15)	2.453(7)
Nb(1)-C(21)	2.468(8)
Nb(1)-C(14)	2.474(8)
Nb(1)-C(12)	2.493(7)
Nb(1)-C(13)	2.499(7)
Nb(1)-C(23)	2.507(7)
Nb(1)-C(25)	2.520(7)
Nb(1)-C(24)	2.550(7)
Si(1)-C(5)	1.854(9)
Si(1)-C(4)	1.858(11)
Si(1)-C(3)	1.865(12)
Si(1)-C(11)	1.888(8)
Si(2)-C(6)	1.825(13)
Si(2)-C(7)	1.875(13)
Si(2)-C(21)	1.882(8)
Si(2)-C(8)	1.892(15)
N(1)-C(41)	1.376(8)
C(1)-C(2)	1.199(10)
C(2)-C(31)	1.459(10)
C(11)-C(15)	1.397(10)
C(11)-C(12)	1.436(9)
C(12)-C(13)	1.373(11)
C(13)-C(14)	1.432(11)
C(14)-C(15)	1.395(10)
C(21)-C(22)	1.384(11)
C(21)-C(25)	1.418(11)
C(22)-C(23)	1.400(11)
C(23)-C(24)	1.393(11)
C(24)-C(25)	1.393(10)
C(31)-C(32)	1.384(12)
C(31)-C(36)	1.402(11)
C(32)-C(33)	1.376(14)
C(33)-C(34)	1.380(17)
C(34)-C(35)	1.381(16)
C(35)-C(36)	1.393(11)
C(41)-C(46)	1.366(10)
C(41)-C(42)	1.382(11)
C(42)-C(43)	1.397(11)
C(43)-C(44)	1.361(14)
C(44)-C(45)	1.371(13)
C(45)-C(46)	1.394(11)
N(1)-Nb(1)-C(1)	95.9(3)
N(1)-Nb(1)-C(22)	90.8(3)
C(1)-Nb(1)-C(22)	124.0(3)
N(1)-Nb(1)-C(11)	103.8(3)
C(1)-Nb(1)-C(11)	130.7(3)
C(22)-Nb(1)-C(11)	100.7(3)
N(1)-Nb(1)-C(15)	81.3(3)
C(1)-Nb(1)-C(15)	110.5(3)
C(22)-Nb(1)-C(15)	125.4(3)
C(11)-Nb(1)-C(15)	33.1(2)
N(1)-Nb(1)-C(21)	87.5(3)
C(1)-Nb(1)-C(21)	92.0(3)
C(22)-Nb(1)-C(21)	32.7(3)
C(11)-Nb(1)-C(21)	133.0(3)
C(15)-Nb(1)-C(21)	155.7(3)

N(1)-Nb(1)-C(14)	93.4(3)
C(1)-Nb(1)-C(14)	79.0(3)
C(22)-Nb(1)-C(14)	156.1(3)
C(11)-Nb(1)-C(14)	55.4(3)
C(15)-Nb(1)-C(14)	32.9(2)
C(21)-Nb(1)-C(14)	170.9(3)
N(1)-Nb(1)-C(12)	135.0(3)
C(1)-Nb(1)-C(12)	105.7(3)
C(22)-Nb(1)-C(12)	107.8(3)
C(11)-Nb(1)-C(12)	33.8(2)
C(15)-Nb(1)-C(12)	54.3(2)
C(21)-Nb(1)-C(12)	129.6(2)
C(14)-Nb(1)-C(12)	54.3(3)
N(1)-Nb(1)-C(13)	126.9(3)
C(1)-Nb(1)-C(13)	76.7(3)
C(22)-Nb(1)-C(13)	137.1(3)
C(11)-Nb(1)-C(13)	55.2(3)
C(15)-Nb(1)-C(13)	54.6(3)
C(21)-Nb(1)-C(13)	144.3(3)
C(14)-Nb(1)-C(13)	33.5(3)
C(12)-Nb(1)-C(13)	31.9(2)
N(1)-Nb(1)-C(23)	121.5(3)
C(1)-Nb(1)-C(23)	124.1(3)
C(22)-Nb(1)-C(23)	32.8(3)
C(11)-Nb(1)-C(23)	82.1(3)
C(15)-Nb(1)-C(23)	114.6(3)
C(21)-Nb(1)-C(23)	54.4(3)
C(14)-Nb(1)-C(23)	131.2(3)
C(12)-Nb(1)-C(23)	77.2(3)
C(13)-Nb(1)-C(23)	104.4(3)
N(1)-Nb(1)-C(25)	116.4(3)
C(1)-Nb(1)-C(25)	74.1(3)
C(22)-Nb(1)-C(25)	53.7(3)
C(11)-Nb(1)-C(25)	130.6(2)
C(15)-Nb(1)-C(25)	161.7(2)
C(21)-Nb(1)-C(25)	33.0(2)
C(14)-Nb(1)-C(25)	141.3(3)
C(12)-Nb(1)-C(25)	107.4(2)
C(13)-Nb(1)-C(25)	111.8(3)
C(23)-Nb(1)-C(25)	53.2(3)
N(1)-Nb(1)-C(24)	140.9(3)
C(1)-Nb(1)-C(24)	92.8(3)
C(22)-Nb(1)-C(24)	53.6(3)
C(11)-Nb(1)-C(24)	98.9(2)
C(15)-Nb(1)-C(24)	130.3(2)
C(21)-Nb(1)-C(24)	54.1(2)
C(14)-Nb(1)-C(24)	125.6(3)
C(12)-Nb(1)-C(24)	77.7(2)
C(13)-Nb(1)-C(24)	92.2(3)
C(23)-Nb(1)-C(24)	32.0(3)
C(25)-Nb(1)-C(24)	31.9(2)
C(5)-Si(1)-C(4)	108.8(6)
C(5)-Si(1)-C(3)	107.3(5)
C(4)-Si(1)-C(3)	112.7(7)
C(5)-Si(1)-C(11)	107.0(4)
C(4)-Si(1)-C(11)	109.5(5)
C(3)-Si(1)-C(11)	111.2(4)
C(6)-Si(2)-C(7)	112.4(8)
C(6)-Si(2)-C(21)	110.7(5)
C(7)-Si(2)-C(21)	105.9(5)
C(6)-Si(2)-C(8)	110.0(7)
C(7)-Si(2)-C(8)	110.5(8)
C(21)-Si(2)-C(8)	107.1(6)

C(2)-C(1)-Nb(1)	177.9(6)
C(1)-C(2)-C(31)	175.4(8)
C(15)-C(11)-C(12)	105.7(7)
C(15)-C(11)-Si(1)	124.3(5)
C(12)-C(11)-Si(1)	128.2(5)
C(15)-C(11)-Nb(1)	73.7(4)
C(12)-C(11)-Nb(1)	74.9(4)
Si(1)-C(11)-Nb(1)	128.3(4)
C(13)-C(12)-C(11)	109.4(7)
C(13)-C(12)-Nb(1)	74.3(4)
C(11)-C(12)-Nb(1)	71.4(4)
C(12)-C(13)-C(14)	107.8(7)
C(12)-C(13)-Nb(1)	73.8(4)
C(14)-C(13)-Nb(1)	72.3(4)
C(15)-C(14)-C(13)	107.0(7)
C(15)-C(14)-Nb(1)	72.7(4)
C(13)-C(14)-Nb(1)	74.2(4)
C(14)-C(15)-C(11)	110.0(7)
C(14)-C(15)-Nb(1)	74.4(4)
C(11)-C(15)-Nb(1)	73.2(4)
C(22)-C(21)-C(25)	106.3(7)
C(22)-C(21)-Si(2)	127.6(7)
C(25)-C(21)-Si(2)	125.4(6)
C(22)-C(21)-Nb(1)	72.5(5)
C(25)-C(21)-Nb(1)	75.5(4)
Si(2)-C(21)-Nb(1)	124.8(4)
C(21)-C(22)-C(23)	109.6(7)
C(21)-C(22)-Nb(1)	74.7(5)
C(23)-C(22)-Nb(1)	76.2(4)
C(24)-C(23)-C(22)	107.5(7)
C(24)-C(23)-Nb(1)	75.7(4)
C(22)-C(23)-Nb(1)	71.0(4)
C(25)-C(24)-C(23)	107.9(7)
C(25)-C(24)-Nb(1)	72.9(4)
C(23)-C(24)-Nb(1)	72.3(4)
C(24)-C(25)-C(21)	108.7(7)
C(24)-C(25)-Nb(1)	75.2(4)
C(21)-C(25)-Nb(1)	71.5(4)
C(32)-C(31)-C(36)	119.1(8)
C(32)-C(31)-C(2)	121.2(8)
C(36)-C(31)-C(2)	119.7(7)
C(33)-C(32)-C(31)	120.0(11)
C(32)-C(33)-C(34)	120.6(11)
C(33)-C(34)-C(35)	120.8(9)
C(34)-C(35)-C(36)	118.6(10)
C(35)-C(36)-C(31)	120.8(9)
C(46)-C(41)-N(1)	121.4(7)
C(46)-C(41)-C(42)	118.9(7)
N(1)-C(41)-C(42)	119.7(7)
C(41)-C(42)-C(43)	120.1(9)
C(44)-C(43)-C(42)	120.9(9)
C(43)-C(44)-C(45)	118.9(9)
C(44)-C(45)-C(46)	120.8(9)
C(41)-C(46)-C(45)	120.4(8)

**Table S4.** Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for **9**. The anisotropic displacement factor exponent takes the form:  $-2\pi^2[h^2a^*U11 + \dots + 2hka^*b^*U12]$ 

	U11	U22	U33	U23	U13	U12
Nb(1)	36(1)	45(1)	39(1)	8(1)	7(1)	-2(1)
Si(1)	56(1)	82(2)	56(1)	-15(1)	3(1)	5(1)
Si(2)	88(2)	57(2)	158(3)	47(2)	10(2)	-2(1)
N(1)	43(3)	65(4)	57(4)	21(3)	11(3)	-8(3)
C(1)	52(4)	60(5)	47(4)	7(4)	9(3)	2(4)
C(2)	47(4)	54(4)	53(5)	3(4)	7(3)	2(3)
C(3)	203(14)	136(11)	57(6)	25(7)	6(7)	91(10)
C(4)	64(7)	252(19)	145(12)	-87(12)	14(7)	-47(9)
C(5)	131(9)	80(7)	56(5)	-7(5)	35(6)	15(6)
C(6)	131(11)	92(9)	187(15)	32(9)	-14(10)	-40(8)
C(7)	130(12)	61(8)	560(40)	108(15)	59(18)	27(8)
C(8)	210(17)	152(14)	222(19)	118(14)	46(14)	-28(12)
C(11)	47(4)	53(4)	57(4)	5(3)	14(3)	5(3)
C(12)	59(4)	43(4)	53(4)	5(3)	17(4)	-7(3)
C(13)	89(6)	50(5)	59(5)	24(4)	22(4)	15(4)
C(14)	61(5)	56(5)	61(5)	6(4)	-4(4)	11(4)
C(15)	42(4)	64(5)	55(5)	-2(4)	9(3)	11(3)
C(21)	54(4)	47(4)	78(6)	18(4)	6(4)	-4(4)
C(22)	58(5)	79(6)	59(5)	25(5)	-1(4)	10(4)
C(23)	46(4)	61(5)	74(6)	9(4)	-12(4)	9(4)
C(24)	44(4)	57(5)	73(5)	8(4)	15(4)	6(3)
C(25)	54(4)	50(4)	60(5)	-1(4)	10(4)	7(4)
C(31)	45(4)	64(5)	47(4)	-2(4)	2(3)	-4(3)
C(32)	95(7)	86(7)	79(7)	8(6)	3(5)	13(6)
C(33)	104(9)	121(10)	78(8)	-47(7)	3(7)	4(7)
C(34)	77(7)	182(14)	36(5)	-32(7)	-7(5)	4(8)
C(35)	61(6)	154(11)	46(5)	10(6)	4(4)	-5(6)
C(36)	45(4)	92(6)	51(5)	6(4)	11(3)	5(4)
C(41)	42(4)	66(5)	57(5)	25(4)	16(3)	-4(3)
C(42)	55(5)	161(10)	64(6)	40(6)	15(4)	-25(6)
C(43)	73(6)	171(12)	90(7)	58(8)	41(6)	-3(7)
C(44)	65(6)	125(9)	106(9)	45(7)	27(6)	-22(6)
C(45)	44(5)	86(7)	113(8)	32(6)	-6(5)	-7(4)
C(46)	60(5)	77(6)	71(5)	25(5)	13(4)	0(4)



**Table S5.** Hydrogen coordinates ( $\times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 9.

	x	y	z	U(eq)
H(3A)	8957	10305	9427	155
H(3B)	7545	10628	9563	155
H(3C)	8739	11291	10390	155
H(4A)	10412	13685	8825	212
H(4B)	10912	12392	8939	212
H(4C)	10652	13357	9900	212
H(5A)	7917	13836	10177	108
H(5B)	6723	13098	9384	108
H(5C)	7642	14141	9095	108
H(6A)	6332	6147	5453	172
H(6B)	6626	4733	5292	172
H(6C)	7404	5688	4806	172
H(7A)	9818	4766	7113	291
H(7B)	10328	5418	6292	291
H(7C)	9298	4211	5955	291
H(8A)	6799	6523	7747	222
H(8B)	8088	6145	8288	222
H(8C)	7015	5091	7621	222
H(12)	9627	12021	6805	63
H(13)	8077	11455	5202	76
H(14)	5823	10976	5629	74
H(15)	6050	11271	7505	67
H(22)	9142	8499	8242	78
H(23)	10496	10344	7946	76
H(24)	10716	9908	6110	70
H(25)	9520	7791	5288	68
H(32)	6467	6014	3011	107
H(33)	6038	5188	1283	135
H(34)	5983	6504	156	131
H(35)	6293	8683	739	108
H(36)	6761	9525	2484	77
H(42)	5953	8842	8724	112
H(43)	3996	8224	9215	126
H(44)	2195	7374	8020	116
H(45)	2369	7065	6319	99
H(46)	4318	7662	5815	82

**Table S6.** Selected torsion angles (deg) for **9**.

Nb(1)-N(1)-C(41)-C(42)	-94(3)
Nb(1)-N(1)-C(41)-C(46)	86(3)
Nb(1)-C(1)-C(2)-C(31)	65(25)
C(1)-C(2)-C(31)-C(32)	49(10)
C(1)-C(2)-C(31)-C(36)	-133(10)

**Table S7.** Least squares planes (x,y,z in crystal coordinates) and deviations from them. for **9**. (\* indicates atom used to define plane).

$$-2.4539 (0.0383) x + 10.6711 (0.0077) y - 1.0723 (0.0524) z = 9.6973 (0.0428)$$

- \* -0.0156 (0.0046) C11
- \* 0.0124 (0.0047) C12
- \* -0.0045 (0.0048) C13
- \* -0.0056 (0.0049) C14
- \* 0.0133 (0.0049) C15

Rms deviation of fitted atoms = 0.0112

$$8.8544 (0.0210) x - 6.0214 (0.0345) y + 2.5529 (0.0518) z = 5.0867 (0.0508)$$

- \* 0.0009 (0.0048) C21
- \* -0.0019 (0.0048) C22
- \* 0.0021 (0.0047) C23
- \* -0.0016 (0.0047) C24
- \* 0.0004 (0.0048) C25

Rms deviation of fitted atoms = 0.0015

$$10.4092 (0.0016) x - 1.1450 (0.0423) y - 2.1570 (0.0481) z = 5.4198 (0.0310)$$

- \* 0.0108 (0.0058) C31
- \* -0.0087 (0.0071) C32
- \* -0.0018 (0.0080) C33
- \* 0.0100 (0.0077) C34
- \* -0.0076 (0.0065) C35
- \* -0.0028 (0.0056) C36

Rms deviation of fitted atoms = 0.0078

$$-3.7800 (0.0406) x + 10.4146 (0.0129) y - 2.0730 (0.0582) z = 5.1613 (0.0478)$$

- \* 0.0094 (0.0067) C41
- \* -0.0036 (0.0079) C42
- \* -0.0054 (0.0087) C43
- \* 0.0087 (0.0084) C44
- \* -0.0029 (0.0073) C45
- \* -0.0062 (0.0063) C46

Rms deviation of fitted atoms = 0.0065

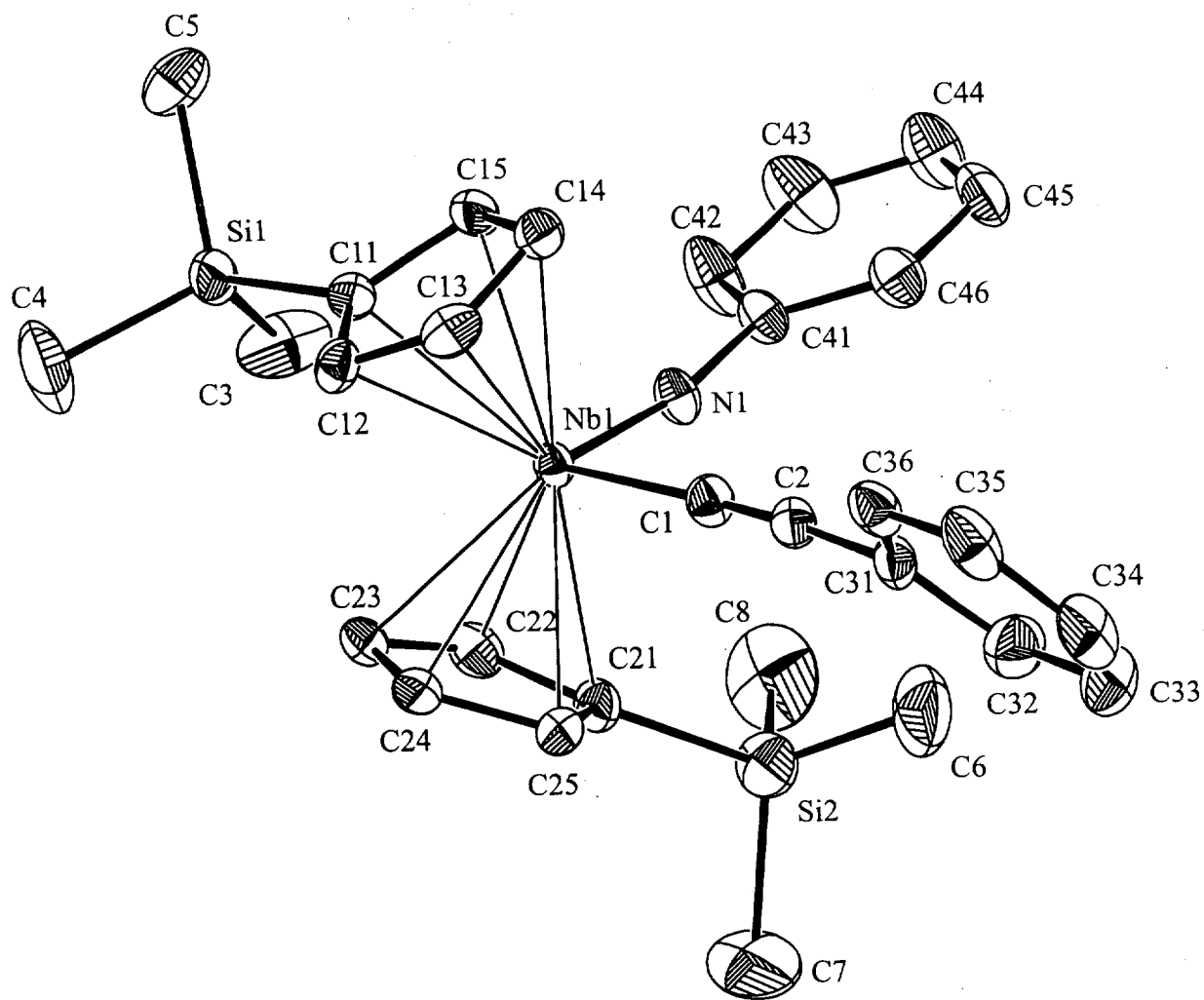


Figure S1

Figure S2

