Supporting Information

Preparation of a High-coordinated-silicon-centered Spiro-cyclic Compound

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1. Materials and methods

All the chemicals were purchased from commercially available sources and were used as received. The solvents were dried by stirring over Na-K alloy for several days. All manipulations were carried out using standard Schlenk and glovebox techniques under high purity dinitrogen gas atmosphere. Deuterated NMR solvents C_6D_6/ THF-D_8 were dried by stirring it for 2 days over Na/K alloy followed by distillation in vacuum and degassed. ^{1}H, ^{13}C and ^{29}Si NMR spectra were recorded on Bruker Avance 400 or 500 MHz, 100 MHz and 99 MHz NMR spectrometers respectively and referenced to the resonances of the solvent used. Amidinato-silylene chloride, **LSiCl** (L = $PhC(N^tBu)_2$) was synthesized as per the procedure reported in the literature.[1]

2. Synthesis

Synthesis of compound 1

Amidinato-silylene chloride, **LSiCl** (2 mmol, 1176 mg) and Ph_2SiCl_2 (2 mmol, 0.4 ml) were mixed together at – 78˚ C and stirred for an hour. The resulting brown colored solution was transferred to a flask containing KC_8 (4 mmol, 540 mg) at – 78˚ C. The solution was slowly brought to the room temperature and stirred overnight. After overnight stirring, the reaction mixture was filtered and solvent was removed under vacuum. The compound was dissolved in hexane and the clear filtrate was concentrated to about 4 ml and kept undisturbed at room temperature for two months. The block-shape colorless crystals of compound **1** were picked up from the flask with 13 % yield (122 mg). ^{1}H NMR (400 MHz, 298K, C_6D_6, ppm): δ = 8.15 (d, *J* = 7.3, 4H, Ar-CH), 7.54 – 7.48 (m, 1H, Ar-CH), 7.22 (t, *J* = 7.4, 4H, Ar-CH), 7.18 – 7.12 (m, 2H, Ar-CH), 7.06 (d, *J* = 7.8, 1H, AR-CH), 7.02 – 6.94 (m, 2H, Ar-CH), 6.94 – 6.86 (m, 1H, Ar-CH), 0.95 (s, 18H, CH_3). ^{13}C NMR (100 MHz, 298K, C_6D_6): δ = 156.4 (NCN), 139.3 (Ar-C), 134.3 (Ar-C), 133.9 (Ar-C), 131.4 (Ar-C), 129.4 (Ar-C), 128.9 (Ar-C), 128.6 (Ar-C), 127.8 (Ar-C), 127.2 (Ar-C), 52.8 (^{t}Butyl-C), 30.9 (CH_3). ^{29}Si NMR (99 MHz, C_6D_6, ppm): δ = 35.9 and 10.2.

Synthesis of compound 2

Compound **1** (0.5 mmol, 238 mg) and 1,2-diphenylethyne (0.5 mmol, 90 mg) were mixed at -77˚ C in toluene and the solution was warmed slowly. Subsequently, the reaction mixture was stirred for 24 h. The resulting reaction mixture was filtered and solvent was removed. The compound was dissolved in hexane and concentrated solution kept for the crystallization at room temperature. Block- shape crystals with 37 % yield (180 mg) were isolated within a week. ^{1}H NMR (500 MHz, 298K, Toluene-D_8, ppm): δ = 8.04 – 8.02 (m, 4H, Ar-CH), 7.83– 7.81 (m, 2H, Ar-CH), 7.26 – 7.24 (m, 6H, Ar-CH), 7.17-7.10 (m, 2H, Ar-CH), *7.01*- 6.98 (m, 2H, Ar-CH), 6.92 – 6.68 (m, 7H, Ar-CH), 6.86 – 6.78 (m, 2H, Ar-CH), 1.00 (s, 18H, CH_3). ^{13}C NMR (125 MHz, 298K, Toluene-D_8, ppm): δ = 167.7 (NCN), 161.0 (Ar-C), 144.3 (Ar-C), 142.5 (Ar-C), 136.7 (Ar-C), 135.1 (Ar-C), 130.4 (Ar-C), 129.9 (Ar-CH), 129.5 (Ar-C), 128.3 (Ar-C), 126.6-126.5 (C=C), 54.8 (^{t}Butyl-C), 32.7 (CH_3). ^{29}Si NMR (99 MHz, 298K, Toluene-D_8, ppm): δ = 17.6 and -71.2.

3. NMR spectra

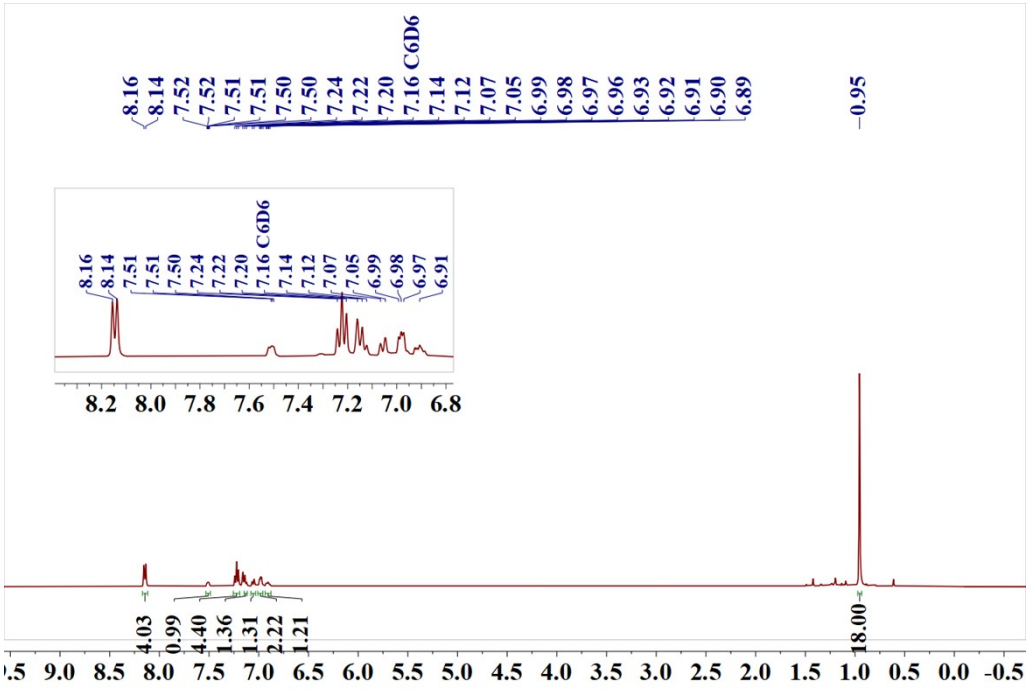

Figure S1. ^{1}H NMR of compound **1**.

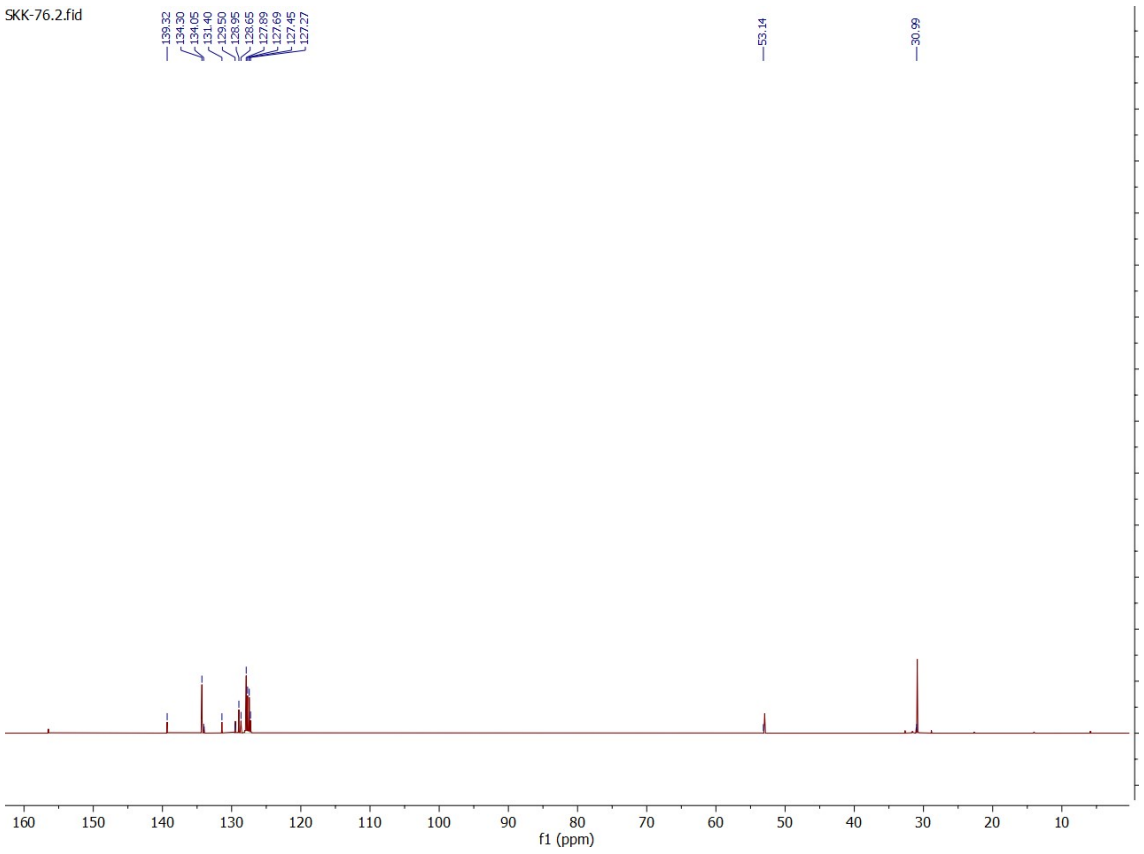

Figure S2. ^{13}C NMR of compound **1**.

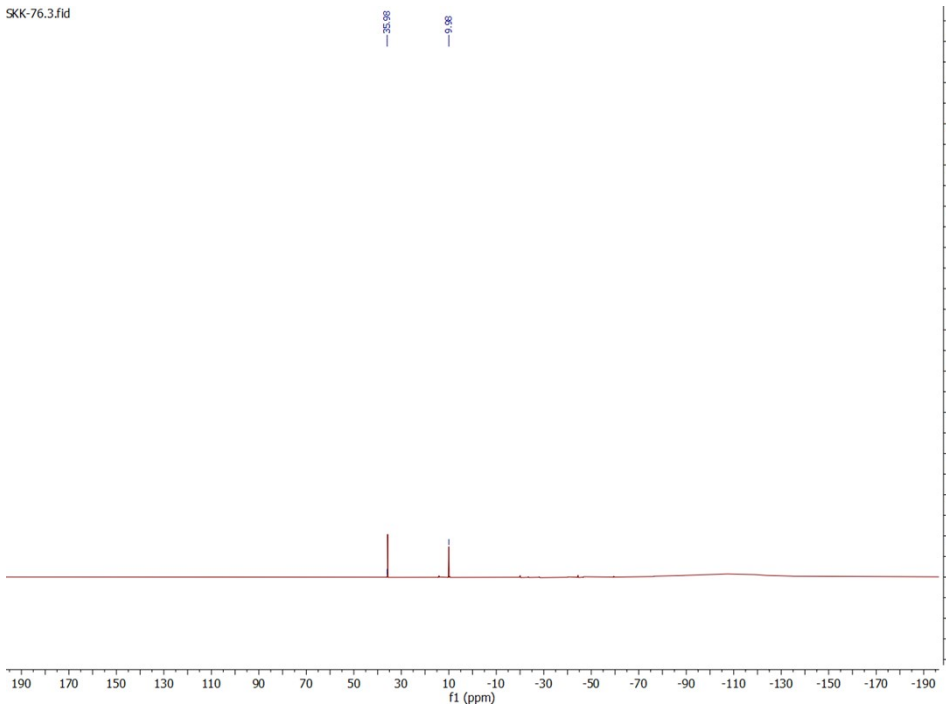

Figure S3. ^{29}Si NMR of compound **1**.

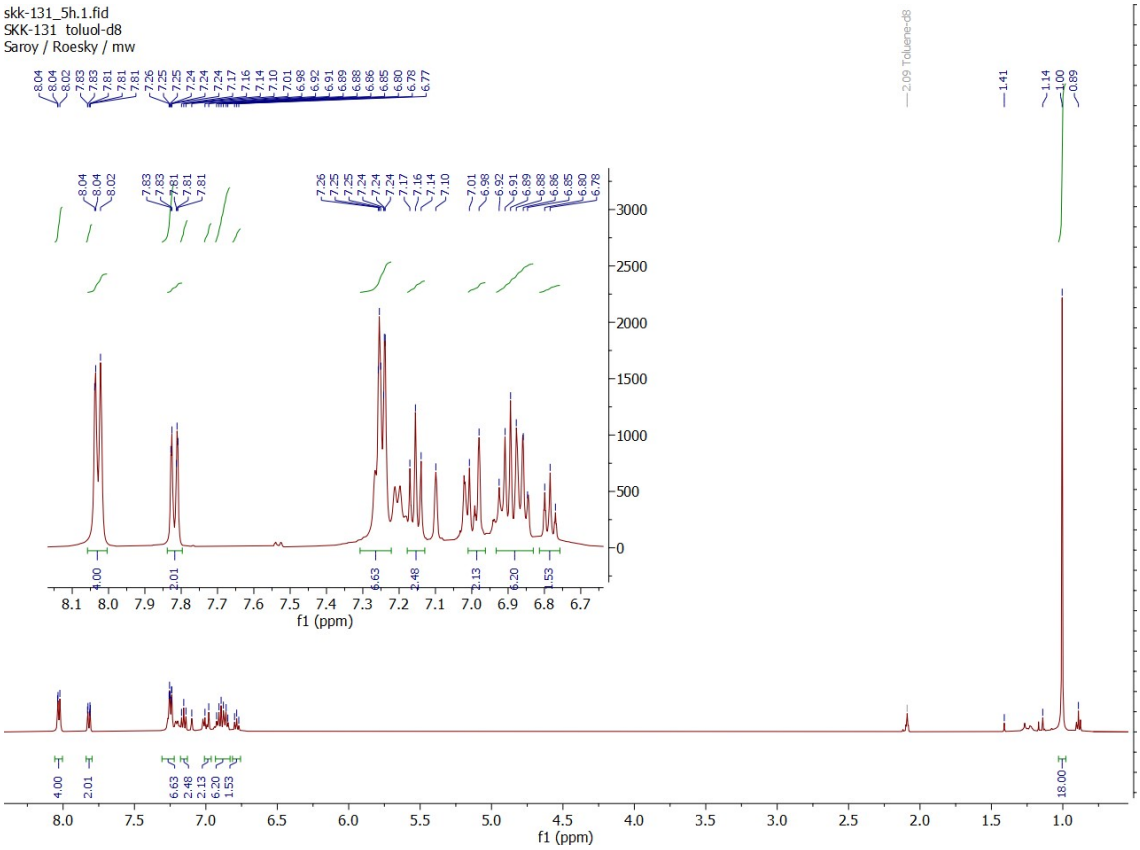

Figure S4. ^{1}H NMR of compound **2**.

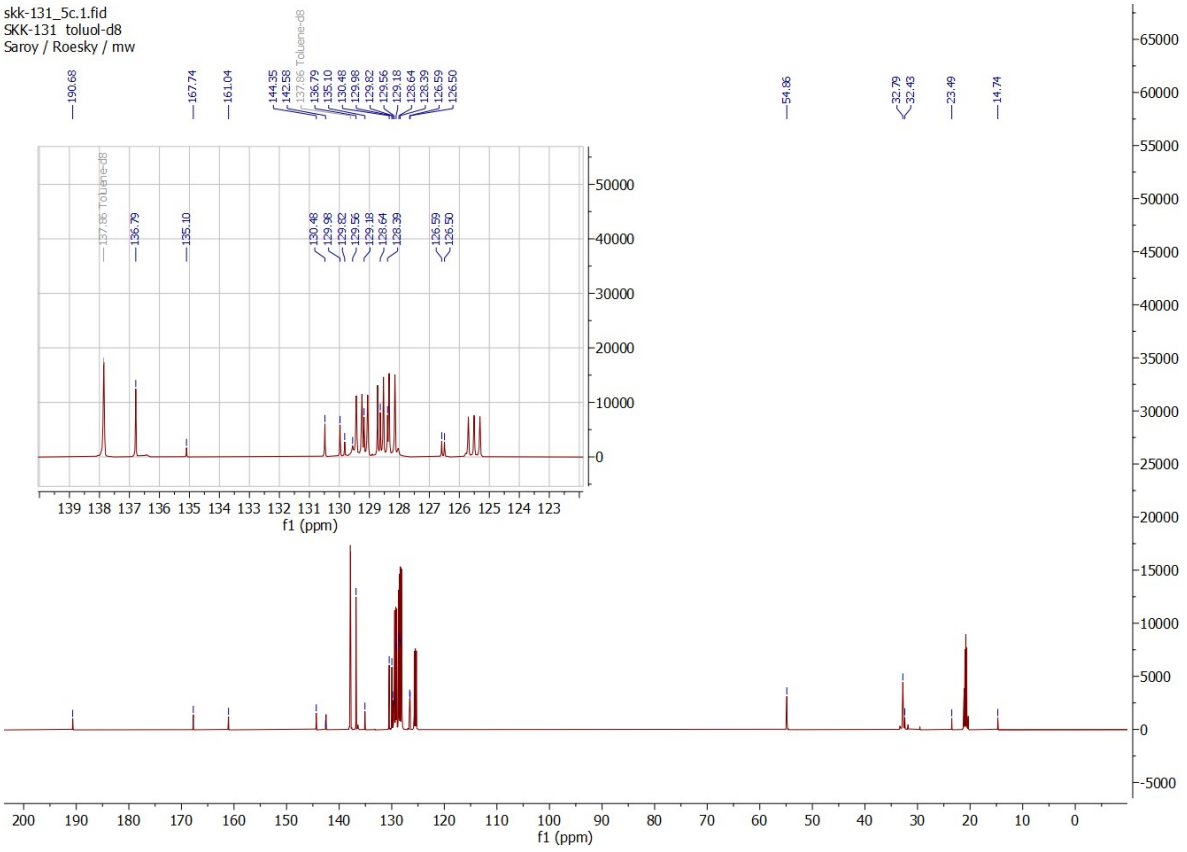

Figure S5. ^{13}C NMR of compound **2**.

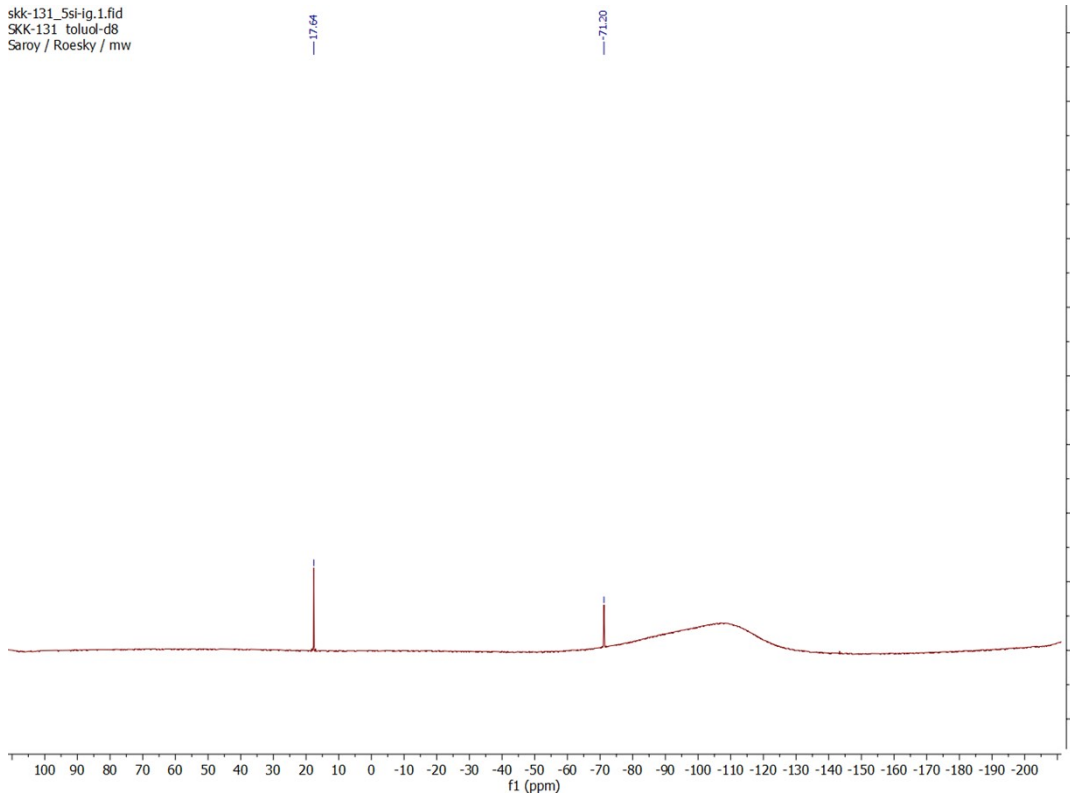

Figure S6. ^{29}Si NMR of compound **2**.

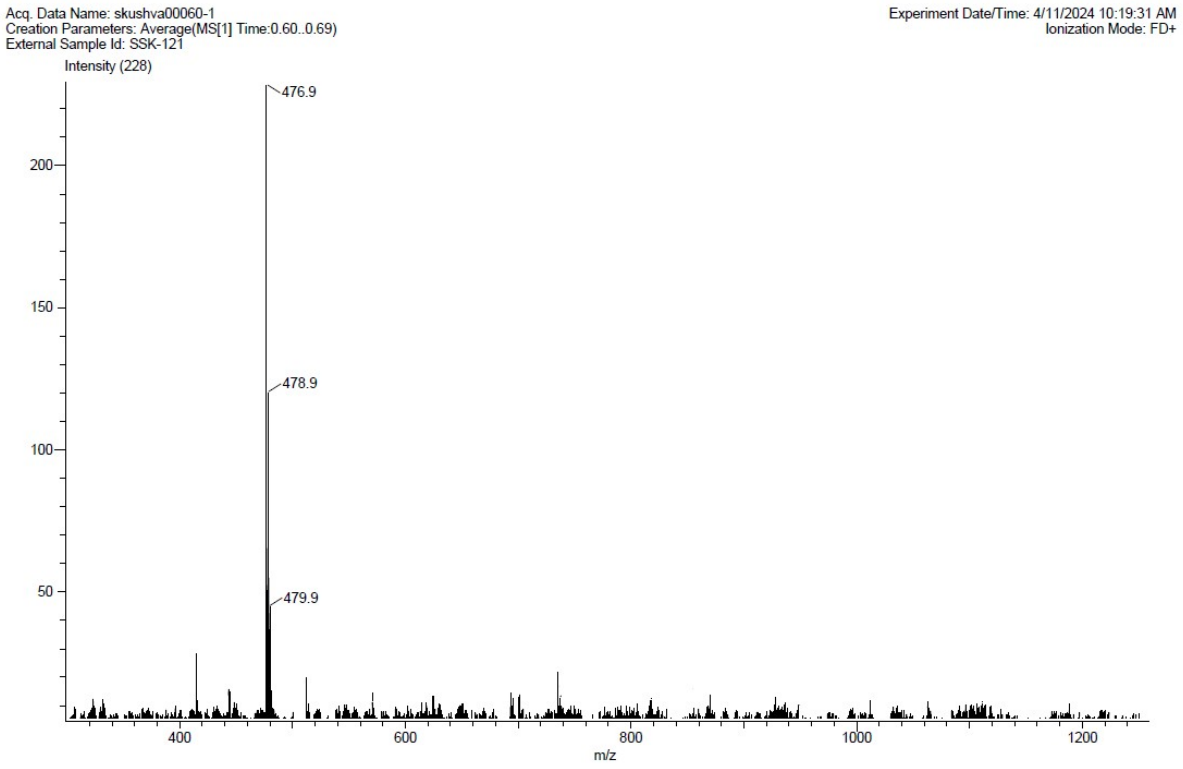

Figure S7. Mass spectrum of **1**.

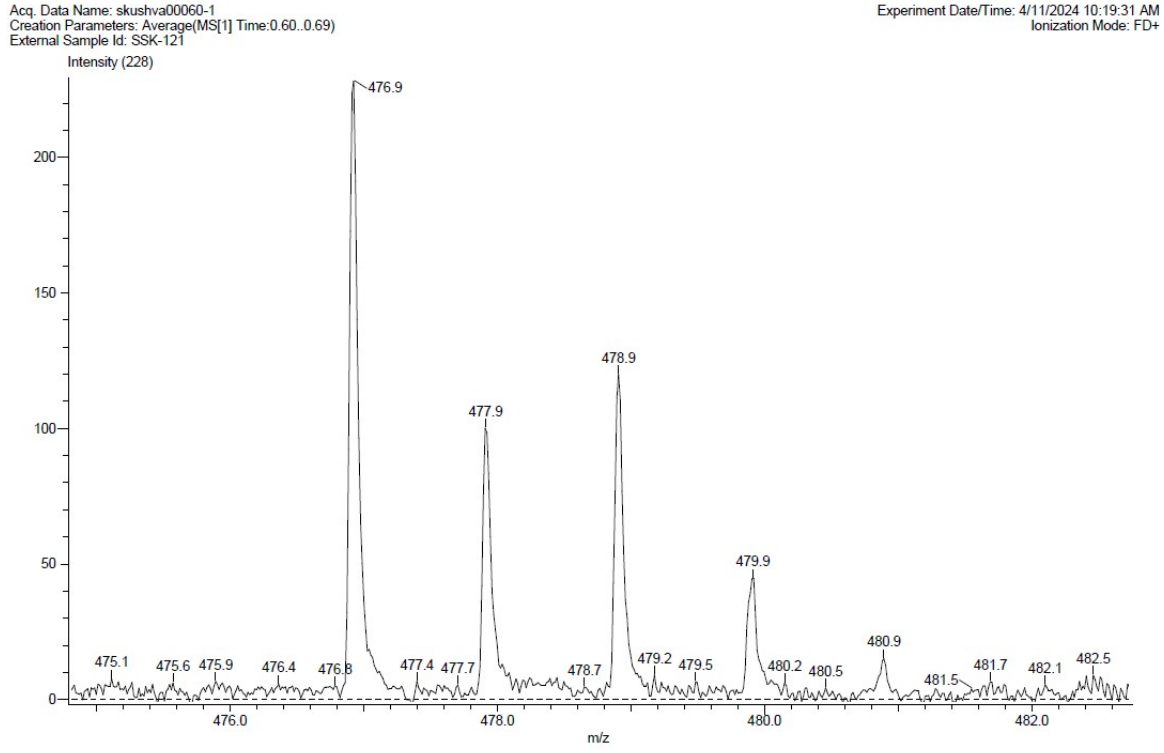

Figure S8. Mass spectrum of **1** (Expanded peak).

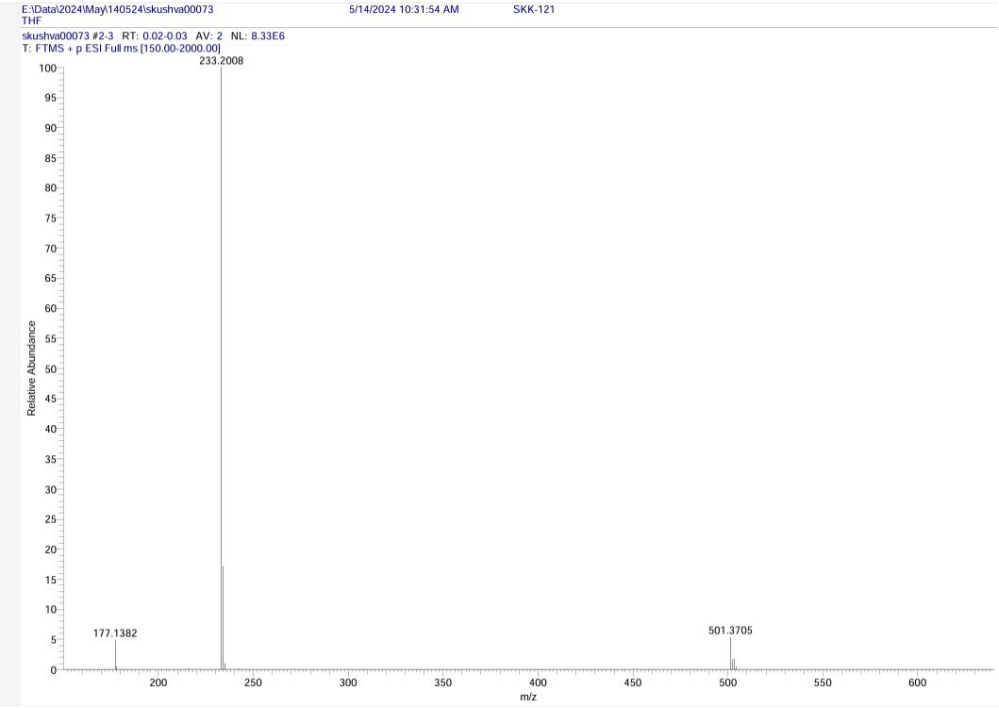

Figure S9. HRMS of compound **1**.

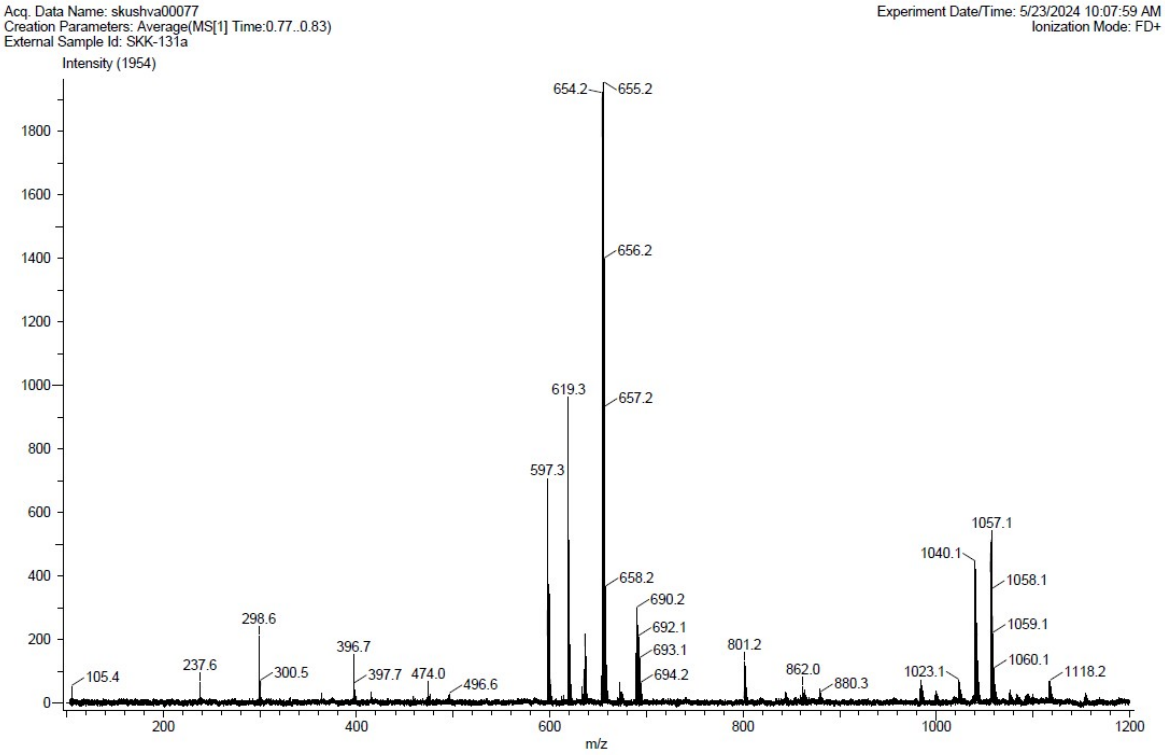

Figure S10. Mass spectrum of **2**.

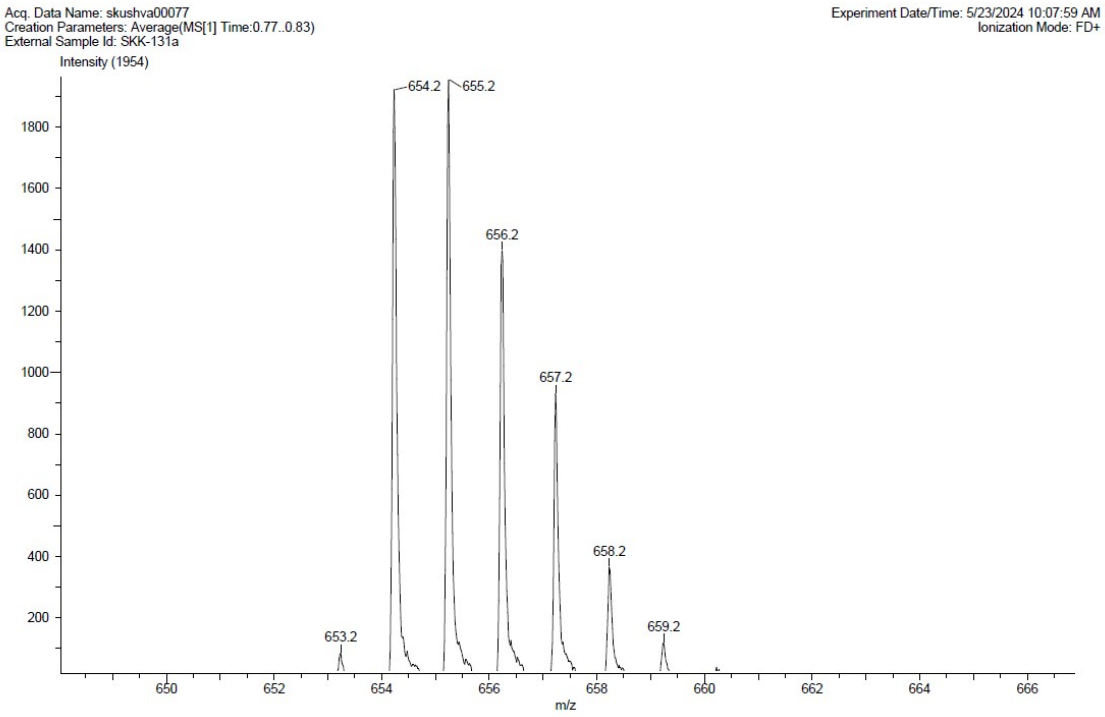

Figure S11. Mass spectrum of **2**(Expanded).

4. X-ray diffraction data

Table S1. Crystal data and structure refinement for compounds **1** and **2**.

Compound	**1**	**2**
CCDC	2292820	2326834
Empirical formula	$C_{27}H_{33}ClN_2Si_2$	$C_{41}H_{43}ClN_2Si_2$
Formula weight	477.18	655.40
Temperature (K)	100(2)	100(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	$Pna2_1$	$P\bar{1}$
a (Å)	25.543(4)	10.498(2)
b (Å)	9.225(2)	10.599(2)
c (Å)	22.485(3)	17.493(4)
α (deg)	90	72.73(2)
β (deg)	90	85.07(3)
γ (deg)	90	75.62(2)
V (Å^3)	5298.2(16)	1800.3(7)
Z	8	2
Density (Mg/m^3)	1.196	1.209
μ/mm^{-1}	0.252	0.204
Crystal size(mm)	0.34 x 0.175 x 0.13	0.183 x 0.152 x 0.124
Crystal color, shape	Yellow block	Colorless block
Θ range (deg)	1.594 to 28.393	1.219 to 27.219
Reflections collected	200799	80583
Independent reflections	13285	8015
R_{int}	0.0488	0.0409
Data/restraints/parameters	13285 / 4077 / 865	8015 / 0 / 421
R_1[a] ($I>2\sigma(I)$)	0.0268	0.0325
wR_2[b](all data)	0.0668	0.0849
Absolute structure parameter	0.104(11)	-
$\Delta\rho_{max}/\Delta\rho_{min}$(e Å^{-3})	0.218 and -0.169	0.343 and -0.271

[a]$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(F_o^2)^2]^{1/2}$

The datasets were collected on a Bruker D8 three circle diffractometer, equipped with a SMART APEX II CCD detector and an INCOATEC microfocus source (Mo K_α radiation) with

INCOATEC Quazar mirror optics. The data were integrated with SAINT[2] and a multi-scan absorption correction was applied using SADABS[3]. The structures were solved by SHELXT[4] and refined on F^2 using SHELXL[4] in the graphical user interface ShelXle.[5]

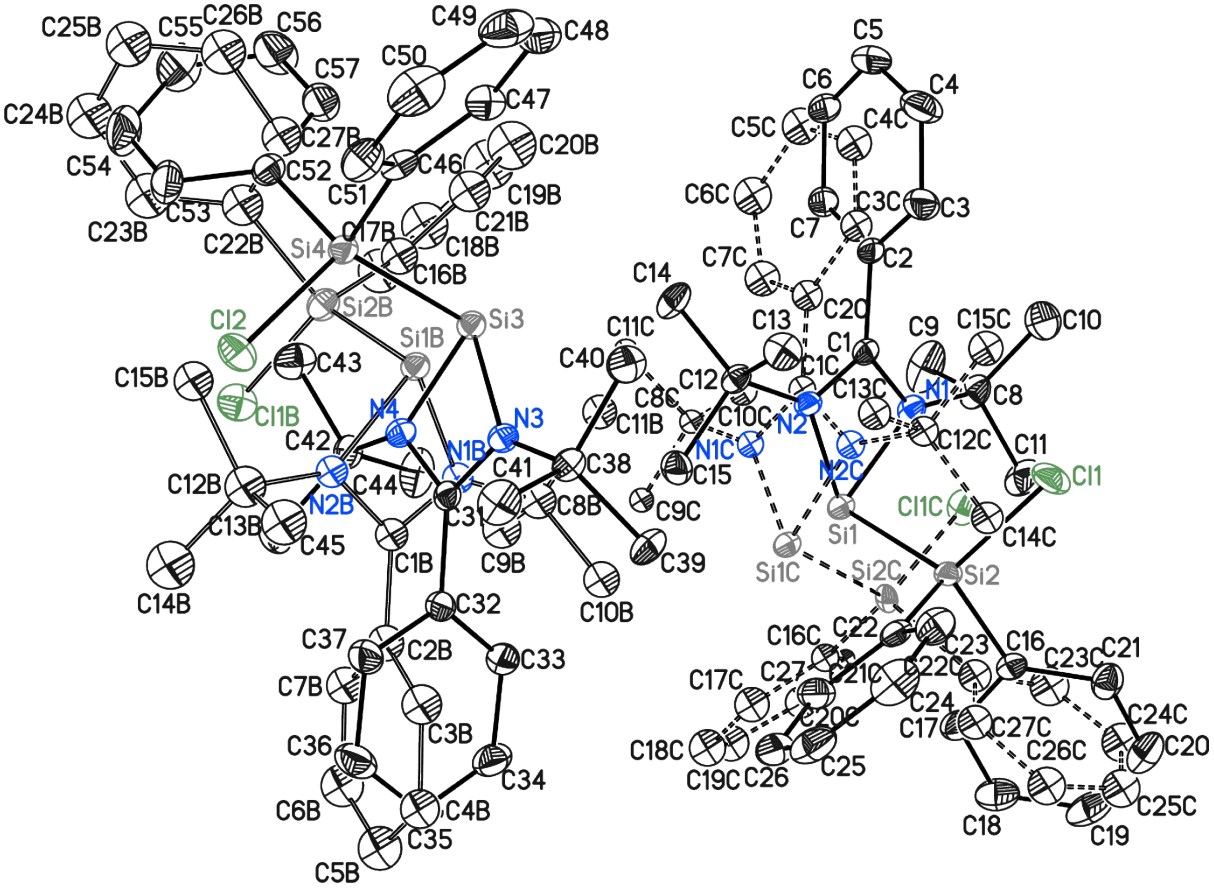

Figure S12. The asymmetric unit of **1** with thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted for clarity. The asymmetric unit contains two molecules, each disordered over two positions. They were refined with distance restraints and restraints for the anisotropic displacement parameters. The occupancy of the main position of one molecule refined to 0.9678(8) and the other molecule refined to 0.9650(8).

Table S2. Bond lengths [Å] and angles [°] for **1**.

Si(1)-N(2)	1.8563(18)	N(2)-C(1)	1.337(3)
Si(1)-N(1)	1.8690(18)	N(2)-C(12)	1.475(2)
Si(1)-C(1)	2.335(2)	C(12)-C(13)	1.528(3)
Si(1)-Si(2)	2.3884(8)	C(12)-C(15)	1.531(3)
N(1)-C(1)	1.338(3)	C(12)-C(14)	1.534(3)
N(1)-C(8)	1.478(3)	C(1)-C(2)	1.492(3)
C(8)-C(9)	1.527(3)	C(2)-C(3)	1.394(3)
C(8)-C(11)	1.527(3)	C(2)-C(7)	1.395(3)
C(8)-C(10)	1.530(4)	C(3)-C(4)	1.395(3)

C(4)-C(5)	1.390(4)	C(36)-C(37)	1.386(3)
C(5)-C(6)	1.389(4)	Cl(2)-Si(4)	2.0898(8)
C(6)-C(7)	1.394(3)	Si(4)-C(46)	1.876(2)
Cl(1)-Si(2)	2.0947(8)	Si(4)-C(52)	1.877(2)
Si(2)-C(16)	1.878(2)	C(46)-C(47)	1.399(3)
Si(2)-C(22)	1.888(2)	C(46)-C(51)	1.401(3)
C(16)-C(21)	1.395(3)	C(47)-C(48)	1.389(3)
C(16)-C(17)	1.410(3)	C(48)-C(49)	1.377(4)
C(17)-C(18)	1.389(3)	C(49)-C(50)	1.376(4)
C(18)-C(19)	1.381(4)	C(50)-C(51)	1.399(4)
C(19)-C(20)	1.387(4)	C(52)-C(53)	1.398(3)
C(20)-C(21)	1.389(3)	C(52)-C(57)	1.399(3)
C(22)-C(23)	1.397(3)	C(53)-C(54)	1.386(4)
C(22)-C(27)	1.402(3)	C(54)-C(55)	1.379(4)
C(23)-C(24)	1.394(3)	C(55)-C(56)	1.386(4)
C(24)-C(25)	1.375(4)	C(56)-C(57)	1.391(3)
C(25)-C(26)	1.383(4)	Si(1B)-N(1B)	1.826(19)
C(26)-C(27)	1.393(3)	Si(1B)-N(2B)	1.857(19)
Si(3)-N(3)	1.8548(17)	Si(1B)-C(1B)	2.310(19)
Si(3)-N(4)	1.8678(18)	Si(1B)-Si(2B)	2.377(16)
Si(3)-C(31)	2.332(2)	N(1B)-C(1B)	1.34(2)
Si(3)-Si(4)	2.3773(8)	N(1B)-C(8B)	1.474(19)
N(3)-C(31)	1.339(3)	C(8B)-C(9B)	1.52(2)
N(3)-C(38)	1.480(2)	C(8B)-C(10B)	1.53(2)
C(38)-C(41)	1.532(3)	C(8B)-C(11B)	1.53(2)
C(38)-C(39)	1.532(3)	N(2B)-C(1B)	1.34(2)
C(38)-C(40)	1.533(3)	N(2B)-C(12B)	1.475(19)
N(4)-C(31)	1.345(2)	C(12B)-C(14B)	1.53(2)
N(4)-C(42)	1.482(3)	C(12B)-C(15B)	1.53(2)
C(42)-C(43)	1.525(3)	C(12B)-C(13B)	1.54(2)
C(42)-C(44)	1.526(3)	C(1B)-C(2B)	1.483(19)
C(42)-C(45)	1.530(3)	C(2B)-C(3B)	1.39(2)
C(31)-C(32)	1.492(3)	C(2B)-C(7B)	1.39(2)
C(32)-C(33)	1.391(3)	C(3B)-C(4B)	1.39(2)
C(32)-C(37)	1.395(3)	C(4B)-C(5B)	1.39(2)
C(33)-C(34)	1.392(3)	C(5B)-C(6B)	1.39(2)
C(34)-C(35)	1.380(4)	C(6B)-C(7B)	1.40(2)
C(35)-C(36)	1.385(4)	Cl(1B)-Si(2B)	2.079(17)

Si(2B)-C(16B)	1.877(18)	C(16C)-C(21C)	1.393(19)
Si(2B)-C(22B)	1.878(18)	C(16C)-C(17C)	1.405(19)
C(16B)-C(17B)	1.399(19)	C(17C)-C(18C)	1.39(2)
C(16B)-C(21B)	1.403(19)	C(18C)-C(19C)	1.37(2)
C(17B)-C(18B)	1.40(2)	C(19C)-C(20C)	1.38(2)
C(18B)-C(19B)	1.37(2)	C(20C)-C(21C)	1.39(2)
C(19B)-C(20B)	1.37(2)	C(22C)-C(27C)	1.383(19)
C(20B)-C(21B)	1.40(2)	C(22C)-C(23C)	1.410(19)
C(22B)-C(23B)	1.391(19)	C(23C)-C(24C)	1.40(2)
C(22B)-C(27B)	1.405(19)	C(24C)-C(25C)	1.37(2)
C(23B)-C(24B)	1.40(2)	C(25C)-C(26C)	1.37(2)
C(24B)-C(25B)	1.37(2)	C(26C)-C(27C)	1.41(2)
C(25B)-C(26B)	1.37(2)		
C(26B)-C(27B)	1.40(2)	N(2)-Si(1)-N(1)	69.65(7)
Si(1C)-N(2C)	1.846(19)	N(2)-Si(1)-C(1)	34.90(7)
Si(1C)-N(1C)	1.861(19)	N(1)-Si(1)-C(1)	34.93(7)
Si(1C)-C(1C)	2.325(18)	N(2)-Si(1)-Si(2)	98.01(6)
Si(1C)-Si(2C)	2.367(16)	N(1)-Si(1)-Si(2)	96.94(6)
N(1C)-C(1C)	1.35(2)	C(1)-Si(1)-Si(2)	101.85(5)
N(1C)-C(8C)	1.472(19)	C(1)-N(1)-C(8)	130.56(17)
C(8C)-C(10C)	1.53(2)	C(1)-N(1)-Si(1)	91.94(13)
C(8C)-C(11C)	1.533(19)	C(8)-N(1)-Si(1)	136.06(14)
C(8C)-C(9C)	1.54(2)	N(1)-C(8)-C(9)	109.78(18)
N(2C)-C(1C)	1.35(2)	N(1)-C(8)-C(11)	105.72(18)
N(2C)-C(12C)	1.475(19)	C(9)-C(8)-C(11)	110.1(2)
C(12C)-C(15C)	1.530(19)	N(1)-C(8)-C(10)	111.59(19)
C(12C)-C(13C)	1.54(2)	C(9)-C(8)-C(10)	110.8(2)
C(12C)-C(14C)	1.54(2)	C(11)-C(8)-C(10)	108.7(2)
C(1C)-C(2C)	1.492(19)	C(1)-N(2)-C(12)	130.75(17)
C(2C)-C(3C)	1.39(2)	C(1)-N(2)-Si(1)	92.52(12)
C(2C)-C(7C)	1.40(2)	C(12)-N(2)-Si(1)	136.34(14)
C(3C)-C(4C)	1.39(2)	N(2)-C(12)-C(13)	109.74(17)
C(4C)-C(5C)	1.39(2)	N(2)-C(12)-C(15)	106.02(16)
C(5C)-C(6C)	1.39(2)	C(13)-C(12)-C(15)	108.74(17)
C(6C)-C(7C)	1.40(2)	N(2)-C(12)-C(14)	112.06(16)
Cl(1C)-Si(2C)	2.082(16)	C(13)-C(12)-C(14)	111.17(18)
Si(2C)-C(16C)	1.872(18)	C(15)-C(12)-C(14)	108.93(18)
Si(2C)-C(22C)	1.903(18)	N(2)-C(1)-N(1)	105.35(17)

N(2)-C(1)-C(2)	125.81(18)	N(3)-Si(3)-Si(4)	99.96(6)
N(1)-C(1)-C(2)	128.80(18)	N(4)-Si(3)-Si(4)	98.64(6)
N(2)-C(1)-Si(1)	52.58(10)	C(31)-Si(3)-Si(4)	104.26(5)
N(1)-C(1)-Si(1)	53.12(10)	C(31)-N(3)-C(38)	130.53(17)
C(2)-C(1)-Si(1)	172.94(15)	C(31)-N(3)-Si(3)	92.37(12)
C(3)-C(2)-C(7)	119.93(19)	C(38)-N(3)-Si(3)	137.08(14)
C(3)-C(2)-C(1)	119.53(18)	N(3)-C(38)-C(41)	109.39(17)
C(7)-C(2)-C(1)	120.44(19)	N(3)-C(38)-C(39)	111.76(16)
C(2)-C(3)-C(4)	120.1(2)	C(41)-C(38)-C(39)	111.01(18)
C(5)-C(4)-C(3)	120.0(2)	N(3)-C(38)-C(40)	106.87(16)
C(6)-C(5)-C(4)	119.8(2)	C(41)-C(38)-C(40)	108.67(18)
C(5)-C(6)-C(7)	120.7(2)	C(39)-C(38)-C(40)	109.00(18)
C(6)-C(7)-C(2)	119.5(2)	C(31)-N(4)-C(42)	130.36(17)
C(16)-Si(2)-C(22)	106.13(9)	C(31)-N(4)-Si(3)	91.58(13)
C(16)-Si(2)-Cl(1)	106.84(7)	C(42)-N(4)-Si(3)	134.66(14)
C(22)-Si(2)-Cl(1)	105.46(7)	N(4)-C(42)-C(43)	106.14(17)
C(16)-Si(2)-Si(1)	108.12(7)	N(4)-C(42)-C(44)	110.15(17)
C(22)-Si(2)-Si(1)	115.96(7)	C(43)-C(42)-C(44)	109.1(2)
Cl(1)-Si(2)-Si(1)	113.73(3)	N(4)-C(42)-C(45)	112.14(17)
C(21)-C(16)-C(17)	117.7(2)	C(43)-C(42)-C(45)	108.84(19)
C(21)-C(16)-Si(2)	125.33(17)	C(44)-C(42)-C(45)	110.38(19)
C(17)-C(16)-Si(2)	116.96(16)	N(3)-C(31)-N(4)	105.44(17)
C(18)-C(17)-C(16)	120.9(2)	N(3)-C(31)-C(32)	128.19(17)
C(19)-C(18)-C(17)	120.3(2)	N(4)-C(31)-C(32)	126.35(18)
C(18)-C(19)-C(20)	119.7(2)	N(3)-C(31)-Si(3)	52.63(10)
C(19)-C(20)-C(21)	120.2(2)	N(4)-C(31)-Si(3)	53.20(10)
C(20)-C(21)-C(16)	121.2(2)	C(32)-C(31)-Si(3)	173.41(14)
C(23)-C(22)-C(27)	117.3(2)	C(33)-C(32)-C(37)	119.7(2)
C(23)-C(22)-Si(2)	124.16(17)	C(33)-C(32)-C(31)	121.38(19)
C(27)-C(22)-Si(2)	118.41(16)	C(37)-C(32)-C(31)	118.86(19)
C(24)-C(23)-C(22)	121.1(2)	C(32)-C(33)-C(34)	119.9(2)
C(25)-C(24)-C(23)	120.3(2)	C(35)-C(34)-C(33)	120.1(2)
C(24)-C(25)-C(26)	120.2(2)	C(34)-C(35)-C(36)	120.1(2)
C(25)-C(26)-C(27)	119.5(3)	C(35)-C(36)-C(37)	120.3(2)
C(26)-C(27)-C(22)	121.6(2)	C(36)-C(37)-C(32)	119.8(2)
N(3)-Si(3)-N(4)	70.01(7)	C(46)-Si(4)-C(52)	109.83(9)
N(3)-Si(3)-C(31)	35.00(7)	C(46)-Si(4)-Cl(2)	106.61(7)
N(4)-Si(3)-C(31)	35.22(7)	C(52)-Si(4)-Cl(2)	106.78(8)

C(46)-Si(4)-Si(3)	111.16(7)	N(2B)-C(12B)-C(15B)	107(2)
C(52)-Si(4)-Si(3)	106.48(7)	C(14B)-C(12B)-C(15B)	112(3)
Cl(2)-Si(4)-Si(3)	115.82(3)	N(2B)-C(12B)-C(13B)	110(2)
C(47)-C(46)-C(51)	117.8(2)	C(14B)-C(12B)-C(13B)	109(2)
C(47)-C(46)-Si(4)	117.57(16)	C(15B)-C(12B)-C(13B)	108(2)
C(51)-C(46)-Si(4)	124.66(18)	N(2B)-C(1B)-N(1B)	105.2(15)
C(48)-C(47)-C(46)	121.5(2)	N(2B)-C(1B)-C(2B)	128.7(17)
C(49)-C(48)-C(47)	119.8(2)	N(1B)-C(1B)-C(2B)	126.1(17)
C(50)-C(49)-C(48)	120.3(2)	N(2B)-C(1B)-Si(1B)	53.5(10)
C(49)-C(50)-C(51)	120.4(2)	N(1B)-C(1B)-Si(1B)	52.2(9)
C(50)-C(51)-C(46)	120.4(2)	C(2B)-C(1B)-Si(1B)	174(2)
C(53)-C(52)-C(57)	117.4(2)	C(3B)-C(2B)-C(7B)	119(2)
C(53)-C(52)-Si(4)	124.59(19)	C(3B)-C(2B)-C(1B)	120(2)
C(57)-C(52)-Si(4)	117.67(17)	C(7B)-C(2B)-C(1B)	121(2)
C(54)-C(53)-C(52)	121.5(2)	C(2B)-C(3B)-C(4B)	121(2)
C(55)-C(54)-C(53)	119.9(2)	C(3B)-C(4B)-C(5B)	120(3)
C(54)-C(55)-C(56)	120.3(2)	C(4B)-C(5B)-C(6B)	120(3)
C(55)-C(56)-C(57)	119.5(2)	C(5B)-C(6B)-C(7B)	120(3)
C(56)-C(57)-C(52)	121.4(2)	C(2B)-C(7B)-C(6B)	120(2)
N(1B)-Si(1B)-N(2B)	70.7(9)	C(16B)-Si(2B)-C(22B)	108.9(18)
N(1B)-Si(1B)-C(1B)	35.5(7)	C(16B)-Si(2B)-Cl(1B)	106.4(12)
N(2B)-Si(1B)-C(1B)	35.4(7)	C(22B)-Si(2B)-Cl(1B)	107.2(12)
N(1B)-Si(1B)-Si(2B)	98.6(13)	C(16B)-Si(2B)-Si(1B)	113.0(14)
N(2B)-Si(1B)-Si(2B)	98.5(13)	C(22B)-Si(2B)-Si(1B)	106.6(13)
C(1B)-Si(1B)-Si(2B)	103.7(12)	Cl(1B)-Si(2B)-Si(1B)	114.5(8)
C(1B)-N(1B)-C(8B)	133(2)	C(17B)-C(16B)-C(21B)	116(2)
C(1B)-N(1B)-Si(1B)	92.3(12)	C(17B)-C(16B)-Si(2B)	123(2)
C(8B)-N(1B)-Si(1B)	134.7(18)	C(21B)-C(16B)-Si(2B)	120(2)
N(1B)-C(8B)-C(9B)	111(2)	C(16B)-C(17B)-C(18B)	122(3)
N(1B)-C(8B)-C(10B)	109(2)	C(19B)-C(18B)-C(17B)	120(3)
C(9B)-C(8B)-C(10B)	111(2)	C(18B)-C(19B)-C(20B)	119(3)
N(1B)-C(8B)-C(11B)	108(2)	C(19B)-C(20B)-C(21B)	121(3)
C(9B)-C(8B)-C(11B)	110(2)	C(20B)-C(21B)-C(16B)	121(2)
C(10B)-C(8B)-C(11B)	108(2)	C(23B)-C(22B)-C(27B)	121(2)
C(1B)-N(2B)-C(12B)	133(2)	C(23B)-C(22B)-Si(2B)	122(2)
C(1B)-N(2B)-Si(1B)	91.1(12)	C(27B)-C(22B)-Si(2B)	117(2)
C(12B)-N(2B)-Si(1B)	134.7(19)	C(22B)-C(23B)-C(24B)	119(2)
N(2B)-C(12B)-C(14B)	111(2)	C(25B)-C(24B)-C(23B)	119(3)

C(26B)-C(25B)-C(24B)	123(3)
C(25B)-C(26B)-C(27B)	119(3)
C(26B)-C(27B)-C(22B)	119(2)
N(2C)-Si(1C)-N(1C)	70.8(9)
N(2C)-Si(1C)-C(1C)	35.4(7)
N(1C)-Si(1C)-C(1C)	35.6(7)
N(2C)-Si(1C)-Si(2C)	101.0(13)
N(1C)-Si(1C)-Si(2C)	98.7(13)
C(1C)-Si(1C)-Si(2C)	104.5(12)
C(1C)-N(1C)-C(8C)	132(2)
C(1C)-N(1C)-Si(1C)	91.3(12)
C(8C)-N(1C)-Si(1C)	136.9(18)
N(1C)-C(8C)-C(10C)	110(2)
N(1C)-C(8C)-C(11C)	111(2)
C(10C)-C(8C)-C(11C)	109(2)
N(1C)-C(8C)-C(9C)	112(2)
C(10C)-C(8C)-C(9C)	106(2)
C(11C)-C(8C)-C(9C)	109(2)
C(1C)-N(2C)-C(12C)	133(2)
C(1C)-N(2C)-Si(1C)	92.1(12)
C(12C)-N(2C)-Si(1C)	134.8(18)
N(2C)-C(12C)-C(15C)	112(2)
N(2C)-C(12C)-C(13C)	108(2)
C(15C)-C(12C)-C(13C)	110(2)
N(2C)-C(12C)-C(14C)	112(2)
C(15C)-C(12C)-C(14C)	107(2)
C(13C)-C(12C)-C(14C)	108(2)
N(2C)-C(1C)-N(1C)	105.4(15)
N(2C)-C(1C)-C(2C)	125.6(17)
N(1C)-C(1C)-C(2C)	129.0(17)
N(2C)-C(1C)-Si(1C)	52.5(9)
N(1C)-C(1C)-Si(1C)	53.1(9)
C(2C)-C(1C)-Si(1C)	177(2)
C(3C)-C(2C)-C(7C)	117(2)
C(3C)-C(2C)-C(1C)	123(2)
C(7C)-C(2C)-C(1C)	120(2)
C(2C)-C(3C)-C(4C)	122(2)
C(3C)-C(4C)-C(5C)	121(3)
C(6C)-C(5C)-C(4C)	118(3)
C(5C)-C(6C)-C(7C)	120(3)
C(2C)-C(7C)-C(6C)	122(2)
C(16C)-Si(2C)-C(22C)	108.4(10)
C(16C)-Si(2C)-Cl(1C)	108.3(11)
C(22C)-Si(2C)-Cl(1C)	101.0(10)
C(16C)-Si(2C)-Si(1C)	109.9(10)
C(22C)-Si(2C)-Si(1C)	112.0(11)
Cl(1C)-Si(2C)-Si(1C)	116.7(8)
C(21C)-C(16C)-C(17C)	116(2)
C(21C)-C(16C)-Si(2C)	126(2)
C(17C)-C(16C)-Si(2C)	118(2)
C(18C)-C(17C)-C(16C)	121(2)
C(19C)-C(18C)-C(17C)	121(3)
C(18C)-C(19C)-C(20C)	119(3)
C(19C)-C(20C)-C(21C)	119(3)
C(16C)-C(21C)-C(20C)	123(2)
C(27C)-C(22C)-C(23C)	117(2)
C(27C)-C(22C)-Si(2C)	127(2)
C(23C)-C(22C)-Si(2C)	115.3(19)
C(24C)-C(23C)-C(22C)	122(2)
C(25C)-C(24C)-C(23C)	118(3)
C(26C)-C(25C)-C(24C)	123(3)
C(25C)-C(26C)-C(27C)	118(3)
C(22C)-C(27C)-C(26C)	121(2)

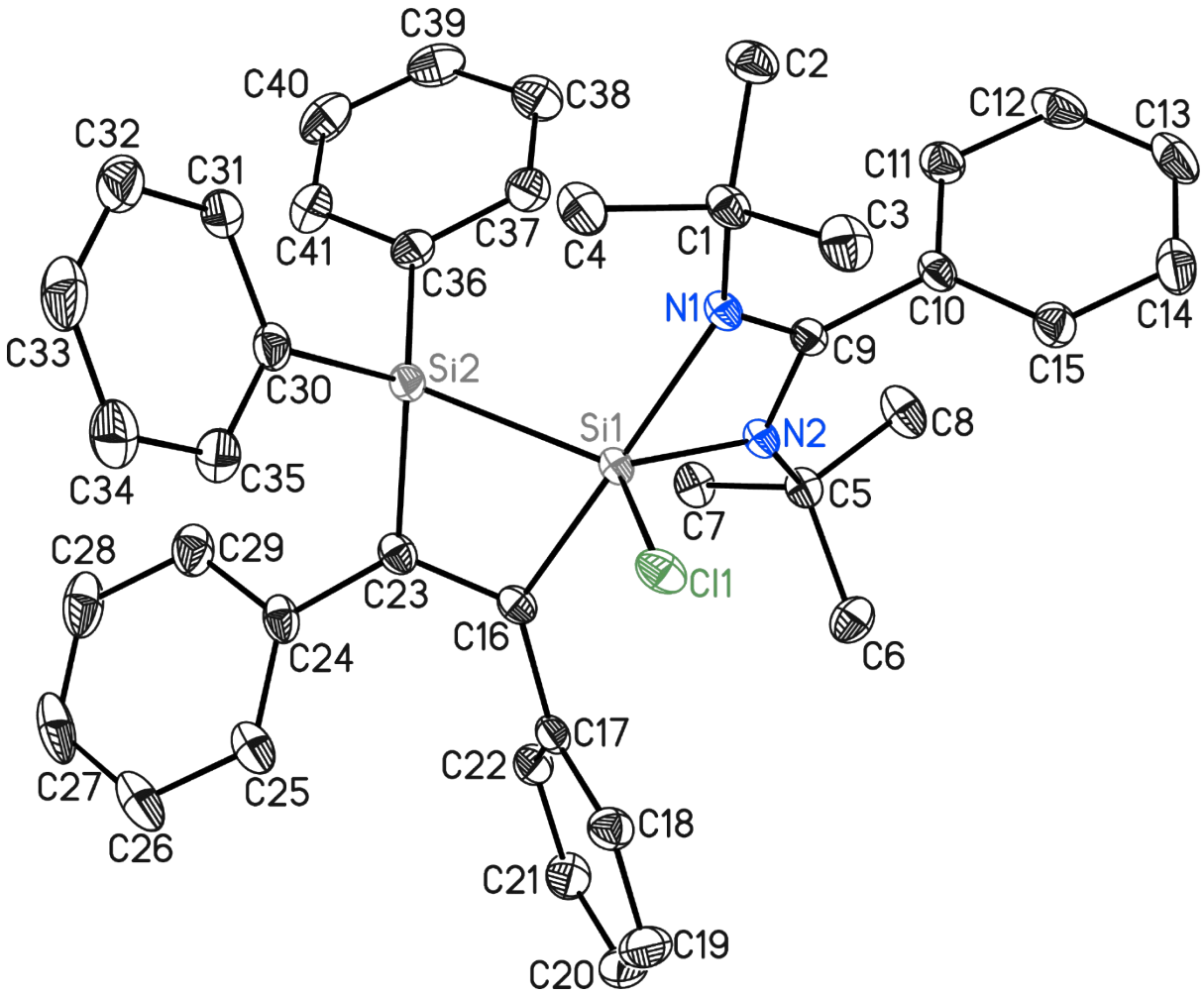

Figure S13. The asymmetric unit of **2** with thermal ellipsoids at 50% probability level. The hydrogen atoms are omitted for clarity.

Table S3. Bond lengths [Å] and angles [°] for **2**.

Cl(1)-Si(1)	2.1218(6)	N(2)-C(5)	1.4971(16)
Si(1)-N(2)	1.8339(12)	C(1)-C(3)	1.5326(19)
Si(1)-C(16)	1.9622(14)	C(1)-C(2)	1.5332(19)
Si(1)-N(1)	2.0022(13)	C(1)-C(4)	1.5340(19)
Si(1)-Si(2)	2.3378(7)	C(7)-C(5)	1.5350(18)
Si(1)-C(9)	2.3799(14)	C(8)-C(5)	1.5314(18)
Si(2)-C(30)	1.8785(15)	C(9)-C(10)	1.4900(17)
Si(2)-C(23)	1.8835(15)	C(10)-C(15)	1.3915(19)
Si(2)-C(36)	1.8842(15)	C(10)-C(11)	1.3932(19)
N(1)-C(9)	1.3033(17)	C(11)-C(12)	1.3849(19)
N(1)-C(1)	1.4852(16)	C(12)-C(13)	1.381(2)
N(2)-C(9)	1.3701(16)	C(13)-C(14)	1.388(2)

C(14)-C(15)	1.396(2)
C(16)-C(23)	1.3669(19)
C(16)-C(17)	1.4885(18)
C(17)-C(18)	1.3992(19)
C(17)-C(22)	1.4037(19)
C(18)-C(19)	1.391(2)
C(19)-C(20)	1.386(2)
C(20)-C(21)	1.387(2)
C(21)-C(22)	1.389(2)
C(23)-C(24)	1.4885(18)
C(24)-C(29)	1.398(2)
C(24)-C(25)	1.404(2)
C(25)-C(26)	1.392(2)
C(26)-C(27)	1.385(3)
C(27)-C(28)	1.380(3)
C(28)-C(29)	1.397(2)
C(30)-C(31)	1.400(2)
C(30)-C(35)	1.403(2)
C(31)-C(32)	1.392(2)
C(32)-C(33)	1.384(2)
C(33)-C(34)	1.387(2)
C(34)-C(35)	1.389(2)
C(36)-C(41)	1.402(2)
C(36)-C(37)	1.403(2)
C(37)-C(38)	1.391(2)
C(38)-C(39)	1.383(2)
C(39)-C(40)	1.383(2)
C(40)-C(41)	1.391(2)
C(5)-C(6)	1.5277(19)

N(2)-Si(1)-C(16)	108.63(6)
N(2)-Si(1)-N(1)	68.16(5)
C(16)-Si(1)-N(1)	175.10(5)
N(2)-Si(1)-Cl(1)	111.64(4)
C(16)-Si(1)-Cl(1)	97.10(4)
N(1)-Si(1)-Cl(1)	87.61(4)
N(2)-Si(1)-Si(2)	127.95(4)
C(16)-Si(1)-Si(2)	73.79(5)
N(1)-Si(1)-Si(2)	105.04(4)
Cl(1)-Si(1)-Si(2)	119.73(3)
N(2)-Si(1)-C(9)	35.00(5)
C(16)-Si(1)-C(9)	143.62(5)
N(1)-Si(1)-C(9)	33.20(5)
Cl(1)-Si(1)-C(9)	99.85(4)
Si(2)-Si(1)-C(9)	122.72(4)
C(30)-Si(2)-C(23)	110.41(6)
C(30)-Si(2)-C(36)	109.38(6)
C(23)-Si(2)-C(36)	120.78(6)
C(30)-Si(2)-Si(1)	123.68(5)
C(23)-Si(2)-Si(1)	76.96(5)
C(36)-Si(2)-Si(1)	113.05(5)
C(9)-N(1)-C(1)	130.13(11)
C(9)-N(1)-Si(1)	89.52(8)
C(1)-N(1)-Si(1)	139.79(8)
C(9)-N(2)-C(5)	130.01(10)
C(9)-N(2)-Si(1)	94.84(8)
C(5)-N(2)-Si(1)	134.61(9)
N(1)-C(1)-C(3)	110.66(11)
N(1)-C(1)-C(2)	111.18(11)
C(3)-C(1)-C(2)	110.59(11)
N(1)-C(1)-C(4)	106.41(10)
C(3)-C(1)-C(4)	109.57(11)
C(2)-C(1)-C(4)	108.31(12)
N(1)-C(9)-N(2)	107.35(11)
N(1)-C(9)-C(10)	127.07(12)
N(2)-C(9)-C(10)	125.51(12)
N(1)-C(9)-Si(1)	57.27(7)
N(2)-C(9)-Si(1)	50.16(6)
C(10)-C(9)-Si(1)	173.36(10)
C(15)-C(10)-C(11)	119.92(12)
C(15)-C(10)-C(9)	119.19(12)
C(11)-C(10)-C(9)	120.88(12)
C(12)-C(11)-C(10)	119.96(14)
C(13)-C(12)-C(11)	120.20(14)
C(12)-C(13)-C(14)	120.40(13)
C(13)-C(14)-C(15)	119.71(14)

C(10)-C(15)-C(14)	119.78(14)	C(40)-C(41)-C(36)	121.25(14)
C(23)-C(16)-C(17)	123.69(11)	N(2)-C(5)-C(6)	108.48(10)
C(23)-C(16)-Si(1)	104.11(9)	N(2)-C(5)-C(8)	114.64(11)
C(17)-C(16)-Si(1)	132.20(9)	C(6)-C(5)-C(8)	108.34(12)
C(18)-C(17)-C(22)	117.80(12)	N(2)-C(5)-C(7)	107.69(10)
C(18)-C(17)-C(16)	122.04(12)	C(6)-C(5)-C(7)	110.97(11)
C(22)-C(17)-C(16)	120.14(12)	C(8)-C(5)-C(7)	106.74(11)
C(19)-C(18)-C(17)	120.90(13)		
C(20)-C(19)-C(18)	120.39(14)		
C(19)-C(20)-C(21)	119.61(14)		
C(20)-C(21)-C(22)	120.13(14)		
C(21)-C(22)-C(17)	121.16(13)		
C(16)-C(23)-C(24)	128.26(12)		
C(16)-C(23)-Si(2)	105.06(9)		
C(24)-C(23)-Si(2)	126.19(10)		
C(29)-C(24)-C(25)	117.79(13)		
C(29)-C(24)-C(23)	119.49(13)		
C(25)-C(24)-C(23)	122.53(13)		
C(26)-C(25)-C(24)	120.82(15)		
C(27)-C(26)-C(25)	120.46(16)		
C(28)-C(27)-C(26)	119.63(14)		
C(27)-C(28)-C(29)	120.28(16)		
C(28)-C(29)-C(24)	121.03(15)		
C(31)-C(30)-C(35)	117.47(13)		
C(31)-C(30)-Si(2)	123.19(11)		
C(35)-C(30)-Si(2)	119.18(11)		
C(32)-C(31)-C(30)	121.09(14)		
C(33)-C(32)-C(31)	120.27(15)		
C(32)-C(33)-C(34)	119.79(15)		
C(33)-C(34)-C(35)	119.87(15)		
C(34)-C(35)-C(30)	121.48(14)		
C(41)-C(36)-C(37)	117.09(13)		
C(41)-C(36)-Si(2)	124.97(11)		
C(37)-C(36)-Si(2)	117.94(10)		
C(38)-C(37)-C(36)	121.76(13)		
C(39)-C(38)-C(37)	119.67(14)		
C(40)-C(39)-C(38)	119.99(14)		
C(39)-C(40)-C(41)	120.23(14)		

5. Computational Methods

Geometry optimizations and vibrational frequencies calculations of LSi-Si(Cl)Ph_2 (**1**) and **2** complexes in singlet and triplet electronic states have been carried out at the BP86-D3(BJ)/Def2TZVPP level in the gas phase.[6] All the calculations were carried out using gaussian 16 program package.[7] The absence of imaginary frequencies assures the minima on the potential energy surface. We have performed NBO [8] calculation using NBO 6.0[9] program to estimate natural bond orbitals, partial charges and Wiberg bond indices (WBI).[10]The nature of Si_L-Si bonds in all three complexes was analyzed by energy decomposition analysis (EDA)[11] coupled with natural orbital for chemical valence (NOCV)[12] using ADF 2018.105 program package.[13] EDA-NOCV calculations were carried out at the BP86-D3(BJ)/TZ2P[14] level using the geometries optimized at BP86-D3(BJ)/def2-TZVPP level. The EDA-NOCV method involves the decomposition of the intrinsic interaction energy (ΔE_{int}) between two fragments into four energy components as follows:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} + \Delta E_{disp} \qquad (1)$$

where the electrostatic ΔE_{elstat} term is originated from the quasi-classical electrostatic interaction between the unperturbed charge distributions of the prepared fragments, the Pauli repulsion ΔE_{Pauli} (repulsion energy due to the interactions of same spins between the fragments) is the energy change associated with the transformation from the superposition of the unperturbed electron densities of the isolated fragments to the wavefunction, which properly obeys the Pauli principle through explicit anti-symmetrisation and renormalization of the production of the wavefunction. Dispersion interaction, ΔE_{disp} (equivalent to attractive forces due to instantaneous fluctuation of electron clouds in the fragment before and after the bond formation) is also obtained as we used D3(BJ). The orbital term ΔE_{orb} comes from (constructive interference during spatial mixing of orbitals of the fragments) the mixing of orbitals, charge transfer and polarization between the isolated fragments. This can be further divided into contributions from each irreducible representation of the point group of an interacting system as follows:

$$\Delta E_{orb} = \sum_{r} \Delta E_{r} \qquad (2)$$

The combined EDA-NOCV method is able to partition the total orbital interactions into pairwise contributions of the orbital interactions which are important in providing a complete picture of the bonding. The charge deformation $\Delta\rho_k(r)$, which comes from the mixing of the

orbital pairs $\psi_k(r)$ and $\psi_{-k}(r)$ of the interacting fragments, gives the magnitude and the shape of the charge flow due to the orbital interactions (Equation 3), and the associated orbital energy ΔE_{orb} presents the amount of orbital energy coming from such interaction (Equation 4).

$$\Delta\rho_{orb}(r) = \sum_{k} \Delta\rho_k(r) = \sum_{k=1}^{N/2} \nu_k [-\psi_{-k}^2(r) + \psi_k^2(r)] \qquad (3)$$

$$\Delta E_{Orb} = \sum_{k} \Delta E_{Orb}^{k} = \sum_{k} \nu_k \left[-F_{-k,-k}^{TS} + F_{k,k}^{TS} \right] \qquad (4)$$

Readers are further referred to the recent review articles to know more about the EDA-NOCV method and its application. [15] Also, a very recent report related to equation (1) has been critically discussed by different researchers. [16]

Optimized coordinates

Compound **1**

Si	14.487402000	6.883366000	13.376831000	C	10.079828000	6.125516000	8.425732000
N	12.804119000	7.411139000	12.673371000	H	9.367242000	6.026873000	7.605884000
C	11.836647000	8.478770000	12.975783000	C	11.089335000	7.090634000	8.362826000
C	12.063526000	9.672710000	12.030045000	H	11.169662000	7.743858000	7.493061000
H	11.839833000	9.396727000	10.991287000	C	12.000755000	7.218722000	9.412848000
H	13.107507000	10.011308000	12.087060000	H	12.797201000	7.961663000	9.363396000
H	11.408657000	10.511230000	12.308110000	Cl	11.637395000	4.543409000	14.223884000
C	10.387635000	7.975704000	12.873200000	Si	13.478939000	5.334587000	14.911219000
H	10.104443000	7.753671000	11.837381000	C	13.122536000	6.149691000	16.568874000
H	9.705112000	8.749318000	13.252859000	C	14.054383000	7.080707000	17.067461000
H	10.256934000	7.066980000	13.475370000	H	14.945094000	7.323978000	16.481906000
C	12.118577000	8.908466000	14.422792000	C	13.847999000	7.720526000	18.291772000
H	13.175287000	9.192609000	14.545289000	H	14.581120000	8.439784000	18.660862000
H	11.897247000	8.095136000	15.125896000	C	12.696406000	7.447851000	19.036162000
H	11.500435000	9.775788000	14.690294000	H	12.528765000	7.951581000	19.989424000
N	13.987312000	5.813200000	11.885157000	C	11.757251000	6.532095000	18.551333000
C	14.623440000	4.745630000	11.092593000	H	10.855366000	6.318797000	19.127923000
C	13.750168000	3.479398000	11.097929000	C	11.970250000	5.887911000	17.330044000
H	12.806206000	3.645273000	10.564123000	H	11.229787000	5.178229000	16.956795000
H	13.522162000	3.178890000	12.128328000	C	14.617301000	3.856799000	15.158721000
H	14.282645000	2.654448000	10.603242000	C	14.270271000	2.536758000	14.825893000
C	14.885649000	5.214932000	9.650679000	H	13.258854000	2.319841000	14.477819000
H	15.455864000	4.448716000	9.106118000	C	15.202341000	1.500866000	14.933666000
H	15.470446000	6.145643000	9.652332000	H	14.914278000	0.481924000	14.668887000
H	13.949061000	5.390163000	9.107063000	C	16.500265000	1.767168000	15.378889000
C	15.962287000	4.438783000	11.779207000	H	17.229192000	0.959315000	15.459065000
H	16.496957000	3.654632000	11.226805000	C	16.860474000	3.074270000	15.723147000
H	15.804876000	4.083261000	12.806360000	H	17.871206000	3.289040000	16.074164000
H	16.597935000	5.335403000	11.811983000	C	15.927852000	4.107077000	15.611756000
C	12.861479000	6.522819000	11.661252000	H	16.228616000	5.124811000	15.873125000
C	11.908245000	6.381224000	10.534241000				
C	10.895182000	5.412616000	10.591990000				
H	10.821536000	4.777769000	11.474843000				
C	9.985302000	5.287343000	9.540917000				
H	9.197104000	4.535443000	9.595445000				

Compound **2**

Cl	8.223945000	10.835352000	13.760381000
Si	7.031568000	9.340427000	12.843446000
Si	7.468024000	7.056354000	13.097125000
N	5.592164000	9.690077000	14.176718000
N	5.492586000	9.966616000	12.054137000
C	5.386085000	9.621062000	15.622717000
C	5.361017000	9.095568000	9.790728000
H	5.223850000	9.356503000	8.740023000
H	4.648475000	8.309172000	10.047376000
H	6.362694000	8.694419000	9.916329000
C	3.685276000	10.755401000	10.479917000
H	3.552750000	10.976801000	9.419622000
H	3.436091000	11.654833000	11.040285000
H	2.977360000	9.972187000	10.746163000
C	4.800388000	10.055010000	13.211375000
C	3.386477000	10.464671000	13.367502000
C	2.366583000	9.528896000	13.240430000
H	2.609288000	8.498954000	13.008911000
C	1.048635000	9.909795000	13.425276000
H	0.258305000	9.175586000	13.329101000
C	0.741620000	11.227190000	13.736319000
H	-0.289798000	11.524058000	13.880903000
C	4.054502000	8.981403000	16.010806000
H	4.057717000	8.788524000	17.085422000
H	3.920996000	8.027458000	15.496681000
H	3.202023000	9.621034000	15.790514000
C	1.757949000	12.161999000	13.863822000
H	1.523455000	13.191202000	14.105906000
C	3.078719000	11.782093000	13.681956000
H	3.875552000	12.509898000	13.775097000
C	8.273815000	8.861954000	11.413248000
C	8.926312000	9.634948000	10.340352000
C	9.632967000	10.809241000	10.608869000
H	9.715054000	11.152016000	11.631183000
C	10.227178000	11.529928000	9.584612000
H	10.777148000	12.434120000	9.817979000
C	10.116558000	11.104627000	8.269272000
H	10.574368000	11.674127000	7.469499000
C	9.416031000	9.940067000	7.987734000
H	9.326729000	9.592748000	6.965120000
C	8.836421000	9.210984000	9.011136000
H	8.306838000	8.293983000	8.784421000
C	8.477256000	7.527192000	11.589091000
C	9.399958000	6.654910000	10.849002000
C	10.715003000	7.036232000	10.574428000
H	11.058989000	8.013553000	10.888912000
C	11.575772000	6.179660000	9.909851000
H	12.594428000	6.491572000	9.711629000
C	11.139252000	4.928653000	9.495755000
H	11.813262000	4.261636000	8.971985000
C	9.836663000	4.535687000	9.765739000
H	9.487208000	3.559139000	9.451779000
C	8.980402000	5.385528000	10.447228000
H	7.965646000	5.072062000	10.664865000
C	8.585523000	6.439499000	14.467544000
C	8.147149000	5.591680000	15.486487000
H	7.126330000	5.224861000	15.479944000
C	8.995990000	5.207695000	16.513640000
H	8.636014000	4.548272000	17.294855000
C	10.304799000	5.666813000	16.539969000
H	10.970279000	5.366442000	17.340682000
C	10.758957000	6.511037000	15.536719000
H	11.780678000	6.871770000	15.551599000
C	9.906232000	6.892895000	14.513103000
H	10.271124000	7.554830000	13.735249000
C	6.059974000	5.840075000	12.840733000
C	4.794483000	6.314606000	12.490528000
H	4.640731000	7.383792000	12.397589000
C	3.740278000	5.447353000	12.247176000
H	2.766052000	5.837148000	11.973751000
C	3.935179000	4.077637000	12.348889000
H	3.114896000	3.395534000	12.159322000
C	5.185776000	3.583795000	12.692853000
H	5.343353000	2.514355000	12.770418000
C	6.234973000	4.457169000	12.938110000
H	7.206577000	4.056735000	13.206781000
C	5.487473000	11.023960000	16.220665000
H	5.428755000	10.969374000	17.309690000
H	4.670967000	11.656637000	15.870967000
H	6.434634000	11.486606000	15.944106000
C	6.506186000	8.752593000	16.184174000
H	6.460222000	8.753979000	17.274165000
H	7.486735000	9.118464000	15.880935000
H	6.405417000	7.721442000	15.846404000
C	5.134070000	10.323043000	10.669733000
C	6.026020000	11.484965000	10.238255000
H	5.830255000	11.744082000	9.196069000
H	7.081464000	11.240780000	10.329509000
H	5.822230000	12.361605000	10.85643800

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