Supplementary Information

Synthesis, Structures and Photophysical Properties of Hexacoordinated Organosilicon Compounds with 2-(2-Pyridyl)phenyl Groups

Shohei Furuta,[b] Toshiaki Mori,[b] Yusuke Yoshigoe,[a] Kohei Sekine,[a,b]
Yoichiro Kuninobu*[a,b]

[a]*Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasugakoen, Kasuga-shi, Fukuoka 816-8580, Japan*
[b]*Department of Molecular and Material Sciences, Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, 6-1 Kasugakoen, Kasuga-shi, Fukuoka 816-8580, Japan*

Contents

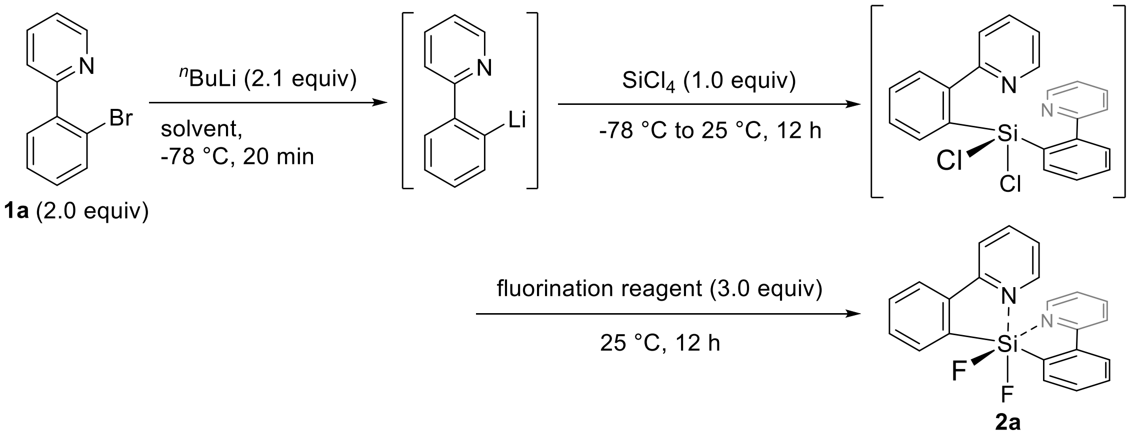
1. General

All reactions were carried out using standard Schlenk techniques under an inert atmosphere. All reagents were purchased from commercial sources and used without further purification unless otherwise noted. NMR spectra were recorded on JEOL JNM-ECA600 (600 MHz for ^{1}H NMR, 150 MHz for ^{13}C NMR, 120 MHz for ^{29}Si NMR), JEOL ECZ-400 (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR), JEOL JNM-LA400 (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR), JEOL JNM-ECA400 (400 MHz for solid-state ^{29}Si NMR) spectrometers. Proton and carbon chemical shifts are reported relative to tetramethylsilane (TMS, δ 0.00 (^{1}H NMR, ^{13}C NMR)) or the residual solvent ($CHCl_3$ (δ 7.26 for ^{1}H NMR or δ 77.16 for ^{13}C NMR), CH_2Cl_2 (δ 5.23 for ^{1}H NMR or δ 53.84 for ^{13}C NMR)) used as an internal reference. HRMS were measured on a JEOL JMS-700 spectrometer. UV/vis absorption and photoluminescence (PL) spectra were measured with a V650 spectrophotometer (JASCO), FP6500 spectrofluorometer (JASCO), UV-3150 UV-vis NIR spectrophotometer (SHIMADZU), and C9920-02 (Hamamatsu Photonics). TG-DTA was measured with DTG-60 (SHIMADZU).

2. Optimization of Reaction Conditions

Screening of reaction conditions was shown in Table S1. In the case of THF or Et_2O as a solvent, the yield of compound **2a** was low (entries 1–6). When cyclopentylmethyl ether (CPME) was used, the target compound **2a** was obtained in a moderate yield (entries 7–9). After examination of fluorination reagents, the target product **2a** was obtained in the highest yield (65%) using silver fluoride (entry 7).

Table S1. Optimization of reaction conditions.

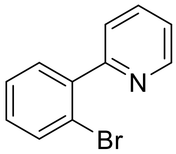


entry	solvent	fluorination reagent	yield [%]
1	THF	$BF_3\cdot OEt_2$	6*
2	THF	AgF	5*
3	THF	$AgBF_4$	trace
4	THF	SbF_3	4*
5	Et_2O	$BF_3\cdot OEt_2$	8
6	Et_2O	AgF	6
7	CPME	AgF	65
8	CPME	$BF_3\cdot OEt_2$	59
9	CPME	SbF_3	28

*^{1}H NMR yield.

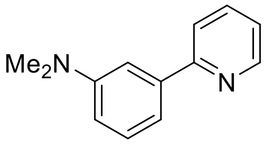
3. Synthesis and Characterization of Substrates

2-(2-Bromophenyl)pyridine[1]



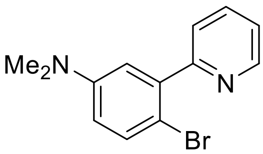
$Pd(OAc)_2$ (144 mg, 0.640 mmol, 0.18 equiv), NBS (685 mg, 3.85 mmol, 1.1 equiv) and 2-phenylpyridine (0.50 mL, 3.50 mmol) were dissolved in acetonitrile (20 mL). The reaction mixture was refluxed for 12 h, then concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (eluent: hexane/EtOAc). The titled compound was isolated as a yellow oil (414 mg, 51%). ^{1}H NMR (400 MHz, $CHCl_3$): δ (ppm) = 7.23–7.31 (m, 2H), 7.40 (ddd, J = 7.6, 7.6, 1.2 Hz, 1H), 7.53 (dd, J = 7.6, 1.6 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.67 (dd, J = 7.6, 1.6 Hz, 1H), 7.76 (ddd, J = 7.6, 7.6, 2.0 Hz, 1H), 8.71 (d, J = 5.2 Hz, 1H). The analytical data is in accordance with the previous report.[1]

N,N-Dimethyl-3-(pyridin-2-yl)aniline[2]



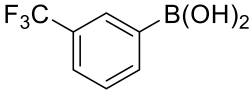
A mixture of 2-bromoprydine (0.98 mL, 10.0 mmol), 3-*(N,N*-dimethylamino)phenylboronic acid (2.48 g, 15.0 mmol, 1.5 equiv), K_2CO_3 (2.76 g, 20.0 mmol, 2.0 equiv), $Pd(OAc)_2$ (26.0 mg, 0.12 mmol, 1.5 mol%), water (40 mL), and ethanol (120 mL) was stirred at 80 °C for 24 h. The reaction mixture was extracted with ethyl acetate (3 x 30 mL). The organic phase was concentrated under reduced pressure, and the crude product was purified by flash chromatography on silica gel (eluent: hexane/EtOAc). The titled compound was isolated as a white solid (1.83 g, 92% yield). ^{1}H NMR (400 MHz, $CHCl_3$): δ (ppm) = 3.02 (s, 6H), 6.79–6.82 (m, 1H), 7.19–7.22 (m, 1H), 7.25–7.28 (m, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.41 (m, 1H), 7.71–7.72 (m, 2H), 8.67–8.69 (m, 1H). The analytical data is in accordance with the previous report.[3]

4-Bromo-*N,N*-dimethyl-3-(pyridin-2-yl)aniline[1]



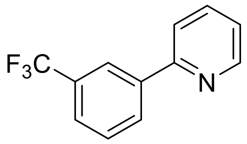
A solution of NBS (979 mg, 5.50 mmol, 1.1 equiv) in acetonitrile (50 mL) was added slowly with stirring to a solution of *N,N*-dimethyl-3-(pyridin-2-yl)aniline (991 mg, 5.0 mmol) in acetonitrile (22.5 mL). The reaction mixture was stirred at room temperature for 1 h, then concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (eluent: hexane/EtOAc). The titled compound was isolated as a yellow oil (1.36 g, 98% yield). ^{1}H NMR (400 MHz, $CHCl_3$): δ (ppm) = 2.96 (s, 6H), 6.63 (dd, J = 8.8, 3.2 Hz, 1H), 6.85 (d, J = 3.2 Hz, 1H), 7.26–7.29 (m, 1H), 7.46 (d, J = 9.2 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), 7.74 (td, J = 8.0, 1.6 Hz, 1H), 8.70 (d, J = 4.8 Hz, 1H). The analytical data is in accordance with the previous report.[1]

(3-(Trifluoromethyl)phenyl)boronic acid[4]



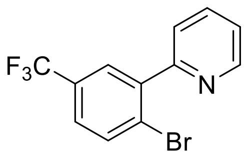
^{n}BuLi (1.6 M in hexane, 22.5 mL, 36.0 mmol, 1.2 equiv) was added dropwise to a solution of 1-bromo-3-(trifluoromethyl)benzene (4.14 mL, 30 mmol) in THF (75 mL) at -78 °C. After the addition was complete, the -78 °C bath was replaced by an ice bath and the solution was warmed up to room temperature to allow thorough mixing of the lithium salts, then re-cooled to -78 °C, and stirred further for 1.5 h. Trimethyl borate (4.20 mL, 37.5 mmol, 1.25 equiv) was added dropwise and solution was stirred for an additional 1 h at -78 °C, following which the reaction mixture was warmed to room temperature and quenched with 2.0 M HCl. The aqueous and organic phases were separated, and the aqueous phase was extracted with ethyl acetate (3 x 30 mL). The organic phases were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by recrystallization (hexane/EtOAc). The titled compound was isolated as a pale white solid (3.74 g, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.68 (dd, J =7.6, 7.2 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 8.43 (d, J = 7.2 Hz, 1H), 8.45 (s, 1H). The analytical data is in accordance with the previous report.[5]

2-(3-(Trifluoromethyl)phenyl)pyridine[6]



To a solution of 2-bromopyridine (0.95 mL, 10.0 mmol) in toluene (35 mL), ethanol (17.5 mL) and water (35 mL) were added Na_2CO_3 (7.95 g, 75.0 mmol, 7.5 equiv), $Pd(PPh_3)_4$ (346 mg, 0.300 mmol) and (3-(trifluoromethyl)phenyl)boronic acid (2.47 g, 13.0 mmol, 1.3 equiv). The reaction mixture was refluxed for 5 h, and cooled to room temperature. To the reaction mixture was added sat. aq. NH_4Cl (75 mL). The aqueous and organic phases were separated, and the aqueous phase was extracted with ethyl acetate (3 x 30 mL). The organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (eluent: hexane/EtOAc). The titled compound was isolated as a white solid (2.05 g, 92% yield). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.28–7.31 (m, 2H), 7.60 (t, J = 8.0 Hz, 1H), 7.68 (d, J = 7.6 Hz, 1H), 7.76–7.82 (m, 1H), 8.18 (d, J = 7.6 Hz, 1H), 8.29 (s, 1H), 8.73 (dd, J = 0.8, 2.4 Hz, 1H). The analytical data is in accordance with the previous report.[7]

2-(2-Bromo-5-(trifluoromethyl)phenyl)pyridine[8]

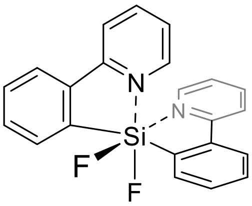


2-(3-(trifluoromethyl)phenyl)pyridine (1.12 g, 5.00 mmol), NBS (1.78 g, 10.0 mmol, 2.0 equiv) and $Pd(OAc)_2$ (56.0 mg, 0.250 mmol, 5.0 mol%) were dissolved in AcOH (83 mL). The reaction mixture was heated at 120 °C for 12 h, and then concentrated under reduced pressure. The crude product was purified by chromatography on silica gel (eluent: hexane/EtOAc). The titled compound was isolated as a colorless oil (718 mg, 48% yield). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.33–7.35 (m, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.62–7.64 (m, 1H), 7.80–7.81 (m, 3H), 8.73 (s, 1H). The analytical data is in accordance with the previous report.[9]

4. General Procedure for the Synthesis of Hexacoordinated Organosilicon Compounds

^{n}BuLi (1.6 M in hexane, 0.34 mL, 0.525 mmol, 2.1 equiv) was slowly added to the solution of 2-(2-bromophenyl)pyridine (117 mg, 0.500 mmol, 2.0 equiv) in cyclopentyl methyl ether (2.5 mL) at -78 °C, and the reaction mixture was stirred at -78 °C for 20 min. Tetrachlorosilane (28.0 μL, 0.250 mmol) was added to the reaction mixture at -78 °C and then allowed to room temperature. After stirring for 12 h, AgF (95.0 mg, 0.750 mmol, 3.0 equiv) was added to the reaction mixture, and stirring for 12 h. The reaction mixture was filtrated and washed with water. The organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (eluent: dichloromethane/methanol), GPC and recrystallization. The titled compound **2a** was isolated as a white solid (60.9 mg, 65%).

Hexacoordinated Organosilicon Compound 2a

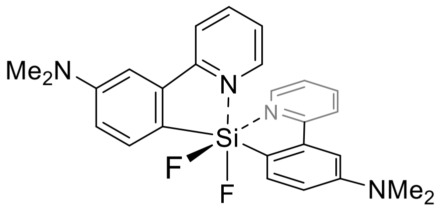


2a was obtained as a white solid (60.9 mg, 65%). ^{1}H NMR (400 M Hz, $CDCl_3$): δ (ppm) = 6.87 (dd, J = 6.4, 6.4 Hz, 2H), 7.15 (d, J = 5.6 Hz, 2H), 7.47 (dd, J = 7.6, 7.6 Hz, 2H), 7.58 (dd, J = 7.6, 7.6 Hz, 2H), 7.71 (dd, J = 7.6, 7.6 Hz, 2H), 7.88 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 7.6 Hz, 2H), 8.20 (d, J = 7.2 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 118.0, 122.7, 122.8, 126.3, 128.4, 131.2, 135.2, 140.4, 144.2, 147.1 (t, J = 41.9 Hz), 154.0; ^{19}F NMR (378 MHz, $CDCl_3$): δ (ppm) = -129.2 (s, 2F); ^{29}Si NMR (120 MHz, $CDCl_3$): δ (ppm) = -129.5 (t, J = 267 Hz); ^{29}Si NMR (79 MHz, CP/MAS): δ (ppm) = -126.0; HRMS(EI$^+$) Calcd for $C_{22}H_{16}F_2N_2Si$ ([M]$^+$) 374.1051, Found 374.1047; TG (in air): Degradation starts at 197.7 °C; DTA (in air): onset temperature = 194.7 °C, peak temperature = 207.9 °C.

The following peaks, which might be derived from hexacoordinated isomers or structures with different coordination number, were observed. ^{19}F NMR (378 MHz, $CDCl_3$): δ (ppm) = -137.3 (d, J = 14.4 Hz), -123.8 (s), -119.5 (d, J = 14.4 Hz); ^{29}Si NMR (120 MHz,

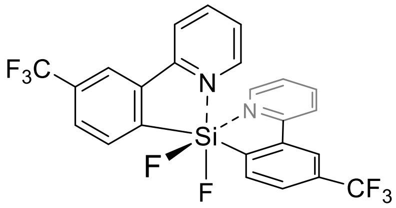
$CDCl_3$): δ (ppm) = -153.3 (t, *J* = 197.0 Hz).

Hexacoordinated Organosilicon Compound 2b



2b was obtained as a yellow solid (15.0 mg, 13%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 6.86 (dd, *J* = 6.4, 6.4 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 7.24 (s, 2H), 7.26-7.38 (m, 2H), 7.66 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.83 (d, *J* = 8.0 Hz, 2H), 8.02-8.12 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) = 41.0, 106.5, 116.1, 117.4, 122.3, 135.9, 136.4, 139.7, 144.4, 150.9, 154.4 (C connected to Si is missing) ; ^{19}F NMR (378 MHz, $CDCl_3$): δ (ppm) = -129.2 (s, 2F); ^{29}Si NMR (120 MHz, $CDCl_3$): δ (ppm) = -125.1 (t, *J* = 262.0 Hz); HRMS (EI$^+$) Calcd for $C_{26}H_{26}F_2N_4Si$ ([M]$^+$) 460.1895, Found 460.1894.

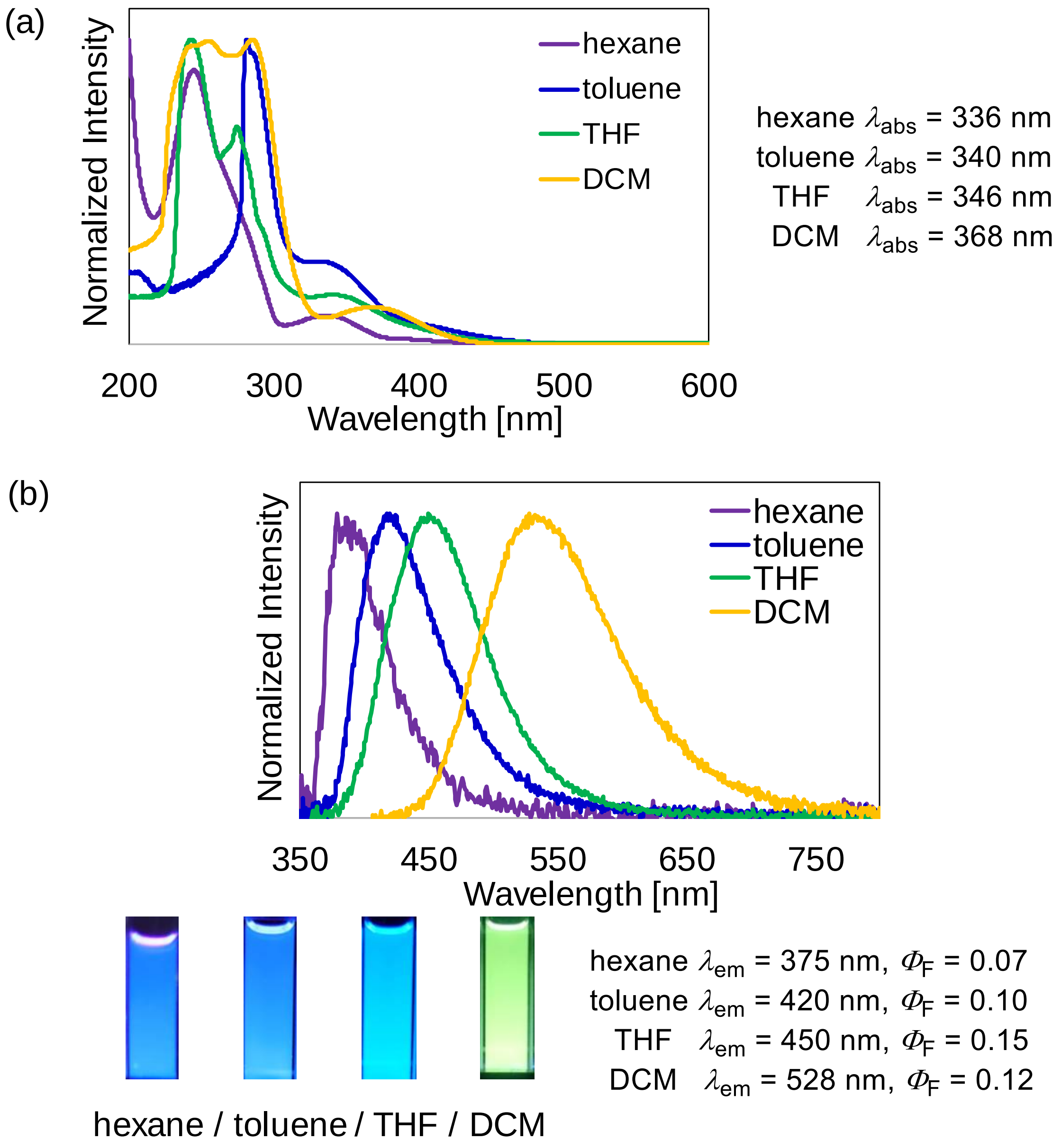
Hexacoordinated Organosilicon Compound 2c



The titled compound was isolated as a white solid (16.0 mg, 13%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.03 (m, 2H), 7.23 (d, *J* = 4.4 Hz, 2H), 7.82–7.89 (m, 4H), 8.01 (d, *J* = 8.0 Hz, 2H), 8.18 (s, 2H), 8.39 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) = 118.6, 119.3, 123.4, 125.2 (q, *J* = 271.7 Hz), 127.6, 131.0 (q, *J* = 32.3 Hz), 134.4, 135.7, 140.9, 144.0, 151.1 (t, *J* = 42.6 Hz), 152.6; ^{19}F NMR (378 MHz, $CDCl_3$): δ (ppm) = -62.3 (s, 6F), -128.4 (s, 2F); HRMS (EI$^+$) Calcd for $C_{24}H_{14}F_8N_2Si$ ([M]$^+$) 510.0799, Found 510.0801.

The following two sets of peaks, which might be derived from isomers or structures with different coordination number, were observed. ^{19}F NMR (378 MHz, $CDCl_3$): δ (ppm) = -62.4 (s), -124.8 (s), and -62.1(s), -62.5(s), -137.5 (d, *J* = 17.3 Hz), -119.9 (d, *J* = 17.3 Hz).

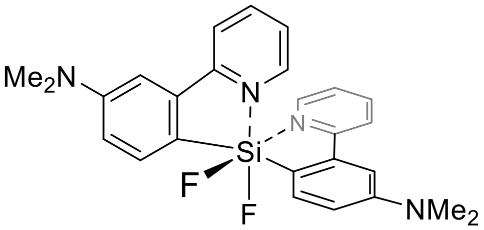
5. Optical Properties



hexane λ_{abs} = 336 nm
toluene λ_{abs} = 340 nm
THF λ_{abs} = 346 nm
DCM λ_{abs} = 368 nm

hexane λ_{em} = 375 nm, Φ_F = 0.07
toluene λ_{em} = 420 nm, Φ_F = 0.10
THF λ_{em} = 450 nm, Φ_F = 0.15
DCM λ_{em} = 528 nm, Φ_F = 0.12

Figure S1. UV/Vis absorption and photoluminescence of **2b** in different solvents.



2b

solution (CH_2Cl_2)
λ_{ex} = 368 nm
λ_{em} = 528 nm
Φ_F = 0.12

solid (powder)
λ_{ex} = 300 nm
λ_{em} = 529 nm
Φ_F = 0.03

crystal
λ_{ex} = 300 nm
λ_{em} = 499 nm
Φ_F = 0.05

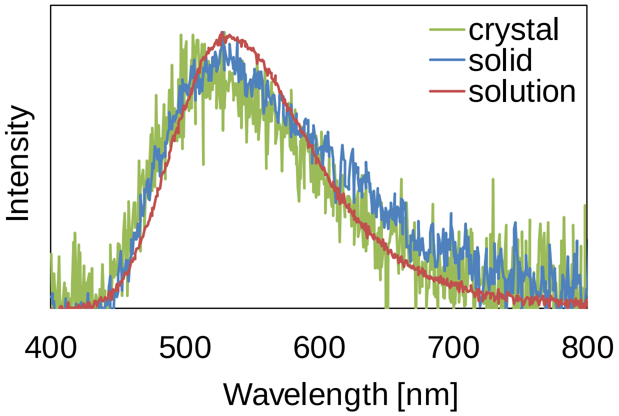


Figure S2. UV/Vis absorption and photoluminescence in solution and the solid states.

The fluorescent colour of silicon compound with two amino groups **2b** can be switched by protonation and deprotonation of the amino groups (Fig. S3). The colour was changed from green to yellow after the addition of trifluoroacetic acid (TFA, 10 µL of 60 mM CH_2Cl_2 solution, 2.0 equiv) to **2b** (3 mL of 0.10 mM CH_2Cl_2 solution, 1.0 equiv). The fluorescent colour can be returned to green by the addition of trimethylamine (TEA, 10 µL of 60 mM CH_2Cl_2 solution, 2.0 equiv).

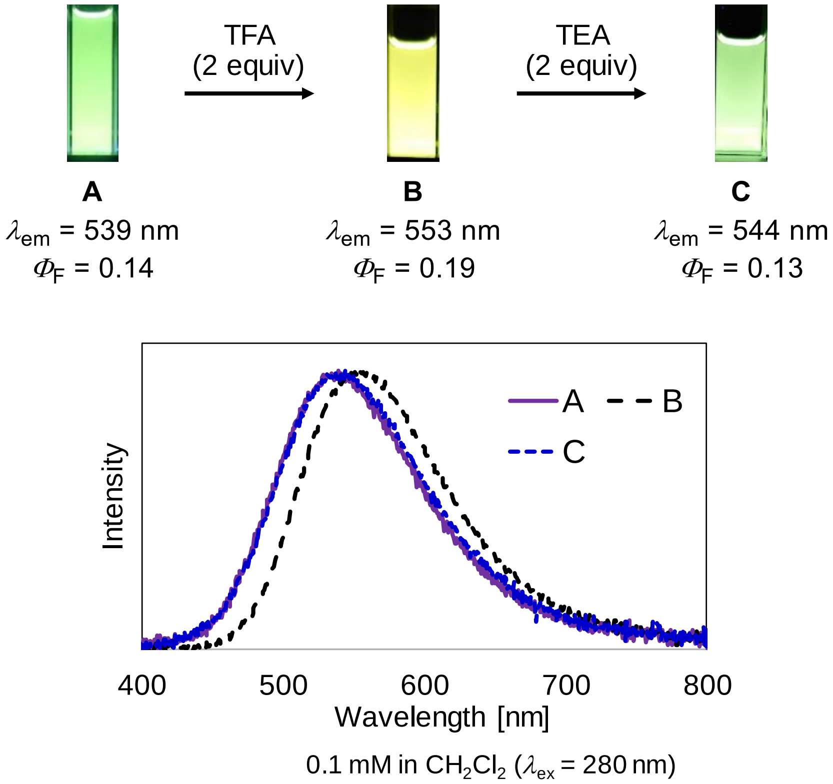
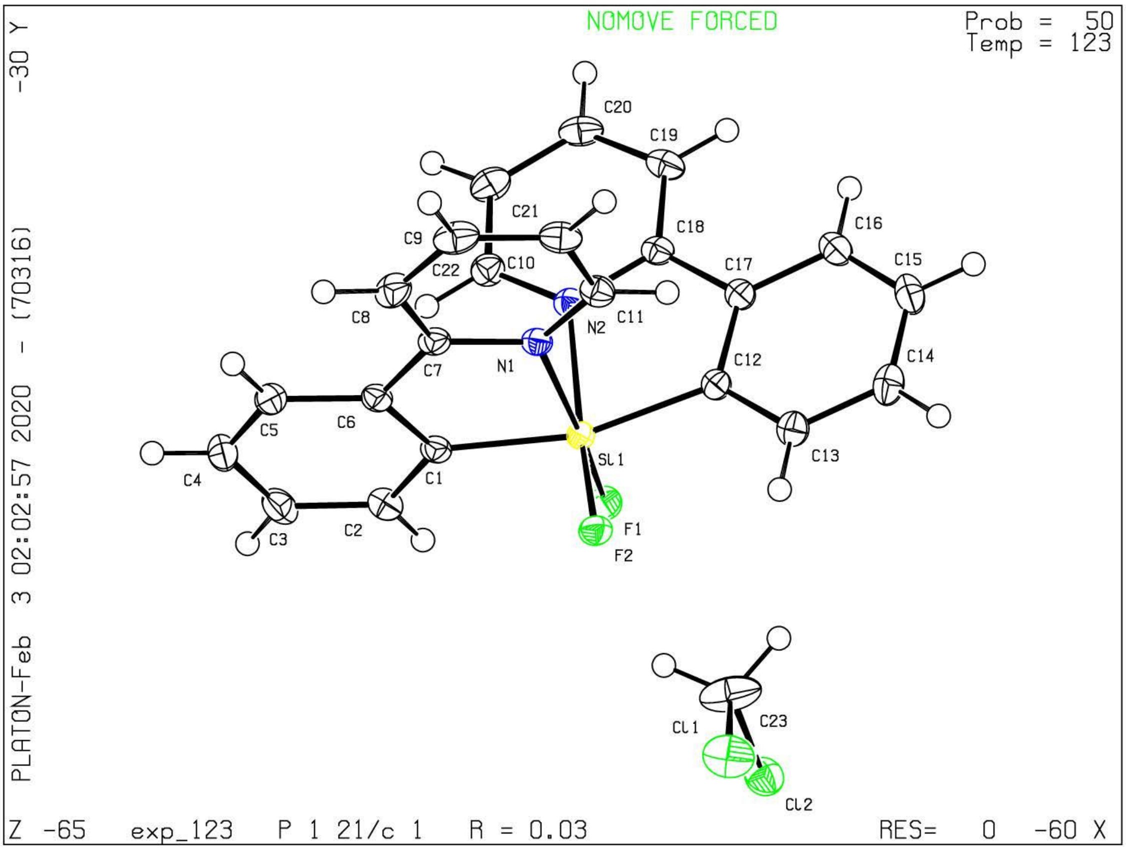


Figure S3. Switching of fluorescent colours of **2b**.

6. X-ray Structure of compound

6-1. X-ray Structure of compound 2a

A single crystal of 6,6-difluoro-6H-5λ4,5'λ4,6λ6-6,6'-spirobi[benzo[3,4][1,2]azasilolo-[1,5-a]pyridine] ($C_{22}H_{26}F_2N_2Si$) (**2a**) was prepared by recrystallization from the dichloromethane solution. A suitable crystal was selected, and the X-ray diffraction was collected on a XtaLAB AFC10 (RCD3): fixed-chi single diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073A). The crystal was kept at 123 K during data collection. The data were collected using ω scan in the θ range of $5.018 \leq \theta \leq 58.782$ deg. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods,[10] and expanded using Fourier techniques.[11] Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F2 was based on 12122 observed reflections and 4808 variable parameters. Neutral atom scattering factors were taken from Cromer and Waber.[12] All calculations were performed using the Olex-2 crystallographic software package except for refinement,[13] which was performed using SHELXL-97.5 Details15 of final refinement as well as the bond lengths and angles are summarized in the supporting information, and the numbering scheme employed is also shown in the supporting information, which were drawn with ORTEP at 50% probability ellipsoid.



Crystal structure determination of 2a

Crystal Data for $C_{23}H_{18}F_2N_2SiCl_2$ (M =459.38 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 9.0006(2) Å, b = 16.2355(4) Å, c =14.0783(4) Å, β = 96.804(3)°, V = 2042.76(9) Å^3, Z = 4, T = 293(2) K, μ(MoKα) = 0.408 mm^{-1}, $Dcalc$ = 1.494 g/cm^3, 12122 reflections measured (5.018°≤ 2Θ ≤ 58.782°), 4808 unique (R_{int} = 0.0161, R_{sigma} = 0.0215) which were used in all calculations. The final R_1 was 0.0302 (I > 2σ(I)) and wR_2 was 0.0843 (all data).

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

Identification code	6,6-difluoro-6H-5λ4,5'λ4,6λ6-6,6'-spirobi [benzo[3,4][1,2]azasilolo[1,5-a]pyridine]
Empirical formula	C23H18F2N2SiCl2
Formula weight	459.38
Temperature/K	123
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.0006(3)
b/Å	16.2355(4)
c/Å	14.0783(4)
α/°	90
β/°	96.804(3)
γ/°	90
Volume/Å3	2042.76(10)
Z	4
ρcalcg/cm3	1.494
μ/mm-1	0.408
F(000)	944.0
Crystal size/mm3	0.5 × 0.5 × 0.1
Radiation	MoKα (λ = 0.71073)
2θrange for data collection/°	5.018 to 58.782
Index ranges	-12 ≤ h ≤ 11, -22 ≤ k ≤ 21, -17 ≤ l ≤ 19
Reflections collected	12122
Independent reflections	4808 [R_{int} = 0.0161, R_{sigma} = 0.0215]
Data/restraints/parameters	4808/0/271
Goodness-of-fit on F2	1.043
Final R indexes [I>=2σ (I)]	R1 = 0.0302, wR2 = 0.0820
Final R indexes [all data]	R1 = 0.0342, wR2 = 0.0843

Largest diff. peak/hole / e Å^{-3} 0.37/-0.24

Table S3. Fractional Atomic Coordinates (×10^{4}) and Equivalent Isotropic Displacement Parameters (Å^{2}×10^{3}) for **2a**. U$_{eq}$ is defined as 1/3 of of the trace of the orthogonalised U$_{IJ}$ tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Cl2	2084.3(4)	3479.1(2)	8114.8(3)	26.42(9)
Si1	3802.9(4)	6272.9(2)	6586.9(2)	14.52(9)
Cl1	627.5(4)	4972.7(2)	8663.3(3)	34.64(11)
F1	3911.4(8)	5257.3(4)	6470.9(5)	19.87(17)
F2	2309.8(8)	6271.2(5)	7173.5(6)	19.66(17)
N2	5797.4(12)	6397.9(6)	5939.5(8)	15.8(2)
N1	3738.8(11)	7562.8(6)	6577.7(8)	15.7(2)
C12	5227.5(14)	6319.7(7)	7705.8(9)	15.9(2)
C7	2926.4(14)	7876.7(8)	5789.0(9)	16.9(2)
C18	7046.0(14)	6421.2(7)	6578.1(10)	16.4(2)
C13	4884.4(15)	6296.9(8)	8646.4(10)	19.5(3)
C1	2714.3(13)	6440.8(8)	5356.2(9)	16.0(2)
C17	6732.3(14)	6402.5(7)	7575.3(9)	16.4(2)
C6	2400.8(13)	7253.8(8)	5076.6(9)	16.7(2)
C11	4299.8(15)	8074.8(8)	7273.2(10)	19.8(3)
C22	5942.5(15)	6411.0(8)	5002.9(10)	19.5(3)
C16	7849.9(15)	6478.8(8)	8348.9(10)	20.7(3)
C2	2247.1(14)	5819.1(8)	4703.7(10)	20.1(3)
C14	5989.4(17)	6363.9(8)	9421.6(10)	23.2(3)
C5	1675.6(14)	7444.4(9)	4170.3(10)	22.0(3)
C4	1246.1(15)	6816.5(10)	3535.1(10)	26.0(3)
C21	7310.3(16)	6455.8(8)	4661.0(11)	22.7(3)
C19	8459.6(15)	6454.6(8)	6275.5(11)	21.3(3)
C20	8588.2(16)	6478.3(8)	5310.6(11)	23.9(3)
C10	4098.5(15)	8919.0(8)	7220.7(11)	23.0(3)

C8	2657.9(16)	8718.8(8)	5707.3(11)	22.7(3)
C15	7473.6(16)	6459.9(8)	9269.6(10)	23.4(3)
C3	1516.5(15)	6003.7(9)	3804.0(10)	24.4(3)
C9	3255.1(16)	9241.4(8)	6426.6(11)	25.3(3)
C23	2113.7(19)	4558.9(10)	8118.4(15)	39.9(4)

Table S4. Anisotropic Displacement Parameters (Å^2×10^3) for **2a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U11	U22	U33	U23	U13	U12
Cl2	27.64(18)	21.90(17)	29.04(19)	-2.81(13)	0.48(14)	-0.74(13)
Si1	14.19(17)	13.15(16)	15.90(17)	1.78(12)	0.49(13)	-0.02(12)
Cl1	30.3(2)	29.65(19)	45.4(2)	-6.29(16)	10.81(17)	2.62(15)
F1	22.1(4)	13.6(3)	23.0(4)	1.7(3)	-1.2(3)	0.2(3)
F2	16.0(4)	21.6(4)	21.8(4)	3.5(3)	3.7(3)	-1.0(3)
N2	15.3(5)	13.8(5)	18.5(5)	1.1(4)	2.4(4)	0.6(4)
N1	13.5(5)	14.8(5)	18.8(5)	0.8(4)	2.3(4)	-0.6(4)
C12	16.8(6)	12.1(5)	18.6(6)	1.1(4)	0.7(5)	1.8(4)
C7	13.0(5)	16.6(6)	21.5(6)	3.1(5)	3.6(5)	0.6(4)
C18	15.9(6)	10.7(5)	22.4(6)	0.4(5)	1.5(5)	0.3(4)
C13	19.7(6)	18.5(6)	20.1(6)	0.6(5)	2.2(5)	3.3(5)
C1	12.1(5)	17.2(6)	18.8(6)	1.0(5)	2.3(5)	-0.6(4)
C17	16.9(6)	11.4(5)	20.4(6)	0.9(4)	-0.4(5)	1.5(4)
C6	11.6(5)	19.0(6)	19.6(6)	1.9(5)	2.3(5)	0.0(5)
C11	18.7(6)	17.6(6)	22.9(7)	-1.3(5)	2.2(5)	-1.0(5)
C22	19.7(6)	18.9(6)	19.9(6)	1.0(5)	3.0(5)	0.7(5)
C16	18.1(6)	17.2(6)	25.5(7)	-0.4(5)	-3.0(5)	-0.2(5)
C2	17.4(6)	19.3(6)	23.4(7)	-1.9(5)	1.4(5)	-0.3(5)
C14	31.6(7)	20.8(6)	16.7(6)	-0.2(5)	0.4(6)	3.3(5)
C5	16.0(6)	25.1(7)	24.5(7)	7.9(5)	0.6(5)	-0.2(5)
C4	19.4(6)	38.6(8)	19.0(7)	5.3(6)	-1.7(5)	-2.0(6)
C21	26.2(7)	20.1(6)	23.6(7)	0.2(5)	10.0(6)	0.5(5)

C19	14.8(6)	19.2(6)	29.9(7)	-2.0(5)	2.0(5)	-1.5(5)
C20	19.2(6)	20.7(6)	33.7(8)	-0.5(6)	11.5(6)	-1.6(5)
C10	22.3(6)	17.2(6)	30.3(7)	-5.3(5)	7.3(6)	-3.1(5)
C8	21.9(6)	17.7(6)	28.8(7)	6.5(5)	4.2(6)	3.8(5)
C15	26.0(7)	20.3(6)	21.5(7)	-1.1(5)	-7.3(6)	1.5(5)
C3	19.9(6)	31.6(7)	20.9(7)	-6.0(6)	-0.4(5)	-4.1(6)
C9	26.3(7)	12.8(6)	38.4(8)	1.0(5)	10.6(6)	0.7(5)
C23	34.8(9)	21.7(7)	67.9(13)	4.0(7)	25.4(9)	0.2(6)

Table S5. Bond Lengths for **2a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl2	C23	1.7533(16)	C18	C19	1.3898(18)
Si1	F1	1.6610(8)	C13	C14	1.3910(19)
Si1	F2	1.6586(8)	C1	C6	1.3966(17)
Si1	N2	2.1172(11)	C1	C2	1.3958(18)
Si1	N1	2.0949(11)	C17	C16	1.3978(18)
Si1	C12	1.9111(13)	C6	C5	1.3973(18)
Si1	C1	1.9064(13)	C11	C10	1.3834(18)
Cl1	C23	1.7528(17)	C22	C21	1.3758(19)
N2	C18	1.3541(16)	C16	C15	1.378(2)
N2	C22	1.3404(17)	C2	C3	1.3890(19)
N1	C7	1.3547(16)	C14	C15	1.387(2)
N1	C11	1.3370(17)	C5	C4	1.381(2)
C12	C13	1.3955(18)	C4	C3	1.386(2)
C12	C17	1.3947(18)	C21	C20	1.383(2)
C7	C6	1.4629(18)	C19	C20	1.378(2)
C7	C8	1.3908(17)	C10	C9	1.378(2)

Table S6. Bond Angles for **2a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
F1	Si1	N2	89.43(4)	N2	C18	C19	121.03(12)

F1	Si1	N1	173.53(5)	C19	C18	C17	125.59(12)
F1	Si1	C12	94.53(5)	C14	C13	C12	121.63(13)
F1	Si1	C1	94.73(5)	C6	C1	Si1	117.14(9)
F2	Si1	F1	96.19(4)	C2	C1	Si1	125.25(10)
F2	Si1	N2	173.17(4)	C2	C1	C6	117.58(12)
F2	Si1	N1	88.94(4)	C12	C17	C18	115.39(11)
F2	Si1	C12	95.38(5)	C12	C17	C16	121.76(12)
F2	Si1	C1	95.35(5)	C16	C17	C18	122.84(12)
N1	Si1	N2	85.74(4)	C1	C6	C7	114.96(11)
C12	Si1	N2	80.25(5)	C1	C6	C5	121.57(12)
C12	Si1	N1	88.89(5)	C5	C6	C7	123.44(12)
C1	Si1	N2	88.03(5)	N1	C11	C10	122.76(13)
C1	Si1	N1	80.83(5)	N2	C22	C21	122.71(13)
C1	Si1	C12	164.98(6)	C15	C16	C17	119.77(13)
C18	N2	Si1	113.34(9)	C3	C2	C1	121.15(13)
C22	N2	Si1	127.69(9)	C15	C14	C13	120.00(13)
C22	N2	C18	118.87(11)	C4	C5	C6	119.51(13)
C7	N1	Si1	113.14(8)	C5	C4	C3	119.95(13)
C11	N1	Si1	127.53(9)	C22	C21	C20	118.61(13)
C11	N1	C7	119.12(11)	C20	C19	C18	119.36(13)
C13	C12	Si1	125.37(10)	C19	C20	C21	119.41(13)
C17	C12	Si1	117.55(10)	C9	C10	C11	118.41(13)
C17	C12	C13	117.07(12)	C9	C8	C7	119.66(13)
N1	C7	C6	113.65(11)	C16	C15	C14	119.76(13)
N1	C7	C8	120.62(12)	C4	C3	C2	120.22(13)
C8	C7	C6	125.73(12)	C10	C9	C8	119.40(12)
N2	C18	C17	113.38(11)	Cl1	C23	Cl2	111.87(9)

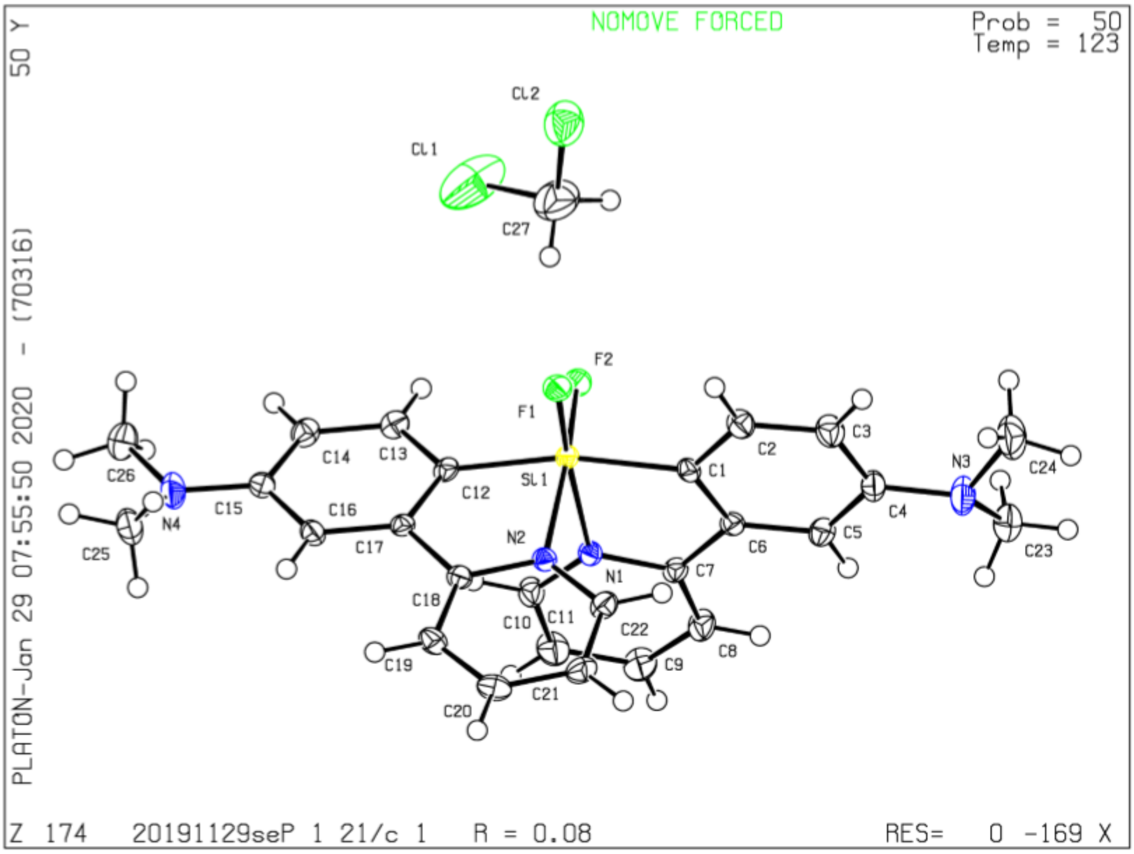
Table S7. Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for **2a**.

Atom	***x***	***y***	***z***	**U(eq)**

H13	3892.4	6235.51	8757.74	23
H11	4848.34	7854.12	7815.12	24
H22	5083.12	6388.88	4566.19	23
H16	8843.87	6542.07	8242.79	25
H2	2428.18	5271.62	4874.3	24
H14	5732.64	6344.16	10041.95	28
H5	1483.6	7990.11	3996.19	26
H4	775.68	6938.72	2927.31	31
H21	7373.82	6470.63	4006.7	27
H19	9310.47	6460.85	6720.19	26
H20	9526.3	6509.24	5097.96	29
H10	4522.24	9260.77	7709.56	28
H8	2078.9	8928.77	5170.8	27
H15	8212.51	6511.41	9786.87	28
H3	1207.69	5580.74	3380.58	29
H9	3089.91	9806	6375.72	30
H23A	3053.13	4747.81	8457.22	48
H23B	2055.29	4756.92	7464.98	48

6-2. X-ray Structure of compound 2b

A single crystal of 6,6-difluoro-N^9,N^9,$N^{9'}$,$N^{9'}$-tetramethyl-6*H*-5λ^4,5'λ^4,6λ^6-6,6'-spirobi[benzo[3,4][1,2]azasilolo[1,5-a]pyridine]-9,9'-diamine ($C_{22}H_{26}F_2N_2Si$) (**2b**) was prepared by recrystallization from the dichloromethane solution. A suitable crystal was selected, and the X-ray diffraction was collected on a XtaLAB AFC10 (RCD3): fixed-chi single diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073A). The crystal was kept at 123 K during data collection. The data were collected using ω scan in the θ range of $4.434 \leq \theta \leq 54.968$ deg. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods, and expanded using Fourier techniques. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F2 was based on 30027 observed reflections and 5995 variable parameters. Neutral atom scattering factors were taken from Cromer and Waber. All calculations were performed using the Olex-2 crystallographic software package except for refinement, which was performed using SHELXL-97.5 Details of final refinement as well as the bond lengths and angles are summarized in the supporting information, and the numbering scheme employed is also shown in the supporting information, which were drawn with ORTEP at 50% probability ellipsoid.



Crystal structure determination of 6,6-difluoro-N^9,N^9,$N^{9'}$,$N^{9'}$-tetramethyl-6*H*-5λ^4,5'λ^4,6λ^6-6,6'-spirobi[benzo[3,4][1,2]azasilolo[1,5-a]pyridine]-9,9'-diamine (2b)

Crystal Data for $C_{27}H_{28}Cl_2F_2N_4Si$ (M =545.52 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 14.1097(4) Å, b = 10.9238(3) Å, c = 17.0344(5) Å, β= 94.326(3)°, V = 2618.06(13) Å^3, Z = 4, T = 123 K, μ(MoKα) = 0.332 mm^{-1}, $Dcalc$ = 1.384 g/cm^3, 30027 reflections measured (4.434°≤ 2Θ ≤ 54.968°), 5995 unique (R_{int} = 0.1704, R_{sigma} = 0.0737) which were used in all calculations. The final R_1 was 0.0818 ($I > 2\sigma(I)$) and wR_2 was 0.2219 (all data).

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

Identification code	6,6-difluoro-N^{9},N^{9},$N^{9'}$,$N^{9'}$-tetramethyl-6*H*-5λ^{4},5'λ^{4},6λ^{6}-6,6'-spirobi[benzo[3,4][1,2]azasilolo[1,5-a]pyridine]-9,9'-diamine
Empirical formula	$C_{27}H_{28}Cl_2F_2N_4Si$
Formula weight	545.52
Temperature/K	123
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.1097(4)
b/Å	10.9238(3)
c/Å	17.0344(5)
α/°	90
β/°	94.326(3)
γ/°	90
Volume/Å^3	2618.06(13)
Z	4
ρ_{calc}g/cm^3	1.384
μ/mm^{-1}	0.332
F(000)	1136.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2θrange for data collection/°	4.434 to 54.968
Index ranges	$-18 \leq h \leq 18$, $-14 \leq k \leq 14$, $-21 \leq l \leq 22$
Reflections collected	30027
Independent reflections	5995 [R_{int} = 0.1704, R_{sigma} = 0.0737]
Data/restraints/parameters	5995/0/329
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0818, wR_2 = 0.2105

Final R indexes [all data] $R_1 = 0.0894$, $wR_2 = 0.2219$

Largest diff. peak/hole / e Å^{-3} 1.07/-1.09

Table S9. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **2b**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Si1	2497.9(4)	2305.3(5)	7368.4(4)	14.13(19)
Cl2	2976.3(6)	7170.0(8)	7266.1(5)	46.6(3)
Cl1	2496.6(11)	5997.8(12)	8732.8(6)	81.4(5)
F1	3184.2(9)	3422.5(12)	7037.2(8)	20.5(3)
F2	1756.0(9)	3221.1(13)	7823.2(8)	20.8(3)
N2	3416.5(12)	995.9(17)	6925.2(11)	14.6(4)
N1	1650.7(12)	792.2(17)	7633.6(11)	15.3(4)
N4	5422.8(16)	1534(2)	10191.8(13)	29.1(5)
N3	-387.9(16)	2058(2)	4449.4(14)	29.8(5)
C1	1682.4(15)	2227(2)	6419.0(14)	15.2(4)
C12	3311.3(14)	2015(2)	8296.7(13)	15.4(4)
C6	919.7(14)	1392(2)	6389.9(13)	15.1(4)
C13	3207.7(16)	2509(2)	9046.4(14)	18.3(5)
C18	4168.3(15)	709(2)	7440.0(13)	15.5(4)
C17	4128.0(15)	1303.5(19)	8219.3(13)	14.2(4)
C7	906.7(15)	590(2)	7088.8(13)	15.8(4)
C2	1711.8(16)	3020(2)	5771.3(14)	20.0(5)
C14	3887.8(17)	2333(2)	9675.1(14)	20.0(5)
C19	4868.8(16)	-108(2)	7228.3(15)	20.5(5)
C8	218.8(16)	-290(2)	7222.6(15)	22.5(5)
C22	3340.7(16)	470(2)	6201.9(14)	19.2(5)
C16	4838.0(15)	1137(2)	8831.6(14)	17.4(4)
C5	224.1(16)	1334(2)	5759.5(14)	20.1(5)
C3	1031.7(18)	2980(2)	5134.1(15)	23.7(5)

C10	1082.8(18)	-791(2)	8456.8(16)	27.3(5)
C21	4012.6(17)	-358(2)	5960.9(15)	22.9(5)
C15	4728.5(17)	1672(2)	9578.6(13)	19.1(5)
C11	1733.4(16)	113(2)	8293.3(14)	20.7(5)
C20	4787.0(18)	-642(2)	6486.5(16)	24.9(5)
C9	303.9(18)	-980(2)	7914.9(16)	26.9(5)
C4	272.7(17)	2128(2)	5107.8(14)	20.6(5)
C23	-1326.6(18)	1564(3)	4551.0(16)	30.4(6)
C25	6375.7(19)	1132(3)	10028.8(17)	30.7(6)
C26	5293(2)	2086(3)	10953.2(16)	33.3(6)
C24	-366(2)	3014(3)	3854.5(19)	40.7(7)
C27	2423(3)	5929(3)	7713(2)	51.7(9)

Table S10. Anisotropic Displacement Parameters (Å^2×10^3) for **2b**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U11**	**U22**	**U33**	**U23**	**U13**	**U12**
Si1	10.6(3)	13.5(3)	18.0(3)	-1.2(2)	-1.1(2)	-0.42(19)
Cl2	47.2(5)	48.9(5)	42.7(5)	6.8(4)	-3.7(4)	-11.0(4)
Cl1	127.7(11)	70.6(8)	49.0(6)	-9.4(5)	27.0(6)	-48.4(7)
F1	16.8(6)	15.8(6)	28.4(7)	2.2(5)	-1.1(5)	-3.9(5)
F2	15.6(6)	21.0(7)	25.6(7)	-5.9(6)	-0.4(5)	4.8(5)
N2	12.6(8)	13.8(8)	17.5(9)	-0.2(7)	0.5(7)	0.6(6)
N1	12.2(8)	14.8(9)	18.5(9)	0.8(7)	-0.8(7)	-0.8(7)
N4	31.8(11)	34.5(12)	19.4(10)	-0.8(9)	-8.9(9)	5.9(10)
N3	27.9(11)	37.1(13)	22.8(11)	4.2(9)	-9.1(9)	-4.6(10)
C1	11.5(9)	14.3(10)	19.4(10)	0.3(8)	-0.8(8)	2.2(7)
C12	10.8(9)	14.5(10)	20.8(11)	-2.1(8)	-0.1(8)	-3.5(7)
C6	12.7(9)	14.2(10)	18.2(10)	-1.3(8)	0.8(8)	1.6(7)
C13	15.0(10)	19.7(10)	20.5(11)	-1.8(9)	3.9(8)	-1.6(8)
C18	14.0(9)	13.8(9)	18.7(10)	0.3(8)	1.0(8)	0.1(8)
C17	13.6(9)	11.8(9)	17.2(10)	-0.4(8)	0.6(8)	-1.4(7)

C7	13.0(9)	15.7(10)	18.5(10)	-2.1(8)	0.6(8)	-1.1(8)
C2	16.9(10)	20.4(11)	22.7(11)	3.0(9)	0.9(9)	-0.9(8)
C14	22.9(11)	20.6(11)	16.5(11)	-0.6(8)	2.4(9)	-2.8(9)
C19	17.2(10)	19.0(11)	25.2(12)	0.0(9)	0.7(9)	5.6(8)
C8	16.1(10)	25.0(12)	25.7(12)	1.6(10)	-2.3(9)	-6.1(9)
C22	17.9(10)	20.1(11)	19.6(11)	-4.4(9)	0.8(8)	-0.4(8)
C16	15.5(10)	16.2(10)	20.3(11)	2.2(8)	-1.3(8)	1.4(8)
C5	16.6(10)	20.4(11)	23.0(11)	-1.5(9)	-1.3(9)	-2.3(8)
C3	23.7(11)	25.4(12)	21.7(12)	5.4(9)	0.0(9)	-2.3(9)
C10	26.8(12)	25.9(12)	28.9(13)	10.3(10)	1.0(10)	-6.9(10)
C21	26.3(11)	19.9(11)	22.5(11)	-7.6(9)	1.2(9)	2.0(9)
C15	23.0(11)	14.9(10)	18.9(11)	3.0(8)	-2.6(9)	-2.7(8)
C11	17.8(10)	21.4(11)	22.3(11)	3.8(9)	-2.5(8)	-3.5(9)
C20	25.9(12)	19.3(11)	29.9(13)	-4.7(10)	4.7(10)	8.5(9)
C9	22.1(11)	25.2(12)	33.3(13)	5.8(10)	1.1(10)	-11.2(10)
C4	18.0(10)	24.8(11)	18.4(11)	-0.9(9)	-2.8(9)	2.2(9)
C23	24.5(12)	36.6(15)	28.9(13)	-0.4(11)	-5.1(10)	-0.3(11)
C25	27.8(13)	32.0(14)	30.5(14)	7.3(11)	-10.3(11)	0.2(11)
C26	42.1(16)	36.5(15)	20.3(13)	-2.8(11)	-5.6(11)	0.3(12)
C24	44.1(17)	46.2(18)	29.4(15)	11.5(13)	-13.0(13)	-6.0(14)
C27	68(2)	37.9(18)	49(2)	1.8(15)	-2.1(18)	-15.7(16)

Table S11. Bond Lengths for **2b**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Si1	F1	1.6816(14)	C12	C13	1.404(3)
Si1	F2	1.6790(14)	C12	C17	1.404(3)
Si1	N2	2.1080(19)	C6	C7	1.479(3)
Si1	N1	2.1087(19)	C6	C5	1.401(3)
Si1	C1	1.915(2)	C13	C14	1.396(3)
Si1	C12	1.909(2)	C18	C17	1.483(3)
Cl2	C27	1.765(4)	C18	C19	1.399(3)

Cl1	C27	1.734(4)	C17	C16	1.403(3)
N2	C18	1.361(3)	C7	C8	1.397(3)
N2	C22	1.356(3)	C2	C3	1.394(3)
N1	C7	1.366(3)	C14	C15	1.409(3)
N1	C11	1.344(3)	C19	C20	1.389(3)
N4	C15	1.385(3)	C8	C9	1.397(4)
N4	C25	1.461(4)	C22	C21	1.394(3)
N4	C26	1.455(3)	C16	C15	1.419(3)
N3	C4	1.405(3)	C5	C4	1.415(3)
N3	C23	1.453(3)	C3	C4	1.417(3)
N3	C24	1.457(4)	C10	C11	1.391(3)
C1	C6	1.409(3)	C10	C9	1.396(4)
C1	C2	1.406(3)	C21	C20	1.394(4)

Table S12. Bond Angles for **2b**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
F1	Si1	N2	89.26(7)	C1	C6	C7	114.26(19)
F1	Si1	N1	172.23(8)	C5	C6	C1	123.1(2)
F1	Si1	C1	94.23(8)	C5	C6	C7	122.7(2)
F1	Si1	C12	94.19(8)	C14	C13	C12	122.1(2)
F2	Si1	F1	96.73(8)	N2	C18	C17	113.29(18)
F2	Si1	N2	172.37(8)	N2	C18	C19	120.8(2)
F2	Si1	N1	89.14(7)	C19	C18	C17	125.9(2)
F2	Si1	C1	93.47(8)	C12	C17	C18	114.43(19)
F2	Si1	C12	94.23(9)	C16	C17	C12	123.2(2)
N2	Si1	N1	85.33(7)	C16	C17	C18	122.39(19)
C1	Si1	N2	90.78(8)	N1	C7	C6	113.31(18)
C1	Si1	N1	80.30(8)	N1	C7	C8	120.5(2)
C12	Si1	N2	80.58(9)	C8	C7	C6	126.1(2)
C12	Si1	N1	90.42(8)	C3	C2	C1	122.2(2)
C12	Si1	C1	167.84(10)	C13	C14	C15	121.1(2)

C18	N2	Si1	113.32(14)	C20	C19	C18	119.4(2)
C22	N2	Si1	127.18(15)	C9	C8	C7	119.5(2)
C22	N2	C18	119.47(19)	N2	C22	C21	122.2(2)
C7	N1	Si1	113.59(14)	C17	C16	C15	119.6(2)
C11	N1	Si1	126.64(15)	C6	C5	C4	120.1(2)
C11	N1	C7	119.52(19)	C2	C3	C4	121.3(2)
C15	N4	C25	119.9(2)	C11	C10	C9	118.1(2)
C15	N4	C26	119.8(2)	C22	C21	C20	118.2(2)
C26	N4	C25	118.3(2)	N4	C15	C14	121.4(2)
C4	N3	C23	118.8(2)	N4	C15	C16	120.8(2)
C4	N3	C24	118.0(2)	C14	C15	C16	117.7(2)
C23	N3	C24	114.6(2)	N1	C11	C10	122.8(2)
C6	C1	Si1	117.87(16)	C19	C20	C21	119.9(2)
C2	C1	Si1	125.73(17)	C10	C9	C8	119.5(2)
C2	C1	C6	116.0(2)	N3	C4	C5	121.6(2)
C13	C12	Si1	126.30(17)	N3	C4	C3	121.0(2)
C17	C12	Si1	117.43(16)	C5	C4	C3	117.3(2)
C17	C12	C13	116.1(2)	Cl1	C27	Cl2	113.8(2)

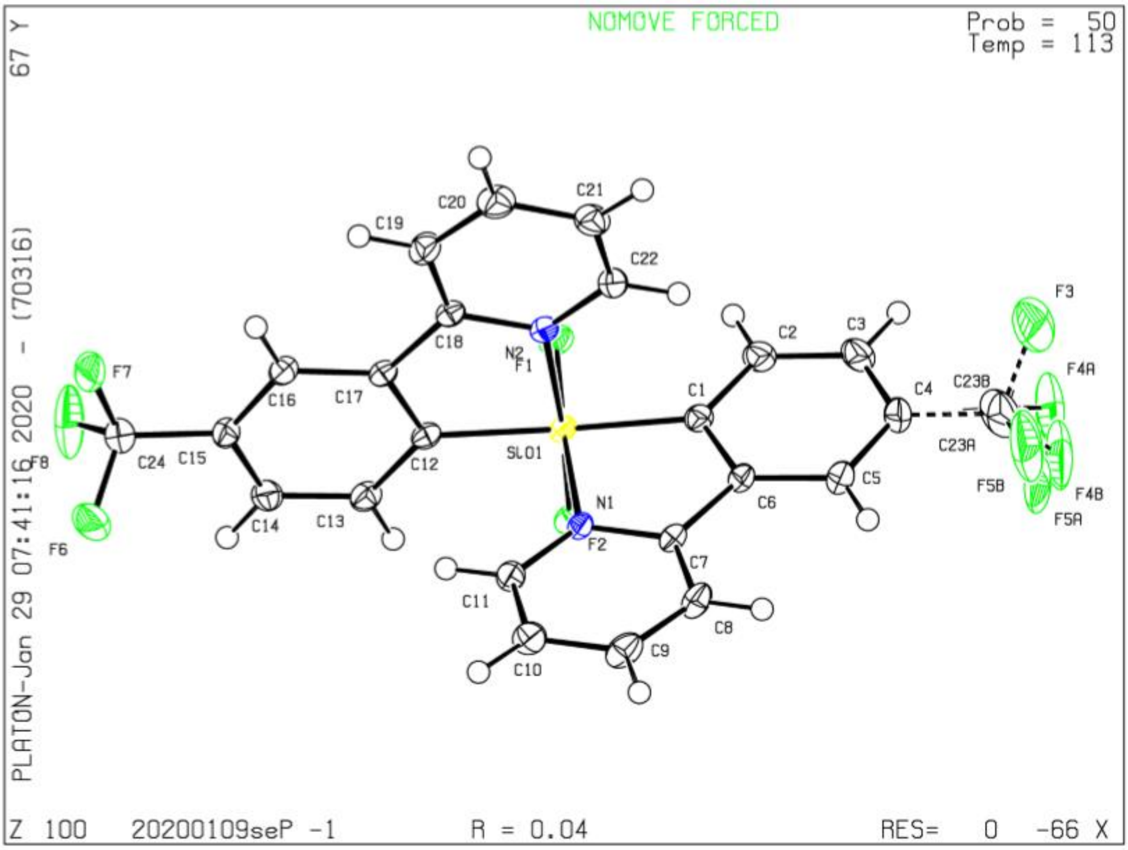
Table S13. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **2b**.

Atom	***x***	***y***	***z***	**U(eq)**
H13	2668.61	2968.06	9126.82	22
H2	2200.91	3590.14	5767.74	24
H14	3783.92	2657.21	10166	24
H19	5384.65	-290.89	7580.99	25
H8	-291.78	-416.09	6853.6	27
H22	2823.07	668.71	5854.89	23
H16	5377.23	679.75	8748.63	21
H5	-270.24	771.86	5769.2	24
H3	1077.24	3522.83	4718.09	28

H10	1164.25	-1256.75	8914.02	33
H21	3946.04	-711.24	5463.03	28
H11	2247.96	253.98	8656.05	25
H20	5247.74	-1188.7	6340.72	30
H9	-154.58	-1559.74	8013.97	32
H23A	-1266.28	753.06	4766.91	46
H23B	-1686.57	1532.26	4050.17	46
H23C	-1647.31	2078.37	4903.07	46
H25A	6362.1	277.24	9898.5	46
H25B	6804.19	1263.63	10486.04	46
H25C	6587.26	1592.47	9594.77	46
H26A	5344.31	2960.1	10912.76	50
H26B	5772.41	1787.58	11335.17	50
H26C	4675.77	1876.38	11114.03	50
H24A	-563.5	3776.33	4070.3	61
H24B	-789.49	2800.66	3407.61	61
H24C	268.19	3094.53	3693.41	61
H27A	1757.96	5906.66	7521.3	62
H27B	2714.04	5173.47	7553.92	62

6-3. X-ray Structure of compound 2c

A single crystal of 6,6-difluoro-9,9'-bis(trifluoromethyl)-6H-5l4,5'l4,6l6-6,6'-spirobi[benzo[3,4][1,2]azasilolo[1,5-a]pyridine] ($C_{24}H_{14}F_8N_2Si$) (**2c**) was prepared by recrystallization from the dichloromethane solution. A suitable crystal was selected, and the X-ray diffraction was collected on a XtaLAB AFC10 (RCD3): fixed-chi single diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073A). The crystal was kept at 113 K during data collection. The data were collected using ω scan in the θ range of $4.072 \leq \theta \leq 54.97$ deg. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods, and expanded using Fourier techniques. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F2 was based on 15251 observed reflections and 4932 variable parameters. Neutral atom scattering factors were taken from Cromer and Waber. All calculations were performed using the Olex-2 crystallographic software package except for refinement, which was performed using SHELXL-97.5 Details of final refinement as well as the bond lengths and angles are summarized in the supporting information, and the numbering scheme employed is also shown in the supporting information, which were drawn with ORTEP at 50% probability ellipsoid.



Crystal structure determination of 2c

Crystal Data for $C_{24}H_{14}F_8N_2Si$ (M =510.46 g/mol): triclinic, space group P-1 (no. 2), a = 7.8983(2) Å, b = 10.1395(3) Å, c = 14.2203(4) Å, α = 80.924(2)°, β = 74.043(2)°, γ = 85.365(2)°, V = 1080.40(5) Å^3, Z = 2, T = 113 K, μ(MoKα) = 0.194 mm^{-1}, $Dcalc$ = 1.569 g/cm^3, 15251 reflections measured (4.072° ≤ 2Θ ≤ 54.97°), 4932 unique (R_{int} = 0.0318, R_{sigma} = 0.0274) which were used in all calculations. The final R_1 was 0.0449 (I > 2σ(I)) and wR_2 was 0.1202 (all data).

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

Identification code	6,6-difluoro-9,9'-bis(trifluoromethyl)-6H-5l4,5'l4,6l6-6,6'-spirobi[benzo[3,4][1,2]azasilolo[1,5-a]pyridine]
Empirical formula	$C_{24}H_{14}F_8N_2Si$
Formula weight	510.46
Temperature/K	113
Crystal system	triclinic
Space group	P-1
a/Å	7.8983(2)
b/Å	10.1395(3)
c/Å	14.2203(4)
α/°	80.924(2)
β/°	74.043(2)
γ/°	85.365(2)
Volume/Å^3	1080.40(5)
Z	2
ρ_{calc}g/cm^3	1.569
μ/mm^{-1}	0.194
F(000)	516.0
Crystal size/mm^3	0.2 × 0.2 × 0.2
Radiation	MoKα (λ = 0.71073)
2θrange for data collection/°	4.072 to 54.97
Index ranges	$-10 \leq h \leq 10$, $-13 \leq k \leq 13$, $-18 \leq l \leq 18$
Reflections collected	15251
Independent reflections	4932 [R_{int} = 0.0318, R_{sigma} = 0.0274]
Data/restraints/parameters	4932/15/344
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0449, wR_2 = 0.1152
Final R indexes [all data]	R_1 = 0.0512, wR_2 = 0.1202

Largest diff. peak/hole / e Å^{-3} 0.43/-0.58

Table S15. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **2c**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
Si01	1927.8(5)	4862.6(4)	2451.2(3)	14.46(12)
F2	1734.1(12)	3721.3(9)	1770.8(7)	18.2(2)
F1	-201.5(12)	5255.8(10)	2856.2(7)	20.5(2)
F6	3281.3(17)	96.7(12)	6124.3(9)	37.8(3)
F7	2142(2)	1618.9(12)	7004.1(8)	43.2(3)
F8	487.3(19)	297.5(16)	6663.7(11)	56.6(4)
N1	4639.3(17)	4634.7(13)	1965.2(9)	14.3(3)
N2	2525.9(17)	6143.3(13)	3343.1(10)	15.9(3)
F3	3215(3)	10591.0(13)	-837.9(12)	67.2(5)
C18	2498.4(19)	5537.0(15)	4264.6(11)	15.8(3)
C17	2151.2(19)	4101.6(15)	4421.4(11)	15.3(3)
C7	5370(2)	5499.9(15)	1156.8(11)	15.5(3)
C11	5684(2)	3734.6(16)	2360.5(12)	18.1(3)
C12	1923.5(19)	3608.7(15)	3605.3(11)	15.7(3)
C13	1647(2)	2244.9(16)	3701.8(12)	18.6(3)
C6	4078(2)	6437.7(15)	807.0(11)	16.8(3)
C1	2339(2)	6285.6(16)	1378.7(12)	17.2(3)
C22	2915(2)	7436.9(16)	3092.9(13)	20.2(3)
C19	2813(2)	6236.9(17)	4957.5(13)	22.0(3)
C15	1882(2)	1929.2(16)	5373.5(12)	19.2(3)
C16	2131(2)	3280.0(16)	5310.7(12)	18.1(3)
C14	1633(2)	1409.9(16)	4573.0(13)	21.0(3)
C8	7178(2)	5477.7(18)	737.6(12)	21.4(3)
C2	1049(2)	7176.6(17)	1107.9(13)	23.1(4)
C10	7487(2)	3673.8(18)	1989.3(13)	21.8(3)

C20	3234(2)	7564.7(18)	4688.5(14)	25.5(4)
C9	8244(2)	4566.9(19)	1163.5(13)	24.0(4)
C5	4546(2)	7430.7(17)	-6.9(12)	22.6(3)
C21	3307(2)	8173.3(17)	3735.4(13)	23.9(4)
C24	1933(2)	1003.8(17)	6292.3(13)	24.7(4)
C4	3237(3)	8300.9(18)	-242.8(13)	28.2(4)
C3	1494(3)	8175.4(19)	306.1(14)	29.3(4)
F4A	2367(9)	9418(5)	-1627(4)	60.6(14)
C23B	3540(13)	9412(7)	-1117(5)	28.6(18)
F5A	5097(7)	9200(6)	-1719(3)	62(2)
C23A	3890(16)	9398(10)	-1058(8)	46(3)
F5B	5571(5)	9738(7)	-1313(6)	67(2)
F4B	3516(17)	9259(4)	-1891(4)	76(4)

Table S16. Anisotropic Displacement Parameters ($Å^2×10^3$) for **2c**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U11**	**U22**	**U33**	**U23**	**U13**	**U12**
Si01	13.2(2)	17.5(2)	11.8(2)	-2.18(16)	-2.06(15)	-0.09(15)
F2	18.7(5)	22.0(5)	15.2(5)	-4.8(4)	-5.2(4)	-0.9(4)
F1	13.9(4)	27.7(5)	18.7(5)	-4.9(4)	-2.0(4)	1.4(4)
F6	52.7(8)	30.2(6)	31.8(6)	-4.6(5)	-18.6(6)	17.3(5)
F7	83.4(10)	27.9(6)	17.4(6)	-2.3(5)	-15.9(6)	9.8(6)
F8	44.8(8)	67.2(10)	49.3(8)	39.5(7)	-18.1(6)	-26.8(7)
N1	14.3(6)	16.9(6)	11.1(6)	-1.8(5)	-2.8(5)	-0.3(5)
N2	16.1(6)	16.1(6)	14.3(6)	-3.4(5)	-1.8(5)	0.1(5)
F3	116.6(15)	22.4(6)	52.4(9)	4.4(6)	-8.3(9)	-12.3(8)
C18	13.3(7)	18.0(7)	14.7(7)	-3.4(6)	-1.1(5)	0.1(5)
C17	13.0(7)	17.6(7)	13.7(7)	-2.9(6)	-0.5(5)	-0.3(5)
C7	16.3(7)	18.9(7)	11.1(7)	-3.0(6)	-2.6(6)	-1.7(6)
C11	16.4(7)	20.6(7)	16.4(8)	-1.2(6)	-4.0(6)	1.2(6)
C12	11.7(7)	18.9(7)	14.7(7)	-3.2(6)	0.1(5)	-1.0(5)

C13	18.9(7)	19.3(8)	17.0(8)	-4.3(6)	-2.0(6)	-3.9(6)
C6	20.5(8)	17.9(7)	11.7(7)	-2.2(6)	-3.8(6)	-0.5(6)
C1	19.5(8)	18.5(7)	14.2(7)	-4.0(6)	-5.4(6)	2.3(6)
C22	22.5(8)	16.8(7)	18.6(8)	-1.5(6)	-1.6(6)	-0.9(6)
C19	26.8(8)	23.5(8)	16.2(8)	-4.1(6)	-5.4(6)	-1.5(7)
C15	18.3(7)	19.7(8)	16.1(8)	0.5(6)	-1.3(6)	0.9(6)
C16	18.5(7)	20.3(8)	14.3(7)	-2.8(6)	-2.7(6)	0.6(6)
C14	22.1(8)	16.4(7)	21.8(8)	-2.0(6)	-1.4(6)	-2.4(6)
C8	17.7(8)	29.8(9)	14.7(8)	-0.6(6)	-1.3(6)	-4.0(6)
C2	24.2(8)	24.5(8)	20.7(8)	-4.8(7)	-7.6(7)	7.2(7)
C10	17.4(8)	27.9(9)	20.7(8)	-3.8(7)	-7.3(6)	3.1(6)
C20	30.7(9)	23.0(8)	25.0(9)	-9.5(7)	-7.2(7)	-3.6(7)
C9	13.0(7)	37.6(10)	20.2(8)	-5.2(7)	-2.0(6)	-0.9(6)
C5	28.6(9)	21.9(8)	14.8(8)	-0.4(6)	-2.6(6)	-1.6(7)
C21	26.9(9)	17.5(8)	26.4(9)	-5.6(7)	-3.9(7)	-2.5(6)
C24	29.0(9)	20.9(8)	21.7(9)	0.5(7)	-4.9(7)	-0.3(7)
C4	44.1(11)	21.6(8)	16.7(9)	0.9(7)	-8.4(8)	4.7(7)
C3	38.6(10)	25.0(9)	24.7(9)	-3.4(7)	-13.4(8)	13.3(7)
F4A	84(3)	56(2)	43(2)	27.9(17)	-35(2)	-12(2)
C23B	41(3)	20(3)	17(3)	11(2)	-5(2)	9(2)
F5A	59(3)	60(3)	37(2)	32(2)	13(2)	6(2)
C23A	67(7)	39(4)	40(5)	-2(3)	-34(5)	15(4)
F5B	52(2)	60(3)	67(4)	44(3)	-7(2)	-12.3(19)
F4B	180(11)	30.8(19)	28(2)	11.5(16)	-48(4)	-25(4)

Table S17. Bond Lengths for **2c**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Si01	F2	1.6619(10)	C12	C13	1.397(2)
Si01	F1	1.6585(10)	C13	C14	1.384(2)
Si01	N1	2.0674(13)	C6	C1	1.398(2)
Si01	N2	2.1133(14)	C6	C5	1.395(2)

Si01	C12	1.9103(16)	C1	C2	1.400(2)
Si01	C1	1.9033(17)	C22	C21	1.377(2)
F6	C24	1.345(2)	C19	C20	1.382(2)
F7	C24	1.322(2)	C15	C16	1.385(2)
F8	C24	1.333(2)	C15	C14	1.393(2)
N1	C7	1.350(2)	C15	C24	1.492(2)
N1	C11	1.342(2)	C8	C9	1.381(2)
N2	C18	1.352(2)	C2	C3	1.386(3)
N2	C22	1.341(2)	C10	C9	1.387(2)
F3	C23B	1.302(8)	C20	C21	1.386(3)
F3	C23A	1.330(11)	C5	C4	1.382(3)
C18	C17	1.474(2)	C4	C3	1.389(3)
C18	C19	1.386(2)	C4	C23B	1.519(6)
C17	C12	1.393(2)	C4	C23A	1.485(10)
C17	C16	1.397(2)	F4A	C23B	1.325(10)
C7	C6	1.472(2)	C23B	F5A	1.314(8)
C7	C8	1.388(2)	C23A	F5B	1.334(11)
C11	C10	1.376(2)	C23A	F4B	1.328(11)

Table S18. Bond Angles for **2c**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
F2	Si01	N1	89.47(5)	C2	C1	Si01	125.66(13)
F2	Si01	N2	171.23(5)	N2	C22	C21	122.59(16)
F2	Si01	C12	94.95(6)	C20	C19	C18	119.33(16)
F2	Si01	C1	94.63(6)	C16	C15	C14	120.65(15)
F1	Si01	F2	97.34(5)	C16	C15	C24	120.20(15)
F1	Si01	N1	172.24(5)	C14	C15	C24	119.12(15)
F1	Si01	N2	90.35(5)	C15	C16	C17	118.34(15)
F1	Si01	C12	92.81(6)	C13	C14	C15	119.96(15)
F1	Si01	C1	94.41(6)	C9	C8	C7	119.32(15)
N1	Si01	N2	83.16(5)	C3	C2	C1	120.92(17)

C12	Si01	N1	90.32(6)
C12	Si01	N2	80.39(6)
C1	Si01	N1	81.26(6)
C1	Si01	N2	88.96(6)
C1	Si01	C12	167.17(7)
C7	N1	Si01	113.86(10)
C11	N1	Si01	126.98(11)
C11	N1	C7	119.15(13)
C18	N2	Si01	113.42(10)
C22	N2	Si01	127.61(11)
C22	N2	C18	118.97(14)
N2	C18	C17	113.25(13)
N2	C18	C19	121.21(14)
C19	C18	C17	125.53(15)
C12	C17	C18	115.24(14)
C12	C17	C16	122.30(14)
C16	C17	C18	122.40(14)
N1	C7	C6	113.45(13)
N1	C7	C8	121.03(15)
C8	C7	C6	125.50(14)
N1	C11	C10	122.65(15)
C17	C12	Si01	117.45(12)
C17	C12	C13	117.72(15)
C13	C12	Si01	124.79(12)
C14	C13	C12	121.01(15)
C1	C6	C7	114.48(14)
C5	C6	C7	123.14(15)
C5	C6	C1	122.35(15)
C6	C1	Si01	116.86(12)
C6	C1	C2	117.47(15)
C11	C10	C9	118.36(15)
C19	C20	C21	119.25(16)
C8	C9	C10	119.46(15)
C4	C5	C6	118.39(16)
C22	C21	C20	118.58(16)
F6	C24	C15	111.52(14)
F7	C24	F6	105.75(15)
F7	C24	F8	107.30(16)
F7	C24	C15	113.39(14)
F8	C24	F6	105.54(15)
F8	C24	C15	112.78(15)
C5	C4	C3	120.81(16)
C5	C4	C23B	124.4(4)
C5	C4	C23A	114.2(5)
C3	C4	C23B	114.8(4)
C3	C4	C23A	124.8(5)
C2	C3	C4	120.05(17)
F3	C23B	C4	112.0(5)
F3	C23B	F4A	100.6(6)
F3	C23B	F5A	116.7(6)
F4A	C23B	C4	111.6(5)
F5A	C23B	C4	108.6(6)
F5A	C23B	F4A	106.9(6)
F3	C23A	C4	112.6(7)
F3	C23A	F5B	95.7(7)
F5B	C23A	C4	121.0(8)
F4B	C23A	F3	106.1(8)
F4B	C23A	C4	113.1(8)
F4B	C23A	F5B	106.2(8)

Table S19. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **2c**.

Atom	***x***	***y***	***z***	**U(eq)**
H11	5157.14	3114.43	2919.09	22
H13	1465.54	1885.11	3160.95	22
H22	2920.04	7861.8	2447.07	24
H19	2740.5	5808.27	5610.74	26
H16	2283.65	3639.06	5858.54	22
H14	1453.15	483.02	4625.15	25
H8	7677.15	6082.91	163.47	26
H2	-147.11	7095.82	1478.65	28
H10	8195.82	3035.59	2291.38	26
H20	3471.87	8054.9	5151.84	31
H9	9486.33	4552.35	892.98	29
H5	5736.21	7506.75	-389.62	27
H21	3619.51	9079.18	3529.73	29
H3	604.56	8774.49	132.07	35

7. Computational Studies

All quantum chemical calculations were conducted by employing the Gaussian 16 rev. B.01 program package.[14] B3LYP[15] functional and 6-31G(d)[16] basis set were used for the optimization in the gas phase. For TD-DFT, B3LYP functional and 6-31G(d) basis set were used.

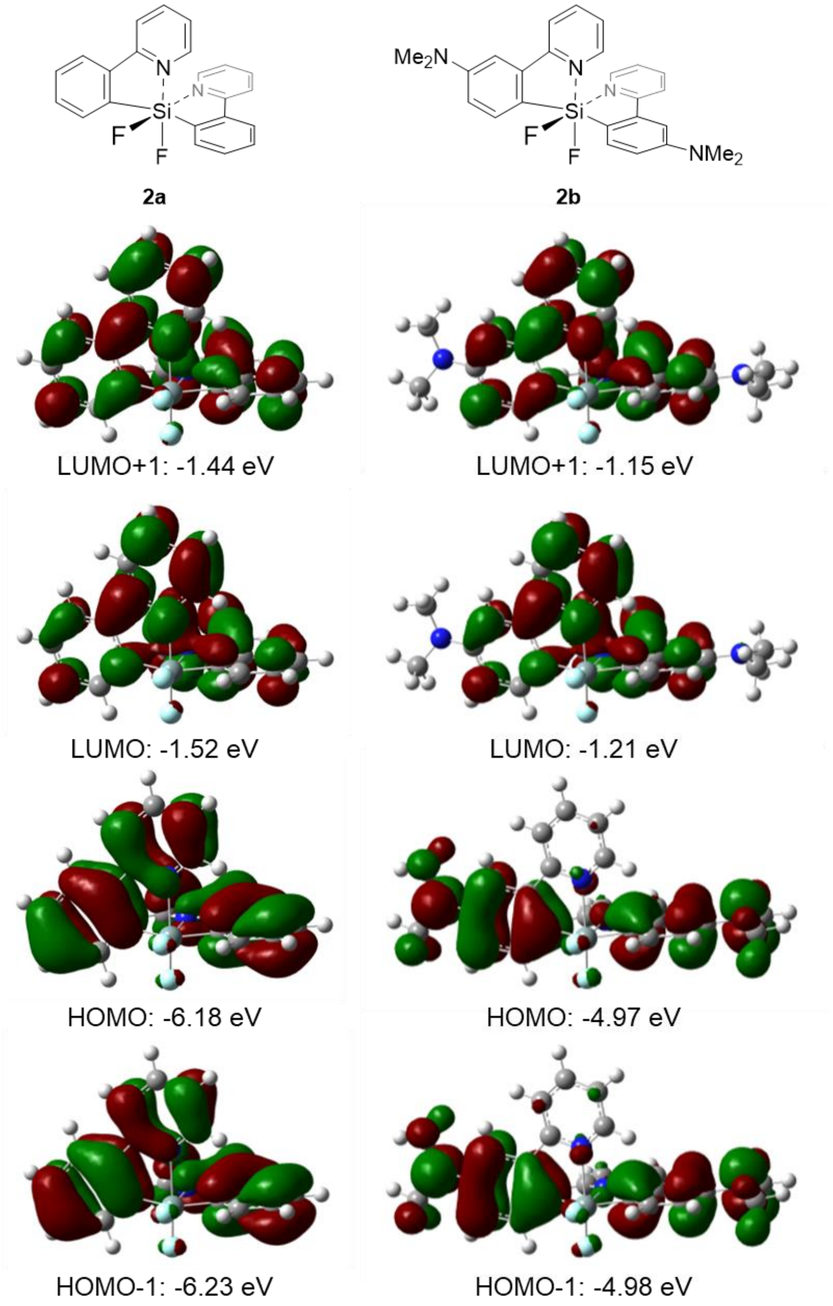


Figure S4. Distributions and energy levels of **2a** and **2b** calculated using B3LYP/6-31G(d) in the gas phase.

Table S20. Transition energies (E), oscillator strengths (f), and orbital assignments for **2b** in the gas phase.

State	λ_{cal} [nm]	ΔE [eV]	Oscillator strength (f)	Assignment	
1	390	3.18	0.0147	HOMO → LUMO	0.67836
				HOMO-1 → LUMO+1	0.1847
2	387	3.20	0.0266	HOMO-1 → LUMO	0.67407
				HOMO → LUMO+1	0.19837
3	381	3.257	0.0123	HOMO-1 → LUMO	-0.20149
				HOMO → LUMO+1	0.67309
4	380	3.265	0.0139	HOMO-1 → LUMO+1	0.6773
				HOMO → LUMO	-0.18716
5	339	3.66	0.016	HOMO-1 → LUMO+3	-0.25484
				HOMO → LUMO+2	0.64966

8. NMR Spectra

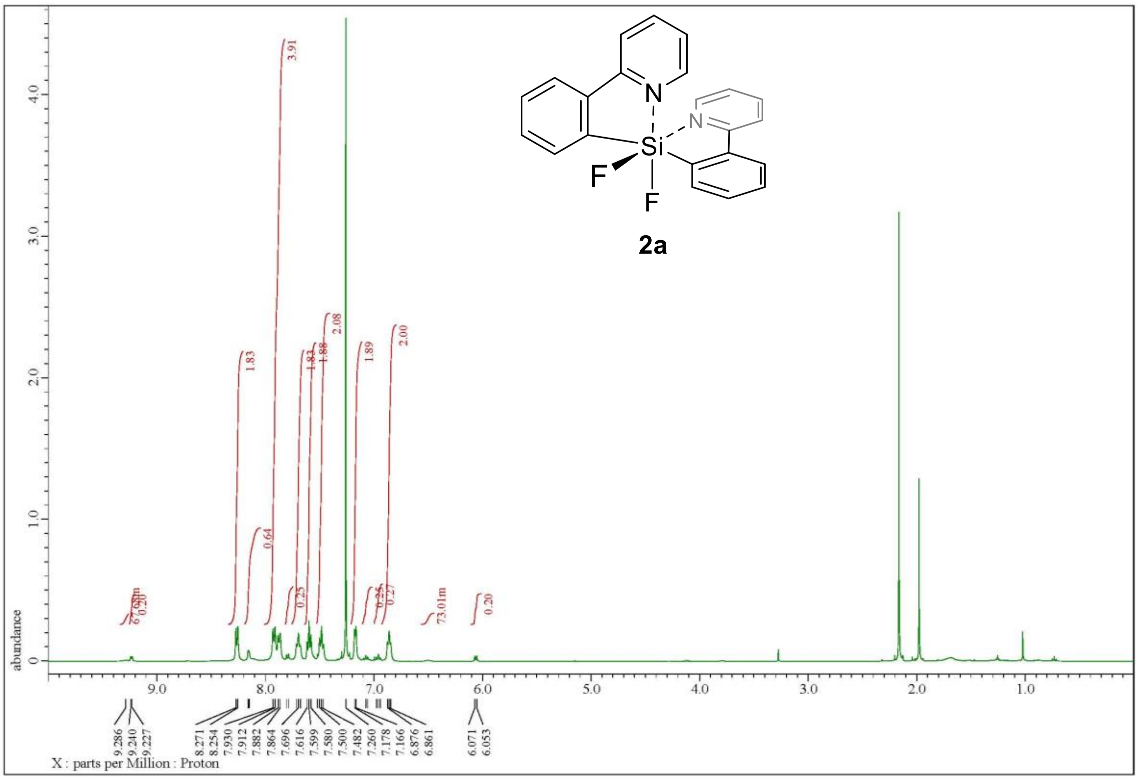


Figure S5. ^{1}H NMR of **2a** in $CDCl_3$.

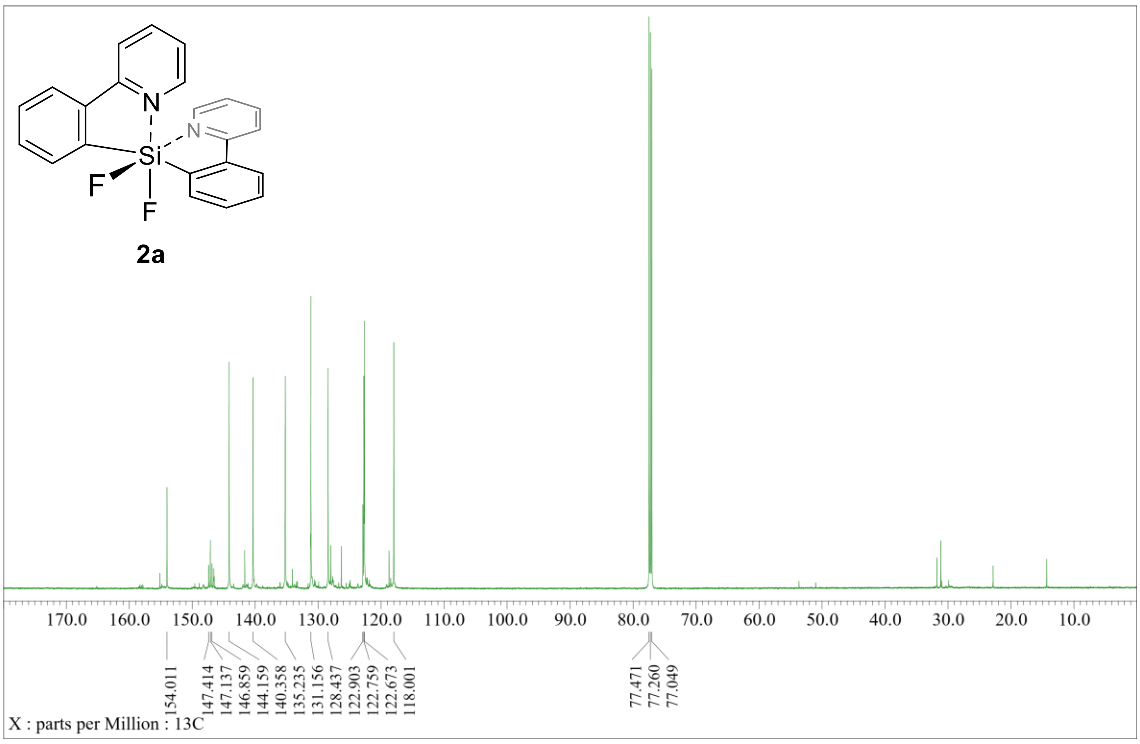


Figure S6. ^{13}C NMR of **2a** in $CDCl_3$.

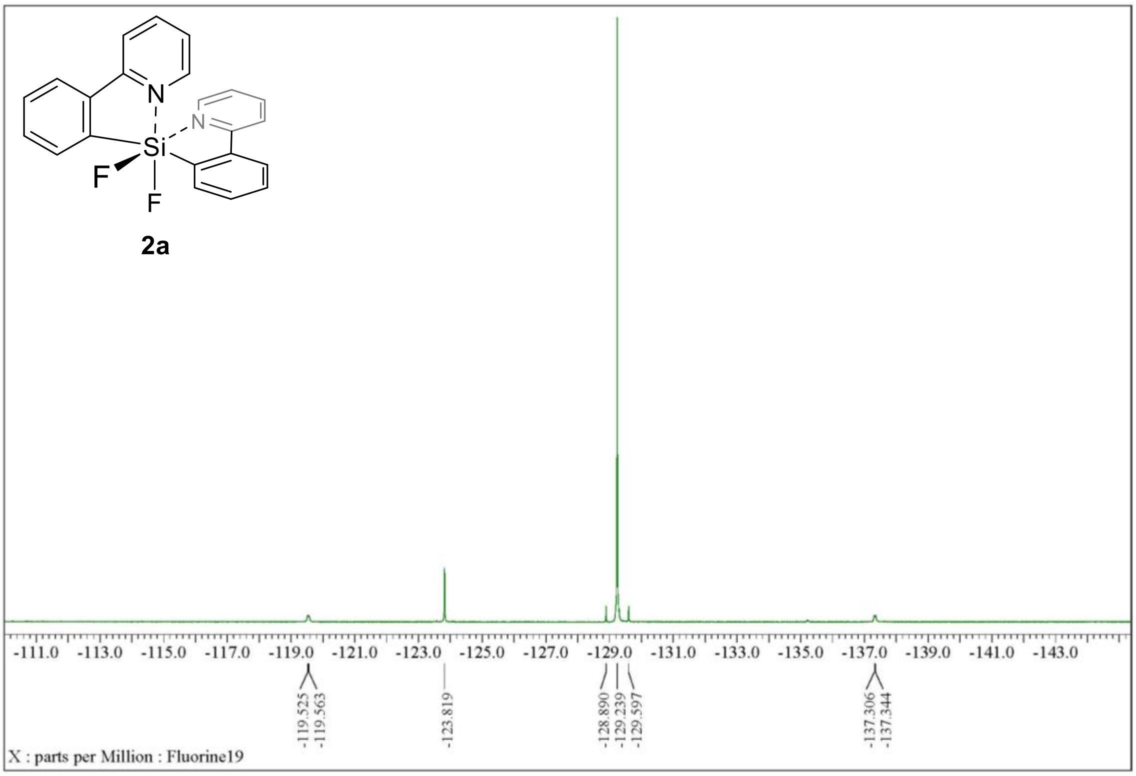


Figure S7. ^{19}F NMR of **2a** in $CDCl_3$.

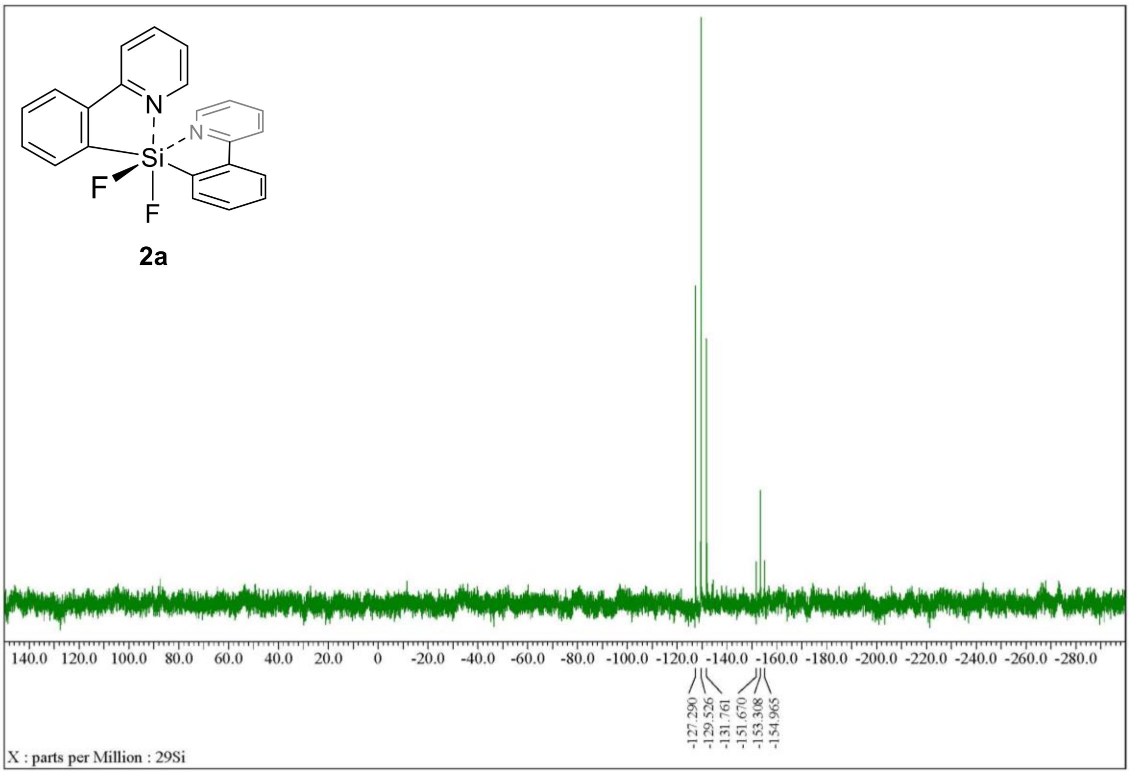


Figure S8. ^{29}Si NMR of **2a** in $CDCl_3$.

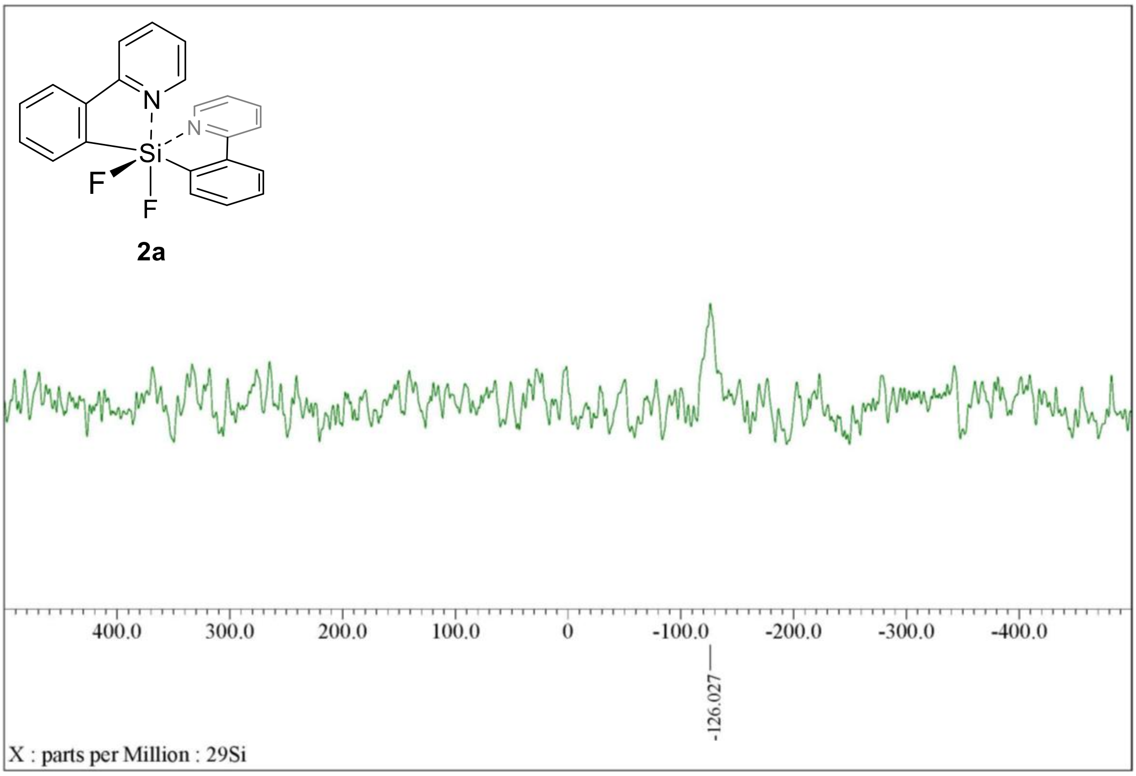


Figure S9. ^{29}Si CP/MAS NMR of **2a** in a solid state.

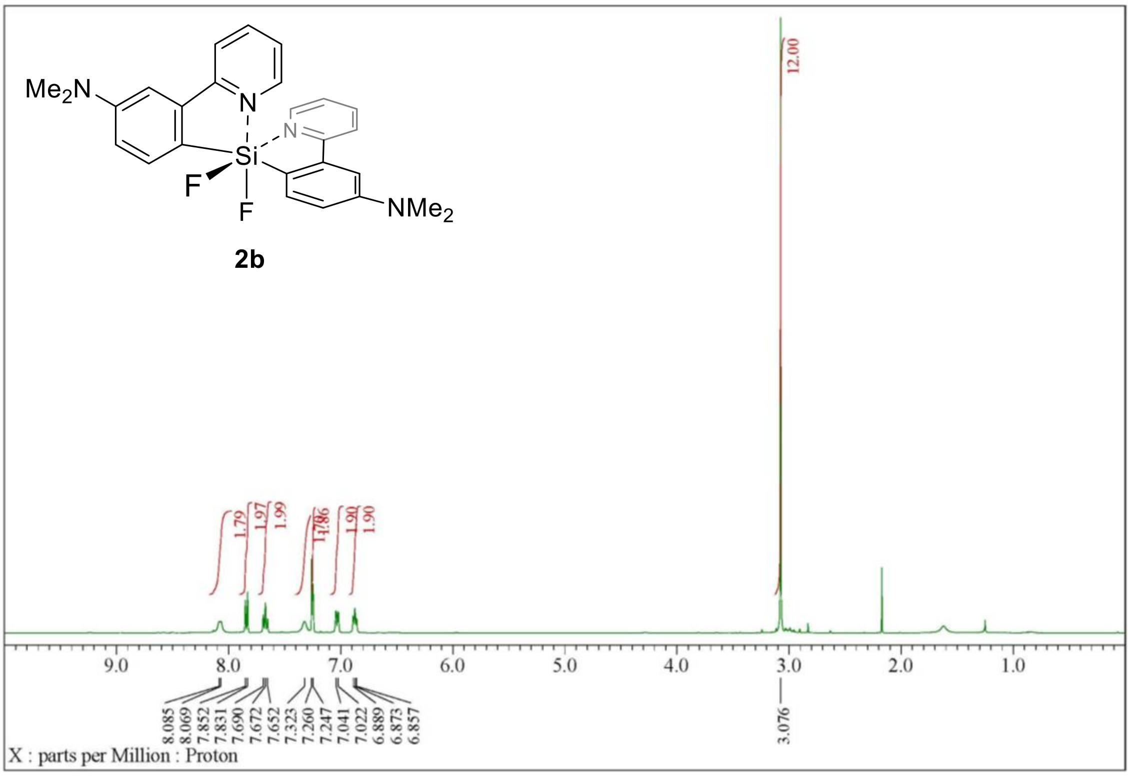


Figure S10. ^{1}H NMR of **2b** in $CDCl_3$.

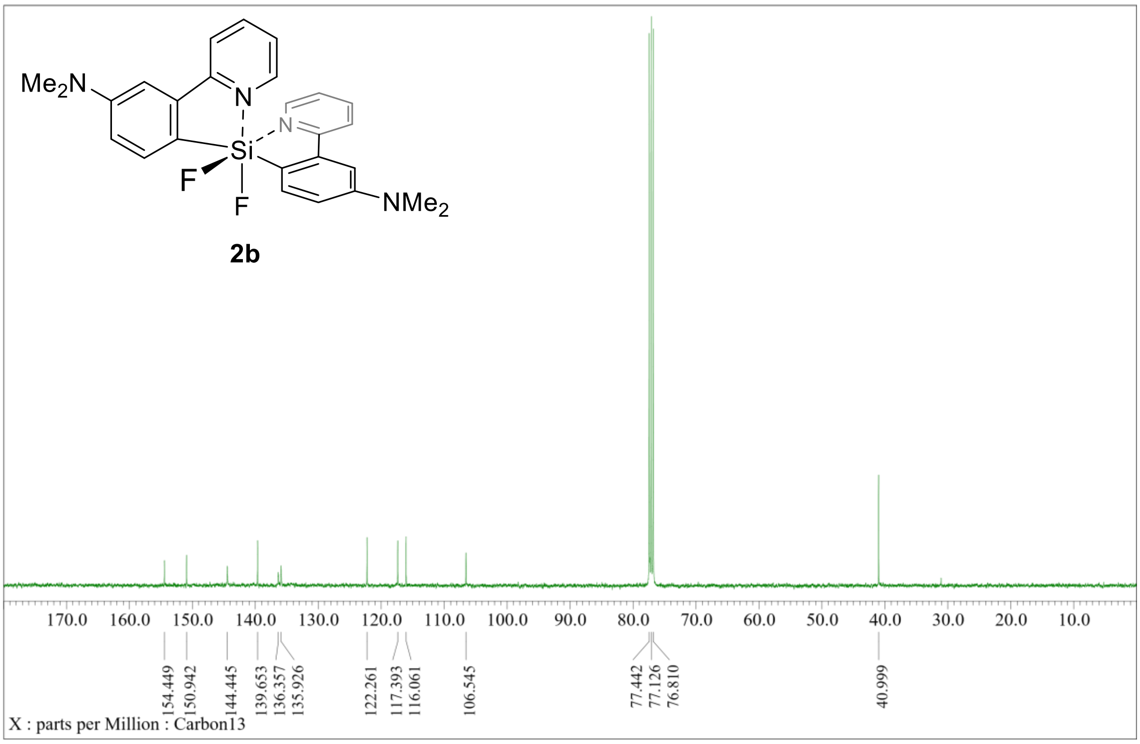


Figure S11. ^{13}C NMR of **2b** in $CDCl_3$.

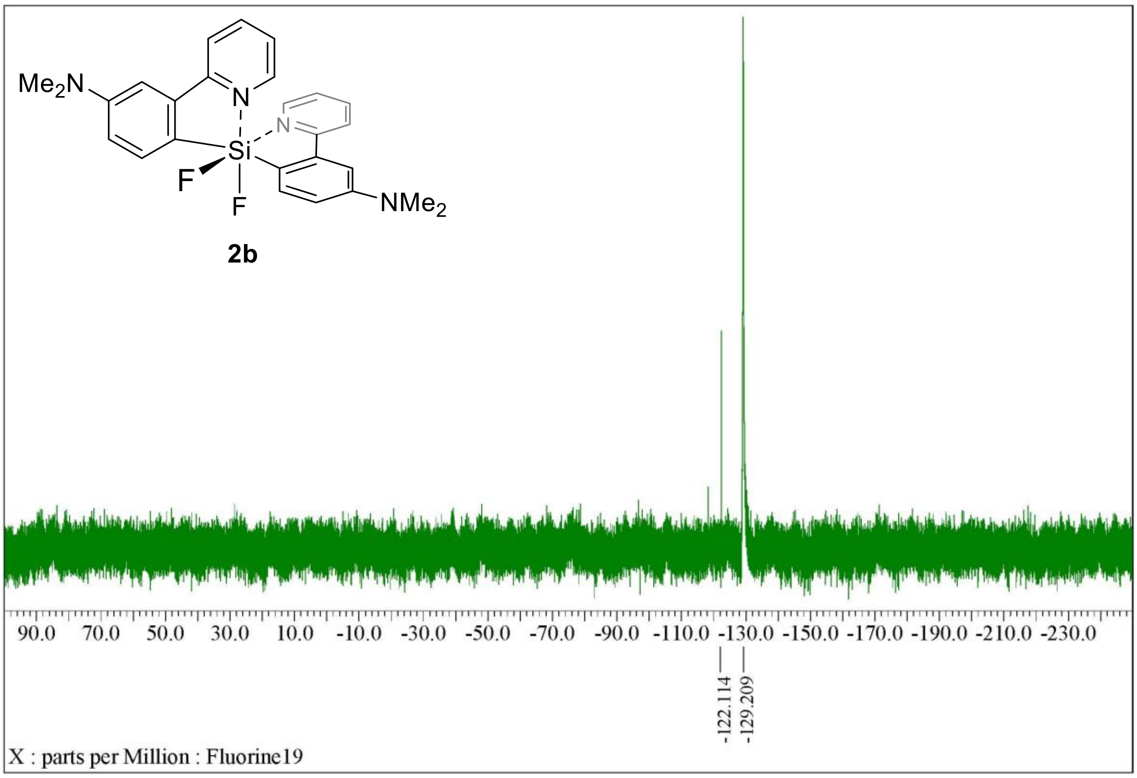


Figure S12. ^{19}F NMR of **2b** in $CDCl_3$.

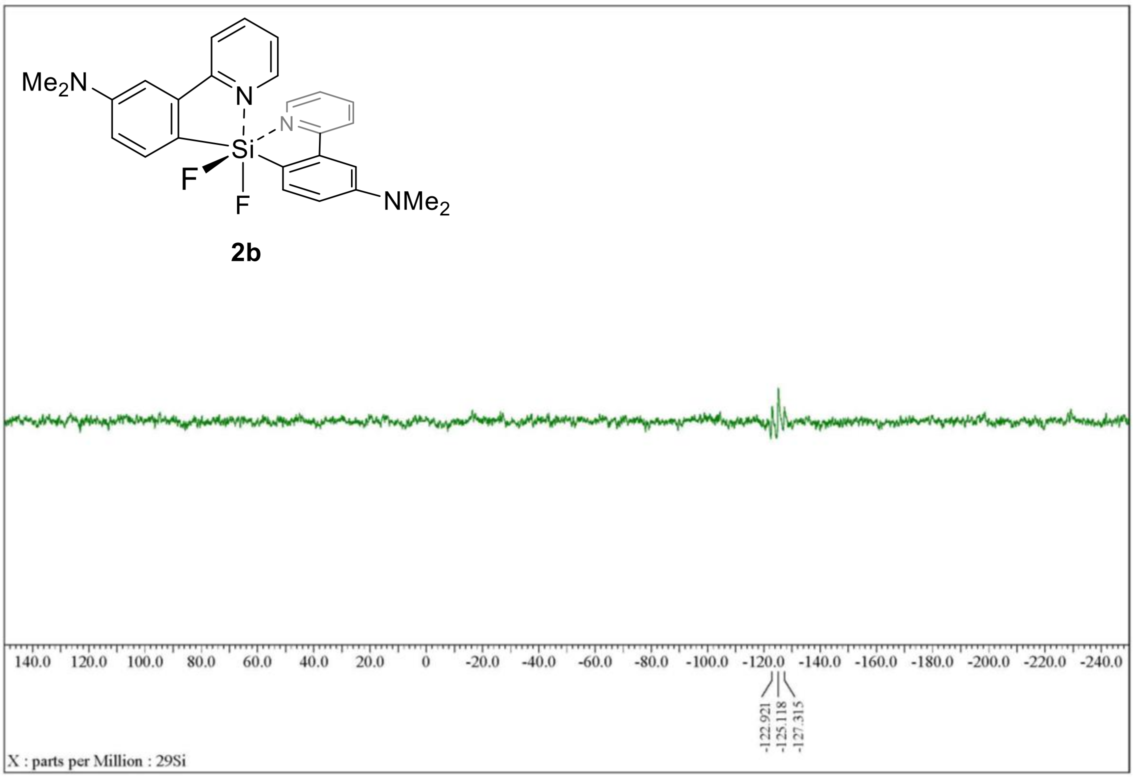


Figure S13. ^{29}Si NMR of **2b** in CDCl₃.

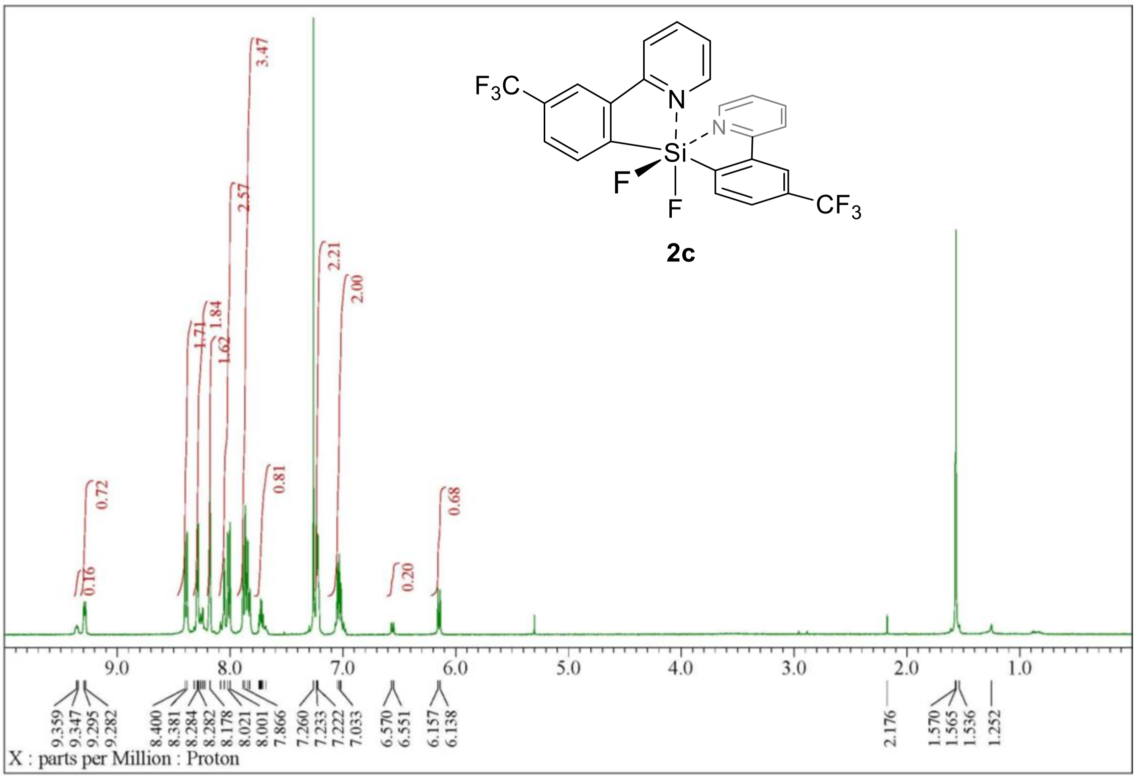


Figure S14. ^{1}H NMR of **2c** in CDCl₃.

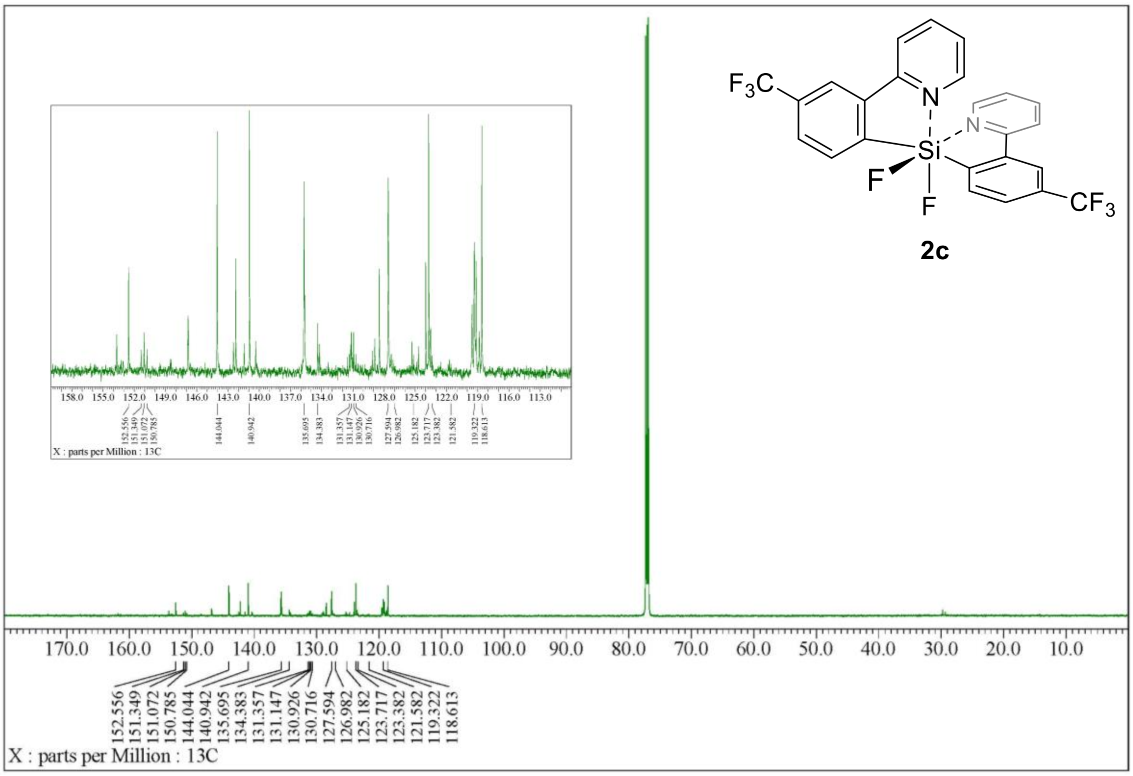


Figure S15. ^{13}C NMR of **2c** in CDCl$_3$.

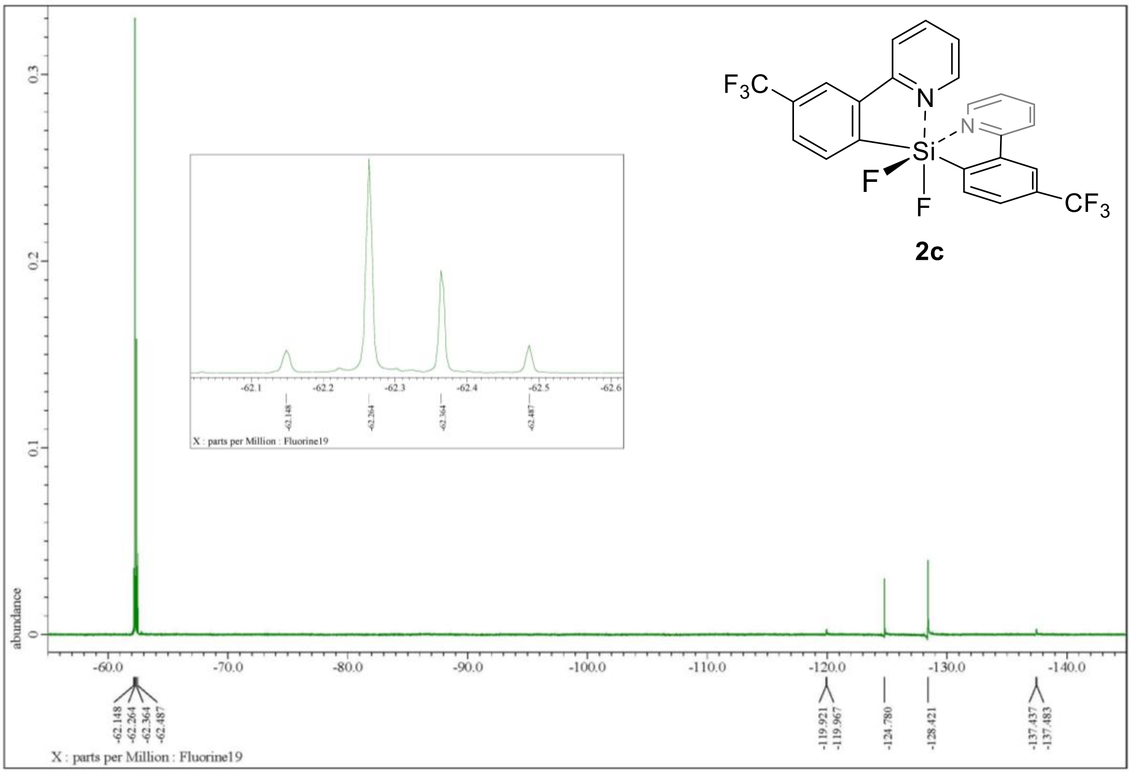


Figure S16. ^{19}F NMR of **2c** in CDCl$_3$.

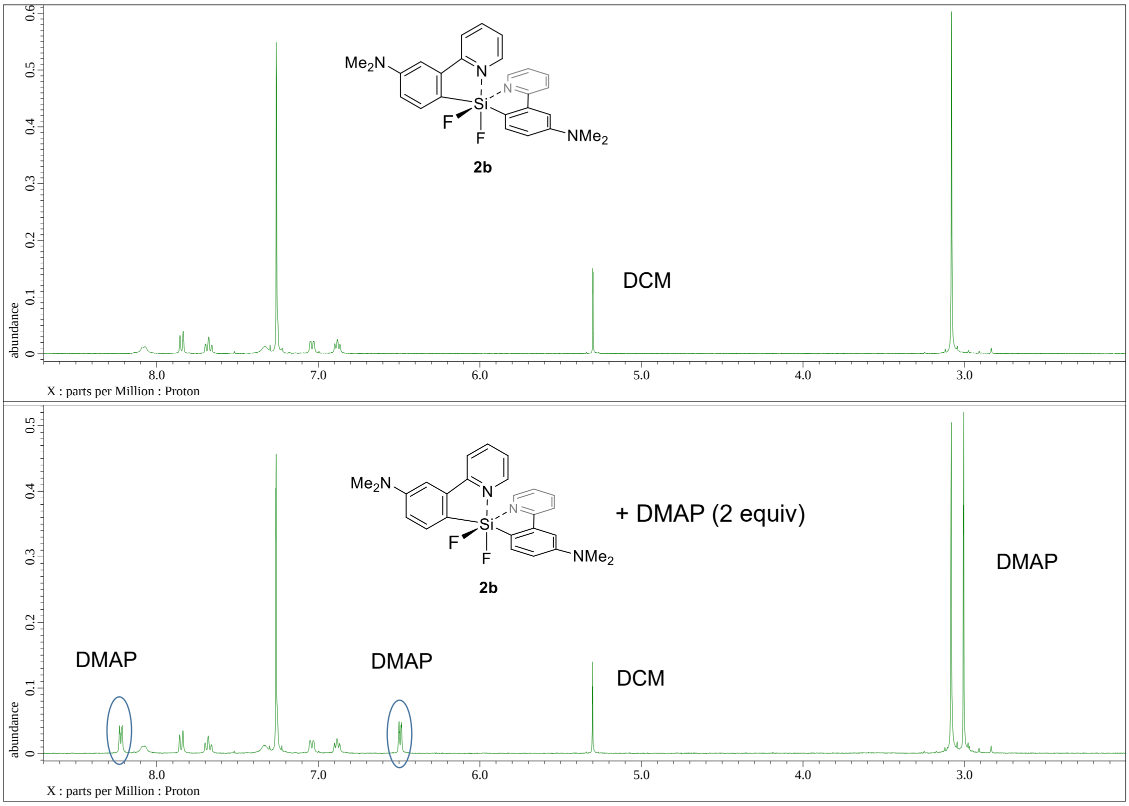


Figure S17. ^{1}H NMR of **2b** and a mixture of **2b** and DMAP in $CDCl_3$.

9. References

1) D. Kalyani, A. R. Dick, W. Q. Anani, and M. S. Sanford, *Tetrahedron*, 2006, **62**, 11483–11489.

2) A. J. Peterson, C. J. Heron, C. L. Mcmullin, M. F. Mahon, N. Press, and C. G. Frost, *Org. Biomol. Chem.*, 2017, **15**, 5993–5998.

3) N. Yoshikai, S. Asako, T. Yamakawa, L. Ilies, and E. Nakamura, *Chem. Asian J.*, 2011, **6**, 3059–3065.

4) O. E. Alawode, V. K. Naganaboina, T. Liyanage, J. Desper, and S. Rayat, *Org. Lett.*, 2014, **16**, 1494–1497.

5) J. T. Gozdali, P. H. Marek, I. D. Madura, B. Gierczyk, Ł. Popenda, G. Schroeder, A. Adamczyk-Woźniak, and A. Sporzyński, *J. Mol. Struct.*, 2019, **1180**, 237–241.

6) C. Zhang, X. M. Chen, Y. Luo, J. L. Li, M. Chen, L. Hai and Y. Wu, *ACS Sustainable Chem. Eng.*, 2018, ***6***, 13473–13481.

7) K. Billingsley and S. L. Buchwald, *Angew. Chem. Int. Ed.*, 2008, **47**, 4695–2698.

8) D. Kalyani, A. R. Dick, W. Q. Anani, and M. S. Sanford, *Org. Lett.*, 2006, ***8***, 2523–2526.

9) Z. J. Du, L. X. Gao, Y. J. Lin and F. S. Han, *ChemCatChem*, 2014, **6**, 123–126.

10) SIR2008: M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, D. Siliqi and R. Spagna, *J. Appl. Crystallogr.*, 2007, **40,** 609–613.

11) DIRDIF99: P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, The DIRDIF-99 program system; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1999.

12) D. T. Cromer and J. T. Waber, International Tables for X-ray Crystallography; Kynoch Press: Birmingham, U.K., 1974, Vol. 4

13) Olex2 program package: O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

14) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian,

J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 16*, Revision B.01, Gaussian, Inc., Wallingford CT, 2016.

15) (*a*) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652; (*b*) C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789.

16) (*a*) R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724–728; (*b*) A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, 1980, **72**, 5639–5648.