

Supporting Information for

Synthesis of Benzo[*h*]quinoline-Based Neutral Pentacoordinate Organosilicon Complexes

Yuichiro Tokoro, Hyeonuk Yeo, Kazuo Tanaka, and Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

chujo@chujo.synchem.kyoto-u.ac.jp.

Experimental Details

Measurements. ^1H (400 MHz), ^{13}C (100 MHz), and ^{11}B (128 MHz) NMR spectra were recorded on a JEOL JNM-EX400 spectrometer. ^1H and ^{13}C NMR spectra used tetramethylsilane (TMS) as an internal standard. ^{29}Si NMR spectra were referenced externally to TMS in CDCl_3 . UV-vis spectra were recorded on a Shimadzu UV-3600 spectrophotometer. Fluorescence emission spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrofluorometer. X-ray crystallographic analysis was carried out by a Rigaku R-Axis RAPID-F graphite-monochromated $\text{Mo K}\alpha$ radiation diffractometer with an imaging plate. A symmetry related absorption correction was carried out by using the program ABSCOR.¹ The analysis was carried out with direct methods (SHELX-97² or SIR97³) using Yadokari-XG.⁴ The program ORTEP3⁵ was used to generate the X-ray structural diagram. Molecular orbital calculations were performed using Gaussian 09. Elemental analysis was performed at the Microanalytical Center of Kyoto University. All reactions were performed under nitrogen or argon atmosphere.

Materials. Tetrahydrofuran (THF), diethyl ether, and triethylamine (Et_3N) were purified using a two-column solid-state purification system (Glasscontour System, Joerg Meyer, Irvine, CA). 10-Bromobenzo[*h*]quinoline,⁶ chlorodiethoxymethylsilane,⁷ and 2-iodo-1,4-bis(trifluoromethyl)benzene⁸ were prepared according to the literature. Other reagents were commercially available and used as received.

Synthesis of 10-trimethylsilylbenzo[*h*]quinoline (1C). 6.25 mL (1.6 M in hexane, 10.0 mmol) of *n*-BuLi was slowly added to a solution of 10-bromobenzo[*h*]quinoline (2.58 g, 10.0 mmol) in 40 mL of THF at $-78\text{ }^\circ\text{C}$,

and the mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 20 min. Trichloromethylsilane (1.26 mL, 10.0 mmol) was added to the reaction mixture at $-78\text{ }^{\circ}\text{C}$ and then allowed to room temperature. After stirring for 12 h, NH_4Cl (aq) was added, followed by extraction with diethyl ether, drying over MgSO_4 , and removal of the solvent under vacuum. The crude products were purified by silica gel column chromatography eluted with hexane. Recrystallization from hexane gave a white solid in 57% yield (1.42 g, 5.66 mmol). ^1H NMR (400 M Hz, CDCl_3): δ = 8.89 (d, J = 4.2 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 6.9 Hz, 1H), 7.94 (d, J = 7.8 Hz, 1H), 7.84 (d, J = 8.8 Hz, 1H), 7.71 (m, 1H), 7.68 (m, 1H), 7.51 (q, J = 4.4 Hz, 1H), 0.46 (s, 3H) ppm. ^{13}C NMR (100 M Hz, CDCl_3): δ = 146.53, 145.52, 138.73, 136.04, 135.81, 135.28, 133.60, 129.28, 128.81, 127.42, 126.62, 124.68, 121.42, 3.16 ppm. ^{29}Si NMR (80 M Hz, CDCl_3): δ = -11.14 ppm. HRMS (EI): m/z : calcd for $\text{C}_{16}\text{H}_{17}\text{NSi}$ (M^+): 251.1130; found : 251.1128.

Synthesis of 10-trifluorosilylbenzo[*h*]quinoline (1F). 7.76 mL (1.6 M in hexane, 12.5 mmol) of *n*-BuLi was slowly added to a solution of 10-bromobenzo[*h*]quinoline (3.20 g, 12.5 mmol) in 60 mL of THF at $-78\text{ }^{\circ}\text{C}$, and the mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for 20 min. Chlorotriethoxysilane (1.26 mL, 10.0 mmol) was added to the reaction mixture at $-78\text{ }^{\circ}\text{C}$ and then allowed to room temperature. After stirring for 12 h, all volatile components were removed under vacuum. Boron trifluoride diethyl etherate (1.8 mL, 14.6 mmol) was added to a suspension of the remaining solid in diethyl ether (30 mL), and stirring for 12 h. The reaction mixture was concentrated under vacuum. The remaining solid was dissolved in a small amount of dichloromethane, and the solution was reprecipitated with hexane. Recrystallization from hexane gave a white solid in 66% yield (2.18 g, 8.29 mmol). ^1H NMR (400 M Hz, CDCl_3): δ = 8.83 (d, J = 4.8 Hz, 1H), 8.44 (d, J = 8.0 Hz, 1H), 8.36 (d, J = 7.0 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.95 (d, J = 9.0 Hz, 1H), 7.87 (t, J = 7.4 Hz, 1H), 7.79 (d, J = 9.0 Hz, 1H), 7.76 (q, J = 4.9 Hz, 1H) ppm. ^{13}C NMR (100 M Hz, CDCl_3): δ = 150.8, 143.8, 142.0, 138.9, 138.1, 137.1, 134.3, 131.1, 128.6, 125.2, 123.4, 123.3 ppm. ^{29}Si NMR (80 M Hz, CDCl_3): δ = -105.3 ppm. HRMS (EI): m/z : calcd for $\text{C}_{13}\text{H}_8\text{F}_3\text{NSi}$ (M^+): 263.0378; found: 263.0388. elemental analysis: calcd for $\text{C}_{13}\text{H}_8\text{F}_3\text{NSi}$: C 59.30,

H 3.06, N 5.32; found: C 59.41, H 3.06, N 5.38.

Synthesis of 10-(diethynylmethylsilyl)benzo[*h*]quinoline (1E). 18.0 mL (1.6 M in hexane, 30.0 mmol) of *n*-BuLi was slowly added to a solution of 10-bromobenzo[*h*]quinoline (7.66 g, 30.0 mmol) in 300 mL of THF at -78 °C, and the mixture was stirred at -78 °C for 20 min. Chlorodiethoxymethylsilane (6.12 mL, 36.0 mmol) was added to the reaction mixture at -78 °C and then allowed to room temperature. After stirring for 12 h, all volatile components were removed under vacuum. Ethynylmagnesium bromide (0.5 M in THF, 120 mL, 60 mmol) was slowly added to a solution of the remaining solid in THF (300 mL), and then the solution was refluxed for 12 h. After the solvent was removed under vacuum, the crude products were purified by silica gel column chromatography eluted with toluene/hexane (2/1). Recrystallization from hexane/dichloromethane gave a white solid in 37% yield (3.02 g, 11.1 mmol). ¹H NMR (400 M Hz, CDCl₃): δ = 8.95 (dd, *J* = 4.4, 1.5 Hz, 1H), 8.82 (dd, *J* = 6.5, 1.0 Hz, 1H), 8.28 (dd, *J* = 6.6, 1.5 Hz, 1H), 8.03 (d, *J* = 6.9 Hz, 1H), 7.91 (d, *J* = 8.9 Hz, 1H), 7.84 (t, *J* = 7.5 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.63 (q, *J* = 4.1 Hz, 1H), 2.52 (s, 2H), 0.77 (t, *J* = 4.1 Hz, 3H) ppm. ¹³C NMR (100 M Hz, CDCl₃): δ = 144.08, 137.94, 135.76, 134.61, 132.38, 130.16, 129.84, 128.34, 128.12, 125.71, 123.99, 122.06, 93.08, 90.95, 4.65 ppm. ²⁹Si NMR (80 M Hz, CDCl₃): δ = -70.85 ppm. HRMS (EI): *m/z*: calcd for C₁₈H₁₃NSi (M⁺): 271.0817; found: 271.0807. elemental analysis: calcd for C₁₈H₁₃NSi: C 79.66, H 4.83, N 5.16; found: C 79.39, H 4.75, N 5.15.

Synthesis of 10-(methylbis(phenylethynyl)silyl)benzo[*h*]quinoline (2C). Triethylamine (5.0 mL) was added to a solution of **1E** (0.271 g, 1.00 mmol), iodobenzene (0.223 g, 2.00 mmol), Pd(PPh₃)₄ (0.115 g, 0.100 mmol), CuI (0.020 g, 0.100 mmol) in toluene (10 mL) at room temperature. After the mixture was stirred at 90 °C for 36 h, the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography eluted with hexane/chloroform (3/2). Recrystallization from hexane/dichloromethane gave a yellow solid in 28% yield (0.120 g, 0.284 mmol). ¹H NMR (400 M Hz, CDCl₃): δ = 9.04 (dd, *J* = 4.4, 1.1 Hz, 1H), 8.93 (dd, *J* = 7.0, 1.0 Hz, 1H), 8.23 (dd, *J* = 7.9, 1.3 Hz, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.60

(q, $J = 4.3$ Hz, 1H), 7.50 (q, $J = 2.7$ Hz, 4H), 7.27 (t, $J = 3.1$ Hz, 6H), 0.89 (s, 3H) ppm. ^{13}C NMR (100 M Hz, CDCl_3): $\delta = 144.8, 144.5, 138.3, 135.7, 135.2, 132.8, 131.9, 129.9, 128.5, 128.0, 126.1, 124.3, 124.1, 122.1, 103.1, 97.2, 4.9$ ppm. ^{29}Si NMR (80 M Hz, CDCl_3): $\delta = -66.2$ ppm. HRMS (EI): m/z : calcd for $\text{C}_{30}\text{H}_{21}\text{NSi}$ (M^+): 423.1443; found: 423.1432.

Synthesis of 10-(bis((2,5-bis(trifluoromethyl)phenyl)ethynyl)-(methyl)silyl)benzo[*h*]quinoline (2F). Triethylamine (10 mL) was added to a solution of **1E** (0.540 g, 2.00 mmol), 2-iodo-1,4-bis(trifluoromethyl)benzene (1.36 g, 4.00 mmol), $\text{Pd}(\text{PPh}_3)_4$ (0.240 g, 0.200 mmol), CuI (0.040 g, 0.200 mmol) in toluene (20 mL) at room temperature. After the mixture was stirred at 90 °C for 18 h, the solvent was removed under vacuum. The crude product was purified by silica gel column chromatography eluted with hexane/ethyl acetate (7/1). Recrystallization from hexane/dichloromethane gave a yellow solid in 56% yield (0.779 g, 1.12 mmol). ^1H NMR (400 M Hz, CDCl_3): $\delta = 8.99$ (s, 1H), 8.88 (d, $J = 6.9$ Hz, 1H), 8.21 (d, $J = 7.8$ Hz, 1H), 7.99 (d, $J = 7.8$ Hz, 1H), 7.93 (s, 2H), 7.85 (d, $J = 7.8$ Hz, 1H), 7.82 (d, $J = 8.5$ Hz, 1H), 7.70 (d, $J = 8.2$ Hz, 2H), 7.66 (d, $J = 9.0$ Hz, 1H), 7.61 (q, $J = 4.9$ Hz, 1H), 7.55 (d, $J = 8.1$ Hz, 2H), 0.96 (s) ppm. ^{13}C NMR (100 M Hz, CDCl_3): $\delta = 144.6, 144.2, 138.1, 136.3, 135.1, 134.8, 134.4, 134.2, 133.8, 133.5, 133.2, 132.6, 131.5, 130.4, 130.2, 128.8, 128.4, 127.9, 127.1, 126.4, 126.0, 124.3, 123.6, 122.3, 121.7, 118.9, 106.9, 96.8, 4.4$ ppm. ^{29}Si NMR (80 M Hz, CDCl_3): $\delta = -72.3$ ppm. HRMS (ESI): m/z : calcd for $\text{C}_{34}\text{H}_{18}\text{F}_{12}\text{NSi}$ ($\text{M}-\text{H}^+$): 696.1017; found: 696.1011.

References

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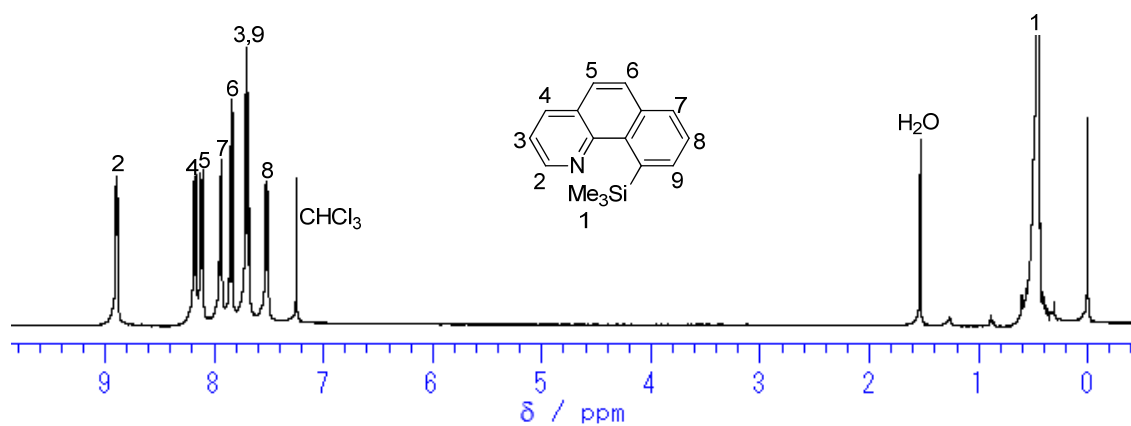


Fig. S1. ^1H NMR spectrum of **1C**.

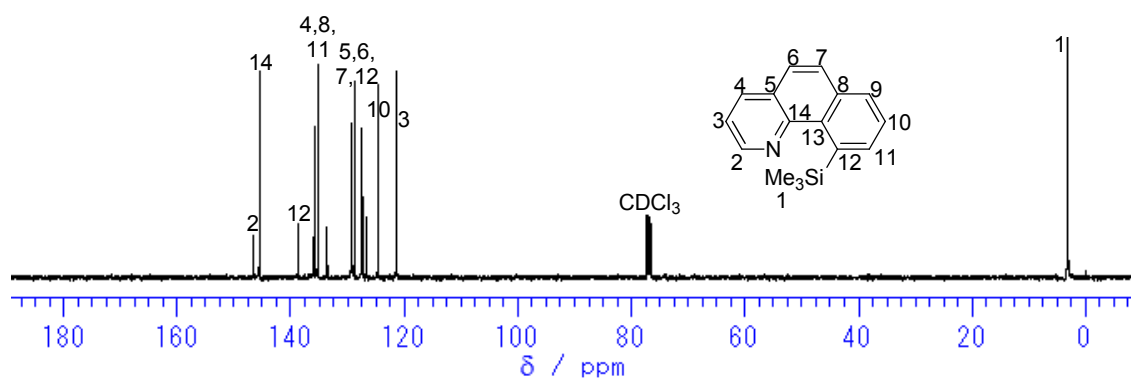


Fig. S2. ^{13}C NMR spectrum of **1C**.

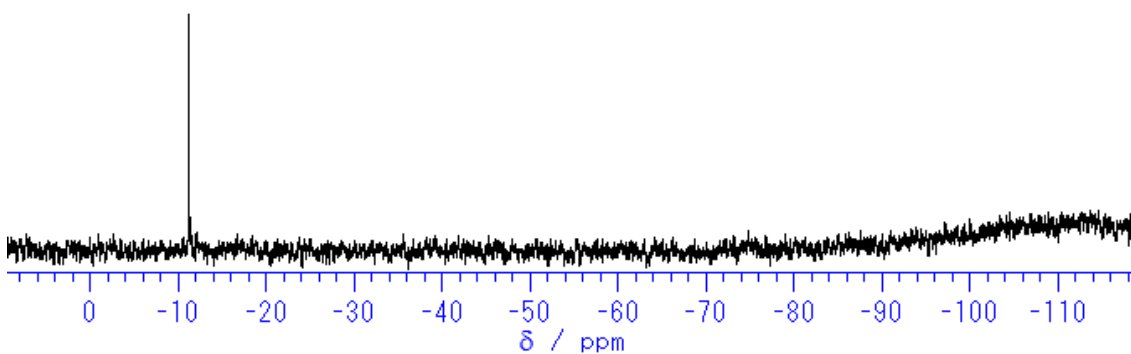


Fig. S3. ^{29}Si NMR spectrum of **1C**.

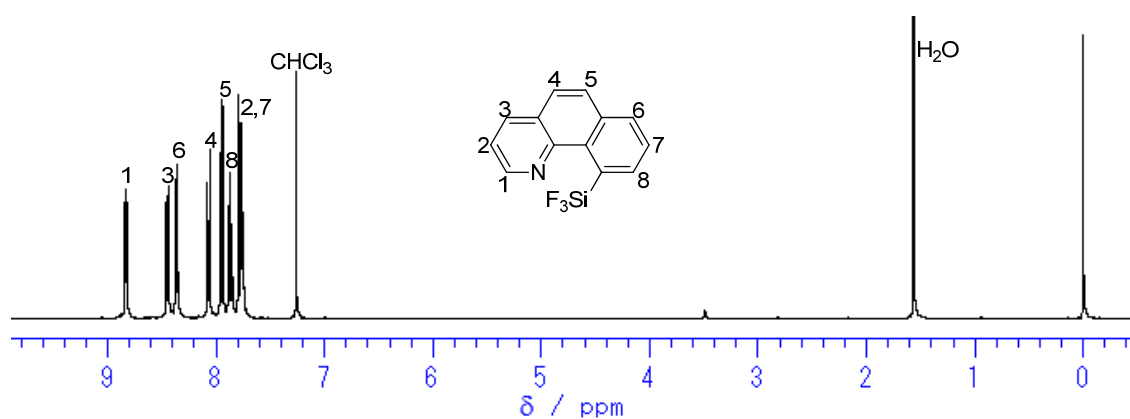


Fig. S4. ^1H spectrum of **1F**.

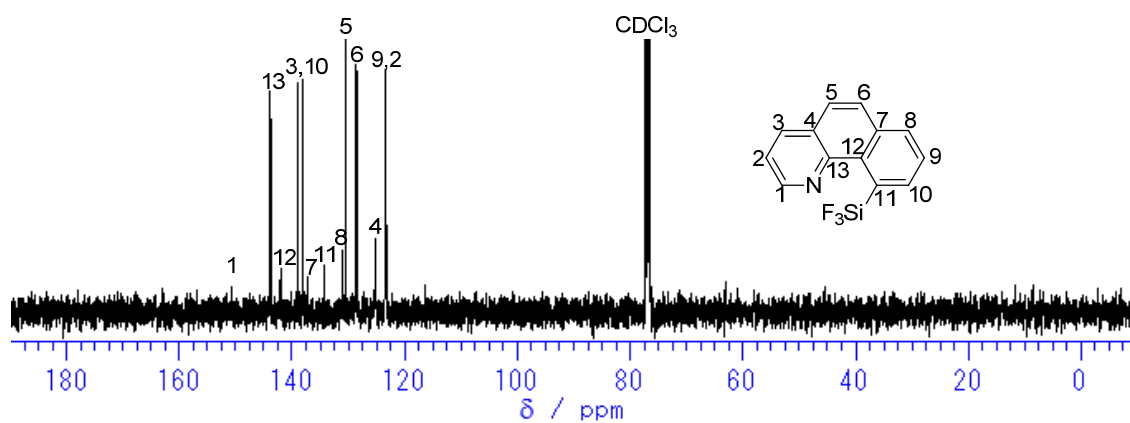


Fig. S5. ^{13}C NMR spectrum of **1F**.

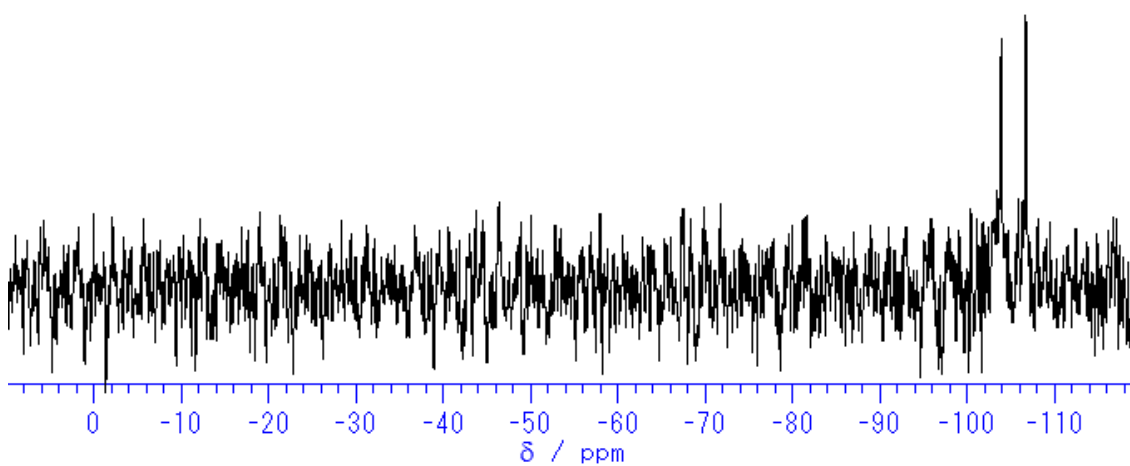


Fig. S6. ^{29}Si NMR spectrum of **1F**.

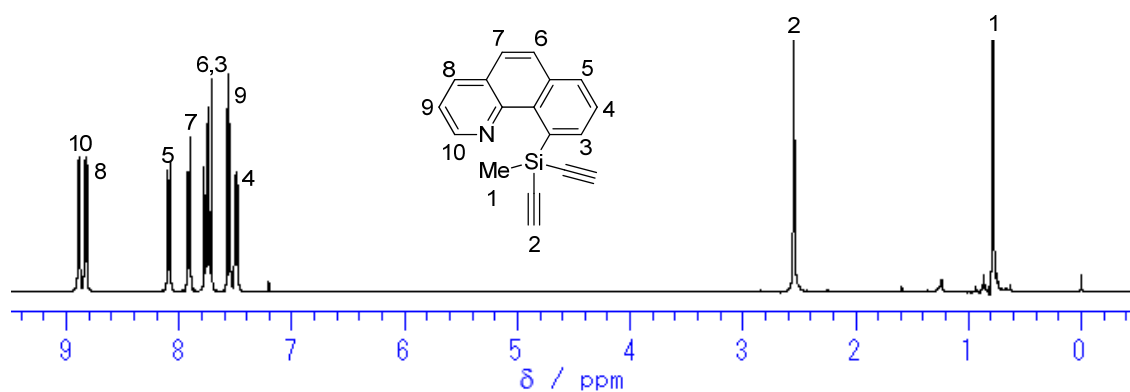


Fig. S7. ^1H NMR spectrum of **1E**.

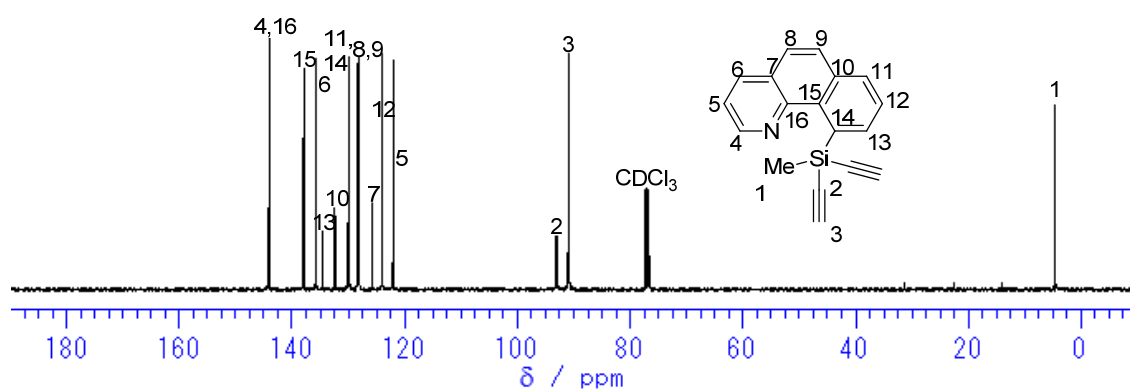


Fig. S8. ^{13}C NMR spectrum of **1E**.

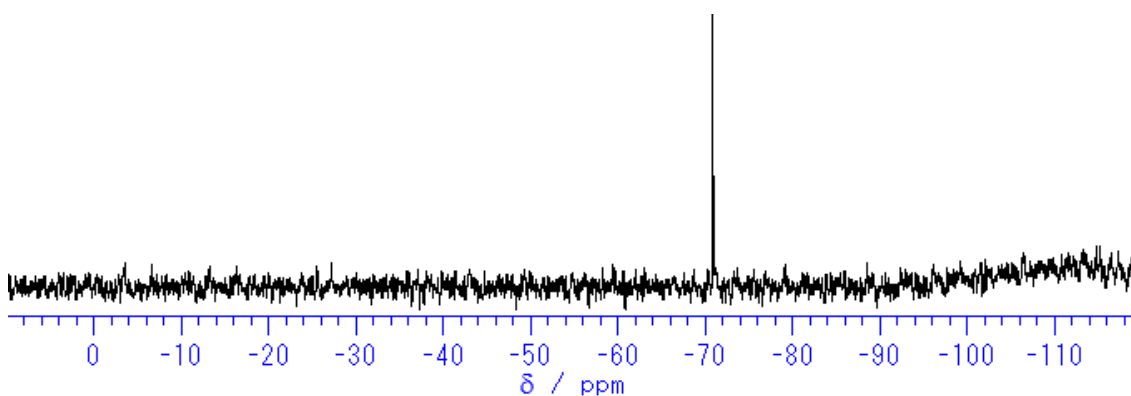
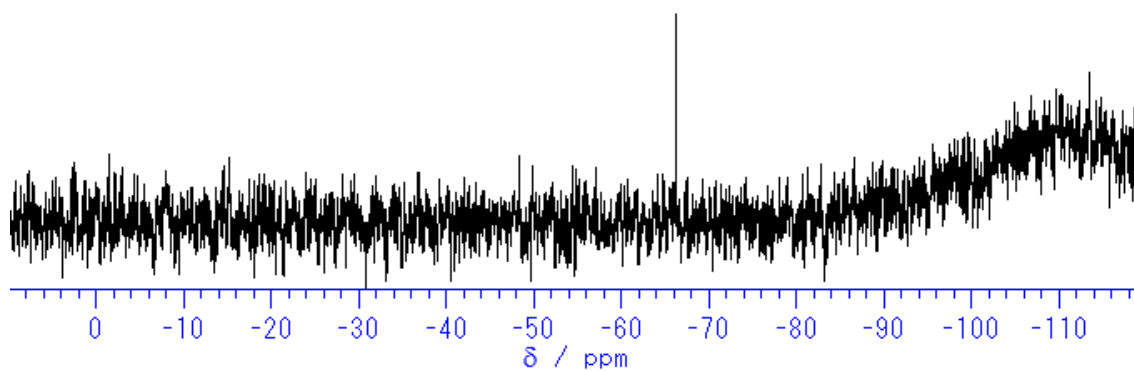
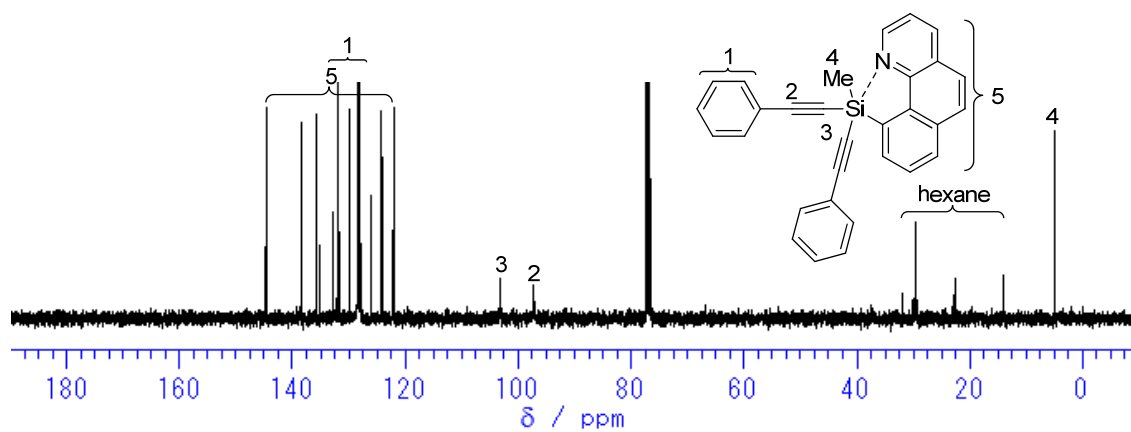
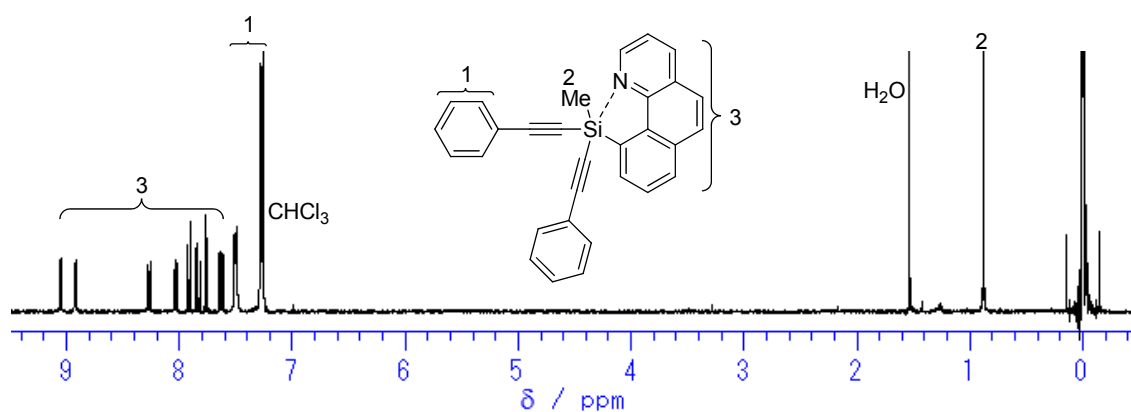


Fig. S9. ^{29}Si NMR spectrum of **1E**.



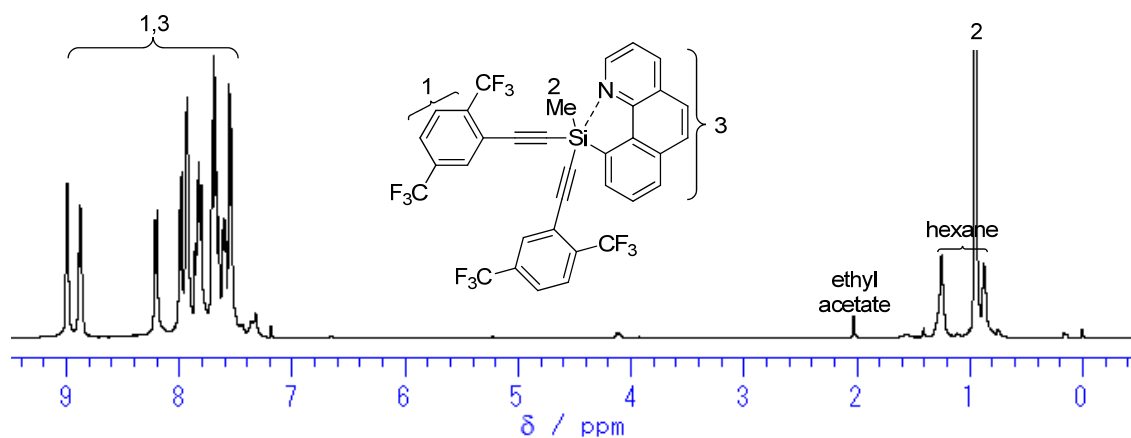


Fig. S13. ^1H NMR spectrum of **2F**.

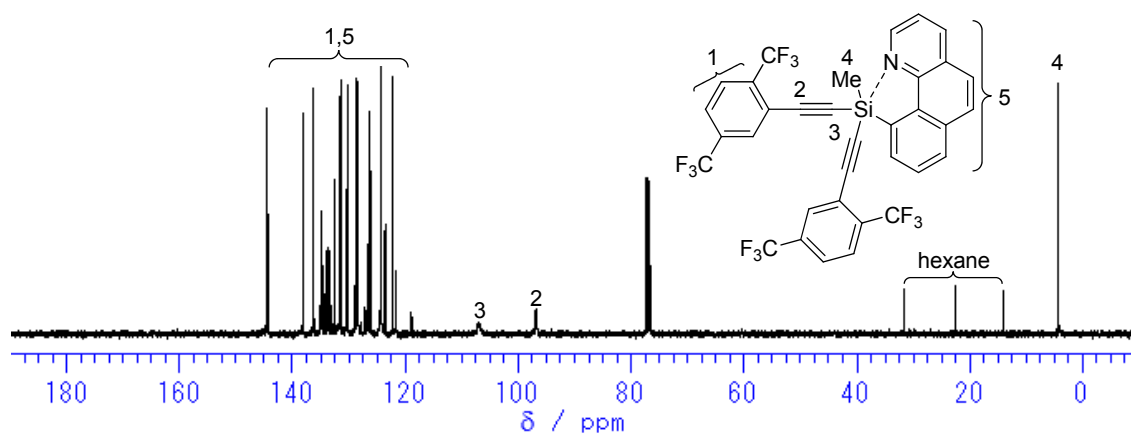


Fig. S14. ^{13}C NMR spectrum of **2F**.

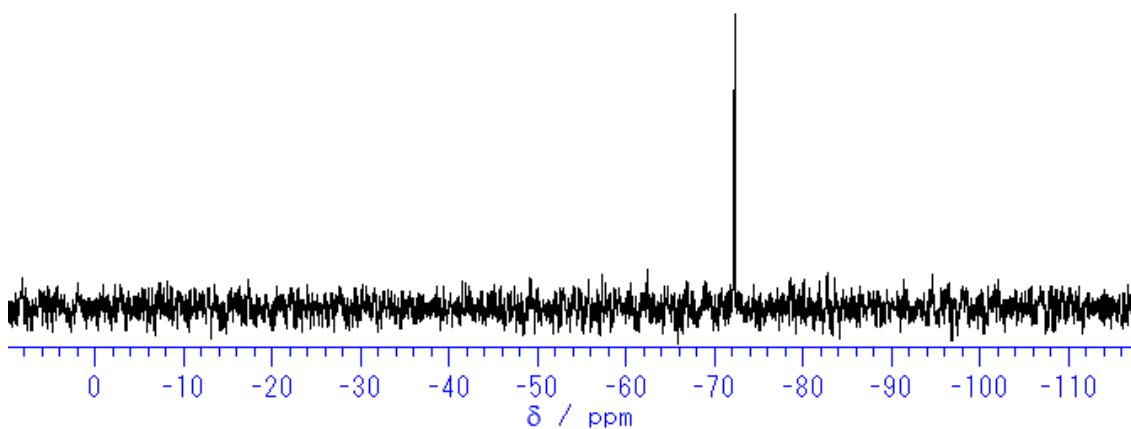


Fig. S15. ^{29}Si NMR spectrum of **2F**.

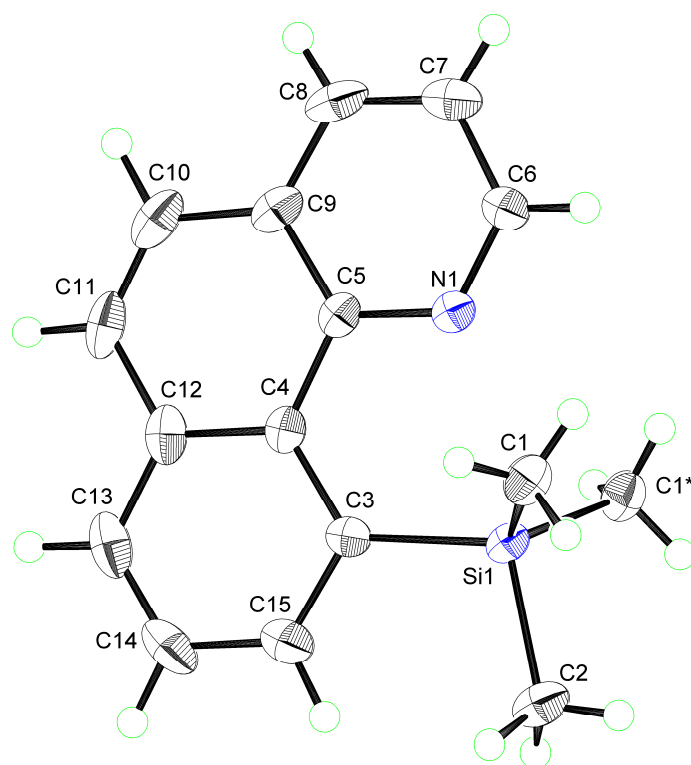


Fig. S16. The X-ray crystal structure of **1C** with thermal ellipsoids drawn to the 50% probability level.

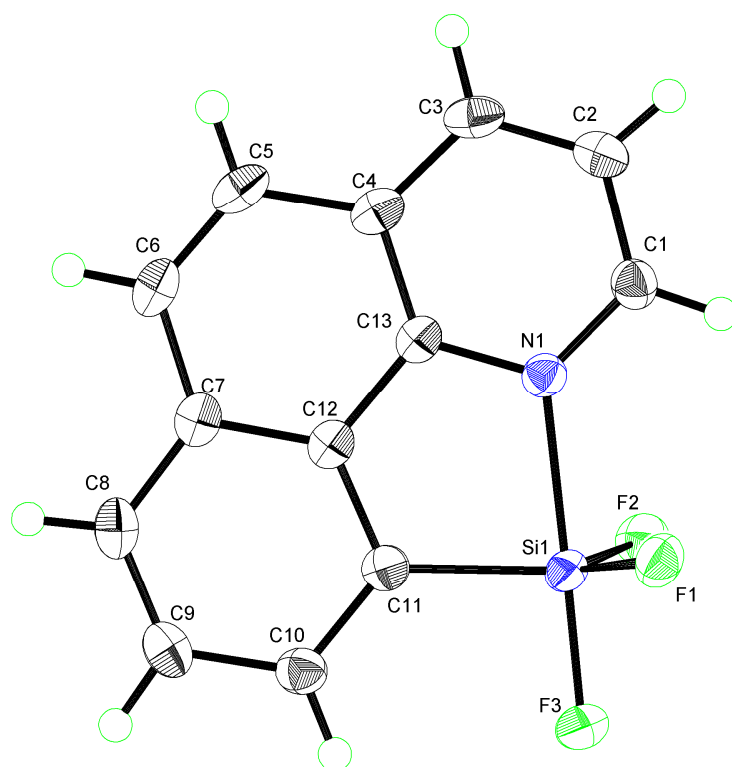


Fig. S17. The X-ray crystal structure of **1F** with thermal ellipsoids drawn to the 50% probability level.

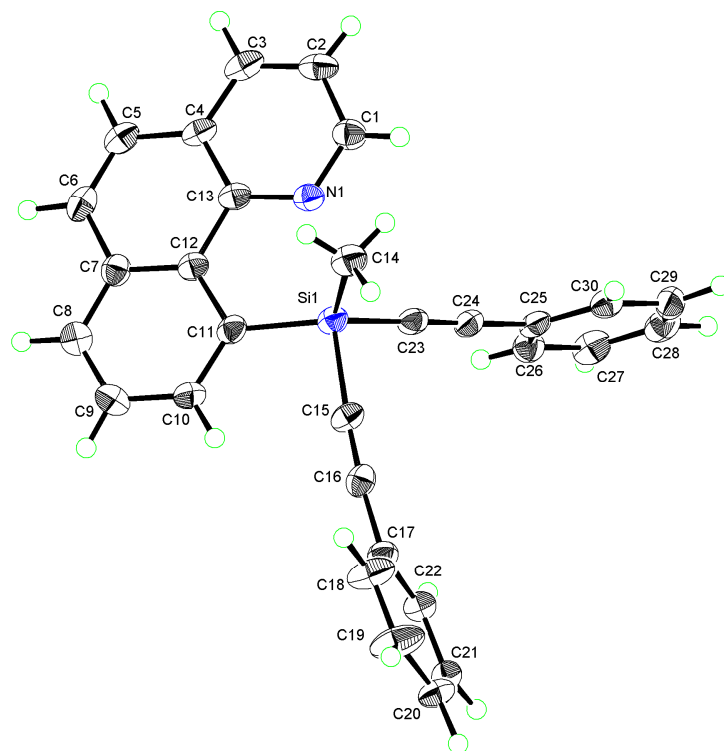


Fig. S18 The X-ray crystal structure of **2C** with thermal ellipsoids drawn to the 50% probability level.