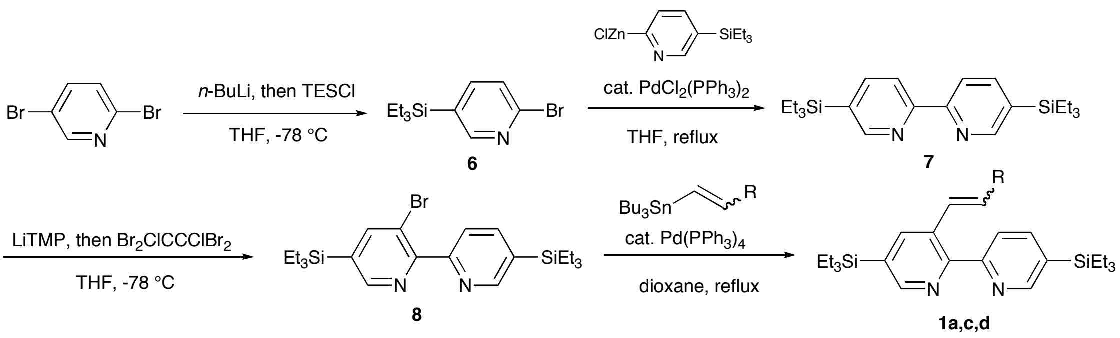
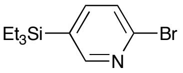
Supporting Information

General. All operations were performed under an argon atmosphere. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) JEOL AL-400, or a JEOL AL-300spedtrometer using $CDCl_3$ (^{1}H: $\delta = 7.26$, ^{13}C: $\delta = 77.0$). IR spectra were recorded on JASCO FT/IR-460plus spectrometer. 250W super high-pressure Hg lamp, SX-UI250HQ(USHIO Co. Ltd.) was used for photoirradiation. UV/vis spectra were measured by a JASCO V-650 spectrophotometer. Flash column chromatography was conducted on Silica gel (Merck Kieselgel 60 Art 7734) and preparative thin layer chromatography (PTLC) was carried out on silica gel (Wako gel B-5F). All solvent were distilled according to usual procedures and stored over molecular sieves.

[1] Preparation of 3-alkenyl-2,2'-bipyridine derivatives 1a, 1c, 1d.



2-Bromo-5-triethylsilylpyridine (6)



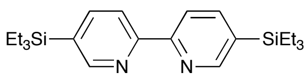
6

To a THF solution (300 ml) of 2,5-dibromopyridine (6.1 g, 26 mmol) was added *n*-BuLi (1.53 M in hexane, 18.6 ml, 29 mmol) at -100 ℃. The reaction mixture was stirred at -100 ℃ for 30 min. Chlorotriethylsilane (5.2 ml, 31 mmol) was added to this solution at -100 ℃, and the mixture was stirred at 0 ℃ for 30 min. The reaction was quenched with pH 7 phosphate buffer. The organic materials were extracted with ethyl acetate three times, and the combined extracts were washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane : ethyl acetate = 9:1) to give **6.** (6.1 g, 85%)

IR (neat) 2955, 2875, 1555, 1452, 1071 cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.76 - 0.83 (6H, m), 0.95 (9H, t, *J* = 7.6 Hz), 7.45 (1H, d, *J* = 7.6 Hz), 7.59 (1H , dd, *J* = 7.6, 2.0 Hz), 8.38 (1H, brs).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 2.8, 6.9, 127.3, 130.8, 142.9, 143.7, 154.3.
Anal. Calcd for $C_{11}H_{18}BrNSi$: C, 48.53; H, 6.66; N, 5.14%.
Found: C, 48.31; H, 6.48; N, 4.91%.

5,5'-Bis(triethylsilyl)-2,2'-bipyridine (7)



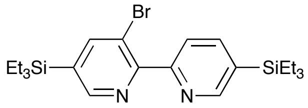
7

(Preparation of Organozinc reagent)
To a THF solution (100 ml) of **6** (3.8 g, 13 mmol) was added *t*-BuLi (1.59 M in pentane, 17.4 ml, 27 mmol) at -78 ℃. After the mixture was stirred at -78 ℃ for 35 min, a THF solution (10 ml) of anhydrous $ZnCl_2$ (3.78 g, 27 mmol) was slowly added to the solution at -78 ℃. The reaction mixture was slowly warmed to room temperature over 1.5 h.

A mixed solution (100 ml) of $Pd(PPh_3)_2Cl_2$ (737 mg, 1 mmol) and **6** (2.6 g, 9.4 mmol) in THF was stirred at room temperature for 30 min. The above THF solution of pyridylzinc chloride was added to the mixture. The reaction mixture was refluxed for 21 h. The reaction was quenched with 1N NaOH. The organic materials were extracted with ethyl acetate three times, and the combined extracts were washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane : ethyl acetate = 9:1) to give **7** quantitatively.

IR (KBr) 2955, 2873, 1574, 1460, 1115, 1005 cm^{-1}
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.80 - 0.87 (12H, m), 0.95 - 1.01 (18H, m), 7.89 (2H, dd, *J* = 8.0, 2.0 Hz), 8.36 (2H, d, *J* = 8.0 Hz), 8.74 (2H, s).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 3.2, 7.3, 120.1, 132.4, 142.8, 154.0, 156.2.
Anal. Calcd for $C_{22}H_{36}N_2Si_2$: C, 68.69; H, 9.43; N, 7.28%.
Found: C, 68.96; H, 9.58; N, 7.08%.

3-Bromo-5,5'-bis(triethylsilyl)-2,2'-bipyridine (8)



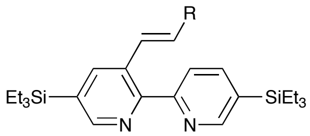
8

To a THF solution (300 ml) of 2,2,6,6-tetramethylpiperidine (2.5 ml, 15 mmol) was added *n*-BuLi

(1.50 M in hexane, 11.4 ml, 17 mmol) at -78 ℃. The mixture was stirred at 0 ℃ for 15 min. After the mixture was cooled to -78 ℃, **7** (3.17 g, 8.2 mmol) in THF (10 ml) was added to the solution. After the reaction mixture was stirred at -78 ℃ for 20 min, a THF solution (10 ml) of 1,2-dibromo-tetrachloroethane (5.9 g, 18 mmol) was added to the solution at -78 ℃. The reaction mixture was stirred at -78 ℃ for 1 h. The reaction was quenched with pH7 phosphate buffer. The organic materials were extracted with ethyl acetate three times, and the combined extracts were washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane : ethyl acetate = 9:1) to give **8**. (1.1 g, 52%)

IR (neat) 2954, 2875, 1561, 1341, 1238, 1071, 1007 cm^{-1}
^1H NMR ($CDCl_3$, 400 MHz): δ = 0.80 - 0.88 (12H, m), 0.90 – 1.00 (18H, m) , 7.69 (1H, d, *J* = 7.6 Hz), 7.86 (1H, d, *J* = 7.6 Hz), 8.00 (1H, s), 8.62 (1H, s), 8.76 (1H, s).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 3.0, 3.1, 7.1, 7.2, 119.7, 123.3, 132.0, 134.4, 142.0, 146.9, 152.5, 153.7, 156.0, 156.9.
Anal. Calcd for $C_{22}H_{35}BrN_2Si_2$: C, 57.00; H, 7.61; N, 6.04%.
Found: C, 57.20; H, 7.53; N, 5.84%.

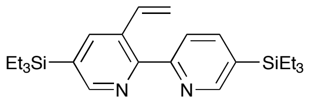
3-alkenyl-5,5'-ditriethylsilyl-2,2'-bipyridine 1a,c,d



1a,c,d

To a dioxane solution (15 ml) of **8** (0.7 mmol) was added $Pd(PPh_3)_4$ (0.03 mmol) and appropriate tributyl(alkenyl)tin (0.8 mmol). After the mixture was refluxed for 10 h, the reaction was quenched with aqueous solution of KF and filtered through a pad of Celite. The organic materials were extracted with ethyl acetate three times, and the combined extracts were washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative thin layer chromatography (hexane : ethyl acetate = 9:1) to give the compound.

3-Vinyl-5,5'-ditriethylsilyl-2,2'-bipyridine (1a)



1a

83% yield

IR (neat) 2954, 2875, 1576, 1459, 1415, 1237, 1034, 1007 cm^{-1}

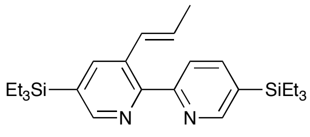
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 0.80 - 0.92 (12H, m), 0.95 - 1.05 (18H, m), 5.34 (1H, d, *J* = 12.6 Hz), 5.74 (1H, d, *J* = 17.6 Hz), 7.18 (1H, dd, *J* = 17.6, 12.6 Hz), 7.82 (1H, d, *J* = 7.6 Hz), 7.90 (1H, dd, *J* = 7.6, 1.6 Hz), 8.02 (1H, d, *J* = 1.6 Hz), 8.65 (1H, d, *J* = 1.6 Hz), 8.76 (1H, s).

^{13}C NMR (CDCl$_3$, 100 MHz): δ = 3.2, 7.3, 115.8, 123.7, 131.21, 131.27, 131.8, 134.8, 140.3, 142.4, 153.1, 153.5, 155.0, 157.9.

Anal. Calcd for $C_{24}H_{38}N_2Si_2$: C, 70.18; H, 9.32; N, 6.82%.

Found: C, 70.04; H, 9.30; N, 6.59%.

_E_-5,5'-Ditriethylsilyl-3-propenyl-2,2'-bipyridine (1c)



1c

16% yield

IR(neat) 2954, 2875, 1577, 1457, 1237, 1007 cm^{-1}

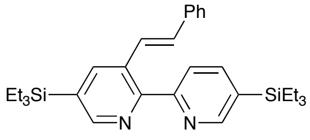
^{1}H NMR (CDCl$_3$, 500 MHz): δ = 0.82 - 0.88 (12H, m), 0.94 - 1.02 (18H, m), 1.89 (3H, dd, *J* = 6.7, 1.7 Hz), 6.21 (1H, dq, *J* = 15.7, 6.7 Hz), 6.83 (1H, dd, *J* = 15.7, 1.7 Hz), 7.76 (1H, dd, *J* = 7.8, 0.9 Hz), 7.89 (1H, dd, *J* = 7.8, 1.7 Hz), 7.95 (1H, d, *J* = 1.5 Hz), 8.59 (1H, d, *J* = 1.5 Hz), 8.76 (1H, dd, *J* = 1.7, 0.9 Hz).

^{13}C NMR (CDCl$_3$, 125 MHz): δ = 3.18, 3.20, 7.26, 7.27, 18.8, 123.8, 128.2, 128.5, 131.2, 131.4, 131.7, 140.4, 142.4, 152.4, 153.6, 154.6, 158.4.

Anal. Calcd for $C_{25}H_{40}N_2Si_2$: C, 70.69; H, 9.49; N, 6.59%.

Found: C, 70.48; H, 9.33; N, 6.37%.

_E_-5,5'-Ditriethylsilyl-3-styryl-2,2'-bipyridine (1d)



1d

63% yield

IR (neat) 2953, 2874, 1576, 1450, 1238, 1007 cm^{-1}

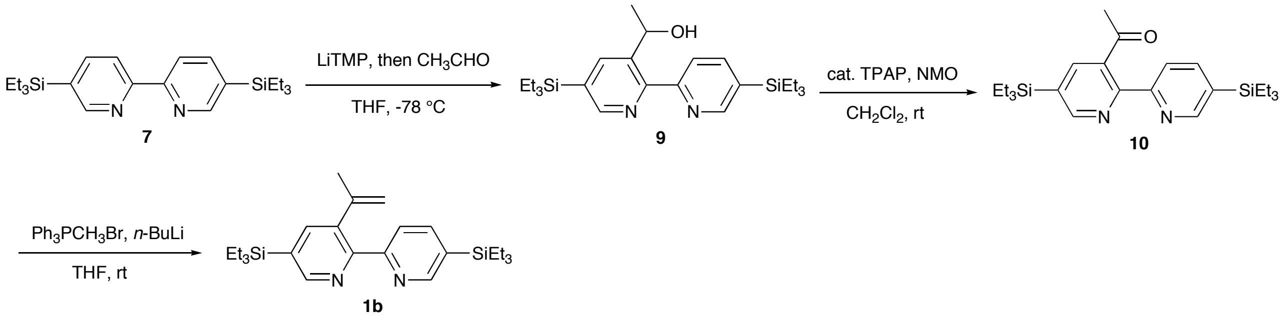
^{1}H NMR (CDCl$_3$, 500 MHz): δ = 0.84 - 0.93 (12H, m), 0.99 - 1.06 (18H, m), 7.03 (1H, d, *J* = 16.3 Hz), 7.24 – 7.28(1H, m), 7.32 – 7.37 (2H, m), 7.46 – 7.49 (2H, m), 7.64 (1H, d, *J* = 16.3 Hz), 7.87 (1H, dd, *J* = 7.7, 1.0 Hz), 7.92 (1H, dd, *J* = 7.7 Hz, 1.7 Hz), 8.12 (1H, d, *J* = 1.4 Hz), 8.67 (1H, d, *J* = 1.4 Hz), 8.78 (1H, dd, *J* = 1.7, 1.0 Hz).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 3.2, 7.3, 123.9, 126.8, 126.9, 127.8, 128.6, 130.7, 131.2, 132.0, 137.5, 140.5, 142.6, 153.0, 153.7, 155.3, 158.2.

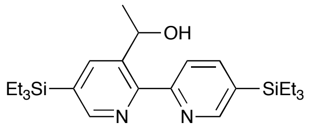
Anal. Calcd for $C_{30}H_{42}N_2Si_2$: C, 74.01; H, 8.70; N, 5.75%.

Found: C, 74.12; H, 8.90; N, 5.53%.

[2] Preparation of 3-alkenyl-2,2'-bipyridine derivatives 1b



5,5'-Bis(triethylsilyl)-3-(1-hydroxyethyl)-2,2'-bipyridine (9)



9

To a THF solution (30 ml) of 2,2,6,6-Tetramethylpiperidine (0.76 ml, 4.5 mmol) was added *n*-BuLi (1.56 M in hexane, 2.9 ml, 4.5 mmol) at -78 ℃. The reaction mixture was stirred at 0 ℃ for 15 min. After the mixture was cooled at -78 ℃, **7** (581 mg, 1.5 mmol) in THF (5 ml) was added to the solution. The reaction mixture was stirred at -78 ℃ for 20 min. A THF solution (5 ml) of distilled CH_3CHO (0.5 ml , 8.9 mmol) was added to the solution at -78 ℃. The reaction mixture was stirred at -78 ℃ for 1 h. The reaction was quenched with pH7 phosphate buffer. The organic materials were extracted with ethyl acetate three times, and the combined extracts were washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane : ethyl acetate = 9:1) to give **9**. (340 mg, 54%)

IR (neat) 3433, 2956, 2876, 1577, 1559, 1402, 1100, 1046 cm^{-1}

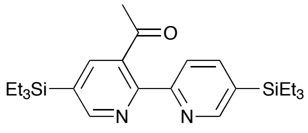
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.82 - 0.90 (12H, m), 0.95 - 1.05 (18H, m), 1.54 (3H, d, J = 6.4 Hz), 4.90 (1H, q, J = 6.4 Hz), 7.38 (1H, brs), 7.94 (1H, d, J = 2.0 Hz), 7.98 (1H, dd, J = 8.0, 2.0 Hz), 8.14 (1H, d, J = 8.0 Hz), 8.66 (2H, d, J = 2.0 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 3.18, 3.23, 7.31, 7.35, 20.2, 66.4, 124.0, 132.3, 132.5, 138.0, 140.8, 143.5, 151.7, 152.5, 155.6, 158.1.

Anal. Calcd for $C_{24}H_{40}N_2OSi_2$: C, 67.23; H, 9.40; N, 6.53%.

Found: C, 67.00; H, 9.61; N, 6.32%.

3-Acetyl-5,5'-bis(triethylsilyl)-2,2'-bipyridine (10)

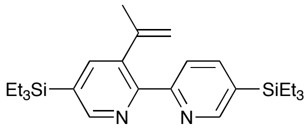


10

A mixed solution of **9** (347 mg 0.8 mmol) and activated MS4A in CH_2Cl_2 (5 ml) was added TPAP (28 mg, 0.08 mmol) and NMO (184 mg, 1.5 mmol). After the reaction mixture was stirred at room temperature overnight, the mixture was directly passd through silica gel. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane : ethyl acetate = 9:1) to give **10** quantitatively.

IR (neat) 2954, 2875, 1699, 1577, 1517, 1348, 1081, 1008 cm^{-1}
^1H NMR ($CDCl_3$, 400 MHz): δ = 0.77 - 0.86 (12H, m), 0.90 - 1.00 (18H, m), 2.35 (3H, s), 7.73 (1H, d, J = 2.0 Hz), 7.90 (1H, d, J = 8.0 Hz), 8.28 (1H, d, J = 8.0 Hz), 8.63 (1H, s), 8.73 (1H, s).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 3.07, 3.10, 7.21, 7.27, 31.3, 121.3, 132.3, 132.9, 136.7, 140.4, 142.8, 152.8, 153.5, 154.2, 155.1, 203.8.
Anal. Calcd for $C_{24}H_{38}N_2OSi_2$: C, 67.55; H, 8.98; N, 6.56%.
Found: C, 67.77; H, 9.15; N, 6.51%.

5,5'-Bis(triethylsilyl)-3-isopropenyl-2,2'-bipyridine (1b)



1b

To a THF solution (2.0 ml) of Ph_3PCH_3Br (0.19 g, 0.54 mmol) was added *n*-BuLi (1.54 M in hexane, 0.33 ml, 0.52 mmol) at -78 ℃. The reaction mixture was stirred at -78 ℃ for 5 min and then a THF solution (6.0 ml) of **10** (0.17 g, 0.42 mmol) was added. The reaction mixture was stirred at room temperature overnight. The reaction was quenched with pH7 phosphate buffer. The organic materials were extracted with ethyl acetate three times, and the combined extracts were washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative thin layer chromatography (hexane : ethyl acetate = 9:1) to give **1b**. (26 mg, 15%)

IR (CH_2Cl_2) 3019, 1522, 1423, 1213, 1046 cm^{-1}

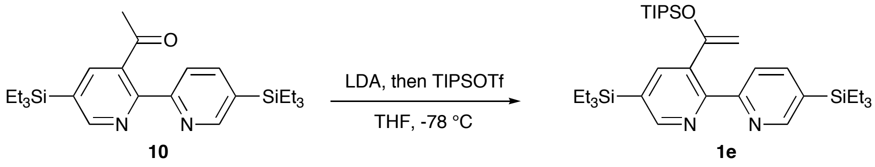
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.86 - 0.90 (12H, m), 0.95 - 1.03 (18H, m), 1.76 (3H, s), 5.02 (1H, s), 5.11 (1H, s), 7.69 (1H, d, *J* = 1.6 Hz), 7.73 (1H, d, *J* = 7.6 Hz), 7.82 (1H, d, *J* = 7.6 Hz), 8.66 (1H, *J* = 1.6 Hz), 8.73 (1H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 3.2, 7.3, 23.5, 116.1, 123.0, 131.1, 131.4, 137.5, 142.1, 143.2, 145.2, 152.8, 154.0, 154.9, 158.3.

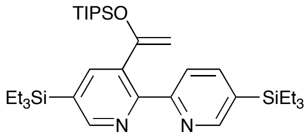
Anal. Calcd for $C_{25}H_{40}N_2Si_2$: C, 70.69; H, 9.49; N, 6.59%.

Found: C, 70.46; H, 9.41; N, 6.40%.

[3] Preparation of 3-alkenyl-2,2'-bipyridine derivatives 1e



5,5'-Bis(triethylsilyl)-3-[1-(triisopropylsilyloxy)ethenyl]-2,2'-bipyridine (1e)



1e

To a 0.3 M THF solution (1.2 ml, 0.36 mmol) of LDA was added a THF solution (2 ml) of **10** (106 mg, 0.24 mmol) at -78 ℃. The reaction mixture was stirred at -78 ℃ for 10 min, and then triisopropylsilyltriflate (93 μl, 0.34 ml) was added at the same temperature. The reaction mixture was further stirred at -78 ℃ for 2 h and the reaction mixture was slowly warmed to room temperature overnight. The reaction was quenched with Et_3N and aqueous $NaHCO_3$ solution. The organic materials were extracted with ethyl acetate three times, and the combined extracts were washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative thin layer chromatography (hexane : ethyl acetate = 9:1) to give **1e.** (51.8 mg, 38%)

IR (neat) 2952, 2873, 1699, 1577, 1458, 1238, 1017 cm^{-1}

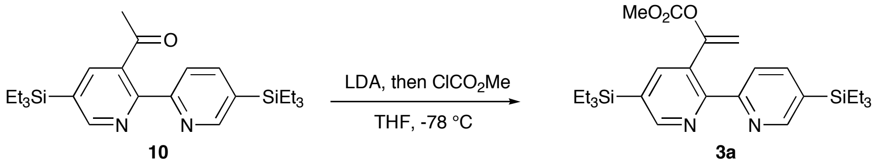
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.80 - 0.90 (30H, m), 0.96 - 1.05 (21H, m), 4.47 (1H, d, *J* = 1.5 Hz), 4.52 (1H, d, *J* = 1.5 Hz), 7.76 (1H, d, *J* = 7.7 Hz), 7.80 (1H, dd, *J* = 7.7, 1.7 Hz), 7.87 (1H, d, *J* = 1.7 Hz), 8.68 (1H, d, *J* = 1.7 Hz), 8.71 (1H, brs).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 3.14, 3.17, 7.19, 12.5, 17.8, 94.6, 122.9, 130.98, 131.03, 133.6, 141.9, 143.4, 153.5, 154.1, 155.6, 157.4, 158.6.

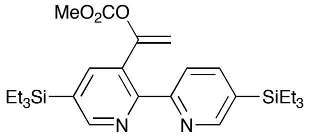
Anal. Calcd for $C_{33}H_{58}N_2OSi_3$: C, 67.98; H, 10.03; N, 4.80%.

Found: C, 67.68; H, 10.25; N, 4.52%.

[4] Preparation of 3-alkenyl-2,2'-bipyridine derivatives 3a



Methyl-1-[(5,5'-ditriethylsilyl-2,2'-bipyridin)-3-yl]-ethenylcarbonate (3a)

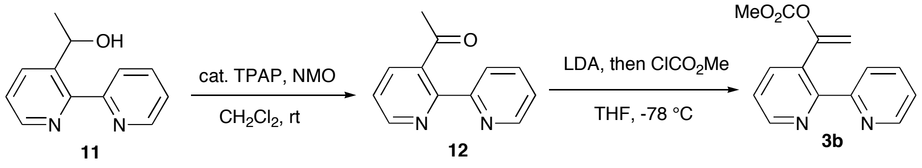


3a

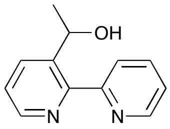
To a 0.3 M THF solution (0.8 ml, 0.24 mmol) of LDA was added a THF solution (2 ml) of **10** (70 mg, 0.16 mmol) at -78 ℃. The reaction mixture was stirred at -78℃ for 10min, and then $ClCO_2Me$ was added at the same temperature. The reaction mixture was further stirred at -78 ℃ for 2 h and then the mixture was slowly warmed to room temperature overnight. The reaction was quenched with pH7 phosphate buffer. The organic materials were extracted with ethyl acetate three times, and the combined extracts were washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane : ethyl acetate = 7:3) to give **3a**. (61 mg, 80%)

IR (CH_2Cl_2) 2985, 1541, 857, 825 cm^{-1}
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.80 - 0.90 (12H, m), 0.92 - 1.05 (18H, m), 3.59 (3H, s), 5.16 (1H, s), 5.32 (1H, s), 7.87 (2H, brs), 7.90 (1H, brs), 8.70 – 8.74 (2H, m).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 3.2, 7.3, 54.8, 105.0, 122.7, 129.0, 131.5, 131.7, 142.3, 143.9, 152.9, 153.2, 153.8, 154.2, 155.1, 157.6.
Anal. Calcd for $C_{26}H_{40}N_2O_3Si_2$: C, 64.42; H, 8.32; N, 5.78%.
Found: C, 64.34; H, 8.38; N, 5.55%.

[5] Preparation of 3-alkenyl-2,2'-bipyridine derivatives 3b



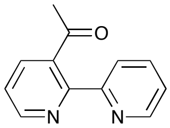
3-(1-Hydroxyethyl)-2,2'-bipyridine (11)



11

11 was prepared according to the literature procedure.[1]

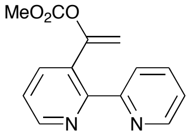
3-Acetyl-2,2'-bipyridine (12)



12

12 was prepared according to the same procedure as that of the synthesis of **10** in quantitative yield.
IR (KBr) 3009, 1693, 1553, 1480, 1417, 1358, 1279, 1105 cm^{-1}
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 2.36 (3H, s), 7.29 - 7.33 (1H, m), 7.37 (1H, dd, *J* = 8.0, 4.8 Hz), 7.71 (1H, dd, *J* = 8.0, 2.0 Hz), 7.85 (1H, dt, *J* = 8.0, 2.0 Hz), 8.31 (1H, d, *J* = 8.0 Hz), 8.60 (1H, d, *J* = 4.8 Hz), 8.71 (1H, dd, *J* = 4.8, 1.6 Hz).
^{13}C NMR (CDCl$_3$, 100 MHz): δ = 31.1, 122.4, 123.1, 123.8, 135.0, 137.0, 137.5, 148.1, 149.6, 153.4, 155.2, 203.1.
Anal. Calcd for $C_{12}H_{10}N_2O$: C, 72.71; H, 5.08; N, 14.13%.
Found: C, 72.50; H, 5.33; N, 14.06%.

Methyl-1- [(2,2'-bipyridin)-3-yl]-ethenylcarbonate (3b)



3b

3b was prepared according to the same procedure as that of the synthesis of **3a** in 70% yield.

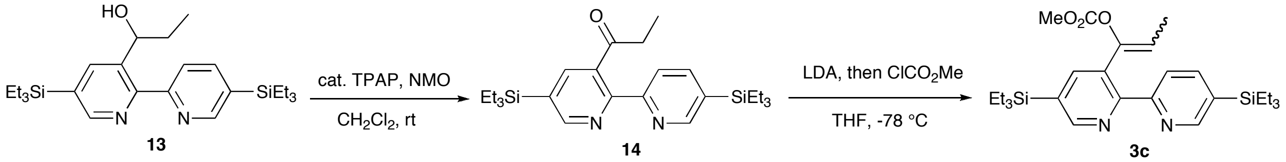
IR (CH$_2$Cl$_2$) 3155, 1762, 1647, 1466, 1382, 1096 cm^{-1}
^{1}H NMR (CDCl$_3$, 500 MHz): δ = 3.62 (3H, s), 5.16 (1H, d, *J* = 2.4 Hz), 5.28 (1H, d, *J* = 2.4 Hz), 7.31 (1H, ddd, *J* = 7.8, 4.8, 1.2 Hz), 7.36 (1H, dd, *J* = 7.8, 4.8 Hz), 7.79 (1H, dt, *J* = 1.7, 7.8 Hz), 7.86 (1H, brd, *J* = 7.8 Hz), 7.89 (1H, dd, *J* = 7.8, 1.7 Hz), 8.67 – 8.70 (1H, m), 8.70 (1H, dd, *J* = 4.8, 1.7 Hz).
^{13}C NMR (CDCl$_3$, 125 MHz): δ = 54.9, 105.9, 122.9, 123.0, 123.6, 129.9, 136.4, 138.1, 149.1,

149.6, 152.6, 153.1, 155.2, 157.7.

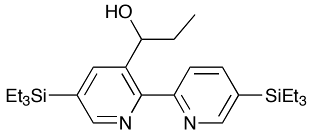
Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93%.

Found: C, 65.45; H, 4.93; N, 10.70%.

[6] Preparation of 3-alkenyl-2,2'-bipyridine derivatives 3c



13 was prepared according to the same procedure as that of the synthesis of 9 by using propanal as an electrophile. **3c** was prepared as a mixture of geometrical isomers according to the same procedure as that of the synthesis of **3b**.



13

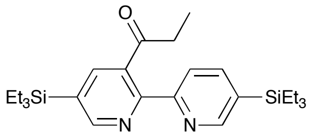
IR (CH_2Cl_2): 3305, 2954, 1577, 1459, 1014, 721 cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.80–0.93 (15H, m), 0.97–1.04 (18H, m), 1.70–1.81 (1H, m), 1.89–2.01 (1H, m), 4.53 (1H, t, J = 7.2 Hz), 7.36 (1H, brs), 7.88 (1H, s), 7.98 (1H, m), 8.14 (1H, dd, J = 8.0, 0.8 Hz), 8.64–8.66 (2H, m).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 3.2, 7.3, 11.2, 27.4, 73.4, 124.0, 132.31, 132.33, 137.3, 142.1, 143.5, 151.7, 152.5, 155.8, 158.2.

Anal. Calcd for $C_{25}H_{42}N_2OSi_2$: C, 67.81; H, 9.56; N, 6.33%.

Found: C, 68.06; H, 9.79; N, 6.10%.



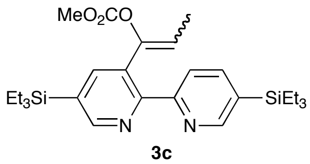
14

IR (CH_2Cl_2): 2954, 1702, 1577, 1518, 1439, 1017 cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.77–0.90 (12H, m), 0.90–1.05 (18H, m), 1.21 (3H, t, J = 7.2 Hz), 2.59 (2H, q, J = 7.2 Hz), 7.68 (1H, s), 7.91 (1H, d, J = 7.8 Hz), 8.32 (1H, d, J = 7.8 Hz), 8.62 (1H, s), 8.74 (1H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 3.1, 7.3, 8.7, 37.4, 121.2, 132.3, 132.8, 136.6, 140.5, 142.9, 152.9, 153.1, 154.1, 155.0, 207.1.

Anal. Calcd for $C_{25}H_{40}N_2OSi_2$: C, 68.12; H, 9.15; N, 6.36%.
Found: C, 67.92; H, 8.94; N, 6.18%.

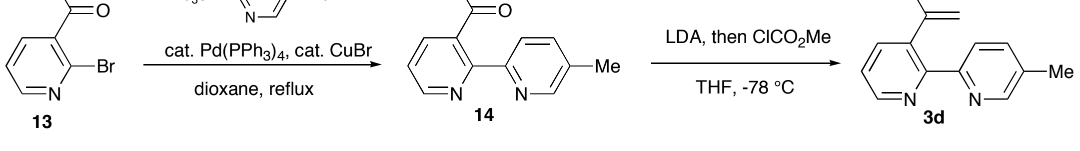


3c

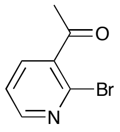
Prepared as ca. 1:1 mixture of *E* and *Z* isomers.
E-isomer:
IR (CH_2Cl_2): 2954, 1758, 1578, 1440, 1247 cm^{-1}
^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.81–0.89$ (12H, m), 0.96–1.02 (18H, m), 1.43 (3H, d, $J = 7.3$ Hz), 3.67 (3H, s), 5.64 (1H, q, $J = 7.3$ Hz), 7.83 (1H, dd, $J = 7.7, 1.7$ Hz), 7.89 (1H, d, $J = 7.7$ Hz), 7.93 (1H, d, $J = 1.7$ Hz), 8.75–8.78 (2H, m).
^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 3.13$, 3.14, 7.20, 7.23, 12.5, 54.9, 116.3, 122.8, 127.1, 131.4, 131.5, 142.1, 145.5, 145.6, 154.1, 154.4, 154.6, 156.2, 157.3.
Anal. Calcd for $C_{27}H_{42}N_2O_3Si_2$: C, 65.01; H, 8.49; N, 5.62%.
Found: C, 64.80; H, 8.79; N, 5.42%.

Z-isomer
IR (CH_2Cl_2): 2957, 1755, 1578, 1441, 1268 cm^{-1}
^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 0.82–0.88$ (12H, m), 0.96–1.02 (18H, m), 1.66 (3H, d, $J = 7.0$ Hz), 3.64 (3H, s), 5.37 (1H, q, $J = 7.0$ Hz), 7.76 (1H, d, $J = 7.7$ Hz), 7.83 (1H, dd, $J = 7.7, 1.7$ Hz), 7.88 (1H, d, $J = 1.7$ Hz), 8.69 (1H, d, $J = 1.7$ Hz), 8.74 (1H, s).
^{13}C NMR ($CDCl_3$, 125 MHz): $\delta = 3.15$, 7.21, 11.4, 55.0, 117.8, 123.0, 129.6, 131.3, 131.6, 142.1, 143.0, 146.0, 153.1, 153.9, 154.2, 155.3, 158.0.
Anal. Calcd for $C_{27}H_{42}N_2O_3Si_2$: C, 65.01; H, 8.49; N, 5.62%.
Found: C, 64.78; H, 8.38; N, 5.40%.

[7] Preparation of 3-Alkenyl-2,2'-bipyridine derivatives 3d



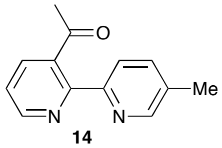
3-Acetyl-2-bromo-pyridine (13)



13

13 was prepared according to the literature procedure.[2]

3-Acetyl-5'-methyl-2,2'-bipyridine (14)



14

To a dioxane solution of **13** (52 mg, 0.26 mmol) was added Pd(PPh_3)$_4$ (16 mg, 0.02 mmol), CuBr (5.1 mg, 0.04 mmol) and 5-methyl-2-tributylstannylpyridine (129 mg, 0.34 mmol). After the mixture was refluxed for 10 h, the reaction was quenched with aqueous KF solution and the mixture was filtered through a pad of Celite. The organic materials were extracted with ethyl acetate three times, and the combined extracts were washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane : ethyl acetate = 9:1) to give **14**. (41 mg, 73%)

IR (KBr): 1686, 1421, 1041 cm^{-1}

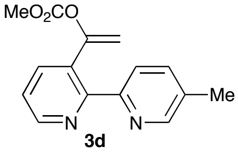
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.34 (3H, s), 2.38 (3H, s), 7.33 (1H, dd, J = 7.6, 4.8 Hz), 7.65 (1H, brd, J = 8.0 Hz), 7.69 (1H, dd, J = 7.6, 1.6 Hz), 8.20 (1H, d, J = 8.0 Hz), 8.42 (1H, s), 8.68 (1H, dd, J = 4.8, 1.6 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 18.4, 31.1, 121.9, 122.8, 133.7, 134.9, 137.2, 137.5, 148.6, 149.5, 152.6, 153.6, 203.2.

Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20%.

Found: C, 73.59; H, 5.80; N, 12.99%.

Methyl-1- [(5'-methyl-2,2'-bipyridin)-3-yl]-ethenylcarbonate (3d)



3d

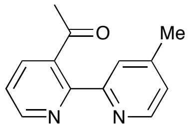
3d was prepared according to the same procedure as that of the synthesis of **3a** in 70% yield.

IR (CH_2Cl_2) 2914, 1541, 1445, 1228, 922 cm^{-1}

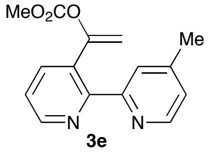
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 2.39 (3H, s), 3.63 (3H, s), 5.14 (1H, d, *J* = 2.0 Hz), 5.26 (1H, d, *J* = 2.0 Hz), 7.33 (1H, dd, *J* = 8.0, 4.0 Hz), 7.59 (1H, d, *J* = 8.0 Hz), 7.75 (1H, d, *J* = 8.0 Hz), 7.87 (1H, d, *J* = 8.0 Hz), 8.50 (1H, s), 8.68 (1H, d, *J* = 4.0 Hz).
^{13}C NMR (CDCl$_3$, 100 MHz): δ = 18.4, 54.9, 105.7, 122.5, 122.6, 123.0, 129.7, 132.6, 136.9, 138.0, 149.4, 152.7, 153.0, 154.8, 155.2.
Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36%.
Found: C, 66.90; H, 5.33; N, 10.13%.

[8] Preparation of 3-Alkenyl-2,2'-bipyridine derivatives 3e

3e was prepared according to the same procedure as that of the synthesis of **3d** described above.



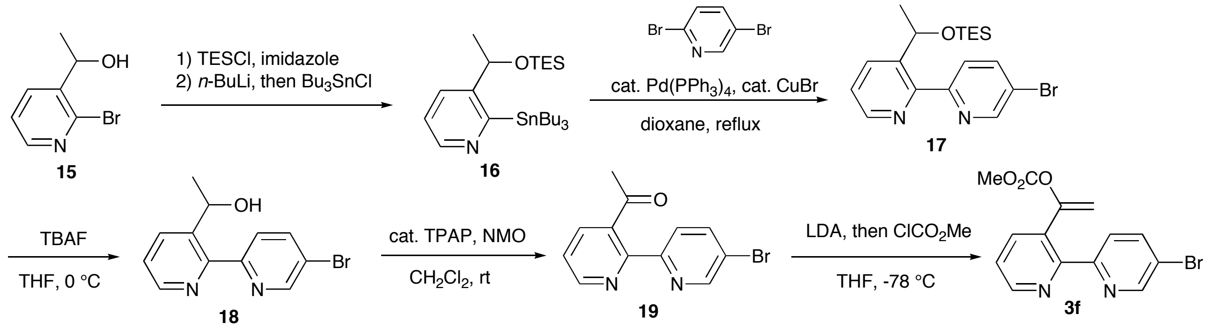
IR (KBr) 1697, 1560, 1361, 1107 cm^{-1}
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 2.33 (3H, s), 2.44 (3H, s), 7.13 (1H, d, *J* = 4.8 Hz), 7.35 (1H, dd, *J* = 8.0, 4.8 Hz), 7.71 (1H, dd, *J* = 7.6 Hz, 1.8 Hz), 8.13 (1H, s), 8.44 (1H, d, *J* = 4.8 Hz), 8.70 (1H, dd, *J* = 4.8 Hz, 1.8 Hz).
^{13}C NMR (CDCl$_3$, 100 MHz): δ = 21.2, 31.1, 123.0, 123.1, 124.8, 135.0, 137.6, 148.0, 148.2, 149.5, 153.7, 155.0, 203.0.
Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20%.
Found: C, 73.36; H, 5.79; N, 13.04%.



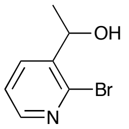
3e

IR (CH$_2$Cl$_2$): 2960, 1762, 1606, 1441, 1252 cm^{-1}
^{1}H NMR (CDCl$_3$, 500 MHz): δ = 2.41 (3H, s), 3.62 (3H, s), 5.18 (1H, d, *J* = 2.4 Hz), 5.28 (1H, d, *J* = 2.4 Hz), 7.11-7.14 (1H, m), 7.34 (1H, dd, *J* = 7.8, 4.8 Hz), 7.67 (1H, s), 7.88 (1H, dd, *J* = 7.8, 1.7 Hz), 8.52 (1H, d, *J* = 4.8 Hz), 8.68 (1H, dd, *J* = 4.8, 1.7 Hz).
^{13}C NMR (CDCl$_3$, 125 MHz): δ = 21.1, 54.9, 105.6, 122.8, 124.0, 124.3, 129.9, 138.2, 147.6, 148.8, 149.5, 152.8, 153.1, 155.4, 157.5.
Anal. Calcd for $C_{15}H_{14}N_2O_3$: C, 66.66; H, 5.22; N, 10.36%.
Found: C, 66.42; H, 5.50; N, 10.14%.

[9] Preparation of 3-Alkenyl-2,2'-bipyridine derivatives 3f



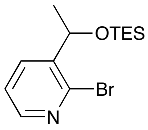
2-Bromo-3-(1-hydroxyethyl)-pyridine (15)



15

15 was prepared according to the literature procedure.[2]

2-Bromo-3-[(1-triethylsilyl)oxyethyl]-pyridine (16)

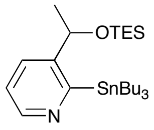


16

To a DMF solution (24 ml) of **15** (2.3 g 11 mmol) was added imidazole (1.1g, 16 mmol) and chlorotriethylsilane (2.4 g, 14 mmol). The reaction mixture was stirred at room temperature for 10 min. The reaction was quenched with pH7 phosphate buffer. The organic materials were extracted with diethyl ether three times, and the combined extracts were washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane : ethyl acetate = 9:1) to give **16** quantitatively.

IR (neat) 2954, 1654, 1459, 1017 cm^{-1}
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.55 - 0.65 (6H, m), 0.89 - 0.96 (9H, m), 1.41 (3H, d, J = 6.4 Hz), 5.10 (1H, q, J = 6.4 Hz), 7.28 (1H, dd, J = 7.6, 4.8 Hz), 7.93 (1H, dd, J = 7.6, 2.0 Hz), 8.25 (1H, dd, J = 4.8, 2.0 Hz).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 4.7, 6.8, 25.4, 68.7, 123.1, 135.8, 140.4, 143.1, 148.4.
Anal. Calcd for $C_{13}H_{22}BrNOSi$: C, 49.36; H, 7.01; N, 4.43%.
Found: C, 49.10; H, 7.24; N, 4.21%.

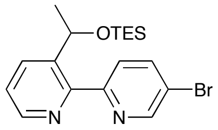
2-Tributylstannyl-3-[(1-triethylsilyl)oxyethyl]-pyridine (17)



17

To a Et_2O solution (300 ml) of **16** (6.1 g, 26 mmol) was added *n*-BuLi (1.53 M in hexane, 18.6 ml, 29 mmol) at -78 ℃. The reaction mixture was stirred at -78 ℃ for 30 min. Tributyltin chloride (5.2 ml, 31 mmol) was added to the solution. After the mixture was stirred at -78 ℃ for 1 h, the reaction was quenched with pH7 phosphate buffer. The organic materials were extracted with ethyl acetate three times, and the combined extracts were washed with brine, and dried over Na_2SO_4. Removal of the solvent under reduced pressure gave crude **17**, which was used for the next step without further purification.

5’-Bromo-3-[(1-triethylsilyl)oxyethyl]-2,2’-bipyridine (18)

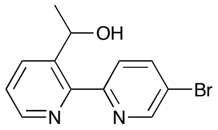


18

To a dioxane solution (68 ml) of 2,5-dibromopyridine (1.83 g, 7.7 mmol) was added $Pd(PPh_3)_4$ (420 mg, 0.4 mmol), CuBr (116 mg, 0.8 mmol) and the above crude **17** (4.3 g, 8.1 mmol). After the mixture was refluxed for 10 h, the reaction was quenched with aqueous KF solution and the mixture was filtered through a pad of Celite. The organic materials were extracted with ethyl acetate three times, and the combined extracts were washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane : ethyl acetate = 9 : 1) to give **18**. (1.78 g, 60%)

IR (neat) 2955, 2875, 1584, 1567, 1547, 1468, 1364, 1087 cm^{-1}
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.40 - 0.51 (6H, m), 0.83 (9H, t, *J* = 7.8 Hz), 1.41 (3H, d, *J* = 6.4 Hz), 5.70 (1H, q, *J* = 6.4 Hz), 7.35 (1H, dd, *J* = 8.0, 4.4 Hz), 7.86 (1H, d, *J* = 8.4 Hz), 7.94 (1H, dd, *J* = 8.4, 2.4 Hz), 8.16 (1H, dd, *J* = 8.0, 1.8 Hz), 8.55 (1H, dd, *J* = 4.4, 1.8 Hz), 8.71 (1H, d, *J* = 2.4 Hz).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 4.7, 6.8, 26.8, 66.0, 120.2, 123.7, 125.6, 135.3, 139.2, 142.1, 147.3, 149.0, 151.6, 156.9.
Anal. Calcd for $C_{18}H_{25}BrN_2OSi$: C, 54.96; H, 6.41; N, 7.12%.
Found: C, 54.73; H, 6.69; N, 6.98%.

5’-Bromo-3-(1-hydroxyethyl)-2,2’-bipyridine (19)

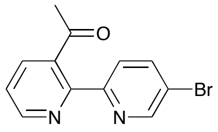


19

To a THF solution (74ml) of **18** (1.7g, 4.5mmol) was added 1.0 M THF solution (9.1 ml, 9.1 mmol) of TBAF at 0 ℃. After the mixture was stirred at room temperature overnight, the reaction was quenched with pH7 phosphate buffer. The organic materials were extracted with ethyl acetate three times, and the combined extracts were washed with brine, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (hexane : ethyl acetate = 7:3) to give **19**. (1.0 g, 70%)

IR (neat) 3054, 2975, 1567, 1547, 1440, 1092, 1068, 1012 cm^{-1}
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.54 (3H, d, *J* = 6.4 Hz), 4.88 – 4.95 (1H, m), 6.12 (1H, d, *J* = 4.0 Hz), 7.36 (1H, dd , *J* = 8.0, 4.6 Hz), 7.92 (1H, dd, *J* = 8.0, 1.4 Hz), 8.02 (1H, dd, *J* = 8.0, 2.0 Hz), 8.06 (1H, d, *J* = 8.0 Hz), 8.60 (1H, dd, *J* = 4.6, 1.4 Hz), 8.69 (1H, d, *J* = 2.0 Hz).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 20.3, 65.6, 120.7, 123.9, 126.3, 134.9, 139.2, 140.2, 147.9, 148.3, 154.3, 156.5.
Anal. Calcd for $C_{12}H_{11}BrN_2O$: C, 51.63; H, 3.97; N, 10.04%.
Found: C, 51.65; H, 4.20; N, 9.81%.

3-Acetyl-5’-bromo-2,2’-bipyridine (20)



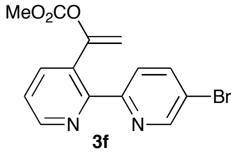
20

20 was prepared according to the same procedure as that of the synthesis of **10** in quantitative yield.

IR (neat) 1686, 1544, 1423, 1360, 1276, 1091, 1008 cm^{-1}
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 2.41 (3H, s), 7.38 (1H, dd , *J* = 7.6, 4.0 Hz), 7.70 (1H, d, *J* = 7.6 Hz), 7.98 (1H, d, *J* = 8.6 Hz), 8.24 (1H, d, *J* = 8.6 Hz), 8.66 (1H, s), 8.71 (1H, d, *J* = 4.0 Hz).
^{13}C NMR ($CDCl_3$, 100 MHz): δ = 31.2, 121.4, 123.4, 123.7, 135.0, 137.5, 139.7, 149.2, 149.6, 152.2, 153.7, 202.9.
Anal. Calcd for $C_{12}H_9BrN_2O$: C, 52.01; H, 3.27; N, 10.11%.

Found: C, 51.87; H, 3.55; N, 9.84%.

Methyl-1-[(5'-bromo-2,2'-bipyridin)-3-yl]-ethenylcarbonate 3f

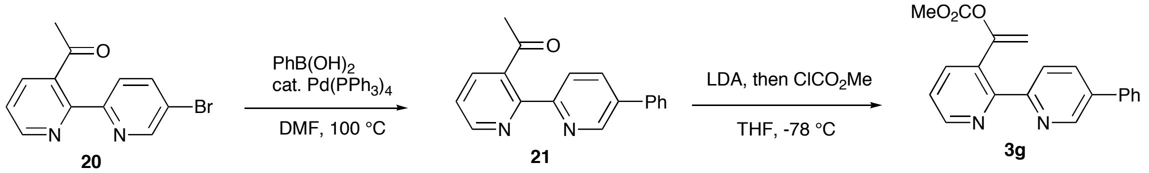


3f

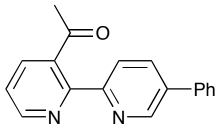
3f was prepared according to the same procedure as that of the synthesis of **3a** in 78% yield**.**

IR (neat) 2955, 1766, 1644, 1428, 1228, 1090 cm^{-1}
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 3.64 (3H, s), 5.15 (1H, d, J = 2.4 Hz), 5.30 (1H, d, J = 2.4 Hz), 7.36 (1H, dd, J = 8.0, 4.8 Hz), 7.81 (1H, d, J = 8.0 Hz), 7.86 - 7.92 (2H, m), 8.68 (1H, dd, J = 4.8, 1.6 Hz), 8.72 (1H, d, J = 1.6 Hz).
^{13}C NMR (CDCl$_3$, 100 MHz): δ = 55.0, 105.9, 120.5, 123.1, 124.9, 129.9, 138.3, 139.0, 149.5, 149.9, 152.3, 153.0, 153.9, 155.9.
Anal. Calcd for $C_{14}H_{11}BrN_2O_3$: C, 50.17; H, 3.31; N, 8.36%.
Found: C, 50.37; H, 3.53; N, 8.47%.

[10] Preparation of 3-Alkenyl-2,2'-bipyridine derivatives 3g



3-Acetyl-5'-phenyl-2,2'-bipyridine (21)



21

To a DMF solution (5 ml) of **20** (0.14 g, 0.53 mmol) was added Pd(PPh$_3$)$_4$, (0.037 g, 0.032 mmol), K$_3$PO$_4$ (0.14 g, 0.66 mmol) and phenylboronic acid (0.096 g, 0.66 mmol). After the mixture was heated at 100 ℃ for 14 h, the reaction was quenched with pH7 phosphate buffer. The organic materials were extracted with diethyl ether three times, and the combined extracts were washed with brine, and dried over Na$_2$SO$_4$. After removal of the solvent under reduced pressure, the residue was purified by preparative thin layer chromatography (hexane : ethyl acetate = 8:2) to give **21**. (128 mg, 88%)

IR (KBr) 3047, 1687, 1579, 1544, 1424, 1352, 1275 cm^{-1}

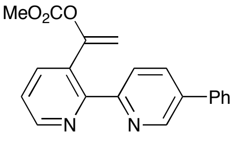
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 2.42 (3H, s), 7.34 - 7.38 (1H, m), 7.41 (1H, t, *J* = 7.2 Hz), 7.46 – 7.51 (2H, m), 7.62 -7.65 (2H, m), 7.71 (1H, dd, *J* = 7.6, 1.6 Hz), 8.05 (1H, dd, *J* = 7.6, 2.4 Hz), 8.40 (1H, d, *J* = 8.0 Hz), 8.71 – 8.73 (1H, m), 8.85 (1H, s).

^{13}C NMR (CDCl$_3$, 100 MHz): δ = 31.2, 122.3, 123.0, 127.0, 128.3, 129.0, 134.9, 135.2, 136.6, 137.0, 137.5, 146.4, 149.6, 152.9, 153.7, 202.7.

Anal. Calcd for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21%.

Found: C, 78.57; H, 5.16; N, 9.98%

Methyl-1- [(5'-phenyl-2,2'-bipyridin)-3-yl]-ethenylcarbonate (3g)



3g

3g was prepared according to the same procedure as that of the synthesis of **3a** in 61% yield**.**

IR (neat) 3054, 1765, 1643, 1429 cm^{-1}

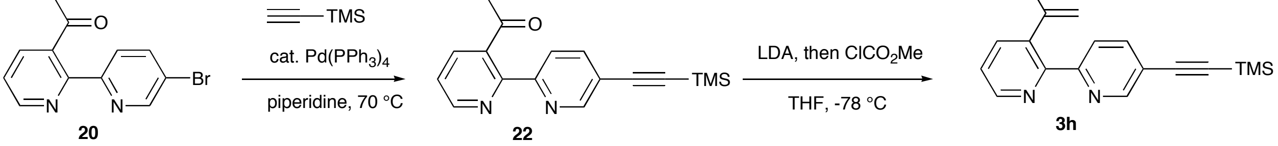
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 3.61 (3H, s), 5.20 (1H, d, *J* = 2.4 Hz), 5.33 (1H, d, *J* = 2.4 Hz), 7.36 (1H, dd, *J* = 7.6, 4.8 Hz), 7.41 (1H, t, *J* = 7.6 Hz), 7.49 (2H, t, *J* = 7.6 Hz), 7.65 (2H, d, *J* = 7.6 Hz), 7.90 (1H, dd, *J* = 7.6, 1.6 Hz), 7.96 – 8.01 (2H, m), 8.71 (1H, dd, *J* = 4.8, 1.6 Hz), 8.93 (1H, brs).

^{13}C NMR (CDCl$_3$, 100 MHz): δ = 55.0, 105.7, 122.8, 123.4, 127.0, 128.1, 129.0, 129.8, 134.6, 135.7, 137.4, 138.1, 147.4, 149.5, 152.6, 153.0, 154.8, 156.2.

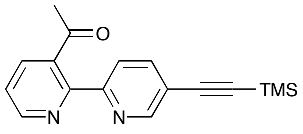
Anal. Calcd for $C_{20}H_{16}N_2O_3$: C, 72.28; H, 4.85; N, 8.43%.

Found: C, 72.05; H, 5.06; N, 8.22%.

[11] Preparation of 3-Alkenyl-2,2'-bipyridine derivatives 3h



3-Acetyl-5'-[(trimethylsilyl)ethynyl]-2,2'-bipyridine (22)

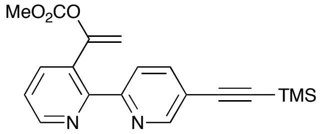


22

To a piperidiene solution (5 ml) of **20** (0.21 g, 0.76 mmol) was added Pd(PPh$_3$)$_4$ (0.088 g, 0.076 mmol) and ethynyltrimethylsilane (0.16 ml, 1.1 mmol). After the mixture was heated at 70 ℃ for 14 h, the reaction was quenched with aqueous solution of NH$_4$Cl. The organic materials were extracted with ethyl acetate three times, and the combined extracts were washed with brine, and dried over Na$_2$SO$_4$. After removal of the solvent under reduced pressure, the residue was purified by preparative thin layer chromatography (hexane : ethyl acetate = 7:3) to give **22**. (40 mg, 17%)

IR (neat) 2959, 2160, 1698, 1578, 1427, 1251 cm^{-1}
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 0.27 (9H, s), 2.36 (3H, s), 7.37 (1H, dd, *J* = 8.0, 4.8 Hz), 7.70 (1H, dd, *J* = 8.0, 1.6 Hz), 7.89 (1H, dd, *J* = 8.0, 1.6 Hz), 8.29 (1H, d, *J* = 8.0 Hz), 8.66 (1H, d, *J* = 1.6 Hz), 8.71 (1H, dd, *J* = 4.8, 1.6 Hz).
^{13}C NMR (CDCl$_3$, 100 MHz): δ = -0.13, 31.2, 99.8, 101.3, 120.4, 121.6, 123.3, 135.0, 137.8, 139.8, 149.6, 150.9, 152.6, 153.9, 202.9.
Anal. Calcd for C$_{17}$H$_{18}$N$_2$OSi: C, 69.35; H, 6.16; N, 9.51%.
Found: C, 69.09; H, 5.94; N, 9.28%.

Methyl-1- [(5’-trimethylsilylethynyl-2,2’-bipyridin)-3-yl]ethenylcarbonate (3h)



3h

3h was prepared according to the same procedure as that of the synthesis of **3a** in 70% yield.

IR (KBr) 2960, 2150, 1759, 1666, 1440, 1428, 1301, 1259 cm^{-1}
^{1}H NMR (CDCl$_3$, 400 MHz): δ = 0.28 (9H, s), 3.65 (3H, s), 5.15 (1H, d, *J* = 2.4 Hz), 5.29 (1H, d, *J* = 2.4 Hz), 7.36 (1H, dd, *J* = 8.0, 4.8 Hz), 7.82 – 7.85 (2H, m), 7.87 (1H, dd, *J* = 8.0, 1.6 Hz), 8.69 (1H, dd, *J* = 4.8, 1.6 Hz), 8.74 (1H, s).
^{13}C NMR (CDCl$_3$, 100 MHz): δ = -0.11, 55.0, 98.9, 101.6, 105.7, 119.5, 122.8, 123.0, 130.0, 138.2, 139.1, 149.5, 151.7, 152.5, 153.0, 154.3, 156.3.
Anal. Calcd for C$_{19}$H$_{20}$N$_2$O$_3$Si: C, 64.75; H, 5.72; N, 7.95%.

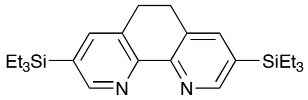
Found: C, 64.96; H, 5.93; N, 7.93%.

Preparation of dihydrophenathroline derivatives

General procedure

An CH_3CN (3.6ml, 0.02 M) solution of 3-alkenyl-2,2'-bipyridine (30.0 mg, 0.07 mmol) and $ZnCl_2$ (10.0 mg 0.07 mmol) was irradiated for 1h with a high pressure Hg lamp. After removal of the solvent under reduced pressure, CH_2Cl_2 (1.5 ml), MeOH (0.5 ml) and 1N NaOH aq. (0.7 ml) were added at room temperature. After the mixture was stirred for 10min, water was added and the organic materials were extracted with CH_2Cl_2 three times, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by preparative thin layer chromatography (hexane : ethyl acetate = 7:3) to give the product.

5,6-dihydro-3,8-bis(triethylsilyl)-1,10-Phenanthroline (2a)



2a

IR (KBr) 2952, 2873, 1580, 1558, 1458, 1365, 1144, 1010 cm^{-1}

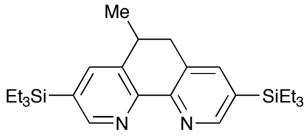
^1H NMR ($CDCl_3$, 400 MHz): δ = 0.78 - 0.90 (12H, m), 0.90 - 1.04 (18H, m), 2.97 (4H, s), 7.58 (2H, s), 8.71 (2H, s).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 3.2, 7.3, 27.5, 132.4, 132.6, 141.5, 151.9, 153.7.

Anal. Calcd for $C_{24}H_{38}N_2Si_2$: C, 70.18; H, 9.32; N, 6.82%.

Found: C, 69.95; H, 9.08; N, 6.67%.

5,6-Dihydro-3,8-ditriethylsilyl-5-Methyl-1,10- Phenanthroline (2b)



2b

IR (KBr) 2954, 2874, 1557, 1456, 1366, 1237, 1145, 1006 cm^{-1}

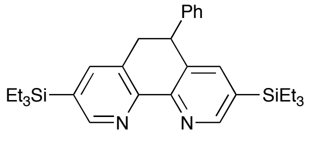
^1H NMR ($CDCl_3$, 400 MHz): δ = 0.80 - 0.88 (12H, m), 0.90 - 1.04 (18H, m), 1.29 (3H, d, *J* = 6.8 Hz), 2.72 – 2.81 (1H, m), 3.10 – 3.20 (2H, m), 7.60 (1H, s), 7.64 (1H, s), 8.74 (2H, s).

^{13}C NMR ($CDCl_3$, 125 MHz at 330 K): δ = 3.2, 7.3, 19.9, 31.9, 35.1, 131.4, 132.7, 132.8, 137.4, 140.2, 142.2, 151.1, 151.5, 153.5, 153.7.

Anal. Calcd for $C_{25}H_{40}N_2Si_2$: C, 70.69; H, 9.49; N, 6.59%.

Found: C, 70.49; H, 9.74; N, 6.35%.

5,6-dihydro-3,8-bis(triethylsilyl)-5-phenyl-1,10-phenanthroline (2d)



2d

IR (neat) 2954, 2875, 1580, 1561, 1455, 1366, 1146, 1008 cm^{-1}

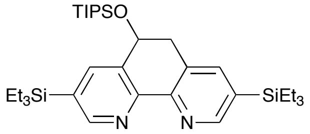
^{1}H NMR (CDCl$_3$, 500 MHz): δ = 0.69 – 0.75 (6H, m), 0.79 – 0.85 (6H, m), 0.89 (9H, t, *J* = 7.8 Hz), 0.96 (9H, t, *J* = 7.8 Hz), 3.24 (1H, dd, *J* = 15.4, 6.3 Hz), 3.30 (1H, dd, *J* = 15.4, 9.9 Hz), 4.34 (1H, dd, *J* = 9.9, 6.3 Hz), 7.17 – 7.20 (2H, m), 7.24 - 7.33 (4H, m), 7.53 (1H, s), 8.74 (2H, brs).

^{13}C NMR (CDCl$_3$, 125 MHz): δ = 3.07, 3.13, 7.1, 7.2, 35.8, 43.7, 127.0, 128.3, 128.7, 131.2, 132.7, 132.8, 135.4, 141.7, 141.9, 142.2, 151.78, 151.83, 153.9, 154.0.

Anal. Calcd for $C_{30}H_{42}N_2Si_2$: C, 74.01; H, 8.70; N, 5.75%.

Found: C, 74.30; H, 8.83; N, 5.66%.

5,6-Dihydro-3,8-bis(triethylsilyl)-5-(triisopropylsilyl)oxy-1,10-phenanthroline (2e)



2e

IR (KBr) 2954, 2873, 1581, 1559, 1460, 1369, 1008 cm^{-1}

^{1}H NMR (CDCl$_3$, 500 MHz): δ = 0.81 - 0.87 (12H, m), 0.95 - 1.00 (18H, m), 1.05 - 1.12 (18H, m), 1.13 – 1.22 (3H, m), 3.08 (1H, dd, *J* = 14.9, 5.4 Hz), 3.14 (1H, dd, *J* = 14.9, 10.5 Hz), 5.18 (1H, dd, *J* = 10.5, 5.4 Hz), 7.61 (1H, s), 8.02 (1H, s), 8.74 (1H, s), 8.76 (1H, s).

^{13}C NMR (CDCl$_3$, 125 MHz): δ = 3.11, 3.12, 7.2, 12.5, 18.1, 37.8, 68.5, 130.0, 132.5, 132.8, 135.6, 139.1, 142.2, 150.8, 151.6, 154.1, 154.3.

Anal. Calcd for $C_{33}H_{58}N_2OSi_3$: C, 67.98; H, 10.03; N, 4.80%.

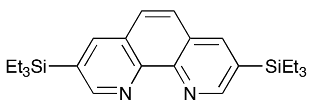
Found: C, 67.76; H, 10.05; N, 4.58%.

Preparation of phenathroline derivatives

General procedure

An CH$_3$CN (3.6 ml, 0.02 M) solution of 3-alkenyl-2,2’-bipyridine (30.0 mg, 0.07 mmol) and ZnCl$_2$ (10.0 mg 0.07 mmol) were irradiated for 1 h with a high pressure Hg lamp. After removal of the solvent under reduced pressure, CH$_2$Cl$_2$ (1.5 ml), MeOH (0.5 ml) and 1N NaOH aq. (0.7 ml) were added at room temperature. After the mixture was stirred for 10 min, water was added and the organic materials were extracted with CH_2Cl_2 three times, and dried over Na_2SO_4. After removal of the solvent under reduced pressure, to the residure was added CH_2Cl_2 (1.5 ml) and DBU (20 μl, 0.14 mmol) at room temperature. The mixture was stirred for 1h. After removal of the solvent under reduced pressure, the residue was purified by preparative thin layer chromatography (hexane : ethyl acetate = 7:3) to give product.

Phenanthroline derivatives **5b, d, e, f, g, h** are the known compounds.[3-6]



5a

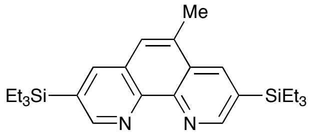
IR (KBr): 2953, 2873, 1548, 1456, 1415, 1137, 1008 cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.90 – 1.05 (30H, m), 7.78 (2H, s), 8.32 (2H, s), 9.21 (2H, s).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 3.3, 7.4, 126.2, 128.0, 132.3, 142.5, 146.2, 154.5.

Anal. Calcd for $C_{24}H_{36}N_2Si_2$: C, 70.53; H, 8.88; N, 6.85%.

Found: C, 70.29; H, 8.63; N, 6.60%.



5c

IR (KBr): 2952, 1551, 1458, 1007 cm^{-1}

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.90 – 1.08 (30H, m), 2.77 (3H, s), 7.59 (1H, s), 8.22 (1H, d, J = 1.6 Hz), 8.45 (1H, d, J = 1.6 Hz), 9.14 (1H, d, J = 1.6 Hz), 9.21 (1H, d, J = 1.6 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 3.3, 7.4, 19.1, 125.6, 127.8, 128.0, 131.8, 132.2, 132.4, 138.6, 141.6, 145.7, 146.2, 153.7, 154.0.

Anal. Calcd for $C_{25}H_{38}N_2Si_2$: C, 71.03; H, 9.06; N, 6.63%.

Found: C, 70.96; H, 9.13; N, 6.33%.

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