

Supporting Information for

2,2'-Bipyridyl Formation from 2-Arylpyridines through Bimetallic Dyttrium Intermediate

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General: All manipulations involving air- and moisture-sensitive organometallic compounds were performed under argon using the standard Schlenk technique or an argon-filled glovebox. ArNHCH₂CH₂NHAr (Ar = 2,6-*i*-Pr₂C₆H₃),^{S1} Y(CH₂SiMe₃)₃(THF)₂,^{S2} Y(ArNCH₂CH₂NAr)(CH₂SiMe₃)₃(THF)₂ (**1**),^{S3} 2-(4-methylphenyl)pyridine (**2b**), and 2-phenylpyridine-*d*₅^{S4} were prepared according to the literature procedure. Other pyridine derivatives were purchased and distilled over CaH₂. Anhydrous pentane, hexane, toluene, and THF were purchased from Kanto Chemical and further purified by passage through activated alumina columns under positive argon pressure as described by Grubbs *et al.*^{S5} Benzene, (Me₃Si)₂O, benzene-*d*₆, toluene-*d*₈, and THF-*d*₈ were dried over CaH₂ and stored in glove box. ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were measured on a BRUKER AVANCEIII-400 spectrometer. Assignment of ¹H and ¹³C{¹H} NMR peaks for some of the complexes was facilitated by 2D ¹H-¹H COSY, 2D ¹H-¹H NOESY, 2D ¹H-¹³C HMQC, and 2D ¹H-¹³C HMBC spectra. Elemental analyses were performed on a Perkin-Elmer 2400 microanalyzer at the Faculty of Engineering Science, Osaka University.

Preparation of Dyttrium Complex Bridged by 6,6'-diphenyl-2,2'-bipyridyl (4a):

A solution of 2-phenylpyridine (**2a**, 11.0 mg, 0.072 mmol) in benzene (0.5 mL) was added to a solution of **1** (50.0 mg, 0.072 mmol) in benzene (0.5 mL) by pipet. The color of the solution turned to green with green-colored powders. The solution was standing for 26 days, and large green crystals were precipitated. After decantation and washing with benzene (1 mL x 2) and pentane (1 mL), dark-green powders of **4a** were obtained quantitatively (51.6 mg, 0.0364 mmol). mp: 116–120 °C (dec.). The dark-green powders were insoluble in non-polar solvents such as C₆D₆ and C₆D₅CD₃. Anal Calcd for (C₈₂H₁₀₆N₆O₂Y₂)·(C₆H₆): C, 72.21; H, 7.71; N, 5.74. Found: C, 72.56; H, 7.82; N, 5.50.

Preparation of 4b:

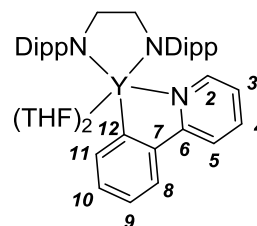
Complex **4b** was obtained quantitatively (52 mg, 0.036 mmol), following similar procedure to the synthesis of **4a**: mp: 116–120 °C (dec.). Anal Calcd for (C₈₄H₁₁₀N₆O₂Y₂)·(C₆H₆): C, 72.46; H, 7.84; N, 5.63. Found: C, 72.75; H, 7.79; N, 5.32.

Preparation of 4c:

A solution of 2-(4-methoxyphenyl)pyridine (**2c**, 13.0 mg, 0.072 mmol) in benzene (0.5 mL) was added to a solution of **1** (50.0 mg, 0.072 mmol) in benzene (0.5 mL) by pipet in an Ar-filled glovebox. The reaction mixture was heated to 50 °C for 68 h to become green suspension. After decantation and washing with benzene (1 mL x 4) and pentane (1 mL), dark-green powders of **4c** were obtained in 36% yield (18.8 mg, 1.29 x 10⁻² mmol). mp: 118–125 °C (dec.). Anal. Calcd. for (C₈₂H₁₀₆N₆O₂Y₂)·(C₆H₆)₂: C, 71.98; H, 7.68; N, 5.25. Found: C, 71.60; H, 7.70; N, 5.49.

Preparation of (ArNCH₂CH₂NAr)Y(2-pyridylphenyl)(THF)₂ (**3a**):

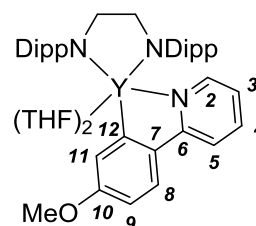
A solution of 2-phenylpyridine (**2a**, 22.3 mg, 0.144 mmol) in THF (1 mL) was added to a solution of complex **1** (100 mg, 0.144 mmol) in THF (1 mL) at room temperature by pipet in an Ar-filled glovebox, and the reaction mixture was stirred for 216 h. All of the solvent



evaporated under reduced pressure, and the residue was washed with (Me₃Si)₂O (1 mL x 5). By drying the formed precipitates in vacuo, yellow powders of **3a** were obtained in 98% yield (107 mg, 0.141 mmol). mp: 72–76 °C (dec.). ¹H NMR (400 MHz, THF-*d*₈, 30 °C) δ 8.26 (d, ³J_{H-H} = 6.5 Hz, 1H, H¹¹ of *PhPy*), 8.20 (d, ³J_{H-H} = 4.6 Hz, 1H, H² of *PhPy*), 8.02 (d, ³J_{H-H} = 8.3 Hz, 1H, H⁸ of *PhPy*), 7.77 (d, ³J_{H-H} = 7.7 Hz, 1H, H⁵ of *PhPy*), 7.74 (t, ³J_{H-H} = 7.7 Hz, 1H, H⁴ of *PhPy*), 7.69–7.12 (m, 3H, H¹⁰, H⁹, and H³ of *PhPy*), 6.83 (d, ³J_{H-H} = 7.5 Hz, 4H, *m*-H of 2,6-*i*-Pr₂C₆H₃), 6.65 (t, ³J_{H-H} = 7.5 Hz, 2H, *p*-H of 2,6-*i*-Pr₂C₆H₃), 4.09 (sept, ³J_{H-H} = 6.8 Hz, 4H, CH(CH₃)₂), 3.78 (s, 4H, N-CH₂), 3.61 (m, 8H, THF), 1.77 (q, ³J_{H-H} = 3.2 Hz, 8H, THF), 1.04 (d, ³J_{H-H} = 6.8 Hz, 24H, CH(CH₃)₂). ¹³C NMR (100 MHz, THF-*d*₈, 30 °C) δ 190.3 (d, ¹J_{Y-C} = 48.8 Hz, Y-C), 165.0 (C⁶ of *PhPy*), 156.5 (*ipso*-C of 2,6-*i*-Pr₂C₆H₃), 146.8 (C² of *PhPy*), 144.4 (C⁷ of *PhPy*), 143.7 (*o*-C of 2,6-*i*-Pr₂C₆H₃), 137.8 (C¹¹ of *PhPy*), 137.8 (C⁴ of *PhPy*), 125.8 (C¹⁰ of *PhPy*), 123.4 (C⁹ of *PhPy*), 122.2 (C⁸ of *PhPy*), 121.2 (*m*-C of 2,6-*i*-Pr₂C₆H₃), 119.4 (C³ of *PhPy*), 118.9 (*p*-C of 2,6-*i*-Pr₂C₆H₃), 118.7 (C⁵ of *PhPy*), 66.3 (THF), 59.6 (N-CH₂), 26.5 (CH(CH₃)₂), 24.4 (CH(CH₃)₂), 23.4 (THF). Anal. Calcd. for C₄₅H₆₀N₃O₂Y: C, 70.75; H, 7.92; N, 5.50. Found: C, 70.38; H, 8.17; N, 5.68.

Preparation of (ArNCH₂CH₂NAr)Y(2-pyridyl-4-MeOC₆H₃)(THF)₂ (**3c**):

Complex **1** (50.2 mg, 0.0720 mmol) and 2-(4-methoxyphenyl)pyridine (**2c**, 13.3 mg, 0.0718 mmol) were dissolved in benzene (0.5 mL) in an Ar-filled glovebox. The reaction mixture was stirred at room



temperature for 3 h. After evaporating the solvent and washing with pentane (1 mL x 2), yellow powders of **3c** were obtained in 83% yield (47.7 mg, 0.0601 mmol). mp: 91–96 °C (dec.). ¹H NMR (400 MHz, C₆D₆, 30 °C) δ 8.09 (brs, 1H, H² of Arpy), 7.79-7.65 (m, 2H, H¹¹ and H⁸ of Arpy), 7.49 (d, ³J_{H-H} = 8.3 Hz, 1H, H⁵ of Arpy), 7.22 (d, ³J_{H-H} = 7.5 Hz, 4H, *m*-H of 2,6-*i*-Pr₂C₆H₃), 7.10 (d, ³J_{H-H} = 7.5 Hz, 2H, *p*-H of 2,6-*i*-Pr₂C₆H₃), 7.01 (m, 1H, H⁴ of Arpy), 6.82 (d, ³J_{H-H} = 8.3 Hz, 1H, H⁹ of Arpy), 6.39 (t, ³J_{H-H} = 6.2 Hz, 1H, H³ of Arpy), 4.26-4.10 (m, 8H, N-CH₂ and CH(CH₃)₂), 3.61 (s, 3H, OCH₃), 3.40 (brs, 8H, THF), 1.30 (d, ³J_{H-H} = 6.7 Hz, 24H, CH(CH₃)₂), 1.09 (brs, 8H, THF). ¹³C NMR (100 MHz, C₆D₆, 30 °C) δ 194.1 (d, ¹J_{Y-C} = 46.8 Hz, Y-C¹²), 166.0 (d, ²J_{Y-C} = 2.4 Hz, C⁶ of ArPy), 159.7 (d, ²J_{Y-C} = 1.3 Hz, C⁷ of Arpy), 156.8 (*ipso*-C of 2,6-*i*-Pr₂C₆H₃), 147.7 (C² of Arpy), 145.1 (*o*-C of 2,6-*i*-Pr₂C₆H₃), 138.6 (C⁴ of Arpy), 133.9 (C¹⁰ of Arpy), 125.3 (C⁸ of Arpy), 123.3 (*m*-C of 2,6-*i*-Pr₂C₆H₃), 123.2 (C¹¹ of Arpy), 121.3 (*p*-C of 2,6-*i*-Pr₂C₆H₃), 119.2 (C³ and C⁵ of Arpy), 111.8 (C⁹ of Arpy), 69.8 (THF), 60.7 (N-CH₂), 54.6 (OCH₃), 28.3 (CH(CH₃)₂), 25.6 (CH(CH₃)₂), 25.0 (THF). Anal. Calcd for C₄₆H₆₂N₃O₃Y₂: C, 69.59; H, 7.87; N, 5.29. Found: C, 69.30; H, 7.96; N, 5.63.

Preparation of (ArNCH₂CH₂NAr)Y(2-pyridyl-4-CF₃C₆H₃)(THF)₂ (**3d**):

Complex **3d** was obtained in 83% yield (49.5 mg, 0.0595 mmol),

following similar procedure to the synthesis of **3c**. mp: 94-99 °C

(dec.). ¹H NMR (400 MHz, C₆D₆, 30 °C) δ 8.56 (s, 1H, H¹¹ of Arpy),

8.33 (d, ³J_{H-H} = 4.8 Hz, 1H, H² of Arpy), 7.51 (d, ³J_{H-H} = 8.3 Hz, 1H,

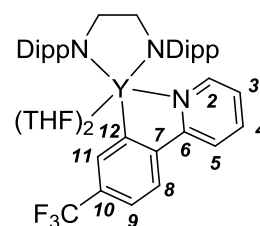
H⁸ of Arpy), 7.50 (d, ³J_{H-H} = 8.3 Hz, 1H, H⁹ of Arpy), 7.44 (d, ³J_{H-H} = 8.2 Hz, 1H, H⁵ of Arpy),

7.18 (d, ³J_{H-H} = 7.5 Hz, 4H, *m*-H of 2,6-*i*-Pr₂C₆H₃), 7.11-7.02 (m, 3H, *p*-H of 2,6-*i*-Pr₂C₆H₃ and

H⁴ of Arpy), 6.49 (t, ³J_{H-H} = 6.3 Hz, 1H, H³ of Arpy), 4.13 (m, 8H, N-CH₂ and CH(CH₃)₂),

3.37 (t, ³J_{H-H} = 6.1 Hz, 8H, THF), 1.27 (d, ³J_{H-H} = 6.8 Hz, 24 H, CH(CH₃)₂), 1.08 (m, 8H,

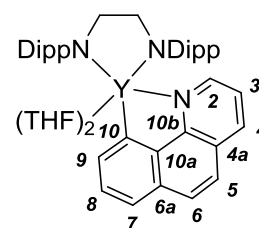
THF). ¹³C NMR (100 MHz, C₆D₆, 30 °C) δ 191.7 (d, ¹J_{Y-C} = 45.3 Hz, Y-C¹²), 164.5 (d, ²J_{Y-C}



= 2.4 Hz, C⁶ of Arpy), 156.6 (d, ²J_{Y-C} = 2.9 Hz, *ipso*-C of 2,6-*i*Pr₂C₆H₃), 149.2 (C⁷ of Arpy), 148.4 (C² of Arpy), 144.9 (*o*-C of 2,6-*i*Pr₂C₆H₃), 139.1 (C⁴ of Arpy), 135.2 (d, ³J_{C-F} = 3.3 Hz, C² of Arpy), 126.5 (q, ¹J_{C-F} = 273.0 Hz, CF₃), 123.3 (C⁸ of Arpy), 123.3 (*m*-C of 2,6-*i*Pr₂C₆H₃), 122.3 (d, ²J_{C-F} = 3.9 Hz, C⁹ of Arpy), 121.5 (*p*-C of 2,6-*i*Pr₂C₆H₃), 121.2 (C³ of Arpy), 120.2 (C⁵ of Arpy), 70.0 (THF), 60.6 (N-CH₂), 28.3 (CH(CH₃)₂), 25.5 (CH(CH₃)₂), 24.9 (THF). ¹³C NMR signal of *ipso*-C of CF₃ is not able to determine because their signal is overlapped with the signal of C₆D₅H. Anal. Calcd for C₄₆H₅₉F₃N₃O₂Y: C, 66.41; H, 7.15; N, 5.05. Found: C, 66.45; H, 7.51; N, 5.34.

Preparation of (ArNCH₂CH₂NAr)Y(κ-(C¹⁰,N)-benzo[*h*]quinolinyl)(THF)₂ (3d):

Complex **3d** was obtained quantitatively (59.5 mg, 0.0755 mmol), following similar procedure to the synthesis of **3c**. mp: 95-100 °C (dec.). ¹H NMR (400 MHz, C₆D₆, 30 °C) δ 8.56 (dd, ³J_{H-H} = 4.9, 1.4 Hz, 1H, H²), 8.51 (d, ³J_{H-H} = 6.0 Hz, 1H, H⁹), 7.71–7.58 (m, 3H, H⁴, H⁷, and H⁸), 7.69 (d, ³J_{H-H} = 8.8 Hz, 1H, H⁶), 7.22 (d, ³J_{H-H} = 8.8 Hz, 1H, H⁵), 7.19 (d, ³J_{H-H} = 7.8 Hz, 4H, *m*-H of 2,6-*i*Pr₂C₆H₃), 7.08 (t, ³J_{H-H} = 7.5 Hz, 2H, *o*-H of 2,6-*i*Pr₂C₆H₃), 6.83 (dd, ³J_{H-H} = 7.9, 4.9 Hz, 1H, H³), 4.23 (s, 4H, N-CH₂), 4.22 (t, ³J_{H-H} = 6.8 Hz, 4H, CH(CH₃)₂), 3.42 (s, 8H, THF), 1.20 (d, ³J_{H-H} = 6.8 Hz, 24H, CH(CH₃)₂), 1.08 (s, 8H, THF). ¹³C NMR (100 MHz, C₆D₆, 30 °C): δ 189.1 (d, ¹J_{Y-C} = 47.7 Hz, Y-C¹⁰), 156.9 (*ipso*-C of 2,6-*i*Pr₂C₆H₃), 154.8 (C^{10b}), 146.9 (C²), 145.1 (*o*-C of 2,6-*i*Pr₂C₆H₃), 138.2 (C⁴), 137.9 (C⁹), 133.6 (C^{6a}), 131.4 (C⁶), 128.4 (C^{10a}), 127.8 (C⁸), 127.3 (C^{4a}), 124.8 (C⁷), 123.3 (*m*-H of 2,6-*i*Pr₂C₆H₃), 122.3 (C⁵), 121.3 (*p*-H of 2,6-*i*Pr₂C₆H₃), 119.6 (C³), 69.7 (THF), 60.8 (N-CH₂), 28.3 (CH(CH₃)₂), 25.5 (CH(CH₃)₂), 25.1 (THF). Anal. Calcd for C₇₁H₆₀N₃O₂Y: C, 71.65; H, 7.68; N, 5.33. Found: C, 71.43; H, 7.82; N, 5.07.



Preparation of Bis(μ,κ -(C,N)-pyridyl)diyttrium Complex **6a**:

A solution of pyridine (**5a**, 11.3 mg, 0.143 mmol) in benzene (1 mL) was added to a solution of **1** (100 mg, 0.144 mmol) in benzene (1 mL) by pipet in an Ar-filled glovebox. The reaction mixture was stand for 48 h at room temperature to form yellow precipitates. After decantation and washing with pentane (1 mL x 5), yellow powders of **6a** were obtained in 43% yield (38 mg, 0.031 mmol). mp: 79–82 °C (dec.). ^1H NMR (400 MHz, C_6D_6 , 30 °C) δ 9.18 (d, $^3J_{\text{H-H}} = 7.4$ Hz, 2H, 3-H of Py), 8.81 (d, $^3J_{\text{H-H}} = 5.0$ Hz, 2H, 6-H of Py), 7.46 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 2H, 4-H of Py), 6.99–6.86 (m, 12H, 2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$), 6.80 (t, $^3J_{\text{H-H}} = 7.4$ Hz, 2H, 5-H of Py), 4.12 (brs, 8H, N- CH_2), 3.94 (sept, $^3J_{\text{H-H}} = 6.8$ Hz, 8H, $\text{CH}(\text{CH}_3)_2$), 2.88 (brs, 8H, α -THF), 1.13 (d, $^3J_{\text{H-H}} = 6.8$ Hz, 48H, $\text{CH}(\text{CH}_3)_2$), 0.68 (brs, 8H, β -THF). Anal. Calcd. for $\text{C}_{70}\text{H}_{98}\text{N}_6\text{O}_2\text{Y}_2$: C, 68.17; H, 8.01; N, 6.81. Found: C, 68.12; H, 8.00; N, 7.16.

Complexes **6b-6d** were prepared according to the similar procedure to **6a**.

Complex **6b** was obtained in 38% yield (34.2 mg, 0.0271 mmol). mp: 82–86 °C (dec.). ^1H NMR (400 MHz, C_6D_6 , 30 °C) δ 9.11 (s, 2H, 3-H of 4-MePy), 8.73 (d, $^3J_{\text{H-H}} = 5.0$ Hz, 2H, 6-H of 4-MePy), 7.04 – 6.80 (m, 12H, 2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$), 6.75 (d, $^3J_{\text{H-H}} = 5.0$ Hz, 2H, 5-H of 4-MePy), 4.13 (brs, 8H, CH_2), 4.00 (sept, $^3J_{\text{H-H}} = 6.4$ Hz, 8H, $\text{CH}(\text{CH}_3)_2$), 2.78 (brs, 8H, α -THF), 2.31 (s, 6H, 4-MePy), 1.16 (br, 48H, $\text{CH}(\text{CH}_3)_2$), 0.61 (brs, 8H, β -THF). Anal. Calcd. for $\text{C}_{72}\text{H}_{102}\text{N}_6\text{O}_2\text{Y}_2$: C, 68.55; H, 8.15; N, 6.66. Found: C, 68.41; H, 8.49; N, 6.69.

Complex **6c** was obtained in 66% yield (58.8 mg, 0.0424 mmol). mp: 92–96 °C (dec.). ^1H NMR (400 MHz, C_6D_6 , 30 °C) δ 9.68 (s, 2H, 3-H of Py), 8.90 (s br, 2H, 6-H of Py), 7.97 (d, $^3J = 6.6$ Hz, 4H, *o*-H of PhPy), 7.36 (t, $^3J = 7.3$ Hz, 4H, *m*-H of PhPy), 7.27-7.18 (m, 4H, 5-H of Py and *p*-H of PhPy), 7.02-6.83 (m, 12H, 2,6- $^i\text{Pr}_2\text{C}_6\text{H}_3$), 4.60-3.80 (m, 16H, $\text{CH}(\text{CH}_3)_2$ and N- CH_2), 2.90 (brs, 8H, α -THF), 1.6-0.9 (br, 48H, $\text{CH}(\text{CH}_3)_2$), 0.63 (brs, 8H, β -THF). Anal. Calcd. for $\text{C}_{82}\text{H}_{106}\text{N}_6\text{O}_2\text{Y}_2$: C, 71.08; H, 7.71; N, 6.07. Found: C, 70.86; H, 7.42; N, 5.70.

Complex **6d** was obtained in 39% yield (36.3 mg, 0.0281 mmol). mp: 98–103 °C (dec.). ¹H NMR (400 MHz, Toluene-*d*₈, -60 °C) δ 8.95 (d, ³*J* = 5.0 Hz, 2H, 6-H of Py), 6.99-6.94 (m, 12H, 2,6-*i*Pr₂C₆H₃), 6.74 (m, 2H, 5-H of Py), 6.25 (d, ³*J* = 8.4 Hz, 2H, 4-H of Py), 4.39-4.00 (m, 16H, N-CH₂ and CH(CH₃)₂), 3.88 (s, 6H, O-CH₃), 2.48 (brs, 8H, α-THF), 1.44 (br d, ³*J* = 5.9 Hz, 12H, CH(CH₃)₂), 1.34 (brd, ³*J* = 5.9 Hz, 12H, CH(CH₃)₂), 0.87 (brd, ³*J* = 5.9 Hz, 12H, CH(CH₃)₂), 0.70 (brd, ³*J* = 5.9 Hz, 12H, CH(CH₃)₂), 0.56-0.30 (m, 8H, β-THF). Anal. Calcd for C₇₂H₁₀₁N₆O₄Y₂: C, 66.91; H, 7.88; N, 6.50. Found: C, 67.16; H, 8.22; N, 6.80.

Preparation of κ-(C,N)-pyridylttrium Complex **7e**:

A solution of 3,5-lutidine (**5e**, 3.0 mg, 0.028 mmol) in C₆D₆ (0.5 mL) was added to **1** (20.0 mg, 0.0287 mmol) in C₆D₆ (0.5 mL) by pipet in an Ar-filled glovebox. The reaction mixture was heated to 60 °C for 24 h to quantitatively form **7e**. Isolation as powder form is difficult due to the high solubility of **7e** in any organic solvents. Complex **7e** was characterized by ¹H and ¹³C NMR spectra. ¹H NMR (400 MHz, C₆D₆, 30 °C) δ 7.97 (s, 1H, 6-H of 3,5-Me₂Py), 7.21 (d, ³*J*_{H-H} = 7.5 Hz, 4H, *m*-H of 2,6-*i*Pr₂C₆H₃), 7.10 (t, ³*J*_{H-H} = 7.5 Hz, 2H, *p*-H of 2,6-*i*Pr₂C₆H₃), 6.88 (s, 1H, 4-H of 3,5-Me₂Py), 4.24 (sept, ³*J*_{H-H} = 6.9 Hz, 4H, CH(CH₃)₂), 4.17 (brs, 4H, NCH₂), 3.48 (brs, 8H, α-THF), 2.65 (s, 3H, 3-Me of 3,5-Me₂Py), 1.91 (s, 3H, 5-Me of 3,5-Me₂Py), 1.37 (d, ³*J*_{H-H} = 6.9 Hz, 24H, CH(CH₃)₂), 1.24 (brs, 8H, β-THF). ¹³C NMR (100 MHz, C₆D₆, 30 °C) δ 219.6 (d, ¹*J*_{Y-C} = 35.2 Hz, Y-C), 157.1 (d, ²*J*_{Y-C} = 2.8 Hz, *ipso*-C of 2,6-*i*Pr₂C₆H₃), 145.0 (*o*-C of 2,6-*i*Pr₂C₆H₃), 142.4 (6-C of 3,5-Me₂Py), 140.0 (d, ²*J*_{Y-C} = 2.0 Hz, 3-C of 3,5-Me₂Py), 133.3 (d, ³*J*_{Y-C} = 1.3 Hz, 4-C of 3,5-Me₂Py), 129.9 (5-C of 3,5-Me₂Py), 123.2 (*m*-C of 2,6-*i*Pr₂C₆H₃), 120.9 (*p*-C of 2,6-*i*Pr₂C₆H₃), 69.0 (α-THF), 61.0 (N-CH₂), 28.4 (CH(CH₃)₂), 25.7 (CH(CH₃)₂), 25.5 (β-THF), 23.8 (3-Me of 3,5-Me₂Py), 18.1 (5-Me of 3,5-Me₂Py). Due to the high solubility of the product, we could not isolate in powder form. The ¹H and ¹³C NMR spectra were shown in Figure S4.

Preparation of (ArNCH₂CH₂NAr)Y(CH₂SiMe₂Py)(THF)₂ (**8f**):

A solution of pyridine (**5a**, 10.9 mg, 0.0721 mmol) in benzene (0.5 mL) was added to a solution of **1** (50.2 mg, 0.0720 mmol) in benzene (0.5 mL) by pipet in an Ar-filled glovebox. The reaction mixture was stand for 24 h at room temperature, and then all the solvent was evaporated. After washing with (Me₃Si)₂O (1 mL x 5), drying the remaining solid in vacuo to give yellow powders of **8f** in 69% yield (37 mg, 0.049 mmol). mp: 111–113 °C (dec.). ¹H NMR (400 MHz, C₆D₆, 30 °C) δ 7.97 (d, ³J_{H-H} = 5.2 Hz, 1H, 6-H of Py), 7.20-7.17 (m, 5H, *m*-H of 2,6-ⁱPr₂C₆H₃ and 3-H of Py), 7.10 (t, ³J_{H-H} = 7.5 Hz, 2H, *p*-H of 2,6-ⁱPr₂C₆H₃), 6.83 (dt, ³J_{H-H} = 7.6 Hz, ⁴J_{H-H} = 1.4 Hz, 1H, 4-H of Py), 6.39-6.34 (m, 1H, 5-H of Py), 4.20 (sept, ³J_{H-H} = 6.9 Hz, 4H, CH(CH₃)₂), 4.10 (s, 4H, NCH₂), 3.50 (brs, 8H, α-THF), 1.36 (d, ³J_{H-H} = 6.9 Hz, 24H, CH(CH₃)₂), 1.17 (brs, 8H, β-THF), 0.29 (s, 6H, SiMe₂). ¹³C NMR (100 MHz, C₆D₆, 30 °C) δ 179.0 (d, ²J_{Y-C} = 1.8 Hz, 2-C of Py), 156.2 (d, ²J_{Y-C} = 2.7 Hz, *ipso*-C of 2,6-ⁱPr₂C₆H₃), 148.8 (6-C of Py), 145.5 (*o*-C of 2,6-ⁱPr₂C₆H₃), 136.2 (4-C of Py), 130.6 (5-C of Py), 123.7 (*m*-C of 2,6-ⁱPr₂C₆H₃), 122.3 (3-C of Py), 121.8 (*p*-C of 2,6-ⁱPr₂C₆H₃), 69.7 (α-THF), 60.8 (N-CH₂), 28.7 (CH(CH₃)₂), 26.0 (CH(CH₃)₂), 25.5 (β-THF), 18.1 (d, ¹J_{Y-C} = 37.2 Hz, Y-C), 3.06 (SiMe₂). Anal. Calcd for C₄₂H₆₄N₃O₂SiY: C, 66.38; H, 8.49; N, 5.53. Found: C, 66.35; H, 8.54; N, 5.69.

Deuterium Labeling Experiment:

Diyttrium complex **3a-d₈,d₉,d₁₀** (100 mg, 0.0702 mmol) was suspended in C₆H₆ (2 mL), and CCl₄ (13.0 mg, 0.087 mmol, 1.2 equiv) was added to quench the reaction mixture. After heating the reaction mixture for 24 h at 60 °C, deuterated 6,6'-diphenyl-2,2'-bipyridyl was isolated by silica-gel column chromatography. ¹H NMR (400 MHz, C₆D₆, 30 °C) δ 8.61 (d, ³J_{H-H} = 7.2 Hz, 2H, 3-H of Py), 8.18 (s, 1.4H, *o*-Ph), 7.92 (t, ³J_{H-H} = 7.2 Hz, 2H, 4H of Py), 7.79 (d, ³J_{H-H} = 7.2 Hz, 2H, 5-H of Py). The ¹H NMR of the isolated product was shown in Figure S5.

X-ray Crystallographic Studies

Single crystals of **3e**, **4a-c**, **6a**, **6c**, and **6d** were obtained from the corresponding saturated solution. Suitable crystals were mounted on a CryoLoop (Hampton Research Corp.) with a layer of light mineral oil and placed in a nitrogen stream at 113 K. Crystal data and structure refinement parameters were summarized in Table S3.

The structures of all these complexes were solved by a direct method (SIR92^{S6} or SHELXS-97^{S7}) and refined on F^2 by full-matrix least-squares methods, using SHELXL-97. Non-hydrogen atoms were anisotropically refined. H-atoms were included in the refinement on calculated positions riding on their carrier atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)^2]$ ($w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$), where $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$ with $\sigma^2(F_o^2)$ from counting statistics. The function $R1$ and $wR2$ were $(\sum ||F_o| - |F_c||) / \sum |F_o|$ and $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^4)]^{1/2}$, respectively. The ORTEP-3 program^{S8} was used to draw each molecule.

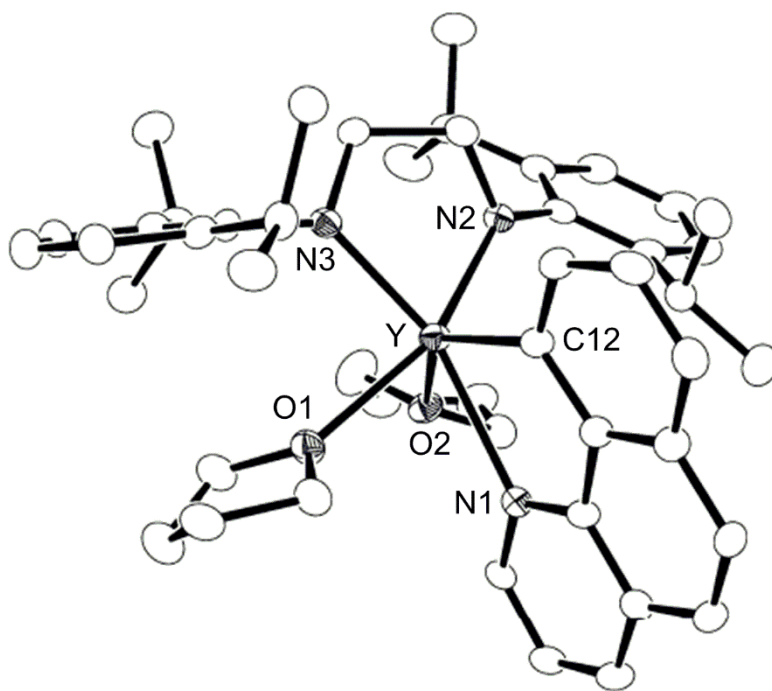


Figure S1. ORTEP drawing of complexes **3e** with 30% thermal ellipsoid. All hydrogen atoms and packing solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (°): Y – N1, 2.631(6); Y – N2, 2.272(6); Y – N3, 2.290(6); Y – C12, 2.497(7); Y – O1, 2.448(5); Y – O2, 2.443(5); N2 – Y – N3, 77.5(2); O1 – Y – O2, 84.95(18).

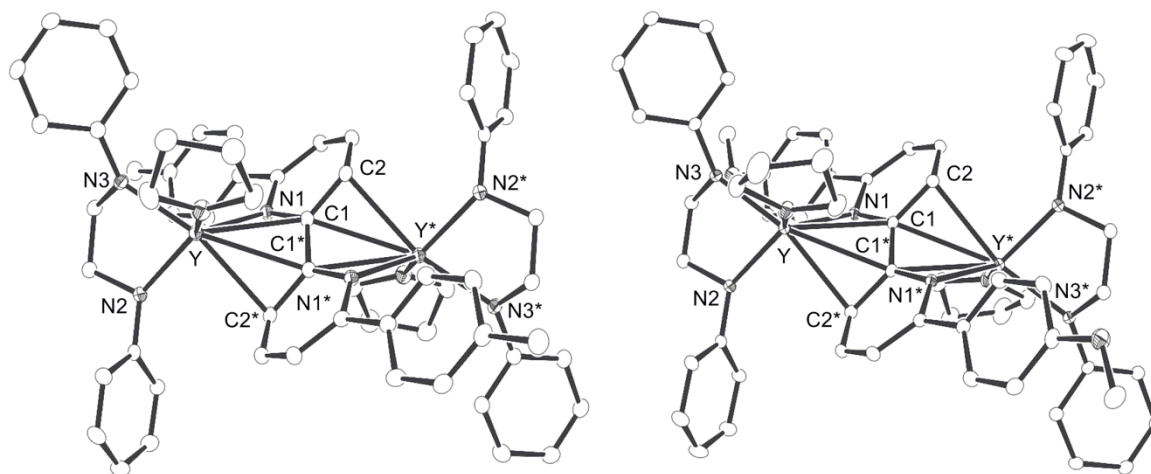


Figure S2. ORTEP drawing of complexes **4b** (left) and **4c** (right) with 30% thermal ellipsoid.

All hydrogen atoms and packing solvent molecules are omitted for clarity.

Table S1. Selected geometries (bond lengths (Å) and angles (deg)) of complexes **4a-c**.

| complex | 4a | 4b | 4c |
|------------------------|-----------|-----------------------|-----------|
| Y—N1 | 2.344(5) | 2.335(3) | 2.333(2) |
| Y—C1 | 2.746(5) | 2.755(4) | 2.771(2) |
| Y—C1* | 2.857(5) | 2.860(4) | 2.888(2) |
| Y—C2* | 2.661(5) | 2.669(4) ^a | 2.686(3) |
| N1—C1 | 1.424(6) | 1.420(4) | 1.429(3) |
| C1—C2 | 1.476(7) | 1.465(5) | 1.470(4) |
| C1—C1* | 1.396(10) | 1.418(7) | 1.392(5) |
| Y—N2 | 2.194(4) | 2.205(3) | 2.213(2) |
| Y—N3 | 2.192(5) | 2.200(3) | 2.183(2) |
| N1—Y—C2* | 70.68(16) | 70.63(11) | 70.14(8) |
| N2—Y—N3 | 80.78(17) | 79.80(11) | 80.60(8) |
| Dihedral angle between | | | |
| N1—Y—C2* and N1— | 109.6 | 110.0 | 110.9 |
| C1—C1*—C2* planes | | | |

^a Y—C2

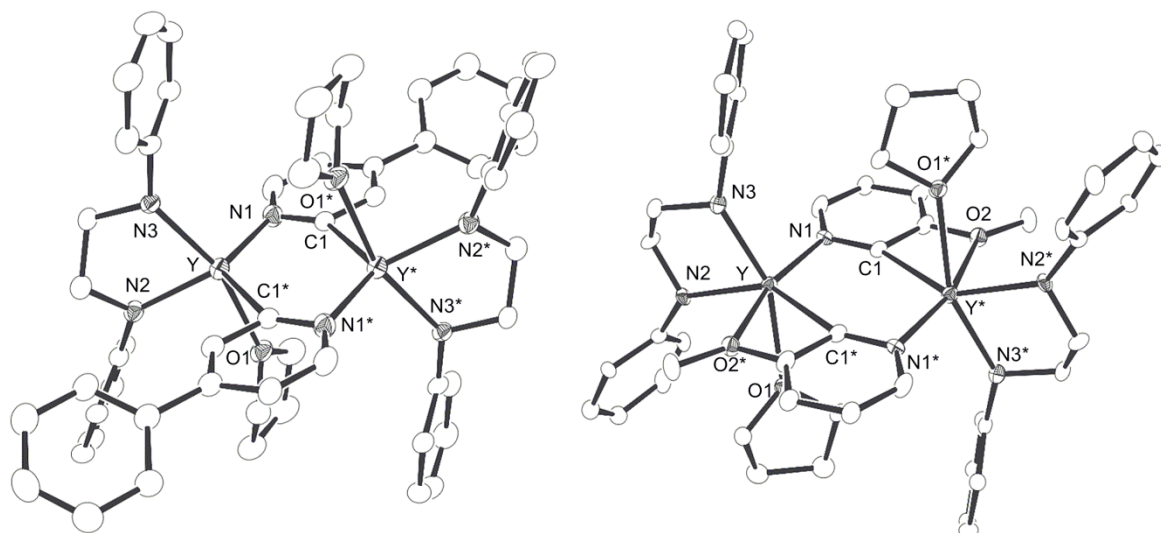


Figure S3. ORTEP drawing of complex **6c** (left) and **6d** (right) with 30% thermal ellipsoid. All hydrogen atoms and packing solvent molecules are omitted for clarity.

Table S2. Selected geometries (bond lengths (Å) and angles (deg)) of complexes **6a**, **6c**, and **6d**.

| complex | 6a | 6c | 6d |
|-----------|-----------|------------------------|------------------------|
| Y—N1 | 2.328(4) | 2.352(5) | 2.366(5) |
| Y—C1 | 2.681(5) | 2.735(6) ^{a)} | 2.850(7) ^{a)} |
| Y—C1* | 2.560(5) | 2.588(6) ^{b)} | 2.685(7) ^{b)} |
| N1—C1 | 1.380(6) | 1.379(7) | 1.376(8) |
| Y—N2 | 2.216(4) | 2.237(5) | 2.239(6) |
| Y—N3 | 2.219(4) | 2.210(5) | 2.252(5) |
| Y—O1(THF) | 2.422(3) | 2.419(4) | - |
| Y—O1* | - | - | 2.504(5) |
| Y—O2(THF) | - | - | 2.404(5) |

^{a)} Y—C1* ^{b)} Y—C1

Table S3. Crystal Data and Data Collection Parameters for **3e**, **4a-c**, **6a**, **6c**, and **6d**.^{a) b)}

| compound | 3e | 4a |
|---|---|--|
| empirical formula | C ₄₇ H ₆₂ N ₃ O ₂ Y | C ₈₂ H ₁₀₈ N ₆ O ₂ Y ₂ ·2(C ₆ H ₆) |
| formula weight | 789.93 | 1543.78 |
| crystal system | <i>monoclinic</i> | <i>monoclinic</i> |
| space group | <i>P2₁/n</i> (#14) | <i>P2₁/n</i> (#14) |
| <i>a</i> , Å | 12.902(11) | 13.160(7) |
| <i>b</i> , Å | 21.925(16) | 16.367(8) |
| <i>c</i> , Å | 16.088(13) | 19.701(10) |
| α , deg. | - | - |
| β , deg. | 106.222(7) | 103.837(4) |
| γ , deg. | - | - |
| <i>V</i> , Å ³ | 4370(6) | 4120(4) |
| <i>Z</i> | 4 | 2 |
| <i>D</i> _{calcd} , g/cm ³ | 1.201 | 1.244 |
| μ [Mo-K α], mm ⁻¹ | 1.375 | 1.453 |
| crystal size, mm ³ | 0.30×0.20×0.05 | 0.28×0.26×0.23 |
| <i>T</i> , K | 113(2) | 113(2) |
| θ range for data collection, deg. | 3.23 to 27.23 | 3.01 to 26.00 |
| no. of reflections measured | 36919 | 35619 |
| unique data (<i>R</i> _{int}) | 8565 (0.1279) | 8083 (0.1303) |
| data / restraints / parameters | 8565 / 0 / 486 | 8083 / 12 / 471 |
| <i>R</i> 1 (<i>I</i> > 2.0 σ (<i>I</i>)) ^{a)} | 0.1188 | 0.0948 |
| <i>wR</i> 2 (<i>I</i> > 2.0 σ (<i>I</i>)) ^{b)} | 0.2648 | 0.1451 |
| <i>R</i> 1 (all data) ^{a)} | 0.1641 | 0.1412 |
| <i>wR</i> 2 (all data) ^{b)} | 0.3028 | 0.1664 |
| GOF on <i>F</i> ² | 1.111 | 1.127 |
| $\Delta\rho$, e Å ⁻³ | 1.87, -0.95 | 0.51, -0.495 |

a) $R1 = (\sum||Fo| - |Fc|)/(\sum|Fo|)$ b) $wR2 = [\{\sum w(Fo^2 - Fc^2)^2\}/\{\sum w(Fo^4)\}]^{1/2}$

Table S3 (continued). Crystal Data and Data Collection Parameters for **3e**, **4a-c**, **6a**, **6c**, and **6d**.^{a) b)}

| compound | 4b | 4c |
|--|---|---|
| empirical formula | C ₈₄ H ₁₁₀ N ₆ O ₂ Y ₂ · 2(C ₇ H ₈) | C ₈₄ H ₁₁₀ N ₆ O ₄ Y ₂ · 2(C ₇ H ₈) |
| formula weight | 1599.88 | 1631.94 |
| crystal system | <i>monoclinic</i> | <i>monoclinic</i> |
| space group | <i>P2₁/n</i> (#14) | <i>P2₁/n</i> (#14) |
| <i>a</i> , Å | 13.324(6) | 13.2137(9) |
| <i>b</i> , Å | 16.849(7) | 17.8164(9) |
| <i>c</i> , Å | 19.590(8) | 18.8346(12) |
| <i>α</i> , deg. | - | - |
| <i>β</i> , deg. | 104.350(5) | 102.372(3) |
| <i>γ</i> , deg. | - | - |
| <i>V</i> , Å ³ | 4261(3) | 4331.1(5) |
| <i>Z</i> | 2 | 2 |
| <i>D</i> _{calcd} , g/cm ³ | 1.247 | 1.251 |
| <i>μ</i> [Mo-Kα], mm ⁻¹ | 1.4095 | 1.3896 |
| crystal size, mm ³ | 0.32×0.29×0.06 | 0.47×0.38×0.10 |
| <i>T</i> , K | 113(2) | 113(2) |
| <i>θ</i> range for data collection, deg. | 3.16 to 27.49 | 3.11 to 27.47 |
| no. of reflections measured | 40751 | 41389 |
| unique data (<i>R</i> _{int}) | 9727 (0.0782) | 9871 (0.0598) |
| data / restraints / parameters | 9727 / 0 / 487 | 9871 / 0 / 496 |
| <i>R</i> 1 (<i>I</i> > 2.0σ(<i>I</i>)) ^{a)} | 0.0661 | 0.0498 |
| <i>wR</i> 2 (<i>I</i> > 2.0σ(<i>I</i>)) ^{b)} | 0.1386 | 0.1025 |
| <i>R</i> 1 (all data) ^{a)} | 0.1024 | 0.0681 |
| <i>wR</i> 2 (all data) ^{b)} | 0.1626 | 0.1130 |
| GOF on <i>F</i> ² | 1.061 | 1.093 |
| Δρ, e Å ⁻³ | 1.45, -0.75 | 0.78, -0.79 |

a) $R1 = (\sum ||Fo| - |Fc||) / (\sum |Fo|)$ b) $wR2 = [\{ \sum w(Fo^2 - Fc^2)^2 \} / \{ \sum w(Fo^4) \}]^{1/2}$

Table S3 (continued). Crystal Data and Data Collection Parameters for **3e**, **4a-c**, **6a**, **6c**, and **6d**.^{a) b)}

| compound | 6a | 6c |
|---|---|--|
| empirical formula | C ₇₀ H ₁₀₀ N ₆ O ₂ Y ₂ | C ₈₂ H ₁₀₆ N ₆ O ₂ Y ₂ ·2(C ₆ H ₆) |
| formula weight | 1235.38 | 1543.83 |
| crystal system | <i>monoclinic</i> | <i>monoclinic</i> |
| space group | <i>C2/c</i> (#15) | <i>P2₁/n</i> (#14) |
| <i>a</i> , Å | 16.313(7) | 15.639(7) |
| <i>b</i> , Å | 20.362(9) | 17.514(8) |
| <i>c</i> , Å | 20.231(9) | 16.240(8) |
| α , deg. | - | - |
| β , deg. | 92.019(4) | 104.711(4) |
| γ , deg. | - | - |
| <i>V</i> , Å ³ | 6716(5) | 4302(3) |
| <i>Z</i> | 4 | 2 |
| <i>D</i> _{calcd} , g/cm ³ | 1.222 | 1.192 |
| μ [Mo-K α], mm ⁻¹ | 1.766 | 1.3935 |
| crystal size, mm ³ | 0.20×0.08×0.08 | 0.21×0.17×0.10 |
| <i>T</i> , K | 113(2) | 113(2) |
| θ range for data collection, deg. | 3.15 to 26.00 | 3.13 to 27.47 |
| no. of reflections measured | 29121 | 35630 |
| unique data (<i>R</i> _{int}) | 6581 (0.1065) | 7992 (0.1016) |
| data / restraints / parameters | 6581 / 0 / 369 | 7992 / 0 / 501 |
| <i>R</i> 1 (<i>I</i> > 2.0 σ (<i>I</i>)) ^{a)} | 0.0784 | 0.1176 |
| <i>wR</i> 2 (<i>I</i> > 2.0 σ (<i>I</i>)) ^{b)} | 0.1337 | 0.1838 |
| <i>R</i> 1 (all data) ^{a)} | 0.1091 | 0.1348 |
| <i>wR</i> 2 (all data) ^{b)} | 0.1492 | 0.1930 |
| GOF on <i>F</i> ² | 1.109 | 1.290 |
| $\Delta\rho$, e Å ⁻³ | 1.214, -0.568 | 0.75, -0.69 |

a) $R1 = (\sum||Fo| - |Fc|)| / (\sum|Fo|)$ b) $wR2 = [\{ \sum w(Fo^2 - Fc^2)^2 \} / \{ \sum w(Fo^4) \}]^{1/2}$

Table S3 (continued). Crystal Data and Data Collection Parameters for **3e**, **4a-c**, **6a**, **6c**, and **6d**.^{a) b)}

| compound | 6d |
|--|---|
| empirical formula | C ₇₂ H ₁₀₄ N ₆ O ₄ Y ₂ |
| formula weight | 1295.46 |
| crystal system | <i>monoclinic</i> |
| space group | <i>P2₁/n</i> (#14) |
| <i>a</i> , Å | 13.492(12) |
| <i>b</i> , Å | 13.673(12) |
| <i>c</i> , Å | 19.029(18) |
| <i>α</i> , deg. | - |
| <i>β</i> , deg. | 101.334(9) |
| <i>γ</i> , deg. | - |
| <i>V</i> , Å ³ | 3442(5) |
| <i>Z</i> | 2 |
| <i>D</i> _{calcd} , g/cm ³ | 1.250 |
| <i>μ</i> [Mo-Kα], mm ⁻¹ | 1.7304 |
| crystal size, mm ³ | 0.17×0.15×0.05 |
| <i>T</i> , K | 113(2) |
| <i>θ</i> range for data collection, deg. | 3.17 to 27.48 |
| no. of reflections measured | 27295 |
| unique data (<i>R</i> _{int}) | 6063 (0.1436) |
| data / restraints / parameters | 6060 / 0 / 379 |
| <i>R</i> 1 (<i>I</i> > 2.0σ(<i>I</i>)) ^{a)} | 0.0914 |
| <i>wR</i> 2 (<i>I</i> > 2.0σ(<i>I</i>)) ^{b)} | 0.1563 |
| <i>R</i> 1 (all data) ^{a)} | 0.1414 |
| <i>wR</i> 2 (all data) ^{b)} | 0.1837 |
| GOF on <i>F</i> ² | 1.063 |
| Δρ, e Å ⁻³ | 1.51, -0.64 |

a) $R1 = (\sum ||Fo| - |Fc||) / (\sum |Fo|)$ b) $wR2 = [\{ \sum w(Fo^2 - Fc^2)^2 \} / \{ \sum w(Fo^4) \}]^{1/2}$

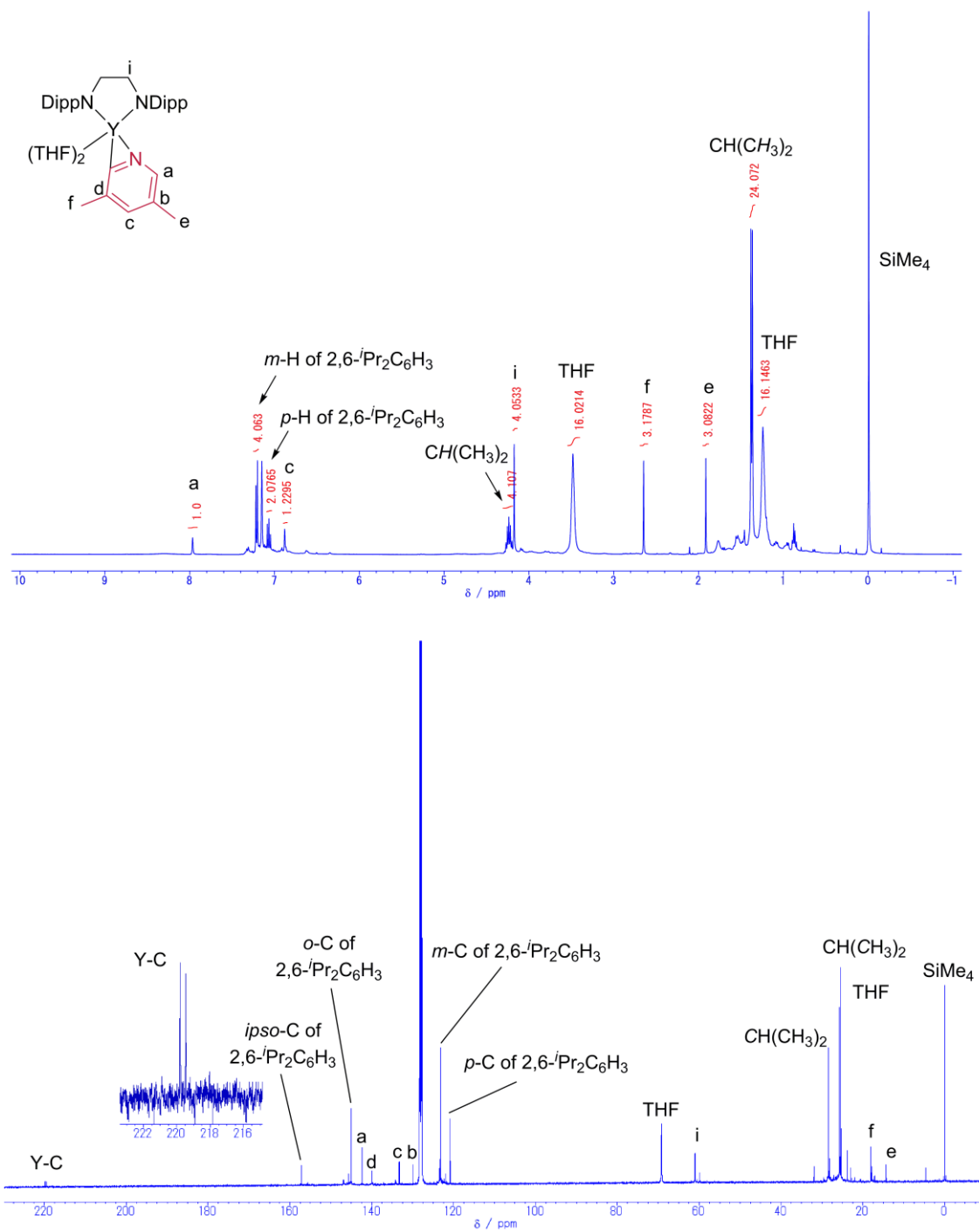


Figure S4. ^1H NMR (top) and ^{13}C NMR (bottom) spectra of **7e**.

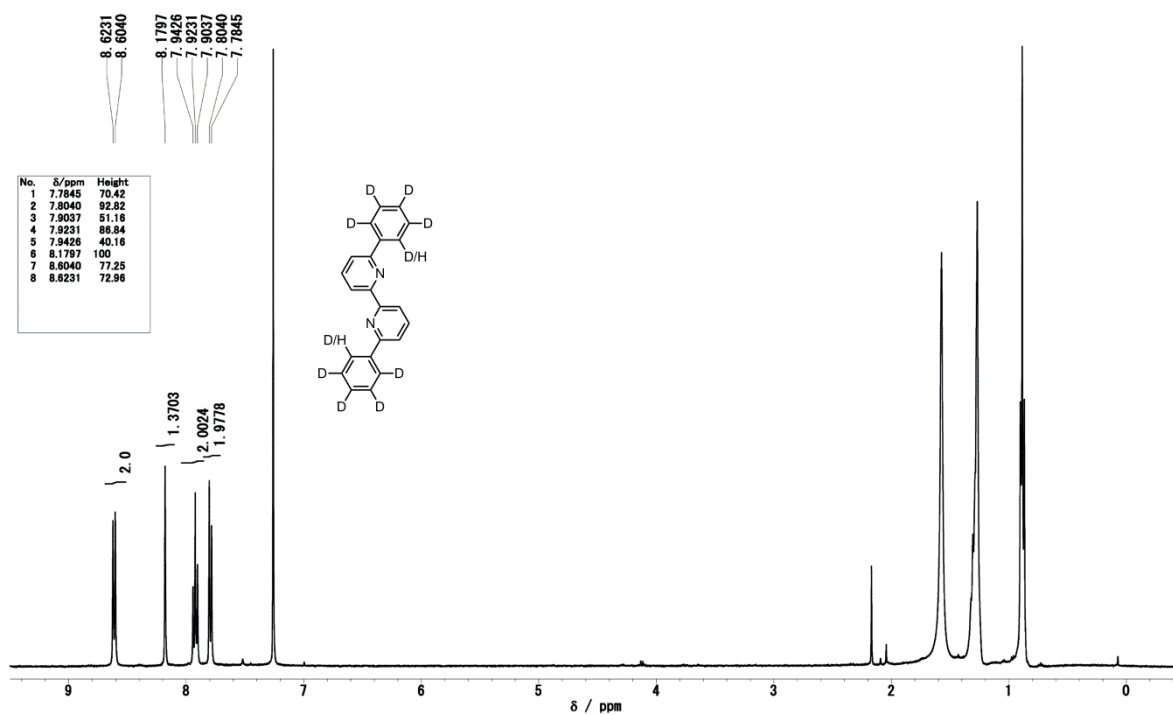


Figure S5. ^1H NMR spectrum of deuterated 6,6'-diphenyl-2,2'-bipyridyl.

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