Supporting Information

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Electroauxiliary-Assisted Sequential Introduction of Two Carbon Nucleophiles on the Same α -Carbon of Nitrogen: Application to the Synthesis of Spiro Compounds

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Experimental Details

General Remarks. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 on a Varian Gemini 2000 spectrometer with Me_4Si as an internal standard unless otherwise noted. Mass spectra were obtained on JEOL JMS SX-102A mass spectrometer. Elemental analyses were carried out at Kyoto University Elemental Analysis Center. IR spectra were measured with a SHIMADZU FTIR 8100 spectrometer. Flash chromatography was carried out on a column of silica gel (Kanto Chem. Co., Silica Gel 60N, spherical, neutral, 40-100 μm). All reactions were carried out under Ar atmosphere.

Materials. Dichloromethane was washed with water, distilled from P_2O_5 , redistilled from dried K_2CO_3 to remove a trace amount of acid, and stored over molecular sieves 4A. Dry ether and THF was purchased from Kanto Chem. Co. as a dehydrated solvent. Bu_4NBF_4 was dried under reduced pressure before use. *N*-(*tert*-Butoxycarbonyl)-2-trimethylsilylpyrrolidine (**1**)¹ were synthesized by known procedures.

***N*-(*tert*-Butoxycarbonyl)-2,2-bis(trimethylsilyl)pyrrolidine (2).** To a solution of *N*-(*tert*-Butoxycarbonyl)-2-trimethylsilylpyrrolidine (**1**) (7.75 g, 31.8 mmol) and HMPA (11.85 g, 66 mmol) in dry ether (70 mL) was added *sec*-butyllithium (1.01 M in cyclohexane / hexane, 64 mL, 64.6 mmol) at $-78\text{ }^{\circ}\text{C}$. The solution was stirred for 4 h at $-78\text{ }^{\circ}\text{C}$ and trimethylsilyl chloride (8.56 g, 78.8 mmol) was added. The solution was warmed to room temperature and stirred for 0.5 h. Saturated aqueous NaHCO_3 was added. The organic phase was separated, the aqueous phase was extracted with ether (20 mL x 3). The combined organic phase was dried over Na_2SO_4 . After removal of the solvent, the crude product was purified with flash column chromatography (hexane/ethyl acetate 50 : 1) to obtain the title compound (8.72 g, 87%): The spectrum data was identical to the literature.²

***N*-Methoxycarbonyl-2,2-bis(trimethylsilyl)pyrrolidine (3).** To a solution of *N*-(*tert*-Butoxycarbonyl)-2,2-bis(trimethylsilyl)pyrrolidine (**2**) (8.72 g, 27.6 mmol) in CH_2Cl_2 (60 mL) was added TFA (15.7 g, 137 mmol) at room temperature. The solution was stirred for 3.5 h at room temperature and dry K_2CO_3 (26.6 g, 192 mmol) was added slowly at $0\text{ }^{\circ}\text{C}$. The solution was stirred for 0.5 h at room temperature and methyl chloroformate (4.23 g, 44.8 mmol) was added at $0\text{ }^{\circ}\text{C}$. The mixture was stirred over night at room temperature, and then water was added. The mixture was extracted with ether (50 mL x 3), and the organic phase was dried over Na_2SO_4 . After removal of the solvent, the crude product was purified with flash column chromatography (hexane/ethyl acetate 25 : 1) to obtain the title compound (6.56 g, 87%): ^1H NMR (300 MHz, CDCl_3) δ 0.05 (s) and 0.09 (s) (total 18H, two rotamers), 1.78-1.88 (m, 2H), 2.00 (t, $J = 6.0\text{ Hz}$) and 2.08 (t, $J = 6.0\text{ Hz}$) (total 2H, two rotamers), 3.37 (t, $J = 6.0\text{ Hz}$) and 3.48 (t, $J = 6.0\text{ Hz}$) (total 2H, two rotamers), 3.64 (s) and 3.65 (s) (total 3H, two rotamers); ^{13}C NMR (75

MHz, CDCl₃) δ -0.5 and -0.3, 24.3 and 25.1, 31.9 and 33.2, 46.7 and 47.1, 48.0 and 49.0, 51.0 and 52.3, 155.3 and 155.5; IR (neat) 1700, 1449, 1379 cm⁻¹; LRMS (EI) m/e 273 (M⁺), 258 (M⁺-CH₃); HRMS (EI) calcd for C₁₂H₂₇O₂NSi₂ (M⁺): 273.1580, found: 273.1583; Anal. calcd for C₁₂H₂₇O₂NSi₂: C, 52.69; H, 9.95; N, 5.12. found: C, 52.45; H, 10.17; N, 5.12.

***N*-Methoxycarbonyl-2-allyl-2-trimethylsilylpyrrolidine (4).** The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca 320 mg, dried at 250 °C / 1 mmHg for 2 h before use) and a platinum plate cathode (40 mm x 20 mm). In the anodic chamber was placed a solution of *N*-methoxycarbonyl-2,2-bis(trimethylsilyl)pyrrolidine (**3**) (115.6 mg, 0.423 mmol) in 0.3 M Bu₄NBF₄ / CH₂Cl₂ (8 mL). In the cathodic chamber was placed 0.3 M Bu₄NBF₄ / CH₂Cl₂ (8 mL) and trifluoromethanesulfonic acid (61.0 mg, 0.406 mmol). The constant current electrolysis (8 mA) was carried out at -78 °C with magnetic stirring until 2.5 F / mol of electricity was consumed. To the cation pool thus generated in the anodic chamber, was added allyltrimethylsilane (299.9 mg, 2.62 mmol) and the solution was stirred for 2 h at -23 °C. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (10 cm) of silica gel to remove Bu₄NBF₄. The silica gel was washed with ether (250 mL). The combined filtrate was concentrated and the crude product was purified with flash column chromatography (hexane/ethyl acetate 25 : 1) to obtain the title compound (89.8 mg, 88%): ¹H NMR (300 MHz, CDCl₃) δ -0.02 (s) and 0.03 (s) (total 9H, two rotamers), 1.62-1.88 (m, 4H), 2.25-2.53 (m, 2H), 3.10-3.29 (m, 1H), 3.42-3.59 (m, 1H), 3.60 (s) and 3.62 (s) (total 3H, two rotamers), 4.94-5.04 (m, 2H), 5.62-5.79 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ -2.1 and -1.8, 22.4 and 23.1, 33.1 and 34.3, 38.6 and 39.7, 47.9 and 48.9,

51.4 and 52.0, 55.1 and 55.7, 117.4 and 117.7, 134.8 and 135.1, 155.06 and 155.11; IR (neat) 1698, 1449, 1381 cm^{-1} ; LRMS (EI) m/e 241 (M^+), 226 ($\text{M}^+ - \text{CH}_3$), 200 ($\text{M}^+ - \text{allyl}$); HRMS (EI) calcd for $\text{C}_{12}\text{H}_{23}\text{O}_2\text{NSi}$ (M^+): 241.1498, found: 241.1495; Anal. calcd for $\text{C}_{12}\text{H}_{23}\text{O}_2\text{NSi}$: C, 59.70; H, 9.60; N, 5.80. found: C, 59.68; H, 9.66; N, 5.86.

***N*-Methoxycarbonyl-2-(3-butenyl)-2-trimethylsilylpyrrolidine (5).** The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca 320 mg, dried at 250 °C / 1 mmHg for 2 h before use) and a platinum plate cathode (50 mm x 30 mm). In the anodic chamber was placed a solution of *N*-methoxycarbonyl-2,2-bis(trimethylsilyl)pyrrolidine (**3**) (812.7 mg, 2.97 mmol) in 0.3 M Bu_4NBF_4 / CH_2Cl_2 (40 mL). In the cathodic chamber was placed 0.3 M Bu_4NBF_4 / CH_2Cl_2 (40 mL) and trifluoromethanesulfonic acid (907.3 mg, 6.05 mmol). The constant current electrolysis (32 mA) was carried out at -78 °C with magnetic stirring until 2.5 F / mol of electricity was consumed. To the cation pool thus generated in the anodic chamber, was added 3-butenylmagnesiumbromide (0.48 M in ether, 12.5 mL, 6.0 mmol) and dry CH_2Cl_2 (12.5 mL) was added to the cathodic chamber. The solution was stirred for 20 min at -78 °C. Acetic acid (314.7 mg, 5.2 mmol) was added. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (15 cm) of silica gel to remove Bu_4NBF_4 . The silica gel was washed with ether (500 mL). The combined filtrate was concentrated and the crude product was purified with flash column chromatography (hexane/ethyl acetate 25 : 1) to obtain the title compound (545.0 mg, 72%): ^1H NMR (300 MHz, CDCl_3) δ 0.00 (s) and 0.06 (s) (total 9H, two rotamers), 1.60-2.04 (m, 8H), 3.14-3.34 (m, 1H), 3.44-3.60 (m, 1H), 3.61 (s) and 3.63 (s) (total 3H, two rotamers), 4.84-5.01 (m, 2H), 5.67-5.82 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ -2.0 and -1.7, 22.7 and 23.4, 29.4 and

29.6, 33.5 and 33.7, 34.6 and 34.7, 47.8 and 48.8, 51.4 and 52.0, 55.3 and 55.8, 114.1 and 114.3, 138.5 and 138.7, 155.1 and 155.3; IR (neat) 1700, 1449, 1381 cm^{-1} ; LRMS (EI) m/e 255 (M^+), 240 ($\text{M}^+ - \text{CH}_3$); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{25}\text{O}_2\text{NSi}$ (M^+): 255.1655, found: 255.1655; Anal. calcd for $\text{C}_{13}\text{H}_{25}\text{O}_2\text{NSi}$: C, 61.13; H, 9.87; N, 5.48. found: C, 60.85; H, 9.98; N, 5.58.

***N*-Methoxycarbonyl-2,2-diallylpyrrolidine (6).** The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca 320 mg, dried at 250 $^{\circ}\text{C}$ / 1 mmHg for 2 h before use) and a platinum plate cathode (40 mm x 20 mm). In the anodic chamber was placed a solution of *N*-methoxycarbonyl-2-allyl-2-trimethylsilylpyrrolidine (**4**) (76.5 mg, 0.317 mmol) in 0.3 M Bu_4NBF_4 / CH_2Cl_2 (8 mL). In the cathodic chamber was placed 0.3 M Bu_4NBF_4 / CH_2Cl_2 (8 mL) and trifluoromethanesulfonic acid (49.3 mg, 0.329 mmol). The constant current electrolysis (8 mA) was carried out at -78°C with magnetic stirring until 2.5 F / mol of electricity was consumed. To the cation pool thus generated in the anodic chamber, was added allyltrimethylsilane (361.6 mg, 3.16 mmol) and the solution was stirred for 2 h at -78°C . The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (10 cm) of silica gel to remove Bu_4NBF_4 . The silica gel was washed with ether (250 mL). The combined filtrate was concentrated and the crude product was purified with flash column chromatography (hexane/ethyl acetate 20 : 1) to obtain the title compound (30.5 mg, 46%): ^1H NMR (300 MHz, CDCl_3) δ 1.65-1.92 (m, 4H), 2.22-2.38 (m, 2H), 2.61 (dd, J = 13.4, 6.8 Hz) and 2.80 (dd, J = 13.5, 6.6 Hz) (total 2H, two rotamers), 3.35 (t, J = 6.9 Hz) and 3.44 (t, J = 6.9 Hz) (total 2H, two rotamers), 3.63 (s) and 3.70 (s) (total 3H, two rotamers), 4.99-5.10 (m, 4H), 5.61-5.77 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.7 and 22.2, 33.8 and 35.1,

41.6 and 42.9, 48.5 and 49.5, 51.8 and 51.9, 64.7 and 65.5, 118.0 and 118.2, 134.0 and 134.4, 154.3 and 155.5; IR (neat) 1705, 1447, 1375 cm^{-1} ; LRMS (FAB) m/e 210 ($\text{M}^+\text{+H}$), 168 ($\text{M}^+\text{-allyl}$); HRMS (FAB) calcd for $\text{C}_{12}\text{H}_{20}\text{O}_2\text{N}$ ($\text{M}^+\text{+H}$): 210.1494, found: 210.1497.

***N*-Methoxycarbonyl-2-allyl-2-(3-butenyl)pyrrolidine (7).** The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca 320 mg, dried at 250 °C / 1 mmHg for 2 h before use) and a platinum plate cathode (40 mm x 20 mm). In the anodic chamber was placed a solution of *N*-methoxycarbonyl-2-(3-butenyl)-2-trimethylsilylpyrrolidine (**5**) (103.6 mg, 0.406 mmol) in 0.3 M Bu_4NBF_4 / CH_2Cl_2 (8 mL). In the cathodic chamber was placed 0.3 M Bu_4NBF_4 / CH_2Cl_2 (8 mL) and trifluoromethanesulfonic acid (60.4 mg, 0.402 mmol). The constant current electrolysis (8 mA) was carried out at -78 °C with magnetic stirring until 2.5 F / mol of electricity was consumed. To the cation pool thus generated in the anodic chamber, was added allyltrimethylsilane (460.0 mg, 4.03 mmol) and the solution was stirred for 2 h at -78 °C and 3 h at -48 °C. The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (10 cm) of silica gel to remove Bu_4NBF_4 . The silica gel was washed with ether (250 mL). The combined filtrate was concentrated and the crude product was purified with flash column chromatography (hexane/ethyl acetate 20 : 1) to obtain the title compound (60.6 mg, 67%): ^1H NMR (300 MHz, CDCl_3) δ 1.60-2.14 (m, 8H), 2.22-2.38 (m, 1H), 2.57 (dd, J = 13.5, 6.9 Hz) and 2.76 (dd, J = 13.7, 7.1 Hz) (total 1H, two rotamers), 3.36 (t, J = 6.8 Hz) and 3.45 (t, J = 6.9 Hz) (total 2H, two rotamers), 3.62 (s) and 3.68 (s) (total 3H, two rotamers), 4.86-5.09 (m, 4H), 5.60-5.85 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.8 and 22.3, 28.6 and 28.7, 34.1 and 35.4, 36.6 and 37.7, 41.7 and 43.1, 48.5 and 49.5, 51.7 and 51.9, 64.9 and 65.6, 114.2 and 114.3, 117.9 and 118.1,

134.1 and 134.5, 138.4 and 138.6, 154.2 and 155.5; IR (neat) 1700, 1447, 1375 cm^{-1} ; LRMS (FAB) m/e 224 ($\text{M}^+\text{+H}$), 182 ($\text{M}^+\text{-allyl}$); HRMS (FAB) calcd for $\text{C}_{13}\text{H}_{22}\text{O}_2\text{N}$ ($\text{M}^+\text{+H}$): 224.1651, found: 224.1653.

***N*-Methoxycarbonyl-2-(3-butenyl)-2-(1-hexenyl)pyrrolidine (8).** The anodic oxidation was carried out in an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca 320 mg, dried at 250 $^{\circ}\text{C}$ / 1 mmHg for 2 h before use) and a platinum plate cathode (40 mm x 20 mm). In the anodic chamber was placed a solution of *N*-methoxycarbonyl-2-(3-butenyl)-2-trimethylsilylpyrrolidine (**5**) (104.4 mg, 0.409 mmol) in 0.3 M Bu_4NBF_4 / CH_2Cl_2 (8 mL). In the cathodic chamber was placed 0.3 M Bu_4NBF_4 / CH_2Cl_2 (8 mL) and trifluoromethanesulfonic acid (120.9 mg, 0.806 mmol). The constant current electrolysis (8 mA) was carried out at -78°C with magnetic stirring until 2.5 F / mol of electricity was consumed. To the cation pool thus generated in the anodic chamber, was added 1-hexenyl ethyl zinc³ (ca 0.5 M in hexane, 4 mL, ca 2 mmol) and dry CH_2Cl_2 (4.0 mL) was added to the cathodic chamber. The solution was stirred for 1 h at -23°C . The solvent was removed under reduced pressure and the residue was quickly filtered through a short column (15 cm) of silica gel to remove Bu_4NBF_4 . The silica gel was washed with ether (250 mL). The combined filtrate was concentrated and the crude product was purified with flash column chromatography (hexane/ethyl acetate 20 : 1) to obtain the title compound (67.6 mg, 62%): ^1H NMR (300 MHz, CDCl_3) δ 0.86 (t, J = 7.1 Hz, 3H), 1.20-1.34 (m, 4H), 1.66-2.08 (m, 10H), 3.23-3.56 (m, 2H), 3.62 (s, 3H), 4.85-5.03 (m, 2H), 5.21-5.48 (m) and 5.60-5.86 (m) (total 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 13.9, 21.1 and 21.9, 22.0 and 22.1, 28.4 and 28.9, 31.6, 31.8 and 31.9, 35.9 and 36.8, 36.2 and 37.6, 48.1 and 49.1, 51.7 and 51.8, 65.8 and 66.5, 114.1 and 114.2, 127.7 and 128.0, 132.2 and 133.3, 138.5

and 138.7, 154.2 and 155.7; IR (neat) 1698, 1445, 1374 cm^{-1} ; LRMS (EI) m/e 265 (M^+), 210 ($\text{M}^+ - \text{C}_4\text{H}_7$); HRMS (EI) calcd for $\text{C}_{16}\text{H}_{27}\text{O}_2\text{N}$ (M^+): 265.2042, found: 265.2043.

***N*-Methoxycarbonyl-1-azaspiro[4,4]non-7-ene (9): Typical Procedure for syntheses of Nitrogen Containing Spiro Compounds.** To a solution of Bis(tricyclohexylphosphine)benzylidineruthenium (IV) dichloride (Grubbs catalyst)⁴ (6.7 mg, 5 mol%) in benzene (2 mL) was added *N*-methoxycarbonyl-2,2-diallylpyrrolidine (**6**) (34.1 mg, 0.163 mmol) at room temperature. The solution was stirred for 2.5 h at room temperature. The reaction mixture was concentrated and the crude product was purified with flash column chromatography (hexane/ethyl acetate 15 : 1) to obtain the title compound (18.8 mg, 64%): ^1H NMR (300 MHz, CDCl_3) δ 1.71-1.82 (m, 2H), 1.85-1.96 (m, 2H), 2.07-2.21 (m, 2H), 2.88 (d, $J = 15.3$ Hz) and 3.08 (d, $J = 14.7$ Hz) (total 2H, two rotamers), 3.41 (t, $J = 6.6$ Hz) and 3.49 (t, $J = 6.5$) (total 2H, two rotamers), 3.62 (s) and 3.65 (s) (total 3H, two rotamers), 5.59 (s) and 5.64 (s) (total 2H, two rotamers); ^{13}C NMR (75 MHz, CDCl_3) δ 22.4 and 22.8, 43.0 and 43.9, 44.3 and 45.2, 47.5 and 48.5, 51.6 and 52.0, 68.0 and 68.8, 128.5 and 128.7, 154.2 and 155.5; IR (neat) 1700, 1447, 1377 cm^{-1} ; LRMS (EI) m/e 181 (M^+), 166 ($\text{M}^+ - \text{Me}$); HRMS (EI) calcd for $\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}$ (M^+): 181.1103, found: 181.1103.

***N*-Methoxycarbonyl-1-azaspiro[4,5]dec-7-ene (10).** Prepared from *N*-methoxycarbonyl-2-allyl-2-(3-butenyl)pyrrolidine (**7**) (38.3 mg, 0.172 mmol) and Grubbs catalyst (7.0 mg, 5 mol%) by the typical procedure. Isolated yield 25.5 mg (76%, purified with flash column chromatography, hexane/ethyl acetate 15 : 1): ^1H NMR (300 MHz, CDCl_3) δ 1.30-1.41 (m, 1H), 1.61-1.82 (m, 4H), 1.83-1.96 (m, 1H), 1.98-2.22 (m, 2H), 2.37-2.50 (m) and 2.91-3.02 (m) (total 1H), 2.64-2.78 (m, 1H), 3.25-3.43 (m, 1H),

3.50-3.59 (m, 1H), 3.62 (s) and 3.67 (s) (total 3H, two rotamers), 5.51-5.65 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 21.5 and 22.0, 24.4 and 24.6, 30.6 and 31.6, 33.3 and 34.4, 36.4 and 37.3, 47.7 and 48.6, 51.5 and 51.8, 61.8 and 62.4, 125.7, 125.9, 154.3 and 155.6; IR (neat) 1696, 1445, 1374 cm^{-1} ; LRMS (EI) m/e 195 (M^+), 180 ($\text{M}^+ - \text{Me}$); HRMS (EI) calcd for $\text{C}_{11}\text{H}_{17}\text{O}_2\text{N}$ (M^+): 195.1259, found: 195.1259.

***N*-Methoxycarbonyl-1-azaspiro[4,4]non-6-ene (11).** Prepared from *N*-methoxycarbonyl-2-(3-butenyl)-2-(1-hexenyl)pyrrolidine (**8**) (22.0 mg, 0.083 mmol) and Grubbs catalyst (3.8 mg, 6 mol%) by the typical procedure. Isolated yield 13.8 mg (92%, purified with flash column chromatography, hexane/ethyl acetate 15 : 1): ^1H NMR (300 MHz, CDCl_3) δ 1.75-1.88 (m, 5H), 2.04-2.69 (m, 3H), 3.33-3.57 (m, 2H), 3.63 (s, 3H), 5.47-5.53 (m, 1H), 5.68-5.75 (m) and 5.80-5.88 (m) (total 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 22.4 and 23.0, 31.1 and 31.4, 34.6 and 35.5, 39.6 and 40.3, 47.1 and 48.0, 51.4 and 51.7, 74.2 and 74.7, 130.0 and 131.3, 134.0 and 135.1, 154.2 and 155.6; IR (neat) 1705, 1447, 1375 cm^{-1} ; LRMS (EI) m/e 181 (M^+), 166 ($\text{M}^+ - \text{Me}$); HRMS (EI) calcd for $\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}$ (M^+): 181.1103, found: 181.1103; Anal. calcd for $\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}$: C, 66.27; H, 8.34; N, 7.73, found: C, 66.06; H, 8.52; N, 7.45.

1-[2-(6-Iodo-3,4-methylenedioxyphenyl)ethyl]-1-azaspiro[4,4]non-6-ene (13). To a solution of *N*-methoxycarbonyl-1-azaspiro[4,4]non-6-ene (**11**) (39.9 mg, 0.220 mmol) in CH_2Cl_2 (1 mL) was added trimethylsilyl iodide (87.2 mg, 0.436 mmol) at room temperature. The solution was stirred for 2.5 h at room temperature. Dry MeOH (1 mL) was added. The reaction mixture was concentrated in reduced pressure. The residue was dissolved to CH_3CN (1 mL) and *i*-Pr₂NEt (289.6 mg, 2.240 mmol) was added. This solution was added to the solution of 2-(6-iodo-3,4-methylenedioxyphenyl)ethyl 4-nitrobenzenesulfonate⁵ (314.2 mg, 0.658 mmol) in acetonitrile (3 mL). The reaction

mixture was stirred over night at 50 °C. 1 M aqueous NaOH (5 mL) was added. The mixture was extracted with ether (3 mL x 3), and the organic phase was dried over Na₂SO₄. After removal of the solvent, the crude product was purified with flash column chromatography (gradient column: ethyl acetate, then ethyl acetate/methanol 15 : 1, + 1% Et₃N) to obtain the title compound (45.1 mg, 52%): ¹H NMR (300 MHz, CDCl₃) δ 1.76-2.02 (m, 6H), 2.30 (tt, *J* = 7.0, 2.2 Hz, 2H), 2.36-2.51 (m, 2H), 2.74-2.90 (m, 3H), 2.94-3.03 (m, 1H), 5.57 (dt, *J* = 5.6, 2.2 Hz, 1H), 5.82 (dt, *J* = 5.6, 2.3 Hz, 1H), 5.92 (s, 2H), 6.75 (s, 1H), 7.19 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 21.3, 29.6, 31.5, 38.1, 40.6, 49.9, 51.2, 77.9, 87.8, 101.4, 109.6, 118.5, 132.5, 134.4, 136.6, 146.8, 148.3; IR (neat) 1476, 1227, 1042 cm⁻¹; LRMS (EI) *m/e* 397 (M⁺), 261 (M⁺-CH₂azaspiro[4,4]non-6-ene); HRMS (EI) calcd for C₁₇H₂₀O₂Ni (M⁺): 397.0539, found: 397.0539.

Cephalotaxine intermediate (14). To a solution of **13** (31.7 mg, 0.080 mmol) in a mixture of acetonitrile, DMF, and water (5 : 5 : 1, 1.7 mL) were added trans-di(μ-acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium⁶ (4.7 mg, 5 mol%) and tetra-*n*-butylammonium acetate (55 mg, 0.18 mmol). The mixture was heated to 120 °C over night, then diluted with 1 M aqueous NaOH (3 mL). The mixture was extracted with ether (3 mL x 3), and the organic phase was extracted with 1 M aqueous HCl (3 mL x 3). The aqueous layer was basified with NaOH solution and extracted with ether (5 mL x 3). The organic phase was dried over Na₂SO₄. After removal of the solvent, the crude product was purified with flash column chromatography (gradient column: ethyl acetate, then ethyl acetate/methanol 15 : 1, + 1% Et₃N) to obtain the title compound (12.8 mg, 60%): The spectrum data was identical to the literature.⁷

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