Cover page for Supporting Information

Title: Zirconocene-mediated Intermolecular Coupling of One Molecule of Si-tethered Diyne with Three Molecules of Organonitriles: One-pot Formation of Pyrrolo[3,2-*c*]pyridine Derivatives via Cleavage of C $\equiv$ N Triple Bonds of Organonitriles

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Contents

- 1) Experimental details and characterization data for all new compounds;
- 2) A proposed reaction mechanism;
- 3) X-ray single-crystal structures for **2b**, **2c**, **2h**, **2j**;
- 4) Copies of ^1H NMR, ^{13}C NMR spectra for all new compounds and DEPT spectra for **2b-d**.

1) Experimental details and characterization data for all new compounds

General Methods: All reactions were conducted under a slightly positive pressure of dry nitrogen using standard Schlenk line techniques. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Toluene was refluxed and distilled from sodium/benzophone ketyl under a nitrogen atmosphere. *n*-BuLi was obtained from Kanto Chemicals Co. Ltd. ¹H and ¹³C NMR spectra were recorded at 300 and 75.4 MHz, respectively, in CDCl₃ unless stated otherwise. GLC analysis was performed on a gas chromatograph (Shimadzu 14B) equipped with a flame ionization detector and a capillary column (CBP1-M25-25).

A Typical Procedure for the Preparation of 2, 3, 4, 6, 7-Pentaphenyl-1*H*-pyrrolo[3,2-*c*]pyridine (2a). To a toluene (10 ml) solution of Cp₂ZrCl₂ (1.05 mmol, 307 mg) at -78 °C (dry ice/acetone) in a 20 ml Schlenk tube was added dropwise *n*-BuLi (2.1 mmol, 1.6 M, 1.32 ml) with a syringe. After the addition was complete, the reaction mixture was stirred at -78 °C for 1 h. Then 1 mmol of bis(phenylethynyl)dimethylsilane (**1a**) was added, and the reaction mixture was warmed up to 50 °C and stirred at this temperature for 3 h. After benzonitrile (3.5 mmol, 361 mg) was added, the reaction mixture was stirred at this temperature for 1 h. The reaction mixture was quenched with saturated aqueous NaHCO₃ and the resulting mixture was extracted with diethyl ether for three times then washed with water and brine. The extract was dried over anhydrous MgSO₄. The solvent was evaporated in vacuo to give a yellow solid, which was subjected to Al₂O₃ column using petroleum ether and diethyl ether (10:1) as the eluent. **2, 3, 4, 6, 7-Pentaphenyl-1*H*-pyrrolo[3,2-*c*]pyridine (2a):** white solid, isolated yield 70% (349 mg). m.p. 285-286 °C; ¹H NMR (CDCl₃, Me₄Si) δ 6.89-7.45 (m, 25H), 8.43 (s, 1H). ¹³C NMR (CDCl₃, Me₄Si) δ 115.99, 117.51, 121.30,

126.02, 126.89, 126.94, 127.12, 127.37, 127.58, 127.70, 127.96, 128.20, 128.47, 128.55, 128.95, 129.20, 129.34, 129.55, 130.04, 130.17, 130.31, 130.52, 130.84, 131.95, 134.51, 135.98, 136.04, 139.42, 140.55, 140.97, 147.97, 152.84. HRMS calcd for $C_{37}H_{26}N_2$: 498.2096, found 498.2083. Anal. Calcd for $C_{37}H_{26}N_2$: C, 89.13; H, 5.26; N, 5.62. Found: C, 89.46; H, 5.28; N, 5.33.

3, 7-Diphenyl-2, 4, 6-tri-*p*-tolyl-1*H*-pyrrolo[3,2-*c*]pyridine (2b): white solid, isolated yield 81% (435 mg). m.p. 264-265 °C; 1H NMR ($CDCl_3$, Me_4Si) δ 2.24 (s, 3H), 2.28 (s, 3H), 2.29 (s, 3H), 6.76-7.44 (m, 22H), 8.33 (s, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 21.18, 21.20, 21.23, 115.65, 117.02, 121.22, 125.76, 127.49, 127.56, 128.31, 128.35, 129.20, 129.27, 129.47, 130.21, 130.43, 130.97, 134.87, 135.86, 136.41, 136.45, 136.47, 136.66, 136.69, 136.71, 136.76, 137.77, 137.87, 140.98, 147.80, 152.73. HRMS calcd for $C_{40}H_{32}N_2$ 540.2566, found 540.2558. Anal. Calcd for $C_{40}H_{32}N_2$: C, 88.85; H, 5.96; N, 5.18. Found: C, 88.61; H, 6.06; N, 5.00. The structure of **2b** was determined by X-ray single-crystal analysis.

3, 7-Diphenyl-2, 4, 6-tri-thiophen-2-yl-1*H*-pyrrolo[3,2-*c*]pyridine (2c): yellow solid, isolated yield 66% (340 mg). m.p. 214-215 °C; 1H NMR ($CDCl_3$, Me_4Si) δ 6.17 -6.25 (m, 1H), 6.46-6.58 (m, 2H), 6.72-6.82 (m, 1H), 6.83-6.95 (m, 3H), 7.02-7.71 (m, 12H), 8.10 (s, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 115.37, 116.20, 119.85, 125.88, 126.24, 126.31, 126.53, 126.62, 126.72, 126.89, 126.98, 127.13, 127.28, 127.47, 128.00, 128.21, 128.70, 128.74, 129.83, 130.07, 131.00, 131.04, 131.45, 133.28, 133.31, 134.64, 134.68, 135.23, 141.31, 141.90, 141.94, 143.09, 145.40, 145.45. HRMS calcd for $C_{31}H_{20}N_2S_3$: 516.0789, found 516.0780. Anal. Calcd for $C_{31}H_{20}N_2S_3$: C, 72.06; H, 3.90; N, 5.42. Found: C, 72.41; H, 4.16; N, 5.07. The structure of **2c** was determined by X-ray single-crystal analysis.

3, 7-Diphenyl-2, 4, 6-tripropyl-1*H*-pyrrolo[3,2-*c*]pyridine (2d): yellow liquid,

isolated yield 72% (284 mg). ^1H NMR (CDCl_3 , Me_4Si) δ 0.61 (t, $J = 7.2$ Hz, 3H), 0.82 (t, $J = 7.2$ Hz, 6H), 1.47-1.69 (m, 6H), 2.46-2.71 (m, 6H), 7.25-7.52 (m, 10H), 7.70 (s, 1H). ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.80, 13.86, 14.02, 14.13, 23.12, 23.90, 24.24, 28.02, 36.70, 37.63, 115.05, 116.90, 120.56, 126.85, 126.89, 127.57, 127.74, 127.86, 128.97, 129.95, 131.24, 136.06, 136.44, 136.47, 136.52, 139.27, 149.33, 154.32. HRMS calcd for $\text{C}_{28}\text{H}_{32}\text{N}_2$: 396.2566, found 396.2558.

3, 7-Diphenyl-2, 4, 6-Tributyl-1*H*-pyrrolo[3,2-*c*]pyridine (2e): yellow solid, isolated yield 64% (281 mg). m.p. 115-116 °C; ^1H NMR (CDCl_3 , Me_4Si) δ 0.64-1.61 (m, 21H), 2.51 (t, $J = 7.5$ Hz, 2H), 2.62-2.74 (m, 4H), 7.24-7.52 (m, 10H), 7.74 (s, 1H). ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.70, 13.79, 13.93, 22.31, 22.34, 22.63, 22.77, 22.80, 25.77, 25.81, 31.98, 32.68, 32.74, 33.19, 34.36, 35.56, 114.95, 116.78, 120.44, 126.90, 127.56, 127.85, 128.97, 129.98, 131.13, 131.24, 136.09, 136.47, 136.73, 139.28, 149.51, 154.47. HRMS calcd for $\text{C}_{31}\text{H}_{38}\text{N}_2$: 438.3035, found 438.3038.

2, 3, 4, 6, 7-Penta-*p*-tolyl-1*H*-pyrrolo[3,2-*c*]pyridine (2f): white solid, isolated yield 46% (261 mg). m.p. 284-285 °C; ^1H NMR (CDCl_3 , Me_4Si) δ 2.25-2.30 (m, 12H), 2.42 (s, 3H), 6.76-6.79 (m, 5H), 6.99-7.41 (m, 15H), 8.32 (s, 1H). ^{13}C NMR (CDCl_3 , Me_4Si) δ 21.12, 21.16, 21.20, 21.32, 115.59, 117.00, 121.44, 127.42, 128.16, 128.23, 128.28, 129.23, 129.35, 129.45, 129.90, 129.99, 130.40, 130.70, 131.83, 133.33, 135.34, 135.45, 136.28, 136.49, 136.87, 137.17, 137.69, 137.97, 141.02, 147.68, 152.64. HRMS calcd for $\text{C}_{42}\text{H}_{36}\text{N}_2$: 568.2879, found 568.2875.

2, 4, 6-Tripropyl-3, 7-di-*p*-tolyl-1*H*-pyrrolo[3,2-*c*]pyridine (2g): yellow liquid, isolated yield 67% (284 mg). ^1H NMR (CDCl_3 , Me_4Si) δ 0.63 (t, $J = 7.5$ Hz, 3H), 0.80-0.85 (m, 6H), 1.45-1.69 (m, 6H), 2.43-2.71 (m, 12H), 7.20-7.32 (m, 8H), 7.70 (s, 1H). ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.81, 14.01, 14.13, 21.27, 21.31, 23.14, 23.90, 24.26, 28.03, 36.73, 37.57,

114.89, 116.75, 120.60, 128.54, 129.67, 129.77, 131.07, 132.97, 133.40, 136.36, 136.37, 137.17, 139.34, 149.38, 154.18. HRMS calcd for $C_{30}H_{36}N_2$: 424.2879, found 424.2889.

3, 7-Diphenyl-2, 4, 6-triisopropyl-1H-pyrrolo[3,2-c]pyridine (2i): white solid, isolated yield 73% (289 mg). m.p. 168-169 °C; 1H NMR ($CDCl_3$, Me_4Si) δ 1.11-1.25 (m, 18H), 2.89-3.11 (m, 3H), 7.34-7.54 (m, 10H), 7.64 (s, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si) δ 22.15, 22.68, 23.18, 25.51, 31.11, 31.28, 113.07, 115.23, 119.48, 126.86, 127.41, 127.86, 128.97, 129.93, 131.06, 136.62, 138.66, 141.34, 153.74, 158.60. HRMS calcd for $C_{28}H_{32}N_2$: 396.2566, found 396.2567; Anal. Calcd for $C_{28}H_{32}N_2$: C, 84.80; H, 8.13; N, 7.06. Found: C, 84.73; H, 8.14; N, 6.92.

A Typical Procedure for the Preparation of 3, 7-Diphenyl-4, 6-di-thiophen-2-yl-2-*p*-tolyl-1H-pyrrolo[3,2-c] -pyridine (2h). The procedure for the preparation of **2h** was the same as that for **2a**. A 1:1 molar ratio mixture of *p*-tolunitrile and 2-thiophenecarbonitrile was used. The products were subjected to SiO_2 column using petroleum ether and diethyl ether (100:1) as the eluent. Parts of **2b** (25 mg) and **2c** (8 mg) were obtained individually. The other parts were a mixture of eight products formed from two different nitriles as determined by TLC and mass and could not be separated. Recrystallization of the mixture these products using CH_2Cl_2 afforded **2h**. HRMS calcd for $C_{34}H_{24}N_2S_2$: 524.1381, found 524.1386. m.p. 294-295 °C. The structure of **2h** was determined by X-ray single-crystal analysis.

Experimental Procedure for the Reaction Described in eq. 4. To a toluene (20 ml) solution of Cp_2ZrCl_2 (2.1 mmol, 614 mg) at - 78 °C (dry ice/acetone) in a 20 ml Schlenk tube was added dropwise *n*-BuLi (4.2 mmol, 1.6 M, 2.64 ml) with a syringe. After the

addition was complete, the reaction mixture was stirred at -78 °C for 1 h. Then 1 mmol of bis(phenylethynyl)dimethylsilane (**1a**) and 1 mmol of bis(tolyethynyl)dimethylsilane (**1b**) were added, and the reaction mixture was warmed up to 50 °C and stirred at this temperature for 3 h. After butyronitrile (7 mmol, 0.63ml) was added, the reaction mixture was stirred at this temperature for 1 h. The reaction mixture was quenched with saturated aqueous NaHCO₃ and the resulting mixture was extracted with diethyl ether for three times then washed with water and brine. The extract was dried over anhydrous MgSO₄. The solvent was evaporated in vacuo to give a yellow solid, which was subjected to SiO₂ column using petroleum ether and diethyl ether (10:1) as the eluent. The final product was obtained as a 1:1 mixture of **2d** and **2g** in 72% combined isolated yield.

A Typical Procedure for the Preparation of 2j and 2k. To a toluene (10 ml) solution of Cp₂ZrCl₂ (1.05 mmol, 307 mg) at - 78 °C (dry ice/acetone) in a 20 ml Schlenk tube was added dropwise *n*-BuLi (2.1 mmol, 1.6 M, 1.32 ml) with a syringe. After the addition was complete, the reaction mixture was stirred at -78 °C for 1 h. Then 1 mmol of bis(phenylethynyl)dimethylsilane (**1a**) was added, and the reaction mixture was warmed up to 50 °C and stirred at this temperature for 3 h. After *iso*-butyronitrile (1.5 mmol, 0.135 ml) was added, the reaction mixture was stirred at this temperature for 1 h. The reaction mixture was quenched with saturated aqueous NaHCO₃ (D₂O for **2k**) and the resulting mixture was extracted with diethyl ether for three times then washed with water and brine. The extract was dried over anhydrous MgSO₄. The solvent was evaporated in vacuo to give a yellow solid, which was subjected to Al₂O₃ column using petroleum ether and diethyl ether (1:1) as the eluent.

1-(2-Benzyl-5-isopropyl-4-phenyl-1*H*-pyrrol-3-yl)-2-methyl-propan-1-one (2j):

white solid, isolated yield 51% (176 mg). m.p. 187 °C; ^1H NMR (CDCl_3 , Me_4Si) δ 0.84 (d, J = 6.9 Hz, 6H), 1.05 (d, J = 6.9 Hz, 6H), 2.46-2.50 (m, 1H), 2.82-2.86 (m, 1H), 4.26 (s, 2H), 7.20-7.38 (m, 10H), 7.97 (s, 1H). ^{13}C NMR (CDCl_3 , Me_4Si) δ 18.89, 22.81, 24.91, 33.65, 37.86, 119.97, 120.76, 126.57, 128.03, 128.72, 128.96, 130.36, 133.92, 134.69, 136.67, 138.62, 205.01. HRMS calcd for $\text{C}_{24}\text{H}_{27}\text{NO}$: 345.2093, found 345.2094 Anal. Calcd for $\text{C}_{24}\text{H}_{27}\text{NO}$: C, 83.44; H, 7.88; N, 4.05. Found: C, 83.42; H, 7.91; N, 4.06. The structure of **2j** was determined by X-ray single-crystal analysis.

1-[2-(Dideuterium-phenyl-methyl)-5-isopropyl-4-phenyl-1H-pyrrol-3-yl]-2-methylpropan-1-one (2k): white solid, isolated yield 53% (184 mg). m.p. 187-188 °C; ^1H NMR (CDCl_3 , Me_4Si) δ 0.84 (d, J = 6.9 Hz, 6H), 1.06 (d, J = 6.9 Hz, 6H), 2.46-2.50 (m, 1H), 2.83-2.87 (m, 1H), 7.20-7.38 (m, 10H), 8.06 (s, 1H). ^{13}C NMR (CDCl_3 , Me_4Si) δ 18.90, 22.81, 24.88, 32.48, 32.74, 33.00, 33.27, 33.58, 37.85, 119.92, 120.69, 126.54, 128.03, 128.69, 128.92, 130.33, 133.94, 134.69, 136.62, 138.53, 205.09. HRMS calcd for $\text{C}_{24}\text{H}_{25}\text{D}_2\text{NO}$: 347.2218, found 347.2205.

A Typical Procedure for the Preparation of 2, 4-Diisopropyl-3, 7-diphenyl-6-*p*-tolyl-1H-pyrrolo[3,2-*c*]pyridine (2l): To a toluene (10 ml) solution of Cp_2ZrCl_2 (1.05 mmol, 307 mg) at -78 °C (dry ice/acetone) in a 20 ml Schlenk tube was added dropwise *n*-BuLi (2.1 mmol, 1.6 M, 1.32 ml) with a syringe. After the addition was complete, the reaction mixture was stirred at -78 °C for 1 h. Then 1 mmol of bis(phenylethynyl)dimethylsilane (**1a**) was added, and the reaction mixture was warmed up to 50 °C and stirred at this temperature for 3 h. After *iso*-butyronitrile (1.5 mmol, 0.135 ml) was added, the reaction mixture was stirred at this temperature for 1 h. *p*-Tolunitrile (234 mg) was then added and the reaction mixture was stirred at 50 °C for 1h. Then the reaction

mixture was quenched with saturated aqueous NaHCO₃. The resulting mixture was extracted with diethyl ether for three times then washed with water and brine. The extract was dried over anhydrous MgSO₄. The solvent was evaporated in vacuo to give a yellow solid, which was subjected to Al₂O₃ column using petroleum ether and diethyl ether (5:1) as the eluent. **2, 4-Diisopropyl-3, 7-diphenyl-6-*p*-tolyl-1*H*-pyrrolo[3,2-*c*]pyridine (2l)**: white solid, isolated yield 67% (300 mg). m.p. 238-239 °C; ¹H NMR (CDCl₃, Me₄Si) δ 0.96-1.28 (m, 12H), 2.28 (s, 3H), 2.77-3.23 (m, 2H), 6.89-7.09 (br, 2H), 7.25-7.50 (m, 12H), 7.96 (s, 1H). ¹³C NMR (CDCl₃, Me₄Si) δ 21.15, 22.06, 22.65, 25.62, 31.26, 113.40, 113.42, 116.05, 120.62, 127.05, 127.16, 127.23, 127.94, 128.16, 129.10, 130.14, 130.36, 131.08, 136.05, 136.08, 136.31, 136.33, 136.97, 136.99, 138.34, 139.00, 139.03, 142.29, 142.32, 146.62, 158.92 HRMS calcd for C₃₂H₃₂N₂: 444.2566, found 444.2574.

2) A proposed reaction mechanism

Based on the preliminary experimental results, a reaction mechanism is proposed as follows.

(1) Insertion of the C≡N triple bond of one organonitrile (R¹CN) into one of the Zr-C bonds affording **4** is proposed to be the first step in this reaction. Insertion of the C≡N triple bond of organonitriles into M-C bonds has been reported.¹ Formation of azazirconacycles has also been well documented.^{2,3}

(2) Skeletal rearrangement of **4** would lead to the formation of **5**, which undergoes insertion of the C≡N triple bond of the second organonitrile (R²CN) to afford **6**. Formation of all the three intermediates **7**, **8**, and **9** might be possible according to literature reports.⁴⁻⁸ Hydrolysis of the reaction mixture of *i*-PrCN with sat. aq. NaHCO₃ afforded an imine **13** as observed by NMR spectroscopy. This imine **13** was completely transformed to the ketone

2j after column chromatography. When the reaction mixture was quenched with D₂O, product **2k** containing a CD₂ moiety was obtained.

(3) Insertion of the C≡N triple bond of the third organonitrile (R³CN) to the Zr-C bond in intermediate **7**, or [2+2] cycloaddition of the C≡N triple bond with intermediates **8** and/or **9**, followed by metathesis would afford **11** and/or **12**, which gave the final product **2** upon hydrolysis.

It should be mentioned that direct evidences for the formation of intermediates **4-12** have not been obtained. Further investigation to elucidate the reaction mechanisms is in progress.

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3) X-ray single-crystal structures for 2b, 2c, 2h, and 2j.

2c

2h

2a

2b

2b (DEPT135)

2c

2c (DEPT135)

2d

2d (DEPT135)

2e

2f

2g

2i

2j

2k

2I