Synthesis of Unsymmetrical, Monosubstituted Bis-terpyridine Derivatives via Suzuki-Miyaura Cross-Coupling

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[2] 1H, 13C and 2D-COSY NMR Spectra -----------------------------------S4
[3] HRMS Spectra ----------------------------------------------------------S21
[1] General Information

Unless otherwise noted, all reagents were reagent grade and were used without purification. Dehydrated CH₂Cl₂, DMF, DMSO, dioxane, H₂SO₄, and acetic acid were used as reaction solvent. These solvents were purchased from Wako or Kanto Chemical Co. Inc. De-ionized H₂O was used in the experiment where required. ¹H-NMR, ¹³C-NMR and 2D-COSY-NMR spectra were recorded at 300 MHz, 75 MHz and 600 MHz, respectively. MALDI-TOF-MS were measured by using AXIMA-CRF, Shimadzu/Kratos TOF Mass spectrometer. High resolution mass spectra (HRMS) were measured by using a Micromass-LCT-LCMS-IT-TOF spectrometer (Toray Research Center Inc.). UV-vis spectra were obtained by using a Shimadzu UV-2550 UV-visible spectrophotometer. Analytical thin layer chromatography (TLC) was Merck aluminium oxide 60 F₂₅₄ neutral or silica gel 60 F₂₅₄ coated on 25 TCC aluminium sheets (20×20 cm). Column chromatographic separations were performed on silica gel 60 N (neutral, 40-100 µM), Kanto Chemical Co. Inc., or activated aluminium oxide (basic, 75 µM), Wako. The preparative HPLC was performed on the high resolution hydrophobic size exclusion column (JAIGEL-1H and -2H) equipped with a controller (LC-9104).

Sodium Hydroxide: NaOH (97%, CICA); Sodium Carbonate: Na₂CO₃ (>99.8%, WAKO); Sodium Hydrogen Carbonate: NaHCO₃ (>99.5%, WAKO); Sodium Methoxide: NaOMe (>96%, TCI) Ammonium Acetate: NH₄OAc (97%, CICA); Potassium Acetate: KOAc (>97%, CICA); Potassium Carbonate: K₂CO₃ (>99.5%, CICA). Magnesium Sulfate: MgSO₄ (anhydrous, 98%, CICA).

Benzene-1,2-dicarboxaldehyde (99%, SIGMA-ALDRICH); 2-Acetyl-6-methylpyridine (98%, Frontier Scientific); 2-Acetyl-6-bromopyridine (97%, ALDRICH); 2-Acetylpyridine (>99%, SIGMA-ALDRICH); Pyridine (>99.5%, WAKO); Iodine: I₂ (>98%, TCI); 4-Bromobenzaldehyde (>95%, TCI); Bis(pinacolato)diboron (>97%, TCI); Bis(triphenylphosphate)palladium(II) dichloride: PdCl₂(PPh₃)₂ (>98%, TCI), M-chloroperoxybenzoic acid (contains ca. 30% water, TCI); Trimethylsilyl cyanide (96%, TCI); Acetyl chloride (>98%, WAKO); Potassium tert-butoxide (>97%, TCI); Thionyl chloride (>98%, TCI); Iron(II) tetrafluoroborate hexahydrate: Fe(BF₄)₂·6H₂O (97%, ALDRICH).

WAKO: WAKO Chemical Co. Inc.
CICI: CICA Chemical Co. Inc.

TCI: TCI Chemical Co. Inc.

ALDRICH: ALDRICH Chemical Co. Inc.
Figure S1. $^1$H-NMR of compound 2

[2] $^1$H, $^{13}$C, 2D-COSY NMR Spectra
Figure S2. $^{13}$C-NMR of compound 2
Figure S3. $^1$H-NMR of compound 3
Figure S4. $^{13}$C-NMR of compound 3
Figure S5. $^1$H-NMR of compound 5
Figure S6. $^{13}$C-NMR of compound 5
Figure S7. $^1$H-NMR of compound 6.
Figure S8. $^{13}$C-NMR of compound 6
Figure S9. 1H-NMR of Compound 8
Figure S10. 13C-NMR of Compound 8
Figure S11. 2D-COSY-NMR of Compound 8
Figure S12: $^1$H-NMR of Compound 9
Figure S13. 13C-NMR of Compound 9
Figure S14. 2D-COSY-NMR of Compound 9
Figure S15. 1H-NMR of Compound 10
Figure S16. $^{13}$C-NMR of Compound 10
Figure S17. 2D-COSY-NMR of Compound 10
[3] HRMS Spectra

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
40 formula(e) evaluated with 4 results within limits (all results (up to 1000) for each mass)

Figure S18. HRMS spectra of compound 2 in CHCl3-MeOH.

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
9 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Figure S19. HRMS spectra of compound 3 in CHCl3-MeOH.
**Elemental Composition Report**

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
45 formula(e) evaluated with 3 results within limits (all results up to 1000) for each mass

**Figure S20.** HRMS spectra of compound 5 in CHCl₃-MeOH.

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**Elemental Composition Report**

**Single Mass Analysis**
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
64 formula(e) evaluated with 3 results within limits (all results up to 1000) for each mass

**Figure S21.** HRMS spectra of compound 6 in CHCl₃-MeOH.
Figure S22. HRMS spectra of Compound 8 in CHCl₃-MeOH.

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 mDa / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
100 formula(e) evaluated with 7 results within limits (all results up to 1000) for each mass
Figure S23. HRMS spectra of Compound 9 in CHCl₃-MeOH.

Elemental Composition Report

Single Mass Analysis
Tolerance = 5.0 mDa  /  DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0  Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
156 formula(e) evaluated with 7 results within limits (all results up to 1000) for each mass

Figure S24. HRMS spectra of Compound 10 in CHCl₃-MeOH.