

Supplementary data for the article entitled

Novel formation of diimidazo[1,2-*a*:2',1'-*c*]quinoxaline derivatives and their optical properties

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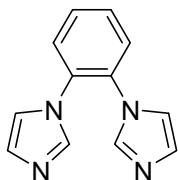
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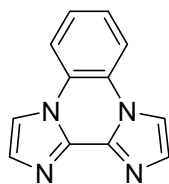
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Generals: Melting points were determined with Yanaco MP-J3 and values were uncorrected. ^1H and ^{13}C NMR measurements were performed on a Varian GEMINI 2000 (300 MHz) spectrometer. Chemical shifts (δ) of ^1H NMR were expressed in parts per million downfield from tetramethylsilane as an internal standard ($\delta = 0$). Multiplicities are indicated as s (singlet), d (doublet), m (multiplet), and coupling constants (J) are reported in Hz unit. Chemical shifts (δ) of ^{13}C NMR (75 MHz) were expressed in parts per million downfield or upfield from CDCl_3 as an internal standard ($\delta = 77.0$). IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer in KBr disk. UV-Vis spectra were measured on a JASCO V570 spectrophotometer. Fluorescence spectra were measured on a JASCO FP-6600 spectrofluorometer. Elemental analyses (EA) were carried out on a Perkin-Elmer 2400CHN in Analytical Chemical Center of Chiba University. Mass spectra were carried out on a JEOL JMS-AX500, a JMS-HX110, or THERMO Scientific Exactive in Analytical Chemical Center of Chiba University. Analytical thin-layer chromatography (TLC) was performed on glass plates pre-coated with silica gel (layer thickness 0.25 mm). Column chromatography was performed on 70-230 mesh silica gel. Preparative GPC was performed on JAIGEL-1H and 2H with a LC-908 (Japan Analytical Industry, Co. Ltd.). The materials not to synthesize in this experimental section were commercially available (Aldrich Chemical Co., Tokyo Kasei Chemical Industry Co., Wako Pure Chemical Co., Kanto Chemical Co., and Nacalai Tesque Inc.). Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl immediately prior to use. *N,N*-Dimethylformamide (DMF) was distilled from P_2O_5 under reduced pressure. The reactions were performed under nitrogen atmosphere otherwise noted.



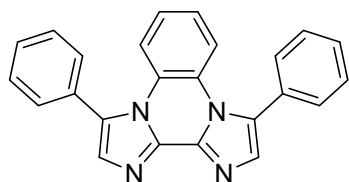
1,2-Di(1*H*-imidazol-1-yl)benzene:¹ In a test tube with a screw cap was added 1,2-dibromobenzene (0.238 g, 1.01 mol), imidazole (0.173 g, 2.54 mmol), K_2CO_3 (0.284 g, 2.04 mmol), Cu_2O (7.8 mg, 0.0055 mmol), and DMSO (1.5 mL). The mixture was stirred at 150 °C for 48 h. The resultant mixture was cooled to room temperature. The mixture was filtered off through Celite with EtOAc. To the organic solution was added H_2O (20 mL). The combined mixture was extracted with EtOAc (total 30 mL). The combined organic layers were dried over Na_2SO_4 . Evaporation in vacuo and column chromatography (silica gel; CHCl_3 : MeOH = 10 : 1) provided 1,2-di(1*H*-imidazol-1-yl)benzene (0.182 g, 0.866 mmol) in 87% yield as a colorless solid: mp 133.1–134.9 °C (lit.¹ 134.3°C); ^1H NMR (CDCl_3 , 300 MHz) δ 6.74 (s, 2H), 7.11 (s, 2H), 7.44 (s, 2H), 7.48–7.52 (m, 2H), 7.54–7.58 (m, 2H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 119.4, 127.1, 129.6, 130.5, 132.1, 136.7; IR (KBr) 3101, 3030, 2360, 1681, 1593, 1520, 1495, 1247, 1176, 1111, 1089, 1065, 1054, 1039, 964, 740 cm^{-1} . MS (FAB): m/z 211 ($[\text{M}+\text{H}]^+$).



Diimidazo[1,2-*a*:2',1'-*c*]quinoxaline (**3**)

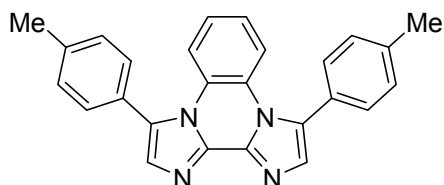
I₂-Mediated Reaction (Method A): To a solution of 1,2-di(imidazol-1-yl)benzene (0.211 g, 1.0 mmol) in THF (5 mL) was added a solution of *n*-BuLi (1.67 M in hexane) (1.44 mL, 2.4 mmol) at -78 °C. After being stirred for 1 h at that temperature, the reaction mixture was added to a solution of I₂ (0.269 g, 1.06 mmol) in THF (4 mL) at -78 °C. The mixture was gradually warmed to 45 °C and stirred for 19 h. To the resultant mixture was added brine (20 mL) and was extracted with CHCl₃ (total 40 mL). The organic layer was dried with Na₂SO₄. After filtration and evaporation, the residue was subjected to column chromatography on silica-gel (CHCl₃ : MeOH =10 : 1) to give **3** (0.147 g, 0.71 mmol) in 71% yield as a white solid. To utilize for measuring a optical properties, the solid was further purified by recrystallization from hexane and CHCl₃ to give colorless plate crystals: mp 260.9–261.4 °C; ¹H NMR (CDCl₃, 300 MHz) δ 7.53 (dd, 2H, *J* = 3.3 and 6.2 Hz), 7.62 (d, 2H, *J* = 1.2 Hz), 7.87 (dd, 2H, *J* = 3.4 and 6.3 Hz), 7.88 (d, 2H, *J* = 1.5 Hz); ¹³C NMR (CDCl₃, 300 MHz) δ 112.3, 116.7, 124.4, 126.5, 132.7, 135.7; IR (KBr) 1630, 1510, 1413, 1324, 1121, 931, 755, 686, 468, 442, 425, 407 cm⁻¹. HRMS (ESI): Calcd for C₁₂H₉N₄ ([M+H]⁺): 209.0822. Found: 209.0819.

Pd-catalyzed Coupling Reaction (Method B): To a solution of 1,2-di(1*H*-imidazol-1-yl)benzene (0.210 g, 1.0 mmol) in THF (5 mL) was added a solution of *n*-BuLi (1.57 M in hexane) (1.53 mL, 2.4 mmol) at -78 °C. After being stirred for 1 h at that temperature, the reaction mixture was added to a solution of Pd(PPh₃)₄ (22.7 mg, 0.024 mmol) in THF (2 mL) at -78 °C. The reaction mixture was gradually warmed to 45 °C and stirred for 19 h. To the reaction mixture was added brine (20 mL) and was extracted with CHCl₃ (total 40 mL). The organic layer was dried with Na₂SO₄. After filtration and evaporation, the residue was subjected to column chromatography on silica-gel (CHCl₃ : MeOH =10 : 1) to give **3** (0.147 g, 0.71 mmol) in 71% yield as a white solid.

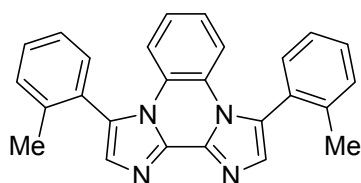


3,10-Diphenyldiimidazo[1,2-*a*:2',1'-*c*]quinoxaline (4a**):** In a test tube with a screw cap was added K₂CO₃ (0.279 g, 1.95 mmol), pre-heated at 150 °C for 2 h with glass tube oven to remove adventitious water, **3** (0.104 g, 0.499 mol), bromobenzene (0.386 g, 2.46 mmol), Pd(OAc)₂ (12.4 mg, 0.055 mmol), PPh₃ (26.4 mg, 0.10 mmol), and DMF (2.5 mL). The mixture was stirred at 140 °C for 48 h. The resultant mixture was cooled down to room temperature. The mixture was filtered off through Celite with CHCl₃. To the organic solution was added brine (20 mL). The combined mixture was extracted with CHCl₃ (total 60 mL). The combined organic layers were dried over

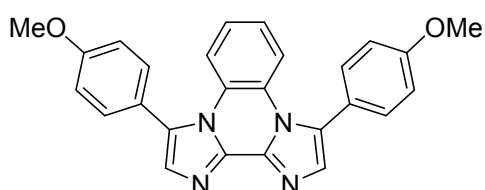
Na₂SO₄. Evaporation in vacuo, column chromatography (silica gel; EtOAc), and preparative GPC provided **4a** (99.1 mg, 0.275 mmol) in 55% yield as a colorless solid: mp 203.1–203.9 °C (hexane and CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 7.04 (dd, 2H, *J* = 3.5 and 6.5 Hz), 7.48–7.57 (m, 14H); ¹³C NMR (CDCl₃, 75 MHz) δ 118.7, 125.3, 126.2, 129.1, 129.2, 129.7, 130.2, 130.8, 133.8, 137.4; IR (KBr) 1624, 1571, 1463, 1476, 1376, 1347, 1160, 954, 851, 762, 704, 645, 567, 506, 485, 450, 439, 409 cm⁻¹. HRMS (ESI): Calcd for C₂₄H₁₇N₄ ([M+H]⁺): 361.1448. Found: 361.1433.



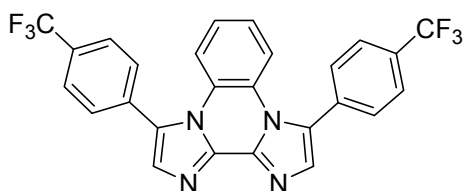
3,10-Di(4-methylphenyl)diimidazo[1,2-*a*:2',1'-*c*]quinoxaline (4b): The titled compound was prepared in 44% yield according to a procedure similar to that mentioned in **4a**: colorless solid, mp 215.7–216.0 °C (hexane and CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 2.48 (s, 6H), 7.04 (dd, 2H, *J* = 3.4 and 6.4 Hz), 7.32 (d, 4H, *J* = 7.9 Hz), 7.43 (d, 4H, *J* = 8.1 Hz), 7.45 (s, 2H), 7.53 (dd, 2H, *J* = 3.5 and 6.4 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 21.4, 118.4, 125.0, 126.1, 127.7, 129.5, 129.7, 130.1, 133.4, 137.2, 139.0; IR (KBr) 1622, 1570, 1493, 1474, 1374, 1346, 1287, 1163, 1079, 1021, 972, 818, 772, 630, 558 cm⁻¹. HRMS (ESI): Calcd for C₂₆H₂₀N₄Na ([M+Na]⁺): 411.1580. Found: 411.1575.



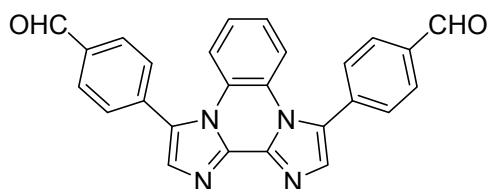
3,10-Di(2-methylphenyl)diimidazo[1,2-*a*:2',1'-*c*]quinoxaline (4c): The titled compound was prepared in 39% yield according to a procedure similar to that mentioned in **4a**: colorless solid, mp 234.9–235.7 °C (hexane and CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 2.12 (s, 6H), 7.00 (dd, 2H, *J* = 3.5 and 6.4 Hz), 7.46 (s, 2H), 7.34–7.53 (m, 10H); ¹³C NMR (CDCl₃, 75 MHz) δ 20.01, 20.03, 116.66, 116.71, 125.54, 125.58, 126.05, 126.08, 126.45, 126.49, 128.7, 128.8, 128.96, 129.04, 129.8 (high intensity), 130.5 (high intensity), 131.18, 131.23, 132.96, 133.01, 136.65, 136.71, 138.7, 138.8 (mixture of atropisomers); IR (KBr) 3053, 1625, 1572, 1495, 1473, 1373, 1288, 1159, 1121, 952, 845, 772, 751, 674 cm⁻¹. HRMS (ESI): Calcd for C₂₆H₂₁N₄ ([M+H]⁺): 389.1761. Found: 389.1753.



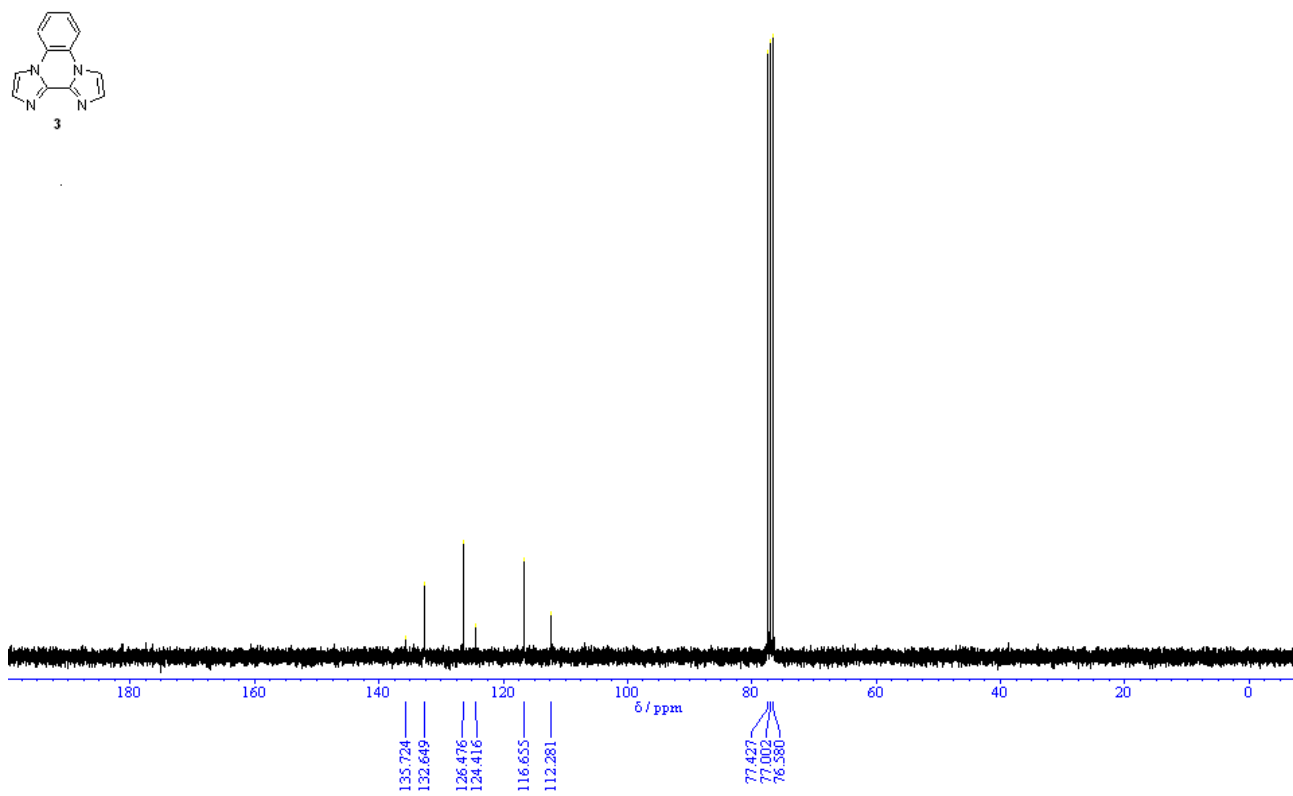
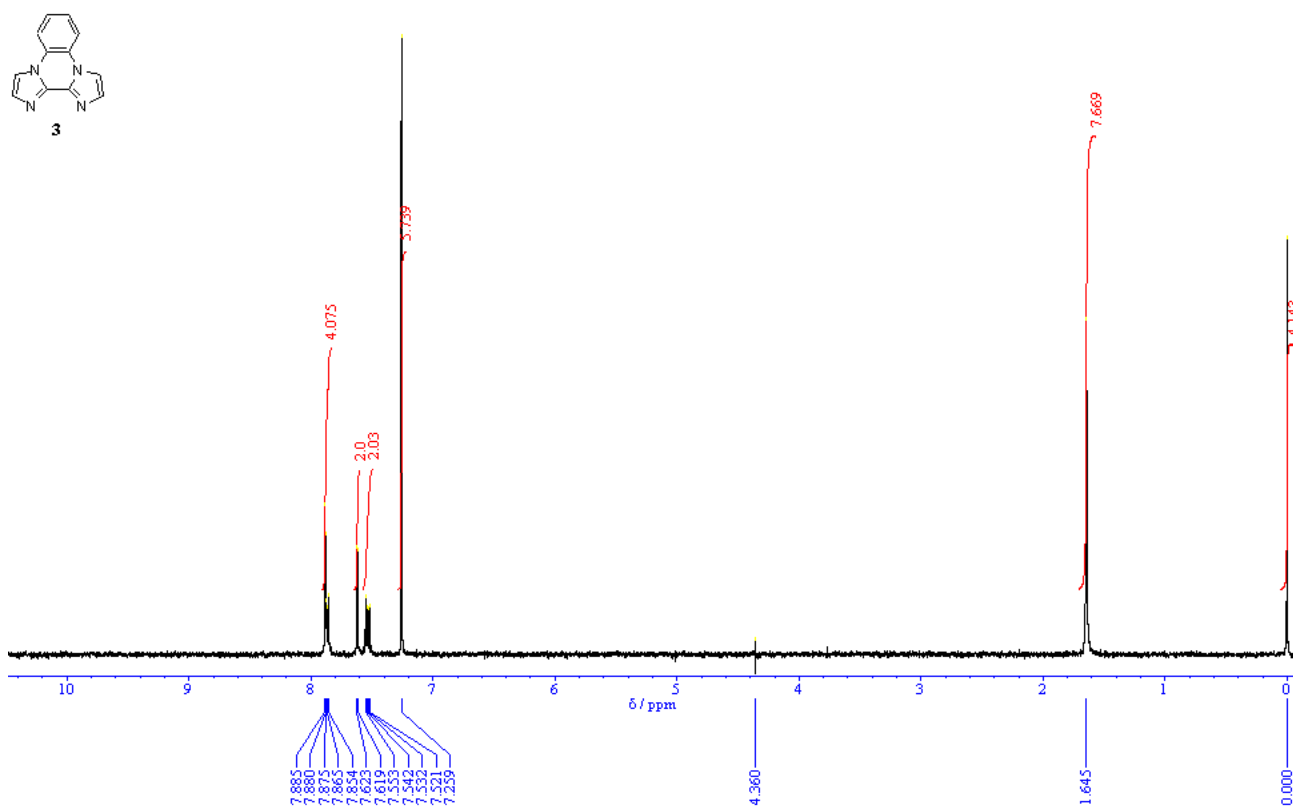
3,10-Di(4-methoxyphenyl)diimidazo[1,2-*a*:2',1'-*c*]quinoxaline (4d): The titled compound was prepared in 34% yield according to a procedure similar to that mentioned in **4a**: colorless solid, mp 219.3–220.1 °C (hexane and CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 3.92 (s, 6H), 7.03–7.06 (m, 2H), 7.05 (d, 4H, *J* = 8.9 Hz), 7.44 (s, 2H), 7.45 (d, 4H, *J* = 8.7 Hz), 7.52 (dd, 2H, *J* = 3.5 and 6.4 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 55.4, 114.4, 118.2, 122.8, 125.0, 126.2, 129.8, 131.0, 133.3, 137.0, 160.2; IR (KBr) 2840, 1611, 1571, 1505, 1376, 1285, 1249, 1177, 1026, 833, 754, 680, 598 cm⁻¹. HRMS (ESI): Calcd for C₂₆H₂₁O₂N₄ ([M+H]⁺): 421.1659. Found: 421.1651.

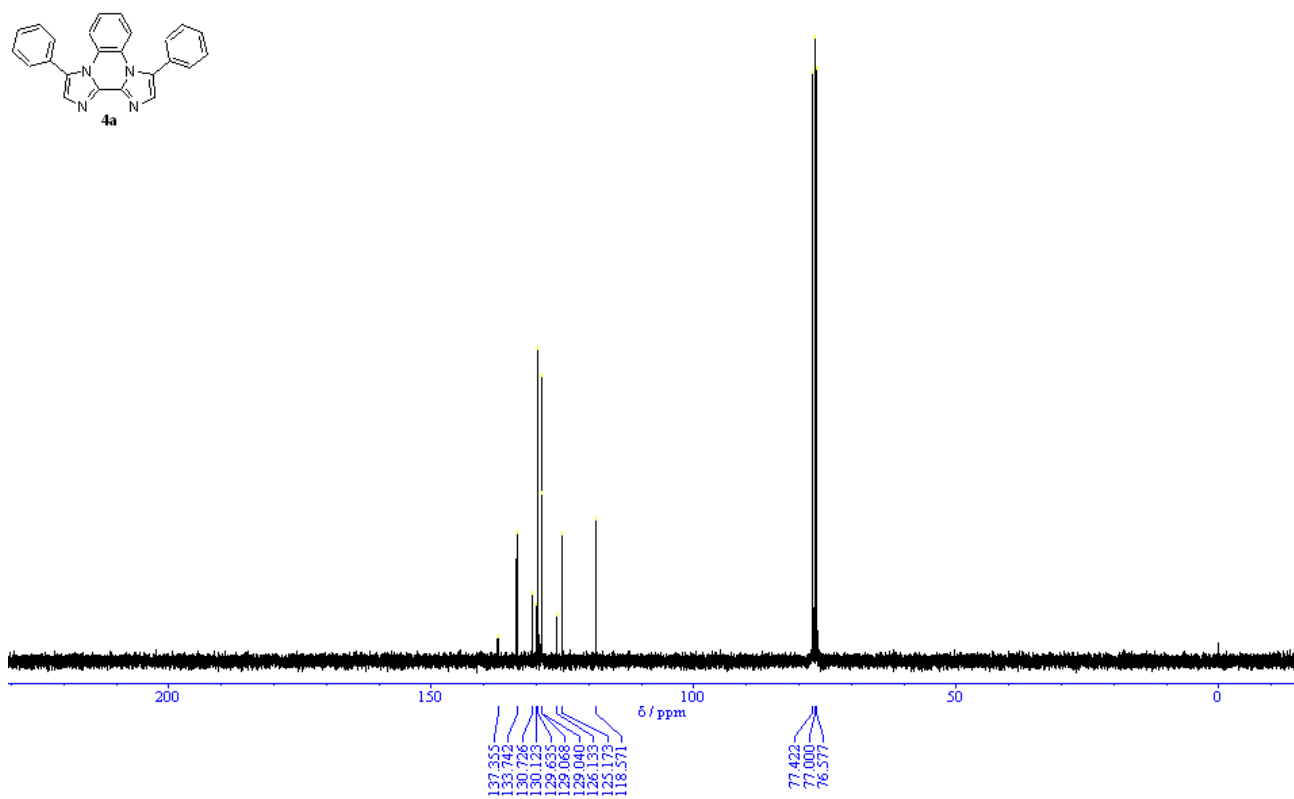
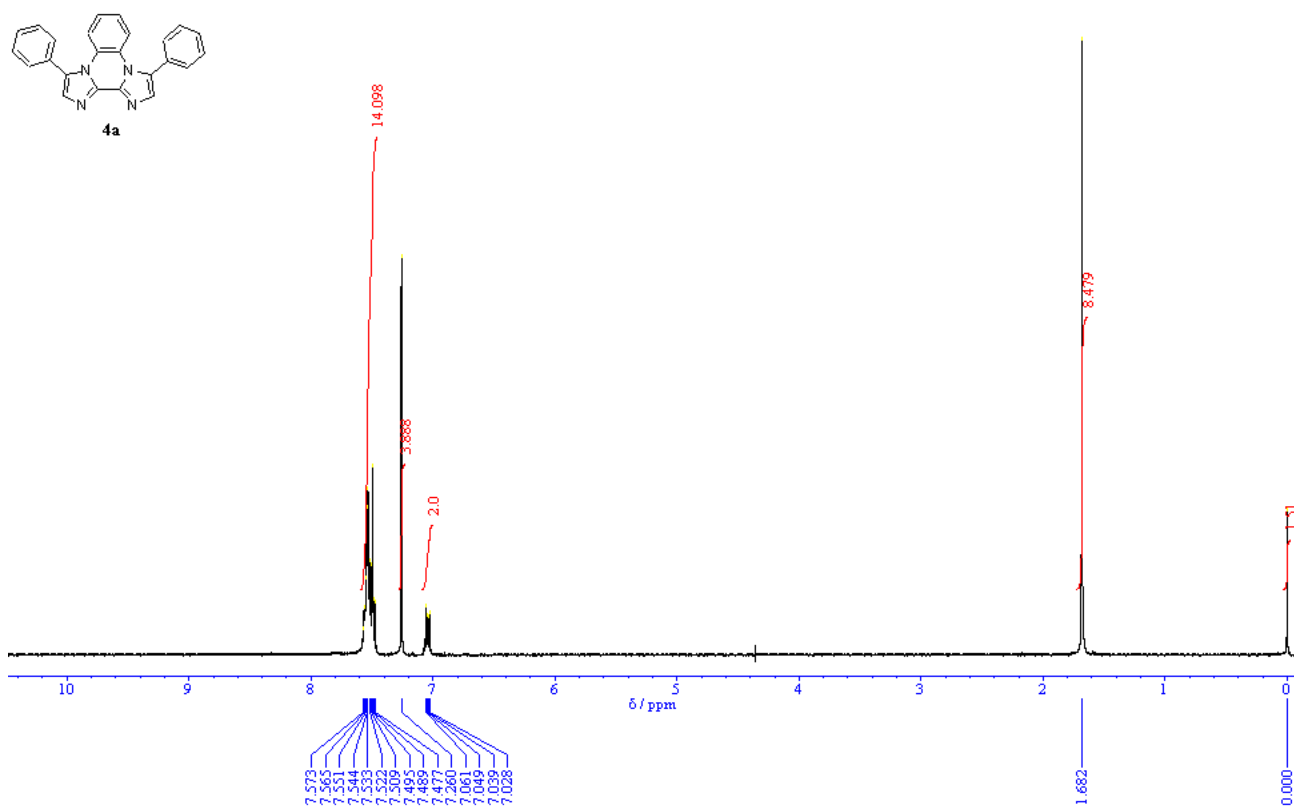


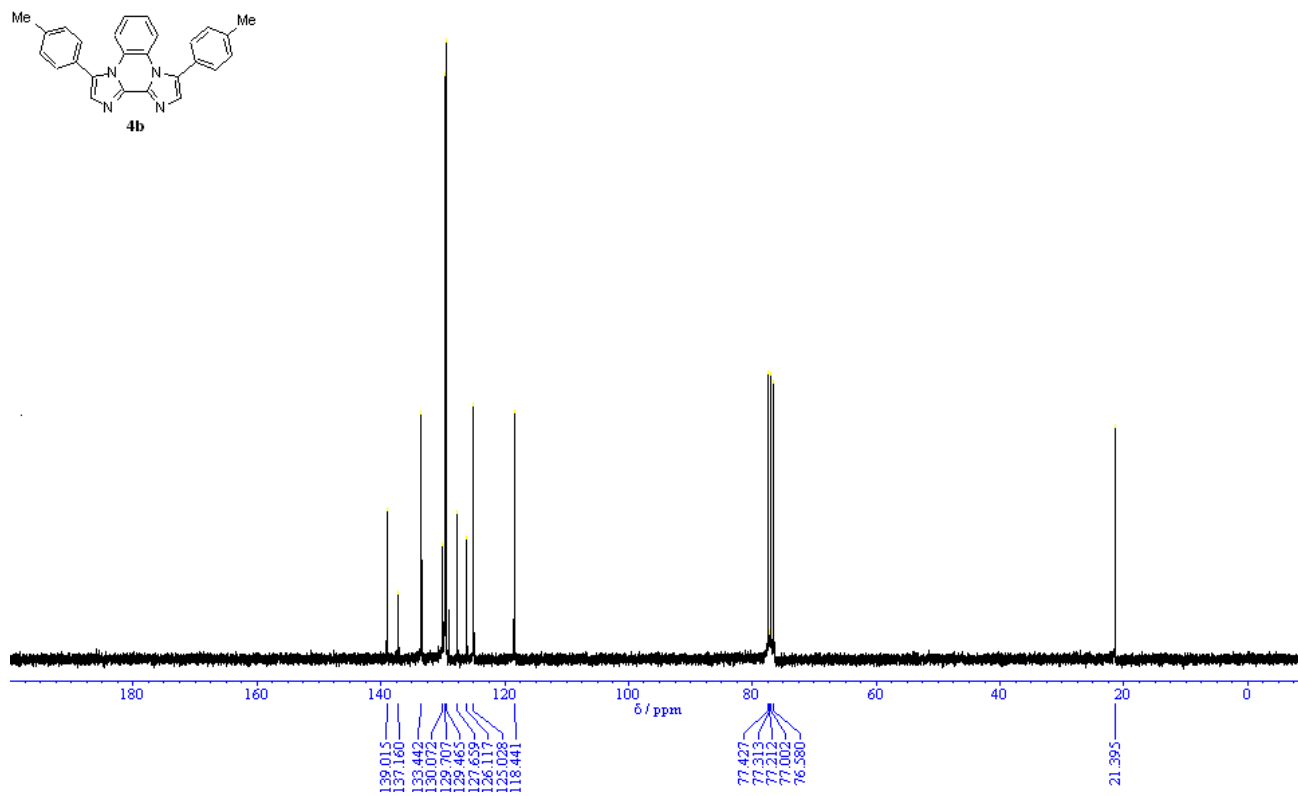
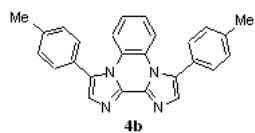
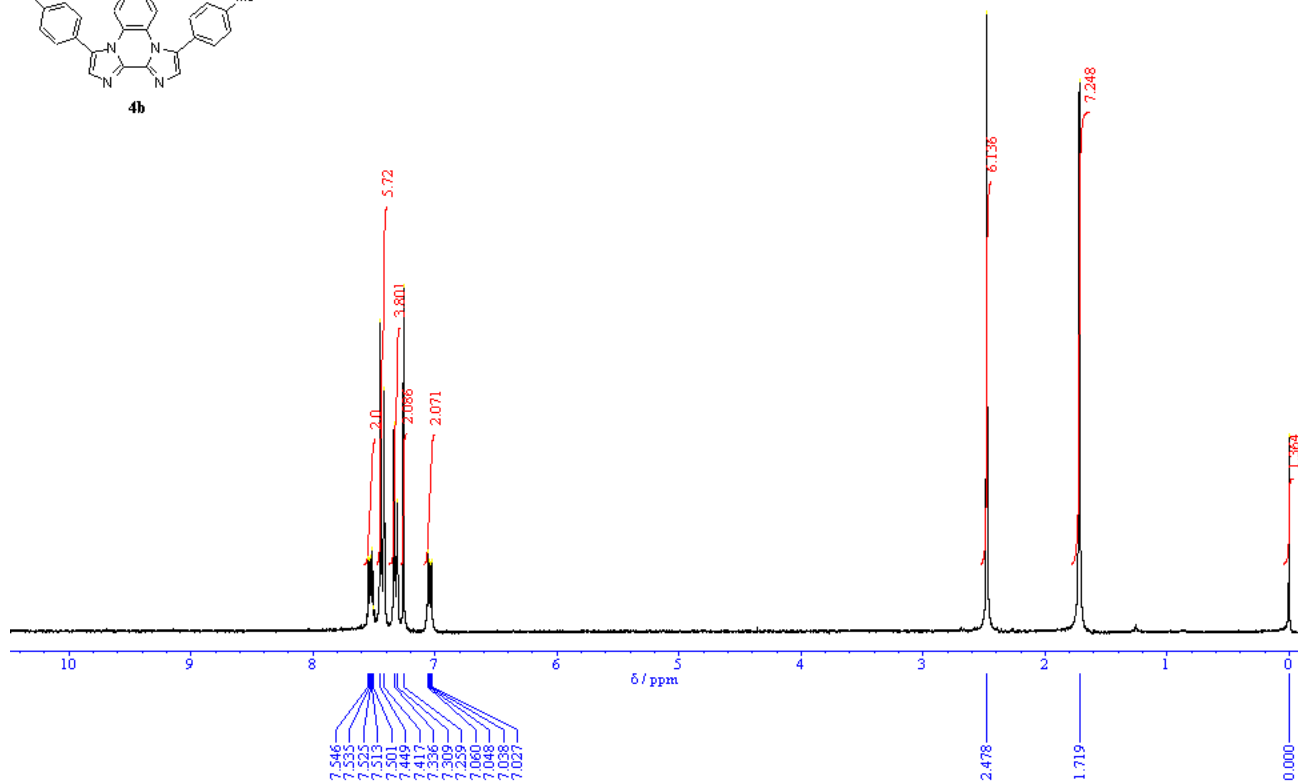
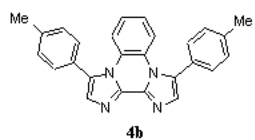
3,10-Di(4-(trifluoromethyl)phenyl)diimidazo[1,2-*a*:2',1'-*c*]quinoxaline (4e): The titled compound was prepared in 47% yield according to a procedure similar to that mentioned in **4a**: colorless solid, mp 287.5–287.9 °C (hexane and CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 7.16 (dd, 2H, *J* = 3.3 and 6.4 Hz), 7.47 (dd, 2H, *J* = 3.4 and 6.3 Hz), 7.58 (s, 2H), 7.71 (d, 4H, *J* = 8.3 Hz), 7.81 (d, 4H, *J* = 8.3 Hz); ¹³C NMR (CDCl₃, 75 MHz) δ 118.8, 123.9 (*J*_{C-F} = 272.4 Hz), 125.7, 125.8, 126.1 (*J*_{C-C-F} = 3.9 Hz), 128.8, 129.5, 131.0 (*J*_{C-C-F} = 32.8 Hz), 134.1, 134.8, 137.9; IR (KBr) 1618, 1573, 1496, 1376, 1327, 1255, 1167, 1122, 1073, 1017, 955, 841, 754, 606, 440cm⁻¹. Anal. Calcd for C₂₆H₁₄F₆N₄: C, 62.91; H, 2.84; N, 11.29%. Found: C, 62.89; H, 2.48; N, 11.18%.

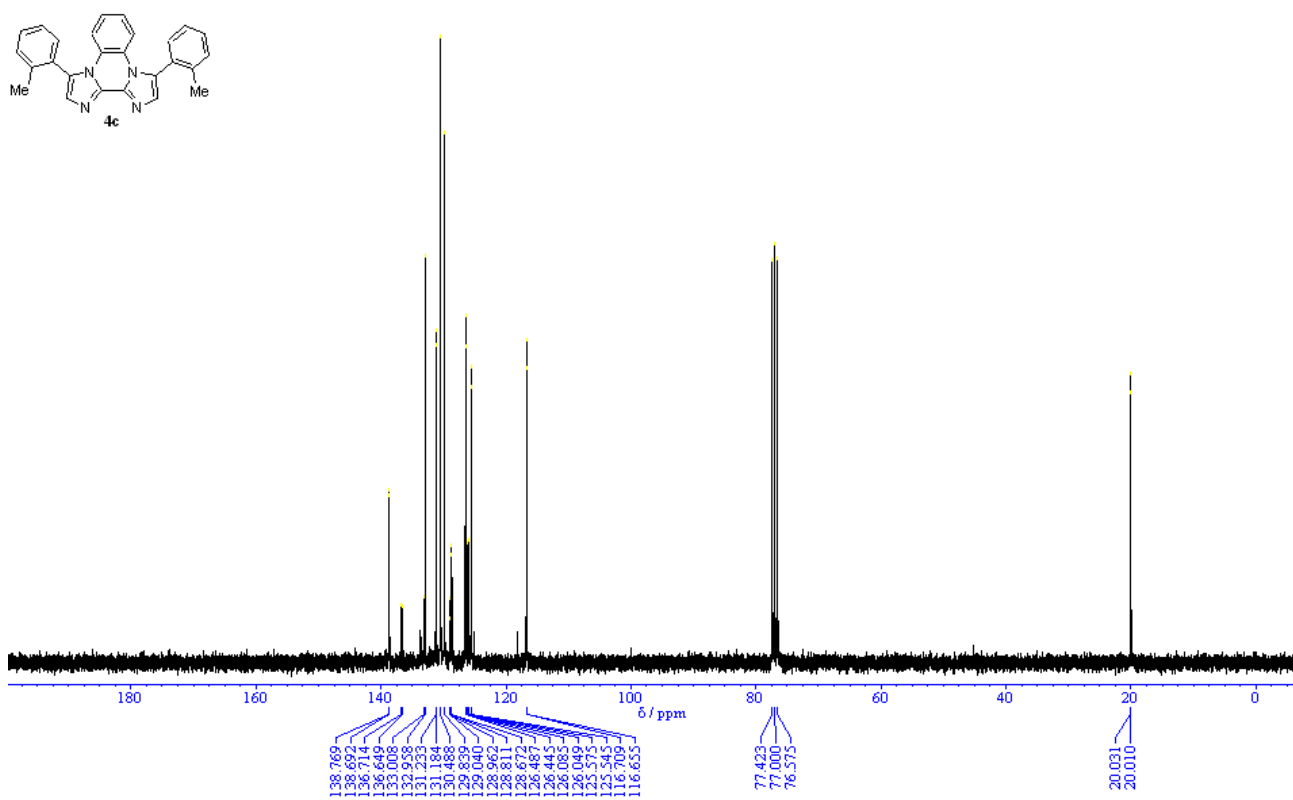
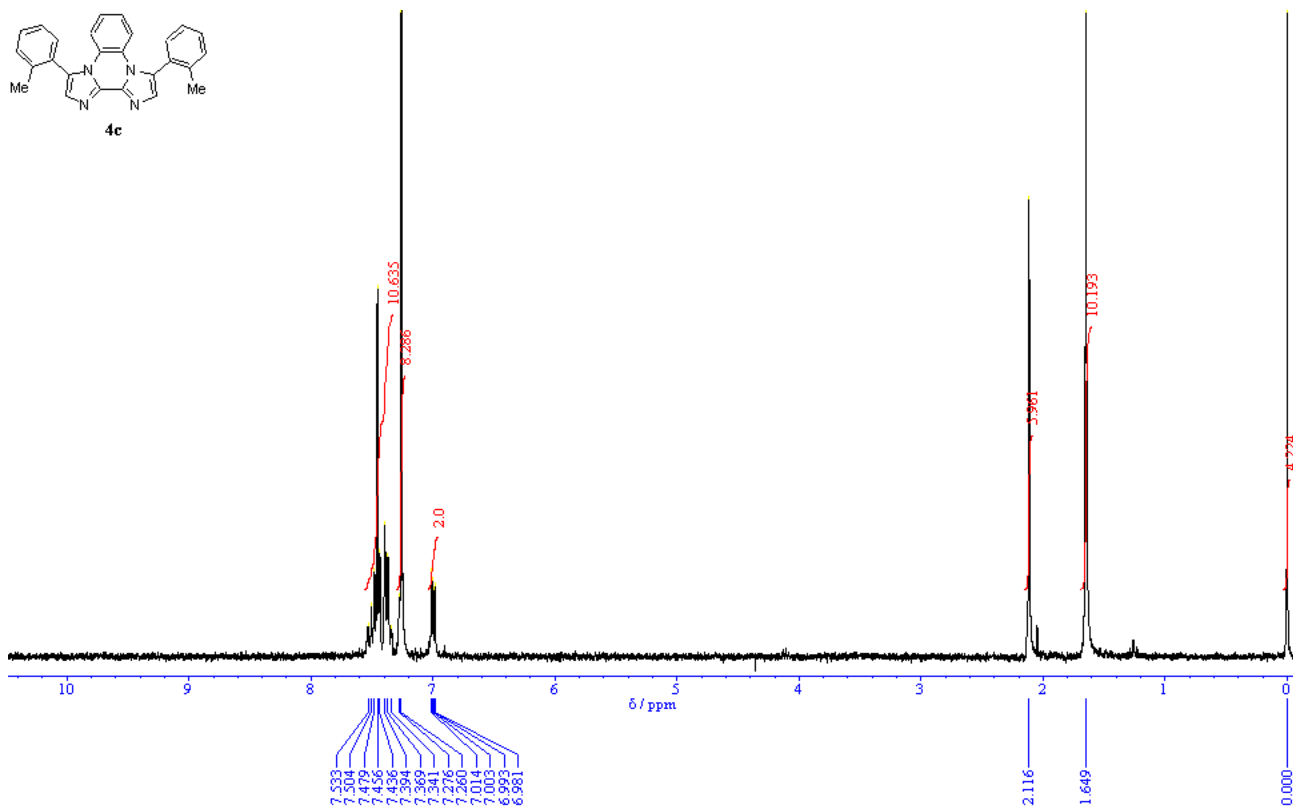


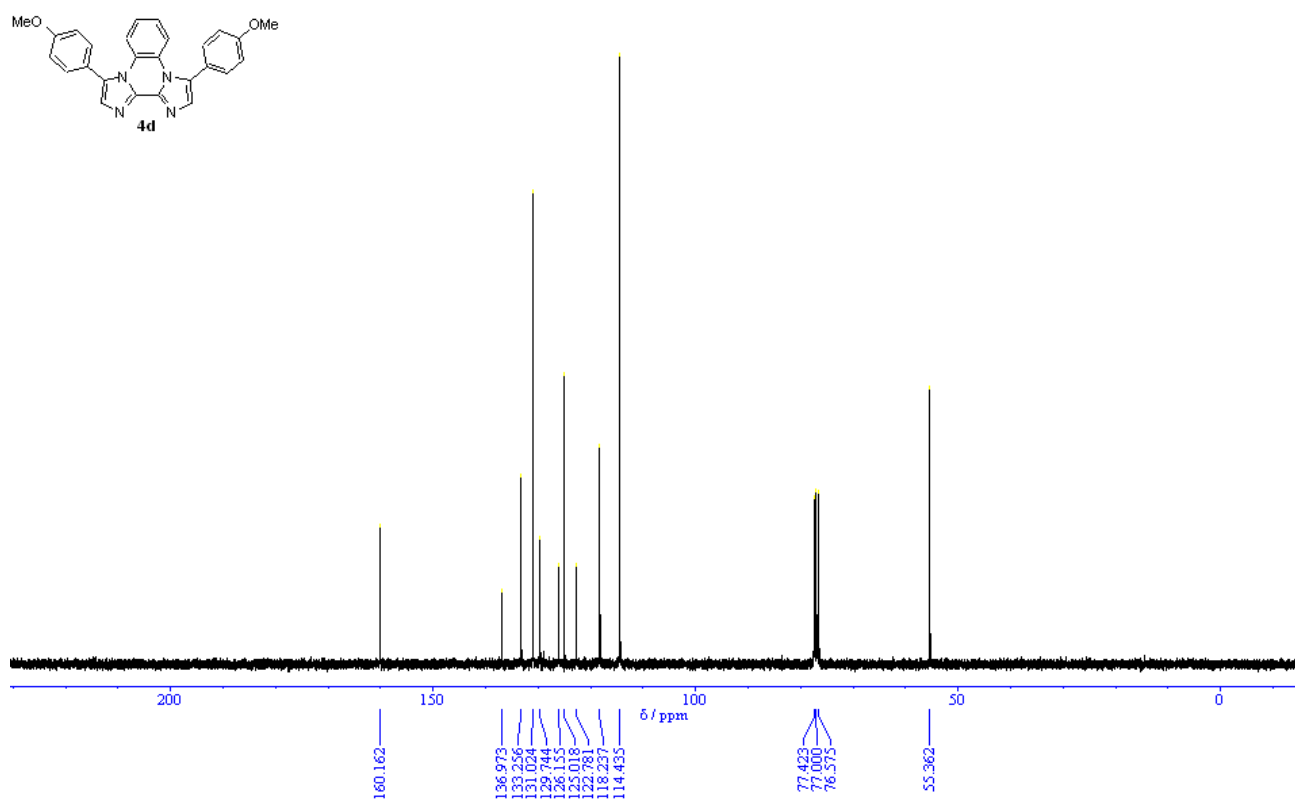
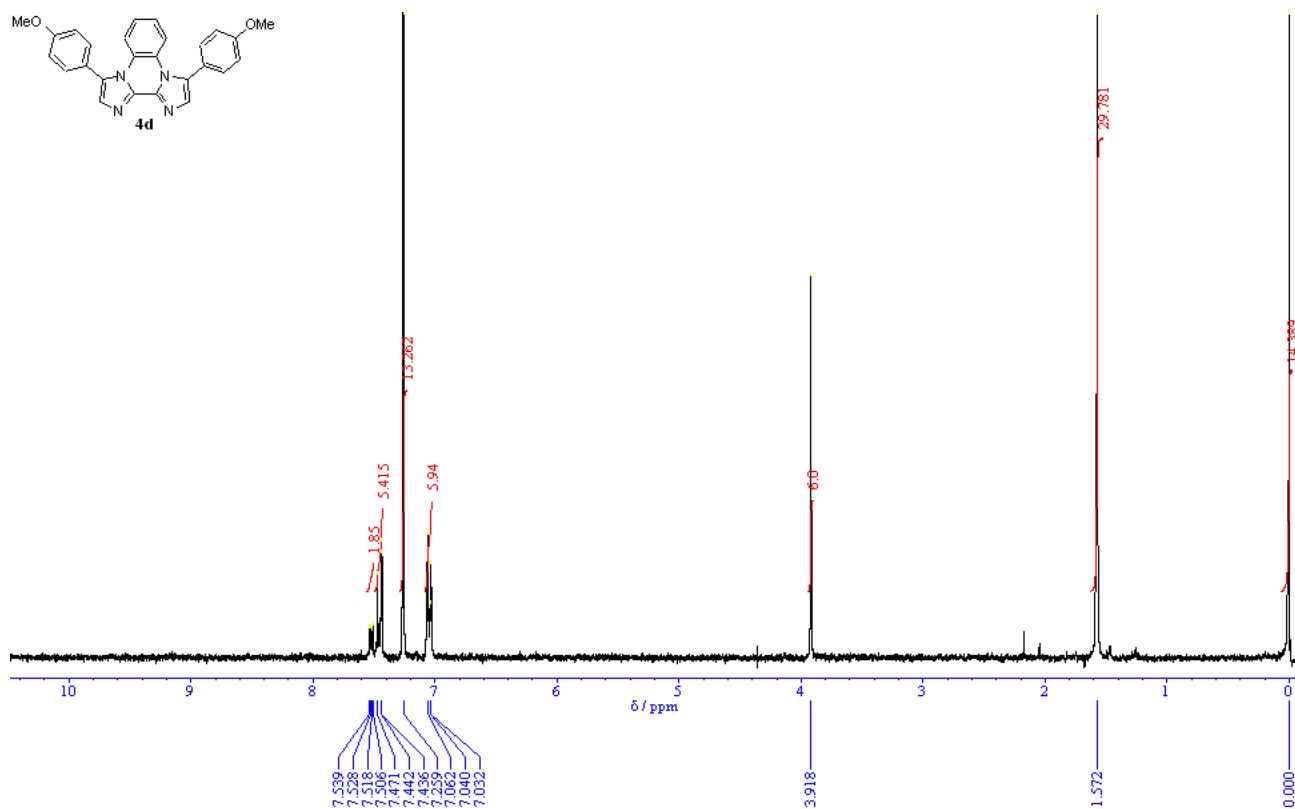
3,10-Di(4-formylphenyl)diimidazo[1,2-*a*:2',1'-*c*]quinoxaline (4f): The titled compound was prepared in 47% yield according to a procedure similar to that mentioned in **4a**: yellow solid, mp 282.2–282.7 °C (hexane and CHCl₃); ¹H NMR (CDCl₃, 300 MHz) δ 7.14 (dd, 2H, *J* = 3.4 and 6.5 Hz), 7.50 (dd, 2H, *J* = 3.5 and 6.3 Hz), 7.64 (s, 2H), 7.77 (d, 4H, *J* = 8.2 Hz), 8.06 (d, 4H, *J* = 8.3 Hz), 10.14 (s, 2H); ¹³C NMR (CDCl₃, 75 MHz) δ 119.0, 125.8, 129.2, 129.4 (includes two types of C), 130.3, 135.1, 136.1, 136.2, 138.1, 191.3; IR (KBr) 3087, 2734, 1993, 1698, 1569, 1209, 1287, 1137, 1082, 1058, 905, 835, 756, 660, 531 cm⁻¹. HRMS (ESI): Calcd for C₂₆H₁₆O₂N₄Na ([M+Na]⁺): 439.1165. Found: 439.1158.

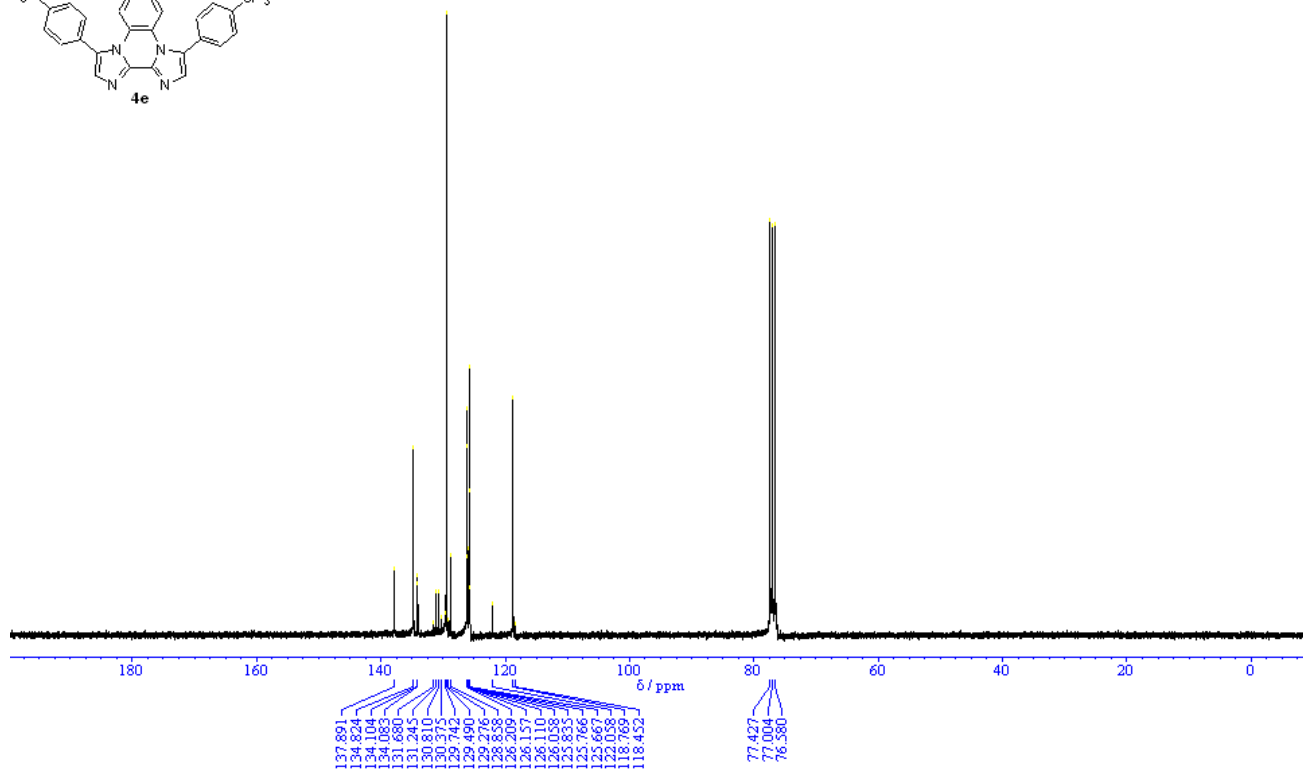
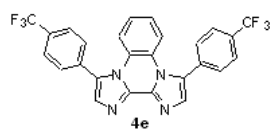
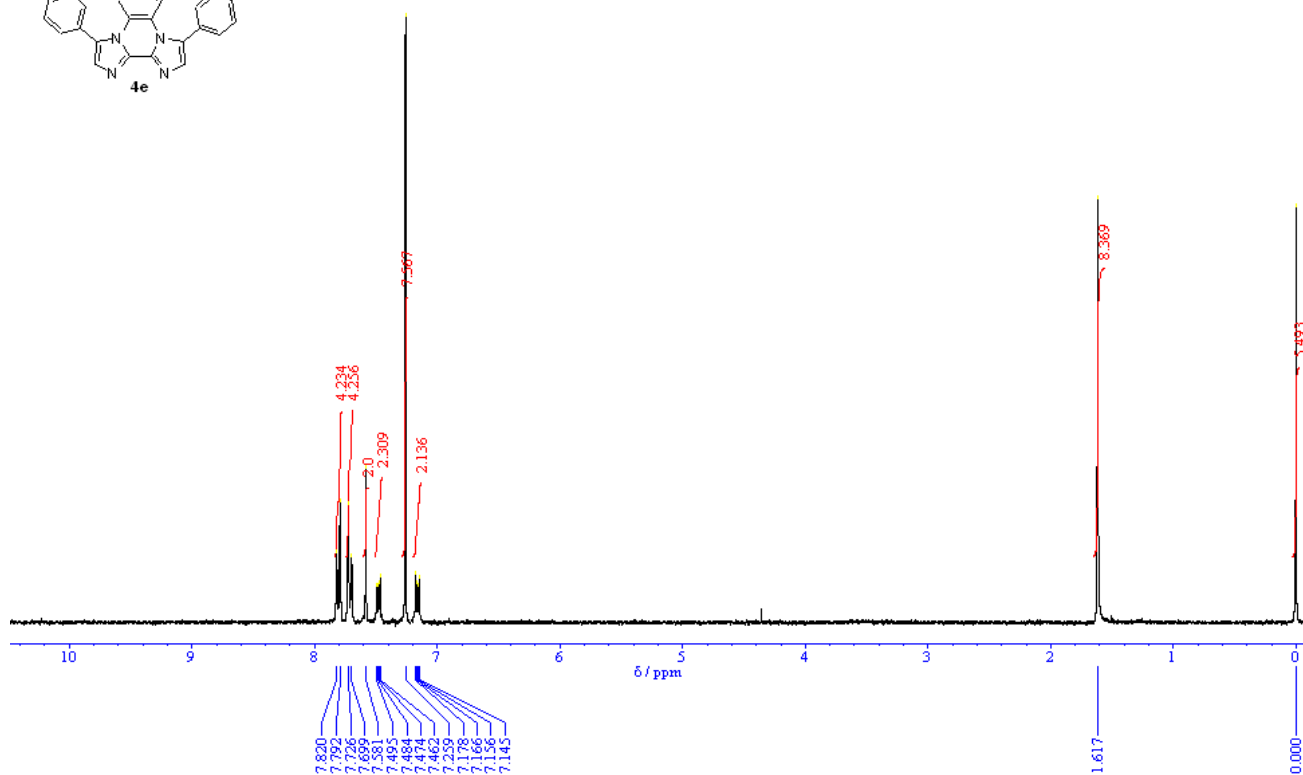
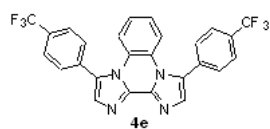


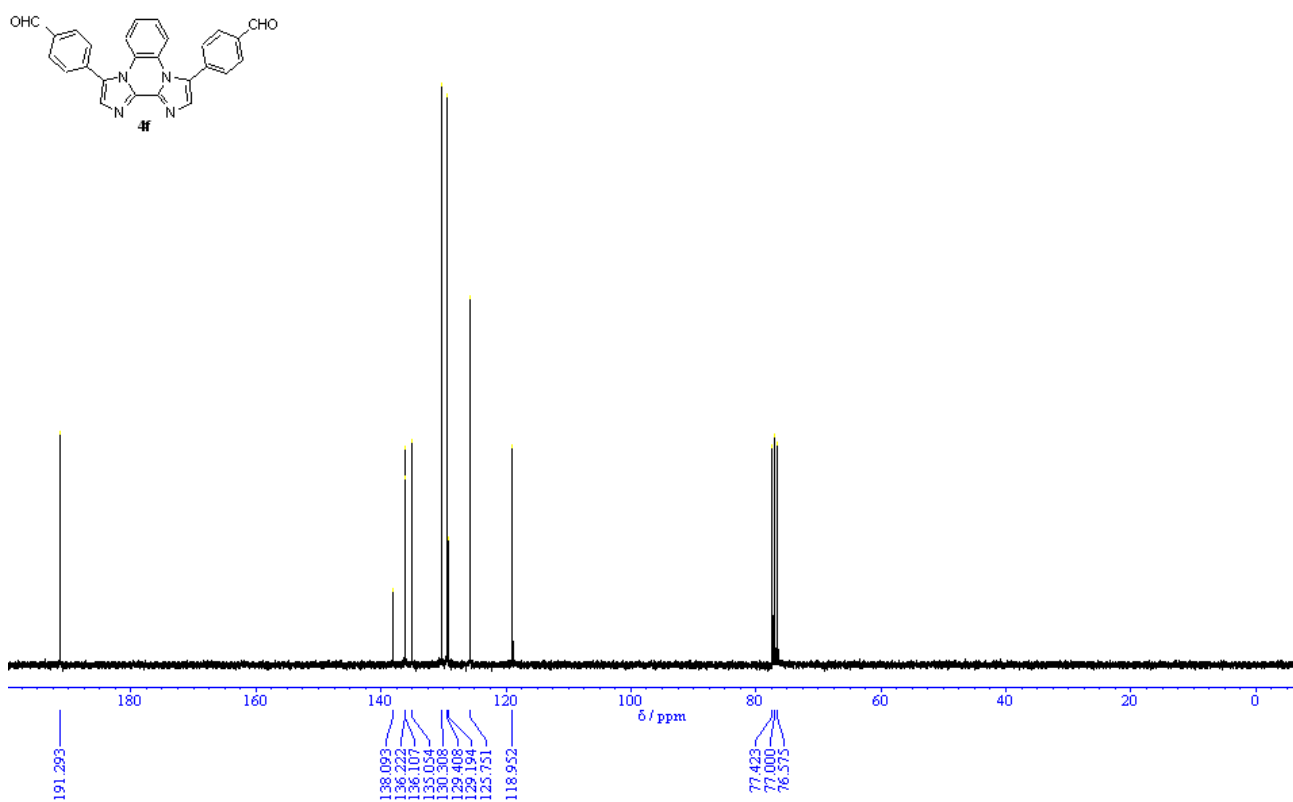
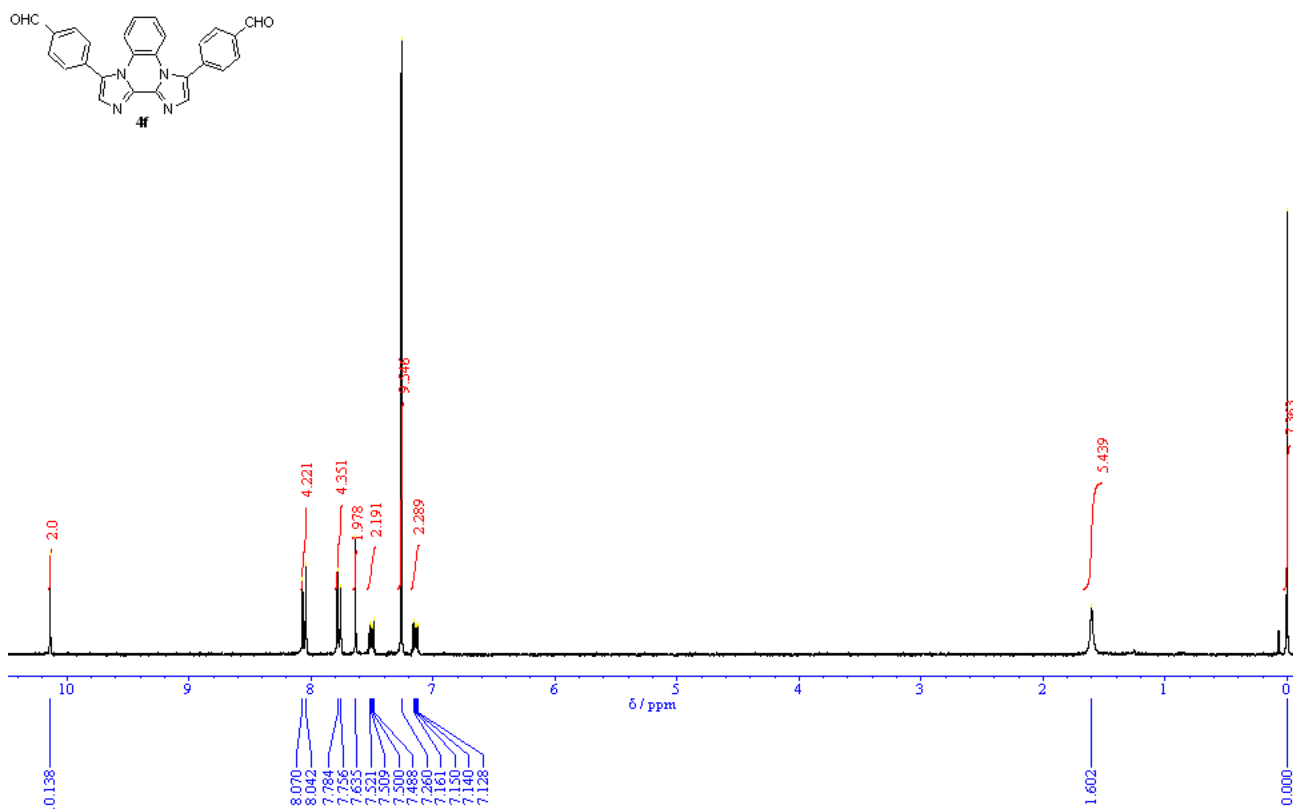












Fabrication and Characterization of OLEDs.

Device A (Spin-coating method): A 50 wt% solution of commercially available PEDOT:PSS (Clevios P VPCH 8000 (H. C. Starck)) in 2-propanol was spin-coated on ITO-coated glass (sheet resistance: $< 10 \Omega/\text{sq.}$, EL Grade of Sanyo Vacuum Industries Co., Ltd.) and dried at $200 \text{ }^\circ\text{C}$ for 30 min under atmospheric pressure. Light-emitting layer was spin-coated at 1000 rpm (60 s) from a 2.0 wt% solution of mixture of compound (**4**), PVK and PBD (3 : 65 : 32 ratio in weight)² in toluene. The film was then dried at $100 \text{ }^\circ\text{C}$ for 60 min under a vacuum. The thickness was measured on a ULVAK DEKTAK 6M surface profiler. A film of TPBI was obtained on the top of the light-emitting layer by evaporation from heated quartz crucibles in a vacuum evaporator (custom-made equipment, Seed Lab., Corporation) below $1.0 \times 10^{-4} \text{ Pa}$. And LiF and aluminum layer were sequentially deposited through a shadow mask to form active diode areas of 4 mm^2 below $5.0 \times 10^{-4} \text{ Pa}$. Thickness was measured on a ULVAC CRTM-9000 quartz crystal deposition controller.

Device B (Vacuum deposition method): A film of α -NPD was obtained on ITO-coated glass by evaporation from heated quartz crucibles in a vacuum evaporator below $1.0 \times 10^{-4} \text{ Pa}$. And films of compound (**4**) and TPBI were sequentially obtained by evaporation under the same conditions. And LiF and aluminum layer were sequentially deposited through a shadow mask to form active diode areas of 4 mm^2 below $5.0 \times 10^{-4} \text{ Pa}$.

Electroluminescence spectra were measured by using a Konica Minolta CS-1000A spectroradiometer with ADVANTEST R6243 DC voltage current source/monitor. Current-voltage-luminance characteristics of OLEDs were measured by using a Keithly Moldel 6485 picoammeter. The luminescence (brightness) was measured by using a Konica Minolta CS-100A spectroradiometer. The current-voltage and luminance-voltage curves were recorded simultaneously under an air.

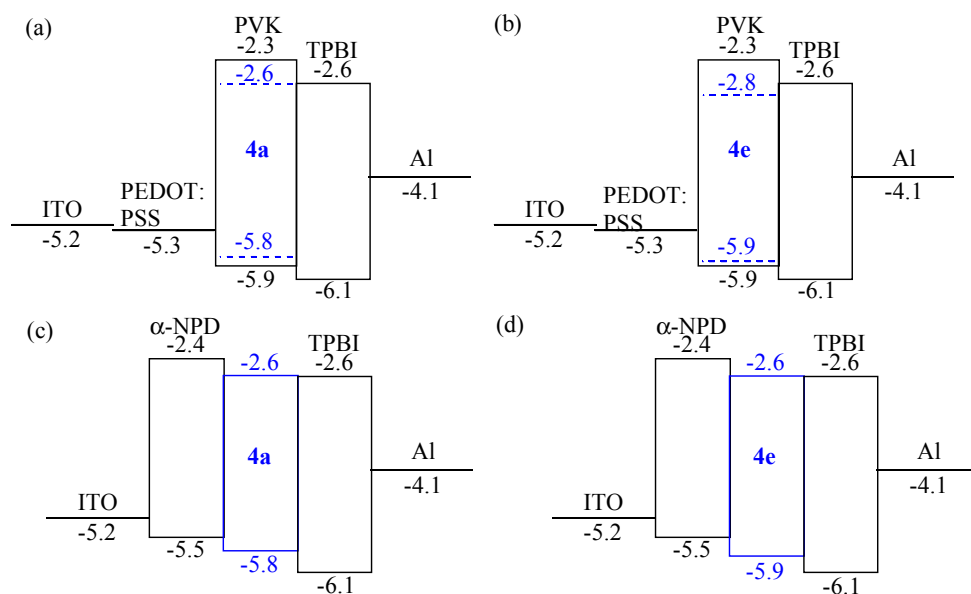


Fig. S1 Schematic energy level (ins eV) diagram of the OLEDs using (a) 4a and (b) 4e as the emitter fabricated by spin-coating method (device A), and using (c) 4a and (d) 4e as the emitter fabricated by vacuum deposition method (device B).

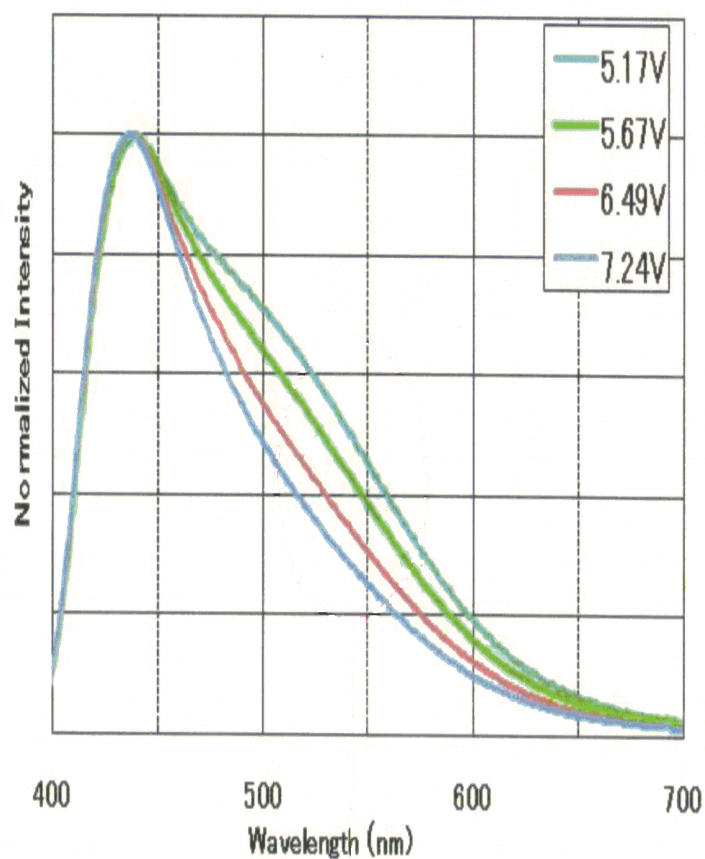


Fig. S2 Voltage dependence of EL spectrum of 4e in device B.

References

- 1 Y.-H. So, *Macromolecules*, 1992, **25**, 516-520.
- 2 C. Jiang, W. Yang, J. Peng, S. Xiao, Y. Cao, *Adv. Mater.*, 2004, **16**, 537-541.