Copper-Promoted *N*-Arylations of Cyclic Imides within Six-Membered Rings: A Facile Route to Arylene-Based Organic Materials

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General: Reagents were purchased from commercial suppliers and used without further purification. Proton nuclear magnetic resonance spectra (¹H NMR) were taken on a 400 MHz or 500 MHz spectrometer. TMS was used as an internal standard for all ¹H NMR. Laser desorption mass spectra were obtained with a time-of-flight MALDI mass spectrometer using dithranol as a matrix. High-resolution fast atom bombardment (HR FAB) measurements were made at the University Illinois at Urbana-Champaign. All column chromatography was performed on standard silica gel, 60 Å, 32-63 µm. Methylene chloride was unstabilized and obtained from a column solvent system in which it is deoxygenated and passed through two alumina columns to remove any water.¹

HPLC measurements were obtained using Phenomenex (4.6 x 250 mm x 5 µm) silica column. All samples were filtered with a 0.2 µm syringe filter prior to injection into the HPLC. An eluent mixture of 80% hexanes to 20% ethyl acetate, both of which

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometal.* **1996**, *15*, 1518-1520.

were HPLC grade was used for the mobile phase. Compound **3** was used as an external standard from which reaction yields were obtained.

General Reaction Conditions for Imide Formation

A 20 mL reaction vial is flame dried and cooled under nitrogen to which 4 Å molecular sieves, 2 mL of dry CH₂Cl₂, a 5 mm stir bar, 0.5 mmol (2-3 equiv) of boronic ester, 0.17 mmol (1 equiv) of imide, 0.5 mmol (3 equiv) triethylamine, and 0.3-0.5 mmol of copper(II) acetate is added. The septum on the reaction vial is pierced with a needle connected to a balloon filled with oxygen. The atmosphere is flushed with oxygen and then the vial is sealed. The reaction is stirred for 19-20 hours with gentle heating (45 °C). Upon consumption of the starting material imide, as judged by HPLC, the reaction mixture was purified directly via flash column chromatography on silica gel, usually using methylene chloride as the eluent.

Compound **2d**, 5,12-Bis-(3,5-di-tert-butyl-phenoxy)-2-octyl-5a,14c-dihydro-anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone.

In a flame dried 100 mL round bottom flask was added *N*-(octyl)-1,7-(3',5'-di-*t*-butylphenoxy)perylene-3,4-dicarboxyanhydride-9,10-dicarboximide (0.11 g, 0.12 mmol), excess urea (55 equiv, 6.6 mmol, 0.40 g), and 12 mL dimethylformamide (DMF). The mixture was heated to reflux under nitrogen overnight. The reaction was judged incomplete via thin layer chromatography (TLC) in the morning and urea was added in 55 equivalent portions each hour (x 2) until all the starting material was consumed (if all

starting material is not consumed, the reaction can still be worked up and the anhydride starting material recovered following purification). Once the reaction is judged complete, it is cooled, diluted with CHCl_3 and washed with saturated aqueous NH_4Cl (1 x 30 mL), brine (1 x 30 mL) and the organic layer is dried over anhydrous sodium sulfate. Removal of solvent under reduced pressure followed by flash column chromatography (100% CHCl_3) yields **2d** in quantitative yield as a dark purple solid. HR FAB found 912.5074 for $\text{C}_{60}\text{H}_{68}\text{N}_2\text{O}_6$ (calc. 912.5077). IR (CH_2Cl_2 cast) 3163, 2958, 2850, 1697, 1604, 1259 cm^{-1} . UV-vis (1.0 cm quartz cuvette, toluene) 401, 508, 545 nm. ^1H NMR (CDCl_3 , 500 MHz): δ 9.68 (t, 2H, $J = 8.85$ Hz), 8.65 (d, 1H, $J = 6.10$ Hz), 8.63 (d, 1H, $J = 6.10$ Hz), 8.45 (s, 1H), 8.37 (s, 1H), 8.36 (s, 1H), 7.37 (s, 1H), 7.36 (s, 1H), 7.03 (d, 2H, $J = 1.53$ Hz), 7.02 (d, 2H, $J = 7.02$ Hz), 4.15 (t, 2H, $J = 7.33$ Hz), 1.34 (m, 48H), 0.86 (t, 3H, $J = 6.71$ Hz).

Compound **7**, 5,12-Bis-(3,5-di-tert-butyl-phenoxy)-2-octyl-9-phenyl-5a,14c-dihydro-anthra[2,1,9-def;6,5,10-d'e'f']diisoquinoline-1,3,8,10-tetraone.

As per general reaction conditions (20 mg, 0.022 mmol) of **2d**, (11 mg, 0.07 mmol) of arylboronic ester **1c**, (12 mg, 0.07 mmol) of copper (II) acetate, and (7 mg, 0.07 mmol) of triethylamine were stirred at 45 °C for 48 hours in 2 mL chloroform. Purification via flash column chromatography (100% CHCl_3) yielded **7** as a dark purple solid (16 mg, 74%). UV-vis (1.0 cm quartz cuvette, toluene) 403, 507, 543 nm. HR FAB found 986.5230 for $\text{C}_{66}\text{H}_{70}\text{N}_2\text{O}_6$ (calc. 986.5234). IR (CH_2Cl_2 cast) 2922, 2852, 1697, 1658, 1602, 1260 cm^{-1} . ^1H NMR (CDCl_3 , 500 MHz): δ 9.71 (d, $J = 8.2$ Hz, 2 H), 8.68 (d, $J = 8.2$ Hz, 1H), 8.64 (d, $J = 8.2$ Hz, 1H), 8.34 (s, 2H), 7.54 (m, 2H), 7.47 (m, 1H), 7.34 (m, 4H), 7.04 (s, 2H), 7.03 (s, 2H), 4.15 (t, $J = 7.9$ Hz, 2H), 1.30 (m, 48H), 0.87 (m, 3H).

Compound **10**, 4-[6,13-Bis-(3,5-di-tert-butyl-phenoxy)-9-octyl-1,3,8,10-tetraoxo-3,5b,8,9,10,10c-hexahydro-1H-anthra[2,1,9-def;6,5,10-d'e'f']diisoquinolin-2-yl]-benzaldehyde.

As per general reaction conditions (20 mg, 0.022 mmol) of **2d**, (13 mg, 0.07 mmol) of 4-formylphenylboronate (**9**), (12 mg, 0.07 mmol) of copper (II) acetate, and (7 mg, 0.07 mmol) of triethylamine were stirred at 40 °C for 48 hours in 4 mL chloroform. Purification via flash column chromatography (100% CHCl₃) yielded **10** as a dark purple/red solid (15 mg, 73%). HR FAB found 1016.5350 for C₆₇H₇₂N₂O₇ (calc. 1016.5340). IR (CH₂Cl₂ cast) 2960, 2854, 1699, 1659, 1600, 1262 cm⁻¹. UV-vis (1.0 cm quartz cuvette, toluene) 401, 509, 546 nm. ¹H NMR (CDCl₃, 500 MHz): δ 10.11 (s, 1H), 9.69 (d, 1H, *J* = 8.55 Hz), 9.66 (d, 1H, *J* = 8.55 Hz), 8.67 (d, 1H, *J* = 8.24 Hz), 8.61 (d, 1H, *J* = 8.55 Hz), 8.22 (s, 1H), 8.17 (s, 1H), 8.06 (d, 2H, *J* = 7.94 Hz), 7.55 (d, 2H, *J* = 8.24 Hz), 7.37 (s, 1H), 7.36 (s, 1H), 7.04 (s, 2H), 7.02 (s, 2H), 4.13 (t, 2H, *J* = 7.63 Hz), 1.33 (m, 48H), 0.87 (t, 3H, *J* = 6.10 Hz).

Compound 11, TPP-(PDI)₄ [Tetraphenylporphyrin-(perylene-diimide)₄]

A 25 mL round bottom flask was flame dried and **10** (21 mg, 0.02 mmol), pyrrole (1.4 mg [0.47 mL of a 3mg/mL solution of pyrrole in CH₂Cl₂], 0.02 mmol) and CH₂Cl₂ (2mL) were added and degassed with nitrogen. Trifluoroacetic acid (TFA) (4.7 mg [0.62 mL of a 8 mg/mL solution of TFA in CH₂Cl₂], 0.04 mmol) was then added to the mixture and stirred at room temperature for 4 hours under a nitrogen atmosphere. *p*-Chloranil (10 mg, 0.04 mmol) was added and the reaction heated to reflux for one hour under nitrogen. Purification via flash column chromatography (96% CHCl₃/4% EtOAc) followed by preparatory thin layer chromatography (gradient: 95% CHCl₃/5% Hexanes followed by 96% CHCl₃/4% EtOAc) yielded **11** as a dark purple solid (5 mg, 23% yield). UV-vis (1.0 cm quartz cuvette, toluene) 422, 515, 550 nm. C₂₈₄H₂₉₄N₁₂O₂₄. Mass spectrum (m/e) 4259.4 (calc.4259.4). IR (CH₂Cl₂ cast) 3553, 2961, 2850, 1699, 1660, 1600, 1260, 1092, 1019, 799 cm⁻¹. Attempts to obtain ¹H NMR only yielded broad spectra due to the strong tendency of this molecule to aggregate as previously reported for a similar porphyrin (van der Boom, T.; Hayes, R. T.; Zhao, Y.; Bushard, P. J.; Weiss, E. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2002**, 124, 9582-9590.) ¹H NMR (CDCl₃, 500 MHz): δ 9.6 (broad, 8H),

8.88 (broad, 4H), 8.8 (broad, 4H), 8.7 (broad, 4H), 8.4 (broad, 4H), 7.7 (broad, 8H), 7.5 (broad, 24H), 7.2 (broad, 24H), 4.2 (broad, 8H), 1.9 (broad, 16H), 1.4 (broad, 188H), -2.8 (broad, 2H).

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Compound	Reference
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1c	Kobayashi, Y.; Mizojiri, R.; Ikeda, E. <i>J. Org. Chem.</i> 1996 , 61, 5391-5399.
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