The Supporting Information published ASAP April 9, 2005, contained errors in the isolated yields for 4-methyl-4'-methoxybiphenyl and 4-fluoro-4'-methylbiphenyl (p S6); the corrected version was published ASAP April 13, 2005.

Electronic Nature of N-Heterocyclic Carbene Ligands:

Effect on the Suzuki Reaction

Niloufar Hadei, Eric Assen B. Kantchev, Christopher J. O'Brien, Michael G. Organ*

Department of Chemistry, York University, 4700 Keele Street, Toronto, Ontario, M3J 1P3

Canada

organ@yorku.ca

Supporting Information

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General Experimental

All reactions were carried out under an atmosphere of argon using Schlenk techniques. Glovebox manipulations were performed in an MBraun Unilab glovebox under an atmosphere of dry argon. All solvents were purchased from Fischer Scientific. CDCl_3 and CD_2Cl_2 were purchased from Cambridge Isotopes. Toluene was dried under argon over CaH_2 ; dioxane was dried under argon over sodium-benzophenone. All reagents were purchased from commercial sources and were used without further purification, unless indicated otherwise. Thin layer chromatography (TLC) was performed on Whatman 60 F₂₅₄ glass plates and were visualized using UV light (254 nm). Column chromatography purifications were carried out using the flash technique on Silicycle silica gel 60 (230-400 mesh). NMR spectra were recorded on a Bruker 300 DPX spectrometer. The chemical shifts (δ) for ^1H and ^{13}C are given in ppm referenced to the residual signals of the deuterated solvent. Gas chromatography was performed on Varian Series GC/MS/MS 4000 System. All melting points are uncorrected.

Synthetic Procedures

Amine Arylation (general procedure): In a pressure vessel, 0.549 g Pd₂(dba)₃, (0.600 mmol, 4 mol %) and 0.747 g *rac*-BINAP (1.20 mmol, 8 mol %) were covered with 70 mL anhydrous toluene and heated to 135 °C for 15 min. After the solution was cooled to room temperature, 5.84 g sodium *tert*-butoxide (60.75 mmol, 405 mol %), 11.35 g 1-adamantylamine (75.0 mmol, 500 mol %) and the corresponding *o*-dibromobenzene (15.0 mmol, 100 mol %) were added in succession, followed by additional 35 mL anhydrous toluene. The mixture was degassed for 10 min with Ar and heated at 135 °C over 20 h. After cooling, the resulting slurry was filtered through a pad of Celite followed by rinsing with dichloromethane. The solvents were removed on a rotary evaporator and the final product was purified by flash chromatography on silicagel.

1,2-di-(1-adamantylamino)-3,4-dimethoxybenzene (8). From 4.44 g 1,2-dibromo-3,4-dimethoxy-benzene, 5.08 g of **8** (47 %) were obtained as off-white solid following column chromatography (hexane-ethyl acetate = 6:1, *R_f* = 0.28), mp 192-193 °C. ¹H NMR (CDCl₃, 300 MHz) δ 6.60 (s, 2H), 3.82 (s, 6H), 3.45 (broad s, 2H), 2.07 (broad s, 6H), 1.77 (broad m, 12H), 1.62 (broad m, 12H). ¹³C NMR (CDCl₃, 75 MHz) δ 143.9, 132.3, 109.7, 56.6, 53.5, 44.2, 36.8, 30.0. Anal. Calcd. for C₂₈H₄₀N₂O₂: C, 77.02; H, 9.23; N, 6.42. Found: C, 77.35; H, 9.41; N, 6.40.

1,2-di-(1-adamantylamino)benzene (9). From 1.78 mL of 1,2-dibromobenzene, 4.42 g of **9** (78 %) was obtained as off-white solid following column chromatography (hexane-dichloromethane = 1:4, containing 0.1 vol % triethylamine, *R_f* = 0.32), mp 168-170 °C. ¹H NMR (CDCl₃, 300 MHz) δ 6.92 (m, 2H), 6.75, (m, 2H), 3.67 (broad s, 2H), 2.09 (broad s, 6H), 1.86 (broad m, 12 H), 1.63 (broad m, 12 H). ¹³C NMR (CDCl₃, 75 MHz) δ 138.4, 122.1, 120.5, 52.8, 43.7, 36.8, 30.0. Anal. Calcd. for C₂₆H₃₆N₂: C, 82.93; H, 9.64; N, 7.44. Found: C, 82.62; H, 10.04; N, 7.24.

1,2-di-(1-adamantylamino)-3,4-difluorobenzene (10). From 4.08 g of 1,2-dibromo-3,4-difluorobenzene, 5.44 g of **10** (89 %) was obtained as off-white solid following column

chromatography (hexane-ethyl acetate = 20:1, R_f = 0.27), mp 159-161 °C. ^1H NMR (CDCl_3 , 300 MHz) δ 6.73, (t, J = 10.5 Hz, 2H), 3.57 (broad s, 2H), 2.11 (broad s, 6H), 1.81 (broad m, 12H), 1.67 (broad m, 12H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 144.1 (dd, $^1J_{\text{C-F}}$ = 241 Hz; $^2J_{\text{C-F}}$ = 14.9 Hz), 134.1 (app. t, $J_{\text{C-F}}$ = 7.0 Hz), 110.0 (dd, $^2J_{\text{C-F}}$ = 14.9 Hz; $^3J_{\text{C-F}}$ = 7.7 Hz), 52.7, 43.2, 36.4, 29.8. Anal. Calcd. for $\text{C}_{26}\text{H}_{34}\text{F}_2\text{N}_2$: C, 75.44; H, 8.62; N, 6.63. Found: C, 75.69; H, 8.31; N, 6.79.

1,3-diadamantylbenzimidazolium chloride formation (general procedure): Diamine (**8-10**) was dissolved with stirring in triethyl orthoformate and conc. HCl was added. The mixture was stirred at room temperature for 30 min and then heated at 80 °C. Hot toluene (equal volume to the triethyl orthoformate) was added and after cooling, the precipitated benzimidazolium salt was vacuum filtered, rinsed successively with toluene and then hexane and dried in high vacuum.

1,3-di-(1-adamantyl)-5,6-dimethoxybenzimidazolium chloride (11). From 1.84 g of **8** (6.35 mmol, 100 mol %), 74 mL of triethyl orthoformate and 0.42 mL of 12.1 N HCl (5.05 mmol, 120 mol %) after heating for 4 h, 1.94 g of **11** (96 %) were obtained as a white solid, mp. 271-272 °C. ^1H NMR (CD_2Cl_2 , 300 MHz) δ 9.14 (s, 1H), 7.36 (s, 2H), 4.00 (s, 6H), 2.58 (broad m, 12H), 2.38 (broad s, 6H), 1.90 (broad m, 12H). ^{13}C NMR (CDCl_3 , 75 MHz) δ 148.8, 135.0, 125.3, 98.9, 62.4, 56.5, 41.1, 35.6, 29.7. Anal. Calcd. for $\text{C}_{29}\text{H}_{39}\text{ClN}_2\text{O}_2$: C, 72.10; H, 8.14; N, 5.80. Found: C, 67.38; H, 8.70; N, 5.36.

1,3-di-(1-adamantyl)-benzimidazolium chloride (12). From 4.53g of **9** (12.0 mmol, 100 mol %), 200 mL of triethyl orthoformate and 1.20 mL of 12.1 N HCl (14.4 mmol, 120 mol %) after heating for 2 h, 3.87 g of **13** (76 %) were obtained as a white solid, mp 322 °C. ^1H NMR (CD_2Cl_2 , 300 MHz) δ 9.31 (s, 1H), 8.07 (m, 2H), 7.56 (m, 2H); 2.59 (broad m, 12H), 2.36 (broad s, 6H), 1.63 (broad m, 12H). ^{13}C NMR (CD_2Cl_2 , 75 MHz) δ 138.8, 131.8, 126.0, 117.4, 63.4, 41.6, 36.1, 30.3. Anal. Calcd. for $\text{C}_{27}\text{H}_{35}\text{ClN}_2$: C, 76.66; H, 8.34; N, 6.62. Found: C, 71.55; H, 8.92; N, 5.82.

1,3-di-(1-adamantyl)-5,6-difluorobenzimidazolium chloride (13). From 2.62 g of **10** (6.35 mmol, 100 mol %), 106 mL of triethyl orthoformate and 0.64 mL of 12.1 N HCl (7.62 mmol, 120 mol %) after heating for 2 h, **13** (2.23 g, 77 %) were obtained as a white solid, mp 319 °C. ¹H NMR (CD₂Cl₂, 300 MHz) δ 9.55 (s, 1H), 7.95 (t, *J* = 8.5 Hz, 2H), 2.60 (broad s, 6H), 1.84 (broad m, 12H), 1.67 (broad m, 12H). ¹³C NMR (CDCl₃, 75 MHz) δ 148.6 (dd, ¹*J*_{C-F} = 252 Hz; ²*J*_{C-F} = 16.7 Hz), 140.5, 126.7 (t, *J*_{C-F} = 6.0 Hz), 105.2 (dd, ²*J*_{C-F} = 16.7 Hz; ³*J*_{C-F} = 5.4 Hz), 63.6, 40.8, 35.4, 29.7. Anal. Calcd. for C₂₇H₃₃ClF₂N₂: C, 70.65; H, 7.25; N, 6.10. Found: C, 70.36; H, 7.63; N, 5.96.

General Method for Suzuki Reactions

In a glovebox a vial was charged with Pd(OAc)₂ (4.5 mg, 0.02 mmol), Ligand **11**, **12** or **13** (0.04 mmol) and Cs₂CO₃ (312 mg, 1.00 mmol). The vial was removed from the glovebox and dioxane (1 mL) was added *via* syringe. The vial was then heated at 80 °C for 30 min, vigorously stirred, the reaction mixture was cooled to room temperature and aryl choride (0.5 mmol) was added followed by a solution of boronic acid (0.75 mmol) in dioxane (0.5 mL) and undecane (50 µL) *via* syringe. The argon inlet was removed, and the reaction vessel was placed in an oil bath at 80 °C. Stirring was continued for 24 hours after which the reaction mixture was cooled to room temperature. GC/MS analysis was conducted by removing an aliquot (2 µL) of the reaction mixture and diluting with distilled hexane (1 mL). The solution was then filtered though a plug of celite and analyzed. Isolation of product was achieved by filtering the reaction mixture through a plug of celite using dichloromethane (20 mL) dry-loaded and purified by column chromatography (Hexane/EtOAc).

4-Methyl-4'-methoxybiphenyl (Table 1, Entry 3).¹ The procedure afforded 98 mg (98 %) of the title compound. The reported yield is the average of two runs. NMR spectra obtained were identical to that previous reported.

4-Fluoro-4'-methylbiphenyl (Table 2, Entry 2).² The procedure afforded 90 mg (97 %) of the title compound. The reported yield is the average of two runs. NMR spectra obtained were identical to that previous reported.

Spectral data:

¹ Farina, V.; Krishnan, B.; Marshall, D.R.; Roth, G.P. *J. Org. Chem.* **1993**, 58, 5434.

² Moore, L. R.; Shaughnessy, K. H. *Org. Lett.* **2004**, 6, 225-228.