

SUPPORTING INFORMATION

Modified (NHC)Pd(allyl)Cl (NHC = *N*-Heterocyclic Carbene)

Complexes for Room Temperature

Suzuki-Miyaura and Buchwald-Hartwig Reactions

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General Information

- All aryl halides, amines and boronic acids were used as received (Aldrich, Acros). Technical grade isopropanol was used to carry out catalytic reactions (Mallinckrodt Chemicals). Anhydrous 1,2-dimethoxyethane (DME), potassium *tert*-butoxide (Acros) and [Pd(crotyl)Cl]₂ (Strem) were stored under argon in a MBraun glovebox.
- [Pd(prenyl)Cl]₂ and [Pd(cinnamyl)Cl]₂¹ were prepared following a literature procedure² and stored in the glovebox.
- IPr·HCl was synthesized according to literature procedures.³
- Dry THF was distilled over Ph₂CO/Na.
- Flash chromatography was performed on silica gel 60 (230-400 mesh, Silicycle).
- ¹H and ¹³C Nuclear Magnetic Resonance (NMR) spectra were recorded on a Varian-300 or Varian-400 MHz spectrometer at ambient temperature in CDCl₃, C₆D₆ or DMSO-*d*₆ (Cambridge Isotope Laboratories, Inc). Assignments of some ¹H and ¹³C NMR signals rely on COSY and/or HMBC experiments.
- Elemental analyses were performed at Robertson Microlit Laboratories, Inc., Madison, NJ, USA.

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Crystallographic determination: All structures were solved by direct methods and refined using the SHEXTL software package. For the structure of compound **5**, refinement of the Flack coefficient yielded a value of 0.50(2) indicating the crystal was a racemic twin. The final structure was obtained by refinement with a racemic twin model.

Suzuki-Miyaura Cross-Coupling Reactions

Preparation of the Catalyst Solutions

In a glovebox, 0.01 mmol of complex (5.7 mg of **3a** or 6.5 mg of **7**) were added to a vial equipped with a magnetic bar, and closed with a screw cap with a septum. Outside the glovebox, technical grade isopropanol (1.0 mL) was injected into the vial and the mixture stirred at room temperature for 15 min prior to the injection of the required amount.

Suzuki-Miyaura Cross-Coupling of Aryl and Heteroaryl Chlorides or Bromides with Boronic Acids at Room Temperature

General Procedure: In a glovebox, potassium *tert*-butoxide (1.1 mmol, 124 mg), boronic acid (1.05 mmol) and aryl halide (if solid, otherwise *vide infra*) were added in turn to a vial equipped with a magnetic bar, and closed with a screw cap fitted with a septum. Outside the glovebox, the required amount of catalyst solution (catalyst loading 0.05 mol %, 200 μ L, catalyst loading 0.005 mol %, 20 μ L) was injected through the septum, followed by addition of technical grade 2-propanol (1 mL). The mixture was then stirred at room temperature unless otherwise indicated. After 15 min, the aryl halide (1 mmol) was injected (if liquid) and the reaction was monitored by gas chromatography. When the reaction reached completion, or no further conversion was observed by gas chromatography, water was added to the reaction mixture, the organic layer was extracted with *tert*-butylmethyl ether (MTBE), dried over magnesium sulfate and the solvent was evaporated *in vacuo*. When necessary the product was purified by flash chromatography on silica gel. The amount of product is the average of two combined runs.

1-Phenylnaphthalene⁴ (Table 5, entry 1)

The procedure afforded, after flash chromatography on silica gel (hexanes/EtOAc, 90/10), 360 mg (88%) of the title compound.

1-(*p*-Methoxyphenyl)-naphthalene⁵ (Table 5, entry 2): The procedure afforded, after flash chromatography on silica gel (hexanes/EtOAc, 90/10), 399 mg (85%) of the title compound.

2-Methoxybiphenyl⁶ (Table 5, entry 3): The procedure afforded, after flash chromatography on silica gel (hexanes/EtOAc, 90/10), 350 mg (95%) of the title compound.

1-(2,4,6-Trimethylphenyl)-naphthalene⁷ (Table 5, entry 4): The procedure afforded, after flash chromatography on silica gel (hexanes/EtOAc, 90/10), 438 mg (89%) of the title compound.

1-(Biphenyl)-naphthalene⁸ (Table 5, entry 5): The procedure afforded, after flash chromatography on silica gel (hexanes/EtOAc, 90/10), 342 mg (61%) of the title compound.

4-Acetylbiphenyl⁹ (Table 6, entry 1): The general procedure afforded, after flash chromatography on silica gel (hexanes/EtOAc, 90/10), 377 mg (96%) of the title compound.

4-Trifluoromethylbiphenyl¹⁰ (Table 6, entry 2): The general procedure afforded, after flash chromatography on silica gel (hexanes/EtOAc, 90/10), 413 mg (93%) of the title compound.

***p*-Terphenyl**¹¹ (Table 6, entry 3): The general procedure afforded, after flash chromatography on silica gel (hexanes/EtOAc, 90/10), 368 mg (80%) of the title compound.

2-Methoxybiphenyl⁶ (Table 6, entry 4): The procedure afforded, after flash chromatography on silica gel (hexanes/EtOAc, 90/10), 313 mg (85%) of the title compound.

2'-Methyl-2-methoxybiphenyl⁴ (Table 6, entry 5): The procedure afforded, after flash chromatography on silica gel (hexanes/EtOAc, 90/10), 337 mg (85%) of the title compound.

2,6-Dimethyl-2'-methoxybiphenyl¹² (Table 6, entry 6): The procedure afforded, after flash chromatography on silica gel (hexanes/EtOAc, 90/10), 352 mg (83%) of the title compound.

1-(2,6-Dimethylphenyl)-naphthalene¹³ (Table 6, entry 7): The procedure afforded, after flash chromatography on silica gel (hexanes/EtOAc, 90/10), 437 mg (94%) of the title compound.

1,1'-Binaphthyl⁴ (Table 6, entry 8): The procedure afforded, after flash chromatography on silica gel (hexanes/EtOAc, 90/10), 488 mg (96%) of the title compound.

Buchwald-Hartwig Cross-Coupling Reactions

Buchwald-Hartwig Cross-Coupling of Aryl Halides with Primary and Secondary Amines

General procedure: In a glovebox, (SIPr)Pd(cinnamyl)Cl (1 mol %, 6.5 mg), potassium *tert*-butoxide (1.1 mmol, 124 mg) and anhydrous dimethoxyethane (DME) (1 mL) were added in turn to a vial equipped with a magnetic bar, and sealed with a screw cap fitted with a septum. Outside the glovebox, the amine (1.1 mmol) and the aryl halide (1 mmol) were injected in turn through the septum. (If one of the two starting materials was a solid, it was added to the vial inside the glovebox and DME and the second starting material were added outside the glovebox under argon). The reaction mixture was then stirred at room temperature unless otherwise indicated. When the reaction reached completion, or no further conversion could be observed by gas chromatography, water was added to the reaction mixture, the organic layer was extracted with *tert*-butylmethyl ether (MTBE), dried over magnesium sulfate and the solvent was evaporated *in vacuo*. When necessary the product was purified by flash chromatography on silica gel. The reported yields are the average of at least two runs.

***N*-(*o*-Tolyl)morpholine**¹⁴ (Table 9, entry 1).

The general procedure yielded, after flash chromatography on silica gel (pentane/MTBE, 90/10), 170 mg (92%) of the title compound.

***N*-(2,4,6-Trimethylphenyl)morpholine**¹⁵ (Table 9, entry 2).

The general procedure yielded, after flash chromatography on silica gel (pentane/MTBE, 90/10), 193 mg (94%) of the title compound.

***N*-(2-Methoxyphenyl)morpholine**¹⁶ (Table 9, entry 3).

The general procedure yielded, after flash chromatography on silica gel (pentane/MTBE, 90/10), 170 mg (92%) of the title compound.

***N*-(4-Cyanophenyl)piperidine**¹⁷ (Table 9, entry 4).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 80/20), 168 mg (90%) of the title compound.

***N*-(4-Biphenyl)piperidine**¹⁸ (Table 9, entry 5).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 90/10), 197 mg (83%) of the title compound.

¹H NMR (300 MHz, CDCl₃): δ 7.55 (d, *J* = 7.2 Hz, 2H, H^{Ar}), 7.48 (d, *J* = 8.4 Hz, 2H, H^{Ar}), 7.40-7.35 (m, 2H, H^{Ar}), 7.25 (t, *J* = 7.2 Hz, 1H, H^{Ar}), 6.98 (d, *J* = 8.4 Hz, 2H, H^{Ar}), 3.19 (t, *J* = 4.8 Hz, 4H, CH₂—N), 1.74-1.67 (m, 4H, CH₂—CH₂—N), 1.61-1.56 (m, 2H, CH₂(CH₂)₂—N).

¹³C NMR (75 MHz, CDCl₃): δ 151.6 (C, N—C^{Ar}), 141.2 (C, C^{Ar}), 131.8 (C, C^{Ar}), 128.8 (CH, C^{Ar}), 127.8 (CH, C^{Ar}), 126.6 (CH, C^{Ar}), 126.4 (CH, C^{Ar}), 116.6 (CH, C^{Ar}), 50.6 (CH₂, CH₂—N), 26.0 (CH₂, CH₂—CH₂—N), 24.5 (CH₂, CH₂(CH₂)₂—N).

Anal. Calcd. for C₁₇H₁₉N (MW 237.34): C, 86.03; H, 8.07; N, 5.90. Found: C, 86.28; H, 7.78; N, 5.87.

***N*-(4-Methoxyphenyl)piperidine¹⁹** (Table 9, entry 6).

The general procedure yielded, after flash chromatography on silica gel (pentane/MTBE, 95/5), 178 mg (93%) of the title compound.

***N,N*-Dibutyl-*N*-(*p*-tolyl)amine²⁰** (Table 9, entry 7).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 80/20), 215 mg (98%) of the title compound.

***N,N*-Dibutyl-*N*-(*o*-tolyl)amine²⁰** (Table 9, entry 8).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 80/20), 193 mg (88%) of the title compound.

***N,N*-Dibutyl-*N*-(4-methoxyphenyl)amine²¹** (Table 9, entry 9).

The general procedure yielded, after flash chromatography on silica gel (pentane/MTBE, 90/10), 222 mg (94%) of the title compound.

***N*-(2,6-dimethylphenyl)benzylamine¹⁷** (Table 9, entry 10).

The general procedure yielded, after filtration through celite, 209 mg (99%) of crude product that was estimated pure enough (> 98%) by NMR and GC.

***N*-Methyl-*N*-(4-cyanophenyl)aniline²²** (Table 9, entry 11).

The general procedure yielded, after flash chromatography on silica gel (pentane/MTBE, 90/10), 202 mg (97%) of the title compound.

***N*-(2,6-Diisopropylphenyl)-*N*-(*o*-tolyl)amine²³** (Table 9, entry 12).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 80/20), 257 mg (96%) of the title compound.

***N*-(2,6-Diisopropylphenyl)-2',6'-dimethylaniline**²³ (Table 9, entry 13).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 80/20), 245 mg (87%) of the title compound.

¹H NMR (300 MHz, CDCl₃): δ 7.13-7.09 (m, 3H, H^{Ar}), 6.91 (d, *J* = 7.5 Hz, 2H, H^{Ar}), 6.69 (t, *J* = 7.5 Hz, 1H, H^{Ar}), 3.15 (septet, *J* = 6.6 Hz, 2H, CH(CH₃)₂), 1.97 (s, 6H, C^{Ar}—CH₃), 1.11 (d, *J* = 6.6 Hz, 12H, CH(CH₃)₂).

¹³C NMR (75 MHz, CDCl₃): δ 144.3 (C, C^{Ar}), 143.3 (C, C^{Ar}), 139.0 (C, C^{Ar}), 129.7 (CH, C^{Ar}), 125.8 (C, C^{Ar}), 125.0 (CH, C^{Ar}), 123.4 (CH, C^{Ar}), 119.8 (CH, C^{Ar}), 28.2 (CH, CH(CH₃)₂), 23.7 (CH₃, CH(CH₃)₂), 19.5 (CH₃, C^{Ar}—CH₃).

***N*-(*p*-Tolyl)morpholine**²⁴ (Table 10, entry 1).

The general procedure yielded, after filtration through celite, 168 mg (95%) of crude product that was estimated pure enough (> 98%) by NMR and GC.

***N*-(*o*-Tolyl)morpholine**¹⁴ (Table 10, entry 2).

The general procedure yielded, after flash chromatography on silica gel (pentane/MTBE, 90/10), 163 mg (92%) of the title compound.

***N*-(2,6-Dimethylphenyl)morpholine**²⁵ (Table 10, entry 3).

The general procedure yielded, after flash chromatography on silica gel (pentane/MTBE, 90/10), 178 mg (93%) of the title compound.

***N*-(4-Cyanophenyl)piperidine**¹⁷ (Table 10, entry 4).

The general procedure yielded, after flash chromatography on silica gel (pentane/MTBE, 80/20), 179 mg (96%) of the title compound.

***N*-(4-Methoxyphenyl)piperidine**¹⁹ (Table 10, entry 5).

The general procedure yielded, after flash chromatography on silica gel (pentane/MTBE, 95/5), 182 mg (95%) of the title compound.

***N*-(2-Methoxyphenyl)morpholine**¹⁶ (Table 10, entry 6).

The general procedure yielded, after flash chromatography on silica gel (pentane/MTBE, 90/10), 178 mg (92%) of the title compound.

***N,N*-Dibutyl-*N*-(*p*-tolyl)amine**²⁰ (Table 10, entry 7).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 80/20), 191 mg (87%) of the title compound.

***N,N*-Dibutyl-*N*-(*o*-tolyl)amine**²⁰ (Table 10, entry 8).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 80/20), 197 mg (90%) of the title compound.

***N,N*-Dibutyl-*N*-(4-methoxyphenyl)amine**²¹ (Table 10, entry 9).

The general procedure yielded, after flash chromatography on silica gel (pentane/MTBE, 90/10), 224 mg (95%) of the title compound.

***N*-(2,6-dimethylphenyl)benzylamine**¹⁷ (Table 10, entry 10).

The general procedure yielded, after filtration through celite, 190 mg (90%) of crude product that was estimated pure enough (> 98%) by NMR and GC.

***N*-(2,6-Dimethylphenyl)-*N*-(*o*-tolyl)amine**²² (Table 10, entry 11).

The general procedure yielded, after flash chromatography on silica gel (pentane/MTBE, 90/10), 190 mg (90%) of the title compound.

***N*-(2,6-Dimethylphenyl)-2',6'-dimethylaniline**²⁶ (Table 10, entry 12).

The general procedure yielded, after flash chromatography on silica gel (pentane/MTBE, 90/10), 194 mg (86%) of the title compound.

***N*-(2,6-Diisopropylphenyl)-*N*-(*p*-tolyl)amine**²⁴ (Table 10, entry 13).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 80/20), 233 mg (87%) of the title compound.

***N*-(2,6-Diisopropylphenyl)-*N*-(*o*-tolyl)amine**²³ (Table 10, entry 14).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 80/20), 249 mg (93%) of the title compound.

***N*-(2,6-Diisopropylphenyl)-2',6'-dimethylaniline**²³ (Table 10, entry 15).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 80/20), 273 mg (97%) of the title compound.

¹H NMR (300 MHz, CDCl₃): δ 7.13-7.09 (m, 3H, H^{Ar}), 6.91 (d, *J* = 7.5 Hz, 2H, H^{Ar}), 6.69 (t, *J* = 7.5 Hz, 1H, H^{Ar}), 3.15 (septet, *J* = 6.6 Hz, 2H, CH(CH₃)₂), 1.97 (s, 6H, C^{Ar}—CH₃), 1.11 (d, *J* = 6.6 Hz, 12H, CH(CH₃)₂).

¹³C NMR (75 MHz, CDCl₃): δ 144.3 (C, C^{Ar}), 143.3 (C, C^{Ar}), 139.0 (C, C^{Ar}), 129.7 (CH, C^{Ar}), 125.8 (C, C^{Ar}), 125.0 (CH, C^{Ar}), 123.4 (CH, C^{Ar}), 119.8 (CH, C^{Ar}), 28.2 (CH, CH(CH₃)₂), 23.7 (CH₃, CH(CH₃)₂), 19.5 (CH₃, C^{Ar}—CH₃).

***N*-(1-Naphthyl)morpholine**²⁷ (Table 11, entry 1).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 90/10), 194 mg (91%) of the title compound.

***N*-(1-Naphthyl)piperidine**²⁸ (Table 11, entry 2).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 90/10), 184 mg (87%) of the title compound.

***N*-Methyl-*N*-(1-naphthyl)aniline**²⁹ (Table 11, entry 3).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 90/10), 208 mg (89%) of the title compound.

***N,N*-Dibutyl-*N*-(1-naphthyl)amine** (Table 11, entry 4).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 95/5), 243 mg (95%) of the title compound.

¹H NMR (300 MHz, CDCl₃): δ 8.31 (d, *J* = 9.0 Hz, 1H, H^{Ar}), 7.76 (d, *J* = 9.0 Hz, 1H, H^{Ar}), 7.50 (d, *J* = 10.8 Hz, 1H, H^{Ar}), 7.46-7.33 (m, 3H, H^{Ar}), 7.13 (d, *J* = 7.5 Hz, 1H, H^{Ar}), 3.10 (t, *J* = 7.2 Hz, 4H, N—CH₂), 1.51-1.42 (m, 4H, N—CH₂—CH₂), 1.33-1.20 (m, 4H, N—(CH₂)₂—CH₂), 0.83 (t, *J* = 7.5 Hz, 6H, CH₃).

¹³C NMR (75 MHz, CDCl₃): δ 148.9 (C, N—C^{Ar}), 135.2 (C, C^{Ar}), 131.5 (C, C^{Ar}), 128.3 (CH, C^{Ar}), 125.8 (CH, C^{Ar}), 125.7 (CH, C^{Ar}), 125.2 (CH, C^{Ar}), 124.5 (CH, C^{Ar}), 123.4 (CH, C^{Ar}), 118.2 (CH, C^{Ar}), 54.3 (CH₂, N—CH₂), 29.6 (CH₂, N—CH₂—CH₂), 20.8 (CH₂, N—(CH₂)₂—CH₂), 14.2 (CH₃, CH₃).

Anal. Calcd. for C₁₈H₂₅N (MW 255.40): C, 84.65; H, 9.87; N, 5.48. Found: C, 84.63; H, 9.83; N, 5.20.

***N,N*-Dibenzyl-*N*-(1-naphthyl)amine**³⁰ (Table 11, entry 5).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 90/10), 239 mg (74%) of the title compound.

***N*-(2-Naphthyl)piperidine**³¹ (Table 11, entry 6).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 80/20), 192 mg (92%) of the title compound.

¹H NMR (400 MHz, CDCl₃): δ 7.69-7.65 (m, 3H, H^{Ar}), 7.39-7.35 (m, 1H, H^{Ar}), 7.28-7.23 (m, 2H, H^{Ar}), 7.11 (s, 1H, H^{Ar}), 3.23 (t, *J* = 4.8 Hz, 4H, CH₂-N), 1.77-1.71 (m, 4H, CH₂—CH₂—N), 1.62-1.58 (m, 2H, CH₂(CH₂)₂—N).

¹³C NMR (100 MHz, CDCl₃): δ 150.3 (C, N—C^{Ar}), 134.9 (C, C^{Ar}), 128.7 (CH, C^{Ar}), 128.5 (C, C^{Ar}), 127.6 (CH, C^{Ar}), 126.9 (CH, C^{Ar}), 126.3 (CH, C^{Ar}), 123.3 (CH, C^{Ar}), 120.4

(CH, C^{Ar}), 110.5 (CH, C^{Ar}), 51.2 (CH₂, CH₂—N), 26.1 (CH₂, CH₂—CH₂—N), 24.6 (CH₂, CH₂(CH₂)₂—N).

***N*-(9-Anthryl)piperidine**³² (Table 11, entry 7).

The general procedure yielded, after flash chromatography on silica gel (pentane/DCM, 90/10), 248 mg (95%) of the title compound.

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