Nickel-Catalyzed Carbon–Carbon Bond-Forming Reactions of Unactivated Tertiary Alkyl Halides: Suzuki Arylations

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I. General Information

The following reagents were purchased and used as received: NiBr$_2$·diglyme (Aldrich; note: hygroscopic), 4,4′-di-ι-butyl-2,2′-bipyridine (Aldrich), LiO-t-Bu (Aldrich, 97%; Strem, 98%), $i$-BuOH (Aldrich; anhydrous), benzene (Aldrich; anhydrous), 2-bromo-2-methylpropane (Aldrich), and 2-chloro-2-methylpropane (Aldrich). Other tertiary alkyl bromides were prepared from the corresponding alcohols, using LiBr and HBr.$^{1}$

All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen. GC analyses were obtained on an HP 6890 Series GC system with a DB-1 column (length 30 m, internal diameter 0.25 mm).

II. Preparation of Electrophiles

The procedure and the yield have not been optimized.

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\text{1-Bromo-1-pentylcyclobutane.} \quad \text{This compound was prepared according to a published method, starting with 1-pentylcyclobutanol (71.3 mmol).}^2 \quad \text{The product was distilled at 73 °C at 20 Torr. Colorless oil (10.6 g, 73%).}
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{^1}H \text{ NMR (400 MHz, CDCl}_3) \delta 2.67–2.60 (m, 2H), 2.38–2.31 (m, 2H), 2.20–2.09 (m, 1H), 1.87–1.77 (m, 3H), 1.49–1.42 (m, 2H), 1.35–1.25 (m, 4H), 0.87 (t, 3H, J = 8.0 Hz).
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{^{13}}C \text{ NMR (100 MHz, CDCl}_3) \delta 69.0, 44.1, 40.1, 31.6, 25.8, 22.6, 17.1, 14.1.
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\text{FT-IR (film) 2932, 2859, 1466, 1240, 1140, 856, 424, 407 cm}^{-1}.
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\text{MS (EI) } m/z \text{ (M}^+) \text{ calcd for C}_{9}H_{17}Br: 204, 206, \text{ found: 204, 206.}
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III. Preparation of Nucleophiles

The procedures and the yields have not been optimized.

Whereas we routinely purified the aryl-(9-BBN) reagents by distillation, we have determined that the reagents can be used without purification by distillation, at the expense of an ~10% reduction in yield in the cross-coupling reaction.

**General Procedure for the synthesis of non-commercially available arylmagnesium bromides.** Magnesium turnings (417 mg, 17.2 mmol, 1.1 equiv) and a crystal of iodine were added to a flame-dried two-neck round-bottom flask under a positive pressure of nitrogen. The magnesium turnings and iodine were allowed to stir under nitrogen for 2 h. THF (anhydrous; 20 mL) was added, and the mixture was allowed to stir until the iodine color disappeared (this can be assisted by gentle heating with a heat gun). A solution of the aryl bromide (17.2 mmol) in anhydrous THF (4 mL) was then added dropwise over 5 min. The mixture was stirred at 40 °C for 3 h. The reaction was then titrated according to a literature procedure,\(^3\) and the Grignard reagent was used directly in the synthesis of the corresponding aryl-(9-BBN) reagent.

**General Procedure for the synthesis of aryl-(9-BBN) reagents from arylmagnesium bromides.** The aryl-(9-BBN) reagents were prepared by following a literature procedure for the synthesis of phenyl-(9-BBN) via the reaction of phenylmagnesium bromide with B-methoxy-(9-BBN) (Aldrich; 1.0 M in hexanes).\(^4\)

\((m\text{-Tolyl})\text{-}(9\text{-BBN})\) was also prepared according to a literature procedure.\(^5\)

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(1s,5s)-9-(3-Isopropylphenyl)-9-borabicyclo[3.3.1]nonane. The title compound was prepared from 3-(isopropylphenyl)magnesium bromide (25.1 mmol). The product was distilled at 96°C at 100 mTorr. Colorless oil (3.2 g, 13.4 mmol, 53%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.96–7.91 (m, 2H), 7.57–7.50 (m, 2H), 3.10 (sept, 1H, $J =$ 6.7 Hz), 2.44–2.42 (m, 2H), 2.18–2.06 (m, 6H), 2.00–1.91 (m, 4H), 1.43 (d, 6H, $J =$ 8.0 Hz), 1.49–1.36 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.3, 132.8, 132.3, 131.0, 128.1, 34.4, 34.3, 29.3, 24.2, 23.6.

$^{11}$B NMR (128 MHz, CDCl$_3$) δ 80.

(1s,5s)-9-([1,1'-Biphenyl]-3-yl)-9-borabicyclo[3.3.1]nonane. The title compound was prepared from [1,1'-biphenyl]-3-ylmagnesium bromide (21.4 mmol). The product was distilled at 135 °C at 150 mTorr. Colorless oil (1.7 g, 6.3 mmol, 29%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.22–8.21 (m, 1H), 8.00–7.98 (m, 1H), 7.83–7.80 (m, 1H), 7.68–7.50 (m, 3H), 7.49–7.41 (m, 2H), 7.40–7.37 (m, 1H), 2.40–2.37 (m, 2H), 2.11–1.98 (m, 6H), 1.93–1.83 (m, 4H), 1.41–1.33 (m, 2H).

$^{13}$C NMR (400 MHz, CDCl$_3$) δ 141.4, 140.9, 133.5, 133.4, 131.6, 128.8, 128.5, 127.32, 127.26, 34.2, 29.4, 23.5.

$^{11}$B NMR (400 MHz, CDCl$_3$) δ 80.

(3-((1s,5s)-9-Borabicyclo[3.3.1]nonan-9-yl)phenoxy)(tert-butyl)dimethylsilane. The title compound was prepared from 3-((tert-butyl(dimethyl)silyl)oxy)phenyl)magnesium bromide (19.4 mmol). The literature procedure was modified as follows: after (3-((tert-butyl(dimethyl)silyl)oxy)phenyl)magnesium bromide was added to the solution of $B$-methoxy-(9-BBN) in diethyl ether, the resulting mixture was stirred for 48 h before continuing to the next step of the reaction. The product was distilled at 165 °C at 500 mTorr. Colorless oil (2.0 g, 6.1 mmol, 31%).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.62–7.57 (m, 1H), 7.46–7.43 (m, 1H), 7.38–7.34 (m, 1H), 7.08–7.04 (m, 1H), 2.28–2.25 (m, 2H), 2.07–1.96 (m, 6H), 1.88–1.80 (m, 4H), 1.38–1.31 (m, 2H), 1.03 (s, 9H), 0.24 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 155.5, 129.0, 127.5, 125.6, 124.4, 34.2, 29.4, 25.8, 23.5, 18.3, 4.3.

$^{11}$B NMR (128 MHz, CDCl$_3$) δ 81.
(1s,5s)-9-(3-Isopropoxyphenyl)-9-borabicyclo[3.3.1]nonane. The title compound was prepared from 3-(isopropoxyphenyl)magnesium bromide, 23.0 mmol (The literature procedure was modified as follows: Once 3-(isopropoxyphenyl)magnesium bromide was added to the solution of B-methoxy-(9-BBN) in diethyl ether, the resulting mixture was stirred for 48 h before continuing to the next step of the reaction). The product was distilled at 124°C at 510 mTorr. Colorless oil (2.5 g, 8.3 mmol, 36%).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.60–7.58 (m, 1H), 7.55–7.54 (m, 1H), 7.43 (t, 1H, $J = 8.0$ Hz), 7.15–7.12 (m, 1H), 4.67 (sept, 1H, $J = 6.0$ Hz), 2.32–2.30 (m, 2H), 2.15–2.04 (m, 6H), 1.92–1.86 (m, 4H), 1.42 (d, 6H, $J = 4.0$ Hz), 1.38–1.32 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.7, 129.1, 126.8, 121.8, 120.0, 69.7, 34.2, 29.4, 23.5, 22.1.

$^{11}$B NMR (128 MHz, CDCl$_3$) $\delta$ 81.

IV. Suzuki Cross-Couplings of Unactivated Tertiary Alkyl Halides

For a glovebox-free procedure, see below.

**General Procedure for the activation of aryl-(9-BBN) reagents.** In a nitrogen-filled glovebox, the aryl-9-BBN reagent (2.50 mmol, 2.5 equiv) was added to a slurry of LiOt-Bu (192 mg, 2.40 mmol, 2.4 equiv), i-BuOH (178 mg, 222 µL, 2.40 mmol, 2.4 equiv), and benzene (1.0 mL) in a 4-mL vial equipped with a magnetic stir bar. The vial was sealed with a PTFE-lined septum cap, and the mixture was stirred vigorously for 20 min and used immediately in the subsequent cross-coupling reaction.

**General Procedure A (Table 2 and eq 4–6).** In a nitrogen-filled glovebox, NiBr$_2$•diglyme (35.5 mg, 0.10 mmol, 0.10 equiv) and 4,4’-di-t-butyl-2,2’-bipyridine (30.0 mg, 0.11 mmol, 0.11 equiv) were added to a 30-mL vial equipped with a magnetic stir bar. Benzene (anhydrous; 24 mL) was added, the vial was sealed with a PTFE-lined cap, and the resulting mixture was stirred vigorously for 2 h (a light-green slurry formed). The solution of the activated aryl-(9-BBN) reagent was then added to the slurry, and the reaction vial was sealed with a PTFE-lined cap and stirred for 20 min (the reaction mixture turned dark-green). The tertiary alkyl halide (neat; 1.0 mmol, 1.0 equiv) was then added to the slurry via microsyringe. The resulting mixture was capped and stirred vigorously at 40 °C for 24 h (outside of the glovebox). Next, the reaction mixture was filtered through a plug of silica gel, which was rinsed with diethyl ether, and the filtrate was concentrated using rotary evaporation. The product was purified by chromatography.

**General Procedure B (Table 3).** General procedure A was followed, except that the reaction was heated to 60 °C, instead of 40 °C.

**General Procedure C (1-iodoadamantane; eq 3).** General procedure A was followed, except that cyclohexane (anhydrous; 1.0 mL) was used in place of benzene for the activation of the aryl-(9-BBN) and that cyclohexane (5.7 mL) was used in place of benzene for the cross-coupling.
Glovebox-free procedure: Cross-coupling of phenyl-(9-BBN) with 1-bromo-1-methylcyclohexane. A 250-mL two-neck round-bottom flask equipped with a stir bar was connected to the outer joint of a swivel frit, and the outer joint on the other end of the swivel frit was connected to a 250-mL one-neck round-bottom flask, also equipped with a stir bar. The swivel frit was connected to a high-vacuum line, and the entire apparatus was flame-dried under vacuum. The apparatus was allowed to cool under vacuum overnight. In the two-neck flask, phenyl-(9-BBN) was synthesized according to the literature procedure (10 mmol scale). At the end of the reaction, the mixture of phenyl-(9-BBN), magnesium salts, and hexanes was filtered into the 250-mL one-neck flask using the swivel frit under a gentle vacuum, to give a clear solution of phenyl-(9-BBN) in hexanes. The hexanes were removed under high vacuum, and the resulting phenyl-(9-BBN) was dried under vacuum for 1 h.

A 25-mL two-neck pear-shaped Schlenk flask equipped with a stir bar was flame-dried under high vacuum and then allowed to cool to room temperature. Under a positive atmosphere of nitrogen, LiOt-Bu (192 mg, 2.40 mmol, 2.4 equiv) was added, and the flask was capped and then placed under high vacuum for 30 min. Under an atmosphere of nitrogen, i-BuOH (anhydrous; 178 mg, 222 µL, 2.40 mmol, 2.4 equiv), freshly synthesized phenyl-(9-BBN) (density = 1.0 g/mL; 495 mg, 2.5 mmol, 2.5 equiv), and benzene (anhydrous; 1.0 mL) were added to the flask, which was subsequently purged with nitrogen for 5 min. The resulting cloudy mixture was allowed to stir for 20 min.

A 100-mL two-neck round-bottom Schlenk flask equipped with a stir bar was flame-dried under high vacuum and then allowed to cool to room temperature. Under a positive atmosphere of nitrogen, NiBr₂·diglyme (35.5 mg, 0.10 mmol, 0.10 equiv) and 4,4′-di-t-butyl-2,2′-bipyridine (30.0 mg, 0.11 mmol, 0.11 equiv) were added, and the flask was capped and then placed under high vacuum, with stirring, for 30 min. Under an atmosphere of nitrogen, benzene (anhydrous; 24 mL) was added to the flask, which was then purged with nitrogen for 5 min. This nickel/ligand mixture was allowed to stir at room temperature for 2 h (light-green slurry). The activated phenyl-(9-BBN) was then transferred via syringe to the nickel/ligand slurry, and the resulting mixture was allowed to stir for 20 min (dark-green reaction mixture). Then, neat 1-bromo-1-methylcyclohexane (177 mg, 1.0 mmol) was added to the reaction mixture, which was purged with nitrogen for 5 min and then heated to 40 °C for 24 h. Next, pentadecane (internal standard to obtain a calibrated yield by GC; 100 µL) was added to the mixture, and the reaction mixture was filtered through a plug of silica, rinsing with diethyl ether. The filtrate was concentrated using rotary evaporation. GC analysis revealed a yield of 70%. The yield of a corresponding reaction, set up in a glovebox with non-distilled phenyl-(9-BBN), was 76%.

(1-Methylcyclohexyl)benzene [828-45-5] (Table 2, entry 1). The title compound was prepared according to general procedure A, using 1-bromo-1-methylcyclohexane (177 mg, 1.0 mmol) and phenyl-(9-BBN) (495 mg, 2.5 mmol). Purification: Biotage, silica, 100% hexanes. Colorless oil.

First run: 148 mg (85%). Second run: 144 mg (83%).

On a larger scale: 1-bromo-1-methylcyclohexane (5.65 mmol): 807 mg (82%).
**tert-Butylbenzene [98-06-6] (Table 2, entry 2).** The title compound was prepared according to general procedure A, using 2-bromo-2-methylpropane (Aldrich; 112 µL, 1.0 mmol) and phenyl-(9-BBN) (495 mg, 2.5 mmol). Purification: Biotage, silica, 100% hexanes. Colorless oil. First run: 94 mg (70%); yield according to GC: 86%. Second run: 97 mg (72%); yield according to GC: 82%. The product is volatile.

**1-H NMR (300 MHz, CDCl₃) δ 7.28–7.25 (m, 2H), 7.18–7.09 (m, 3H), 2.40–2.31 (m, 2H), 2.17–2.03 (m, 3H), 1.86–1.72 (m, 3H), 1.27–1.12 (m, 4H), 1.06–0.98 (m, 2H), 0.82 (t, 3H, J = 6.0 Hz).

**13C NMR (100 MHz, CDCl₃) δ 150.7, 127.7, 125.7, 124.9, 46.5, 42.7, 32.8, 32.3, 24.2, 22.6, 16.0, 14.1.

FT-IR (film) 3024, 2928, 2856, 1601, 1495, 1466, 764, 700, 563, 419, 410 cm⁻¹.

**MS (El) m/z (M⁺) calcd for C₁₅H₂₀: 202, found: 202.**

**PhMe**

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**1-Pentylcyclobutyl)benzene (Table 2, entry 4).** The title compound was prepared according to general procedure A, using 1-bromo-1-pentylcyclobutane (205 mg, 1.0 mmol) and phenyl-(9-BBN) (495 mg, 2.5 mmol). Purification: Biotage, silica, 100% hexanes. Colorless oil. First run: 105 mg (52%). Second run: 113 mg (54%).

**1-H NMR (300 MHz, CDCl₃) δ 7.28–7.25 (m, 2H), 7.18–7.09 (m, 3H), 2.40–2.31 (m, 2H), 2.17–2.03 (m, 3H), 1.86–1.72 (m, 3H), 1.27–1.12 (m, 4H), 1.06–0.98 (m, 2H), 0.82 (t, 3H, J = 6.0 Hz).

**13C NMR (100 MHz, CDCl₃) δ 150.7, 127.7, 125.7, 124.9, 46.5, 42.7, 32.8, 32.3, 24.2, 22.6, 16.0, 14.1.

FT-IR (film) 3024, 2928, 2856, 1601, 1495, 1466, 764, 700, 563, 419, 410 cm⁻¹.

**MS (El) m/z (M⁺) calcd for C₁₅H₂₀: 202, found: 202.**

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**PhMe**

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**PhMe**
4-Methyl-4-phenyltetrahydro-2H-pyran [67768-01-8] (Table 2, entry 6). The title compound was prepared according to general procedure A, using 4-bromo-4-methyltetrahydro-2H-pyran (179 mg, 1.0 mmol) and phenyl-(9-BBN) (495 mg, 2.5 mmol). Purification: Biotage, reverse-phase silica (C-18), 40% → 100% acetonitrile/water, followed by Biotage, silica, 10% → 80% Et₂O/hexanes. Colorless oil.

First run: 102 mg (58%). Second run: 97 mg (55%).

(2,6-Dimethylhept-5-en-2-yl)benzene (Table 2, entry 7). The title compound was prepared according to general procedure A, using 6-bromo-2,6-dimethylhept-2-ene (205 mg, 1.0 mmol) and phenyl-(9-BBN) (495 mg, 2.5 mmol). Purification: Biotage, silica, 100% hexanes. Colorless oil.

First run: 151 mg (75%). Second run: 155 mg (77%).

¹H NMR (300 MHz, CDCl₃) δ 7.28–7.23 (m, 4H), 7.16–7.14 (m, 1H), 5.04 (t, 1H, J = 8.0 Hz), 1.75–1.69 (m, 2H), 1.65–1.63 (m, 5H), 1.48 (s, 3H), 1.31 (s, 6H).

¹³C NMR (100 MHz, CDCl₃) δ 149.4, 131.1, 128.0, 125.9, 125.4, 124.9, 44.6, 37.7, 28.9, 25.7, 23.6, 17.5.

FT-IR (film) 2965, 2926, 1496, 1446, 1385, 1366, 764, 699 cm⁻¹.

MS (EI) m/z (M⁺) calcd for C₁₅H₂₂: 202, found: 202.

(6-Chloro-2-methylhexan-2-yl)benzene (Table 2, entry 8). The title compound was prepared according to general procedure A, using 5-bromo-1-chloro-5-methylhexane (214 mg, 1.0 mmol) and phenyl-(9-BBN) (495 mg, 2.5 mmol). Purification: Biotage, silica, 100% hexanes. Colorless oil.

First run: 140 mg (67%). Second run: 141 mg (67%).

¹H NMR (300 MHz, CDCl₃) δ 7.34–7.28 (m, 4H), 7.19–7.17 (m, 1H), 3.44 (t, 2H, J = 8.0 Hz), 1.71–1.60 (m, 4H), 1.31 (s, 6H), 1.24–1.18 (m, 2H).

¹³C NMR (100 MHz, CDCl₃) δ 149.2, 128.1, 125.8, 125.5, 44.9, 43.8, 37.7, 33.3, 28.9, 22.2.

FT-IR (film) 2961, 2868, 1497, 1445, 1387, 1367, 1311, 1031, 765, 700, 652, 569 cm⁻¹.

MS (EI) m/z (M⁺) calcd for C₁₃H₁₈Cl: 210, found: 210.
1-Methyl-3-(1-methylcyclohexyl)benzene [14962-11-9] (Table 3, entry 1). The title compound was prepared according to general procedure B, using 1-bromo-1-methylcyclohexane (177 mg, 1.0 mmol) and (1s,5s)-9-[(m-tolyl)-9-borabicyclo[3.3.1]nonane (530 mg, 2.5 mmol). Purification: Biotage, silica, 100% hexanes. Colorless oil.

First run: 112 mg (60%). Second run: 115 mg (61%).

1-Isopropyl-3-(1-methylcyclohexyl)benzene [14962-14-2] (Table 3, entry 2). The title compound was prepared according to general procedure B, using 1-bromo-1-methylcyclohexane (177 mg, 1.0 mmol) and (1s,5s)-9-[(3-isopropylphenyl)-9-borabicyclo[3.3.1]nonane (601 mg, 2.5 mmol). Purification: Biotage, silica, 100% hexanes. Colorless oil.

First run: 134 mg (62%). Second run: 127 mg (59%).

3-(1-Methylcyclohexyl)-1,1'-biphenyl (Table 3, entry 3). The title compound was prepared according to general procedure B, using 1-bromo-1-methylcyclohexane (177 mg, 1.0 mmol) and (1s,5s)-9-[(1,1'-biphenyl)-3-yl)-9-borabicyclo[3.3.1]nonane (686 mg, 2.5 mmol). Purification: Biotage, reverse-phase silica (C-18), 40% → 100% acetonitrile/water. Colorless oil.

First run: 183 mg (73%). Second run: 187 mg (75%).

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.64–7.60 (m, 3H), 7.49–7.33 (m, 6H), 2.13–2.05 (m, 2H), 1.70–1.44 (m, 8H), 1.26 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.5, 142.0, 141.1, 128.7, 128.6, 127.3, 127.1, 125.0, 124.9, 124.2, 38.1, 38.0, 30.6, 26.4, 22.7.

FT-IR (film) 3029, 2929, 2856, 1598, 1481, 1466, 1449, 1410, 1075, 894, 798, 756 cm$^{-1}$.

MS (EI) m/z (M$^+$) calcd for C$_{19}$H$_{22}$: 250, found: 250.
**tert-Butyldimethyl(3-(1-methylcyclohexyl)phenoxy)silane (Table 3, entry 4).** The title compound was prepared according to general procedure B, using 1-bromo-1-methylcyclohexane (177 mg, 1.0 mmol) and (3-((1S,5S)-9-borabicyclo[3.3.1]nonan-9-yl)phenoxy)(tert-butyl)dimethylsilane (821 mg, 2.5 mmol). Purification: Biotage, reverse-phase silica (C-18), 40% → 100% acetonitrile/water. Colorless oil.

First run: 164 mg (54%). Second run: 161 mg (53%).

$^1$H NMR (300 MHz, CDCl$_3$) δ 6.96 (t, 1H, $J = 12.0$ Hz), 6.78–6.75 (m, 1H), 6.65 (t, 1H, $J = 3.0$ Hz), 6.47–6.43 (m, 1H), 1.80–1.72 (m, 2H), 1.37–1.22 (m, 8H), 0.96 (s, 3H), 0.79 (s, 9H), 0.00 (s, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 170.0, 155.5, 128.9, 118.8, 118.0, 116.8, 37.9, 37.9, 30.5, 26.4, 25.8, 22.7, 18.3, 4.4.

FT-IR (film) 2929, 2858, 1600, 1581, 1487, 1472, 1361, 1302, 1251, 1190, 1002, 981, 953, 874, 835, 781 cm$^{-1}$.

MS (EI) $m/z$ (M$^+$) calcd for C$_{19}$H$_{32}$O$_{1}$Si: 304, found: 304.

**1-Isopropoxy-3-(1-methylcyclohexyl)benzene (Table 3, entry 5).** The title compound was prepared according to general procedure B, using 1-bromo-1-methylcyclohexane (177 mg, 1.0 mmol) and (1S,5S)-9-(3-isopropoxyphenyl)-9-borabicyclo[3.3.1]nonane (641 mg, 2.5 mmol). Purification: Biotage, reverse-phase silica (C-18), 40% → 100% acetonitrile/water. Colorless oil.

First run: 133 mg (57%). Second run: 130 mg (56%).

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.25–7.20 (m, 1H), 6.98–6.91 (m, 2H), 6.73–6.69 (m, 1H), 4.60–4.51 (m, 1H), 2.02–1.95 (m, 2H), 1.59–1.42 (m, 8H), 1.35 (d, 6H, $J = 9.0$ Hz), 1.18 (s, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.8, 152.0, 128.9, 118.2, 114.6, 111.7, 69.6, 38.0, 37.9, 30.5, 26.4, 22.7, 22.2.

FT-IR (film) 2975, 2930, 2857, 1605, 1579, 1487, 1467, 1452, 1383, 1372, 1289, 1239, 1188, 1122, 1000, 985, 961, 873, 773 cm$^{-1}$.

MS (EI) $m/z$ (M$^+$) calcd for C$_{16}$H$_{24}$O: 232, found: 232.

**Ph (3r,5r,7r)-1-Phenyladamantane [780-68-7] (eq 3).** The title compound was prepared according to general procedure C, using 1-iodoadamantane (262 mg, 1.0 mmol) and phenyl-(9-BBN) (495 mg, 2.5 mmol). Purification: Biotage, silica, 100% hexanes. White solid.

First run: 157 mg (74%). Second run: 155 mg (73%).
(3r,5r,7r)-1-(3-Isopropylphenyl)adamantane [183967-44-4] (eq 3). The title compound was prepared according to general procedure C, using 1-iodoadamantane (262 mg, 1.0 mmol) and (1s,5s)-9-(3-isopropylphenyl)-9-borabicyclo[3.3.1]nonane (601 mg, 2.5 mmol). Purification: Biotage, silica, 100% hexanes. Colorless oil.
First run: 158 mg (62%). Second run: 150 mg (59%).

Diphenylmethane [101-81-5] (eq 5). This compound was prepared according to general procedure A (except that toluene was used in place of benzene), using 1-bromo-1-methylcyclohexane (177 mg, 1.0 mmol) and phenyl-(9-BBN) (495 mg, 2.5 mmol). Purification: Biotage, reverse-phase silica (C-18), 40% → 100% ACN/water, followed by Biotage, silica, 100% hexanes. Colorless oil.
First run: 48 mg (29%). Second run: 53 mg (32%).

1H NMR (300 MHz, CDCl3) δ 7.34–7.19 (m, 10H), 4.02 (s, 2H).

13C NMR (100 MHz, CDCl3) δ 141.1, 128.9, 128.5, 126.1, 42.0.

The direct cross-coupling product, (1-methylcyclohexyl)benzene, was also isolated using the aforementioned purification procedure.
First run: 66 mg (38%). Second run: 72 mg (41%).

(1-Methylcyclohexane-1,4-diyl)dibenzene (eq 6). The title compound was prepared according to general procedure A, using ((1s,4s)-4-bromo-4-methylcyclohexyl)benzene (cis, dr >20:1; 253 mg, 1.0 mmol) and phenyl-(9-BBN) (495 mg, 2.5 mmol). Purification: Biotage, reverse-phase silica (C-18), 40% → 100% acetonitrile/water. White solid. Isolated product is a mixture of diastereomers (1.2:1).
First run: 181 mg (72%). Second run: 185 mg (74%).

1H NMR (300 MHz, CDCl3); diastereomer 1: δ 7.38–6.93 (m, 10H), 6.78–6.75 (m, 9H), 1.27 (s, 3H).

1H NMR (300 MHz, CDCl3); diastereomer 2: δ 7.38–6.93 (m, 10H), 6.78–6.75 (m, 9H), 1.09 (s, 3H).

13C NMR (100 MHz, CDCl3) δ 152.4, 147.44, 147.39, 147.2, 128.6, 128.5, 128.3, 127.0, 126.9, 126.5, 126.1, 125.9, 125.7, 125.4, 125.2, 44.7, 44.2, 38.3, 38.09, 38.05, 36.6, 35.5, 30.6, 30.2, 24.5.

FT-IR (film) 3085, 3058, 3025, 2928, 2857, 1943, 1869, 1800, 1602, 1581, 1494, 1450, 1376, 1098, 1077, 1032, 1023, 964, 762 cm⁻¹.

MS (EI) m/z (M⁺) calcd for C19H22: 250, found: 250.
V. Examples of Recalcitrant Aryl-(9-BBN) Coupling Partners

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Table 2, entry 1
$^1$H NMR (300 MHz, CDCl$_3$)
Table 2, entry 2
$^{1}H$ NMR (300 MHz, CDCl$_3$)
Table 2, entry 3
$^1$H NMR (300 MHz, CDCl$_3$)
Table 2, entry 4

$^1$H NMR (300 MHz, CDCl$_3$)
Table 2, entry 5
$^1$H NMR (300 MHz, CDCl$_3$)
Table 2, entry 6
$^1$H NMR (300 MHz, CDCl$_3$)
Table 2, entry 7
$^1$H NMR (300 MHz, CDCl$_3$)
Table 2, entry 8
$^1$H NMR (300 MHz, CDCl$_3$)
Table 3, entry 1
$^1$H NMR (300 MHz, CDCl$_3$)
Table 3, entry 2
$^1$H NMR (300 MHz, CDCl$_3$)
Table 3, entry 3
$^1$H NMR (300 MHz, CDCl$_3$)
Table 3, entry 4
$^1$H NMR (300 MHz, CDCl$_3$)
Table 3, entry 5
$^1$H NMR (300 MHz, CDCl$_3$)
eq 3

$^1$H NMR (300 MHz, CDCl$_3$)
eq 3

$^{1}H$ NMR (300 MHz, CDCl$_3$)
$\text{eq 5}$

$^1\text{H NMR (300 MHz, CDCl}_3\text{)}$
eq 6

$^1$H NMR (300 MHz, CDCl$_3$)