Catalytic Enantioselective Cyclization/Cross-Coupling with Alkyl Electrophiles

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I. General

The following reagents were purchased and used as received: NiBr₂•glyme (Aldrich; note: hygroscopic), ligands (R,R)-1 and (S,S)-1 (Aldrich), KOt-Bu (Strem), i-BuOH (anhydrous; Aldrich), i-Pr₂O (anhydrous; Aldrich), and THF (anhydrous; Aldrich). 9-BBN dimer (Aldrich) was purified by recrystallization in DME (anhydrous; Aldrich) prior to use.

All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen, unless otherwise noted.

HPLC analyses were carried out on an Agilent 1100 Series system, using Daicel CHIRALCEL® columns or Daicel CHIRALPAK® columns (internal diameter 4.6 mm, column length 250 mm, particle size 5 µm).

II. Preparation of Nucleophiles

General procedure for the preparation of B-aryl-(9-BBN) reagents. These reagents were prepared according to a literature procedure,¹ with minor modifications. In a glovebox, a 20 mL vial equipped with a stir bar was charged with magnesium turnings (243 mg, 10.0 mmol), a small piece of iodine (5-10 mg), and THF (4.0 mL). The aryl bromide (7.60 mmol) and THF (2.0 mL) were added to a 4 mL vial. Each vial was sealed with a teflon-lined septum cap and removed from the glovebox. A portion (~0.5 mL) of the solution of aryl bromide was added by

¹ Fang, G. Y.; Wallner, O. A.; Di Blasio, N.; Ginesta, X.; Harvey, J. N.; Aggarwal, V. K. J. Am. Chem. Soc. 2007, 129, 14632–14639.
syringe to the 20 mL vial with vigorous stirring. After the yellow color of iodine had faded (within 1 min), the rest of the aryl bromide solution was added over 5 min. The vial containing the solution of aryl bromide was rinsed with THF (0.5 mL x 2), and the washings were added to the reaction vial. The reaction mixture was stirred vigorously at 50 °C for 2 h. Next, the reaction mixture was filtered in a glovebox through an acrodisc with the aid of THF (1.0 mL). A portion of the resulting solution (~0.25 mL) was immediately titrated using an accurately prepared solution of 10/90 i-BuOH/toluene as the titrant with 1,10-phenanthroline as the indicator (final concentration of the Grignard solution: 0.90 to 1.10 M; the average of two titrations).

In a glovebox, a 40 mL vial equipped with a stir bar was charged with 9-BBN dimer (854 mg, 3.50 mmol) and THF (5.0 mL). Methanol (0.284 mL, 7.00 mmol) was added dropwise under gentle stirring (Caution: Gas evolution). The mixture was stirred at r.t. until gas evolution stopped (~15 min; covered with a cap without tightening), during which time it became a homogenous colorless solution. The vial was sealed with a teflon-lined septum cap and taken out of the glovebox. The titrated Grignard solution from the previous step (7.00 mmol of ArMgBr) was then added via syringe at −78 °C over 1 min. The reaction mixture was warmed to r.t., and stirred for 30 min.

The reaction solution was concentrated under high vacuum (attached through a liquid nitrogen-cooled trap) until all of the volatiles had been removed. The resulting sticky gel was mixed with pentane (12 mL) and allowed to stand at r.t. for 12 h, during which time the gel solidified. In a glovebox, the solid was broken up with a spatula. The spatula was rinsed with pentane (~2 mL), and the washings were added to the reaction vial. The vial was then sealed with a teflon-lined septum cap, and vigorously stirred at r.t. for 3 h. The resulting white suspension was filtered through a pad of oven-dried celite in the glovebox with the aid of pentane (~2 mL). The colorless filtrate was concentrated under high vacuum. The extraction/filtration/evaporation sequence was repeated once (except it was not allowed to stand for 12 h). The resulting B-aryl-(9-BBN) reagent (neat) could be stored in the glovebox at −10 °C for at least 5 weeks without noticeable decomposition.

\[ \text{9-(2-Allyloxyphenyl)-9-borabicyclo[3.3.1]nonane. Prepared from 1-allyloxy-2-bromobenzene. White solid.} \]

\[ ^{1}H \text{ NMR (CD}_{6} \text{, 400 MHz)} \delta 7.68 (dd, J = 1.8, 7.3 Hz, 1H), 7.25 (ddd, J = 1.8, 7.3, 8.3 Hz, 1H), 6.97 (ddd, J = 0.8, 7.3, 7.3 Hz, 1H), 6.58 (dd, J = 0.8, 8.3 Hz, 1H), 5.81 (tdd, J = 5.3, 10.5, 17.3 Hz, 1H), 5.18 (d, J = 17.3 Hz, 1H), 5.02 (d, J = 10.5 Hz, 1H), 4.12 (d, J = 5.3 Hz, 2H), 2.44 (br s, 2H), 1.96–2.12 (m, 10H), 1.36–1.43 (m, 2H); \]

\[ ^{13}C \text{ NMR (CD}_{6} \text{, 125 MHz)} \delta 164.0, 135.6, 134.1, 133.5, 128.7, 121.2, 117.4, 111.8, 69.2, 34.7, 33.9, 24.1; \]

\[ ^{11}B \text{ NMR (CD}_{6} \text{, 128 MHz)} \delta 82. \]
9-(2-Allyloxy-4-methoxyphenyl)-9-borabicyclo[3.3.1]nonane. Prepared from 2-allyloxy-1-bromo-4-methoxybenzene. Colorless white oil.

$^1$H NMR (C$_6$D$_6$, 500 MHz) $\delta$ 7.74 (d, $J = 8.2$ Hz, 1H), 6.45 (dd, $J = 2.2$, 8.2 Hz, 1H), 6.38 (d, $J = 2.2$ Hz, 1H), 5.81 (tdd, $J = 5.2$, 10.6, 17.3 Hz, 1H), 5.19 (d, $J = 17.3$ Hz, 1H), 5.02 (d, $J = 10.6$ Hz, 1H), 4.13 (d, $J = 5.2$ Hz, 2H), 3.40 (s, 3H), 2.50 (br s, 2H), 1.98–2.10 (m, 10H), 1.38–1.45 (m, 2H);

$^{13}$C NMR (C$_6$D$_6$, 125 MHz) $\delta$ 166.4, 165.2, 138.1, 133.6, 123.4, 117.0, 104.8, 99.3, 68.8, 54.8, 34.4, 30.9, 23.9;

$^{11}$B NMR (C$_6$D$_6$, 128 MHz) $\delta$ 80.

9-[2-(3-Buten-1-yl)phenyl]-9-borabicyclo[3.3.1]nonane. Prepared from 4-(2-bromophenyl)-1-butene. Colorless oil.

$^1$H NMR (C$_6$D$_6$, 500 MHz) $\delta$ 7.53 (dd, $J = 1.3$, 7.4 Hz, 1H), 7.24 (ddd, $J = 1.6$, 7.4, 7.4 Hz, 1H), 7.18 (ddd, $J = 1.3$, 7.4, 7.4 Hz, 1H), 7.11 (dd, $J = 1.6$, 7.4 Hz, 1H), 5.79 (tdd, $J = 6.5$, 10.2, 17.0 Hz, 1H), 5.02 (d, $J = 17.0$ Hz, 1H), 4.95 (d, $J = 10.2$ Hz, 1H), 2.80–2.87 (m, 2H), 2.23–2.32 (m, 2H), 2.06 (br s, 2H), 1.88–2.04 (m, 10H), 1.35–1.43 (m, 2H);

$^{13}$C NMR (C$_6$D$_6$, 125 MHz) $\delta$ 146.4, 138.6, 132.6, 130.7, 129.5, 128.7, 126.1, 115.3, 38.6, 36.3, 34.9, 33.3, 23.9;

$^{11}$B NMR (C$_6$D$_6$, 128 MHz) $\delta$ 85.

9-[2-(3-Buten-1-yl)-4-fluorophenyl]-9-borabicyclo[3.3.1]nonane. Prepared from 4-(2-bromo-5-fluorophenyl)-1-butene. Colorless oil.

$^1$H NMR (C$_6$D$_6$, 400 MHz) $\delta$ 7.37 (dd, $J = 6.7$, 8.1 Hz, 1H), 6.80–6.89 (m, 2H), 5.70 (tdd, $J = 6.5$, 10.2, 16.9 Hz, 1H), 4.89–4.98 (m, 2H), 2.67–2.77 (m, 2H), 2.08–2.18 (m, 2H), 1.80–2.15 (m, 12H), 1.30–1.40 (m, 2H);

$^{13}$C NMR (C$_6$D$_6$, 100 MHz) $\delta$ 165.0 (d, $J = 248$ Hz), 149.9 (d, $J = 7.6$ Hz), 137.7, 135.0 (d, $J = 8.3$ Hz), 116.1 (d, $J = 19.7$ Hz), 115.19, 115.17, 112.6 (d, $J = 19.8$ Hz), 37.6, 35.4, 34.5, 32.7, 23.5;

$^{11}$B NMR (C$_6$D$_6$, 128 MHz) $\delta$ 84;

$^{19}$F NMR (C$_6$D$_6$, 376 MHz) $\delta$ –110.9.

S–3
9-[2-(3-Methyl-3-buten-1-yl)phenyl]-9-borabicyclo[3.3.1]nonane. Prepared from 4-(2-bromophenyl)-2-methyl-1-butene. Colorless oil.

\(^1\)H NMR (CD\(_6\), 400 MHz) \(\delta\) 7.54 (dd, \(J = 1.6, 7.4\) Hz, 1H), 7.25 (ddd, \(J = 1.6, 7.4, 7.4\) Hz, 1H), 7.19 (ddd, \(J = 1.3, 7.4, 7.4\) Hz, 1H), 7.13 (ddd, \(J = 1.3, 7.4\) Hz, 1H), 4.81 (d, \(J = 8.1\) Hz, 2H), 2.87–2.95 (m, 2H), 2.18–2.27 (m, 2H), 2.08 (br s, 2H), 1.92–2.03 (m, 10H), 1.65 (s, 3H), 1.35–1.42 (m, 2H); \(^13\)C NMR (CD\(_6\), 125 MHz) \(\delta\) 146.4, 145.5, 132.2, 130.4, 129.1, 128.3, 125.7, 110.3, 42.2, 34.9, 34.5, 32.7, 23.6, 22.8;

\(^11\)B NMR (CD\(_6\), 128 MHz) \(\delta\) 85.

III. Asymmetric Cyclization/Cross-Coupling Reactions

General procedure for asymmetric cyclization/cross-coupling reactions. In a glovebox, anhydrous THF (2.0 mL) and \(i\)-Pr\(_2\)O (2.0 mL) were thoroughly mixed in a 4 mL vial (hereafter referred to as the “mixed solvent”). The B-aryl-\((9\text{-}BBN)\) reagent (neat, 1.47 mmol) was added with the aid of 1 mL of the mixed solvent to a 4 mL vial that contained KO\(_t\)-Bu (132 mg, 1.18 mmol) and \(i\)-BuOH (0.140 mL, 1.52 mmol). The total volume of the mixture was adjusted to 1.75 mL by adding the mixed solvent. The vial was sealed with a teflon-lined septum cap, and the reaction mixture was stirred vigorously for 50 min, affording a solution of the activated organoboron reagent.

In a glovebox, NiBr\(_2\)-glyme (21.6 mg, 0.070 mmol), \((R,R)-1\) (20.2 mg, 0.084 mmol), and the mixed solvent (1.25 mL) were added in turn to a 20 mL vial equipped with a stir bar. The vial was sealed with a teflon-lined septum cap, and the reaction mixture was stirred vigorously for 30 min (a bright green slurry forms). The electrophile (0.70 mmol, neat) was then added in one portion to the slurry at r.t. The vial was sealed with a teflon-lined septum cap, the seal was wrapped with electrical tape, and the vial was taken out of the glovebox and kept at the designated reaction temperature hereafter. Next, the solution of the organoboron reagent was transferred via syringe to the vigorously stirred reaction slurry in a continuous flow over 10 seconds. The vial that had contained the solution of the organoboron reagent was rinsed with the mixed solvent (0.50 mL), and the rinse was added to the reaction slurry. After addition of the organoboron reagent, the reaction mixture turned from bright green to orange. The puncture in the septum cap was covered with vacuum grease, and the mixture was stirred vigorously at the designated reaction temperature. The reaction time was 36 h, unless otherwise noted. Next, the reaction mixture was passed through a short plug of silica gel, eluting with Et\(_3\)O. The resulting solution was concentrated under vacuum and purified by chromatography.

A second run was conducted with \((S,S)-1\).
3-(4-Phenylbutyl)-2,3-dihydrobenzofuran (Table 2, entry 1). The title compound was prepared according to the general procedure, using 1-bromo-3-phenylpropane (0.106 mL, 0.70 mmol) and 9-(2-allyloxyphenyl)-9-borabicyclo[3.3.1]nonane (374 mg, 1.47 mmol). The reactions were conducted at 25 °C for 36 h. Purification: flash chromatography (0–2% EtO/hexanes). Colorless oil.

First run: 134 mg (76%, 96% ee). Second run: 138 mg (78%, 94% ee).

This compound was also prepared on a 6.3 mmol scale, using 1-bromo-3-phenylpropane (0.954 mL, 6.30 mmol) and 9-(2-allyloxyphenyl)-9-borabicyclo[3.3.1]nonane (3.37 g, 13.2 mmol). The same reaction conditions (with (R,R)-1) and purification method were employed: 1.07 g (67%, 96% ee). Colorless oil.

The ee was determined by HPLC analysis (CHIRALCEL OJ-H, 2% i-PrOH in hexanes; 1.0 mL/min; retention times (when (R,R)-1 is employed): 17.6 min (major), 19.7 min (minor).

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.27 (dd, $J = 7.5$, 7.5 Hz, 2H), 7.09–7.19 (m, 5H), 6.84 (dd, $J = 7.5$, 7.5 Hz, 1H), 6.77 (d, $J = 7.5$ Hz, 1H), 4.59 (dd, $J = 8.5$, 8.5 Hz, 1H), 4.17 (dd, $J = 6.1$, 8.5 Hz, 1H), 3.39 (dddd, $J = 6.1$, 6.1, 8.5, 8.5 Hz, 1H), 2.56–2.66 (m, 2H), 1.75–1.83 (m, 1H), 1.54–1.68 (m, 3H), 1.33–1.50 (m, 2H);

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 160.0, 142.4, 131.0, 128.33, 128.27, 128.0, 125.7, 124.3, 120.2, 110.4, 76.8, 41.8, 35.7, 34.7, 31.4, 26.8;

IR (film) 3024, 2929, 2854, 1596, 1478, 1455, 1226, 961, 747 cm$^{-1}$;

MS (El): calcd for C$_{18}$H$_{24}$O (M) 252, found 252;

$[\alpha]^{25}_D = +8.8^\circ$ (c = 0.27, CHCl$_3$, obtained with (S,S)-1).

3-(2-Trimethylsilylethyl)-2,3-dihydrobenzofuran (Table 2, entry 2). The title compound was prepared according to the general procedure, using allyl(bromomethyl)dimethylsilane (0.100 mL, 0.70 mmol) and 9-(2-allyloxyphenyl)-9-borabicyclo[3.3.1]nonane (374 mg, 1.47 mmol). The reactions were conducted at 25 °C for 36 h. Purification: flash chromatography (100% hexanes). Colorless oil.

First run: 67 mg (44%, 97% ee). Second run: 77 mg (50%, 95% ee).

The ee was determined by HPLC analysis (CHIRALCEL OJ-H, 100% hexanes; 0.6 mL/min; retention times (when (R,R)-1 is employed): 10.1 min (major), 11.2 min (minor).

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.16 (d, $J = 7.4$ Hz, 1H), 7.10 (dd, $J = 7.7$, 7.7 Hz, 1H), 6.84 (dd, $J = 7.4$, 7.4 Hz, 1H), 6.77 (d, $J = 7.7$ Hz, 1H), 4.61 (dd, $J = 8.8$, 8.8 Hz, 1H), 4.22 (dd, $J = 6.2$, 8.8 Hz, 1H), 3.36–3.40 (m, 1H), 1.69–1.75 (m, 1H), 1.49–1.57 (m, 1H), 0.56 (dt, 1H, $J = 4.7$, 13.6 Hz), 0.46 (dt, 1H, $J = 4.2$, 13.7 Hz), −0.03 (s, 9H);

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 160.0, 130.9, 128.1, 124.3, 120.2, 109.4, 76.5, 44.7, 29.1, 13.7, −1.8;
IR (film) 2952, 2912, 1596, 1482, 1248, 1229, 863, 834, 748 cm⁻¹;  
MS (EI): calcd for C₁₃H₂₀O₃ (M) 220, found 220;  
[α]D²₅ = −5.2° (c = 0.11, CHCl₃, obtained with (R,R)-1).

3-[3-(1,3-Dioxan-2-yl)propyl]-2,3-dihydrobenzofuran (Table 2, entry 3).  The title compound was prepared according to the general procedure, using 2-(2-bromoethyl)-1,3-dioxane (0.095 mL, 0.70 mmol) and 9-(2-allyloxyphenyl)-9-borabicyclo[3.3.1]nonane (374 mg, 1.47 mmol). The reactions were conducted at 25 °C for 36 h. Purification: flash chromatography (0→7% EtO/hexanes), followed by preparative TLC (5% EtO/hexanes). Colorless oil.

First run: 115 mg (66%, 96% ee).  Second run: 123 mg (71%, 97% ee).

The ee was determined by HPLC analysis (CHIRALCEL OJ-H, 2% i-PrOH in hexanes; 1.0 mL/min; retention times (when (R,R)-1 is employed): 23.8 min (major), 27.7 min (minor).

¹H NMR (CDCl₃, 500 MHz) δ 7.15 (d, J = 7.4 Hz, 1H), 7.09 (dd, J = 7.7, 7.7 Hz, 1H), 6.83 (dd, J = 7.4, 7.4 Hz, 1H), 6.76 (d, J = 8.0 Hz, 1H), 4.61 (dd, J = 8.8, 8.8 Hz, 1H), 4.51 (t, J = 5.1Hz, 1H), 4.18 (dd, J = 6.6, 8.7 Hz, 1H), 4.08 (ddd, J = 1.2, 4.9, 12.0 Hz, 2H), 3.74 (dd, J = 12.0 Hz, 2H), 3.36–3.44 (m, 1H), 2.00–2.11 (m, 1H), 1.74–1.81 (m, 1H), 1.40–1.65 (m, 5H), 1.30–1.35 (m, 1H);

¹³C NMR (CDCl₃, 100 MHz) δ 159.8, 130.9, 128.0, 124.3, 120.3, 109.4, 102.0, 76.8, 66.9, 41.9, 35.2, 34.7, 25.8, 21.6;

IR (film) 2952, 2851, 1596, 1482, 1459, 1230, 1141, 1089, 997, 751 cm⁻¹;  
MS (ESI+): calcd for C₁₃H₂₀O₃ (M+H) 249, found 249;  
[α]D²₅ = +4.5° (c = 0.34, CHCl₃, obtained with (R,R)-1).

2-[5-(2,3-Dihydrobenzofuran-3-yl)pentyl]isoindoline-1,3-dione (Table 2, entry 4).  The title compound was prepared according to the general procedure, using N-(4-bromobutyl) phthalimide (197 mg, 0.70 mmol) and 9-(2-allyloxyphenyl)-9-borabicyclo[3.3.1]nonane (374 mg, 1.47 mmol). The reactions were conducted at 25 °C for 36 h. Purification: flash chromatography (5→15% EtO/hexanes).  White solid.

First run: 151 mg (64%, 98% ee).  Second run: 163 mg (69%, 96% ee).

The ee was determined by HPLC analysis (CHIRALCEL OJ-H, 7% i-PrOH in hexanes; 1.0 mL/min; retention times (when (R,R)-1 is employed): 45.4 min (major), 57.1 min (minor).

¹H NMR (CDCl₃, 500 MHz) δ 7.80–7.84 (m, 2H), 7.67–7.71 (m, 2H), 7.12 (d, J = 7.4 Hz, 1H), 7.08 (dd, J = 7.7, 7.7 Hz, 1H), 6.82 (dd, J = 7.4, 7.4 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H), 4.59 (dd, J = 8.8,
8.8 Hz, 1H), 4.16 (dd, J = 6.5, 8.8 Hz, 1H), 3.67 (t, J = 7.5 Hz, 2H), 3.34–3.42 (m, 1H), 1.71–1.78 (m, 1H), 1.64–1.71 (m, 2H), 1.49–1.58 (m, 1H), 1.32–1.46 (m, 4H);

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 168.4, 159.8, 139.3, 132.1, 130.9, 128.0, 124.2, 123.1, 120.3, 109.4, 76.8, 41.8, 37.8, 34.7, 28.4, 26.8, 26.7;

IR (film) 2932, 2856, 1771, 1712, 1596, 1482, 1396, 1370, 1229, 1057, 752, 719 cm$^{-1}$;

MS (ESI+): calcd for C$_{28}$H$_{32}$NO$_3$ (M+H) 336, found 336;

$[\alpha]^{\text{D}}_2$ = +9.6° (c = 0.35, CHCl$_3$, obtained with (S,S)-1).

6-Methoxy-3-(4-phenylbutyl)-2,3-dihydrobenzofuran (Table 2, entry 5).  The title compound was prepared according to the general procedure, except that a different catalyst loading was used: NiBr$_2$-glyme (32.4 mg, 0.105 mmol, 15%) and 1 (28.6 mg, 0.119 mmol, 17%). The reactions were conducted with 1-bromo-3-phenylpropane (0.106 mL, 0.70 mmol) and 9-(2-allyloxy-4-methoxyphenyl)-9-borabicyclo[3.3.1]nonane (417 mg, 1.47 mmol) at 25 °C for 36 h. Purification: flash chromatography (0 → 1% Et$_2$O/hexanes). Colorless oil.

First run: 89 mg (45%, 93% ee).  Second run: 86 mg (44%, 94% ee).

The ee was determined by HPLC analysis (CHIRALCEL OJ-H, 5% i-PrOH in hexanes; 1.0 mL/min; retention times (when (R,R)-1 is employed): 28.0 min (minor), 37.1 min (major).

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.24–7.28 (m, 2H), 7.14–7.18 (m, 3H), 6.99 (d, J = 8.0 Hz, 1H), 6.38 (dd, J = 2.0, 8.0 Hz, 1H), 6.37 (d, J = 2.0 Hz, 1H), 4.60 (dd, J = 8.8, 8.8 Hz, 1H), 4.18 (dd, J = 6.3, 8.8 Hz, 1H), 3.75 (s, 3H), 3.28–3.36 (m, 1H), 2.61 (t, J = 7.7 Hz, 2H), 1.70–1.77 (m, 1H), 1.60–1.68 (m, 2H), 1.50–1.58 (m, 1H), 1.31–1.48 (m, 2H);

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 161.2, 160.4, 142.4, 128.4, 128.3, 125.7, 124.3, 123.1, 105.8, 96.2, 77.8, 55.5, 41.2, 35.8, 35.0, 31.5, 26.8;

IR (film) 2928, 2854, 1615, 1596, 1495, 1446, 1278, 1192, 1143, 1111, 1028, 975 cm$^{-1}$;

MS (ESI+): calcd for C$_{28}$H$_{32}$NO$_3$ (M+H) 283, found 283;

$[\alpha]^{\text{D}}_2$ = +30.4° (c = 0.30, CHCl$_3$, obtained with (S,S)-1).

3-(2-Cyclohexylethyl)-2,3-dihydrobenzofuran (Table 2, entry 6).  The title compound was prepared according to the general procedure, using bromomethylcyclohexane (0.098 mL, 0.70 mmol) and 9-(2-allyloxyphenyl)-9-borabicyclo[3.3.1]nonane (374 mg, 1.47 mmol). The reactions were conducted at 25 °C for 48 h. Purification: flash chromatography (100% hexanes). Colorless oil.

First run: 89 mg (55%, 96% ee).  Second run: 96 mg (60%, 96% ee).

The ee was determined by HPLC analysis (CHIRALCEL OJ-H, 100% hexanes; 0.6 mL/min; retention times (when (R,R)-1 is employed): 12.4 min (major), 13.6 min (minor).
$^1$H NMR (CDCl$_3$, 500 MHz) δ 7.14 (d, $J = 7.4$ Hz, 1H), 7.09 (dd, $J = 7.7$ Hz, 1H), 6.83 (dd, $J = 7.4$ Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 1H), 4.60 (dd, $J = 8.8, 8.8$ Hz, 1H), 4.17 (dd, $J = 6.6, 8.8$ Hz, 1H), 3.34–3.40 (m, 1H), 1.73–1.80 (m, 1H), 1.59–1.72 (m, 5H), 1.50–1.58 (m, 1H), 1.08–1.33 (m, 6H), 0.81–0.93 (m, 2H);

$^{13}$C NMR (CDCl$_3$, 125 MHz) δ 159.9, 131.2, 128.0, 124.3, 120.2, 109.4, 76.9, 42.1, 37.8, 34.9, 33.4, 33.2, 32.2, 26.6, 26.34, 26.32;

IR (film) 2917, 2848, 1596, 1480, 1460, 1226, 963, 747 cm$^{-1}$;

MS (EI): calcd for C$_{15}$H$_{25}$O (M) 230, found 230;

$[\alpha]^{25}_{D} = +15.7^\circ$ (c = 0.26, CHCl$_3$, obtained with (S,S)-1).

3-[(2,3-Dihydro-1H-inden-2-yl)methyl]-2,3-dihydrobenzofuran (Table 2, entry 7). The title compound was prepared according to the general procedure, using 2-bromo-2,3-dihydro-1H-indene (138 mg, 0.70 mmol) and 9-(2-allyloxyphenyl)-9-borabicyclo[3.3.1]nonane (374 mg, 1.47 mmol). The reactions were conducted at 25 °C for 36 h. Purification: flash chromatography (0→0.5% Et$_3$O/hexanes). Colorless oil.

First run: 90 mg (51%, 97% ee). Second run: 93 mg (53%, 95% ee).

The ee was determined by HPLC analysis (CHIRALCEL OJ-H, 2% i-PrOH in hexanes; 1.0 mL/min; retention times (when (R,R)-1 is employed): 19.0 min (major), 21.9 min (minor).

$^1$H NMR (CDCl$_3$, 500 MHz) δ 7.09–7.20 (m, 6H), 6.84 (dd, $J = 7.4, 7.4$ Hz, 1H), 6.79 (d, $J = 8.0$ Hz, 1H), 4.67 (dd, $J = 8.8, 8.8$ Hz, 1H), 4.24 (dd, $J = 6.5, 8.8$ Hz, 1H), 3.49–3.56 (m, 1H), 3.08 (dddd, $J = 5.7, 7.2, 15.1$ Hz, 2H), 2.54–2.69 (m, 3H), 2.00 (dddd, $J = 5.8, 7.6, 13.4$ Hz, 1H), 1.78 (dd, $J = 6.8, 8.9, 13.4$ Hz, 1H);

$^{13}$C NMR (CDCl$_3$, 125 MHz) δ 159.8, 143.0, 142.9, 130.9, 128.2, 126.3, 124.42, 124.40, 124.3, 120.4, 109.6, 77.1, 40.84, 40.81, 39.5, 39.1, 38.2;

IR (film) 2923, 2841, 1596, 1481, 1463, 1227, 969, 744 cm$^{-1}$;

MS (EI): calcd for C$_{15}$H$_{25}$O (M) 250, found 250;

$[\alpha]^{25}_{D} = +60^\circ$ (c = 0.11, CHCl$_3$, obtained with (S,S)-1).
1-[4-(4-Methoxyphenyl)butyl]-2,3-dihydro-1H-indene (eq 2). The title compound was prepared according to the general procedure, except that a different catalyst loading was used: NiBr₂·glyme (16.2 mg, 0.0525 mmol, 7.5%) and 1 (15.1 mg, 0.0630 mmol, 9.0%). The reactions were conducted with 1-bromo-3-(4-methoxyphenyl)propane (0.122 mL, 0.70 mmol) and 9-[2-(3-butyl-1-yl)phenyl]-9-borabicyclo[3.3.1]nonane (371 mg, 1.47 mmol) at −5 °C for 48 h. Purification: flash chromatography (0→1% Et₂O/hexanes), followed by preparative TLC (1% Et₂O/hexanes). Colorless oil.

First run: 89 mg (45%, 95% ee). Second run: 92 mg (47%, 94% ee). The ee was determined by HPLC analysis (CHIRALCEL OJ-H, 2% i-PrOH in hexanes; 1.0 mL/min; retention times (when (R,R)-1 is employed): 15.6 min (major), 32.5 min (minor).

¹H NMR (CDCl₃, 500 MHz) δ 7.12–7.21 (m, 4H), 7.10 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 3.78 (s, 3H), 3.03–3.11 (m, 1H), 2.87–2.94 (m, 1H), 2.76–2.85 (m, 1H), 2.52–2.63 (m, 2H), 2.21–2.30 (m, 1H), 1.82–1.90 (m, 1H), 1.59–1.70 (m, 3H), 1.38–1.52 (m, 3H);

¹³C NMR (CDCl₃, 125 MHz) δ 157.6, 147.7, 144.0, 134.8, 129.2, 126.2, 125.9, 124.4, 123.5, 113.7, 55.2, 44.8, 35.0, 34.9, 32.1, 32.0, 31.4, 27.3;

IR (film) 3018, 2927, 2852, 1611, 1511, 1456, 1245, 1175, 1037, 826, 744 cm⁻¹;

MS (EI): calcd for C₂₀H₂₄O (M) 280, found 280;

[α]²⁵D = −5.0° (c = 0.75, CHCl₃, obtained with (S,S)-1).

5-Fluoro-1-[4-(4-methoxyphenyl)butyl]-2,3-dihydro-1H-indene (eq 2). The title compound was prepared according to the general procedure, except that a different catalyst loading was used: NiBr₂·glyme (16.2 mg, 0.0525 mmol, 7.5%) and 1 (15.1 mg, 0.0630 mmol, 9.0%). The reactions were conducted with 1-bromo-3-(4-methoxyphenyl)propane (0.122 mL, 0.70 mmol) and 9-[2-(3-butyl-1-yl)-4-fluorophenyl]-9-borabicyclo[3.3.1]nonane (397 mg, 1.47 mmol) at −5 °C.
for 48 h. Purification: flash chromatography (0→1% EtO/hexanes), followed by reverse-phase (C18) chromatography (1:1→4:1 CH3CN/H2O). Colorless oil.

First run: 89 mg (43%, 98% ee). Second run: 90 mg (43%, 95% ee).

The ee was determined by HPLC analysis (CHIRALCEL OJ-H, 2% i-PrOH in hexanes; 1.0 mL/min; retention times (when (R,R)-1 is employed): 15.2 min (major), 24.1 min (minor).

1H NMR (CDCl3, 500 MHz) δ 7.04–7.10 (m, 3H), 6.79–6.88 (m, 4H), 3.77 (s, 3H), 2.97–3.04 (m, 1H), 2.83–2.90 (m, 1H), 2.73–2.81 (m, 1H), 2.50–2.62 (m, 2H), 2.22–2.30 (m, 1H), 1.76–1.83 (m, 1H), 1.56–1.70 (m, 3H), 1.35–1.46 (m, 3H);

13C NMR (CDCl3, 125 MHz) δ 162.0 (d, J = 241 Hz), 157.6, 146.1 (d, J = 7.6 Hz), 143.1, 134.8, 129.2, 124.2 (d, J = 8.6 Hz), 113.7, 112.6 (d, J = 22.9 Hz), 111.3 (d, J = 22.0 Hz), 55.2, 44.0, 35.02, 34.96, 32.5, 31.9, 31.4, 27.2;

19F NMR (CDCl3, 282 MHz) δ –118.0;

IR (film) 2924, 2852, 1610, 1511, 1483, 1463, 1242, 1175, 1036, 809 cm⁻¹;

MS (EI): calcd for C26H23FO (M) 298, found 298;

[α]Dⁿ = +11.5° (c = 0.25, CHCl₃, obtained with (R,R)-1).

1-Methyl-1-(4-phenylbutyl)-2,3-dihydro-1H-indene (eq 3). The title compound was prepared according to the general procedure, using 1-iodo-3-phenylpropane (0.112 mL, 0.70 mmol) and 9-[2-(3-methyl-3-buten-1-yl)phenyl]-9-borabicyclo[3.3.1]nonane (392 mg, 1.47 mmol). The reactions were conducted at 25 °C for 36 h. Purification: flash chromatography (100% hexanes). Colorless oil.

First run: 149 mg (81%, 57% ee). Second run: 155 mg (84%, 58% ee).

The ee was determined by HPLC analysis (CHIRALCEL OD-H, 100% hexanes; 1.0 mL/min; retention times (when (R,R)-1 is employed): 22.8 min (major), 31.0 min (minor).

1H NMR (CDCl3, 500 MHz) δ 7.23–7.26 (m, 2H), 7.08–7.19 (m, 7H), 2.86 (dd, J = 7.3, 7.3 Hz, 2H), 2.54–2.59 (m, 2H), 1.96–2.02 (m, 1H), 1.78–1.83 (m, 1H), 1.49–1.65 (m, 4H), 1.31–1.40 (m, 1H), 1.20–1.29 (m, 1H), 1.22 (s, 3H);

13C NMR (CDCl3, 125 MHz) δ 151.6, 143.2, 142.8, 128.3, 128.2, 126.2, 126.1, 125.5, 124.5, 122.6, 47.3, 41.2, 38.6, 35.9, 32.3, 30.3, 26.7, 24.7;

IR (film) 3062, 3023, 2929, 2856, 1453, 1372, 1024, 756 cm⁻¹;

MS (EI): calcd for C26H24 (M) 264, found 264;

[α]Dⁿ = +2.4° (c = 0.50, CHCl₃, obtained with (R,R)-1).
5-(2,3-Dihydrobenzofuran-3-yl)-4-methyl-N,N-diphenylpentanamide (eq 4). The title compound was prepared according to the general procedure, using 4-bromo-N,N-diphenylpentanamide (230 mg, 0.70 mmol) and 9-(2-allyloxyphenyl)-9-borabicyclo[3.3.1]nonane (374 mg, 1.47 mmol). The reactions were conducted at 25 °C for 36 h. Purification: flash chromatography (5→20% EtO/hexanes). Colorless viscous oil.

First run: 144 mg (54%, 89:11 d.r., major diastereomer 99% ee, minor diastereomer 86% ee). Second run: 141 mg (52%, 90:10 d.r., major diastereomer 98% ee, minor diastereomer 85% ee). The ee was determined by HPLC analysis (CHIRALPAK AD-H, 4% i-PrOH in hexanes; 1.0 mL/min; retention times (when (R,R)-1 is employed): for major diastereomer, 63.9 min (major), 72.1 min (minor); for minor diastereomer, 53.5 min (major), 57.8 min (minor).

1H NMR (CDCl3, 500 MHz, major diastereomer) δ 7.15–7.45 (m, 10H), 7.06–7.12 (m, 2H), 6.82 (ddd, J = 1.0, 7.4, 7.4 Hz, 1H), 6.76 (d, J = 7.9 Hz, 1H), 4.57 (dd, J = 8.7 Hz, 1H), 4.08 (dd, J = 6.9, 8.7 Hz, 1H), 3.42–3.48 (m, 1H), 2.21–2.35 (m, 2H), 1.70–1.78 (m, 1H), 1.44–1.58 (m, 4H), 0.84 (d, J = 6.2 Hz, 3H);

13C NMR (CDCl3, 125 MHz, major diastereomer) δ 173.1, 159.7 142.9, 131.3, 129.5, 129.0, 128.0, 126.2, 124.2, 120.3, 109.5, 77.0, 42.1, 39.4, 32.81, 32.77, 30.4, 19.1;
IR (film) 3062, 2955, 2925, 1668, 1596, 1492, 1455, 1373, 1289, 1273, 1232, 753 cm⁻¹;
MS (ESI+): calcd for C26H₂₈NO₃ (M+H) 386, found 386;
[α]D⁻²⁸ = +5.3° (c = 0.28, CHCl₃, obtained with (R,R)-1).

2-(6-Methoxy-2,3-dihydrobenzofuran-3-yl)ethanol (Scheme 1). The title compound was prepared through a three-step sequence.

Step 1: The Ni-catalyzed cyclization/cross-coupling (1.4 mmol scale) was conducted according to the general procedure, using allyl(bromomethyl)dimethylsilane (270 mg, 1.40 mmol) and 9-(2-allyloxy-4-methoxy phenyl)-9-borabicyclo[3.3.1]nonane (835 mg, 2.94 mmol). The reactions were conducted at 10 °C for 36 h. Purification by flash chromatography (1% Et₂O/hexanes) afforded a mixture of the desired cyclization-coupling product and 1-allyloxy-3-methoxybenzene (derived from excess nucleophile) as light-yellow oil.

Step 2: In air, the product from Step 1 was mixed with CHCl₃ (reagent grade; 1.5 mL), KHF₂ (164 mg, 2.10 mmol), and TFA (0.21 mL, 2.8 mmol) in a 20 mL vial equipped with a stir bar. The vial was sealed with a teflon-lined septum cap, and the mixture was stirred at 50 °C for 3 h. During this time, the reaction mixture became bright blue. The volatiles were then carefully removed under vacuum.
**Step 3**: In air, the resulting residue was mixed with THF (reagent grade, 2.0 mL), methanol (reagent grade, 2.0 mL), H₂O₂ (30 wt% commercial solution, 1.4 mL, 14 mmol), and NaHCO₃ (0.35 g, 4.2 mmol). The vial was sealed with a teflon-lined septum cap, and the mixture was stirred at 65 °C for 12 h (Caution: Gas evolution. Use safety shield). During this time, the reaction mixture became light yellow. The reaction was cooled to 0 °C and quenched with a saturated solution of sodium sulfite (10 mL) with vigorous stirring. The mixture was transferred to a separatory funnel that contained brine (20 mL), the aqueous layer was extracted with EtOAc (50 mL x 2), and the combined organic layers were washed with brine, dried over sodium sulfate, and concentrated. Purification: flash chromatography (10→40% EtOAc/hexanes). Pale-yellow oil.

First run (with (R,R)-1): 101 mg (37% over three steps, 96% ee).
Second run (using (S,S)-1): 106 mg (39% over three steps, 96% ee).

The ee was determined by HPLC analysis (CHIRALCEL OD-H, 5% i-PrOH in hexanes; 1.0 mL/min; retention times (when (R,R)-1 is employed): 22.6 min (minor), 25.0 min (major).

1H NMR (CDCl₃, 500 MHz) δ 7.03 (d, J = 8.1 Hz, 1H), 6.40 (dd, J = 2.3, 8.1 Hz, 1H), 6.38 (d, J = 2.3 Hz, 1H), 4.66 (dd, J = 8.8, 8.8 Hz, 1H), 4.26 (dd, J = 2.0, 8.8 Hz, 1H), 3.75 (s, 3H), 3.74 (dd, J = 6.3, 6.3 Hz, 2H), 3.51 (dddd, J = 6.0, 6.0, 8.5, 8.5 Hz, 1H), 1.94–2.02 (m, 1H), 1.76–1.84 (m, 1H), 1.37 (br s, 1H);

13C NMR (CDCl₃, 125 MHz) δ 161.1, 160.5, 124.3, 122.5, 106.0, 96.3, 77.9, 60.8, 55.5, 38.5, 37.7; IR (film) 3400 (br), 2934, 2886, 1622, 1596, 1495, 1446, 1281, 1195, 1145, 1114, 1029, 978 cm⁻¹; MS (ESI+): calcd for C₃₁H₅₉O₃ (M+H) 195, found 195; [α]²⁵D = +22.8° (c = 0.56, CHCl₃, obtained with (S,S)-1).

**IV. Determination of Absolute Configuration**

The absolute configuration of the product of the cross-coupling illustrated in eq 4 (prepared with (R,R)-1) was determined by converting the compound into a crystalline phthalimide derivative, the structure of which was determined by X-ray crystallography.
N-((S)-5-((R)-2,3-dihydrobenzofuran-3-yl)-4-methylpentyl)isoindoline-1,3-dione  The title compound was prepared through a three-step sequence.

Step 1: Under nitrogen, an oven-dried 4 mL vial was charged with LiAlH₄ (58 mg, 1.5 mmol) and anhydrous THF (2 mL). The resulting gray suspension was added over 5 min to a 20 mL vial that contained a solution of 5-(2,3-dihydrobenzofuran-3-yl)-4-methyl-N,N-diphenylpentanamide (77 mg, 0.20 mmol, prepared with (R,R)-1) in THF (4 mL) at 0 °C under nitrogen. The vial that had contained the solution of LiAlH₄ was rinsed with anhydrous THF (1 mL), and the rinse was added to the reaction mixture. The reaction mixture was warmed to 25 °C and stirred for 12 h, during which time a light-gray suspension formed.

The reaction mixture was carefully quenched at 0 °C with ice water (20 mL). The resulting suspension was extracted with EtO (20 mL x 2). The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated under vacuum. Purification by flash chromatography (1:2→1:1 EtOAc/hexanes) afforded the alcohol (36 mg, 82% yield) as a colorless oil.

Step 2: Under nitrogen, an oven-dried 20 mL vial equipped with a stir bar was charged with the product from Step 1 (31 mg, 0.14 mmol), CH₂Cl₂ (2 mL), triethylamine (39 μL, 0.28 mmol), and MsCl (17 μL, 0.17 mmol) at 0 °C. The reaction mixture was warmed to 25 °C and stirred for 4 h.

The reaction was then quenched at 0 °C with water (10 mL). The resulting suspension was extracted with EtOAc (10 mL x 2), and the combined organic layers were washed with brine, dried over sodium sulfate, and concentrated under vacuum, furnishing the desired tosylate (light-yellow oil), which was used in the next step without purification.

Step 3: Under nitrogen, a 4 mL vial equipped with a stir bar was charged with the unpurified mesylate from Step 2, DMF (anhydrous, 1.0 mL), and phthalimide potassium salt (32 mg, 0.17 mmol). The vial was sealed with a teflon-lined septum cap, and the reaction mixture was vigorously stirred at 25 °C for 12 h, and then at 60 °C for 1 h.

The reaction was quenched at 0 °C with water (10 mL). The resulting suspension was extracted with EtOAc (10 mL x 2), and the combined organic layers were washed with brine, dried over sodium sulfate, and concentrated. Purification by flash chromatography (5→10% EtOAc/hexanes) afforded the product (43 mg, 88% yield for two steps) as a white solid.

A crystal suitable for X-ray crystallography was obtained by slow vapor diffusion in EtO/pentane at −20 °C.

¹H NMR (CDCl₃, 500 MHz) δ 7.82 (dd, J = 3.0, 5.5 Hz, 2H), 7.69 (dd, J = 3.0, 5.5 Hz, 2H), 7.06–7.13 (m, 2H), 6.82 (dd, J = 7.4, 7.4 Hz, 1H), 6.75 (d, J = 7.9 Hz, 1H), 4.59 (dd, J = 8.7, 8.7 Hz, 1H), 4.12 (dd, J = 7.1, 8.6 Hz, 1H), 3.66 (t, J = 7.3 Hz, 2H), 3.45–3.53 (m, 1H), 1.63–1.77 (m, 2H), 1.50–1.59 (m, 3H), 1.33–1.40 (m, 1H), 1.20–1.28 (m, 1H), 0.94 (d, J = 6.3 Hz, 3H);

¹³C NMR (CDCl₃, 125 MHz) δ 168.4, 159.7, 133.9, 132.1, 131.3, 128.0, 124.0, 123.2, 120.3, 109.4, 76.9, 42.3, 39.4, 38.1, 34.4, 30.6, 26.0, 19.1;

IR (film) 3464, 2928, 1770, 1712, 1596, 1482, 1397, 1226, 1064, 1016, 968, 752 cm⁻¹;

MS (ESI+): calcd for C₂₅H₂₄NO₅ (M+H) 350, found 350;

[α]D²⁵ = −3.7° (c = 0.26, CHCl₃).
A suitable crystal of C$_{22}$H$_{23}$NO$_3$ was selected for analysis. All measurements were made on a Bruker APEX-II CCD with filtered Cu-K$_\alpha$ radiation at a temperature of 120 K. Using Olex2,$^1$ the structure was solved with the ShelXS$^2$ structure solution program using Direct Methods and refined with the ShelXL$^2$ refinement package using Least Squares minimization. The absolute stereochemistry was determined on the basis of the absolute structure parameter.

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. Appl. Crystallogr. 2009, 42, 339.

2. Sheldrick, G. M. Acta Crystallogr. A 2008, 64, 112.

Table S–1. Crystal data and structure refinement for crystal01.

| Identification code  | crystal01          |
|----------------------|--------------------|
| Empirical formula    | C$_{22}$H$_{23}$NO$_3$ |
| Formula weight       | 349.41             |
| Temperature          | 120 K              |
| Wavelength           | 1.54178 Å          |
| Crystal system       | Orthorhombic       |
| Space group          | P2$_1$2$_1$2$_1$    |
| Unit cell dimensions |                     |
| a = 4.95310(10) Å   | $\alpha$ = 90°    |
| b = 12.3326(3) Å    | $\beta$ = 90°     |
| c = 29.4659(7) Å    | $\gamma$ = 90°    |
| Volume               | 1799.91(7) Å$^3$  |
| Z                    | 4                  |
| Density (calculated) | 1.289 Mg/m$^3$     |
| Absorption coefficient| 0.684 mm$^{-1}$   |
| F(000)               | 744                |
| Crystal size         | 0.147 x 0.142 x 0.071 mm$^3$ |
| Theta range for data collection | 2.999 to 71.513° |
| Index ranges         | -6< h< 6, -15< k< 15, -36< l< 35 |
| Reflections collected| 31273              |
| Independent reflections| 3492 [R(int) = 0.0238] |
| Completeness to theta= 67.679° | 99.9 % |
| Absorption correction | Numerical          |
| Max. and min. transmission | 1.0000 and 0.9407 |
| Refinement method    | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 3492 / 0 / 236 |
Goodness-of-fit on $F^2$  
Final R indices [I>2sigma(I)]  
R1 = 0.0244, wR2 = 0.0617  
R indices (all data)  
R1 = 0.0249, wR2 = 0.0627  
Absolute structure parameter  
0.04(4)  
Largest diff. peak and hole  
0.186 and -0.128 e/Å$^3$  

Table S–2. Atomic coordinates (x 10$^4$) and equivalent isotropic displacement parameters (Å$^2$x 10$^3$) for crystal01. U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

|   | x     | y     | z     | U(eq) |
|---|-------|-------|-------|-------|
| O(1)| 1865(2)| 2969(1)| 566(1)| 24(1) |
| O(2)| 3365(2)| -1139(1)| -1800(1)| 31(1) |
| O(3)| -3380(2)| -3456(1)| -1368(1)| 33(1) |
| N(1)| -202(2)| -2116(1)| -1499(1)| 24(1) |
| C(1)| 206(3)| 2746(1)| 926(1)| 21(1) |
| C(2)| -1328(3)| 3513(1)| 1150(1)| 27(1) |
| C(3)| -3012(3)| 3149(1)| 1496(1)| 32(1) |
| C(4)| -3105(3)| 2061(1)| 1615(1)| 31(1) |
| C(5)| -1520(3)| 1302(1)| 1386(1)| 26(1) |
| C(6)| 136(3)| 1652(1)| 1038(1)| 20(1) |
| C(7)| 1847(3)| 1038(1)| 697(1)| 20(1) |
| C(8)| 3416(3)| 1986(1)| 481(1)| 24(1) |
| C(9)| 46(3)| 435(1)| 356(1)| 21(1) |
| C(10)| 1550(3)| -283(1)| 13(1)| 20(1) |
| C(11)| 2713(3)| -1288(1)| 246(1)| 26(1) |
| C(12)| -366(3)| -581(1)| -375(1)| 23(1) |
| C(13)| 828(3)| -1306(1)| -744(1)| 21(1) |
| C(14)| -1050(3)| -1345(1)| -1152(1)| 28(1) |
| C(15)| 1940(3)| -1936(1)| -1797(1)| 24(1) |
| C(16)| 2034(3)| -2904(1)| -2100(1)| 24(1) |
| C(17)| 3734(3)| -3143(1)| -2458(1)| 30(1) |
| C(18)| 3401(4)| -4150(1)| -2667(1)| 35(1) |
| C(19)| 1438(4)| -4868(1)| -2524(1)| 35(1) |
| C(20)| -325(3)| -4612(1)| -2170(1)| 31(1) |
| C(21)| 32(3)| -3617(1)| -1961(1)| 24(1) |
| C(22)| -1455(3)| -3114(1)| -1577(1)| 24(1) |
Table S–3. Anisotropic displacement parameters (Å^2 x 10^3) for crystal01. The anisotropic displacement factor exponent takes the form: -2π^2 [ h^2 a^*2U11 + ... + 2 h k a^* b^* U12 ]

|   | U11  | U22  | U33  | U12  | U13  | U23  |
|---|------|------|------|------|------|------|
| O(1) | 27(1) | 20(1) | 26(1) | 1(1) | 3(1) | -1(1) |
| O(2) | 35(1) | 26(1) | 33(1) | 2(1) | 0(1) | -4(1) |
| O(3) | 31(1) | 39(1) | 28(1) | 2(1) | 1(1) | -6(1) |
| N(1) | 25(1) | 25(1) | 22(1) | -4(1) | -1(1) | 2(1) |
| C(1) | 20(1) | 22(1) | 20(1) | -1(1) | -4(1) | -1(1) |
| C(2) | 32(1) | 20(1) | 30(1) | -3(1) | -4(1) | 2(1) |
| C(3) | 33(1) | 31(1) | 31(1) | -9(1) | 3(1) | 7(1) |
| C(4) | 33(1) | 35(1) | 24(1) | -3(1) | 7(1) | -1(1) |
| C(5) | 32(1) | 24(1) | 23(1) | 1(1) | 2(1) | -1(1) |
| C(6) | 21(1) | 21(1) | 19(1) | -1(1) | -2(1) | 1(1) |
| C(7) | 20(1) | 19(1) | 22(1) | -1(1) | 0(1) | 1(1) |
| C(8) | 23(1) | 23(1) | 27(1) | -4(1) | 3(1) | -1(1) |
| C(9) | 20(1) | 20(1) | 24(1) | -2(1) | 2(1) | 1(1) |
| C(10) | 21(1) | 17(1) | 23(1) | -1(1) | 3(1) | 1(1) |
| C(11) | 31(1) | 20(1) | 26(1) | -1(1) | -1(1) | 4(1) |
| C(12) | 21(1) | 21(1) | 26(1) | -3(1) | 0(1) | 3(1) |
| C(13) | 22(1) | 17(1) | 23(1) | -1(1) | 1(1) | 0(1) |
| C(14) | 27(1) | 29(1) | 26(1) | -6(1) | 0(1) | 6(1) |
| C(15) | 24(1) | 24(1) | 23(1) | 2(1) | -2(1) | 4(1) |
| C(16) | 25(1) | 26(1) | 21(1) | 0(1) | -5(1) | 5(1) |
| C(17) | 28(1) | 39(1) | 24(1) | 0(1) | -1(1) | 6(1) |
| C(18) | 36(1) | 45(1) | 24(1) | -8(1) | -5(1) | 15(1) |
| C(19) | 44(1) | 32(1) | 30(1) | -12(1) | -15(1) | 12(1) |
| C(20) | 34(1) | 27(1) | 31(1) | -2(1) | -12(1) | 2(1) |
| C(21) | 26(1) | 26(1) | 21(1) | 0(1) | -6(1) | 4(1) |
| C(22) | 25(1) | 27(1) | 21(1) | 2(1) | -6(1) | 1(1) |
Table S–4. Hydrogen coordinates ($x \times 10^4$) and isotropic displacement parameters ($\AA^2 \times 10^3$) for crystal01.

|      | x   | y   | z   | U(eq) |
|------|-----|-----|-----|-------|
| H(2) | -1235 | 4260 | 1071 | 33    |
| H(3) | -4118 | 3654 | 1653 | 38    |
| H(4) | -4258 | 1831 | 1853 | 37    |
| H(5) | -1579 | 558  | 1468 | 32    |
| H(7) | 3102  | 525  | 854  | 24    |
| H(8A) | 5235 | 2046 | 618  | 29    |
| H(8B) | 3622 | 1868 | 150  | 29    |
| H(9A) | -1025 | 978  | 186  | 26    |
| H(9B) | -1237 | -24  | 527  | 26    |
| H(10) | 3082 | 145  | -116 | 24    |
| H(11A) | 1243 | -1710 | 381 | 39    |
| H(11B) | 3978 | -1064 | 484 | 39    |
| H(11C) | 3664 | -1734 | 22  | 39    |
| H(12A) | -1960 | -951 | -245 | 27    |
| H(12B) | -1008 | 97   | -518 | 27    |
| H(13A) | 2610 | -1020 | -838 | 25    |
| H(13B) | 1092 | -2048 | -623 | 25    |
| H(14A) | -2885 | -1541 | -1047 | 33    |
| H(14B) | -1150 | -613 | -1288 | 33    |
| H(17) | 5069 | -2644 | -2558 | 36    |
| H(18) | 4546 | -4346 | -2913 | 42    |
| H(19) | 1284 | -5552 | -2669 | 42    |
| H(20) | -1705 | -5098 | -2077 | 37    |
(R)-1-(4-(4-Methoxyphenyl)butyl)-2,3-dihydro-1H-indene. The product (X=H) in eq 2 was synthesized according to a literature method.² On the basis of a comparison of HPLC data, the absolute stereochemistry of the product in eq 2 was determined to be R when using (S,S)-1.

The absolute configurations for other cyclization/cross-coupling products were assigned by analogy.

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(2) Arp, F. O.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 10482–10483.
V. $^1$H NMR Spectra

Table 2, entry 1
(CDCl$_3$, 500 MHz)
Table 2, entry 2
(CDCl₃, 500 MHz)
Table 2, entry 3
(CDCl₃, 500 MHz)
Table 2, entry 4
(CDCl₃, 500 MHz)
Table 2, entry 5
(CDCl₃, 500 MHz)
Table 2, entry 6
(CDCl₃, 500 MHz)
Table 2, entry 7
(CDCl₃, 500 MHz)
eq 2
(CDCl$_3$, 500 MHz)
eq 2
(CDCl$_3$, 500 MHz)
eq 3
(CDCl₃, 500 MHz)
CONPh₂

eq 4

(CDCl₃, 500 MHz)
Scheme 1
(CDCl₃, 500 MHz)