Stereospecific Pd-Catalyzed Cross-Coupling Reactions of Secondary Alkylboron Nucleophiles and Aryl Chlorides

Ling Li, Shibin Zhao, Amruta Joshi-Pangu, Mohamed Diane, and Mark R. Biscoe*

Supporting Information

Table of Contents

General Reagent/Analytical Information.............................................. S2
General Procedural Information...................................................... S2-S4
Single Crystal X-Ray Structure..................................................... S4-S5
Compound Characterization Data.................................................... S5-S16
References......................................................................................... S16
Chiral GC and HPLC data................................................................. S17-S27
$^1$H and $^{13}$C NMR Spectra............................................................. S28-S55
General Reagent Information

BDH brand ethyl ether was purchased from VWR. EMD brand Omnisolv THF (unstabilized) was also purchased from VWR. These solvents were transferred to separate 20 L solvent-delivery kegs and vigorously purged with argon for 2 h. The solvents were further purified by passing them under argon pressure through two packed columns of neutral alumina. Water used in Suzuki reactions was distilled and degassed prior to use. Reagents and solvents were used as received unless otherwise noted. Flash chromatography was performed using Silicycle silica gel (ultra pure grade).

General Analytical Information

All compounds were characterized by $^1$H NMR and $^{13}$C NMR spectroscopy. Copies of the $^1$H and $^{13}$C spectra for all new compounds can be found at the end of the Supporting Information. All previously unreported compounds were additionally characterized by high resolution MS. Nuclear Magnetic Resonance spectra were recorded on a Varian 300 or 500 MHz instrument. All $^1$H NMR experiments are reported in $\delta$ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) or residual acetone (2.05 ppm). All $^{13}$C NMR spectra are reported in ppm relative to deuterochloroform (77.23 ppm) or residual acetone (29.84 ppm), and were obtained with $^1$H decoupling. High-resolution MS analyses were performed on an Agilent 6520 Q-TOF instrument. All GC analyses were performed on a Shimadzu GC-2010 gas chromatograph with an FID detector using a 25 m x 0.20 mm capillary column with cross-linked methyl siloxane as the stationary phase. All GC yields were calibrated using dodecane or tetradecane as an internal standard. Chiral GC analyses were performed using a 30 m x 0.32 mm chiral column (Rt®-βDEXsm from Restek). Chiral HPLC analyses were performed by Chiral Technologies Inc. Polarimetry measurements were performed using a Rudolph Autopol IV digital polarimeter.

Procedural Information

**General procedure 1 for cross-coupling reactions**

On the benchtop, the aryl chloride (0.50 mmol), alkyl boronic acid or trifluoroborate (0.75 mmol), K$_2$CO$_3$ (207 mg, 1.5 mmol), and third generation $t$-Bu$_3$P Buchwald precatalyst$^1$ (0.025 mmol) were added to an oven-dried 10 mL screw-top test tube equipped with a stirbar. The test tube was sealed with a screw-top septum and electrical tape. The reaction vessel was evacuated (ca. 200 mtorr) and backfilled with argon four times. If the aryl chloride was a liquid, it was added to the reaction vessel via syringe at this point. Toluene (1.0 mL) and degassed water (0.5 mL) were then added via syringe. The septum was covered with electrical tape, and the reaction vessel was heated to 100 °C for 24 h. The cooled reaction mixture was transferred to a separatory funnel, diluted with saturated NH$_4$Cl solution (10 mL), and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine (10 mL) and dried over Na$_2$SO$_4$. The organic layer was filtered, concentrated under reduced pressure, and purified by column chromatography.
General procedure 2 for cross-coupling reactions

On the benchtop, the aryl chloride (0.50 mmol), alkyl trifluoroborate (0.75 mmol), K$_2$CO$_3$ (207 mg, 1.5 mmol), and third generation $t$-Bu$_3$P Buchwald precatalyst$^1$ (0.05 mmol) were added to an oven-dried Schlenk tube equipped with a stirbar. The Schlenk tube was capped with a rubber septum and evacuated (ca. 50 mTorr) and backfilled five times with argon through the side arm of the Schlenk flask. If the aryl chloride were a liquid, it was added to the reaction vessel via syringe at this point. Benzene (1.0 mL) or toluene (1.0 mL) and degassed water (1.0 mL for benzene, 0.5 mL for toluene) were then added via syringe. Under a flow of argon, the rubber septum was replaced with a Teflon stopper and the Schlenk tube was sealed. The reaction vessel was heated to 60 ºC for 48 h in an oil bath. The cooled reaction mixture was transferred to a separatory funnel, diluted with saturated NH$_4$Cl solution (10 mL), and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine (10 mL) and dried over Na$_2$SO$_4$. The organic layer was filtered, concentrated under reduced pressure, and purified by column chromatography on silica gel.

Formation of optically active secondary alkyltrifluoroborates (R)-7 and (R)-8 (see chiral GC and HPLC data below for comparisons versus standards):

H.C. Brown’s protocol$^{2a}$ was employed to prepare (R)-7 (Figure S1):

![Figure S1](image_url)
Matteson’s protocol\textsuperscript{2b} was employed to prepare \((R)\)-8 via the process shown in Figure S2.

![Chemical Structure](image)

**Figure S2**

**Single Crystal X-Ray Structure Determination**

**Experimental Description**

A colorless block-like crystal with the size of \(0.18 \times 0.36 \times 0.52\) mm\(^3\) (grown by slow diffusion of hexane into methylene chloride) was selected for geometry and intensity data collection with a Bruker SMART APEXII CCD area detector on a D8 goniometer at 100 K. The temperature during the data collection was controlled with an Oxford Cryosystems Series 700+ instrument. Preliminary lattice parameters and orientation matrices were obtained from three sets of frames. Data were collected using graphite-monochromated and 0.5 mm-MonoCap-collimated Mo-K\(\alpha\) radiation (\(\lambda = 0.71073\) Å) with the \(\omega\) scan method. Data were processed with the INTEGRATE program of the APEX2 software for reduction and cell refinement. Multi-scan absorption corrections were applied by using the SCALE program for the area detector. The structure was solved by the direct method and refined on \(F^2\) (SHELXTL). Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms on carbons were placed in idealized positions (C-H = 0.95-1.00 Å) and included as riding with \(U_{iso}(H) = 1.2\) or 1.5 \(U_{eq}(\text{non-H})\), and the hydrogen atom on the nitrogen atom was refined with a restrained distance of N-H 0.86 Å (Figure S3).
Crystal structure of derivatized (S)-3-phenylbutyric acid (9) to confirm stereochemical assignment by Sigma-Aldrich:

\[
\begin{align*}
\text{N} & \quad \text{H} \\
\text{Br} & \quad \text{H}
\end{align*}
\]

\[
\text{HO} \quad \text{CH}_3
\]

\[
\text{(S)-9} \quad \text{Sigma Aldrich}
\]

**Figure S3**

**Compound Characterization**

**Potassium (4-phenylbutan-2-yl)trifluoroborate.** 4,4,5,5-tetramethyl-2-(4-phenylbutan-2-yl)-1,3,2-dioxaborolane\(^3\) (1.3 g, 5.0 mmol) was added to a 10 mL round bottom flask. The flask was sealed with a rubber septum and evacuated/backfilled with argon three times. Anhydrous methanol (3 mL) was added via syringe. KHF\(_2\) (3.5 g, 45 mmol) was added to a separate 25 mL round bottom flask with a stirbar. The flask was sealed with a rubber septum and evacuated/backfilled with argon three times. Degassed water (3.75 mL) was added to the 25 mL flask via syringe. The methanol solution was then transferred dropwise into the aqueous solution of KHF\(_2\). The reaction mixture was allowed to stir for 30 min, after which the solvent was removed under reduced pressure. The remaining solid was extracted acetone three times. The combined acetone washes were concentrated under reduced pressure. The resulting solid was triturated with hexane until no starting boronate or pinacol remained in solid. After drying under reduced pressure, a white solid (750 mg, 62%) remained. \(^1\)H NMR (500 MHz, acetone-\(d_6\)): \(\delta\)
7.15-7.21 (m, 4H), 7.07 (t, J = 7.1 Hz, 1H), 2.67 (m, 1H), 2.52 (m, 1H), 1.74 (m, 1H), 1.30 (m, 1H), 0.82 (d, J = 7.2 Hz, 3H), 0.33 (br s, 1H) ppm. \(^{13}\)C NMR (125 MHz, acetone-d\(_6\)): \(\delta\) 145.9, 129.2, 128.7, 125.6, 37.0, 36.3, 16.2 ppm. \(^{11}\)B NMR (160 MHz, DMSO): \(\delta\) 1.23 ppm.

**(S)-1,3-Diphenylbutane.** (Figure 3c) NiI\(_2\) (3.75 mg, 0.012 mmol, 6 mol %), trans-2-aminohexanol hydrochloride (1.8 mg, 0.012 mmol, 6 mol %), phenylboronic acid (27 mg, 0.22 mmol, 1.1 equiv), and NaHMDS (73 mg, 0.4 mmol, 2.0 equiv) were added to a 4-mL vial equipped with stir bar. The vial was sealed with a septum-containing screw cap, and purged with argon. \(t\)-PrOH (0.6 mL) was added via syringe, and the resulting mixture was stirred for 5 min at rt. The bromide (42 mg, 0.2 mmol, 1.0 equiv) was then added via syringe. The reaction mixture was heated to 60 ºC in an oil bath for 6 h, allowed to cool to rt, and filtered through a short pad of silica gel using a 1:1 hexanes/ether mixture (20 mL). A pale yellow liquid (26 mg, 61%) was obtained after concentration under reduced pressure. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.31-7.35 (m, 2H), 7.26-7.30 (m, 2H), 7.17-7.24 (m, 4H), 7.13-7.16 (m, 2H), 2.74 (app. sextet, \(J = 7.0\) Hz, 1H), 2.48-2.58 (m, 2H), 1.87-1.99 (m, 2H), 1.29 (d, \(J = 7.0\) Hz, 3H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 147.5, 142.8, 128.59, 128.57, 128.46, 127.3, 126.2, 125.8, 40.2, 39.7, 34.1, 22.8 ppm. \(\alpha\) \(^{20}\)D (c 1.00, CHCl\(_3\)) = +13.2 ±0.2º. (Figure 3d) Using general procedure 2 with (R)-8, a pale yellow liquid (67 mg, 64%) was obtained. \(\alpha\) \(^{20}\)D (c 1.00, CHCl\(_3\)) = +13.1 ±0.5º.

1-(iso-Propyl)-4-methoxybenzene\(^6\) (Table 2, entry 1). General procedure 1 was employed using 4-chloroanisole (71 mg, 0.5 mmol) and iso-propylboronic acid (66 mg, 0.75 mmol). A colorless liquid (run 1: 57 mg, 76%; run 2: 62 mg, 82%) was isolated by column chromatography (99.5:0.5 Hex/ether). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.16 (d, \(J = 8.2\) Hz, 2H), 6.85 (d, \(J = 8.3\) Hz, 2H), 3.80 (s, 3H), 2.87 (septet, \(J = 7.0\) Hz, 1H), 1.23 (d, \(J = 7.0\) Hz, 6H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 157.8, 141.2, 127.4, 113.8, 55.4, 33.5, 24.4 ppm.

(Table 2, entry 3). General procedure 1 was employed using 4-chloroanisole (71 mg, 0.5 mmol) and potassium iso-propyltrifluoroborate (112 mg, 0.75 mmol). A colorless liquid (run 1: 61 mg, 81%; run 2: 63 mg, 84%) was isolated by column chromatography (99.5:0.5 Hex/ether).
1-(sec-Butyl)-4-methoxybenzene\(^5\) (Table 2, entry 2). General procedure 1 was employed using 4-chloroanisole (71 mg, 0.5 mmol) and sec-butylboronic acid (77 mg, 0.75 mmol). A colorless liquid (run 1: 68 mg, 83%; run 2: 51 mg, 62%) was isolated by column chromatography (98:2 Hex/ether). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.10 (d, \(J = 8.6\), 2H), 6.84 (d, \(J = 8.7\) Hz, 2H), 3.79 (s, 3H), 2.55 (m, 1H), 1.56 (m, 2H), 1.21 (d, \(J = 7.0\) Hz, 3H), 0.81 (t, \(J = 7.4\) Hz, 3H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 157.8, 139.9, 128.0, 113.7, 55.4, 41.0, 31.5, 22.3, 12.5 ppm.

(Table 2, entry 4). General procedure 1 was employed using 4-chloroanisole (71 mg, 0.5 mmol) and potassium (\(R\))-sec-butyltrifluoroborate (123 mg, 0.75 mmol). A colorless liquid (run 1: 65 mg, 79%; run 2: 76 mg, 92%) was isolated by column chromatography (98:2 Hex/ether). (Figure 3, row 1, column 3). General procedure 1 was employed at 60 °C using (\(R\))-sec-butyltrifluoroborate. Optical rotation of product: \([\alpha]^{20}_D\) (c 1.00, CHCl\(_3\)) = +18.6°.

**1-(iso-Propyl)-4-nitrobenzene\(^6\)** (Table 2, entry 5). General procedure 1 was employed using 1-chloro-4-nitrobenzene (79 mg, 0.5 mmol) and iso-propylboronic acid (66 mg, 0.75 mmol). An oily, yellow liquid (run 1: 72 mg, 87%; run 2: 63 mg, 76%) was isolated by column chromatography (99:1 Hex/ether). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.15 (d, \(J = 8.5\) Hz, 2H), 7.37 (d, \(J = 8.6\) Hz, 2H), 3.02 (septet, \(J = 6.8\) Hz, 1H), 1.29 (d, \(J = 6.9\) Hz, 6H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 256.8, 146.3, 127.4, 123.8, 34.4, 23.8 ppm.

(Table 2, entry 7). General procedure 1 was employed using 1-chloro-4-nitrobenzene (79 mg, 0.5 mmol) and potassium iso-propyltrifluoroborate (112 mg, 0.75 mmol). An oily, yellow liquid (run 1: 60 mg, 73%; run 2: 50 mg, 61%) was isolated by column chromatography (99:1 Hex/ether).

**1-(sec-Butyl)-4-nitrobenzene\(^7\)** (Table 2, entry 6). General procedure 1 was employed using 1-chloro-4-nitrobenzene (79 mg, 0.5 mmol) and sec-butylboronic acid (77 mg, 0.75 mmol). An oily, yellow liquid (run 1: 70 mg, 78%; run 2: 62 mg, 69%) was isolated by column chromatography (99:1 Hex/ether). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.15 (d, \(J = 8.7\) Hz, 2H), 7.33 (d, \(J = 8.6\) Hz, 2H), 2.73 (m, 1H), 1.63 (m, 2H), 1.27 (d, \(J = 6.9\) Hz, 3H), 0.83 (t, \(J = 7.4\) Hz, 3H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 155.7, 146.4, 128.0, 123.8, 41.9, 31.0, 21.7, 12.3 ppm.

(Table 2, entry 8). General procedure 1 was employed using 1-chloro-4-nitrobenzene (79 mg, 0.5 mmol) and potassium sec-butyltrifluoroborate (123 mg, 0.75 mmol). An oily,
yellow liquid (run 1: 64 mg, 71%; run 2: 65 mg, 72%) was isolated by column chromatography (99:1 Hex/ether).

\[
\text{MeO} \begin{array}{c}
\text{i-Pr}
\end{array}
\]

1-(iso-Propyl)-3-methoxybenzene$^5$ (Table 2, entry 9). General procedure 1 was employed using 3-chloroanisole (71 mg, 0.5 mmol) and iso-propylboronic acid (66 mg, 0.75 mmol). A colorless liquid (run 1: 62 mg, 83%; run 2: 62 mg, 83%) was isolated by column chromatography (99:1 Hex/ether). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.23 (t, $J = 7.8$ Hz, 1H), 6.84 (d, $J = 7.5$ Hz, 1H), 6.79 (m, 1H), 6.73 (d, $J = 7.8$ Hz, 1H), 3.82 (s, 3H), 2.89 (septet, $J = 6.8$ Hz, 1H), 1.26 (d, $J = 6.8$ Hz, 6H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ 159.7, 150.8, 129.4, 119.1, 112.6, 110.8, 55.3, 34.4, 24.2 ppm. (Table 2, entry 11).

1-(sec-Butyl)-3-methoxybenzene$^5$ (Table 2, entry 10). General procedure 1 was employed using 3-chloroanisole (71 mg, 0.5 mmol) and sec-butylboronic acid (77 mg, 0.75 mmol). A colorless liquid (run 1: 62 mg, 75%; run 2: 72 mg, 87%) was isolated by column chromatography (99:1 Hex/ether). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.21 (t, $J = 7.6$ Hz, 1H), 6.79 (d, $J = 7.7$ Hz, 1H), 6.74 (s, 1H), 6.73 (m, 1H), 3.81 (s, 3H), 2.57 (app. sextet, $J = 7.0$ Hz, 1H), 1.59 (m, 2H), 1.23 (d, $J = 6.9$ Hz, 3H), 0.83 (t, $J = 7.4$ Hz, 3H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ 159.7, 149.6, 129.3, 119.7, 113.2, 110.8, 55.3, 42.0, 31.3, 22.1, 12.5 ppm. (Table 2, entry 12).

1-(4-(iso-Propyl)phenyl)-IH-pyrrole (Table 2, entry 13). General procedure 1 was employed using 1-(4-chlorophenyl)-1H-pyrrole (89 mg, 0.5 mmol) and iso-propylboronic acid (66 mg, 0.75 mmol). A brownish liquid (81 mg, 88%) was isolated by column chromatography (99:5:0.5 Hex/ether). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.32 (d, $J = 8.5$ Hz, 2H), 7.28 (d, $J = 8.5$ Hz, 2H), 7.06 (t, $J = 2.1$ Hz, 2H), 6.33 (t, $J = 2.1$ Hz, 2H), 2.94 (septet, $J = 6.9$ Hz, 1H), 1.27 (d, $J = 6.9$ Hz, 6H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ
146.5, 138.9, 127.6, 120.8, 119.5, 110.2, 33.8, 24.2 ppm. HRMS (FAB\(^+\)): Calcd (M+H\(^+\)) 186.1283; Found 186.1275.

(Table 2, entry 15). General procedure 1 was employed using 1-(4-chlorophenyl)-1\(H\)-pyrrole (89 mg, 0.5 mmol) and potassium iso-propyltrifluoroborate (112 mg, 0.75 mmol). A brownish liquid (run 1: 54 mg, 58%; run 2: 75 mg, 81%; run 3: 77 mg, 83%) was isolated by column chromatography (99.5:0.5 Hex/ether).

![1-(sec-Butyl)phenyl]-1\(H\)-pyrrole\(^a\) (Table 2, entry 14). General procedure 1 was employed using 1-(4-chlorophenyl)-1\(H\)-pyrrole (89 mg, 0.5 mmol) and sec-butylboronic acid (77 mg, 0.75 mmol). A brownish liquid (84 mg, 84%) was isolated by column chromatography (99.4:0.6 Hex/ether). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.32 (d, \(J = 8.5\) Hz, 2H), 7.23 (d, \(J = 8.5\) Hz, 2H), 7.08 (t, \(J = 2.1\) Hz, 2H), 6.34 (t, \(J = 2.1\) Hz, 2H), 2.64 (m, 1H), 1.62 (m, 2H), 1.26 (d, \(J = 6.9\) Hz, 3H), 0.85 (t, \(J = 7.4\) Hz, 3H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 145.4, 138.9, 128.2, 120.8, 119.6, 110.2, 41.3, 31.4, 22.1, 12.5 ppm. (Table 2, entry 16). General procedure 1 was employed using 1-(4-chlorophenyl)-1\(H\)-pyrrole (89 mg, 0.5 mmol) and potassium sec-butyltrifluoroborate (123 mg, 0.75 mmol). A brownish liquid (run 1: 53 mg, 53%; run 2: 83 mg, 83%; run 3: 79 mg, 79%) was isolated by column chromatography (99.4:0.6 Hex/ether). (Figure 3, row 1, column 3). General procedure 1 was employed using \((R)\)-sec-butytrifluoroborate. Optical rotation of product: \([\alpha]^{20}_D\) (c 1.00, CHCl\(_3\)) = +17.1°.

1-(iso-Propyl)-2,4-dimethylbenzene\(^9\) (Table 2, entry 17). General procedure 1 was employed using 1-chloro-2,4-dimethylbenzene (66 \(\mu\)L, 0.5 mmol) and iso-propylboronic acid (66 mg, 0.75 mmol). A colorless liquid (run 1: 62 mg, 84%; run 2: 54 mg, 72%) was isolated by column chromatography (99.8:0.2 Hex/ether). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 144.0, 135.06, 135.05, 131.2, 127.0, 124.8, 29.1, 23.5, 21.1, 19.5 ppm.

(Table 2, entry 19). General procedure 1 was employed using 1-chloro-2,4-dimethylbenzene (66 \(\mu\)L, 0.5 mmol) and potassium iso-propyltrifluoroborate (112 mg, 0.75 mmol). A colorless liquid (run 1: 70 mg, 95%; run 2: 64 mg, 87%) was isolated by column chromatography (99.8:0.2 Hex/ether).
1-(sec-Butyl)-2,4-dimethylbenzene (Table 2, entry 18). General procedure 1 was employed using 1-chloro-2,4-dimethylbenzene (67 µL, 0.5 mmol) and sec-butylboronic acid (77 mg, 0.75 mmol). A colorless liquid (run 1: 70 mg, 86%; run 2: 76 mg, 94%) was isolated by column chromatography (99.8:0.2 Hex/ether). ¹H NMR (500 MHz, CDCl₃): δ 7.08 (d, J = 7.9 Hz, 1H), 7.00 (d, J = 7.9 Hz, 1H), 6.97 (s, 1H), 2.84 (m, 1H), 2.29 (s, 6H), 1.58 (m, 2H), 1.18 (d, J = 6.9 Hz, 3H), 0.86 (t, J = 7.4 Hz, 3H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 143.0, 135.5, 134.9, 131.1, 127.0, 125.3, 36.0, 30.8, 21.5, 21.1, 19.7, 12.6 ppm.

(Table 2, entry 20). General procedure 1 was employed using 1-chloro-2,4-dimethylbenzene (67 µL, 0.5 mmol) and potassium sec-butyltrifluoroborate (123 mg, 0.75 mmol). A colorless liquid (run 1: 76 mg, 93%; run 2: 71 mg, 88%) was isolated by column chromatography (99.8:0.2 Hex/ether).

5-(iso-Propyl)-3-methyl-1-benzothiophene (Table 2, entry 21). General procedure 1 was employed using 5-chloro-3-methyl-1-benzothiophene (91 mg, 0.5 mmol) and iso-propylboronic acid (66 mg, 0.75 mmol). A colorless liquid (run 1: 86 mg, 90%; run 2: 88 mg, 92%) was isolated by column chromatography (99.8:0.2 Hex/ether). ¹H NMR (500 MHz, CDCl₃): δ 7.77 (d, J = 8.3 Hz, 1H), 7.55 (s, 1H), 7.26 (dd, J = 8.2, 1.2 Hz, 1H), 7.05 (s, 1H), 3.07 (septet, J = 6.9 Hz, 1H), 2.45 (s, 3H), 1.34 (d, J = 6.9 Hz, 6H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 145.0, 140.0, 137.9, 132.1, 123.6, 122.7, 121.8, 119.2, 34.5, 24.6, 14.2 ppm. HRMS (FAB⁺): Calcd (M⁺) 190.0816; Found 190.0814.

(Table 2, entry 23): General procedure 1 was employed using 5-chloro-3-methyl-1-benzothiophene (91 mg, 0.5 mmol) and potassium iso-propyltrifluoroborate (112 mg, 0.75 mmol). A colorless liquid (run 1: 93 mg, 98%; run 2: 95 mg, 99%) was isolated by column chromatography (99.8:0.2 Hex/ether).

5-(sec-Butyl)-3-methyl-1-benzothiophene (Table 2, entry 22). General procedure 1 was employed using 5-chloro-3-methyl-1-benzothiophene (91 mg, 0.5 mmol) and sec-butylboronic acid (77 mg, 0.75 mmol). A colorless liquid (run 1: 92 mg, 90%; run 2: 91 mg, 89%) was isolated by column chromatography (99.8:0.2 Hex/ether). ¹H NMR (500 MHz, CDCl₃): δ 7.77 (d, J = 8.2 Hz, 1H), 7.50 (s, 1H), 7.21 (dd, J = 8.3, 1.5 Hz, 1H),
7.05 (s, 1H), 2.74 (m, 1H), 2.44 (s, 3H), 1.68 (m, 2H), 1.32 (d, J = 6.9 Hz, 3H), 0.85 (d, J = 7.4 Hz, 3H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ 143.8, 140.0, 138.0, 132.1, 123.9, 122.7, 121.7, 120.0, 42.1, 31.7, 22.6, 14.2, 12.6 ppm. HRMS (FAB$^+$): Calcd (M$^+$) 204.0973; Found 204.0982.

(Table 2, entry 24). General procedure 1 was employed using 5-chloro-3-methyl-1-benzothiophene (91 mg, 0.5 mmol) and potassium sec-butyltrifluoroborate (123 mg, 0.75 mmol). A colorless liquid (run 1: 96 mg, 94%, run 2: 101 mg, 99%) was isolated by column chromatography (99.8:0.2 Hex/ether). (Figure 3, row 1, column 1). General procedure 1 was employed using ($R$)-sec-butyltrifluoroborate. Optical rotation of product: $[\alpha]_{D}^{20}$ (c 1.00, CHCl$_3$) = +24.5º.

6-Isopropylquinoline$^{11}$ (Table 2, entry 25). General procedure 1 was employed using 6-chloroquinoline (82 mg, 0.5 mmol) and iso-propylboronic acid (66 mg, 0.75 mmol). A yellow liquid (run 1: 70 mg, 82%; run 2: 69 mg, 81%) was isolated by column chromatography (80:20 Hex/ether). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.86 (dd, J = 4.2, 2.0 Hz, 1H), 8.11 (d, J = 8.6 Hz, 1H), 8.04 (d, J = 8.6 Hz, 1H), 7.63 (dd, J = 8.7, 1.8 Hz, 1H), 7.60 (s, 1H), 7.35 (dd, J = 8.3, 4.2 Hz, 1H), 3.11 (septet, J = 6.9 Hz, 1H), 1.34 (d, J = 6.9 Hz, 6H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ 149.6, 147.18, 147.17, 135.8, 129.5, 129.3, 128.4, 123.9, 121.1, 34.1, 23.9 ppm.

(Table 2, entry 27): General procedure 1 was employed using 6-chloroquinoline (82 mg, 0.5 mmol) and potassium iso-propyltrifluoroborate (112 mg, 0.75 mmol). A yellow liquid (run 1: 70 mg, 82%; run 2: 65 mg, 75%) was isolated by column chromatography (80:20 Hex/ether).

6-sec-Butylquinoline$^{12}$ (Table 2, entry 26). General procedure 1 was employed using 6-chloroquinoline (82 mg, 0.5 mmol) and sec-butylboronic acid (77 mg, 0.75 mmol). A yellow liquid (run 1: 77 mg, 83%; run 2: 71 mg, 76%) was isolated by column chromatography (85:15 Hex/ether to 80:20 Hex/ether gradient). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.86 (dd, J = 4.1, 1.6 Hz, 1H), 8.11 (d, J = 8.3 Hz, 1H), 8.04 (d, J = 8.6 Hz, 1H), 7.59 (m, 2H), 7.37 (dd, J = 8.3, 4.2 Hz, 1H), 2.80 (m, 1H), 1.70 (m, 2H), 1.33 (d, J = 6.9 Hz, 3H), 0.85 (d, J = 7.4 Hz, 3H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ 149.7, 147.3, 146.0, 135.8, 129.6, 129.3, 128.4, 123.9, 121.1, 41.7, 31.1, 21.9, 12.4 ppm.

(Table 2, entry 28): General procedure 1 was employed using 6-chloroquinoline (82 mg, 0.5 mmol) and potassium sec-butyltrifluoroborate (123 mg, 0.75 mmol). A yellow liquid
(run 1: 70 mg, 76%; run 2: 63 mg, 74%) was isolated by column chromatography (85:15 Hex/ether to 80:20 Hex/ether gradient).

tert-Butyl 6-isopropyl-1H-indole-1-carboxylate (Table 2, entry 29). General procedure 1 was employed using 1-(tert-butoxycarbonyl)-6-chloroindole (126 mg, 0.5 mmol) and iso-propylboronic acid (66 mg, 0.75 mmol). A colorless liquid (run 1: 110 mg, 85%; run 2: 113 mg, 87%) was isolated by column chromatography (98:2 Hex/ether). Peaks of major rotamer given: \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.06 (br s, 1H), 7.53 (br s, 1H), 7.47 (d, \(J = 8.0\) Hz, 1H), 7.12 (d, \(J = 8.0, 1.1\) Hz, 1H), 6.52 (d, \(J = 3.6\) Hz, 1H), 3.04 (septet, \(J = 6.9\) Hz, 1H), 1.68 (s, 9H), 1.32 (d, \(J = 6.9\) Hz, 6H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 150.1, 145.7, 128.8, 126.0, 121.9, 120.8, 112.9, 107.3, 83.6, 34.8, 28.4, 24.7 ppm. HRMS (FAB\(^+\)): Calcd (M\(^+\)) 259.1572; Found 259.1586.

(Table 2, entry 30): General procedure 1 was employed using 1-(tert-butoxycarbonyl)-6-chloroindole (126 mg, 0.5 mmol) and potassium iso-propyltrifluoroborate (112 mg, 0.75 mmol). A colorless liquid (run 1: 115 mg, 89%, run 2: 119 mg, 92%) was isolated by column chromatography (98:2 Hex/ether).

tert-Butyl 6-(sec-butyl)-1H-indole-1-carboxylate (Table 2, entry 30). General procedure 1 was employed using 1-(tert-butoxycarbonyl)-6-chloroindole (126 mg, 0.5 mmol) and sec-butylboronic acid (77 mg, 0.75 mmol). A colorless liquid (run 1: 125 mg, 92%; run 2: 121 mg, 89%) was isolated by column chromatography (98:2 Hex/ether). Peaks of major rotamer given: \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 8.01 (br s, 1H), 7.52 (br s, 1H), 7.46 (d, \(J = 8.0\) Hz, 1H), 7.07 (dd, \(J = 8.0, 1.2\) Hz, 1H), 6.52 (d, \(J = 3.6\) Hz, 1H), 2.72 (app. sextet, \(J = 7.0\) Hz, 1H), 1.66 (s, 9H), 1.65 (m, 2H), 1.29 (d, \(J = 6.9\) Hz, 3H), 0.84 (t, \(J = 7.4\) Hz, 3H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \(\delta\) 150.1, 144.5, 128.8, 125.5, 122.4, 120.7, 113.7, 107.3, 83.5, 43.4, 31.7, 28.4, 28.3, 22.6 ppm. HRMS (FAB\(^+\)): Calcd (M\(^+\)) 273.1729; Found 273.1740.

(Table 2, entry 32): General procedure 1 was employed using 1-(tert-butoxycarbonyl)-6-chloroindole (126 mg, 0.5 mmol) and potassium sec-butyltrifluoroborate (123 mg, 0.75 mmol). A colorless liquid (run 1: 126 mg, 93%; run 2: 122 mg, 89%; run 3: 133 mg, 97%) was isolated by column chromatography (98:2 Hex/ether).
3-Methyl-5-(4-phenylbutan-2-yl)benzo[b]thiophene (Table 3, entry 1). General procedure 2 was employed using 5-chloro-3-methyl-1-benzothiophene (91 mg, 0.5 mmol) and potassium (4-phenylbutan-2-yl)trifluoroborate (180 mg, 0.75 mmol). A pale yellow, waxy solid (run 1: 109 mg, 78%; run 2: 120 mg, 86%) was isolated by column chromatography (99:5:0.5 Hex/ether). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.79 (d, $J$ = 8.3 Hz, 1H), 7.51 (s, 1H), 7.27 (m, 2H), 7.23 (d, $J$ = 8.4 Hz, 1H), 7.17 (t, $J$ = 7.4 Hz, 1H), 7.14 (d, $J$ = 7.8 Hz, 2H), 7.07 (s, 1H), 2.87 (app. sextet, $J$ = 7.2 Hz, 1H), 2.53 (m, 2H), 2.44 (s, 3H), 1.99 (m, 2H), 1.34 (d, $J$ = 7.0 Hz, 3H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 143.4, 142.7, 140.1, 138.1, 132.2, 128.6, 128.5, 125.9, 123.9, 122.9, 121.9, 120.2 40.4, 39.9, 34.2, 23.3, 14.3 ppm. HRMS (FAB): Calcd (M$^+$) 280.1286; Found 280.1292.

2,4-Dimethyl-1-(4-phenylbutan-2-yl)benzene (Table 3, entry 2). General procedure 2 was employed using 1-chloro-2,4-dimethylbenzene (67 μL, 0.5 mmol) and potassium (4-phenylbutan-2-yl)trifluoroborate (180 mg, 0.75 mmol). A pale yellow liquid (run 1: 97 mg, 81%; run 2: 100 mg, 84%) was isolated by column chromatography (99:1 Hex/ether). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.27 (m, 2H), 7.17 (t, $J$ = 7.4 Hz, 1H), 7.14 (m, 3H), 7.02 (d, $J$ = 7.7 Hz, 1H), 6.97 (s, 1H), 2.95 (app. sextet, $J$ = 7.0 Hz, 1H), 2.55 (m, 2H), 2.30 (s, 3H), 2.22 (s, 3H), 1.94 (m, 1H), 1.88 (m, 1H), 1.22 (d, $J$ = 6.9 Hz, 3H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 142.8, 142.5, 135.5, 135.1, 131.3, 128.6, 128.5, 127.1, 125.8, 125.3, 39.5, 34.1, 33.8, 22.1, 21.1, 19.6 ppm. HRMS (FAB): Calcd (M$^+$) 238.1722; Found 238.1731.

Ethyl 4-(4-phenylbutan-2-yl)benzoate (Table 3, entry 3). General procedure 2 was employed using ethyl 4-chlorobenzoate (92 mg, 0.5 mmol) and potassium (4-phenylbutan-2-yl)trifluoroborate (180 mg, 0.75 mmol). A pale yellow liquid (run 1: 98 mg, 78%; run 2: 100 mg, 71%) was isolated by chromatography (98:2 Hex/ether). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.99 (d, $J$ = 8.3 Hz, 2H), 7.25-7.28 (m, 4H), 7.17 (t, $J$ = 7.4 Hz, 1H), 7.11 (d, $J$ = 7.5 Hz, 2H), 4.37 (q, $J$ = 7.1 Hz, 2H), 2.78 (m, 1H), 2.44-2.54 (m, 2H), 1.93 (m, 2H), 1.39 (t, $J$ = 7.1 Hz, 3H), 1.28 (d, $J$ = 7.0 Hz, 3H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 166.8, 152.8, 142.3, 129.96, 129.95, 128.50, 128.49, 127.3, 125.9, 61.0, 39.9, 39.7, 34.0, 22.4, 14.6 ppm. HRMS (FAB): Calcd (M+H$^+$) 283.1698; Found 283.1691.
**tert-Butyl 6-(4-phenylbutan-2-yl)-1H-indole-1-carboxylate** (Table 3, entry 4). General procedure 2 was employed using 1-((tert-butoxycarbonyl)-6-chloroindole (126 mg, 0.5 mmol) and potassium (4-phenylbutan-2-yl)trifluoroborate (180 mg, 0.75 mmol). A colorless liquid (run 1: 103 mg, 59%; run 2: 95 mg, 55%) was isolated by column chromatography (97:3 Hex/ether). Peaks of major rotamer given: $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.04 (br s, 1H), 7.54 (br s, 1H), 7.49 (d, $J$ = 8.0 Hz, 1H), 7.26 (m, 2H), 7.16 (m, 3H), 7.10 (dd, $J$ = 8.0, 1.2 Hz, 1H), 6.53 (d, $J$ = 3.6 Hz, 1H), 2.85 (m, 1H), 2.53 (m, 2H), 1.97 (m, 2H), 1.67 (s, 9H), 1.33 (d, $J$ = 7.0 Hz, 3H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$), $\delta$ 150.0, 144.0, 142.8, 128.9, 128.6, 128.4, 125.8, 125.6, 122.3, 120.9, 113.7, 107.3, 83.55, 40.6, 40.2, 34.2, 28.4, 23.2 ppm. HRMS (FAB$^+$): Calcd (M$^{+}$) 349.2042; Found 349.2038.

**2-Methyl-8-(4-phenylbutan-2-yl)quinolone** (Table 3, entry 5). General procedure 2 was employed using 8-chloro-2-methylquinoline (89 mg, 0.50 mmol) and potassium (4-phenylbutan-2-yl)trifluoroborate (180 mg, 0.75 mmol). A light brown liquid (run 1: 74 mg, 54%; run 2: 65 mg, 48%) was isolated by column chromatography (96:4 Hex/ether). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.06 (d, $J$ = 8.4 Hz, 1H), 7.66 (m, 2H), 7.52 (t, $J$ = 7.6 Hz, 1H), 7.33 (m, 2H), 7.24 (m, 3H), 4.47 (app. sextet, $J$ = 7.0 Hz, 1H), 2.81 (s, 3H), 2.73 (m, 1H), 2.61 (m, 1H), 2.23 (m, 1H), 2.08 (m, 1H), 1.48 (d, $J$ = 7.0 Hz, 3H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$), $\delta$ 157.7, 146.1, 145.6, 143.3, 136.5, 128.6, 128.3, 125.8, 125.6, 125.64, 125.6, 125.5, 121.7, 40.2, 34.3, 32.0, 25.9, 22.0 ppm. HRMS (FAB$^+$): Calcd (M$^{+}$H$^+$) 276.1752; Found 276.1753.

**Ethyl 4-(1-phenylpropan-2-yl)benzoate** (Table 3, entry 6). General procedure 2 was employed using ethyl 4-chlorobenzoate (92 mg, 0.5 mmol) and potassium (1-phenylpropan-2-yl)trifluoroborate (170 mg, 0.75 mmol). A colorless liquid (run 1: 86 mg, 64%; run 2: 88 mg, 66%) was isolated by column chromatography (98:2 Hex/ether). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.94 (d, $J$ = 8.2 Hz, 2H), 7.22 (m, 4H) 7.17 (t, $J$ = 7.2 Hz,
1H), 7.04 (d, J = 7.5 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 3.06 (m, 1H), 2.91 (dd, J = 13.4 Hz, 7.0 Hz, 1H), 2.81 (dd, J = 13.4 Hz, 7.8 Hz, 1H), 1.38 (t, J = 7.1 Hz, 3H), 1.27 (d, J = 7.0 Hz, 3H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$), δ 166.8, 152.3, 140.3, 129.8, 129.2, 128.5, 128.3, 127.2, 126.1, 60.9, 44.9, 42.2, 21.2, 14.5 ppm. HRMS (FAB$^+$): Calcd (M+H$^+$) 269.1541; Found 269.1532.

1-Cyclopropyl-4-nitrobenzene$^{13}$ (Table 3, entry 7). General procedure 1 was employed using 1-chloro-4-nitrobenzene (79 mg, 0.5 mmol) and potassium cyclopropyltrifluoroborate (111 mg, 0.75 mmol). A yellow oil (run 1: 77 mg, 95%; run 2: 78 mg, 96%) was isolated by column chromatography (98:2 Hex/ether). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.09 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.8 Hz, 2H), 1.98 (m, 1H), 1.12 (m, 2H), 0.81 (m, 2H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ 152.9, 145.8, 126.0, 123.8, 16.0, 11.4 ppm.

1-(4-cyclobutylphenyl)-1H-pyrrole$^{14}$ (Table 3, entry 8). General procedure 1 was employed using 1-(4-chlorophenyl)-1H-pyrrole (89 mg, 0.5 mmol) and potassium cyclobutyltrifluoroborate (122 mg, 0.75 mmol). An off-white solid (run 1: 82 mg, 84%; run 2: 87 mg, 88%) was isolated by column chromatography (98:2 Hex/ether). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.31 (s, 2H), 7.27 (s, 2H), 7.07 (s, 2H), 6.34 (s, 2H), 3.56 (quintet, J = 8.6 Hz, 1H), 2.36 (m, 2H), 2.15 (m, 2H), 2.05 (dt, J = 19.6, 9.1 Hz, 1H), 1.87 (dd, J = 19.4, 8.8 Hz, 1H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ 144.0, 138.8, 127.5, 120.7, 119.6, 110.2, 40.0, 30.1, 18.4 ppm.

6-Cyclopentylquinoline (Table 3, entry 9). General procedure 1 was employed using 6-chloroquinoline (82 mg, 0.5 mmol) and potassium cyclopentyltrifluoroborate (132 mg, 0.75 mmol). A slightly brown liquid (run 1: 86 mg, 87%; run 2: 86 mg, 87%) was isolated by column chromatography (70:30 Hex/ether). $^1$H NMR (500 MHz, CDCl$_3$): δ 8.81 (dd, J = 4.1, 1.4 Hz, 1H), 8.03 (d, J = 8.0, 1H), 8.02 (d, J = 8.6, 1H), 7.59 (d, J = 8.7 Hz, 1H), 7.57 (s, 1H), 7.29 (dd, J = 8.2, 4.2 Hz, 1H), 3.12 (m, 1H), 2.09-2.11 (m, 2H), 1.80-1.82 (m, 2H), 1.64-1.70 (m, 4H) ppm. $^{13}$C NMR (125 MHz, CDCl$_3$): δ 149.6, 147.2,
144.9, 135.7, 129.9, 129.2, 128.3, 124.6, 121.1, 45.9, 34.6, 25.6 ppm. HRMS (FAB+): Calcd (M+H\(^+\)) 198.1283; Found 198.1287.

MeO
\(-\)
\(\text{Cyclohexyl-3-methoxybenzene}\)\(^{15}\) (Table 3, entry 10). General procedure 1 was employed using 3-chloroanisole (71 mg, 0.5 mmol) and potassium cyclohexyltrifluoroborate (143 mg, 0.75 mmol). A pale yellow oil (run 1: 81 mg, 85%; run 2: 90 mg, 95%) was isolated by column chromatography (99:1-97:3 gradient of Hex/ether). \(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 7.21 (t, \(J = 7.9\) Hz, 1H), 6.81 (d, \(J = 7.5\) Hz, 1H), 6.76 (s, 1H), 6.72 (d, \(J = 8.2\) Hz, 1H), 3.80 (s, 3H), 2.48 (m, 1H), 1.72-1.87 (m, 5H), 1.40 (m, 5H) ppm. \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): δ 159.8, 150.0, 129.4, 119.5, 113.0, 111.0, 55.3, 44.9, 34.6, 27.1, 26.4 ppm.

References

1) Bruno, N. C.; Tudge, M. T.; Buchwald, S. L. Chem. Sci. 2013, 4, 916.
2) (a) Joshi N. N.; Pyun, C.; Mahindroo, V.; Singaram, B.; Brown, H. C. J. Org. Chem. 1992, 57, 504. (b) Matteson, D. S. Tetrahedron 1998, 54, 10555.
3) (a) Dudnik, A. S.; Fu, G. C. J. Am. Chem. Soc. 2012, 134, 10693. (b) Gonzalez-Bobes, F.; Fu, G. C. J. Am. Chem. Soc. 2006, 128, 5360.
4) Lennox, A. J. J.; Lloyd-Jones, G. C. Angew. Chem. Int. Ed. 2012, 51, 9385.
5) Joshi-Pangu, A.; Ganesh, M.; Biscoe, M. R. Org. Lett. 2011, 13, 1218.
6) Jacoway, J.; Kumar, G. G. K. S. N.; Laali, K. K. Tetrahedron Lett. 2012, 53, 6782.
7) Laszlo, P.; Vandormael, J. Chem. Lett. 1988, 1843.
8) Johnson, F.; Subramanian, R. J. Org. Chem. 1986, 51, 5040.
9) Kumar, V. G.; Shoba, T. S.; Rao, K. V. C. Tetrahedron Lett. 1985, 26, 3281.
10) Nitta, Y.; Arakawa, Y.; Ueyama, N. Chem. Pharm. Bull. 1986, 34, 2710.
11) Li, L.; Wang, C.-Y.; Huang, R.; Biscoe, M. R. Nature Chem. 2013, 5, 607.
12) Cho, C. S.; Oh, B. H.; Shim, S. C. J. Heterocyclic Chem. 1999, 36, 1175.
13) Crist, D. R.; Jordan, G. J.; Moore, D. W.; Hashmall, J. A.; Borsetti, A. P.; Saleh, A. J. Am. Chem. Soc. 1983, 105, 4136.
14) Molander, G. A.; Gormisky, P. E. J. Org. Chem. 2008, 73, 7481.
15) Guo, X.; Li, C.-J. Org. Lett. 2011, 13, 4977.
MeOH (R) from oxdn. of 98% ee

Sigma-Aldrich

MeOH Me (R)

BF₃·K (R) from oxdn. of 98% ee

Sigma-Aldrich
Me

Me

(95% ee) Me

Me

(98% ee) Me

Me

Me

(S) Me

(R) Me

BF$_3$K

t from

min

100 110 120 130

1000 750 500 250 0

Peak

Ret.Time

Height

Area

Area%

1
117.310
760
41740
50.44

2
119.057
719
41012
49.56

Total

62752
100.00

Peak

Ret.Time

Height

Area

Area%

1
116.893
3575
225175
97.86

2
119.072
105
4914
2.14

Total

230089
100.00
Chromatographic Conditions for the Separation of the Enantiomers of MRB-4-phenyl-2-butanol on CHIRAPAK IB-3

- **Column**: CHIRALPAK IB-3 (150 x 4.6 mm i.d., 3 micron) Part # 81524
- **Mobile Phase**: Hexane/Isopropanol 95:5
- **Flow Rate**: 1.0 mL/min
- **Detection**: UV, 210 nm; ref 600 nm
- **Temperature**: 25°C
- **Sample**: ca. 2.0 mg/mL in mobile phase
- **Inject. Volume**: 3.0 microL
Chiralcel OJ-RH (150 x 4.6 mm i.d., 5 micron)

Mobile Phase
Acetonitrile/Water 60:40
Chromatographic Conditions for the Separation of the Enantiomers of MRB-Phen-Thio on CHIRACEL OJ-3

| Parameter          | Specification                           |
|--------------------|-----------------------------------------|
| **Column**         | CHIRALCEL OJ-3 (150 x 4.6 mm i.d., 3 micron) Part # 17524 |
| **Mobile Phase**   | Hexane/ Isopropanol 95:5                |
| **Flow Rate**      | 0.5 mL/min                              |
| **Detection**      | UV, 254 nm; ref 600 nm                   |
| **Temperature**    | 25°C                                    |
| **Sample**         | ca. 2.0 mg /mL in mobile phase          |
| **Inject. Volume** | 5.0 microL                              |
### Chromatographic Conditions for the Separation of the Enantiomers of MRB-Phen-Indole on CHIRAPAK OJ-3

| Column       | Two of CHIRALPAK OJ-3 (150 x 4.6 mm i.d., 3 micron) Part # 17524 |
|--------------|------------------------------------------------------------------|
| Mobile Phase | Hexane / Ethanol 95:5                                             |
| Flow Rate    | 0.6 mL/min                                                       |
| Detection    | UV, 230 nm; ref 600 nm                                            |
| Temperature  | 25°C                                                             |
| Sample       | ca. 2.0 mg/mL in Mobile Phase                                     |
| Inject. Volume | 2.0 microL                                                       |
Chromatographic Conditions for the Separation of the Enantiomers of MRB-Phen-2-Quin on CHIRAPAK OJ-3

| Column                  | CHIRALPAK OJ-3 (150 x 4.6 mm i.d., 3 micron) Part # 17524 |
|-------------------------|----------------------------------------------------------|
| Mobile Phase            | Hexane / Ethanol 95:5                                     |
| Flow Rate               | 0.6 mL/min                                               |
| Detection               | UV, 254 nm; ref 600 nm                                    |
| Temperature             | 25°C                                                     |
| Sample                  | ca. 2.0 mg/mL in Mobile Phase                            |
| Inject. Volume          | 2.0 microL                                               |
Me $\text{H} - \text{BF}_3\text{K}$

(R) 98% ee in acetone-\text{d}_6
BF$_3$·K$_2$Me in acetone-d$_6$
Table 2, entry 13
Table 2, entry 13
Table 2, entry 21
Table 2, entry 21
Table 2, entry 22
Table 2, entry 29
Table 2, entry 29
Table 2, entry 30
Table 2, entry 30

![Chemical Structure Image]
Table 3, entry 1
Table 3, entry 2
Table 3, entry 2

Me

Me

Ph

Me
Table 3, entry 3
Table 3, entry 3
Table 3, entry 4
Table 3, entry 5
Table 3, entry 6
Table 3, entry 6
Table 3, entry 9
Table 3, entry 9