New Directing Groups
for Metal-Catalyzed Asymmetric Carbon–Carbon Bond-Forming Processes:
Stereoconvergent Alkyl–Alkyl Suzuki Cross-Couplings of Unactivated Electrophiles

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Supporting Information

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I. General

The following reagents were purchased and used as received: 9-BBN dimer (Aldrich), NiBr₂·diglyme (Aldrich; somewhat hygroscopic), diamine ligands (Aldrich), KO-t-Bu (Acros or Strem), n-hexanol (Aldrich; anhydrous), i-BuOH (Aldrich; anhydrous), and i-Pr₂O (Aldrich; anhydrous). Unless otherwise noted, reactions were conducted with stirring in oven-dried glassware under an inert atmosphere. All NMR spectra were recorded on a 400 MHz spectrometer.

II. Preparation of Materials

These procedures have not been optimized.
Representative Procedure A (synthesis of dialkylamines).\textsuperscript{1} Calcium trifluoromethanesulfonate (30 mmol, 0.5 equiv) was added to a solution of the epoxide (60 mmol) and amine (60 mmol) in acetonitrile (150 mL) at 0 °C. The resulting mixture was stirred at room temperature overnight, and then the acetonitrile was removed by rotary evaporation. Water (50 ml) was added to the residue, and the mixture was extracted with CH$_2$Cl$_2$ (3 x 50 ml). The combined organic extracts were dried over MgSO$_4$ and then concentrated. The amino alcohol can be used without purification, or it can be purified by column chromatography.

Representative Procedure B (synthesis of carbamate-containing electrophiles). Dry Et$_2$O (180 mL) and 2,6-lutidine (20 mmol) were added to a dry flask charged with the secondary amine (18 mmol). The reaction mixture was cooled to −78 °C, and then the chloroformate (18 mmol) was added. The mixture was allowed to warm to room temperature, and it was stirred overnight. Next, the reaction was quenched by the addition of aqueous HCl (1 M; 70 mL). The organic layer was separated, dried over MgSO$_4$, and then concentrated. The product was purified by column chromatography.

Representative Procedure C (synthesis of sulfonamide-containing electrophiles). Dry CH$_2$Cl$_2$ (18 mL) and 2,6-lutidine (3.95 mmol) were added to a dry flask was charged with the secondary amine (3.59 mmol). The reaction mixture was cooled to 0 °C, and then the sulfonyl chloride (3.59 mmol) was added. The mixture was allowed to warm to room temperature, and it was stirred overnight. Next, the reaction was quenched by the addition of aqueous HCl (1 M; 10 mL). The organic layer was separated, dried over MgSO$_4$, and then concentrated. The product was purified by column chromatography.

Representative Procedure D (synthesis of alkyl bromides). Dry CH₂Cl₂ (25 mL) and imidazole (2.1 mmol) were added to a dry flask charged with the alcohol (1.9 mmol). The reaction mixture was cooled to 0 °C, and then PPh₃Br₂ (2.1 mmol) was added. The mixture was allowed to warm to room temperature, and it was stirred overnight. Next, the reaction was quenched by the addition of water (15 mL). The organic layer was separated, dried over MgSO₄, and then concentrated. The product was purified by column chromatography.

Representative Procedure E (synthesis of alkyl chlorides). PPh₃ (4.0 mmol) and NCS (4.0 mmol) were added in turn to a stirred solution of the alcohol (3.6 mmol) in dry CH₂Cl₂ (20 mL) at 0 °C. The mixture was allowed to warm to room temperature, and it was stirred overnight. Next, the reaction was quenched by the addition of water (10 mL). The organic layer was separated, dried over MgSO₄, and then concentrated. The product was purified by column chromatography.

Representative Procedure F (synthesis of arylamines). Triethylamine (4.2 mL, 30 mmol) and the α-bromo acid bromide (20 mmol) were added dropwise in turn to a solution of the aniline (20 mmol) in CH₂Cl₂ (150 mL) at 0 °C. The mixture was allowed to warm to room temperature, and it was stirred for 2 h. Next, aqueous HCl (1 M; 50 mL) was added. The organic layer was separated, washed with water (50 mL) and brine (50 mL), dried over MgSO₄, filtered, and concentrated. The material may be used without purification in the next step.

Representative procedure G (synthesis of arylamines). Borane–THF (1.0 M; 1.0 equiv) was added dropwise to a solution of the amide in dry THF (100 mL). After the addition was complete, the solution was heated at 50 °C for 18 h. Next, it was allowed to cool to room temperature, and then the reaction was quenched by the addition of water (10 mL). The THF
was removed by rotary evaporation, and the resulting mixture was diluted with \( \text{Et}_2\text{O} \) (100 mL). The organic layer was separated, washed with water (100 mL) and brine (100 mL), dried over MgSO\(_4\), filtered, and concentrated. The material may be used without purification in the next step.

The arylamines were protected via reaction with chloroformates or sulfonyl chlorides, following Representative Procedures B and C.

![Diagram of halo sulfones reaction]

**Preparation of halo sulfones**: The alcohols were prepared according to a literature procedure,\(^2\) and they were converted to the bromide/chloride as described above.

**Phenyl 2-hydroxybutyl(4-methoxybenzyl)carbamate**. The title compound was synthesized from phenyl 2-hydroxybutyl(4-methoxybenzyl)carbamate (1.00 g, 3.0 mmol) and triphenylphosphine dibromide (1.40 g, 3.3 mmol). Purification by chromatography (5% → 100% \( \text{Et}_2\text{O}/\text{hexanes} \)) yielded 0.87 g (74%) of a colorless oil.

\(^1\)H NMR (CDCl\(_3\)) \( \delta \) 7.38–7.33 (m, 2H), 7.26–7.18 (m, 3H), 7.13–7.09 (m, 2H), 6.90–6.86 (m, 2H), 4.88–4.60 (m, 2H), 4.35–4.17 (m, 1H), 3.80 (s, 3H), 3.69–3.38 (m, 2H), 1.93–1.70 (m, 2H), 1.04 (t, 3H, \( J = 7.2 \) Hz).

\(^13\)C NMR (CDCl\(_3\)) \( \delta \) 159.1, 155.0, 151.2, 129.6, 129.3, 128.7, 125.4, 121.6, 114.13, 114.08, 56.03, 55.56, 55.3, 54.2, 52.8, 51.8, 51.0, 29.5, 29.2, 12.0, 11.9 [mixture of rotamers].

FT-IR (film) 3018, 2936, 2838, 1717, 1613, 1513, 1457, 1409, 1203, 1114, 1035, 754, 668 cm\(^{-1}\).

MS (ESI) [M+H]\(^+\) calcd for C\(_{19}\)H\(_{23}\)BrNO\(_3\): 392.0856, found: 392.0850.

**Phenyl 2-bromohexyl(butyl)carbamate**. The title compound was synthesized from phenyl butyl(2-hydroxyhexyl)carbamate (1.00 g, 3.4 mmol) and triphenylphosphine dibromide (1.58 g, 3.3 mmol). Purification by chromatography (5% → 100% \( \text{Et}_2\text{O}/\text{hexanes} \)) yielded 0.87 g (74%) of a colorless oil.

\(^1\)H NMR (CDCl\(_3\)) \( \delta \) 7.38–7.33 (m, 2H), 7.26–7.18 (m, 3H), 7.13–7.09 (m, 2H), 6.90–6.86 (m, 2H), 4.88–4.60 (m, 2H), 4.35–4.17 (m, 1H), 3.80 (s, 3H), 3.69–3.38 (m, 2H), 1.93–1.70 (m, 2H), 1.04 (t, 3H, \( J = 7.2 \) Hz).

\(^13\)C NMR (CDCl\(_3\)) \( \delta \) 159.1, 155.0, 151.2, 129.6, 129.3, 128.7, 125.4, 121.6, 114.13, 114.08, 56.03, 55.56, 55.3, 54.2, 52.8, 51.8, 51.0, 29.5, 29.2, 12.0, 11.9 [mixture of rotamers].

FT-IR (film) 3018, 2936, 2838, 1717, 1613, 1513, 1457, 1409, 1203, 1114, 1035, 754, 668 cm\(^{-1}\).

MS (ESI) [M+H]\(^+\) calcd for C\(_{19}\)H\(_{23}\)BrNO\(_3\): 392.0856, found: 392.0850.

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3.7 mmol). Purification by chromatography (5% → 100% Et₂O/hexanes) yielded 0.88 g (73%) of a colorless oil.

1H NMR (CDCl₃) δ 7.36–7.33 (m, 2H), 7.20–7.18 (m, 1H), 7.10–7.08 (m, 2H), 4.39–4.23 (m, 1H), 3.83–3.58 (m, 2H), 3.45–3.37 (m, 2H), 1.94–1.73 (m, 2H), 1.67–1.55 (m, 3H), 1.46–1.26 (m, 5H), 0.97–0.87 (m, 6H).

13C NMR (CDCl₃) δ 153.1, 151.3, 129.3, 125.3, 121.6, 55.4, 54.3, 54.0, 49.2, 48.7, 36.0, 35.8, 30.8, 29.6, 29.5, 22.1, 20.0, 13.9 [mixture of rotamers].

FT-IR (film) 3018, 2958, 2931, 1717, 1684, 1653, 1559, 1457, 1419, 1206, 755, 668 cm⁻¹.

MS (ESI) [M+H]+ calcd for C₁₇H₂₇BrNO₂: 356.1220, found: 356.1217.

Phenyl 2-bromo-3-cyclohexylpropyl(methyl)carbamate. The title compound was synthesized from phenyl 3-cyclohexyl-2-hydroxypropyl(methyl)carbamate (1.50 g, 5.1 mmol) and triphenylphosphine dibromide (2.40 g, 5.7 mmol). Purification by chromatography (5% → 100% Et₂O/hexanes) yielded 1.29 g (72%) of a yellow solid.

Mp: 60–62 °C.

1H NMR (CDCl₃) δ 7.37–7.33 (m, 4H), 7.20–7.17 (m, 2H), 7.12–7.07 (m, 4H), 4.46–4.35 (m, 2H), 3.87–3.72 (m, 3H), 3.43–3.38 (m, 1H), 3.20 (s, 3H), 3.07 (s, 3H), 1.76–1.73 (m, 16H), 1.27–1.11 (m, 16H), 1.00–0.95 (m, 2H), 0.81–0.79 (m, 2H) [~1:1 mixture of rotamers].

13C NMR (CDCl₃) δ 155.0, 154.5, 151.3, 151.2, 129.31, 129.26, 125.4, 125.3, 121.7, 121.6, 57.5, 56.6, 51.8, 51.1, 43.8, 43.6, 36.9, 36.2, 35.5, 35.4, 33.8, 33.6, 31.9, 31.7, 26.4, 26.1, 25.9 [mixture of rotamers].

FT-IR (film) 2922, 2851, 1723, 1594, 1495, 1394, 1205, 1131, 855, 750, 690 cm⁻¹.


Phenyl 2-bromobutyl(phenyl)carbamate. The title compound was synthesized from N-(2-bromobutyl)aniline (0.70 g, 2.2 mmol) and phenyl chloroformate (0.30 mL, 2.2 mmol). Purification by chromatography (0% → 50% Et₂O/hexanes) yielded 0.83 g (77%) of a clear oil.

1H NMR (CDCl₃) δ 7.43–7.30 (m, 7H), 7.18–7.07 (m, 3H), 4.09–4.06 (m, 3H), 1.91–1.84 (m, 1H), 1.82–1.74 (m, 1H), 1.04 (t, 3H, J = 7.6 Hz).

13C NMR (CDCl₃) δ 151.1, 129.2, 127.4, 125.4, 121.5, 65.8, 54.8, 31.5, 28.9, 22.6, 15.2, 14.1, 11.8.

FT-IR (film) 3064, 2969, 2936, 1725, 1596, 1495, 1456, 1390, 1325, 1294, 1206, 1164, 1137, 1072, 1025, 1004, 988, 925, 748, 699 cm⁻¹.
**Benzyl 2-bromobutyl(phenyl)carbamate.** The title compound was synthesized from N-(2-bromobutyl)aniline (1.40 g, 6.1 mmol) and benzyl chloroformate (0.90 mL, 6.1 mmol). Purification by chromatography (5%→100% Et₂O/hexanes) yielded 1.40 g (64%) of a colorless oil.

¹H NMR (CDCl₃) δ 7.38–7.24 (m, 10H), 5.16 (d, 2H, J = 18.4 Hz), 4.13–3.95 (m, 3H), 1.93–1.67 (m, 2H), 1.00 (t, 3H, J = 7.2 Hz).

¹³C NMR (CDCl₃) δ 155.4, 141.1, 136.3, 129.0, 128.3, 127.8, 127.4, 127.0, 67.3, 56.3, 55.0, 28.8, 11.7.

FT-IR (film) 3019, 2945, 2930, 2338, 1700, 1598, 1495, 1405, 1215, 757, 698, 668 cm⁻¹.


**S-(1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 2-bromopropyl(phenyl)carbamate.** The title compound was synthesized from N-(2-bromobutyl)aniline (1.34 g, 6.1 mmol) and (S)-menthyl chloroformate (97% ee; 1.33 mL, 6.1 mmol). Purification by chromatography (5%→100% Et₂O/hexanes) yielded 2.18 g (88%) of a light-yellow oil.

¹H NMR (CDCl₃) δ 7.36–7.32 (m, 2H), 7.25–7.20 (m, 3H), 4.58 (br s, 1H), 4.12–3.86 (m, 3H), 2.04 (br s, 1H), 1.79–1.44 (m, 7H), 1.02–0.73 (m, 13H) [mixture of diastereomers].

¹³C NMR (CDCl₃) δ 155.4, 141.5, 128.9, 127.5, 126.8, 76.1, 57.6, 47.0, 46.5, 46.4, 41.1, 34.2, 31.3, 26.29, 26.27, 23.4, 23.2, 22.0, 20.7, 16.4 [mixture of diastereomers].

FT-IR (film) 2956, 2870, 1703, 1598, 1496, 1454, 1397, 1276, 1196, 1148, 1013, 966, 836, 766, 699 cm⁻¹.

MS (ESI) [M+H]⁺ calcd for C₂₀H₃₁BrNO₂: 396.1533, found: 396.1553.
Phenyl butyl(2-chlorohexyl)carbamate. The title compound was synthesized from phenyl butyl(2-hydroxyhexyl)carbamate (1.00 g, 3.4 mmol) and NCS (0.50 g, 3.7 mmol). Purification by chromatography (5% → 100% Et₂O/hexanes) yielded 0.62 g (58%) of a colorless oil.

¹H NMR (CDCl₃) δ 7.37–7.33 (m, 2H), 7.20–7.16 (m, 1H), 7.10–7.08 (m, 2H), 4.29–4.15 (m, 1H), 3.78–3.23 (m, 4H), 1.87–1.26 (m, 10H), 0.97–0.87 (m, 6H).

¹³C NMR (CDCl₃) δ 155.0, 154.3, 151.3, 151.2, 129.2, 125.3, 121.6, 61.1, 61.0, 55.0, 53.9, 49.3, 48.8, 35.5, 35.4, 30.8, 28.4, 28.3, 22.2, 22.1, 20.0, 19.9, 13.9, 13.8 [mixture of rotamers].

FT-IR (film) 3018, 2958, 2936, 1717, 1653, 1595, 1496, 1465, 1413, 1206, 1163, 753, 690 cm⁻¹.

MS (ESI) [M+H]⁺ calcd for C₁₇H₂₇ClNO₂: 312.1725, found: 312.1712.

Phenyl 3-bromobutyl(butyl)carbamate. The title compound was synthesized from 4-(butylamino)butan-2-ol (2.00 g, 14 mmol). Purification by chromatography (5% → 100% Et₂O/hexanes) yielded 3.2 g (71% over 2 steps) of a light-yellow oil.

¹H NMR (CDCl₃) δ 7.36–7.32 (m, 2H), 7.17 (t, 1H, J = 7.4 Hz), 7.10–7.08 (m, 2H), 4.18–4.10 (m, 1H), 3.58–3.30 (m, 4H), 2.19–2.03 (m, 2H), 1.76–1.73 (m, 3H), 1.66–1.58 (m, 2H), 1.38–1.35 (m, 2H), 0.98–0.92 (m, 3H) [mixture of rotamers].

¹³C NMR (CDCl₃) δ 154.7, 151.3, 129.2, 125.1, 121.6, 48.6, 48.0, 46.7, 46.0, 40.0, 39.2, 30.9, 30.1, 26.6, 26.5, 19.9, 13.8 [mixture of rotamers].

FT-IR (film) 3044, 2959, 2873, 1722, 1595, 1496, 1469, 1417, 1379, 1297, 1206, 1139, 1069, 1025, 1002, 911, 854, 753, 691, 616, 499 cm⁻¹.

MS (ESI) [M+H]⁺ calcd for C₁₅H₂₃BrNO₂: 328.0907, found: 328.0928.

N-(2-Bromobutyl)-N-(4-methoxybenzyl)-4-methylbenzenesulfonamide. The title compound was synthesized from N-(2-hydroxybutyl)-N-(4-methoxybenzyl)-4-methylbenzenesulfonamide (1.40 g, 3.8 mmol) and triphenylphosphine dibromide (1.79 g, 4.2 mmol). Purification by chromatography (5% → 100% Et₂O/hexanes) yielded 1.03 g (63%) of a white solid.
$^1$H NMR (CDCl$_3$) δ 7.71 (d, 2H, $J = 8.4$ Hz), 7.31 (d, 2H, $J = 8.4$ Hz), 7.17 (d, 2H, $J = 8.4$ Hz), 6.82 (d, 2H, $J = 8.4$ Hz), 4.40–4.15 (m, 2H), 3.77 (s, 3H), 3.41–3.34 (m, 1H), 3.08–2.93 (m, 2H), 2.42 (s, 3H), 1.29–1.22 (m, 2H), 0.76 (t, 3H, $J = 7.6$ Hz).

$^{13}$C NMR (CDCl$_3$) δ 159.5, 143.6, 136.1, 129.9, 129.8, 129.7, 129.5, 127.7, 127.3, 127.2, 114.0, 55.6, 55.2, 54.8, 53.3, 28.4, 21.5, 11.8 [mixture of rotamers].

FT-IR (film) 3020, 2967, 2805, 1612, 1513, 1456, 1339, 1252, 1160, 1090, 904, 814, 755, 667, 658 cm$^{-1}$.

MS (ESI) [M+H]$^+$ calcd for C$_{19}$H$_{25}$BrNO$_3$S: 428.0733, found: 428.0701.

N-(2-Bromo-3-cyclohexylpropyl)-N-butyl-4-methylbenzenesulfonamide. The title compound was synthesized from N-butyl-N-(3-cyclohexyl-2-hydroxypropyl)-4-methylbenzenesulfonamide (2.9 g, 7.9 mmol) and triphenylphosphine dibromide (3.3 g, 8.7 mmol). Purification by chromatography (5%→100% Et$_2$O/hexanes) yielded 2.45 g (73%) of a light-yellow oil.

$^1$H NMR (CDCl$_3$) δ 7.67 (d, 4H, $J = 8.4$ Hz), 7.29 (d, 4H, $J = 8.0$ Hz), 4.26–4.19 (m, 2H), 3.70–3.69 (m, 1H), 3.54–3.42 (m, 2H), 3.32–3.27 (m, 2H), 3.21–3.13 (m, 2H), 3.07–3.00 (m, 2H), 2.40 (s, 3H), 2.39 (s, 3H), 1.82–0.86 (m, 39H) [~1:1 mixture of rotamers].

$^{13}$C NMR (CDCl$_3$) δ 143.4, 142.8, 141.2, 136.2, 129.7, 129.5, 127.3, 127.1, 121.9, 55.8, 51.7, 50.0, 35.5, 33.9, 32.6, 31.4, 30.6, 26.4, 26.2, 25.9, 25.8, 21.5, 19.9, 13.6 [mixture of rotamers].

FT-IR (film) 2925, 2852, 1599, 1494, 1449, 1342, 1305, 1222, 1160, 1120, 1091, 1030, 966, 922, 892, 866, 841, 815, 750, 728, 705, 657, 549 cm$^{-1}$.

MS (ESI) [M+H]$^+$ calcd for C$_{20}$H$_{33}$BrNO$_2$S: 432.1402, found: 432.1409.

N-(2-Bromoctyl)-N-butylmethanesulfonamide. The title compound was synthesized from N-butyl-N-(2-hydroxyoctyl)methanesulfonamide (3.70 g, 13.2 mmol) and triphenylphosphine dibromide (6.10 g, 14.5 mmol). Purification by chromatography (5%→100% Et$_2$O/hexanes) yielded 2.10 g (46%) of a colorless oil.

$^1$H NMR (CDCl$_3$) δ 4.17–4.10 (m, 1H), 3.57–3.38 (m, 2H), 3.32–3.10 (m, 2H) 2.87 (s, 3H), 1.95–1.87 (m, 1H), 1.72–1.24 (m, 13H), 0.93–0.83 (m, 6H).

$^{13}$C NMR (CDCl$_3$) δ 54.6, 54.2, 49.0, 39.0, 35.7, 31.5, 30.5, 28.5, 27.3, 22.5, 19.9, 14.0, 13.7.

FT-IR (film) 3020, 2953, 2932, 1653, 1559, 1457, 1335, 1216, 1148, 759, 668 cm$^{-1}$.

MS (ESI) [M+H]$^+$ calcd for C$_{13}$H$_{29}$BrNO$_2$S: 344.1097, found: 344.1068.
**N-(2-Bromobutyl)-N-phenylmethanesulfonylamide.** The title compound was synthesized from N-(2-bromobutyl)aniline (0.70 g, 3.1 mmol) and methanesulfonyl chloride (0.40 mL, 4.6 mmol). Purification by chromatography (5%→100% Et₂O/hexanes) yielded 0.193 g (20%) of a white solid.

Mp: 82–84 °C.

¹H NMR (CDCl₃) δ 7.43–7.33 (m, 5H), 4.07–4.02 (m, 1H), 3.95–3.80 (m, 2H), 2.91 (s, 3H), 2.04–1.96 (m, 1H), 1.76–1.67 (m, 1H), 0.99 (t, 3H, J = 7.2 Hz).

¹³C NMR (CDCl₃) δ 139.0, 129.7, 128.6, 128.5, 56.9, 54.9, 37.6, 28.3, 11.4.

FT-IR (film) 2971, 2935, 1595, 1493, 1455, 1342, 1222, 1192, 1155, 1070, 1027, 1005, 961, 879, 776, 697, 544, 522 cm⁻¹.


**N-(2-Chloroctyl)-N-butylmethanesulfonylamide.** The title compound was synthesized from N-butyl-N-(2-hydroxyoctyl)methanesulfonylamide (1.00 g, 3.6 mmol) and NCS (0.53 g, 4.0 mmol). Purification by chromatography (5%→100% Et₂O/hexanes) yielded 0.60 g (56%) of a colorless oil.

¹H NMR (CDCl₃) δ 4.09–4.03 (m, 1H), 3.49–3.28 (m, 4H), 2.87 (s, 3H), 1.75–1.63 (m, 1H), 1.51–1.25 (m, 13H), 0.90 (t, 3H, J = 7.2 Hz), 0.85 (t, 3H, J = 7.2 Hz).

¹³C NMR (CDCl₃) δ 61.0, 54.1, 48.9, 39.1, 35.5, 31.6, 30.5, 28.7, 26.1, 22.5, 19.9, 14.0, 13.7.

FT-IR (film) 3020, 2955, 2932, 1333, 1215, 1149, 758, 668 cm⁻¹.

MS (ESI) [M+H]⁺ calcd for C₁₃H₂₉ClNO₂S: 298.1602, found: 298.1606.

**N-(3-Bromobutyl)-N-butylmethanesulfonylamide.** The title compound was synthesized from 4-(N-butylmethylsulfonylamido)butan-2-yl methanesulfonate (2.42 g, 14 mmol) and LiBr (2.8 g, 32 mmol) in acetone. Purification by chromatography (0%→50% Et₂O/hexanes) yielded 1.72 g (61%) of a light-yellow oil.

¹H NMR (CDCl₃) δ 4.14–4.06 (m, 1H), 3.35–3.33 (m, 2H), 3.24–3.13 (m, 2H), 2.81 (s, 3H), 2.16–1.97 (m, 2H), 1.71 (d, 3H, J = 6.4 Hz), 1.62–1.53 (m, 2H), 1.36–1.27 (m, 2H), 0.91 (t, 3H, J = 7.4 Hz).

¹³C NMR (CDCl₃) δ 48.5, 48.1, 46.7, 40.5, 37.8, 30.7, 26.5, 19.8, 13.7.

FT-IR (film) 2960, 2933, 2873, 1458, 1379, 1332, 1241, 1203, 1147, 1047, 961, 928, 880, 774, 705, 520 cm⁻¹.
3-Bromo-N,N-dimethylpentane-1-sulfonamide. The title compound was synthesized from 3-hydroxy-N,N-dimethylpentane-1-sulfonamide (2.00 g, 10.2 mmol) and triphenylphosphate dibromide (4.80 g, 11.4 mmol). Purification by chromatography (30% → 50% Et<sub>2</sub>O/hexanes) yielded 2.16 g (82%) of a colorless oil.

1H NMR (CDCl<sub>3</sub>) δ 4.07–4.00 (m, 1H), 3.23–3.16 (m, 1H), 3.06–2.99 (m, 1H), 2.87 (s, 6H), 2.39–2.30 (m, 1H), 2.30–2.14 (m, 1H), 1.91–1.83 (m, 2H), 1.04 (t, 3H, J = 7.2 Hz).

13C NMR (CDCl<sub>3</sub>) δ 57.3, 46.5, 37.5, 32.3, 32.1, 12.0.

FT-IR (film) 2969, 1459, 1333, 1143, 959, 748, 709 cm<sup>–1</sup>.

MS (ESI) [M+Na]<sup>+</sup> calcd for C<sub>7</sub>H<sub>16</sub>BrNNaO<sub>2</sub>S: 281.9961, found: 281.9967.

3-Bromo-1-( tert-butylsulfonyl )pentane. The title compound was synthesized from 1-( tert-butylsulfonyl )pentan-3-ol (1.50 g, 7.2 mmol) and triphenylphosphate dibromide (3.3 g, 7.9 mmol). Purification by chromatography (10% → 100% EtOAc/hexanes) yielded 1.48 g (76%) of a colorless liquid.

1H NMR (CDCl<sub>3</sub>) δ 4.03–3.97 (m, 1H), 3.16–3.09 (m, 1H), 2.99–2.92 (m, 1H), 2.37–2.29 (m, 1H), 2.20–2.10 (m, 1H), 1.84–1.73 (m, 2H), 1.31 (s, 9H), 0.96 (t, 3H, J = 7.4 Hz).

13C NMR (CDCl<sub>3</sub>) δ 58.8, 57.6, 43.9, 32.1, 29.5, 23.1, 11.7.

FT-IR (film) 2972, 2878, 1464, 1398, 1366, 1294, 1211, 1116, 1050, 1019, 953, 903, 806, 755, 722, 664, 601, 536 cm<sup>–1</sup>.

MS (ESI) [M+Na]<sup>+</sup> calcd for C<sub>9</sub>H<sub>19</sub>BrNaO<sub>2</sub>S: 293.0181, found: 293.0198.

(3-Bromo-5-( tert-butylsulfonyl )pentyl)benzene. The title compound was synthesized from 1-( tert-butylsulfonyl )-5-phenylpentan-3-ol (1.5 g, 5.3 mmol) and triphenylphosphate dibromide.

(2.5 g, 5.8 mmol). Purification by chromatography (5%→100% Et₂O/hexanes) yielded 1.53 g (83%) of a white solid.

1H NMR (CDCl₃) δ 7.30–7.27 (m, 2H), 7.21–7.18 (m, 3H), 4.07–4.01 (m, 1H), 3.27–3.20 (m, 1H), 3.03–2.96 (m, 1H), 2.94–2.87 (m, 1H), 2.80–2.73 (m, 1H), 2.50–2.41 (m, 1H), 2.35–2.12 (m, 3H), 1.41 (s, 9H).

13C NMR (CDCl₃) δ 140.3, 128.6, 128.5, 126.3, 59.2, 55.1, 44.2, 40.8, 33.5, 30.1, 23.4.

FT-IR (film) 3062, 3027, 2939, 1603, 1496, 1455, 1398, 1366, 1287, 1205, 1115, 1017, 986, 806, 750, 722, 701, 665 cm⁻¹.


(2-Bromo-4-(isopropylsulfonyl)butyl)cyclohexane. The title compound was synthesized from 1-cyclohexyl-4-(isopropylsulfonyl)butan-2-ol (2.0 g, 7.6 mmol) and triphenylphosphine dibromide (3.5 g, 8.3 mmol). Purification by chromatography (5%→100% Et₂O/hexanes) yielded 1.44 g (56%) of a white solid.

1H NMR (CDCl₃) δ 4.20–4.14 (m, 1H), 3.28–3.21 (m, 1H), 3.15–3.00 (m, 2H), 2.45–2.36 (m, 1H), 2.23–2.13 (m, 1H), 1.85–1.78 (m, 1H), 1.74–1.54 (m, 7H), 1.39 (d, 6H, J = 6.8 Hz), 1.29–1.07 (m, 3H), 0.98–0.90 (m, 1H), 0.84–0.76 (m, 1H).

13C NMR (CDCl₃) δ 53.31, 53.28, 47.5, 46.8, 35.5, 33.4, 32.0, 30.9, 26.3, 26.0, 25.9, 15.5, 15.1.

FT-IR (film) 2924, 2852, 1448, 1308, 1231, 1169, 1122, 1052, 964, 879, 839, 758, 689 cm⁻¹.


1-(tert-Butylsulfonyl)-3-chloropentane. The title compound was synthesized from 1-(tert-butylsulfonyl)pentan-3-ol (1.50 g, 7.2 mmol), NCS (1.10 g, 8.2 mmol), and triphenylphosphine (2.10 g, 8.0 mmol). Purification by chromatography (5%→100% Et₂O/hexanes) yielded 1.24 g (75%) of a white solid.

Mp: 32–34 °C.

1H NMR (CDCl₃) δ 3.93–3.86 (m, 1H), 3.14–3.07 (m, 1H), 2.98–2.90 (m, 1H), 2.31–2.23 (m, 1H), 2.09–1.99 (m, 1H), 1.80–1.61 (m, 2H), 1.31 (s, 9H), 0.94 (t, 3H, J = 7.4 Hz).

13C NMR (CDCl₃) δ 63.5, 58.8, 42.8, 31.4, 28.9, 23.1, 10.6.

FT-IR (film) 2973, 2940, 2879, 1464, 1399, 1366, 1293, 1200, 1116, 1051, 1019, 958, 906, 860, 808, 756, 723, 666, 601, 544 cm⁻¹.

MS (ESI) [M+H]⁺ calcd for C₉H₁₅ClNaO₂S: 249.0686, found: 249.0698.
III. Stereoconvergent Suzuki Cross-Coupling Reactions

General Procedure (carbamates) (conducted in a glovebox; however, see the note below). The trialkylborane was prepared by adding 9-BBN dimer (2.28 g, 9.3 mmol), i-Pr$_2$O (5.0 mL), and the alkene (18.7 mmol) in turn to a 20-mL vial. The vial was capped and removed from the glovebox. The reaction mixture was stirred at 60 °C for 1.5 h, and then it was allowed to cool to r.t. The vial was taken back into the glovebox, and the reaction mixture was diluted with i-Pr$_2$O to furnish a 1.5 M solution. Next, a portion of this solution (0.67 mL, 1.00 mmol) was added to a solution of KOt-Bu (78 mg, 0.70 mmol) in n-hexanol (113 µL, 0.90 mmol) in a 4-mL vial. The resulting mixture was stirred at r.t. for 45 min.

A solution of NiBr$_2$•diglyme (17.6 mg, 0.050 mmol) and (1R,2R)-(+)N,N'-dimethyl-1,2-diphenyl-1,2-ethanediamine ((R,R)-DMPEDA; 14.7 mg, 0.061 mmol) in i-Pr$_2$O (2.5 mL) in a 20-mL vial was stirred at r.t. for 30 min. Next, a solution of the electrophile (0.50 mmol) in i-Pr$_2$O (2.0 mL) was added, along with an i-Pr$_2$O rinsing (0.5 mL) (Note: if the electrophile is not soluble in i-Pr$_2$O, then it was added as a solid, followed by 2.5 mL of i-Pr$_2$O), and then the solution of the activated trialkylborane was added dropwise over 30 seconds. The reaction mixture was stirred at r.t. for 72 h, and then it was filtered through silica gel, eluting with Et$_2$O (20 mL). The solvent was removed by rotary evaporation, and the residue was diluted with hexanes (10 mL). The resulting solution was filtered through an acrodisc and then concentrated by rotary evaporation.

A second run was performed with the (1S,2S) enantiomer ((S,S)-DMPEDA) of the ligand.

General Procedure (sulfonamides and sulfones) (conducted in a glovebox; however, see the note below). The trialkylborane was prepared by adding 9-BBN dimer (2.28 g, 9.3 mmol), i-Pr$_2$O (5.0 mL), and the alkene (18.7 mmol) in turn to a 20-mL vial. The vial was capped and removed from the glovebox. The reaction mixture was stirred at 60 °C for 1.5 h, and then it was allowed to cool to r.t. The vial was taken back into the glovebox, and the reaction mixture was diluted with i-Pr$_2$O to furnish a 1.5 M solution. Next, a portion of this solution (0.67 mL, 1.00 mmol) was added to a solution of KOt-Bu (78 mg, 0.70 mmol) in i-butanol (83 µL, 0.90 mmol) in a 4-mL vial. The resulting mixture was stirred at r.t. for 45 min.

A solution of NiBr$_2$•diglyme (17.6 mg, 0.050 mmol) and (1R,2R)-(+)N,N'-dimethyl-1,2-bis[3-trifluoromethyl]phenyl]-1,2-ethanediamine ((R,R)-m-CF$_3$-DMPEDA; 22.6 mg, 0.060 mmol) in i-Pr$_2$O (2.5 mL) in a 20-mL vial was stirred at r.t. for 30 min. Next, a solution of the electrophile (0.50 mmol) in i-Pr$_2$O (2.0 mL) was added, along with an i-Pr$_2$O rinsing (0.5 mL) (Note: if the electrophile is not soluble in i-Pr$_2$O, then it was added as a solid, followed by 2.5 mL of i-Pr$_2$O), and then the solution of the activated trialkylborane was added dropwise over 30 seconds. The reaction mixture was stirred at r.t. for 72 h, and then it was filtered through silica gel, eluting with Et$_2$O (20 mL). The solvent was removed by rotary evaporation, and the residue was diluted with hexanes (10 mL). The resulting solution was filtered through an acrodisc and then concentrated by rotary evaporation.

A second run was performed with the (1S,2S) enantiomer ((S,S)-m-CF$_3$-DMPEDA) of the ligand.
**Note:** For the sake of convenience, the stereoconvergent Suzuki cross-couplings were conducted in a glovebox. However, this method does not require the use of a glovebox. When carried out using Schlenk techniques without a glovebox, the coupling illustrated in entry 3 of Table 2 proceeded in 92% ee and 89% yield.

![Chemical Structure 1]

(R)-Phenyl 2-ethyl-6-(2-methyl-1,3-dioxolan-2-yl)hexyl(4-methoxybenzyl)carbamate (Table 1, entry 1). Phenyl 2-hydroxybutyl(4-methoxybenzyl)carbamate (196 mg, 0.50 mmol) and a solution of the alkyborane prepared by hydroboration of 2-(but-3-enyl)-2-methyl-1,3-dioxolane with 9-BBN dimer (1.5 M in i-Pr$_2$O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water→acetonitrile). Colorless oil. First run: 125 mg (55%, 92% ee). Second run: 128 mg (56%, 90% ee).

The ee was determined by HPLC on an AD-H column (5.0% i-PrOH in hexanes, 1.0 mL/min) with $t_r = 28.8$ min (minor), 30.1 min (major).

$^1$H NMR (CDCl$_3$) δ 7.36–7.33 (m, 2H), 7.25–7.07 (m, 5H), 6.88–6.85 (m, 2H), 4.55 (s, 1H), 4.48 (s, 1H), 3.93–3.89 (m, 4H), 3.80 (s, 3H), 3.14–3.13 (m, 2H), 1.72–1.65 (m, 1H), 1.61–1.20 (m, 13H), 0.86 (t, 3H, $J = 7.6$ Hz) [mixture of rotamers].

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.0, 155.5, 155.0, 151.5, 129.5, 129.2, 128.6, 125.1, 121.7, 121.6, 113.9, 110.0, 64.6, 55.2, 50.4, 50.2, 50.0, 49.5, 39.1, 37.7, 37.4, 30.8, 29.7, 26.6, 24.4, 23.8, 23.7, 10.6 [mixture of rotamers].

FT-IR (film) 3016, 2936, 1717, 1708, 1615, 1513, 1457, 1418, 1205, 1037, 734, 667, 649 cm$^{-1}$.

MS (ESI) [M+H]$^+$ calcd for C$_{27}$H$_{38}$NO$_5$: 456.2744, found: 456.2755.

$[\alpha]_{D}^{22} = -2.4$ (c 1.0, CHCl$_3$) obtained with (R,R)-DMPEDA.

![Chemical Structure 2]

(R)-Phenyl butyl(2-(3-(2-methoxyphenyl)propyl)hexyl)carbamate (Table 1, entry 2). Phenyl 2-bromohexyl(butyl)carbamate (178 mg, 0.50 mmol) and a solution of the alkyborane prepared by hydroboration of 1-allyl-2-methoxybenzene with 9-BBN dimer (1.5 M in i-Pr$_2$O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water→acetonitrile). Colorless oil. First run: 177 mg (83%, 90% ee). Second run: 176 mg (83%, 89% ee).
The ee was determined by HPLC on an AD-H column (1.0% i-PrOH in hexanes, 1.0 mL/min) with \( t_r = 9.6 \) min (major), 16.0 min (minor).

\(^1\)H NMR (CDCl\(_3\)) \( \delta 7.36–7.32 (m, 2H), 7.19–7.12 (m, 5H), 6.89–6.82 (m, 2H), 3.80 (s, 3H), 3.38–3.18 (m, 4H), 2.60 (t, 2H, \( J = 7.6 \) Hz), 1.79–1.66 (m, 1H), 1.65–1.55 (m, 4H), 1.40–1.25 (m, 10H), 0.97–0.87 (m, 6H).

\(^{13}\)C NMR (CDCl\(_3\)) \( \delta 157.3, 154.8, 151.5, 130.9, 130.8, 129.7, 129.1, 126.9, 126.8, 124.9, 121.70, 121.66, 120.3, 110.2, 55.1, 51.6, 51.1, 47.7, 47.5, 36.7, 36.2, 31.3, 31.2, 31.0, 30.6, 30.5, 29.7, 28.6, 26.7, 23.1, 20.1, 20.0, 14.1, 13.8 [mixture of rotamers].

FT-IR (film) 3019, 2950, 2936, 1717, 1700, 1653, 1559, 1457, 1419, 1215, 758, 669 cm\(^{-1}\).

MS (ESI) [M+H]\(^+\) calcd for C\(_{27}\)H\(_{40}\)NO\(_3\): 426.3003, found: 426.3016.

\([\alpha]\)\(^{22}\)\(_D\) = –2.1 (c 1.0, CHCl\(_3\)) obtained with (S,S)-DMPEDA.

Phenyl 2-bromo-3-cyclohexylpropyl(methyl)carbamate (180 mg, 0.50 mmol) and a solution of the alkylborane prepared by hydroboration of 1-allyl-2-methylbenzene with 9-BBN dimer (1.5 M solution in i-Pr\(_2\)O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water→acetonitrile). Colorless oil. First run: 149 mg (72%, 89% ee). Second run: 158 mg (76%, 90% ee).

The ee was determined by HPLC on an AD-H column (1.0% i-PrOH in hexanes, 1.0 mL/min) with \( t_r = 13.9 \) min (major), 16.4 min (minor).

\(^1\)H NMR (CDCl\(_3\)) \( \delta 7.40–7.36 (m, 4H), 7.23–7.10 (m, 14H), 3.40–3.26 (m, 4H), 3.07 (s, 3H), 3.00 (s, 3H), 2.62 (t, 4H, \( J = 7.8 \) Hz), 2.34 (s, 3H), 2.32 (s, 3H), 1.95–1.14 (m, 32H), 1.00–0.84 (m, 4H) [~1:1 mixture of rotamers].

\(^{13}\)C NMR (CDCl\(_3\)) \( \delta 155.0, 151.5, 140.9, 140.6, 140.5, 135.7, 135.6, 130.1, 130.03, 129.98, 129.9, 129.14, 129.10, 128.7, 125.8, 125.7, 125.6, 125.5, 125.02, 124.97, 121.7, 121.6, 53.9, 53.6, 39.7, 39.6, 35.3, 35.1, 34.9, 34.8, 33.9, 33.8, 33.6, 33.4, 33.3, 33.2, 32.9, 31.9, 31.7, 30.2, 29.5, 26.8, 26.5 [mixture of rotamers].

FT-IR (film) 3016, 2922, 2851, 1725, 1595, 1494, 1449, 1400, 1293, 1206, 1164, 1128, 1026, 908, 854, 748, 691 cm\(^{-1}\).

MS (ESI) [M+H]\(^+\) calcd for C\(_{25}\)H\(_{38}\)NO\(_2\): 408.2897, found: 408.2896.

\([\alpha]\)\(^{24}\)\(_D\) = +4.8° (c 0.50, CH\(_2\)Cl\(_2\)) obtained with (R,R)-DMPEDA.
(R)-Phenyl 2-ethyloctyl(phenyl)carbamate (Table 1, entry 4). Phenyl 2-bromobutyl(phenyl)carbamate (175 mg, 0.50 mmol) and a solution of the reagent prepared by hydroboration of 1-hexene with 9-BBN dimer (1.5 M solution in i-Pr$_2$O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water → acetonitrile). Colorless oil. First run: 102 mg (57%, 90% ee). Second run: 97 mg (54%, 91% ee).

The ee was determined by HPLC on an AD-H column (1.0% i-PrOH in hexanes, 1.0 mL/min) with $t_r = 9.2$ min (minor), 10.2 min (major).

$^1$H NMR (CDCl$_3$) $\delta$ 7.39–7.29 (m, 7H), 7.16–7.06 (m, 3H), 3.74–3.71 (m, 2H), 1.52–1.19 (m, 13H), 0.86–0.80 (m, 6H).

$^{13}$C NMR (CDCl$_3$) $\delta$ 154.3, 151.4, 141.7, 129.2, 129.1, 129.0, 127.3, 126.8, 125.2, 121.6, 53.9, 31.8, 30.5, 29.6, 26.2, 23.5, 22.6, 14.1, 10.4.

FT-IR (film) 3043, 2928, 2857, 1718, 1597, 1495, 1457, 1394, 1274, 1204, 1164, 1133, 1072, 1026, 1006, 749, 699, 638 cm$^{-1}$.

MS (ESI) [M+H]$^+$ calcd for C$_{23}$H$_{32}$NO$_2$: 354.2428, found: 354.2423.

$[\alpha]^{25}_{D} = -7.6^\circ$ (c 0.25, CH$_2$Cl$_2$) obtained with (R,R)-DMPEDA.

(R)-Benzyl 4-cyclohexyl-2-ethylbutyl(phenyl)carbamate (Table 1, entry 5). Benzyl 2-bromobutyl(phenyl)carbamate (181 mg, 0.50 mmol) and a solution of the alkylborane prepared by hydroboration of vinylcyclohexane with 9-BBN dimer (1.5 M solution in i-Pr$_2$O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water → acetonitrile). Colorless oil. First run: 130 mg (66%, 79% ee). Second run: 132 mg (66%, 82% ee).

The ee was determined by HPLC on an AD-H column (1.0% i-PrOH in hexanes, 1.0 mL/min) with $t_r = 9.6$ min (minor), 10.6 min (major).

$^1$H NMR (CDCl$_3$) $\delta$ 7.36–7.18 (m, 10H), 5.14 (s, 2H), 3.62 (d, 2H, $J = 7.2$ Hz), 1.63–1.04 (m, 18H), 0.77 (t, 3H, $J = 7.6$ Hz).

$^{13}$C NMR (CDCl$_3$) $\delta$ 155.7, 136.7, 128.8, 128.3, 127.7, 127.3, 126.4, 67.0, 53.3, 37.9, 33.8, 33.31, 33.26, 27.5, 26.6, 26.3, 23.4, 10.3 [mixture of rotamers].

FT-IR (film) 3014, 2928, 2857, 1718, 1597, 1495, 1457, 1394, 1274, 1204, 1164, 1133, 1072, 1026, 1006, 749, 699, 638 cm$^{-1}$.

MS (ESI) [M+H]$^+$ calcd for C$_{26}$H$_{36}$NO$_2$: 394.2741, found: 394.2736.

$[\alpha]^{22}_{D} = +6.5^\circ$ (c 1.0, CHCl$_3$) obtained with (R,R)-DMPEDA.
(1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl (R)-2-methyloctyl(phenyl)carbamate (eq 2). (1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 2-bromopropyl(phenyl)carbamate (200 mg, 0.50 mmol) and a solution of the alkylborane prepared by hydroboration of hexene with 9-BBN dimer (1.5 M solution in i-Pr₂O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water→acetonitrile). Colorless oil. Run with (R,R) ligand: 116 mg (57%, 79% de).

The de was determined by HPLC on an AD-H column (1.0% i-PrOH in hexanes, 1.0 mL/min) with tₘ = 6.5 min (minor), 7.1 min (major).

¹H NMR (CDCl₃) δ 7.33–7.29 (m, 2H), 7.20–7.17 (m, 3H), 4.58–4.54 (m, 1H), 3.61–3.44 (m, 2H), 2.07–2.04 (m, 1H), 1.82–1.80 (m, 1H), 1.60–0.96 (m, 15H), 0.85–0.74 (m, 18H) [mixture of rotamers].

¹³C NMR (CDCl₃) δ 155.7, 142.3, 128.7, 127.3, 126.1, 75.5, 55.9, 47.1, 41.2, 34.3, 34.1, 32.0, 31.8, 31.3, 29.5, 26.7, 26.2, 23.4, 22.6, 22.0, 20.7, 17.3, 16.4, 14.1.

FT-IR (film) 2956, 2927, 2871, 1702, 1598, 1497, 1457, 1400, 1293, 1274, 1148, 1013, 766, 698 cm⁻¹.


(1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl (S)-2-methyloctyl(phenyl)carbamate (eq 3). (1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl 2-bromopropyl(phenyl)carbamate (200 mg, 0.50 mmol) and a solution of the alkylborane prepared by hydroboration of 1-hexene with 9-BBN dimer (1.5 M solution in i-Pr₂O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water→acetonitrile). Colorless oil. Run with (S,S) ligand: 110 mg (54%, 80% de).

The de was determined by HPLC on an AD-H column (1.0% i-PrOH in hexanes, 1.0 mL/min) with tₘ = 6.3 min (major), 6.9 min (minor).

¹H NMR (CDCl₃) δ 7.33–7.29 (m, 2H), 7.20–7.15 (m, 3H), 4.58–4.54 (m, 1H), 3.61–3.44 (m, 2H), 2.07–2.05 (m, 1H), 1.82–1.80 (m, 1H), 1.60–1.00 (m, 15H), 0.87–0.74 (m, 18H) [mixture of rotamers].

¹³C NMR (CDCl₃) δ 155.7, 142.3, 128.7, 127.3, 126.1, 55.8, 47.1, 41.2, 34.3, 34.0, 32.0, 31.8, 31.3, 29.5, 26.7, 26.3, 23.4, 22.6, 22.0, 20.7, 17.3, 16.4.
FT-IR (film) 3040, 2925, 2871, 1705, 1598, 1497, 1456, 1400, 1343, 1274, 1181, 1148, 1080, 1039, 1013, 984, 968, 920, 879, 847, 766, 698, 649 cm\(^{-1}\).

MS (ESI) [M+H]\(^+\) calcd for C\(_{26}\)H\(_{44}\)NO\(_2\): 402.3367, found: 402.3375.

(R)-Phenyl butyl(2-(3-(2-methoxyphenyl)propyl)hexyl)carbamate (eq 4). Phenyl 2-chlorohexyl(butyl)carbamate (156 mg, 0.50 mmol) and a solution of the alkylborane prepared by hydroboration of 1-allyl-2-methoxybenzene with 9-BBN dimer (1.5 M in \(i\)-Pr\(_2\)O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water→acetonitrile). Colorless oil. First run: 166 mg (78%, 90% ee). Second run: 172 mg (81%, 89% ee).

The ee was determined by HPLC on an AD-H column (1.0% \(i\)-PrOH in hexanes, 1.0 mL/min) with \(t_r = 9.6\) min (major), 16.0 min (minor).

For characterization data, see Table 1, entry 2 (above).

(R)-Phenyl butyl(6-(2-methoxyphenyl)-3-methylhexyl)carbamate (eq 5). Phenyl 3-bromobutyl(butyl)carbamate (160 mg, 0.50 mmol) and a solution of the alkylborane prepared by hydroboration of 1-allyl-2-methoxybenzene with 9-BBN dimer (1.5 M solution in \(i\)-Pr\(_2\)O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water→acetonitrile). Colorless oil. First run: 184 mg (94%, 52% ee). Second run: 184 mg (94%, 55% ee). Third run with (1R,2R)-(+)\(-\)N,N’-dimethyl-1,2-bis[(3-trifluoromethyl)phenyl]-1,2-ethanediame: 174 mg (89%, 76% ee).

The ee was determined by HPLC on an OD-H column (5.0% \(i\)-PrOH in hexanes, 1.0 mL/min) with \(t_r = 9.8\) min (minor), 11.1 min (major).

\(^1\)H NMR (CDCl\(_3\)) \(\delta 7.40–7.36\) (m, 2H), 7.23–7.15 (m, 5H), 6.91–6.86 (m, 2H), 3.82 (s, 3H), 3.42–3.35 (m, 4H), 2.66–2.63 (m, 2H), 1.86–1.30 (m, 11H), 0.99 (d, 6H, \(J = 5.6\) Hz) [mixture of rotamers].

\(^13\)C NMR (CDCl\(_3\)) \(\delta 157.3, 154.4, 151.5, 131.0, 130.8, 129.6, 129.0, 126.7, 124.8, 121.6, 121.1, 120.2, 110.0, 55.0, 47.3, 47.0, 45.9, 45.5, 36.7, 36.6, 35.6, 34.8, 30.8, 30.5, 30.4, 30.2, 30.0, 27.1, 19.9, 19.5, 19.4, 13.8 [mixture of rotamers].
FT-IR (film) 3426, 2932, 2049, 1716, 1599, 1494, 1378, 1205, 1031, 942, 909, 887, 853, 751, 690 cm\(^{-1}\).

MS (ESI) [M+H]\(^+\) calcd for C\(_{25}\)H\(_{36}\)NO\(_3\): 398.2690, found: 398.2695.

\([\alpha]\)^{24}\text{D} = -11.5° (c 0.50, CH\(_2\)Cl\(_2\)) obtained with (R,R)-m-CF\(_3\)-DMPEDA.

(R)-N-butyl-6-(2-methoxyphenyl)-3-methylhexan-1-amine (eq 6). A solution of (R)-phenyl butyl(6-(2-methoxyphenyl)-3-methylhexyl)carbamate (176 mg, 0.46 mmol) in DMSO (2.3 mL) and aqueous KOH (6 M; 2.3 mL) in a 20 mL-vial was heated at 95 °C for 24 h. Next, the reaction mixture was cooled to r.t., diluted with water (20 mL), and extracted with Et\(_2\)O (3 x 20 mL). The combined organic layers were washed with brine (4 x 20 mL), and the solvent was removed. CH\(_2\)Br\(_2\) was added as an internal standard, and the yield (83%) was determined by \(^1\)H NMR spectroscopy.

The amine can be purified and isolated as the p-toluenesulfonic acid salt: The unpurified amine was dissolved in Et\(_2\)O (11.5 mL), and p-toluenesulfonic acid monohydrate (96 mg, 0.50 mmol) was added. The mixture was stirred at r.t. for 1.75 h, and then it was concentrated, and the residue was purified by flash column chromatography (5% MeOH/CH\(_2\)Cl\(_2\)→20% MeOH/CH\(_2\)Cl\(_2\)). Beige powder. First run: 147 mg (71%). Second run: 156 mg (76%).

\(^1\)H NMR (CDCl\(_3\)) \(\delta\) 8.65 (br s, 2H), 7.71 (d, 2H, J = 8.0 Hz), 7.16–7.06 (m, 4H), 2.93–2.81 (m, 4H), 2.58–2.44 (m, 2H), 2.31 (s, 3H), 1.75–1.68 (m, 3H), 1.59–1.41 (m, 3H), 1.33–1.24 (m, 3H), 1.14–1.04 (m, 1H), 0.86 (t, 3H, J = 7.4 Hz), 0.80 (d, 3H, J = 6.4 Hz).

\(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 157.3, 142.0, 140.3, 130.8, 129.6, 128.8, 126.8, 125.7, 120.3, 110.1, 55.1, 47.4, 46.1, 36.3, 32.5, 30.8, 30.2, 27.7, 27.0, 21.2, 19.9, 19.0, 13.5.

MS (ESI) [M+H]\(^+\) calcd for C\(_{18}\)H\(_{32}\)NO: 278.2478, found: 278.2489.

(R)-N-(2-Ethyl-5-(4-fluorophenyl)pentyl)-N-(4-methoxybenzyl)-4-methylbenzenesulfonamide (Table 2, entry 1). N-(2-Bromobutyl)-N-(4-methoxybenzyl)-4-methylbenzenesulfonamide (213 mg, 0.50 mmol) and a solution of the alkylborane prepared by hydroboration of 1-allyl-4-fluorobenzene with 9-BBN dimer (1.5 M in i-Pr\(_2\)O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10%
acetonitrile/water→acetonitrile). Colorless oil. First run: 135 mg (56%, 89% ee). Second run: 143 mg (59%, 90% ee).

The ee was determined by HPLC on an AD-H column (5.0% i-PrOH in hexanes, 1.0 mL/min) with t<sub>r</sub> = 20.0 min (major), 26.1 min (minor).

1H NMR (CDCl<sub>3</sub>) δ 7.68 (d, 2H, <i>J</i> = 8.4 Hz), 7.29 (d, 2H, <i>J</i> = 8.0 Hz), 7.13 (d, 2H, <i>J</i> = 8.4 Hz), 7.04–7.00 (m, 2H), 6.93–6.89 (m, 2H), 6.77 (d, 2H, <i>J</i> = 8.0 Hz), 4.21–4.11 (m, 2H), 3.74 (s, 3H), 2.91–2.89 (m, 2H), 2.42 (s, 3H), 2.39–2.35 (m, 2H), 1.40–1.07 (m, 7H), 0.63 (t, 3H, <i>J</i> = 7.6 Hz).

13C NMR (CDCl<sub>3</sub>) δ 159.1, 143.1, 136.7, 129.8, 129.63, 129.60, 129.5, 128.6, 127.3, 115.0, 114.8, 113.8, 55.2, 52.8, 52.6, 37.2, 35.3, 30.1, 28.3, 23.5, 21.5, 10.5.

FT-IR (film) 3020, 2965, 2811, 1700, 1653, 1558, 1540, 1507, 1457, 1215, 756, 669 cm<sup>−1</sup>.

MS (ESI) [M+H]<sup>+</sup> calcd for C<sub>28</sub>H<sub>35</sub>FNO<sub>3</sub>S: 484.2316, found: 484.2336.

<sup>[α]</sup><sub>D</sub> = +3.9 (c 1.0, CHCl<sub>3</sub>) obtained with (R,R)-m-CF<sub>3</sub>-DMPEDA.

(S)-N-Butyl-N-(2-cyclohexylmethyl)-5-(2-methoxyphenyl)pentyl-4-methylbenzenesulfonamide (Table 2, entry 2). N-(2-Bromo-3-cyclohexylpropyl)-N-butyl-4-methylbenzenesulfonamide (220 mg, 0.50 mmol) and a solution of the alkylborane prepared by hydroboration of 1-allyl-2-methoxybenzene with 9-BBN dimer (1.5 M solution in i-Pr<sub>2</sub>O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water→acetonitrile). Colorless oil. First run: 143 mg (56%, 90% ee). Second run: 131 mg (51%, 91% ee).

The ee was determined by HPLC on an AD-H column (1.0% i-PrOH in hexanes, 0.9 mL/min) with t<sub>r</sub> = 15.3 min (major), 16.4 min (minor).

1H NMR (CDCl<sub>3</sub>) δ 7.67 (d, 2H, <i>J</i> = 8.4 Hz), 7.27 (d, 2H, <i>J</i> = 8.0 Hz), 7.18–7.10 (m, 2H), 6.89–6.82 (m, 2H), 3.80 (s, 3H), 3.11–2.87 (m, 4H), 2.56 (t, 2H, <i>J</i> = 7.6 Hz), 2.40 (s, 3H), 1.86–1.07 (m, 19H), 0.87 (t, 3H, <i>J</i> = 7.4 Hz), 0.77–0.74 (m, 3H).

13C NMR (CDCl<sub>3</sub>) δ 157.3, 142.8, 136.9, 130.9, 129.7, 129.4, 127.2, 126.8, 120.2, 110.1, 55.1, 52.9, 48.5, 39.5, 34.7, 33.9, 33.3, 33.0, 31.4, 30.5, 30.4, 26.6, 26.3, 26.2, 21.4, 20.0, 13.7.

FT-IR (film) 3546, 2927, 1600, 1494, 1464, 1340, 1243, 1159, 1091, 1051, 1030, 927, 815, 753, 656 cm<sup>−1</sup>.

MS (ESI) [M+H]<sup>+</sup> calcd for C<sub>30</sub>H<sub>46</sub>NO<sub>3</sub>S: 500.3193, found: 500.3185.

<sup>[α]</sup><sub>D</sub> = −6.5° (c 0.50, CH<sub>2</sub>Cl<sub>2</sub>) obtained with (R,R)-m-CF<sub>3</sub>-DMPEDA.
(R)-N-Butyl-N-(2-(3-(2-methoxyphenyl)propyl)octyl)methanesulfonamide (Table 2, entry 3).  

N-(2-Bromooctyl)-N-butylmethanesulfonamide (171 mg, 0.50 mmol) and a solution of the alkylborane prepared by hydroboration of 1-allyl-2-methoxybenzene with 9-BBN dimer (1.5 M in i-Pr₂O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water→acetonitrile). Colorless oil. First run: 158 mg (77%, 90% ee). Second run: 156 mg (76%, 90% ee).

The ee was determined by HPLC on an AS-H column (5.0% i-PrOH in hexanes, 1.0 mL/min) with tᵣ = 10.5 min (minor), 18.1 min (major).


\[ ^1H\text{ NMR (CDCl}_3\text{)} \delta 7.17–7.09 \text{ (m, 2H)}, 6.88–6.81 \text{ (m, 2H)}, 3.79 \text{ (s, 3H)}, 3.12–2.99 \text{ (m, 4H)}, 2.77 \text{ (s, 3H)}, 2.57 \text{ (t, 2H, } J = 7.6 \text{ Hz)}, 1.65–1.24 \text{ (m, 19H)}, 0.91 \text{ (t, 3H, } J = 7.2 \text{ Hz)}, 0.86 \text{ (t, 3H, } J = 6.8 \text{ Hz)}.\]

\[ ^{13}C\text{ NMR (CDCl}_3\text{)} \delta 157.3, 130.8, 129.7, 126.9, 120.3, 110.2, 55.2, 51.9, 48.0, 37.8, 36.1, 31.8, 31.0, 30.9, 30.6, 30.5, 29.6, 26.6, 26.2, 22.6, 20.1, 14.0, 13.7.\]

FT-IR (film) 3019, 2951, 2935, 1559, 1457, 1215, 760, 669 cm⁻¹.

MS (ESI) [M+H]** calcd for C₂₃H₄₂NO₃S: 412.2880, found: 412.2872.

\[ [\alpha]^{22}_D = -4.9 \text{ (c 1.0, CHCl}_3\text{)} \] obtained with (S,S)-m-CF₃-DMPEDA.

(R)-N-(4-Cyclohexyl-2-ethylbutyl)-N-phenylmethanesulfonamide (Table 2, entry 4).  

N-(2-Bromobutyl)-N-phenylmethanesulfonamide (155 mg, 0.50 mmol) and a solution of the alkylborane prepared by hydroboration of vinylcyclohexane with 9-BBN dimer (1.5 M solution in i-Pr₂O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water→acetonitrile). White solid. First run: 122 mg (71%, 71% ee). Second run: 111 mg (65%, 73% ee).

The ee was determined by HPLC on an OJ-H column (5.0% i-PrOH in hexanes, 1.0 mL/min) with tᵣ = 8.2 min (major), 9.3 min (minor).


\[ ^1H\text{ NMR (CDCl}_3\text{)} \delta 7.40–7.28 \text{ (m, 5H)}, 3.57–3.48 \text{ (m, 2H)}, 2.82 \text{ (s, 3H)}, 1.64–1.61 \text{ (m, 5H)}, 1.41–0.98 \text{ (m, 12H)}, 0.78 \text{ (t, 3H, } J = 7.2 \text{ Hz)}, 0.80–0.76 \text{ (m, 1H)}.\]

\[ ^{13}C\text{ NMR (CDCl}_3\text{)} \delta 139.4, 129.3, 128.2, 127.9, 53.7, 37.9, 37.6, 36.2, 33.7, 33.4, 33.3, 27.3, 26.7, 26.4, 26.3, 23.2, 10.2.\]

FT-IR (film) 2923, 2851, 1493, 1457, 1342, 1158, 1067, 964, 883, 775, 697 cm⁻¹.

MS (ESI) [M+H]** calcd for C₁₉H₃₂NO₃S: 338.2148, found: 338.2144.

\[ [\alpha]^{24}_D = -19.4^° \text{ (c 0.50, CH}_2\text{Cl}_2\text{)} \] obtained with (S,S)-m-CF₃-DMPEDA.
(R)-N-Butyl-N-(2-(3-(2-methoxyphenyl)propyl)octyl)methanesulfonamide (eq 7). N-(2-Chlorooctyl)-N-butylmethanesulfonamide (149 mg, 0.50 mmol) and a solution of the alkylborane prepared by hydroboration of 1-allyl-2-methoxybenzene with 9-BBN dimer (1.5 M in i-Pr₂O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water→acetonitrile). Colorless oil. First run: 148 mg (72%, 92% ee). Second run: 150 mg (73%, 91% ee).

The ee was determined by HPLC on an AS-H column (5.0% i-PrOH in hexanes, 1.0 mL/min) with $t_r = 9.0$ min (minor), 15.5 min (major).

For characterization data, see Table 2, entry 3 (above).

(R)-N-Butyl-N-(6-(2-methoxyphenyl)-3-methylhexyl)methanesulfonamide (eq 8). N-(3-Bromobutyl)-N-butylmethanesulfonamide (150 mg, 0.50 mmol) and a solution of the alkylborane prepared by hydroboration of 1-allyl-2-methoxybenzene with 9-BBN dimer (1.5 M solution in i-Pr₂O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water→acetonitrile). Colorless oil. First run: 149 mg (80%, 65% ee). Second run: 146 mg (78%, 62% ee).

The ee was determined by HPLC on an OJ-H column (5.0% i-PrOH in hexanes, 1.0 mL/min) with $t_r = 20.0$ min (major), 24.6 min (minor).

$^1$H NMR (CDCl₃) $\delta$ 7.15 (t, 1H, $J = 7.8$ Hz), 7.11 (d, 1H, $J = 7.2$ Hz), 6.88–6.82 (m, 2H), 3.80 (s, 3H), 3.22–3.11 (m, 4H), 2.78 (s, 3H), 2.63–2.52 (m, 2H), 1.67–1.17 (m, 11H), 0.95–0.90 (m, 6H).

$^{13}$C NMR (CDCl₃) $\delta$ 157.2, 130.8, 129.6, 126.7, 120.1, 110.1, 55.1, 47.2, 45.8, 38.1, 36.5, 35.5, 30.6, 30.4, 30.2, 27.0, 19.8, 19.3, 13.6.

FT-IR (film) 2932, 1601, 1588, 1494, 1464, 1377, 1331, 1243, 1147, 1098, 1051, 1032, 960, 926, 877, 754 cm⁻¹.

MS (ESI) [M+H]$^+$ calcd for C₁₉H₃₄NO₃S: 356.2254, found: 356.2243.

$[\alpha]_{D}^{24} = -8.1^\circ$ (c 0.50, CH₂Cl₂) obtained with (R,R)-m-CF₃-DMPEDA.
(R)-N-Butyl-N-(2-phenyloctyl)methanesulfonamide (eq 9). \(N-(2-\text{Bromoocyt})-N\)-butylmethanesulfonamide (170 mg, 0.50 mmol) and a solution of the distilled phenylborane prepared according to a literature procedure\(^4\) (0.20 mL of Ph-(9-BBN) in 0.47 mL of \(i\)-Pr\(_2\)O) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water \(\rightarrow\) acetonitrile). Colorless oil. First run: 149 mg (88%, 96% ee). Second run: 151 mg (89%, 94% ee).

The ee was determined by HPLC on an AS-H column (2.0% \(i\)-PrOH in hexanes, 1.0 mL/min) with \(t_r = 15.4\) min (major), 18.3 min (minor).

\(^1\)H NMR (CDCl\(_3\)) \(\delta 7.30–7.27\) (m, 2H), 7.21–7.17 (m, 3H), 3.38 (d, 2H, \(J = 7.2\) Hz), 3.08–2.95 (m, 2H), 2.87–2.79 (m, 1H), 2.38 (s, 3H), 1.72–1.58 (m, 1H), 1.58–1.41 (m, 2H), 1.25–1.11 (m, 11H), 0.87 (t, 3H, \(J = 6.8\) Hz).

\(^{13}\)C NMR (CDCl\(_3\)) \(\delta 142.8, 128.5, 128.0, 126.7, 53.3, 47.2, 44.8, 38.3, 33.3, 31.6, 29.9, 29.2, 27.2, 22.5, 19.8, 13.9, 13.6.

FT-IR (film) 3062, 3028, 2929, 2858, 1603, 1559, 1495, 1455, 1413, 1332, 1149, 1030, 962, 926, 783, 702, 518 cm\(^{-1}\).

MS (ESI) [M+Na\(^+\)] calcd for C\(_{19}\)H\(_{33}\)NNaO\(_2\)S: 362.2124, found: 362.2137.

\([\alpha]^{24}_D = +15.2\) (c 0.55, CH\(_2\)Cl\(_2\)) obtained with (R,R)-\(m\)-CF\(_3\)-DMPEDA.

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(R)-3-Ethyl-6-(2-methoxyphenyl)-\(N,N\)-dimethylhexane-1-sulfonamide (eq 10). 3-Bromo-\(N,N\)-dimethylpentane-1-sulfonamide (150 mg, 0.50 mmol) and a solution of the alkylborane prepared by hydroboration of 1-allyl-2-methoxybenzene with 9-BBN dimer (1.5 M solution in \(i\)-Pr\(_2\)O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water \(\rightarrow\) acetonitrile). Colorless oil. First run: 148 mg (78%, 86% ee). Second run: 147 mg (77%, 84% ee).

The ee was determined by HPLC on an OD-H column (5.0% \(i\)-PrOH in hexanes, 1.0 mL/min) with \(t_r = 16.3\) min (major), 17.7 min (minor).

\(^1\)H NMR (CDCl\(_3\)) \(\delta 7.15\) (t, 1H, \(J = 7.6\) Hz), 7.10 (d, 1H, \(J = 7.2\) Hz), 6.88–6.81 (m, 2H), 3.80 (s, 3H), 2.84 (s, 8H), 2.58 (t, 2H, \(J = 7.6\) Hz), 1.77–1.71 (m, 2H), 1.60–1.52 (m, 2H), 1.44–1.24 (m, 5H), 0.85 (t, 3H, \(J = 7.4\) Hz).

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$^{13}$C NMR (CDCl$_3$) $\delta$ 157.2, 130.5, 129.6, 126.8, 120.1, 110.1, 55.0, 45.8, 37.7, 37.3, 32.2, 30.2, 26.4, 25.8, 25.3, 10.5.

FT-IR (film) 2929, 1601, 1587, 1464, 1410, 1243, 1143, 1051, 1031, 960, 752, 703, 667 cm$^{-1}$.

MS (ESI) $[\text{M}+\text{H}]^{+}$ calc'd for C$_{17}$H$_{30}$NO$_3$S: 328.1941, found: 328.1945.

$[\alpha]_{25}^{D} = -9.6^\circ$ (c 0.50, CH$_2$Cl$_2$) obtained with (R,R)$-m$-CF$_3$-DMPEDA.

(R)-1-(6-(tert-Butylsulfonyl)-4-ethylhexyl)-2-methoxybenzene (Table 3, entry 1). 1-(tert-Butylsulfonyl)-3-bromopentane (125 mg, 0.46 mmol) and a solution of the alkylborane prepared by hydroboration of 1-allyl-2-methoxybenzene with 9-BBN dimer (1.5 M solution in $i$-Pr$_2$O; 0.60 mL, 0.92 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water$\rightarrow$acetonitrile). Clear oil. First run: 122 mg (78%, 88% ee). Second run: 125 mg (80%, 88% ee).

The ee was determined by HPLC on an IA column (1.0% $i$-PrOH in hexanes, 1.0 mL/min) with $t_r$: 25.5 min (major), 27.8 min (minor).

For characterization data, see eq 11 (below).

(R)-tert-Butyl(6-(tert-butylsulfonyl)-4-phenethylhexyloxy)dimethylsilane (Table 3, entry 2). (3-Bromo-5-(tert-butylsulfonyl)pentyl)benzene (175 mg, 0.50 mmol) and a solution of the alkylborane prepared by hydroboration of allyloxy(tert-butyl)dimethylsilane with 9-BBN dimer (1.5 M solution in $i$-Pr$_2$O; 0.67 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water$\rightarrow$acetonitrile). Clear oil. First run: 184 mg (83%, 88% ee). Second run: 175 mg (79%, 86% ee).

The ee was determined by HPLC on an IB column (1.0% $i$-PrOH in hexanes, 1.0 mL/min) with $t_r$: 11.6 min (minor), 12.8 min (major).

$^1$H NMR (CDCl$_3$) $\delta$ 7.27–7.23 (m, 2H), 7.15–7.14 (m, 3H), 3.58 (t, 2H, $J = 5.8$ Hz), 2.89–2.78 (m, 2H), 2.61 (t, 2H, $J = 7.6$ Hz), 1.96–1.82 (m, 2H), 1.67–1.48 (m, 5H), 1.38 (s, 11H), 0.87 (s, 9H), 0.03 (s, 6H).

$^{13}$C NMR (CDCl$_3$) $\delta$ 142.2, 128.3, 128.2, 125.7, 63.0, 58.8, 43.1, 36.1, 35.1, 32.7, 29.3, 28.9, 25.9, 23.7, 23.4, 18.2, –5.4.
FT-IR (film) 3062, 3027, 2933, 2857, 1604, 1496, 1462, 1388, 1363, 1293, 1256, 1116, 1007, 939, 836, 809, 776, 745, 700, 660 cm\(^{-1}\).

MS (ESI) [M+Na]\(^+\) calcd for C\(_{24}\)H\(_{44}\)NaO\(_3\)Si: 463.2673, found: 463.2660.

\([\alpha]\)\(^D\)\(_{24}\) = –2.5\(^\circ\) (c 1.25, CH\(_2\)Cl\(_2\)) obtained with (S,S)-\(m\)-CF\(_3\)-DMPEDA.

(S)-1-(4-(Cyclohexylmethyl)-6-(isopropylsulfonyl)hexyl)-2-methoxybenzene (Table 3, entry 3). (2-Bromo-4-(isopropylsulfonyl)butyl)cyclohexane (165 mg, 0.51 mmol) and a solution of the alkylborane prepared by hydroboration of 2-methoxyallyl benzene with 9-BBN dimer (1.5 M solution in \(i\)-Pr\(_2\)O; 0.68 mL, 1.0 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water→acetonitrile). Clear oil. First run: 170 mg (85%, 89% ee). Second run: 167 mg (84%, 90% ee).

The ee was determined by HPLC on an AD-H column (5.0% \(i\)-PrOH in hexanes, 1.0 mL/min) with \(t_r\): 9.9 min (major), 11.2 min (minor).

\(^1\)H NMR (CDCl\(_3\)) \(\delta\) 7.15 (t, 1H, \(J = 7.6\) Hz), 7.09 (d, 1H, \(J = 7.2\) Hz), 6.87–6.81 (m, 2H), 3.80 (s, 3H), 3.07 (septet, 1H, \(J = 6.8\) Hz), 2.82 (t, 2H, \(J = 8.2\) Hz), 2.57 (t, 2H, \(J = 7.4\) Hz), 1.77–1.52 (m, 10H), 1.42–0.99 (m, 14H), 0.85–0.77 (m, 2H).

\(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 157.2, 130.5, 129.7, 126.9, 120.2, 110.1, 55.1, 52.2, 46.7, 41.5, 34.6, 33.54, 33.48, 33.1, 32.8, 30.3, 26.5, 26.2, 26.1, 24.9, 15.2, 15.1.

FT-IR (film) 2921, 1601, 1587, 1494, 1464, 1411, 1388, 1243, 1176, 1123, 1051, 1031, 967, 926, 880, 753, 683, 644, 565 cm\(^{-1}\).

MS (ESI) [M+Na]\(^+\) calcd for C\(_{23}\)H\(_{38}\)NaO\(_3\)S: 417.2434, found: 417.2436.

\([\alpha]\)\(^D\)\(_{24}\) = +4.2\(^\circ\) (c 0.5, CH\(_2\)Cl\(_2\)) obtained with (R,R)-\(m\)-CF\(_3\)-DMPEDA.

(R)-1-(6-(tert-Butylsulfonyl)-4-ethylhexyl)-2-methoxybenzene (eq 11). 1-(tert-Butylsulfonyl)-3-chloropentane (120 mg, 0.53 mmol) and a solution of the alkylborane prepared by hydroboration of 1-allyl-2-methoxybenzene with 9-BBN dimer (1.5 M solution in \(i\)-Pr\(_2\)O; 0.70 mL, 1.1 mmol) were used. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water→acetonitrile). Clear oil. First run: 138 mg (77%, 88% ee). Second run: 132 mg (73%, 88% ee).
The ee was determined by HPLC on an IA column (1.0% i-PrOH in hexanes, 1.0 mL/min) with $t_r = 24.7$ min (major), 27.1 min (minor).

$^1$H NMR (CDCl$_3$) $\delta$ 7.15 (t, 1H, $J = 7.8$ Hz), 7.10 (d, 1H, $J = 7.2$ Hz), 6.87–6.81 (m, 2H), 3.80 (s, 3H), 2.84–2.80 (m, 2H), 2.57 (t, 2H, $J = 7.6$ Hz), 1.86–1.80 (m, 2H), 1.57 (quintet, 2H, $J = 7.8$ Hz), 1.46–1.26 (m, 14H), 0.85 (t, 3H, $J = 7.4$ Hz).

$^{13}$C NMR (CDCl$_3$) $\delta$ 157.4, 130.7, 129.7, 126.9, 120.3, 110.2, 58.9, 55.2, 43.4, 38.1, 32.4, 30.3, 26.5, 25.5, 23.5, 23.4, 10.6.

FT-IR (film) 2936, 1600, 1494, 1463, 1365, 1288, 1242, 1114, 1051, 1031, 806, 753, 657 cm$^{-1}$.


$[\alpha]_D^{24} = +0.31^\circ$ (c 1.0, CH$_2$Cl$_2$) obtained with (R,R)-m-CF$_3$-DMPEDA.

IV. Transmetalation Study

1-(tert-Butyldiphenylsiloxy)-2,3-cis-dideuterio-2-propene. Quinoline (1.6 mL, 14 mmol) was added to a flask that contained 5% Pd on CaCO$_3$ (12% w/w; 120 mg) and pentane (8.1 mL). The flask was evacuated and backfilled with argon three times. tert-Butyldiphenyl(prop-2-ynyloxy)silane (1.0 g, 3.4 mmol) was then added to the reaction mixture. The flask was evacuated and backfilled with D$_2$ three times. The reaction mixture was stirred for 45 min, and then it was filtered through celite. The filtrate was concentrated, and the residue was purified by chromatography (0%→50% Et$_2$O/hexanes), which furnished a colorless liquid (0.96 g, 95%).

$^1$H NMR (CDCl$_3$) $\delta$ 7.70 (d, 4H, $J = 9.6$ Hz), 7.45–7.36 (m, 6H), 5.37–5.36 (m, 1H), 4.22 (d, 2H, $J = 1.2$ Hz), 1.08 (s, 9H).

$^{13}$C NMR (CDCl$_3$) $\delta$ 136.6 (t, $J = 22.5$ Hz), 135.5, 133.7, 129.6, 127.6, 113.5 (t, $J = 24.0$ Hz), 64.5, 26.8, 19.3.

FT-IR (film) 3072, 2960, 2932, 2858, 1473, 1428, 1391, 1374, 1362, 1260, 1188, 1134, 1112, 1087, 1008, 938, 883, 823, 739, 615, 505 cm$^{-1}$.

MS (ESI) [M+Na]$^+$ calcd for C$_{19}$H$_{22}$D$_2$NaOSi: 321.1614, found: 321.1634.

1-(tert-Butyldiphenylsiloxy)-2,3-trans-dideuterio-2-propene. The title compound was synthesized from (E)-2,3-dideuterioprop-2-en-1-ol$^5$ (1.0 g, 18 mmol), TBDPSCI (5.6 mL, 21

(5) Synthesized according to Baldwin, J. E.; Black, K. A. J. Org. Chem. 1983, 48, 2778–2779, using diethyl ether as solvent, with the addition of LiAlD$_4$ at 0 °C. After quenching and
mmol), and imidazole (2.7 g, 39 mmol) in DMF (13 mL), and purified by chromatography on reverse-phase silica (0%→100% acetonitrile/H$_2$O), which furnished a colorless oil (2.4 g; 46% over 2 steps). The $^1$H NMR spectrum matched the reported data.\(^6\)

![Eq 12. Bromocyclohexane-d$_{11}$ (25 µL, 0.20 mmol) and a solution of the alkylborane prepared by hydroboration of 1-(tert-butyldiphenylsiloxyl)-2,3-trans-dideutero-2-propene with 9-BBN dimer (1.5 M solution in $i$-Pr$_2$O; 0.30 mL, 0.40 mmol) were used, and the General Procedure (sulfonamides and sulfones) was followed. The product was purified by flash chromatography on silica gel (0%→50% Et$_2$O/hexane) and then again on reverse-phase silica gel (10% acetonitrile/water→acetonitrile), which furnished a colorless oil (51 mg, 64%). $^1$H NMR (500 MHz, CDCl$_3$; deuterium decoupled) δ 7.63–7.62 (m, 4H), 7.39–7.32 (m, 6H), 3.58 (d, 2H, $J$ = 7.0 Hz), 1.47 (br s, 1H), 1.11 (d, 1H $J$ = 10.0 Hz), 1.00 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 135.6, 134.2, 129.5, 127.5, 64.3, 32.7 (t, $J$ = 19.5 Hz), 29.4 (t, $J$ = 18.5 Hz), 26.9, 19.2. FT-IR (film) 3071, 3050, 3000, 2930, 2858, 2197, 2102, 1590, 1472, 1428, 1389, 1361, 1112, 1008, 823, 739, 701, 613 cm$^{-1}$. MS (ESI) [M+H]$^+$ calcld for C$_{26}$H$_{24}$D$_{13}$OSi: 394.3424, found: 394.3412.

![Eq 13. Bromocyclohexane-d$_{11}$ (25 µL, 0.20 mmol) and a solution of the alkylborane prepared by hydroboration of 1-(tert-butyldiphenylsiloxyl)-2,3-cis-dideutero-2-propene with 9-BBN dimer (1.5 M solution in $i$-Pr$_2$O; 0.30 mL, 0.40 mmol) were used, and the General Procedure (sulfonamides and sulfones) was followed. The product was purified by flash chromatography on reverse-phase silica gel (10% acetonitrile/water→acetonitrile), which furnished a colorless oil (64 mg, 80%). $^1$H NMR (500 MHz, CDCl$_3$; deuterium decoupled) δ 7.66–7.65 (m, 4H), 7.38–7.36 (m, 6H), 3.61 (d, 2H, $J$ = 6.5 Hz), 1.51 (br s, 1H), 1.14 (d, 1H $J$ = 5.0 Hz), 1.03 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 135.6, 134.2, 129.5, 127.6, 64.3, 32.8 (t, $J$ = 19.5 Hz), 29.4 (t, $J$ = 19.5 Hz), 26.9, 19.2. filtration over Celite, the solvent was removed at atmospheric pressure. Due to the low boiling point of the deuteriated alcohol, it was silylated immediately.\(^6\) Ridgway, B. H.; Woerpel, K. A. J. Org. Chem. 1998, 63, 458–460.
FT-IR (film) 3071, 3050, 3000, 2930, 2858, 2197, 2102, 1590, 1472, 1428, 1389, 1361, 1188, 1112, 1008, 823, 739, 701, 613 cm⁻¹.

MS (ESI) [M+H]⁺ calcd for C₂₅H₂₄D₁₃OSi: 394.3424, found: 394.3424.

V. Assignment of Absolute Stereochemistry

These procedures have not been optimized.

For one member of each family of directed reactions (three total), the absolute stereochemistry of the cross-coupling products was determined by correlation. The absolute stereochemistry of the other reaction products is assigned by analogy.

**Absolute stereochemistry: carbamates.**

\[
\begin{align*}
\text{Ph} & \quad \text{N} & \quad \text{O} & \quad \text{Me} \\
\text{Ph} & \quad \text{N} & \quad \text{O} & \quad \text{Me} \\
\end{align*}
\]

prepared with (R,R) ligand according to:
Owston, N. A.; Fu, G. C.

(R)-Phenyl 2-ethyloctyl(phenyl)carbamate. (R)-2-Ethyloctyl benzyl(phenyl)carbamate was prepared with (R,R) ligand according to:
Owston, N. A.; Fu, G. C.

\[
\begin{align*}
\text{Ph} & \quad \text{N} & \quad \text{O} & \quad \text{Me} \\
\text{Ph} & \quad \text{N} & \quad \text{O} & \quad \text{Me} \\
\end{align*}
\]

\[
\begin{align*}
1) & \text{LiAlH}_4 \\
2) & \text{TsCl} \\
3) & \text{PhNH}_2 \\
4) & \text{PhOCl} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{N} & \quad \text{O} & \quad \text{Me} \\
\text{Ph} & \quad \text{N} & \quad \text{O} & \quad \text{Me} \\
\end{align*}
\]

1) LiAlH₄ (1.0 M in Et₂O; 0.65 mL, 0.64 mmol) was added to a solution of (R)-2-ethyloctyl benzyl(phenyl)carbamate (78 mg, 0.21 mmol) in THF (7.1 mL) in a 25-mL round-bottom flask equipped with a stir bar and a condenser under nitrogen. The reaction mixture was heated to 65 °C for 2 h, and then it was allowed to cool to r.t. Next, it was cooled to 0 °C, and the reaction was quenched with water (5 mL) and then aqueous HCl (1.0 M; 10 mL). The mixture was extracted with Et₂O (3 x 10 mL), and the organic extracts were dried over MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (5% → 100% Et₂O/hexanes): 21 mg (64%).

Tosyl chloride (51 mg, 0.27 mmol) was added to a solution of the alcohol (21 mg, 0.13 mmol) in anhydrous pyridine (0.5 mL) in a 4-mL vial. The reaction mixture was stirred at r.t. for 24 h. Next, the reaction was quenched with H₂O (10 mL), and the mixture was extracted with Et₂O (3 x 10 mL). The organic extracts were washed with saturated aqueous NaHCO₃ (10 mL), dried over MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (5% → 100% Et₂O/hexanes): 34 mg (83%).

A 4-mL vial containing the tosylate (34 mg, 0.11 mmol), K₂CO₃ (30 mg, 0.22 mmol), NaI (0.027 mmol), and aniline (12 µL, 0.13 mmol) in MeCN (0.7 mL) was heated at 70 °C for 24 h. Next, the reaction mixture was allowed to cool to r.t., and the reaction was quenched with H₂O (20 mL), then aqueous HCl (1.0 M; 10 mL). The mixture was extracted with Et₂O (3 x 10 mL), and the organic extracts were dried over MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (5% → 100% Et₂O/hexanes): 28 mg (60%).
(10 mL). The mixture was extracted with Et₂O (3 x 10 mL), and the organic extracts were dried over MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (5% → 100% Et₂O/hexanes; not completely pure). The impure aniline was transferred to a 4-mL vial and dissolved in Et₂O (1.1 mL). Next, 2,6-lutidine (15 µL, 0.13 mmol) and then phenyl chloroformate (15 µL, 0.13 mmol) were added to the reaction mixture. The mixture was stirred at r.t. for 6 h, and then the reaction was quenched by the addition of HCl (1.0 M; 10 mL). The mixture was extracted with Et₂O (3 x 10 mL), and the organic extracts were dried over MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (5% → 100% Et₂O/hexanes): 2 mg (5% over two steps).

HPLC conditions: AD-H column, 1.0% i-PrOH/hexanes, 1.0 mL/min. Retention times: 10.4 min (minor, S), 11.4 min (major, R).

The product from Table 1, entry 4, generated with (R,R)-DMPEDA: Retention times: 9.2 min (minor, S), 10.2 min (major, R).

**Absolute stereochemistry: sulfonamides.**

![Reaction Scheme]

Prepared with (R,R) ligand according to:

Owston, N. A.; Fu, G. C.


**(R)-N-Butyl-N-(2-(3-(2-methoxyphenyl)propyl)octyl)phenylmethanesulfonamide.** (R)-2-(3-(2-Methoxyphenyl)propyl)octyl benzyl(phenyl)carbamate was obtained as described above.

LiAlH₄ (1.0 M in Et₂O; 0.30 mL, 0.26 mmol) was added to a solution of (R)-2-(3-(2-methoxyphenyl)propyl)octyl phenylbenzyl(phenyl)carbamate (43 mg, 0.088 mmol) in THF (2.9 mL) in a 25-mL round-bottom flask equipped with a stir bar and a condenser under nitrogen. The reaction mixture was heated to 65 °C for 3.5 h, and then it was allowed to cool to r.t. Next, the reaction mixture was cooled to 0 °C and quenched with water (5 mL) and then aqueous HCl (1.0 M; 10 mL). The mixture was extracted with Et₂O (3 x 10 mL), and the organic extracts were dried over MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (5% → 100% Et₂O/hexanes).

The alcohol was transferred to a 4-mL vial and dissolved in anhydrous pyridine (0.3 mL). Tosyl chloride (34 mg, 0.18 mmol) was added, and the reaction mixture was stirred at r.t. for 24 h. The reaction was quenched with H₂O (10 mL), and the mixture was extracted with Et₂O (3 x 10 mL). The organic extracts were washed with saturated aqueous NaHCO₃ (10 mL), dried over MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (5% → 100% Et₂O/hexanes).
The tosylate, DMF (1.3 mL), \( i\)-Pr\(_2\)NEt (46 µL, 0.26 mmol), and \( n\)-BuNH\(_2\) (87 µL, 0.88 mmol) were added to a 20-mL vial. The reaction mixture was heated at 60 °C for 48 h. Next, the reaction mixture was cooled to r.t., diluted with H\(_2\)O (10 mL), and extracted with Et\(_2\)O (3 x 10 mL). The organic extracts were washed with brine (4 x 10 mL), dried over MgSO\(_4\), filtered, and concentrated by rotary evaporation.

The residue was transferred to a 20-mL vial and dissolved in CH\(_2\)Cl\(_2\) (0.45 mL). Next, 2,6-lutidine (0.10 mL, 0.88 mmol) and mesyl chloride (70 µL, 0.88 mmol) were added sequentially. The reaction was stirred at r.t. for 7.5 h. Then, the reaction was quenched with aqueous HCl (1.0 M; 10 mL), and the mixture was extracted with Et\(_2\)O (3 x 10 mL). The organic extracts were dried over MgSO\(_4\), filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (5% → 100% Et\(_2\)O/hexanes): 19 mg (53% over four steps).

HPLC conditions: AS-H column, 1.0% \( i\)-PrOH/hexanes, 0.8 mL/min. Retention times: 12.3 min (minor, \( S\)), 18.3 min (major, \( R\)).

The product from Table 2, entry 3, generated with (\( S,S\))-\( m\)-CF\(_3\)-DMPEDA: Retention times: 12.2 min (major, \( R\)), 18.4 min (minor, \( R\)).

Absolute stereochemistry: sulfones.

![Diagram](image.png)

prepared with \((R,R)\) ligand according to:

Owston, N. A.; Fu, G. C.


(\(R\))-1-(6-(\( tert\)-Butylsulfonyl)-4-ethylhexyl)-2-methoxybenzene. \( R\)-2-Ethyl-5-(2-methoxyphenyl)pentyl benzyl(phenyl)carbamate was obtained as described above.

LiAlH\(_4\) (1.0 M in Et\(_2\)O; 1.3 mL, 1.3 mmol) was added to a solution of \( R\)-2-ethyl-5-(2-methoxyphenyl)pentyl benzyl(phenyl)carbamate (186 mg, 0.43 mmol) in THF (14.4 mL) in a 50-mL round-bottom flask equipped with a stir bar and a condenser under nitrogen. The reaction mixture was heated to 65 °C for 4.5 h, and then it was allowed to cool to r.t. The mixture was then cooled to 0 °C, and the reaction was quenched by the addition of water (5 mL) and then aqueous HCl (1.0 M; 10 mL). The mixture was extracted with Et\(_2\)O (3 x 10 mL), and the combined organic extracts were dried over MgSO\(_4\), filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (5% → 100% Et\(_2\)O/hexanes): 79 mg (82%).

The alcohol (79 mg, 0.36 mmol) was transferred to a 4-mL vial and dissolved in anhydrous pyridine (1 mL). Tosyl chloride (137 mg, 0.72 mmol) was added, and the reaction mixture was
stirred at r.t. for 12 h. The reaction was quenched by the addition of H₂O (10 mL), and the mixture was extracted with Et₂O (3 x 10 mL). The organic extracts were washed with saturated aqueous NaHCO₃ (10 mL), dried over MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (5%→100% Et₂O/hexanes): 126 mg (93%).

n-BuLi (2.3 M, 0.15 mL) was added to a 20-mL vial containing a solution of 2-methyl-2-(methylsulfonyl)propane (46 mg, 0.34 mmol) in THF (2.3 mL) at –20 °C. The reaction mixture was allowed to warm to r.t. and then stirred for 30 min. The tosylate (126 mg, 0.33 mmol) was dissolved in THF (0.3 mL) and added to the reaction mixture at r.t. After 24 h, the reaction was quenched with H₂O (10 mL), and the mixture was extracted with Et₂O (3 x 10 mL). The organic extracts were dried over MgSO₄, filtered, and concentrated by rotary evaporation. The residue was purified by flash chromatography (5%→100% Et₂O/hexanes): 75 mg (65%).

HPLC conditions: IA column, 1.0% i-PrOH/hexanes, 1.0 mL/min. Retention times: 20.0 min (major, R), 22.0 min (minor, S).

The product from Table 3, entry 1, generated with (R,R)-m-CF₃-DMPEDA: Retention times: 20.0 min (major, R), 21.1 min (minor, S).
VI. $^1$H NMR Spectra

Table 1, entry 1
Table 3, entry 1

![Chemical Structure](image)
... end of report ...

---

Table 1, entry 1

![Chemical Structure](image)

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Table 1. Entry 3

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Data file: CHROM/GRAPPIR/DATA-02-98-00-00
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End of report...

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with (R)-m-CF<sub>3</sub>-D-Phe

---

\[ \text{Me} \quad \text{Me} \quad \text{N} \quad \text{Ph} \quad \text{OMe} \]

---

Page 2 of 2
Table 2, entry 2 with 4-CH3T-DMPEDA

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Data from C18, C19, and C20 column separations.
with (S)-n-Cl-DMPEDA

Table 2: only 3

\[ \text{MeO} \quad \text{n-bu} \quad \text{n-hex} \]

\[ \text{MeN} \quad \text{BF}_3 \]

---

Results obtained with ethanol/water mixture:

**Table 1:**

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Appendix:

Figure 1: Spectral data for compound A.

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Acknowledgments:

This work was supported by the Chemical Sciences, Geosciences, and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U.S. Department of Energy.
Data File: C6NCH34F27H27N2O3S10

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Figure 1: Graph with organic compound structure.

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Figure 2: Graph with organic compound structure.

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Figure 3: Graph with organic compound structure.
Table 3. Entry 2

Data File: ['file://testfile1.csv', 'file://testfile2.csv']

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Signal 2: Delay 0, Start=300, End=1000

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Signal 3: Delay 0, Start=300, End=1000

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Signal 4: Delay 0, Start=300, End=1000

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Note: The file paths provided are placeholders for actual file locations.