Supplementary Information

**Enantioselective Rhodium-Catalyzed Arylation of Electron-Deficient Alkenylarenes**

Aakarsh Saxena and Hon Wai Lam*

*EaStCHEM, School of Chemistry, University of Edinburgh, Joseph Black Building, The King’s Buildings, West Mains Road, Edinburgh, EH9 3JJ, United Kingdom*

**Supporting Information**

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**General Information**

CH$_2$Cl$_2$, MeCN, and THF were dried and purified by passage through activated alumina columns using a solvent purification system from http://www.glasscontoursolventsystems.com. All commercially available reagents were used as received. Thin layer chromatography (TLC) was performed on Merck DF-Alufolien 60F$_254$ 0.2 mm precoated plates. Product spots were visualized by UV light at 254 nm, and subsequently developed using potassium permanganate or ceric ammonium molybdate solution as appropriate. Flash column chromatography was carried out using silica gel (Fisher Scientific 60Å particle size 35-70 micron) employing the method of Still and co-workers. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Infra-red spectra were recorded.

on a Jasco FT/IR-460 Plus instrument as a thin film on sodium chloride plates or as a dilute solution in CHCl₃. ¹H NMR spectra were recorded on a Bruker AVA500 (500 MHz), a Bruker AVA400 (400 MHz), or a Bruker DPX360 (360 MHz) spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using residual protonated solvent as internal standard (CDCl₃ at 7.27 ppm). Abbreviations used in the description of resonances are: s (singlet), d (doublet), t (triplet), q, (quartet), app (apparent), br (broad), m (multiplet). Coupling constants (J) are quoted to the nearest 0.1 Hz. Proton-decoupled¹³C NMR spectra were recorded on a Bruker AVA500 (125.8 MHz) spectrometer, a Bruker AVA400 (100.6 MHz), or a Bruker ARX250 (62.9 MHz) spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of tetramethylsilane, using deuterated solvent as internal standard (CDCl₃ at 77.0 ppm). Assignments were made using the DEPT sequence with secondary pulses at 90° and 135°. ¹⁹F NMR spectra were recorded on a Bruker AVA400 (376 MHz) spectrometer. Chemical shifts (δ) are quoted in parts per million (ppm) downfield of CFCl₃ (δ = 0 ppm), using fluorobenzene as internal standard (C₆H₅F at –113.5 ppm). High resolution mass spectra were recorded using electrospray ionization (ES), electron impact (EI), or atmospheric solids analysis probe (ASAP) techniques on a Finnigan MAT 900 XLT spectrometer, a Finnigan MAT 95XP spectrometer, or a Thermofisher LTQ Orbitrap XL spectrometer at the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea. Optical rotations were performed on an Optical Activity POLAAR 20 polarimeter. Chiral HPLC analysis was performed on an Agilent 1100 instrument using 4.6 x 250 mm columns. Authentic racemic samples of products for chiral HPLC assay determinations were obtained using [Rh(cod)Cl]₂ (2.5 mol %) as an achiral precatalyst, using thermal heating. Reactions using microwave heating were carried out in a Biotage microwave synthesizer.

Preparation of Chiral Dienes

Chiral dienes L₁ and L₃ were prepared as described previously.²

To a solution of carboxylic acid L8 (83 mg, 0.40 mmol), HBTU (167 mg, 0.44 mmol), and Et3N (70 µL, 0.44 mmol) in MeCN (8 mL) at room temperature was added cyclohexylamine (55 µL, 0.48 mmol) in one portion, and the reaction was stirred at room temperature for 1 h. The reaction was diluted with brine (8 mL) and the mixture was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with 2 M HCl (30 mL), saturated aqueous NaHCO3 solution (30 mL), and brine (30 mL), and then dried (MgSO4), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (10% EtOAc/hexane) gave the amide L2 (95 mg, 83%) as a colorless solid. m.p. 32-34 °C; [α]D20 +23.5 (c 1.10, CHCl3); IR (film) 3312 (NH), 2930, 1628 (C=O), 1528, 1449, 1256, 908, 814 cm⁻¹; 1H NMR (500 MHz, CDCl3) δ 6.76 (1H, dd, J = 6.2, 1.8 Hz, =CHH), 5.81 (1H, d, J = 6.0 Hz, =CHH), 5.51 (1H, br d, J = 7.2 Hz, NH), 4.02 (1H, dt, J = 6.0, 1.9 Hz, =CHCHH), 3.86-3.76 (1H, m, =CHCHH), 3.35-3.29 (1H, m, =CHCHH), 1.99-1.89 (2H, m), 1.82 (3H, d, J = 1.6 Hz, =CCH3), 1.75-1.66 (2H, m), 1.64-1.55 (2H, m), 1.42-1.34 (2H, m), 1.32-1.03 (5H, m), 1.00 (3H, d, J = 6.4 Hz, CH(CH3)2), 0.95 (1H, ddd, J = 11.5, 4.8, 2.4 Hz, CH), 0.82 (3H, d, J = 6.4 Hz, CH(CH3)2); 13C NMR (125.8 MHz, CDCl3) δ 165.1 (C), 145.3 (C), 143.9 (C), 137.1 (CH), 124.2 (CH), 48.0 (CH), 47.8 (CH), 43.5 (CH), 40.0 (CH), 33.8 (CH), 33.3 (CH2), 33.2 (CH2), 31.8 (CH2), 25.6 (CH2), 24.9 (CH2), 24.9 (CH2), 21.8 (CH3), 21.3 (CH3), 19.0 (CH3); HRMS (ES) Exact mass calculated for C19H30NO [M+H]+: 288.2322, found: 288.2325.

(1R,4R,7R)-7-Isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylic acid diisopropylamide (L4)

To a solution of carboxylic acid L82,3 (70 mg, 0.34 mmol) and DMF (6 μL, 0.68 mmol) in CH₂Cl₂ (0.6 mL) at 0 °C was added oxalyl chloride (32 μL, 0.37 mmol) dropwise over 1 min. The mixture was stirred at 0 °C for 1.5 h (until no more effervescence was observed) to give a solution of the corresponding acid chloride. To a separate mixture of diisopropylamine (50 μL, 0.35 mmol) in CH₂Cl₂ (1 mL) and saturated aqueous Na₂CO₃ solution (1 mL) at 0 °C was added the solution of the acid chloride dropwise via cannula. The mixture was then stirred at room temperature for 20 h. The mixture was partitioned between saturated aqueous NaHCO₃ solution (4 mL) and CH₂Cl₂ (4 mL). The aqueous layer was separated and extracted with CH₂Cl₂ (3 x 4 mL). The combined organic layers were washed with 10% HCl solution (5 mL), dried (MgSO₄), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (1% EtOAc/hexane→8% EtOAc/hexane) gave the diisopropyl amide L4 (57 mg, 58%) as a colorless oil. [α]²⁰D +28.6 (c 0.41, CHCl₃); IR (film) 2963, 2870, 1609 (C=O), 1439, 1369, 1213, 1159, 1079, 885, 732 cm⁻¹; ¹H NMR (360 MHz, CDCl₃) δ 6.20 (1H, dd, J = 6.1, 1.6 Hz, =CH), 5.77 (1H, d, J = 5.8 Hz, =CH), 3.73 (2H, br s, 2 x NCH) 3.58 (1H, dt, J = 5.7, 1.8 Hz, =CHCH), 3.25 (1H, app dd, J = 5.8, 2.3 Hz, =CHCH), 1.80 (3H, d, J = 1.6 Hz, =CH₃), 1.62 (1H, ddd, J = 11.6, 8.9, 2.9 Hz, CH), 1.50-1.32 (12H, m, 4 x CH₃), 1.27-1.11 (2H, m, CH₂), 0.94 (3H, d, J = 6.3 Hz, CH₃), 0.89 (1H, ddd, J = 11.6, 8.9, 2.9 Hz, CH), 0.79 (3H, d, J = 6.3 Hz, CH₃); ¹³C NMR (62.9 MHz, CDCl₃) δ 170.7 (C), 146.1 (C), 144.3 (C), 131.2 (CH), 123.5 (CH), 48.1 (CH), 43.1 (CH), 42.7 (CH), 34.0 (CH), 32.1 (CH₂), 21.7 (CH₃), 21.3 (CH₃), 20.9 (2 x CH₃), 20.8 (2 x CH₃), 19.1 (CH₃) (2 x CH next to nitrogen were not observed); HRMS (ES) Exact mass calcd for C₁₉H₃₂NO [M+H]⁺: 290.2478, found: 290.2473.
(1R,4R,7R)-7-Isopropyl-5-methylbicyclo[2.2.2]octa-2,5-diene-2-carboxylic acid dibenzylamide (L5)

To a solution of carboxylic acid L8 (500 mg, 2.42 mmol) and DMF (42 μL, 0.55 mmol) in CH₂Cl₂ (4.5 mL) at 0 °C was added oxalyl chloride (230 μL, 2.67 mmol) dropwise over 2 min. The mixture was stirred at 0 °C for 1.5 h (until no more effervescence was observed) to give a solution of the corresponding acid chloride. To a separate mixture of dibenzylamine (423 μL, 2.20 mmol) in CH₂Cl₂ (5 mL) and saturated aqueous Na₂CO₃ solution (5 mL) at 0 °C was added the solution of the acid chloride dropwise via cannula over 1 min. The mixture was then stirred at room temperature for 21 h. The mixture was partitioned between saturated aqueous NaHCO₃ solution (10 mL) and CH₂Cl₂ (10 mL). The aqueous layer was separated and extracted with CH₂Cl₂ (3 x 10 mL). The combined organic layers were washed with 10% HCl solution (15 mL), dried (MgSO₄), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (3% EtOAc/hexane) gave the dibenzyl amide L5 (820 mg, 97%) as a colorless oil. \([\alpha]_{D}^{20} +14.1 \ (c \ 0.72, \ CHCl₃)\); IR (film) 2958, 2862, 1608 (C=O), 1542, 1426, 1259, 1099, 1017, 892, 733 cm⁻¹; ¹H NMR (360 MHz, CDCl₃) δ 7.37-7.29 (6H, m, ArH), 7.20-7.18 (4H, m, ArH), 6.50 (1H, dd, J = 6.1, 1.6 Hz, =CH), 5.77 (1H, d, J = 5.8 Hz, =CH), 4.60-4.41 (4H, m, 2 x NCH₂), 3.83 (1H, dt, J = 5.8, 1.8 Hz, =CHCH), 3.28 (1H, app dd, J = 5.8, 2.2 Hz, =CHCH), 1.79 (3H, d, J = 1.4 Hz, =CH₃), 1.64 (1H, ddd, J = 11.5, 8.9, 2.9 Hz, CH), 1.46-1.40 (1H, m, CH), 1.13-1.01 (1H, m, CH₂), 0.96 (3H, d, J = 6.4 Hz, CH₃), 0.95-0.90 (1H, m, CH₂), 0.82 (3H, d, J = 6.4 Hz, CH₃); ¹³C NMR (62.9 MHz, CDCl₃) δ 171.2 (C), 144.4 (C), 143.8 (C), 137.2 (2 x C), 135.0 (CH), 128.6 (6 x CH), 127.3 (4 x CH), 123.5 (CH), 48.1 (CH), 43.3 (CH), 42.8 (CH), 33.9 (CH), 32.0 (CH₂), 21.7 (CH₃), 21.3 (CH₃), 19.1 (CH₃) (2 x CH₂ next to nitrogen were not observed); HRMS (ES) Exact mass calcd for C₂₇H₃₂NO [M+H]+: 386.2478, found: 386.2471.
(1R,4R,7R)-7-Isopropyl-5-methyl-bicyclo[2.2.2]octa-2,5-diene-2-carboxylic acid benzylamide (L6)

To a solution of carboxylic acid L8 (83 mg, 0.40 mmol), HBTU (167 mg, 0.44 mmol), and Et₃N (70 µL, 0.44 mmol) in MeCN (8 mL) at room temperature was added benzylamine (53 µL, 0.48 mmol) in one portion, and the reaction was stirred at room temperature for 1 h. The reaction was diluted with brine (8 mL) and the mixture was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with 2 M HCl (30 mL), saturated aqueous NaHCO₃ solution (30 mL), and brine (30 mL), and then dried (MgSO₄), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (10% EtOAc/hexane) gave the amide L6 (81 mg, 68%) as a white solid. R f = 0.40 (20% EtOAc/hexane); m.p. 112-114 °C; [α] D²⁰ +25.4 (c 1.10, CHCl₃); IR (film) 3314 (NH), 2949, 2864, 1631 (C=O), 1535, 1282, 1028, 802, 678 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.34-7.21 (5H, m, ArH), 6.79 (1H, dd, J = 6.2, 1.4 Hz, =CH), 5.90 (1H, br s, NH), 5.77 (1H, d, J = 5.7 Hz, =CH), 4.51-4.41 (2H, m, NCH₂), 4.07-3.99 (1H, m, =CHCH), 3.34-3.26 (1H, m, =CHCH), 1.78 (3H, br s, =CH₃), 1.54 (1H, ddd, J = 11.5, 9.1, 2.8 Hz, CH), 1.30-1.17 (1H, m, CH₂), 1.11-1.01 (1H, m, CH₂), 0.97 (3H, d, J = 6.4 Hz, CH(CH₃)₂), 0.92 (1H, ddd, J = 11.5, 5.6, 2.5 Hz, CH), 0.79 (3H, d, J = 6.4 Hz, CH(CH₃)₂); ¹³C NMR (125.8 MHz, CDCl₃) δ 165.8 (C), 144.8 (C), 143.8 (C), 138.5 (C), 138.0 (CH), 128.7 (2 x CH), 127.9 (2 x CH), 127.4 (CH), 124.1 (CH), 47.8 (CH), 43.6 (CH₂), 43.6 (CH), 40.0 (CH), 33.8 (CH), 31.7 (CH₂), 21.8 (CH₃), 21.4 (CH₃), 19.0 (CH₃); HRMS (ES) Exact mass calculated for C₂₀H₂₆NO [M+H]+: 296.2009, found: 296.2012.

Preparation of Alkenylboronic Esters

Alkenylboronic esters 14, 15, 16, and 18 were prepared according to previously reported procedures. Alkenylboronic ester 16 is commercially available from Sigma-Aldrich.

4,4,5,5-Tetramethyl-2-[(E)-4-phenylbut-1-enyl]-[1,3,2]dioxaborolane (19)

To a mixture of 4-phenylbut-1-yne (5.62 mL, 40.0 mmol), Cp₂ZrHCl (292 mg, 1.00 mmol), and Et₃N (0.56 mL, 4.00 mmol) at room temperature was added pinacolborane (5.80 mL, 40.0 mmol) over 2 min, and the mixture was stirred for 16 h. The reaction was quenched carefully with H₂O (75 mL) and after effervescence had ceased, the mixture was extracted with Et₂O (2 x 100 mL). The combined organic extracts were dried (MgSO₄), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (5% EtOAc/hexane) gave the alkenylboronic ester 19 (7.86 g, 76%) as a colorless oil that displayed spectroscopic data consistent with those observed previously. ⁶

Preparation of Alkenylarenes

1-Nitro-4-[(E)-4-phenylbut-1-enyl]benzene (1a)

A solution of 1-iodo-4-nitrobenzene (1.49 g, 6.00 mmol), alkenylboronic ester 19⁶ (1.70 g, 6.60 mmol), Pd(OAc)₂ (67 mg, 0.30 mmol), PPh₃ (315 mg, 1.20 mmol), and NaOH (720 mg, 18.0 mmol) in THF (60 mL) was heated to reflux for 16 h. The mixture was cooled to room temperature, and partitioned between Et₂O (100 mL) and H₂O (50 mL). The aqueous layer was separated and extracted with Et₂O (2 x 50 mL) and the combined organic layers were washed with saturated aqueous NH₄Cl solution (80 mL), dried (MgSO₄), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (20% CH₂Cl₂/hexane → 40% CH₂Cl₂/hexane) gave the alkenylarene 1a (1.11 g, 73%) as a yellow solid. m.p. 68-70 °C; IR (film) 3028, 2937, 1595 (C=C), 1514, 1340, 1107, 968, 864, 744, 698 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.18 (2H, d, J = 8.9 Hz, ArH), 7.46 (2H, d, J = 8.9 Hz, ArH), 7.41-7.35 (2H, m, ArH), 7.32-7.26 (3H, m, ArH), 6.53-6.49 (2H, m, CH=CH), 2.93-2.86 (2H, m,

CH$_2$Ph), 2.70-2.61 (2H, m, =CHCH$_2$); $^{13}$C NMR (125.8 MHz, CDCl$_3$) δ 146.3 (C), 144.0 (C), 141.0 (C), 135.1 (CH), 128.5 (CH), 128.30 (2 x CH), 128.27 (2 x CH), 126.2 (2 x CH), 125.9 (CH), 123.7 (2 x CH), 35.2 (CH$_2$), 34.8 (CH$_2$); HRMS (EI) Exact mass calcd for C$_{16}$H$_{15}$NO$_2$ [M]$^+$: 253.1097, found: 253.1096.

1-[(E)-Hex-1-enyl]-4-nitrobenzene (1b)

A solution of 1-iodo-4-nitrobenzene (1.25 g, 5.00 mmol), alkenylboronic ester 14 (1.16 g, 5.50 mmol), Pd(OAc)$_2$ (56 mg, 0.25 mmol), PPh$_3$ (262 mg, 1.00 mmol), and NaOH (600 mg, 15.0 mmol) in THF (50 mL) was heated to reflux for 16 h. The mixture was cooled to room temperature, and partitioned between Et$_2$O (100 mL) and H$_2$O (50 mL). The aqueous layer was separated and extracted with Et$_2$O (2 x 50 mL) and the combined organic layers were washed with saturated aqueous NH$_4$Cl solution (80 mL), dried (MgSO$_4$), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (20% CH$_2$Cl$_2$/hexane $\rightarrow$ 40% CH$_2$Cl$_2$/hexane) gave the alkenylarene 1b (906 mg, 88%) as a yellow oil. IR (film) 2929, 2858, 1649 (C=C), 1597, 1518 (N-O), 1346 (N-O), 1109, 970, 862, 744 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 8.08 (2H, d, $J$ = 8.9 Hz, ArH), 7.38 (2H, d, $J$ = 8.9 Hz, ArH), 6.43-6.35 (2H, m, CH=CH), 2.23-2.19 (2H, m, =CHCH$_2$), 1.47-1.41 (2H, m, CH$_2$CH$_2$CH$_3$), 1.38-1.31 (2H, m, CH$_2$CH$_3$), 0.91 (3H, t, $J$ = 7.3 Hz, CH$_3$); $^{13}$C NMR (125.8 MHz, CDCl$_3$) δ 146.1 (C), 144.2 (C), 136.4 (CH), 127.8 (CH), 126.0 (2 x CH), 123.6 (2 x CH), 32.7 (CH$_2$), 30.9 (CH$_2$), 22.1 (CH$_2$), 13.7 (CH$_3$); HRMS (EI) Exact mass calcd for C$_{12}$H$_{15}$NO$_2$ [M]$^+$: 205.1097, found: 205.1096.

1-[(E)-2-Cyclopropylvinyl]-4-nitrobenzene (1c)

A solution of 1-iodo-4-nitrobenzene (996 mg, 4.00 mmol), alkenylboronic ester 16 (854 mg, 4.40 mmol), Pd(OAc)$_2$ (45 mg, 0.20 mmol), PPh$_3$ (210 mg, 0.80 mmol), and NaOH (480 mg, 12.0 mmol) in THF (40 mL) was heated to reflux for 16 h. The mixture was cooled to room temperature, and partitioned between Et$_2$O (50 mL) and H$_2$O (30 mL). The aqueous layer was separated and extracted with Et$_2$O (2 x 40 mL) and the combined organic layers were washed with saturated aqueous NH$_4$Cl solution (50 mL), dried (MgSO$_4$), filtered, and concentrated in vacuo. Purification of the residue by
column chromatography (20% CH₂Cl₂/hexane→40% CH₂Cl₂/hexane) gave the alkenylarene 1c (717 mg, 95%) as a yellow solid. m.p. 64-66 °C; IR (film) 3014, 1649, 1593, 1508 (N-O), 1342 (N-O), 1111, 1049, 858, 746 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.15-8.07 (2H, m, ArH), 7.41-7.34 (2H, m, ArH), 6.50 (1H, d, J = 15.7 Hz, ArC=H), 5.90 (1H, dd, J = 15.7, 9.3 Hz, ArCH=CH), 1.69-1.54 (1H, m, =CHCH₂), 0.98-0.83 (2H, m, CH₂CH₂), 0.65-0.52 (2H, m, CH₂CH₂); ¹³C NMR (100.6 MHz, CDCl₃) δ 146.0 (C), 144.2 (C), 125.7 (2 x CH), 125.4 (CH), 123.9 (2 x CH), 15.0 (CH), 7.9 (2 x CH₂); HRMS (EI) Exact mass calcd for C₁₁H₁₁NO₂ [M]+: 189.0784, found: 189.0787.

1-[(E)-3-Methoxypropenyl]-4-nitrobenzene (1d)

A solution of 1-iodo-4-nitrobenzene (1.01 g, 5.00 mmol), alkenylboronic ester 17 (1.09 g, 5.50 mmol), Pd(OAc)₂ (56 mg, 0.25 mmol), PPh₃ (262 mg, 1.00 mmol), and NaOH (600 mg, 15.0 mmol) in THF (50 mL) was heated to reflux for 5 h. The mixture was cooled to room temperature, and partitioned between Et₂O (50 mL) and H₂O (30 mL). The aqueous layer was separated and extracted with Et₂O (2 x 50 mL) and the combined organic layers were washed with saturated aqueous NH₄Cl solution (50 mL), dried (MgSO₄), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (10% EtOAc/hexane) gave the alkenylarene 1d (857 mg, 89%) as a cream solid. m.p. 34-36 °C; IR (film) 2930, 1594, 1515 (N-O), 1188, 1120, 1077, 976, 957, 860 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.11-8.04 (2H, m, ArH), 7.48-7.38 (2H, m, ArH), 6.61 (1H, d, J = 16.0 Hz, ArC=H), 6.39 (1H, dt, J = 16.0, 5.3 Hz, ArCH=CH), 4.07 (2H, dd, J = 5.4, 1.7 Hz, CH₂OCH₃), 3.36 (3H, s, OCH₃); ¹³C NMR (100.6 MHz, CDCl₃) δ 146.6 (C), 143.0 (C), 131.1 (CH), 129.0 (CH), 126.6 (2 x CH), 123.6 (2 x CH), 72.1 (CH₂), 58.1 (CH₃); m/z (EI) 193 ([M]⁺, 44), 147 (43), 115 (100).

(4-Chlorophenyl)methyl-[(E)-3-(4-nitrophenoxy)allyl]amine (1e)

A solution of trans-4-nitrocinnamaldehyde (532 mg, 3.00 mmol) and 4-chloro-N-methylaniline (363 µL, 3.00 mmol) in CH₂Cl₂ (20 mL) was stirred at room temperature for 2 h. NaBH(OAc)₃ (1.91 g, 9.00 mmol) was added in one portion and the reaction was stirred for a further 3 h. The mixture was partitioned between CH₂Cl₂ (20 mL) and H₂O (10 mL). The aqueous layer was separated and extracted
with CH₂Cl₂ (2 x 20 mL) and the combined organic layers were washed with saturated aqueous NaHCO₃ solution (20 mL), brine (20 mL), dried (Na₂SO₄), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (20% CH₂Cl₂/hexane→50% CH₂Cl₂/hexane) gave the alkenylarene 1e (800 mg, 88%) as a yellow solid. m.p. 88-90 °C; IR (film) 2896, 1594, 1501 (N-O), 1341 (N-O), 1211, 1110, 968, 859, 810, 737 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.20-8.13 (2H, m, ArH), 7.50-7.44 (2H, m, ArH), 7.22-7.16 (2H, m, ArH), 6.71-6.64 (2H, m, ArH), 6.55 (1H, d, J = 16.0 Hz, ArC=H), 6.42 (1H, dt, J = 16.0, 4.9 Hz, ArCH=CH), 4.12 (2H, dd, J = 4.9, 1.5 Hz, CH₂N), 3.01 (3H, s, NC₃H₃); 13C NMR (100.6 MHz, CDCl₃) δ 147.7 (C), 146.8 (C), 143.1 (C), 130.6 (CH), 129.2 (CH), 129.0 (2 x CH), 126.8 (2 x CH), 124.0 (2 x CH), 121.7 (C), 113.6 (2 x CH), 54.9 (CH₂), 38.5 (CH₃); m/z (EI) 302 ([M⁺, 41), 207 (47), 116 (100).

2-Fluoro-4-nitro-1-[{(E)}-4-phenylbut-1-enyl]benzene (1g)

A solution of 4-bromo-3-fluoronitrobenzene (1.32 g, 6.00 mmol), alkenylboronic ester 19 (1.70 g, 6.60 mmol), Pd(OAc)₂ (67 mg, 0.30 mmol), PPh₃ (315 mg, 1.20 mmol), and CsF (2.73 g, 18.0 mmol) in THF (60 mL) was heated to reflux for 16 h. The mixture was cooled to room temperature, and partitioned between Et₂O (100 mL) and H₂O (50 mL). The aqueous layer was separated and extracted with Et₂O (2 x 50 mL) and the combined organic layers were washed with saturated aqueous NH₄Cl solution (80 mL), dried (MgSO₄), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (5% CH₂Cl₂/hexane→20% CH₂Cl₂/hexane) gave the alkenylarene 1g (517 mg, 48%) as a green solid. m.p. 36-38 °C; IR (film) 3028, 2927, 1603, 1523 (N-O), 1348 (N-O), 1232, 970, 806, 741, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.99 (1H, dd, J = 8.6, 2.2 Hz, ArH), 7.92 (1H, dd, J = 10.2, 2.3 Hz, ArH), 7.60-7.54 (1H, m, ArH), 7.38-7.32 (2H, m, ArH), 7.29-7.23 (3H, m, ArH), 6.67-6.54 (2H, m, CH=CH), 2.91-2.85 (2H, m, CH₂Ph), 2.71-2.62 (2H, m, =CHCH₂); ¹³C NMR (125.8 MHz, CDCl₃) δ 158.8 (C, d, J = 252.8 Hz), 146.7 (C, d, J = 8.9 Hz), 141.0 (C), 137.8 (CH, d, J = 4.6 Hz), 132.2 (C, d, J = 12.6 Hz), 128.4 (2 x CH), 128.3 (2 x CH), 127.2 (CH, d, J = 4.4 Hz), 126.1 (CH), 121.4 (CH, d, J = 3.3 Hz), 119.3 (CH, d, J = 3.5 Hz), 111.6 (CH, d, J = 27.6 Hz), 35.3 (CH₂), 35.2 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ −115.3 (1F, dd, J = 10.2, 7.5 Hz); HRMS (EI) Exact mass calcd for C₁₆H₁₄FNO₂ [M⁺]: 271.1003, found: 271.1004.
4-[(E)-Hex-1-enyl]-2-methyl-1-nitrobenzene (1h)

A solution of 5-chloro-2-nitrotoluene (858 mg, 5.00 mmol), alkenylboronic ester 14 (1.16 g, 5.50 mmol), Pd(OAc)$_2$ (56 mg, 0.25 mmol), PPh$_3$ (262 mg, 1.00 mmol), and CsF (2.28 g, 15.0 mmol) in THF (50 mL) was heated to reflux for 16 h. The mixture was cooled to room temperature, and partitioned between Et$_2$O (100 mL) and H$_2$O (50 mL). The aqueous layer was separated and extracted with Et$_2$O (2 x 50 mL) and the combined organic layers were washed with saturated aqueous NH$_4$Cl solution (80 mL), dried (MgSO$_4$), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (20% CH$_2$Cl$_2$/hexane) gave the alkenylarene 1h (407 mg, 31%) as a yellow oil. IR (film) 2958, 2929, 2858, 1604, 1583, 1514 (N-O), 1340 (N-O), 968, 839, 752 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.97 (1H, d, $J$ = 8.5 Hz, ArH), 7.31-7.26 (1H, m, ArH), 7.25 (1H, br s, ArH), 6.45-6.34 (2H, m, C=CH$_2$), 2.62 (3H, s, ArCH$_3$), 2.30-2.22 (2H, m, CH$_2$CH$_2$CH$_2$CH$_3$), 1.53-1.44 (2H, m, CH$_2$CH$_2$CH$_3$), 1.43-1.34 (2H, m, CH$_2$CH$_3$), 0.94 (3H, t, $J$ = 7.3 Hz, CH$_2$CH$_3$); $^{13}$C NMR (125.8 MHz, CDCl$_3$) $\delta$ 147.2 (C), 142.9 (C), 136.0 (CH), 134.3 (C), 130.1 (CH), 128.0 (CH), 125.4 (CH), 123.9 (CH), 32.8 (CH$_2$), 31.1 (CH$_2$), 22.2 (CH$_2$), 21.0 (CH$_3$), 13.9 (CH$_3$); HRMS (ASAP) Exact mass calc'd for C$_{13}$H$_{18}$N$_1$O$_2$ [M+H]$^+$: 220.1332, found: 220.1329.

5-[(E)-Hex-1-enyl]-2-nitrobenzoic acid methyl ester (1i)

A solution of methyl 5-chloro-2-nitrobenzoate (1.08 g, 5.00 mmol), alkenylboronic ester 14 (1.16 g, 5.50 mmol), Pd(OAc)$_2$ (56 mg, 0.25 mmol), PPh$_3$ (262 mg, 1.00 mmol), and CsF (2.28 g, 15.0 mmol) in THF (50 mL) was heated to reflux for 16 h. The mixture was cooled to room temperature, and partitioned between Et$_2$O (100 mL) and H$_2$O (50 mL). The aqueous layer was separated and extracted with Et$_2$O (2 x 50 mL) and the combined organic layers were washed with saturated aqueous NH$_4$Cl solution (80 mL), dried (MgSO$_4$), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (20% CH$_2$Cl$_2$/hexane→40% CH$_2$Cl$_2$/hexane) gave the alkenylarene 1i (407 mg, 31%) as a yellow oil. IR (film) 2956, 1739 (C=O), 1585, 1525 (N-O), 1437, 1344 (N-O), 1259, 1209, 1068, 845 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.86 (1H, d, $J$ = 8.5 Hz, ArH), 7.56 (1H, d, $J$ = 1.9 Hz, ArH), 7.46 (1H, dd, $J$ = 8.5, 1.9 Hz, ArH), 6.48-6.33 (2H, m, CH=CH$_2$), 3.89 (3H, s, OCH$_3$),
2.25-2.21 (2H, m, =CHCH₃), 1.50-1.40 (2H, m, CH₂CH₃), 1.39-1.29 (2H, m, CH₂CH₃), 0.90 (3H, t, J = 7.3 Hz, CH₃); ¹³C NMR (125.8 MHz, CDCl₃) δ 166.3 (C), 145.3 (C), 143.3 (C), 137.4 (CH), 128.6 (C), 128.0 (CH), 127.0 (CH), 126.3 (CH), 124.4 (CH), 53.0 (CH₃), 32.7 (CH₂), 30.8 (CH₂), 22.1 (CH₂), 13.7 (CH₃); HRMS (ASAP) Exact mass calcd for C₁₄H₁₇NO₄ [M]−: 263.1163, found: 263.1156.

4-[(E)-Hex-1-enyl]-1-nitro-2-trifluoromethylbenzene (1j)

A solution of 4-bromo-1-nitro-2-(trifluoromethyl)benzene (1.08 g, 4.00 mmol), alkanylboronic ester 14 (925 mg, 4.40 mmol), Pd(OAc)₂ (45 mg, 0.20 mmol), PPh₃ (210 mg, 0.80 mmol), and NaOH (480 mg, 12.0 mmol) in THF (40 mL) was heated to reflux for 16 h. The mixture was cooled to room temperature, and partitioned between Et₂O (50 mL) and H₂O (30 mL). The aqueous layer was separated and extracted with Et₂O (2 x 40 mL) and the combined organic layers were washed with saturated aqueous NH₄Cl solution (50 mL), dried (MgSO₄), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (5% CH₂Cl₂/hexane→20% CH₂Cl₂/hexane) gave the alkanylarene 1j (640 mg, 59%) as a yellow oil. IR (film) 2931, 1651, 1591, 1537 (N-O), 1354 (N-O), 1273, 1147, 1045, 966, 839 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.87 (1H, d, J = 8.4 Hz, ArH), 7.74 (1H, d, J = 1.8 Hz, ArH), 7.61 (1H, dd, J = 8.4, 1.8 Hz, ArH), 6.54-6.41 (2H, m, =CHCH₃), 1.55-1.46 (2H, m, CH₂CH₂CH₃), 1.43-1.36 (2H, m, CH₂CH₃), 0.95 (3H, t, J = 7.3 Hz, CH₃); ¹³C NMR (125.8 MHz, CDCl₃) δ 145.9 (C), 143.0 (C), 138.0 (CH), 129.3 (CH), 125.8 (CH), 125.0 (CH, q, J = 5.5 Hz), 124.2 (C, q J = 33.8 Hz), 122.0 (C, q, J = 273.4 Hz), 32.8 (CH₂), 30.9 (CH₂), 22.2 (CH₂), 13.8 (CH₃); ¹⁹F NMR (376 MHz, CDCl₃) δ −60.5 (3F, s); HRMS (ASAP) Exact mass calcd for C₁₃H₁₄F₃NO₂ [M]−: 273.0982, found: 273.0982.

1-Nitro-4-[(E)-4-phenylbut-1-enyl]naphthalene (1k)

A solution of 4-nitronaphthalen-1-yl trifluoromethanesulfonate 7 (1.93 g, 6.00 mmol), alkanylboronic ester 19 (1.70 g, 6.60 mmol), Pd(OAc)₂ (67 mg, 0.30 mmol), PPh₃ (315 mg, 1.20 mmol), and NaOH

(720 mg, 18.0 mmol) in THF (60 mL) was heated to reflux for 16 h. The mixture was cooled to room temperature, and partitioned between Et₂O (100 mL) and H₂O (50 mL). The aqueous layer was separated and extracted with Et₂O (2 x 50 mL) and the combined organic layers were washed with saturated aqueous NH₄Cl solution (80 mL), dried (MgSO₄), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (5% CH₂Cl₂/hexane) gave the alkenylarene 1k (980 mg, 54%) as a red solid. m.p. 52-54 °C; IR (film) 3026, 2925, 1572, 1512 (N-O), 1454, 1334 (N-O), 1167, 968, 829, 766 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.61 (1H, d, J = 8.7 Hz, ArH), 8.19 (1H, d, J = 8.0 Hz, ArH), 7.75-7.68 (1H, m, ArH), 7.64-7.58 (1H, m, ArH), 7.55 (1H, d, J = 8.0 Hz, ArH), 7.37-7.31 (2H, m, ArH), 7.29-7.22 (3H, m, ArH), 7.08 (1H, d, J = 15.6 Hz, ArCH=), 6.37 (1H, dt, J = 15.6, 6.9 Hz, ArCH=CH), 2.92 (2H, t, J = 7.5 Hz, CH₂Ph), 2.76-2.68 (2H, m, CH₂CH₂Ph); ¹³C NMR (125.8 MHz, CDCl₃) δ 145.4 (C), 142.6 (C), 141.2 (C), 137.1 (CH), 131.7 (C), 129.1 (CH), 128.6 (2 x CH), 128.5 (2 x CH), 127.1 (CH), 127.0 (CH), 126.1 (CH), 125.4 (C), 124.7 (CH), 124.0 (CH), 123.5 (CH), 122.0 (CH), 35.4 (CH₂), 35.2 (CH₂); HRMS (ES) Exact mass calcd for C₂₀H₁₈NO₂ [M+H]⁺: 304.1332, found: 304.1335.

Trimethyl[(E)-2-(4-nitrophenyl)vinyl]silane (3)

A solution of 1-iodo-4-nitrobenezene (747 mg, 3.00 mmol), alkenylboronic ester 18 (679 mg, 3.00 mmol), Pd(OAc)₂ (34 mg, 0.15 mmol), PPh₃ (157 mg, 0.60 mmol), and NaOH (360 mg, 9.00 mmol) in THF (30 mL) was heated to reflux for 16 h. The mixture was cooled to room temperature, and partitioned between Et₂O (40 mL) and H₂O (25 mL). The aqueous layer was separated and extracted with Et₂O (2 x 40 mL) and the combined organic layers were washed with saturated aqueous NH₄Cl solution (40 mL), dried (MgSO₄), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (10% CH₂Cl₂/hexane→40% CH₂Cl₂/hexane) gave the alkenylarene 3 (523 mg, 79%) as a yellow solid. m.p. 37-39 °C; IR (film) 2956, 1591, 1521 (N-O), 1341 (N-O), 1240, 1109, 993, 861, 839, 750 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.24-8.18 (2H, m, ArH), 7.61-7.53 (2H, m, ArH), 6.95 (1H, d, J = 19.1 Hz, ArCH=), 6.74 (1H, d, J = 19.1 Hz, ArCH=CH), 6.47 (2H, m, ArH), 6.02 (2H, m, ArH); ¹³C NMR (100.6 MHz, CDCl₃) δ 147.1 (C), 144.4 (C), 141.2 (CH), 136.1 (CH), 126.8 (2 x CH), 123.9 (2 x CH), −1.5 (3 x CH₃); m/z (EI) 221 ([M]+, 10), 206 (100), 147 (91).
1-[(E)-5-tert-Butyldimethylsilyloxy-1-ethyl]-4-nitrobenzene (4)

A solution of 1-iodo-4-nitrobenzene (4.98 g, 20.0 mmol), alkenylboronic ester 15⁴ (7.18 g, 22.0 mmol), Pd(OAc)₂ (225 mg, 1.00 mmol), PPh₃ (1.05 g, 4.00 mmol), and NaOH (2.40 g, 60.0 mmol) in THF (200 mL) was heated to reflux for 16 h. The mixture was cooled to room temperature, and partitioned between Et₂O (150 mL) and H₂O (100 mL). The aqueous layer was separated and extracted with Et₂O (2 x 150 mL) and the combined organic layers were washed with saturated aqueous NH₄Cl solution (200 mL), dried (MgSO₄), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (5% EtOAc/hexane) gave the alkenylarene 4 (4.91 g, 76%) as a yellow oil. IR (film) 2931, 1651, 1597, 1518 (N-O), 1344 (N-O), 1255, 1107, 968, 839, 742 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.08-8.02 (2H, m, ArH), 7.39-7.33 (2H, m, ArH), 6.45-6.34 (2H, m, CH=CH₂), 3.63 (2H, t, J = 6.2 Hz, C₂H₂O), 2.34-2.24 (2H, m, =CHCH₂), 1.72-1.62 (2H, m, =CHCH₂CH₂), 0.87 (9H, s, C(CH₃)₃), 0.02 (6H, s, Si(CH₃)₂); ¹³C NMR (125.8 MHz, CDCl₃) δ 146.1 (C), 144.1 (C), 135.8 (CH), 128.1 (CH), 126.0 (2 x CH), 123.6 (2 x CH), 62.0 (CH₂), 31.8 (CH₂), 29.4 (CH₂), 25.7 (3 x CH₃), 18.0 (C), –5.6 (2 x CH₃); HRMS (ES) Exact mass calcd for C₁₇H₂₈NO₃Si [M+H]⁺: 322.1833, found: 322.1838.

1-Nitro-3-[(E)-4-phenylbut-1-enyl]benzene (8)

A solution of 1-iodo-3-nitrobenzene (996 mg, 4.00 mmol), alkenylboronic ester 19⁶ (1.14 g, 4.40 mmol), Pd(OAc)₂ (45 mg, 0.20 mmol), PPh₃ (210 mg, 0.80 mmol), and NaOH (480 mg, 12.0 mmol) in THF (40 mL) was heated to reflux for 16 h. The mixture was cooled to room temperature, and partitioned between Et₂O (50 mL) and H₂O (30 mL). The aqueous layer was separated and extracted with Et₂O (2 x 40 mL) and the combined organic layers were washed with saturated aqueous NH₄Cl solution (50 mL), dried (MgSO₄), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (20% CH₂Cl₂/hexane→40% CH₂Cl₂/hexane) gave the alkenylarene 8 (957 mg, 95%) as a dark yellow oil. IR (film) 3028, 2925, 2856, 1529 (N-O), 1350 (N-O), 1076, 964, 820, 733, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.19 (1H, s, ArH), 8.10-8.02 (1H, m, ArH), 7.62 (1H, d, J = 7.7 Hz, ArH), 7.46 (1H, t, J = 7.9 Hz, ArH), 7.33 (2H, m, ArH), 7.29-7.20 (3H, m, ArH),...
6.51-6.38 (2H, m, CH=CH), 2.89-2.80 (2H, m, CH\textsubscript{2}Ph), 2.65-2.55 (2H, m, CH\textsubscript{2}CH\textsubscript{2}Ph); \textsuperscript{13}C NMR (125.8 MHz, CDCl\textsubscript{3}) \(\delta\) 148.6 (C), 141.2 (C), 139.4 (C), 133.4 (CH), 131.8 (CH), 129.3 (CH), 128.41 (2 x CH), 128.39 (2 x CH), 128.3 (CH), 126.0 (CH), 121.5 (CH), 120.5 (CH), 35.5 (CH), 34.7 (CH\textsubscript{2}); HRMS (EI) Exact mass calcd for C\textsubscript{16}H\textsubscript{15}NO\textsubscript{2} [M]\textsuperscript{+}: 253.1097, found: 253.1095.

1-[(\textit{E})-Hex-1-enyl]-2-nitrobenzene (9)

A solution of 1-iodo-2-nitrobenzene (747 mg, 3.00 mmol), alkenylboronic ester 14\textsuperscript{2} (693 mg, 3.30 mmol), Pd(OAc)\textsubscript{2} (34 mg, 0.15 mmol), PPh\textsubscript{3} (157 mg, 0.60 mmol), and NaOH (360 mg, 9.00 mmol) in THF (30 mL) was heated to reflux for 16 h. The mixture was cooled to room temperature, and partitioned between Et\textsubscript{2}O (50 mL) and H\textsubscript{2}O (30 mL). The aqueous layer was separated and extracted with Et\textsubscript{2}O (2 x 25 mL) and the combined organic layers were washed with saturated aqueous NH\textsubscript{4}Cl solution (40 mL), dried (MgSO\textsubscript{4}), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (20% CH\textsubscript{2}Cl\textsubscript{2}/hexane→40% CH\textsubscript{2}Cl\textsubscript{2}/hexane) gave the alkenylarene 9 (575 mg, 93%) as a yellow oil. IR (film) 2929, 2858, 1606, 1522 (N-O), 1466, 1346 (N-O), 964, 860, 783, 739 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.84 (1H, dd, \(J\) = 8.2, 1.1 Hz, ArH), 7.57 (1H, dd, \(J\) = 7.9, 1.1 Hz, ArH), 7.50 (1H, t, \(J\) = 7.6 Hz, ArH), 7.35-7.28 (1H, m, ArH), 6.82 (1H, d, \(J\) = 15.7 Hz, ArCH=), 6.23 (1H, td, \(J\) = 15.7, 6.9 Hz, ArCH=CH), 2.56 (2H, app ddd, \(J\) = 8.3, 7.3, 1.4 Hz, =CHCH\textsubscript{2}), 1.51-1.45 (2H, m, CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{3}), 1.42-1.34 (2H, m, CH\textsubscript{2}CH\textsubscript{3}), 0.93 (3H, t, \(J\) = 7.3 Hz, CH\textsubscript{3}); \textsuperscript{13}C NMR (125.8 MHz, CDCl\textsubscript{3}) \(\delta\) 147.5 (C), 136.8 (CH), 133.2 (C), 132.7 (CH), 128.2 (CH), 127.2 (CH), 124.7 (CH), 124.2 (CH), 32.8 (CH\textsubscript{2}), 31.0 (CH\textsubscript{2}), 22.1 (CH\textsubscript{2}), 13.8 (CH\textsubscript{3}); HRMS (EI) Exact mass calcd for C\textsubscript{12}H\textsubscript{15}NO\textsubscript{2} [M]\textsuperscript{+}: 205.1097, found: 205.1095.

2-[(\textit{E})-Hex-1-enyl]-5-nitropyridine (10)

A solution of 2-bromo-5-nitropyridine (1.02 g, 5.00 mmol), alkenylboronic ester 14\textsuperscript{2} (1.16 g, 5.50 mmol), Pd(OAc)\textsubscript{2} (56 mg, 0.25 mmol), PPh\textsubscript{3} (262 mg, 1.00 mmol), and CsF (2.28 g, 15.0 mmol) in THF (50 mL) was heated to reflux for 16 h. The mixture was cooled to room temperature, and partitioned between Et\textsubscript{2}O (100 mL) and H\textsubscript{2}O (50 mL). The aqueous layer was separated and extracted
with Et$_2$O (2 x 50 mL) and the combined organic layers were washed with saturated aqueous NH$_4$Cl solution (80 mL), dried (MgSO$_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (40% CH$_2$Cl$_2$/hexane→60% CH$_2$Cl$_2$/hexane) gave the 2-alkenylpyridine 10 (581 mg, 56%) as a red oil. IR (film) 2958, 2929, 1649, 1593, 1576, 1518 (N-O), 1468, 1348 (N-O), 972, 866 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.30 (1H, s, ArH), 8.35 (1H, dd, $J = 8.7, 2.7$ Hz, ArH), 7.34 (1H, d, $J = 8.7$ Hz, ArH), 7.02 (1H, td, $J = 15.5, 7.1$ Hz, ArCH=CH), 6.55 (1H, d, $J = 15.6$ Hz, ArCH=), 2.30 (2H, app qd, $J = 7.5, 1.4$ Hz, =CHC$_2$H$_5$), 1.55-1.45 (2H, m, C$_2$H$_5$CH$_2$CH$_3$), 1.41-1.34 (2H, C$_2$H$_5$), 0.91 (3H, t, $J = 7.3$ Hz, C$_3$H$_7$); $^{13}$C NMR (125.8 MHz, CDCl$_3$) $\delta$ 161.3 (C), 145.1 (CH), 142.3 (CH), 142.1 (C), 131.5 (CH), 128.3 (CH), 120.5 (CH), 32.7 (CH$_2$), 30.6 (CH$_2$), 22.2 (CH$_2$), 13.8 (CH$_3$); HRMS (ASAP) Exact mass calcd for C$_{11}$H$_{14}$N$_2$O$_2$ [M$^-\]$: 206.1061, found: 206.1060.

4-[(E)-Hex-1-enyl]-2-trifluoromethylbenzonitrile (12)

A solution of 2-trifluoromethyl-4-iodobenzonitrile (1.19 g, 4.00 mmol), alkenylboronic ester 14 (925 mg, 4.40 mmol), Pd(OAc)$_2$ (45 mg, 0.20 mmol), PPh$_3$ (210 mg, 0.80 mmol), and NaOH (480 mg, 12.0 mmol) in THF (40 mL) was heated to reflux for 16 h. The mixture was cooled to room temperature, and partitioned between Et$_2$O (50 mL) and H$_2$O (30 mL). The aqueous layer was separated and extracted with Et$_2$O (2 x 40 mL) and the combined organic layers were washed with saturated aqueous NH$_4$Cl solution (50 mL), dried (MgSO$_4$), filtered, and concentrated *in vacuo*. Purification of the residue by column chromatography (20% CH$_2$Cl$_2$/hexane→40% CH$_2$Cl$_2$/hexane) gave the alkenylarene 12 (917 mg, 91%) as a colorless oil. IR (film) 2960, 2931, 2229 (C≡N), 1649 (C=C), 1608, 1323, 1178, 1138, 1053, 966 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.74 (1H, d, $J = 8.0$ Hz, ArH), 7.71 (1H, br s, ArH), 7.58 (1H, dd, $J = 8.0, 1.2$ Hz, ArH), 6.53-6.41 (2H, m, CH=CH), 2.31-2.27 (2H, m, =CHCH$_2$), 1.53-1.47 (2H, m, CH$_2$CH$_2$CH$_3$), 1.42-1.35 (2H, CH$_2$CH$_3$), 0.94 (3H, t, $J = 7.3$ Hz, CH$_3$); $^{13}$C NMR (125.8 MHz, CDCl$_3$) $\delta$ 142.8 (C), 137.8 (CH), 134.7 (CH), 132.7 (C, q, $J = 32.3$ Hz), 128.8 (CH), 127.1 (CH), 123.6 (CH, q, $J = 4.7$ Hz), 122.4 (C, q, $J = 273.8$ Hz), 115.6 (C), 106.9 (C, q, $J = 2.0$ Hz), 32.6 (CH$_2$), 30.8 (CH$_3$), 22.1 (CH$_2$), 13.6 (CH$_3$); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ −62.5 (3F, s); HRMS (ES) Exact mass calcd for C$_{14}$H$_{18}$N$_2$F$_3$ [M+NH$_4$]$^+$: 271.1417, found: 271.1415.
Enantioselective Rhodium-Catalyzed Addition of Arylboronic Acids to Alkenylarenes: General Procedure

A solution of [Rh(C2H4)2Cl2] (1.9 mg, 0.005 mmol) and ligand L5 (4.6 mg, 0.012 mmol) in dioxane (0.3 mL) was stirred under nitrogen at room temperature for 15 min. This solution was then added via cannula to a sealed nitrogen-flushed microwave vial containing the appropriate alkenylarene (0.20 mmol), the appropriate arylboronic acid (0.48 mmol), KOH (28 mg, 0.50 mmol), and H2O (0.1 mL), using further dioxane (0.2 mL) as a rinse. The resulting mixture was irradiated in a microwave reactor at 80 °C for 30 min. After cooling to room temperature, the mixture was filtered through a short plug of SiO2 using CH2Cl2 as eluent and concentrated in vacuo. Purification of the residue by column chromatography gave the arylated product.

1-[(S)-2,4-Diphenylbutyl]-4-nitrobenzene (2a). Using microwave irradiation: The title compound was prepared according to the General Procedure from alkenylarene 1a (51 mg, 0.20 mmol) and phenylboronic acid (59 mg, 0.48 mmol) and purified by column chromatography (5% CH2Cl2/hexane→20% CH2Cl2/hexane) to give a yellow oil (61 mg, 92%). [α]24D +72.9 (c 0.85, CHCl3); IR (film) 3026, 2927, 2856, 1603, 1518 (N-O), 1452, 1344 (N-O), 852, 758, 700 cm−1; 1H NMR (400 MHz, CDCl3) δ 8.06-7.99 (2H, m, ArH), 7.34-7.15 (6H, m, ArH), 7.13-7.05 (6H, m, ArH), 3.06 (1H, dd, J = 13.2, 6.3 Hz, ArCH2), 2.96 (1H, dd, J = 13.2, 8.5 Hz, ArCH2), 2.92-2.81 (1H, m, ArCH2), 2.60-2.40 (2H, m, CH2CH2Ph), 2.10-1.99 (2H, m, CH2CH2Ph); 13C NMR (100.6 MHz, CDCl3) δ 148.3 (C), 146.3 (C), 143.2 (C), 141.9 (C), 129.8 (2 x CH), 128.5 (2 x CH), 128.3 (2 x CH), 128.3 (2 x CH), 127.7 (2 x CH), 126.6 (CH), 125.8 (CH), 123.3 (2 x CH), 47.2 (CH), 43.7 (CH2), 37.5 (CH2), 33.6 (CH2); HRMS (ES) Exact mass calcd for C22H25N2O2 [M+NH4]+: 349.1911, found: 349.1911. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (99:1 hexane:isopropanol, 0.8 mL/min, 254 nm, 25 °C); tR (major) = 18.1 min, tR (minor) = 19.9 min; 95% ee.

Using thermal heating: A repeat of the above reaction using thermal heating (oil bath temperature 80 °C) under otherwise identical conditions gave the alkenylarene 1a (60 mg, 90%) in 94% ee.
2-[(S)-1-(4-Nitrobenzyl)-3-phenylpropyl]naphthalene (2b). The title compound was prepared according to the General Procedure from alkenylarene 1a (51 mg, 0.20 mmol) and 2-naphthylboronic acid (83 mg, 0.48 mmol) and purified by column chromatography (5% CH₂Cl₂/hexane→20% CH₂Cl₂/hexane) to give a dark brown viscous oil (60 mg, 79%). 

\[ \alpha \] \text{D} +108.0 (c 0.69, CHCl₃); IR (film) 3057, 2933, 1601, 1518 (N-O), 1454, 1344 (N-O), 1109, 856, 746, 700 cm⁻¹; \[ \text{H NMR (500 MHz, CDCl}_3] \delta 8.03-7.97 (2H, m, ArH), 7.87-7.80 (2H, m, ArH), 7.79-7.47 (1H, m, ArH), 7.52-7.43 (3H, m, ArH), 7.33-7.24 (3H, m, ArH), 7.22-7.16 (1H, m, ArH), 7.13-7.04 (4H, m, ArH), 3.19-3.00 (3H, m, ArC₂H₂), 2.60-2.43 (2H, m, C₂H₂C₂H₂); 13C NMR (125.8 MHz, CDCl₃) δ 148.2 (C), 146.3 (C), 141.8 (C), 140.6 (C), 133.4 (C), 132.4 (C), 129.8 (2 x CH), 128.34 (2 x CH), 128.31 (2 x CH), 127.6 (CH), 127.5 (CH), 126.7 (CH), 126.1 (CH), 125.9 (CH), 125.5 (2 x CH), 123.3 (2 x CH), 47.3 (CH), 43.5 (CH₂), 37.4 (CH₂), 33.6 (CH₂); m/z (ES) 404 ([M+Na]+, 100). Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (99:1 hexane:isopropanol, 0.8 mL/min, 225 nm, 25 °C); tᵣ (minor) = 45.2 min, tᵣ (major) = 48.3 min; 89% ee.

1-Nitro-4-[(S)-2-phenylhexyl]benzene (2c)

A solution of [Rh(C₂H₄)₂Cl]₂ (4.9 mg, 0.0125 mmol) and ligand L₅ (11.6 mg, 0.030 mmol) in dioxane (1.5 mL) was stirred under nitrogen at room temperature for 15 min. This solution was then added via cannula to a sealed nitrogen-flushed microwave vial containing alkenylarene 1b (205 mg, 1.00 mmol), phenylboronic acid (293 mg, 2.40 mmol), KOH (140 mg, 2.50 mmol), and H₂O (0.5 mL), using further dioxane (1.0 mL) as a rinse. The resulting mixture was heated to 80 °C in an oil bath for 1 h. After cooling to room temperature, the mixture was filtered through a short plug of SiO₂ using CH₂Cl₂ as eluent and concentrated in vacuo. Purification of the residue by column chromatography (5% CH₂Cl₂/hexane→20% CH₂Cl₂/hexane) gave the arylation product 2c (236 mg, 83%) as a yellow oil. 

\[ \alpha \] \text{D} +137.0 (c 1.07, CHCl₃); IR (film) 2956, 2929, 2858, 1603, 1518 (N-O), 1346 (N-O), 1109, 850, 760, 700 cm⁻¹; \[ \text{H NMR (500 MHz, CDCl}_3] \delta 8.07-8.01 (2H, m, ArH), 7.30-7.23 (2H, m, ArH), 7.22-7.16 (1H, m, ArH), 7.15-7.10 (2H, m, ArH), 7.09-7.04 (2H, m, ArH), 3.06 (1H, dd, J = 13.3, 6.1 Hz, 1H, m, ArH), 2.60-2.43 (2H, m, C₂H₂C₂H₂); 13C NMR (125.8 MHz, CDCl₃) δ 148.2 (C), 146.3 (C), 141.8 (C), 140.6 (C), 133.4 (C), 132.4 (C), 129.8 (2 x CH), 128.34 (2 x CH), 128.31 (2 x CH), 127.6 (CH), 127.5 (CH), 126.7 (CH), 126.1 (CH), 125.9 (CH), 125.5 (2 x CH), 123.3 (2 x CH), 47.3 (CH), 43.5 (CH₂), 37.4 (CH₂), 33.6 (CH₂); m/z (ES) 404 ([M+Na]+, 100). Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (99:1 hexane:isopropanol, 0.8 mL/min, 225 nm, 25 °C); tᵣ (minor) = 45.2 min, tᵣ (major) = 48.3 min; 89% ee.
ArCH₂), 2.94 (1H, dd, J = 13.3, 8.8 Hz, ArCH), 2.88-2.78 (1H, m, ArCHCH₂), 1.71 (2H, app q, J = 7.6 Hz, CH₂CH₂CH₂CH₃), 1.37-1.10 (4H, m, CH₂C₂H₂CH₃), 0.84 (3H, t, J = 7.2 Hz, CH₃); ¹³C NMR (125.8 MHz, CDCl₃) δ 148.7 (C), 146.2 (C), 143.8 (C), 129.8 (2 x CH), 128.3 (2 x CH), 127.6 (2 x CH), 126.3 (CH), 123.2 (2 x CH), 47.9 (CH), 43.6 (CH₂), 35.6 (CH₂), 29.6 (CH₂), 22.6 (CH₂), 13.9 (CH₃); HRMS (ES) Exact mass calcd for C₁₉H₂₁NO₂ [M+NH₄]+: 315.2067, found: 315.2068. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (99.3:0.7 hexane:isopropanol, 0.8 mL/min, 280 nm, 25 °C); tᵣ (major) = 8.2 min, tᵣ (minor) = 9.0 min; 94% ee.

4-[(S)-2-(4-Methylphenyl)hexyl]-1-nitrobenzene (2d). The title compound was prepared according to the General Procedure from alkenylarene 1b (41 mg, 0.20 mmol) and 4-methylphenylboronic acid (65 mg, 0.48 mmol) and purified by column chromatography (5% CH₂Cl₂/hexane→20% CH₂Cl₂/hexane) to give a yellow oil (52 mg, 87%). [α]²⁴D +154.6 (c 0.97, CHCl₃); IR (film) 2956, 2927, 2858, 1603, 1518 (N-O), 1344 (N-O), 1109, 860, 781, 704 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.06-8.01 (2H, m, ArH), 7.15-7.09 (2H, m, ArH), 7.06 (2H, d, J = 7.8 Hz, ArH), 6.97-6.92 (2H, m, ArH), 3.02 (1H, dd, J = 13.3, 6.2 Hz, ArCH₂), 2.91 (1H, dd, J = 13.3, 8.7 Hz, ArCH₂), 2.83-2.73 (1H, m, ArCH₂), 2.31 (3H, s, ArCH₃), 1.70-1.63 (2H, m, CH₂CH₂CH₂CH₃), 1.35-1.09 (4H, m, CH₂C₂H₂CH₃), 0.83 (3H, t, J = 7.2 Hz, CH₂C₂H₃); ¹³C NMR (125.8 MHz, CDCl₃) δ 148.9 (C), 146.2 (C), 140.8 (C), 135.8 (C), 129.8 (2 x CH), 129.0 (2 x CH), 127.5 (2 x CH), 123.2 (2 x CH), 47.4 (CH), 43.7 (CH₂), 35.7 (CH₂), 29.7 (CH₂), 22.6 (CH₂), 21.0 (CH₃), 13.9 (CH₃); HRMS (ES) Exact mass calcd for C₁₀H₂₇N₂O₂ [M+NH₄]+: 315.2067, found: 315.2068. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (98:1 hexane:isopropanol, 0.8 mL/min, 254 nm, 25 °C); tᵣ (major) = 8.2 min, tᵣ (minor) = 9.2 min; 95% ee.

4-[(S)-2-(3-Methylphenyl)hexyl]-1-nitrobenzene (2e). The title compound was prepared according to the General Procedure from alkenylarene 1b (41 mg, 0.20 mmol) and 3-methylphenylboronic acid (65 mg, 0.48 mmol) and purified by column chromatography (5% CH₂Cl₂/hexane→20% CH₂Cl₂/hexane) to give a yellow oil (53 mg, 90%). [α]²⁴D +130.9 (c 0.83, CHCl₃); IR (film) 2927, 2858, 1604, 1518 (N-O), 1456, 1344 (N-O), 1109, 860, 781, 704 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.07-8.02 (2H, m, ArH), 7.17-7.10 (3H, m, ArH), 7.00 (1H, d, J = 7.5 Hz, ArH), 6.89-6.82 (2H, m, ArH), 3.01 (1H, dd, J = 13.4, 6.4 Hz, ArCH₂), 2.93 (1H, dd, J = 13.4, 8.4 Hz, ArCH₂), 2.82-2.72 (1H, m, ArCH₂CH₂), 2.31 (3H, s, ArCH₃), 1.70-1.62 (2H, n-BuO₂NMe)
m, CH₂CH₂CH₂CH₃), 1.35-1.08 (4H, m, CH₂CH₂CH₃), 0.83 (3H, t, J = 7.2 Hz, CH₃); ¹³C NMR (125.8 MHz, CDCl₃) δ 148.9 (C), 146.2 (C), 143.9 (C), 137.9 (C), 129.8 (2 x CH), 128.4 (CH), 128.2 (CH), 127.1 (CH), 124.6 (CH), 123.2 (2 x CH), 47.8 (CH), 43.6 (CH₂), 35.6 (CH₂), 29.7 (CH₂), 22.6 (CH₂), 21.5 (CH₃), 13.9 (CH₃); HRMS (ASAP) Exact mass calcd for C₁₉H₂₄NO₂ [M+H]⁺: 298.1802, found: 298.1804. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (99.3:0.7 hexane:isopropanol, 0.8 mL/min, 280 °C); tᵣ (major) = 8.0 min, tᵣ (minor) = 8.7 min; 92% ee.

4-[(S)-2-(2-Methylphenyl)hexyl]-1-nitrobenzene (2f). The title compound was prepared according to the General Procedure from alkenylarene 1b (41 mg, 0.20 mmol) and 2-methylphenylboronic acid (65 mg, 0.48 mmol) but for a reaction time of 1 h and purified by column chromatography (5% CH₂Cl₂/hexane→20% CH₂Cl₂/hexane) to give a yellow oil (36 mg, 61%). [α]²⁴D +107.9 (c 0.95, CHCl₃); IR (film) 2929, 2858, 1603, 1518 (N-O), 1462, 1344 (N-O), 1109, 852, 760, 727 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.06-8.00 (2H, m, ArH), 7.26-7.18 (2H, m, ArH), 7.13-7.01 (4H, m, ArH), 3.22-3.11 (1H, m, ArCH₂CH₃), 3.02 (1H, dd, J = 13.2, 6.0 Hz, ArCH₂), 2.90 (1H, dd, J = 13.2, 8.8 Hz, ArCH₂), 2.04 (3H, s, ArCH₃), 1.69-1.64 (2H, m, CH₂CH₂CH₂CH₃), 1.35-1.09 (4H, m, CH₂CH₂CH₃), 0.84 (3H, t, J = 7.2 Hz, CH₃); ¹³C NMR (125.8 MHz, CDCl₃) δ 148.8 (C), 146.2 (C), 142.2 (C), 136.1 (C), 130.2 (CH), 129.8 (2 x CH), 126.2 (CH), 125.9 (CH), 125.7 (CH), 123.2 (2 x CH), 43.5 (CH₂), 42.0 (CH), 35.7 (CH₂), 29.6 (CH₂), 22.8 (CH₂), 19.7 (CH₃), 13.9 (CH₃); HRMS (ASAP) Exact mass calcd for C₁₉H₂₄NO₂ [M+H]⁺: 298.1802, found: 298.1804. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (99:1 hexane:isopropanol, 0.8 mL/min, 254 nm, 25 °C); tᵣ (major) = 7.3 min, tᵣ (minor) = 8.3 min; 97% ee.

4-[(S)-2-(4-Chlorophenyl)hexyl]-1-nitrobenzene (2g). The title compound was prepared according to the General Procedure from alkenylarene 1b (41 mg, 0.20 mmol) and 4-chlorophenylboronic acid (75 mg, 0.48 mmol) and purified by column chromatography (5% CH₂Cl₂/hexane→20% CH₂Cl₂/hexane) to give a yellow oil (56 mg, 89%). [α]²⁴D +158.6 (c 0.90, CHCl₃); IR (film) 2927, 2858, 1601, 1518 (N-O), 1491, 1454, 1344 (N-O), 1093, 1014, 829 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.07-8.02 (2H, m, ArH), 7.25-7.19 (2H, m, ArH), 7.13-7.08 (2H, m, ArH), 7.01-6.95 (2H, m, ArH), 3.04 (1H, dd, J = 13.2, 5.8 Hz, ArCH₂), 2.88 (1H, dd, J = 13.2, 9.0 Hz, ArCH₂), 2.84-2.75 (1H, m, ArCH₂CH₂), 1.75-1.59 (2H, m, CH₂CH₂CH₂CH₃), 1.35-1.06 (4H, m, CH₂CH₂CH₃), 0.83 (3H, t, J = 7.3 Hz, CH₃); ¹³C NMR
(125.8 MHz, CDCl$_3$) $\delta$ 148.2 (C), 146.3 (C), 142.3 (C), 132.0 (C), 129.8 (2 x CH), 128.9 (2 x CH), 128.5 (2 x CH), 123.3 (2 x CH), 47.4 (CH), 43.5 (CH$_2$), 35.6 (CH$_2$), 29.6 (CH$_2$), 22.6 (CH$_2$), 13.9 (CH$_3$); HRMS (ASAP) Exact mass calcd for C$_{18}$H$_{20}$ClNO$_2$ [M] –: 317.1188, found: 317.1186. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (99:1 hexane:isopropanol, 0.8 mL/min, 254 nm, 25 °C); $t_c$ (major) = 12.3 min, $t_c$ (minor) = 13.3 min; 94% ee.

4-[(S)-2-(4-Fluorophenyl)hexyl]-1-nitrobenzene (2h). The title compound was prepared according to the General Procedure from alkenylarene 1b (41 mg, 0.20 mmol) and 4-fluorophenylboronic acid (67 mg, 0.48 mmol) and purified by column chromatography (5% CH$_2$Cl$_2$/hexane→20% CH$_2$Cl$_2$/hexane) to give a yellow oil (49 mg, 81%). $[\alpha]_{D}^{24}$ +119.1 (c 0.94, CHCl$_3$); IR (film) 2929, 2858, 1603, 1510 (N-O), 1346 (N-O), 1223, 1159, 1109, 835, 750 cm$^{-1}$; $^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.07-8.01 (2H, m, ArH), 7.13-7.06 (2H, m, ArH), 7.03-6.89 (4H, m, ArH), 3.04 (1H, dd, $J$ = 12.8, 5.5 Hz, ArCH$_2$H), 2.92-2.75 (2H, m, ArCH$_2$H), 1.77-1.58 (2H, m, C$_2$H$_2$CH$_2$CH$_3$), 1.37-1.05 (4H, m, C$_2$H$_2$CH$_3$), 0.83 (3H, t, $J$ = 7.2 Hz, CH$_3$)$_3$; $^{13}$C NMR (125.8 MHz, CDCl$_3$) $\delta$ 161.4 (C, d, $J$ = 244.3 Hz), 148.4 (C), 146.3 (C), 139.4 (C, d, $J$ = 3.2 Hz), 129.8 (2 x CH), 128.9 (2 x CH, d, $J$ = 7.7 Hz), 123.3 (2 x CH), 115.2 (2 x CH, d, $J$ = 21.1 Hz), 47.2 (CH), 43.7 (CH$_2$), 35.8 (CH$_2$), 29.6 (CH$_2$), 22.6 (CH$_2$), 13.9 (CH$_3$)$_3$; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –117.0 (1F, tt, $J$ = 8.6, 5.5 Hz); HRMS (ASAP) Exact mass calcd for C$_{18}$H$_{20}$FNO$_2$ [M] : 301.1484, found: 301.1483. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (99:1 hexane:isopropanol, 0.8 mL/min, 254 nm, 25 °C); $t_c$ (major) = 11.5 min, $t_c$ (minor) = 12.5 min; 94% ee.

4-[(S)-2-(4-Methoxyphenyl)hexyl]-1-nitrobenzene (2i). The title compound was prepared according to the General Procedure from alkenylarene 1b (41 mg, 0.20 mmol) and 4-methoxyphenylboronic acid (73 mg, 0.48 mmol) and purified by column chromatography (5% CH$_2$Cl$_2$/hexane→20% CH$_2$Cl$_2$/hexane) to give a yellow amorphous solid (52 mg, 83%). $[\alpha]_{D}^{24}$ +147.6 (c 0.75, CHCl$_3$); IR (film) 2929, 2856, 1606, 1514 (N-O), 1344 (N-O), 1248, 1178, 1038, 831, 748 cm$^{-1}$; $^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.06-8.01 (2H, m, ArH), 7.13-7.07 (2H, m, ArH), 6.98-6.92 (2H, m, ArH), 6.81-6.76 (2H, m, ArH), 3.78 (3H, s, OCH$_3$)$_3$, 3.01 (1H, dd, $J$ = 13.3, 5.9 Hz, ArCH$_2$H), 2.88 (1H, dd, $J$ = 13.3, 8.9 Hz, ArCH$_2$H), 2.81-2.71 (1H, m, ArCH$_2$CH$_3$), 1.73-1.59 (2H, m, CH$_2$CH$_2$CH$_2$CH$_3$), 1.35-1.09 (4H, m, CH$_2$CH$_2$CH$_3$), 0.83 (3H, t, $J$ = 7.2 Hz, CH$_3$)$_3$; $^{13}$C NMR (125.8 MHz, CDCl$_3$) $\delta$ 158.0 (C), 148.9 (C), 146.2 (C), 135.8 (C), 129.8 (2 x n-BuO$_2$N), 129.8 (2 x n-BuO$_2$N).
CH), 128.5 (2 x CH), 123.2 (2 x CH), 113.7 (2 x CH), 55.2 (CH₃), 47.1 (CH), 43.8 (CH₂), 35.9 (CH₂),
29.7 (CH₂), 22.6 (CH₂), 14.0 (CH); HRMS (ASAP) Exact mass calcd for C₁₉H₂₃NO₃ [M]−: 313.1683,
found: 313.1688. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (98:2
hexane:isopropanol, 0.8 mL/min, 280 nm, 25 °C); tᵣ (major) = 10.8 min, tᵣ (minor) = 12.2 min; 93% ee.

1-[(R)-2-Cyclopropyl-2-phenylethyl]-4-nitrobenzene (2j). The title compound
was prepared according to the General Procedure from alkenylarene 1c (38 mg,
0.20 mmol) and phenylboronic acid (59 mg, 0.48 mmol) and purified by column
chromatography (5% CH₂Cl₂/hexane→20% CH₂Cl₂/hexane) to give a yellow oil (40 mg, 74%). [α]D²⁴
+49.4 (c 0.89, CHCl₃); IR (film) 3078, 3001, 2925, 1599, 1516 (N-O), 1344 (N-O), 1109, 1018, 750,
698 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.08-8.03 (2H, m, ArH), 7.32-7.26 (2H, m, ArH), 7.25-7.20
(1H, m, ArH), 7.18-7.09 (4H, m, ArH), 3.23 (1H, dd, J = 13.3, 6.2 Hz, ArCH₂), 3.13 (1H, dd, J = 13.3,
8.4 Hz, ArCH₂), 2.15-2.07 (1H, m, ArCH₂CH₂), 1.18-1.06 (1H, m, CH₂CH₂CH₂), 0.65-0.57 (1H, m,
CH₂CH₂), 0.50-0.42 (1H, m, CH₂CH₂), 0.17-0.11 (2H, m, CH₂CH₂); ¹³C NMR (125.8 MHz, CDCl₃) δ
148.4 (C), 146.3 (C), 143.8 (C), 130.0 (2 x CH), 128.3 (2 x CH), 127.6 (2 x CH), 126.5 (CH), 123.2 (2
x CH), 52.9 (CH), 43.4 (CH₂), 16.8 (CH), 5.9 (CH₂), 4.0 (CH₂); HRMS (EI) Exact mass calcd for
C₁₇H₁₇NO₂ [M]+: 267.1254, found: 267.1252. Enantiomeric excess was determined by HPLC with a
Chiralpak AD-H column (99:1 hexane:isopropanol, 0.8 mL/min, 280 nm, 25 °C); tᵣ (minor) = 9.3 min,
tᵣ (major) = 10.2 min; 92% ee.

1-[(S)-3-Methoxy-2-phenylpropyl]-4-nitrobenzene (2k). The title compound
was prepared according to the General Procedure from alkenylarene 1d (39 mg,
0.20 mmol) and phenylboronic acid (59 mg, 0.48 mmol) and purified by column
chromatography (40% CH₂Cl₂/hexane) to give a colorless oil (45 mg, 82%). [α]D²⁴
+106.0 (c 1.00, CHCl₃); IR (film) 2921, 1644, 1604, 1516 (N-O), 1494, 1453, 1343 (N-O), 1110, 760, 699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ
8.07-8.01 (2H, m, ArH), 7.31-7.24 (2H, m, ArH), 7.24-7.18 (1H, m, ArH), 7.18-7.13 (2H, m, ArH),
7.13-7.07 (2H, m, ArH), 3.58-3.56 (2H, m, ArH), 3.37 (3H, s, OC₃H₃), 3.29 (1H, dd, J = 13.3, 5.5 Hz,
ArCH₂), 3.21-3.10 (1H, m, ArCH₂CH₂), 2.96 (1H, dd, J = 13.3, 9.1 Hz, ArCH₂); ¹³C NMR (100.6 MHz, CDCl₃) δ
148.2 (C), 146.3 (C), 141.1 (C), 129.9 (2 x CH), 128.5 (2 x CH), 127.8 (2 x CH), 126.9 (CH), 123.3 (2 x CH), 76.0 (CH₂), 58.9 (CH₃), 47.7 (CH), 39.1 (CH₂); m/z (ES) 294
([M+Na]⁺, 100). Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column (99:1
hexane:isopropanol, 0.8 mL/min, 280 nm, 25 °C); tᵣ (minor) = 19.8 min, tᵣ (major) = 21.0 min; 91% ee.
(4-Chlorophenyl)methyl-[(S)-3-(4-nitrophenyl)-2-phenylpropyl]amine (2l). The title compound was prepared according to the General Procedure from alkenylarene 1e (61 mg, 0.20 mmol) and phenylboronic acid (59 mg, 0.48 mmol) and purified by column chromatography (20% CH₂Cl₂/hexane→40% CH₂Cl₂/hexane) to give a yellow gum (65 mg, 85%). [α]₂⁴D –28.7 (c 1.05, CHCl₃); IR (film) 1597, 1510, 1500 (N-O), 1344 (N-O), 1235, 1110, 848, 808, 766, 699 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.06-8.00 (2H, m, ArH), 7.30-7.24 (2H, m, ArH), 7.24-7.19 (1H, m, ArH), 7.18-7.12 (4H, m, ArH), 7.11-7.06 (2H, m, ArH), 6.53-6.47 (2H, m, ArH), 3.70 (1H, dd, J = 14.8, 7.0 Hz, CH₂N), 3.46 (1H, dd, J = 14.8, 7.6 Hz, CH₂N), 3.34-3.24 (1H, m, ArCH₂C), 3.16 (1H, dd, J = 13.6, 5.5 Hz, ArCH₂), 3.02 (1H, dd, J = 13.6, 9.8 Hz, ArCH₂), 2.72 (3H, s, CH₃); ¹³C NMR (125.8 MHz, CDCl₃) δ 147.8 (C), 147.3 (C), 146.4 (C), 141.4 (C), 129.7 (2 x CH), 129.0 (2 x CH), 128.7 (2 x CH), 127.8 (2 x CH), 127.1 (CH), 123.4 (2 x CH), 121.2 (C), 113.1 (2 x CH), 59.3 (CH₂), 46.0 (CH), 39.8 (CH₂), 39.7 (CH₃); m/z (ES) 381 ([M+H]+, 100). Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column (98:2 hexane:isopropanol, 0.8 mL/min, 280 nm, 25 °C); tᵣ (minor) = 18.0 min, tᵣ (major) = 19.8 min; 91% ee.

1-[(S)-2,4-Diphenylbutyl]-2-fluoro-4-nitrobenzene (2n). The title compound was prepared according to the General Procedure from alkenylarene 1g (54 mg, 0.20 mmol) and phenylboronic acid (59 mg, 0.48 mmol) and purified by column chromatography (5% CH₂Cl₂/hexane→20% CH₂Cl₂/hexane) to give a yellow oil (63 mg, 90%). [α]₂⁴D +75.9 (c 0.90, CHCl₃); IR (film) 3028, 2927, 1639, 1525 (N-O), 1493, 1350 (N-O), 1230, 1072, 741, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.86-7.80 (2H, m, ArH), 7.34-7.17 (6H, m, ArH), 7.16-7.08 (4H, m, ArH), 7.04-6.98 (1H, m, ArH), 3.22-3.11 (1H, m, ArCH₂), 3.00-2.90 (2H, m, ArCH₂), 2.60-2.45 (2H, m, CH₃CH₂Ph), 2.15-2.02 (2H, m, CH₃CH₂Ph); ¹³C NMR (125.8 MHz, CDCl₃) δ 160.3 (C, d, J = 249.6 Hz), 147.0 (C, d, J = 8.9 Hz), 143.0 (C), 141.8 (C), 135.5 (C, d, J = 16.2 Hz), 131.8 (CH, d, J = 5.4 Hz), 128.5 (2 x CH), 128.3 (2 x CH), 128.3 (2 x CH), 127.6 (2 x CH), 126.7 (CH), 125.8 (CH), 118.7 (CH, d, J = 3.5 Hz), 110.9 (CH, d, J = 27.9 Hz), 45.9 (CH), 37.5 (CH₂), 36.8 (CH₂), 33.6 (CH₂); ¹⁹F NMR (376 MHz, CDCl₃) δ –114.1 (1F, t, J = 8.3 Hz); HRMS (ASAP) Exact mass calcd for C₂₂H₂₁FNO₂ [M+H]+: 350.1551, found: 350.1549. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (99:1 hexane:isopropanol, 0.8 mL/min, 280 nm, 25 °C); tᵣ (minor) = 27.1 min, tᵣ (major) = 32.9 min; 88% ee.
2-Methyl-1-nitro-4-[((S)-2-phenylhexyl]benzene (2o)

A solution of [Rh(C₂H₄)₂Cl]₂ (9.8 mg, 0.025 mmol) and ligand L₅ (23 mg, 0.060 mmol) in dioxane (2.0 mL) was stirred under nitrogen at room temperature for 15 min. This solution was then added via cannula to a sealed nitrogen-flushed microwave vial containing alkenylarene 1h (219 mg, 1.00 mmol), phenylboronic acid (293 mg, 2.40 mmol), KOH (140 mg, 2.50 mmol), and H₂O (0.5 mL), using further dioxane (0.5 mL) as a rinse. The resulting mixture was irradiated in a microwave reactor at 80 °C for 30 min. After cooling to room temperature, the mixture was filtered through a short plug of SiO₂ using CH₂Cl₂ as eluent and concentrated in vacuo. Purification of the residue by column chromatography (20% CH₂Cl₂/hexane) gave the arylation product 2o (235 mg, 79%) as a yellow oil. [α]D²⁴ +104.7 (c 1.05, CHCl₃); IR (film) 2956, 2929, 2858, 1610, 1587, 1516 (N-O), 1452, 1342 (N-O), 837, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.87-7.81 (1H, m, ArH), 7.31-7.24 (2H, m, ArH), 7.22-7.16 (1H, m, ArH), 7.11-7.05 (2H, m, ArH), 6.96-6.90 (2H, m, ArH), 2.97 (1H, dd, J = 13.2, 6.3 Hz, ArCH₂), 2.88 (1H, dd, J = 13.2, 8.3 Hz, ArCH₂), 2.85-2.76 (1H, m, ArCH₂Ar), 2.53 (3H, s, ArCH₃), 1.73-1.64 (2H, m, CH₂CH₂CH₂CH₃), 1.37-1.09 (4H, m, CH₂CH₂CH₂CH₃), 1.04 (3H, t, J = 7.2 Hz, CH₂CH₃); ¹³C NMR (125.8 MHz, CDCl₃) δ 147.0 (C), 146.9 (C), 144.1 (C), 133.5 (C), 133.4 (CH), 128.3 (2 x CH), 127.6 (2 x CH), 127.4 (CH), 126.3 (CH), 124.6 (CH), 47.7 (CH), 43.4 (CH₂), 35.5 (CH₂), 29.7 (CH₂), 22.6 (CH₂), 20.7 (CH₃), 13.9 (CH₃); HRMS (ASAP) Exact mass calcd for C₁₀H₂₄NO₂ [M+H]⁺: 298.1802, found: 298.1800. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (98:2 hexane:isopropanol, 0.8 mL/min, 254 nm, 25 °C); t₁ (major) = 7.2 min, t₂ (minor) = 8.1 min; 87% ee.

2-Nitro-5-[(S)-2-phenylhexyl]benzoic acid methyl ester (2p). The title compound was prepared according to the General Procedure from alkenylarene 1i (53 mg, 0.20 mmol) and phenylboronic acid (59 mg, 0.48 mmol) and purified by column chromatography (5% CH₂Cl₂/hexane→20% CH₂Cl₂/hexane) to give a colorless oil (54 mg, 80%). [α]D²⁴ +90.0 (c 0.76, CHCl₃); IR (film) 2929, 1738 (C=O), 1645, 1527 (N-O), 1437, 1348 (N-O), 1294, 1205, 1070, 702 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.74 (1H, d, J = 8.3 Hz, ArH), 7.32 (1H, d, J = 1.8 Hz, ArH), 7.29-7.23 (2H, m, ArH), 7.22-7.16 (1H, m, ArH), 7.10 (1H, dd, J = 8.3, 1.9 Hz, ArH),
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7.07-7.02 (2H, m, ArH), 3.91 (3H, s, OCH₃), 3.03 (1H, dd, J = 13.4, 6.1 Hz, ArCH₂), 2.92 (1H, dd, J = 13.4, 8.7 Hz, ArCH₂), 2.85-2.75 (1H, m, ArCH₂C₂H), 1.69 (2H, app q, J = 7.6 Hz, C₂H₂CH₂CH₂), 1.35-1.05 (4H, m, C₂H₂C₂H₃), 0.83 (3H, t, J = 7.2 Hz, CH₂C₃H); 13C NMR (125.8 MHz, CDCl₃) δ 166.3 (C), 147.3 (C), 145.8 (C), 143.5 (C), 131.9 (CH), 130.1 (CH), 128.5 (2 x CH), 127.7 (C), 127.6 (2 x CH), 126.5 (CH), 123.7 (CH), 53.2 (CH₃), 47.8 (CH), 43.4 (CH₂), 35.6 (CH₂), 29.7 (CH₂), 22.6 (CH₂), 13.9 (CH₃); HRMS (ES) Exact mass calcd for C₂₀H₂₇N₂O₄ [M+NH₄]+: 359.1965, found: 359.1965. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (99:1 hexane:isopropanol, 0.8 mL/min, 254 nm, 25 °C); tᵣ (major) = 19.7 min, tᵣ (minor) = 23.2 min; 91% ee.

1-Nitro-4-[(S)-2-phenylhexyl]-2-trifluoromethylbenzene (2q). The title compound was prepared according to the General Procedure from alkenylarene 1j (55 mg, 0.20 mmol) and phenylboronic acid (59 mg, 0.48 mmol) and purified by column chromatography (5% CH₂Cl₂/hexane→20% CH₂Cl₂/hexane) to give a colorless oil (60 mg, 85%). [α]₂⁴D +89.7 (c 0.98, CHCl₃); IR (film) 2931, 1643, 1539 (N-O), 1454, 1358 (N-O), 1313, 1176, 1144, 1049, 702 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.71 (1H, d, J = 8.3 Hz, ArH), 7.34 (1H, d, J = 1.4 Hz, ArH), 7.30-7.17 (4H, m, ArH), 7.07-7.00 (2H, m, ArH), 3.09 (1H, dd, J = 13.4, 5.7 Hz, ArC₂H₂), 2.95 (1H, dd, J = 13.4, 9.2 Hz, ArCH₂), 1.79-1.66 (2H, m, C₂H₂CH₂CH₂), 1.38-1.11 (4H, m, C₂H₂CH₂CH₂), 0.85 (3H, t, J = 7.2 Hz, CH₂C₃H); ¹³C NMR (125.8 MHz, CDCl₃) δ 146.9 (C), 146.0 (C), 143.1 (C), 133.2 (CH), 128.5 (CH), 128.4 (CH, q, J = 5.4 Hz), 127.6 (CH), 126.7 (CH), 124.9 (CH), 123.3 (C, q, J = 33.7 Hz), 121.9 (C, q, J = 273.4 Hz), 47.8 (CH), 43.4 (CH₂), 35.6 (CH₂), 29.6 (CH₂), 22.6 (CH₂), 13.9 (CH₃); ¹⁹F NMR (376 MHz, CDCl₃) δ –60.4 (3F, s); HRMS (ASAP) Exact mass calcd for C₁₉H₂₁F₃NO₂ [M+H]+: 352.1519, found: 352.1521. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (99:1 hexane:isopropanol, 0.8 mL/min, 254 nm, 25 °C); tᵣ (major) = 19.7 min, tᵣ (minor) = 23.2 min; 91% ee.

1-[(S)-2,4-diphenylbutyl]-4-nitronaphthalene (2r). The title compound was prepared according to the General Procedure from alkenylarene 1k (61 mg, 0.20 mmol) and phenylboronic acid (59 mg, 0.48 mmol) and purified by column chromatography (5% CH₂Cl₂/hexane→20% CH₂Cl₂/hexane) to give a yellow oil (41 mg, 54%). [α]₂⁴D +55.9 (c 1.36, CHCl₃); IR (film) 3026, 2927, 2856, 1736, 1514 (N-O), 1454, 1338 (N-O), 1219, 769, 700 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.59 (1H, d, J = 8.6 Hz, ArH), 8.06 (1H, d, J = 8.5 Hz, ArH), 7.98 (1H, d, J = 7.8 Hz, ArH), 7.74-7.67 (1H, m, ArH), 7.64-7.58 (1H, m, ArH), 7.32-7.22
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(5H, m, ArH), 7.20-7.17 (1H, m, ArH), 7.13-7.05 (5H, m, ArH), 3.50 (1H, dd, J = 13.8, 6.7 Hz, ArCH₂CH), 3.34 (1H, dd, J = 13.8, 7.9 Hz, ArCH₂CH), 3.10-2.99 (1H, m, ArCH₂C), 2.58-2.39 (2H, m, CH₂Ph), 2.17-2.08 (2H, m, CH₂CH₂Ph); ¹³C NMR (125.8 MHz, CDCl₃) δ 145.5 (C), 144.3 (C), 143.8 (C), 141.8 (C), 132.6 (C), 128.7 (CH), 128.6 (2 x CH), 128.33 (2 x CH), 128.27 (2 x CH), 127.6 (2 x CH), 127.1 (CH), 126.7 (CH), 125.8 (CH), 125.7 (CH), 125.5 (C), 124.4 (CH), 123.8 (CH), 123.3 (CH), 46.5 (CH), 41.7 (CH₂), 37.7 (CH₂), 33.7 (CH₂); HRMS (ASAP) Exact mass calcd for C₂₆H₂₄NO₂ [M+H]+: 382.1802, found: 382.1802. Enantiomeric excess was determined by HPLC with a Chiralcel IB-3 column (99:1 hexane:isopropanol, 0.8 mL/min, 210 nm, −2.5 °C); tᵣ (minor) = 15.1 min, tᵣ (major) = 15.6 min; 84% ee.

[(S)-1-(4-Methoxyphenyl)-2-(4-nitrophenyl)ethyl]trimethylsilane (2s)

A solution of [Rh(C₂H₄)₂Cl₂] (3.8 mg, 0.010 mmol) and ligand L₅ (9.2 mg, 0.024 mmol) in dioxane (0.6 mL) was stirred under nitrogen at room temperature for 15 min. This solution was then added via cannula to a sealed nitrogen-flushed microwave vial containing alkenylarene 3 (89 mg, 0.40 mmol), 4-methoxyphenylboronic acid (146 mg, 0.96 mmol), KOH (56 mg, 1.00 mmol), and H₂O (0.2 mL), using further dioxane (0.4 mL) as a rinse. The resulting mixture was irradiated in a microwave reactor at 80 °C for 30 min. After cooling to room temperature, the mixture was filtered through a short plug of SiO₂ using CH₂Cl₂ as eluent and concentrated in vacuo. Purification of the residue by column chromatography (20% CH₂Cl₂/hexane→40% CH₂Cl₂/hexane) gave the arylation product 2s (75 mg, 57%) as a yellow oil. [α]D⁺14 +142.2 (c 0.97, CHCl₃); IR (film) 2953, 1605, 1509 (N-O), 1344 (N-O), 1247, 1178, 1108, 1037, 856, 841 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.03-7.97 (2H, m, ArH), 7.20-7.14 (2H, m, ArH), 6.91-6.84 (2H, m, ArH), 6.78-6.71 (2H, m, ArH), 3.75 (3H, s, OCH₃), 3.15 (1H, dd, J = 14.5, 4.2 Hz, ArCH₂), 3.09 (1H, dd, J = 14.5, 11.8 Hz, ArCH₂), 2.30 (1H, dd, J = 11.8, 4.2 Hz, ArCH₂), 0.02 (9H, s, Si(CH₃)₃); ¹³C NMR (125.8 MHz, CDCl₃) δ 157.0 (C), 150.0 (C), 146.1 (C), 133.6 (C), 129.2 (2 x CH), 128.6 (2 x CH), 123.3 (2 x CH), 113.7 (2 x CH), 55.1 (CH₃), 37.6 (CH), 36.0 (CH₂), −2.9 (3 x CH₃); m/z (ES) 352 ([M+Na]+, 100). Enantiomeric excess was determined by
HPLC with a Chiralcel OD-H column (99:1 hexane:isopropanol, 0.8 mL/min, 280 nm, 25 °C); \( t_r \) (major) = 8.4 min, \( t_r \) (minor) = 9.1 min; 91% ee.

**4-[(S)-5-tert-Butyldimethylsilyloxy-2-phenylpentyl]-1-nitrobenzene (2t)**

A solution of \([\text{Rh}(\text{C}_2\text{H}_4)\text{Cl}]_2\) (24 mg, 0.0625 mmol) and ligand L5 (58 mg, 0.15 mmol) in dioxane (7.5 mL) was stirred under nitrogen at room temperature for 15 min. This solution was then added via cannula to a sealed nitrogen-flushed microwave vial containing alkenylarene 4 (1.61 g, 5.00 mmol), phenylboronic acid (1.46 g, 12.0 mmol), KOH (701 mg, 2.50 mmol), and H\(_2\)O (2.5 mL), using further dioxane (5.0 mL) as a rinse. The resulting mixture was heated to 80 °C in an oil bath for 1.5 h. After cooling to room temperature, the mixture was filtered through a short plug of SiO\(_2\) using CH\(_2\)Cl\(_2\) as eluent and concentrated in vacuo. Purification of the residue by column chromatography (5% CH\(_2\)Cl\(_2\)/hexane→20% CH\(_2\)Cl\(_2\)/hexane) gave the arylation product 2t (1.75 g, 88%) as a yellow oil. \([\alpha]_{D}^{24} +79.3 \ (c \ 1.12, \text{CHCl}_3); \) IR (film) 2929, 2856, 1603, 1520 (N-O), 1346 (N-O), 1255, 1105, 837, 775, 700 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.09-8.02 (2H, m, ArH), 7.31-7.24 (2H, m, ArH), 7.23-7.17 (1H, m, ArH), 7.17-7.12 (2H, m, ArH), 7.11-7.05 (2H, m, ArH), 3.61-3.51 (2H, m, CH\(_2\)O), 3.06 (1H, dd, \( J = 13.3, 6.4 \) Hz, ArCH\(_2\)), 2.97 (1H, dd, \( J = 13.3, 8.4 \) Hz, ArCH\(_2\)), 2.91-2.81 (1H, m, ArCH\(_2\)CH\(_2\)), 1.85-1.78 (1H, m, CH\(_2\)CH\(_2\)CH\(_2\)O), 1.75-1.68 (1H, m, CH\(_2\)CH\(_2\)CH\(_2\)O), 1.48-1.36 (2H, m, CH\(_2\)CH\(_2\)O), 0.89 (9H, s, C(CH\(_3\))\(_3\)), 0.02 (3H, s, SiCH\(_3\)), 0.01 (3H, s, SiCH\(_3\)); \(^{13}\)C NMR (125.8 MHz, CDCl\(_3\)) \( \delta \) 148.6 (C), 146.3 (C), 143.6 (C), 129.8 (2 x CH), 128.4 (2 x CH), 127.6 (2 x CH), 126.4 (CH), 123.2 (2 x CH), 62.8 (CH\(_2\)), 47.6 (CH), 43.7 (CH\(_2\)), 31.9 (CH\(_2\)), 30.6 (CH\(_2\)), 25.9 (3 x CH\(_3\)), 18.3 (C), –5.4 (2 x CH\(_3\)); HRMS (ES) Exact mass calcd for C\(_{23}\)H\(_{34}\)NO\(_3\)Si [M+H]: 400.2302, found: 400.2306. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (99:1 hexane:isopropanol, 0.8 mL/min, 254 nm, 25 °C); \( t_r \) (major) = 7.1 min, \( t_r \) (minor) = 7.8 min; 93% ee.

**5-Nitro-2-[(S)-2-phenylhexyl]pyridine (11).** The title compound was prepared according to the General Procedure from alkenylpyridine 10 (41 mg, 0.20 mmol) and phenylboronic acid (59 mg, 0.48 mmol) and purified by column chromatography (5%
CH$_2$Cl$_2$/hexane $\rightarrow$ 20% CH$_2$Cl$_2$/hexane) to give a yellow oil (52 mg, 91%). $[\alpha]_D^{24} +125.1$ (c 0.90, CHCl$_3$); IR (film) 2956, 2927, 2858, 1645, 1599, 1577, 1522 (N-O), 1468, 1350 (N-O), 702 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.33 (1H, d, $J = 2.6$ Hz, ArH), 8.19 (1H, dd, $J = 8.5$ Hz, 2.7 Hz, ArH), 7.26-7.20 (2H, m, ArH), 7.19-7.12 (1H, m, ArH), 7.10-7.05 (2H, m, ArH), 6.96 (1H, d, $J = 8.5$ Hz, ArH), 3.32-3.21 (1H, m, ArCH$_2$), 3.18-3.05 (2H, m, ArCH$_2$CH$_2$), 1.78-1.67 (2H, m, C$_2$H$_5$CH$_2$CH$_2$CH$_3$), 1.37-1.08 (4H, m, C$_2$H$_5$C$_2$H$_3$), 0.83 (3H, t, $J = 7.2$ Hz, C$_3$); $^{13}$C NMR (125.8 MHz, CDCl$_3$) $\delta$ 167.7 (C), 144.6 (CH), 143.8 (C), 142.4 (C), 130.7 (CH), 128.4 (2 x CH), 127.5 (2 x CH), 126.4 (CH), 123.6 (CH), 46.4 (CH), 46.0 (CH$_2$), 36.0 (CH$_2$), 29.6 (CH$_2$), 22.6 (CH$_2$), 13.9 (CH$_3$); HRMS (ASAP) Exact mass calcd for C$_{17}$H$_{20}$N$_2$O$_2$ [M$- $]: 284.1530, found: 284.1522. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (99:1 hexane:isopropanol, 0.8 mL/min, 280 nm, 25 °C); $t_r$ (minor) = 13.1 min, $t_r$ (major) = 19.7 min; 91% ee.

4-[(S)-2-Phenylhexyl]-2-trifluoromethylbenzonitrile (13)

A solution of [Rh(C$_2$H$_4$)$_2$Cl]$_2$ (3.8 mg, 0.010 mmol) and ligand L5 (9.2 mg, 0.024 mmol) in dioxane (0.3 mL) was stirred under nitrogen at room temperature for 15 min. This solution was then added via cannula to a sealed nitrogen-flushed microwave vial containing alkenylarene 12 (51 mg, 0.20 mmol), phenylboronic acid (59 mg, 0.48 mmol), KOH (28 mg, 0.50 mmol), and H$_2$O (0.1 mL), using further dioxane (0.2 mL) as a rinse. The resulting mixture was irradiated in a microwave reactor at 80 °C for 1.5 h. After cooling to room temperature, the mixture was filtered through a short plug of SiO$_2$ using CH$_2$Cl$_2$ as eluent and concentrated in vacuo. Purification of the residue twice by column chromatography (5% CH$_2$Cl$_2$/hexane) gave the arylation product 13 (39 mg, 59%) as a colorless oil. $[\alpha]_D^{24} +58.9$ (c 1.39, CHCl$_3$); IR (film) 2931, 2860, 2231 (C= N), 1606, 1496, 1321, 1178, 1138, 1057, 700 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.61 (1H, d, $J = 7.9$ Hz, ArH), 7.32 (1H, s, ArH), 7.27-7.23 (2H, m, ArH), 7.22-7.16 (2H, m, ArH), 7.04-6.98 (2H, m, ArH), 3.07 (1H, dd, $J = 13.4$, 5.8 Hz, ArCH$_2$), 2.93 (1H, dd, $J = 13.4$, 9.2 Hz, ArCH$_2$), 2.83-2.74 (1H, m, ArCH$_2$CH$_2$), 1.77-1.66 (2H, m, CH$_2$CH$_2$CH$_2$CH$_3$), 1.39-1.09 (4H, m, CH$_2$CH$_2$CH$_3$), 0.84 (3H, t, $J = 7.2$ Hz, CH$_3$); $^{13}$C NMR (125.8 MHz, CDCl$_3$) $\delta$ 147.1 (C), 143.2 (C), 134.3 (CH), 132.7 (CH), 132.3 (C, d, $J = 32.4$ Hz), 128.5
(2 x CH), 127.6 (2 x CH), 127.4 (CH, q, \(J = 4.6\) Hz), 126.6 (CH), 122.4 (C, q, \(J = 273.8\) Hz), 115.7 (C), 107.3 (C, q, \(J = 2.2\) Hz), 47.8 (CH), 43.8 (CH\(_2\)), 35.6 (CH\(_2\)), 29.6 (CH\(_2\)), 22.6 (CH\(_2\)), 13.9 (CH\(_3\)); \(^{19}\text{F}\) NMR (376 MHz, CDCl\(_3\)) \(\delta -62.4\) (3F, s); HRMS (ASAP) Exact mass calcd for C\(_{20}\)H\(_{21}\)NF\(_3\) [M+H]\(^+\): 332.1621, found: 332.1624. Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column (99:1 hexane:isopropanol, 0.8 mL/min, 230 nm, 25 °C); \(t_r\) (major) = 8.1 min, \(t_r\) (minor) 9.2 min; 84% ee.

**Determination of Absolute Configurations**

*N-{4-[\((S)\)-5-\((\text{tert-Butyldimethylsilyloxy})-2\)-phenylpenty]phenyl}-4-methylbenzenesulfonamide (6)*

A solution of nitroarene 2t (400 mg, 1.00 mmol) and 10% Pd/C (100 mg) in EtOH (20 mL) at room temperature was stirred under an atmosphere of hydrogen (balloon) for 3 h. The solution was filtered through a short plug of celite using CH\(_2\)Cl\(_2\) as eluent (50 mL) and concentrated *in vacuo* to leave the amine 5 which was used immediately without further purification. To the amine 5 was added a solution of TsCl (210 mg, 1.10 mmol), Et\(_3\)N (153 µL, 1.10 mmol), and DMAP (147 mg, 1.20 mmol) in CH\(_2\)Cl\(_2\) (7.5 mL) *via* cannula and the resulting solution was stirred at room temperature for 16 h. The reaction was concentrated *in vacuo* and the residue was purified by column chromatography (20% CH\(_2\)Cl\(_2\)/hexane→40% CH\(_2\)Cl\(_2\)/hexane) to give the sulfonamide 6 (477 mg, 91%) as an off-white solid. Slow diffusion of hexane into a solution of 6 in EtOAc provided crystals that were suitable for X-ray
crystallography. m.p. 84-86 °C; [α]$_D^{24}$ +45.2 (c 1.06, CHCl$_3$); IR (film) 3255 (NH), 2927, 1512, 1462, 1394, 835, 700 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) δ 7.65 (2H, d, $J = 8.3$ Hz, ArH), 7.07-7.01 (2H, m, ArH), 6.93 (2H, d, $J = 8.5$ Hz, ArH), 6.86 (2H, d, $J = 8.5$ Hz, ArH), 3.53 (2H, t, $J = 6.5$ Hz, CO$_2$H), 2.90-2.69 (3H, m, ArCH$_2$CH$_2$O), 2.39 (3H, s, ArCH$_3$), 1.78-1.71 (1H, m, CH$_2$CH$_2$O), 1.66-1.60 (1H, m, CH$_2$CH$_2$O), 1.42-1.34 (2H, m, CH$_2$CH$_2$CH$_2$O), 0.88 (9H, s, C(CH$_3$)$_3$), 0.02 (3H, s, SiCH$_3$), 0.01 (3H, s, SiCH$_3$); $^{13}$C NMR (125.8 MHz, CDCl$_3$) δ 144.5 (C), 143.5 (C), 137.9 (C), 136.0 (C), 134.1 (C), 129.8 (2 x CH), 129.4 (2 x CH), 128.1 (2 x CH), 127.7 (2 x CH), 127.2 (2 x CH), 126.0 (CH), 121.7 (2 x CH), 63.0 (CH$_2$), 47.7 (CH), 43.2 (CH$_2$), 31.6 (CH$_2$), 30.7 (CH$_2$), 25.9 (3 x CH$_3$), 21.5 (CH$_3$), 18.2 (C), −5.4 (2 x CH$_3$); HRMS (ES) Exact mass calcd for C$_{30}$H$_{42}$NO$_3$SSi [M+H]: 524.2649 found: 524.2638.

The sense of enantioinduction observed using ligand L$_5$ is consistent with reported examples of arylation of acyclic electron-deficient alkenes using structurally similar chiral dienes$^{,2,8}$ and the absolute configurations of the remaining arylation products in this study were assigned by analogy with that of 2t.

**Preparation of Indole 7**

7-Methyl-5-[(S)-2-phenylhexyl]-1H-indole (7)

To a solution of nitroarene 2o (119 mg, 0.40 mmol) in THF (4 mL) at −40 °C was added vinylmagnesium bromide (1 M in THF, 1.32 mL, 1.32 mmol) over 1 min and the resulting mixture was stirred at −40 °C for 2 h. The reaction was warmed to room temperature and quenched carefully with saturated aqueous NH$_4$Cl solution (20 mL). The aqueous layer was extracted with Et$_2$O (3 x 40 mL) and the combined organic layers were washed with H$_2$O (20 mL), brine (20 mL), dried (MgSO$_4$), filtered, and concentrated in vacuo. Purification of the residue by column chromatography (10% CH$_2$Cl$_2$/hexane) gave the indole 7 (78 mg, 67%) as a pale yellow gum. [α]$_D^{24}$ +57.6 (c 1.25, CHCl$_3$); IR (film) 3419 (N-H), 2925, 2856, 1597, 1452, 1344, 1111, 760, 725, 700 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.97 (1H, br s, NH), 7.33-7.24 (2H, m, ArH), 7.23-7.14 (5H, m, ArH), 6.74 (1H, br s, NCH=CH), 6.48 (1H, d, $J = 3.2$, 2.0 Hz, NCH=CH), 3.04-2.79 (3H, m, ArCH$_2$CH), 2.45 (3H, s, ArCH$_3$).

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Supplementary Information

ArCH₃), 1.79-1.52 (2H, m, CH₂CH₂CH₂CH₃), 1.32-1.05 (4H, m, CH₂CH₂CH₃), 0.79 (3H, t, J = 7.2 Hz, CH₃); ¹³C NMR (100.6 MHz, CDCl₃) δ 146.2 (C), 134.0 (C), 132.5 (C), 128.1 (2 x CH), 127.8 (2 x CH), 127.3 (C), 125.7 (CH), 124.4 (CH), 123.7 (CH), 119.5 (C), 118.4 (CH), 102.8 (CH), 48.4 (CH), 44.0 (CH₂), 35.0 (CH₂), 29.8 (CH₂), 22.8 (CH₂), 16.7 (CH₃), 14.0 (CH₃); HRMS (ES) Exact mass calcd for C₂₁H₂₆N [M+H]: 292.2060 found: 292.2061.
NMR Spectra of New Compounds

Me
Me
HN
L2
Me

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![Chemical Structure](image)

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[Chemical structure image]

[Chemical spectra images]

[Table of chemical shifts]

ppm (1H)

ppm (13C)
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### NMR Spectra

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**Chemical Structures**

- [Structure 1](#)

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**References**

1. [Reference 1](#)
2. [Reference 2](#)
Supplementary Information

HPLC Traces

Data File name: AEM0091K
Data acquired by: ESI
ok: 1/15/2015
Location: Trial 1
Sample: A0562

Data File name: AEM0091L
Data acquired by: ESI
ok: 1/15/2015
Location: Trial 2
Sample: A0562

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