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General. $^1$H NMR and $^{13}$C NMR spectra were recorded at ambient temperature using 500 MHz or 300 MHz spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the $\delta$ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. High resolution mass spectra were obtained by peak matching. Melting points are reported uncorrected. Infrared spectroscopy was obtained using a diamond attenuated total reflectance (ATR) accessory. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Liquid chromatography was performed using forced flow (flash chromatography) of the indicated solvent system on 60Å (40 – 60 µm) mesh silica gel (SiO$_2$). Medium pressure liquid chromatography (MPLC) was performed to force flow the indicated solvent system down columns that had been packed with 60Å (40 – 60 µm) mesh silica gel (SiO$_2$). All reactions were carried out under an atmosphere of nitrogen in glassware, which had been oven-dried. Unless otherwise noted, all reagents were commercially obtained and, where appropriate, purified prior to use. Acetonitrile, Methanol, Toluene, THF, Et$_2$O, and CH$_2$Cl$_2$ were dried by filtration through alumina according to the procedure of Grubbs.$^1$ Metal salts were stored in a nitrogen atmosphere dry box.
I. Preparation of Substrates using Wittig Reaction.

A. Routes to Substrates

The styryl azides investigated in this study were synthesized by one three different routes (Scheme s1). The majority of the substrates were formed in two steps from commercially available ortho-nitro-substituted benzaldehydes starting by a nucleophilic aromatic substitution using NaN₃ followed by a Wittig reaction. Alternatively the styryl azides were constructed from phosphonate s3 using a Horner–Wadworth–Emmons reaction of phosphonate s3, followed by an iron-mediated reduction to form aniline s4. Azidation then provided the required styryl azide. Finally styryl azides, 14b and 14c, were accessed from boronic acid s5 and the corresponding vinyl triflate s6.

Scheme s1. Routes to Styryl Azides.

I. Wittig Reaction Route

\[ \text{R} \quad \text{CHO} \quad \overset{\text{NaN₃, HMPA}}{\longrightarrow} \quad \text{R} \quad \text{CHO} \quad \overset{\text{Ph₃P, R}}{\longrightarrow} \quad \text{R} \quad \text{N₃} \]

II. Horner–Wadsworth–Emmons Route

\[ \text{NO}_2 \quad \overset{\text{PO(OEt)}_2}{\longrightarrow} \quad \overset{\text{R¹, R²}}{\longrightarrow} \quad \overset{\text{Fe(0)}}{\longrightarrow} \quad \text{R} \quad \text{NH₂} \quad \overset{\text{TiN₃}}{\longrightarrow} \quad \text{R} \quad \text{N₃} \]

III. Suzuki Route

\[ \text{R} \quad \text{B(OH)}₂ \quad \overset{(dpdf)PdCl₂}{\longrightarrow} \quad \text{R} \quad \text{NH₂} \quad \overset{\text{TiN₃}}{\longrightarrow} \quad \text{R} \quad \text{N₃} \]

B. General Procedure for the Nucleophilic Substitution of 2-Nitrobenzaldehydes.

Following the procedure of Driver and co-workers,² the 2-azidobenzaldehydes were prepared. Yields were not optimized.

To a dry, stir bar-equipped scintillation vial were added 0.453 g of 2-nitro-benzaldehyde (3.0 mmol), 0.585 g of NaN₃ (9.0 mmol), and 9.0 mL of HMPA. The reaction was stirred overnight at room temperature, then was taken up in diethyl ether (100 mL) and washed with water (5 × 50 mL). The organic layer was dried over Na₂SO₄ and filtered. The filtrate was concentrated in vacuo. Purification with MPLC afford the 2-azidobenzaldehyde.
C. Synthesis of 2-Azidobenzaldehydes.

**Benzaldehyde s9.** The general procedure was followed using 2.10 g of 2-nitrobenzaldehyde (13.9 mmol) and 2.92 g of NaN₃ (45.0 mmol, 3.3 eq) in 40 mL of HMPA. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a light yellow solid (1.70 g, 83%); mp 33 - 36 °C; The spectral data matched that reported by Driver and co-workers: ¹H NMR (500 MHz, CDCl₃) δ 10.25 (s, 1H), 7.79 (dd, J = 1.5 Hz, 7.5 Hz, 1H), 7.54 (dt, J = 1.5 Hz, 8.0 Hz, 1H) 7.14 – 7.19 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 188.4 (CH), 142.8 (C), 135.4 (CH), 128.9 (CH), 126.9 (C), 124.8 (C), 119.1 (CH); IR (thin film): 2971, 2121, 1690, 1594, 1477, 1290, 1274 cm⁻¹.

**Benzaldehyde s10.** The general procedure was followed using 1.81 g of 2-nitro-3-methoxybenzaldehyde (10 mmol) and 1.31 g of NaN₃ (20 mmol) in 50 mL of HMPA at 50 °C. Purification of the reaction mixture using MPLC (1:30 EtOAc:hexanes) afforded the product as a white solid (1.61 g, 91%); mp 54 – 56 °C; ¹H NMR (500 MHz; CDCl₃) δ 10.15 (s, 1H), 7.82 (d, J = 8.5 Hz, 1H), 6.72 (dd, J = 2.5 Hz, 8.5 Hz, 1H), 6.67 (d, J = 2.5 Hz, 1H), 3.88 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 187.2 (CH), 165.3 (C), 144.9 (C), 131.1 (CH), 121.0 (C), 111.1 (CH), 103.9 (CH), 55.8 (CH₃); IR (thin film): 2359, 2341, 2110, 1723, 1264, 730, 703 cm⁻¹. HRMS (EI) m/z calcd for C₈H₇O₂N₃ (M)+ 177.05383, found 177.05529.

**Benzaldehyde s11.** The general procedure was followed using 1.81 g of 2-nitro-4-methoxybenzaldehyde (10 mmol) and 1.31 g of NaN₃ (20 mmol) in 50 mL of HMPA at 50 °C. Purification of the reaction mixture using MPLC (1:30 EtOAc:hexanes) afforded the product as a white solid (1.62 g, 92%); mp 73 – 75 °C; ¹H NMR (500 MHz; CDCl₃) δ 10.17 (s, 1H), 7.84 (d, J = 9.0 Hz, 1H), 6.74 (dd, J = 2.5 Hz, 9.0 Hz, 1H), 6.68 (d, J = 2.5 Hz, 1H), 3.90 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 187.2 (CH), 165.3 (C), 144.9 (C), 131.1 (CH), 121.1 (C), 111.1 (CH), 104.0 (CH), 55.8 (CH₃); IR (thin film): 3457, 3015, 2970, 2116, 1744, 1367, 1229, 750, 528 cm⁻¹. HRMS (EI) m/z calcd for C₈H₇O₂N₃ (M)+ 177.05383, found 177.05520.

**Benzaldehyde s12.** The general procedure was followed using 1.85 g of 2-nitro-4-chlorobenzaldehyde (10 mmol) and 0.98 g of NaN₃ (15 mmol) in 50 mL of HMPA. Purification of the reaction mixture using MPLC (1:100 EtOAc:hexanes) afforded the product as a white solid (1.45 g, 80%); mp 91 – 93 °C; ¹H NMR (500 MHz; CDCl₃) δ 10.28 (s, 1H), 7.82 (d, J = 8.5 Hz, 1H), 7.26 (d, J = 2.0 Hz, 1H), 7.21 (dd, J = 1.5 Hz, 8.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 187.4 (CH), 144.0 (C), 141.7 (C), 130.2 (CH), 125.6 (CH), 125.4 (C),
119.2 (CH); IR (thin film): 3455, 3016, 2969, 2123, 1739, 1366, 1216, 750, 528 cm\textsuperscript{-1}. HRMS (EI) \textit{m/z} calcd for C\textsubscript{7}H\textsubscript{4}ON\textsubscript{3}Cl (M)+ 183.00134, found 183.00217.

**Benzaldehyde s13.** The general procedure was followed using 2.09 g of methyl 4-formyl-3-nitrobenzoate (10 mmol) and 1.31 g of NaN\textsubscript{3} (20 mmol) in 50 mL of HMPA. Purification of the reaction mixture using M PLC (1:30 EtOAc: hexanes) afforded the product as a white solid (1.95 g, 95 %); mp 112 – 114 °C; \textsuperscript{1}H NMR (500 MHz; CDCl\textsubscript{3}) \(\delta\) 10.38 (s, 1H), 7.94 – 7.92 (m, 2H), 7.85 – 7.83 (m, 1H), 3.97 (s, 3H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 188.1 (CH), 165.3 (C), 143.1 (C), 136.2 (C), 129.4 (C), 129.1 (CH), 125.6 (CH), 120.3 (C), 52.8 (CH\textsubscript{3}); IR (thin film): 3458, 3015, 2970, 2122, 1738, 1366, 1216, 762, 527 cm\textsuperscript{-1}. HRMS (EI) \textit{m/z} calcd for C\textsubscript{9}H\textsubscript{7}O\textsubscript{3}N\textsubscript{3} (M)+ 205.04875, found 205.04990.

**Benzaldehyde s14.**\textsuperscript{3} The general procedure was followed using 2.69 g of 2-nitro-4-trifluoromethylbenzaldehyde (12.3 mmol) and 2.21 g of NaN\textsubscript{3} (34.0 mmol) in 50 mL of HMPA. Purification by M PLC (1:100 EtOAc: hexanes) afforded the product as a yellow solid (2.49 g, 94%): mp 89 -91 °C; The spectral data matched that reported by Driver and co-workers: \textsuperscript{2} \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) 10.38 (s, 1H), 8.00 (d, \(J = 8.0\) Hz, 1H), 7.50 (s, 1H) 7.48 (d, \(J = 8.0\) Hz, 1H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 187.5 (CH), 143.5 (C), 136.8 (q, \(J_{CF} = 31.4\) Hz, C), 129.8 (CH), 126.1 (C), 122.9 (q, \(J_{CF} = 270.9\) Hz, C), 121.6 (q, \(J_{CF} = 3.5\) Hz, CH) 116.3 (q, \(J_{CF} = 36.3\) Hz, CH); \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 282 MHz) \(\delta\) –61.10; IR (thin film): 2980, 2901, 2122, 1689, 1414, 1392, 1328, 1072, 750 cm\textsuperscript{-1}.

**Benzaldehyde s15.** The general procedure was followed using 2.29 g of 4-(methylsulfonyl)-2-nitrobenzaldehyde (10 mmol) and 1.31 g of NaN\textsubscript{3} (20 mmol) in 50 mL of HMPA. Purification of the reaction mixture using M PLC (1:10 EtOAc: hexanes) afforded the product as a white solid (1.96 g, 87%); mp 125 – 127 °C; \textsuperscript{1}H NMR (500 MHz; CDCl\textsubscript{3}) \(\delta\) 10.40 (s, 1H), 8.05 (d, \(J = 8.0\) Hz, 1H), 7.85 (s, 1H), 7.5 (d, \(J = 8.0\) Hz, 1H), 3.12 (s, 3H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 187.3 (CH), 146.5 (C), 144.1 (C), 130.3 (CH), 129.8 (CH), 118.4 (CH), 44.2 (CH\textsubscript{3}); IR (thin film): 3023, 2925, 2852, 2115, 1681, 1398, 1279, 1159, 1135 cm\textsuperscript{-1}.

**Benzaldehyde s16.**\textsuperscript{4} The general procedure was followed using 2.03 g of 2-nitro-5-bromobenzaldehyde (10 mmol) and 1.3 g of NaN\textsubscript{3} (20 mmol) in 40 mL of DMSO at 50 °C. Purification of the reaction mixture using M PLC (1:100 EtOAc:hexanes) afforded the product as a white solid (2.19 g, 97%); mp 94 – 96 °C; \textsuperscript{1}H NMR (500 MHz; CDCl\textsubscript{3}) \(\delta\) 10.27 (s, 1H), 7.98 (d, \(J = 2.5\) Hz, 1H), 7.70 (dd, \(J = 2.5\) Hz, 8.5 Hz, 1H), 7.16 (d, \(J = 8.5\) Hz, 1H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \(\delta\) 187.1 (CH), 141.9 (C), 138.0 (CH), 131.7 (CH), 128.0 (C), 120.8
Benzaldehyde s17. The general procedure was followed using 2.09 g of methyl 3-formyl-4-nitrobenzoate (10 mmol) and 1.31 g of NaN₃ (20 mmol) in 50 mL of HMPA. Purification of the reaction mixture using MPLC (1:30 EtOAc:hexanes) afforded the product as a white solid (1.97 g, 96%); mp 118 –110 °C; ¹H NMR (500 MHz; CDCl₃) δ 10.31 (s, 1H), 8.49 (d,  J = 2.0 Hz, 1H), 8.23 (dd,  J = 2.0 Hz, 8.5 Hz, 1H), 7.31 (d,  J = 8.5 Hz, 1H), 3.97 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 187.7 (CH), 165.4 (C), 146.8 (C), 136.0 (CH), 130.8 (CH), 127.0 (C), 127.6 (C), 119.2 (CH), 52.4 (CH₃); IR (thin film): 3458, 3015, 2970, 2122, 1738, 1366, 1216, 762, 527 cm⁻¹. HRMS (EI) m/z calcd for C₉H₇O₃N₃ (M)+ 205.04875, found 205.04980.

D. General Procedure for the Phosphonium Salt Synthesis.

Unless otherwise noted, the phosphonium salt was synthesized from the corresponding cycloketone. Yields were not optimized.

To a solution of 2.92 g of α-tetralone (20 mmol) in 30 mL of EtOH was added 1.52 g of NaBH₄ (40 mmol). The mixture was monitored by thin layer chromatography. Once the starting material spot had disappeared, the mixture was concentrated in vacuo, and the resulting material was diluted with 50 mL of water. The resulting aqueous mixture was extracted with dichloromethane (3 × 10 mL). The organic phase (containing the alcohol) was treated with proportional HBr. The progress of the reaction was monitored by thin layer chromatography. Once the alcohol completely consumed, the mixture was diluted with 100 mL of water, then extracted with dichloromethane (3 × 20 mL). The resulting organic phase was dried over Na₂SO₄. The mixture was filtered and the filtrate was concentrated in vacuo to afford bromide. To a solution of the bromide in 60 mL of PhMe was added 5.76 g of PPh₃. The reaction mixture was heated to reflux. After 16h, the mixture was cooled down to room temperature, then filtrated. The solid was washed with diethyl ether (3 × 30 mL), and dried under high vacuum to afford phosphonium salt.

E. General Procedure for the Wittig Reaction of 2-Azidobenzaldehydes.

Following the procedure of Scott and co-workers, the 2-azidobenzaldehydes were prepared. Yields were not optimized.

To a solution of 4.0 mmol of the phosphonium salt in 12 mL of THF at −78 °C, was added 1.6 mL of n-BuLi (2.5 M in hexanes, 4.0 mmol) dropwise. After stirring 1h at −78 °C, the mixture was warmed to room
temperature and stirred additional one hour. Then 0.647 g of 2-azidobenzaldehyde (4.4 mmol) was added and the mixture was stirred for 1 h at ambient temperature. The resulting mixture was diluted with 15 mL of water and extracted with CH$_2$Cl$_2$ ($3 \times 10$ mL). The resulting organic phase was washed with 20 mL of brine and dried over Na$_2$SO$_4$. After filtration, the filtrate was concentrated in vacuo. Purification of the reaction mixture using MPLC afforded the product.

### E. Synthesis of Styryl Azides.

#### Styryl Azide 8.
The general procedure was followed using 1.94 g of 2-azidobenzaldehyde s9 (13.2 mmol), 6.85 g of the phosphonium salt (14.5 mmol), 5.8 mL of a 2.5 M solution of BuLi in hexanes in 50 mL of THF. Purification by MPLC (pure hexanes) afforded the product as a white powder, as an 84:16 mixture of E- and Z-isomers (2.24 g, 65%): R$_f$ = 0.45 (18:82 EtOAc: hexane). Selected spectral data for the major (E) isomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.80 - 7.99 (m, 1H), 7.33 - 7.37 (m, 2H), 7.13 - 7.26 (m, 5H), 7.07 (s, 1H), 2.91 (t, $J$ = 6.5 Hz, 2H), 2.71 (t, $J$ = 6.0 Hz, 2H), 1.87 - 1.92 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 138.7 (C), 138.6 (C), 137.9 (C), 135.9 (C), 130.9 (CH), 130.1 (C), 129.2 (CH), 128.1 (CH), 127.6 (CH), 126.2 (CH), 124.7 (CH), 124.3 (CH), 118.7 (CH), 118.4 (CH); 30.4 (CH$_2$), 28.2 (CH$_2$), 23.8 (CH$_2$); Selected spectral data for the minor (Z) isomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.13 - 7.26 (m, 5H), 7.07 - 7.08 (m, 1H), 6.95 - 6.98 (m, 1H), 6.85 - 6.88 (m, 1H), 6.47 (s, 1H), 2.95 (t, $J$ = 6.5 Hz, 2H), 2.63 (t, $J$ = 6.5 Hz, 2H), 2.05 - 2.10 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 139.8 (C), 138.7 (C), 138.0 (C), 134.7 (C), 131.3 (CH), 130.1 (C), 128.9 (CH), 128.0 (CH), 127.6 (CH), 124.7 (CH), 142.5 (CH), 199.9 (CH), 119.5 (CH), 118.5 (CH), 35.0 (CH$_2$), 29.7 (CH$_2$), 24.2 (CH$_2$); Selected spectral data for the mixture: $^\text{IR}$ (thin film): 2117, 2083, 1486, 1445, 756, 745 cm$^{-1}$. HRMS (EI) $m$ / $z$ calcd for C$_{17}$H$_{15}$N$_3$ (M – N$_2$)$^+$ 261.12660, found 261.12679.

#### Styryl Azide 11a.
The general procedure was followed using 0.58 g of 2-azido-3-methoxybenzaldehyde s10 (3.3 mmol), 1.42 g of the phosphonium salt (3.0 mmol), 1.2 mL of a 2.5 M solution of BuLi in hexanes in 25 mL of THF. Purification by MPLC (1:50 EtOAc:hexanes) afforded the product as a white powder, as a 76:24 mixture of E- and Z-isomers (0.63 g, 72%). Selected spectral data for the major (E) isomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.76 - 7.74 (m, 1H), 7.23 - 7.21 (m, 2H), 7.14 - 7.04 (m, 3H), 6.93 - 6.90 (m, 1H), 6.84 - 6.82 (m, 1H), 3.93 (s, 3H), 2.88 (t, $J$ = 6.5 Hz, 2H), 2.66 (dt, $J$ = 1.5 Hz, 6.0 Hz, 2H), 1.86 (pent, $J$ = 6.5 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 153.9 (C), 138.5 (C), 137.8 (C), 135.9 (C), 131.8 (C), 129.2 (CH), 127.6 (CH), 126.9 (C), 126.2 (CH), 124.6 (CH), 124.6 (CH), 122.8 (CH), 119.4 (CH), 110.2 (CH), 56.1 (CH$_3$), 30.3 (CH$_2$), 28.2 (CH$_2$), 23.7 (CH$_3$); Selected spectral data for the minor (Z) isomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.27 - 7.25 (m, 1H), 7.14 - 7.04 (m, 3H), 6.88 - 6.85 (m, 1H), 6.75 - 6.71 (m, 2H), 6.41 (s, 1H), 3.91 (s, 3H), 2.92 (t, $J$ = 6.5 Hz, 2H), 2.60 (dt, $J$ = 1.5 Hz, 6.0 Hz, 2H), 2.04 (pent, $J$ = 6.5 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 153.9 (C), 139.5 (C), 138.8 (C), 134.8 (C), 132.5 (C), 129.0 (CH), 128.8 (CH), 127.5 (CH), 125.7 (CH), 125.0 (C), 124.8 (CH), 123.1 (CH), 120.5 (CH), 109.9 (CH), 56.0 (CH$_3$), 34.9 (CH$_2$), 29.7 (CH$_2$), 24.2 (CH$_2$); Selected
spectral data for the mixture: δ IR (thin film): 2933, 2103, 1756, 1450, 1262, 1087, 737 cm⁻¹. HRMS (EI) m/z calcd for C₁₈H₁₇ON (M-N₂)+ 263.13102, found 163.132000.

**Styryl Azide 11b.** The general procedure was followed using 0.58 g of 2-azido-4-methoxybenzaldehyde s₁₁ (3.3 mmol), 1.42 g of the phosphonium salt (3.0 mmol), 1.2 mL of a 2.5 M solution of BuLi in hexanes in 25 mL of THF. Purification by MPLC (1:50 EtOAc: hexanes) afforded the product as a white powder, as an 83:17 mixture of E- and Z-isomers (0.37 g, 43%). Selected spectral data for the major (E) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.74 – 7.72 (m, 1H), 7.26 – 7.19 (m, 2H), 7.14 – 7.12 (m, 1H), 6.97 (s, 1H), 6.74 – 6.71 (m, 2H), 3.87 (s, 3H), 2.87 (t, J = 6.5 Hz, 2H), 2.67 (dt, J = 1.5 Hz, 6.0 Hz, 2H), 1.87 (pent, J = 6.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 159.5 (C), 139.6 (C), 137.7 (C), 137.5 (C), 136.1 (C), 131.7 (CH), 129.1 (CH), 127.4 (CH), 126.2 (CH), 124.5 (CH), 122.8 (C), 118.3 (CH), 110.0 (CH), 104.2 (CH), 55.5 (CH₃), 30.3 (CH₂), 28.1 (CH₂), 23.7 (CH₂); Selected spectral data for the minor (Z) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.71 – 7.70 (m, 1H), 7.26 – 7.20 (m, 3H), 7.16 (d, J = 6.5 Hz, 1H), 6.86 (t, J = 6.5 Hz, 1H), 6.69 (d, J = 2.5 Hz, 1H), 6.51 (dd, J = 2.5 Hz, 8.5 Hz, 1H), 6.33 (s, 1H), 3.83 (s, 3H), 2.91 (t, J = 6.5 Hz, 2H), 2.57 (dt, J = 1.5 Hz, 6.0 Hz, 2H), 2.03 (pent, J = 6.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 139.8 (C), 139.3 (C), 137.9 (C), 135.6 (C), 133.3 (C), 131.8 (CH), 129.2 (CH), 128.6 (CH), 128.5 (C), 124.7 (CH), 123.1 (C), 119.4 (CH), 110.6 (CH), 104.0 (CH), 55.4 (CH₃), 34.9 (CH₂), 29.7 (CH₂), 24.2 (CH₂); Selected spectral data for the mixture: δ IR (thin film): 2935, 2101, 1753, 1436, 1266, 1084, 739 cm⁻¹. HRMS (EI) m/z calcd for C₁₈H₁₇ON₃ (M)+ 291.13717, found 291.13649.

**Styryl Azide 11c.** The general procedure was followed using 0.60 g of 2-azido-4-chlorobenzaldehyde s₁₂ (3.3 mmol), 1.42 g of the phosphonium salt (3.0 mmol), 1.2 mL of a 2.5 M solution of BuLi in hexanes in 25 mL of THF. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a white powder, as an 82:18 mixture of E- and Z-isomers (0.49 g, 55%). Selected spectral data for the major (E) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.71 – 7.70 (m, 1H), 7.26 – 7.20 (m, 3H), 7.16 (d, J = 2.0 Hz, 1H), 7.13 – 7.12 (m, 2H), 6.91 (s, 1H), 2.86 (t, J = 6.5 Hz, 2H), 2.62 (dt, J = 1.5 Hz, 6.5 Hz, 2H), 1.85 (pent, J = 6.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 139.8 (C), 139.3 (C), 137.9 (C), 135.6 (C), 133.3 (C), 131.8 (CH), 129.2 (CH), 128.6 (CH), 128.5 (C), 124.7 (CH), 123.1 (C), 119.4 (CH), 110.6 (CH), 104.0 (CH), 55.4 (CH₃), 34.9 (CH₂), 29.7 (CH₂), 24.2 (CH₂); Selected spectral data for the minor (Z) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.23 – 7.19 (m, 1H), 7.10 – 7.05 (m, 3H), 6.86 (t, J = 6.5 Hz, 1H), 6.69 (d, J = 2.5 Hz, 1H), 6.51 (dd, J = 2.5 Hz, 8.5 Hz, 1H), 6.33 (s, 1H), 3.83 (s, 3H), 2.91 (t, J = 6.5 Hz, 2H), 2.57 (dt, J = 1.5 Hz, 6.0 Hz, 2H), 2.03 (pent, J = 6.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 140.6 (C), 139.2 (C), 139.0 (C), 134.4 (C), 133.2 (C), 132.3 (CH), 129.1 (C), 129.0 (CH), 128.8 (CH), 124.8 (CH), 124.8 (CH), 124.6 (CH), 118.7 (CH), 118.6 (CH), 34.9 (CH₂), 29.7 (CH₂), 24.1 (CH₂); Selected spectral data for the mixture: δ IR (thin film): 2931, 2109, 1738, 1486, 1286, 756 cm⁻¹. HRMS (EI) m/z calcd for C₁₇H₁₄N₃Cl (M)+ 295.08762, found 295.08889.
**Styryl Azide 11d.** The general procedure was followed using 0.68 g of methyl 3-azido-4-formylbenzoate s13 (3.3 mmol), 1.42 g of the phosphonium salt (3.0 mmol), 1.2 mL of a 2.5 M solution of BuLi in hexanes in 25 mL of THF. Purification by MPLC (1:50 EtOAc: hexanes) afforded the product as a white powder, as an 83:17 mixture of E- and Z-isomers (0.39 g, 41%). Selected spectral data for the major (E) isomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.85 (d, $J = 1.5$ Hz, 1H), 7.80 (dd, $J = 1.5$ Hz, 8.0 Hz, 1H), 7.73 (dd, $J = 3.5$ Hz, 5.5 Hz, 1H), 7.39 (d, $J = 3.0$ Hz, 1H), 7.22 (dd, $J = 3.5$ Hz, 5.5 Hz, 2H), 7.14 – 7.12 (m, 1H), 7.00 (s, 1H), 3.95 (s, 3H), 2.87 (t, $J = 6.5$ Hz, 2H), 2.67 (dt, $J = 1.5$ Hz, 6.5 Hz, 2H), 1.86 (pent, $J = 6.5$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 166.2 (C), 140.4 (C), 139.1 (C), 138.1 (C), 135.5 (C), 134.6 (C), 130.7 (CH), 129.6 (C), 129.2 (CH), 128.0 (CH), 125.0 (CH), 124.7 (CH), 119.4 (CH), 117.9 (CH), 52.4 (CH$_3$), 30.2 (CH$_2$), 28.3 (CH$_2$), 23.7 (CH$_2$); Selected spectral data for the minor (Z) isomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 1.5$ Hz, 1H), 7.35 (dd, $J = 3.0$ Hz, 8.0 Hz, 1H), 7.14 – 7.12 (m, 2H), 6.94 (d, $J = 8.5$ Hz, 1H), 6.80 (t, $J = 8.5$ Hz, 1H), 3.92 (s, 3H), 2.90 (t, $J = 6.5$ Hz, 2H), 2.59 (dt, $J = 1.5$ Hz, 6.5 Hz, 2H), 2.03 (pent, $J = 6.5$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 141.1 (C), 138.3 (C), 135.5 (C), 134.2 (C), 131.2 (CH), 129.2 (CH), 128.8 (CH), 128.0 (C), 125.0 (CH), 124.8 (CH), 119.6 (CH), 119.0 (CH), 52.3 (CH$_3$), 34.9 (CH$_2$), 29.6 (CH$_2$), 24.0 (CH$_2$); Selected spectral data for the mixture: IR (thin film): 3456, 3015, 2970, 2116, 1739, 1436, 1367, 1228, 1092, 748, 527 cm$^{-1}$. HRMS (EI) $m/z$ calcd for C$_{19}$H$_{17}$O$_2$N$_3$ (M)$^+$ 319.13208, found 319.13140.

**Styryl Azide 11e.** The general procedure was followed using 0.95 g of 2-azidobenzaldehyde s14 (4.4 mmol), 1.89 g of the phosphonium salt (4.0 mmol), 1.8 mL of a 2.5 M solution of BuLi in hexanes in 20 mL of THF. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a light yellow powder, as a 87:13 mixture of E- and Z-isomers (1.81 g, 81%): Selected spectral data for the major (E) isomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.75 – 7.77 (m, 1H), 7.40 – 7.46 (m, 3H), 7.24 – 7.28 (m, 2H), 7.14 – 7.18 (m, 1H), 7.02 (s, 1H), 2.91 (m, $J = 6.5$ Hz, 2H), 2.67 – 2.69 (m, 2H), 1.89 (pent, $J = 6.5$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 166.2 (C), 141.1 (C), 139.0 (C), 138.3 (C), 135.5 (C), 134.2 (C), 131.2 (CH), 129.2 (CH), 128.8 (CH), 128.0 (C), 125.0 (CH), 124.8 (CH), 119.6 (CH), 119.0 (CH), 52.3 (CH$_3$), 34.9 (CH$_2$), 29.6 (CH$_2$), 24.0 (CH$_2$); Selected spectral data for the minor (Z) isomer: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.40 – 7.46 (m, 1H), 7.24 – 7.28 (m, 1H), 7.14 – 7.18 (m, 2H), 6.94 (d, $J = 8.5$ Hz, 1H), 6.80 (t, $J = 8.5$ Hz, 1H), 3.92 (s, 3H), 2.90 (t, $J = 6.5$ Hz, 2H), 2.59 (dt, $J = 1.5$ Hz, 6.5 Hz, 2H), 2.03 (pent, $J = 6.5$ Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 141.9 (C), 138.8 (C), 134.3 (C), 131.8 (CH), 131.8 (CH), 128.8 (CH), 124.9 (CH), 118.5 (CH), 115.5 (q, $J_{CF} = 3.8$ Hz, CH), 34.9 (CH$_3$), 29.6 (CH$_2$), 24.0 (CH$_2$); $^{19}$F NMR (CDCl$_3$, 282 MHz) $\delta$ –63.12; Selected spectral data for the mixture: IR (thin film): 2111, 1739, 1328, 1273, 1123, 913, 745 cm$^{-1}$. HRMS (EI) $m/z$ calcd for C$_{19}$H$_{17}$O$_2$N$_3$F$_3$ (M)$^+$ 329.11398, found 329.11303.
Styryl Azide 11f. The general procedure was followed using 0.74 g of 2-azido-4-(methylsulfonyl)benzaldehyde s15 (3.3 mmol), 1.42 g of the phosphonium salt (3.0 mmol), 1.2 mL of a 2.5 M solution of BuLi in hexanes in 25 mL of THF. Purification by MPLC (1:20 EtOAc: hexanes) afforded the product as a white powder as one isomer (0.47 g, 46%): 1H NMR (500 MHz, CDCl3) δ 7.73 (d, J = 1.5 Hz, 2H), 7.68 (dd, J = 1.5 Hz, 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.15 – 7.13 (m, 1H), 6.98 (s, 1H), 3.11 (s, 3H), 2.88 (t, J = 6.5 Hz, 2H), 2.66 (dt, J = 1.5 Hz, 6.5 Hz, 2H), 1.87 (pent, J = 6.5 Hz, 2H); 13C NMR (125 MHz, CDCl3) δ 141.5 (C), 140.1 (C), 139.7 (C), 138.2 (C), 135.5 (C), 135.1 (C), 131.7 (CH), 129.3 (CH), 128.3 (CH), 126.3 (CH), 124.7 (CH), 123.0 (CH), 117.2 (CH), 117.1 (CH), 44.6 (CH3), 30.1 (CH2), 23.7 (CH2); IR (thin film): 3454, 3026, 2969, 2116, 1738, 1366, 1206, 738, 536 cm–1. HRMS (EI) m/z calcd for C18H17O2NS (M-N2)+ 311.09800, found 311.09698.

Styryl Azide 11g. The general procedure was followed using 0.75 g of 2-azido-5-bromobenzaldehyde s16 (3.3 mmol), 1.42 g of the phosphonium salt (3.0 mmol), 1.2 mL of a 2.5 M solution of BuLi in hexanes in 25 mL of THF. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a white powder, as an 83:17 mixture of E- and Z-isomers (0.62 g, 61%). Selected spectral data for the major (E) isomer: 1H NMR (500 MHz, CDCl3) δ 7.73 – 7.71 (m, 1H), 7.45 (d, J = 2.5 Hz, 1H), 7.42 (dd, J = 2.5 Hz, 8.5 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.17 – 7.14 (m, 1H), 7.05 (d, J = 8.5 Hz, 1H), 6.92 (s, 1H), 2.88 (t, J = 6.5 Hz, 2H), 2.66 (dt, J = 1.5 Hz, 6.5 Hz, 2H), 1.87 (pent, J = 6.5 Hz, 2H); 13C NMR (125 MHz, CDCl3) δ 139.9 (C), 138.0 (C), 137.8 (C), 135.4 (C), 133.4 (CH), 131.9 (C), 130.7 (CH), 129.2 (CH), 128.0 (C), 127.9 (CH), 126.2 (CH), 124.8 (CH), 120.0 (CH), 117.4 (CH), 30.3 (CH2), 28.1 (CH2), 23.7 (CH2); Selected spectral data for the minor (Z) isomer: 1H NMR (500 MHz, CDCl3) δ 7.34 (dd, J = 2.0 Hz, 8.5 Hz, 1H), 7.27 (d, J = 2.0 Hz, 1H), 7.17 – 7.14 (m, 2H), 7.01 (d, J = 8.0 Hz, 2H), 6.90 – 6.87 (m, 1H), 6.28 (s, 1H), 2.92 (t, J = 6.5 Hz, 2H), 2.59 (dt, J = 1.5 Hz, 6.5 Hz, 2H), 2.04 (pent, J = 6.5 Hz, 2H); 13C NMR (125 MHz, CDCl3) δ 141.1 (C), 138.9 (C), 137.2 (C), 134.0 (C), 133.7 (CH), 132.6 (C), 129.0 (CH), 128.6 (CH), 128.0 (C), 124.8 (CH), 124.8 (CH), 120.1 (CH), 118.3 (CH), 117.2 (CH), 35.0 (CH3), 29.7 (CH2), 24.1 (CH2); Selected spectral data for the mixture: δ IR (thin film): 3454, 3026, 2969, 2116, 1738, 1366, 1206, 738, 536 cm–1; HRMS (EI) m/z calcd for C17H14N3Br (M)++ 339.03710, found 339.03776.

Styryl Azide 11h. The general procedure was followed using 0.68 g of methyl 3-azido-4-formylbenzoate s17 (3.3 mmol), 1.42 g of the phosphonium salt (3.0 mmol), 1.2 mL of a 2.5 M solution of BuLi in hexanes in 25 mL of THF. Purification by MPLC (1:50 EtOAc: hexanes) afforded the product as a white powder, as an 87:13 mixture of E- and Z-isomers (0.38 g, 40%). Selected spectral data for the major (E) isomer: 1H NMR (500 MHz,
CDCl₃) δ 8.03 (d, J = 1.5 Hz, 1H), 7.98 (dd, J = 1.5 Hz, 8.0 Hz, 1H), 7.74 (dd, J = 3.5 Hz, 5.5 Hz, 1H), 7.23 – 7.20 (m, 3H), 7.15 – 7.14 (m, 1H), 6.98 (s, 1H), 3.94 (s, 3H), 2.87 (t, J = 6.5 Hz, 2H), 2.69 (dt, J = 1.5 Hz, 6.5 Hz, 2H), 1.86 (pent, J = 6.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 166.5 (C), 143.2 (C), 139.6 (C), 138.0 (C), 135.6 (C), 132.2 (CH), 129.9 (C), 129.3 (CH), 129.2 (CH), 127.8 (CH), 126.2 (CH), 126.1 (C), 124.6 (CH), 118.2 (CH), 52.1 (CH₃), 30.3 (CH₂), 28.2 (CH₂), 23.7 (CH₂); Selected spectral data for the minor (Z) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.92 (dd, J = 3.0, 8.5 Hz, 1H), 7.83 (d, J = 3.0 Hz, 1H), 7.23 – 7.20 (m, 1H), 7.13 – 7.10 (m, 1H), 6.95 (d, J = 8.5 Hz, 1H), 6.80 (t, J = 6.5 Hz, 1H), 6.33 (s, 1H), 3.82 (s, 3H), 2.92 (t, J = 6.5 Hz, 2H), 2.60 (dt, J = 1.5 Hz, 6.5 Hz, 2H), 2.05 (pent, J = 6.5 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 166.3 (C), 142.6 (C), 140.9 (C), 138.9 (C), 135.5 (C), 134.2 (C), 132.7 (CH), 130.8 (CH), 129.0 (CH), 128.4 (CH), 126.4 (CH), 126.1 (C), 124.8 (CH), 118.7 (CH), 118.4 (CH), 52.0 (CH₃), 35.0 (CH₂), 29.7 (CH₂), 24.1 (CH₂); Selected spectral data for the mixture: δ IR (thin film): 3024, 2969, 2121, 1753, 1372, 1292, 762, 528 cm⁻¹. HRMS (EI) m/z calcld for C₁₉H₁₇ON (M)+ 291.12593, found 291.12443.

Styryl Azide 14a. The general procedure was followed using 0.92 g of 2-azidobenzaldehyde s₉ (6.54 mmol), 2.40 g of the phosphonium salt (5.24 mmol), 2.3 mL of a 2.5 M solution of BuLi in hexanes in 15 mL of THF. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a light yellow powder, as a 82:18 mixture of E- and Z-isomers (0.24 g, 19%): Rf = 0.45 (18:82 EtOAc: hexane). Selected spectral data for the major (E) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.65 – 7.67 (m, 1H), 7.54 (dd, J = 1.5 Hz, 7.5 Hz, 1H), 7.10 – 7.35 (m, 7H), 3.00 – 3.08 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 146.0 (C), 145.6 (C), 142.4 (C), 137.8 (C), 130.0 (C), 130.9 (CH), 128.5 (CH), 127.6 (CH), 126.8 (CH), 125.3 (CH), 124.5 (CH), 120.7 (CH), 118.4 (CH), 113.4 (CH), 30.8 (CH₂), 30.7 (CH₂); Selected spectral data for the minor (Z) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, J = 8.0 Hz, 1H), 7.10 – 7.23 (m, 3H), 3.18 – 3.24 (m, 2H), 3.05 – 3.08 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 149.0 (C), 145.0 (C), 139.4 (C), 138.0 (C), 130.8 (CH), 130.1 (C), 129.0 (CH), 128.5 (CH), 125.9 (CH), 124.7 (CH), 124.2 (CH), 118.7 (CH), 116.8 (CH), 33.9 (CH₂), 30.2 (CH₂); Selected spectral data for the mixture: δ IR (thin film): 2117, 2084, 1570, 1483, 1277, 1264, 749 cm⁻¹. HRMS (EI) m/z calcld for C₁₉H₁₇ON (M)+ 291.12593, found 291.12443.

Styryl Azide 14b. The general procedure was followed using 0.76 g of 2-azidobenzaldehyde s₉ (5.18 mmol), 2.48 g of the phosphonium salt (4.70 mmol), 2.1 mL of a 2.5 M solution of BuLi in hexanes in 15 mL of THF. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a light yellow oil, as a 72:28 mixture of E- and Z-isomers (0.52 g, 35%): Rf = 0.45 (18:82 EtOAc: hexane). Selected spectral data for the major (E) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.81 (d, J = 7.5 Hz, 1H), 7.51 – 7.54 (m, 2H), 7.30 – 7.39 (m, 2H), 7.11 – 7.23 (m, 3H), 3.18 – 3.24 (m, 2H), 3.05 – 3.08 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 144.3 (C), 143.7 (C), 143.5 (C), 143.3 (C), 138.0 (C), 129.4 (C), 128.9 (CH), 128.1 (CH), 127.1 (CH), 125.1 (q, J₇CF = 4.0 Hz, CH), 124.6 (CH), 124.2 (q, J₇CF = 271.9, C), 123.9 (CH), 118.4 (CH), 115.0 (CH), 30.4 (CH₂), 29.6 (CH₂); Selected spectral data for the minor (Z) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, J = 7.5 Hz, 1H), 7.30 – 7.39 (m,
Styryl Azide 14d. The general procedure was followed using 0.65 g of 2-azidobenzaldehyde s9 (4.42 mmol), 1.87 g of the phosphonium salt (3.95 mmol), 1.73 mL of a 2.5 M solution of BuLi in hexanes in 20 mL of THF. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a white powder, as an 83:17 mixture of E- and Z-isomers (0.28 g, 27%): Rf = 0.45 (18:82 EtOAc: hexane). Selected spectral data for the major (E) isomer: 1H NMR (500 MHz, CDCl3) δ 7.70 (dd, J = 1.5 Hz, 8.0 Hz, 1H), 7.32 – 7.35 (m, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.19 – 7.22 (m, 2H), 7.08 (s, 1H), 6.95 – 6.98 (m, 1H), 6.83 – 6.85 (m, 1H), 4.20 (t, J = 6.0 Hz, 2H), 2.80 – 2.83 (m, 2H); 13C NMR (125 MHz, CDCl3) δ 154.9 (C), 138.7 (C), 132.5 (C), 129.5 (CH), 128.8 (C), 128.3 (CH), 124.8 (CH), 124.3 (CH), 122.4 (C), 120.9 (CH), 118.4 (CH), 117.5 (CH), 117.0 (CH), 66.2 (CH2), 26.9 (CH2); Selected spectral data for the minor (Z) isomer: 1H NMR (500 MHz, CDCl3) δ 7.38 (d, J = 7.5 Hz, 1H), 7.29 – 7.30 (m, 1H), 7.09 – 7.11 (m, 1H), 7.00 – 7.04 (m, 2H), 6.84 (dd, J = 1.0 Hz, 8.0 Hz, 1H), 6.65 – 6.58 (m, 1H), 6.29 (s, 1H), 4.38 (t, 5.5 Hz, 2H), 2.71- 2.73 (m, 2H); 13C NMR (125 MHz, CDCl3) δ 154.9 (C), 138.1 (C), 132.5 (C), 131.1 (CH), 129.7 (CH), 128.53 (CH), 128.50 (CH), 124.7 (CH), 120.6 (C), 120.0 (CH), 119.3 (CH), 118.6 (CH), 117.1 (CH), 67.4 (CH2), 33.3 (CH2); Selected spectral data for the mixture: δ IR (thin film): 2117, 2091, 1603, 1572, 1468, 1450, 1281, 1049, 749 cm⁻¹. HRMS (EI) m/z calcd for C16H13ON3 (M)⁺ 263.10587, found 263.10672.

II. Preparation of Substrates using a Horner–Wadsworth–Emmons Reaction.

A. General Procedure for the Horner–Wadsworth–Emmons Reaction and Fe-Mediated Nitro-Group Reduction

2-Amino substituted styrenes were synthesized via a two-step procedure of Horner-Wadsworth-Emmons reaction followed by nitro-group reduction. Yields were not optimized.

To a −78 °C solution of LDA (4.4 mmol) in 10 mL of THF was added dropwise ortho-nitrobenzylphosphonate in 3 mL of THF. After an additional hour, a solution of the ketone in 5 mL of THF was added slowly to the mixture at −78 °C. The reaction mixture was allowed to warm to ambient temperature slowly. After 1h, 10 mL water was added to quench the reaction. The resulting mixture was taken up by dichloromethane and separated. The aqueous phase was washed with 3 × 5 mL dichloromethane. The resulting organic phase was washed with
20 mL of brine and dried over Na$_2$SO$_4$. After filtration, the filtrate was concentrated *in vacuo* to produce 2-nitrostyrene, which was submitted to the subsequent Fe-mediated nitro-group reduction without further purification.

To a solution of nitro-substituted styrene (prepared from 4.0 mmol of ortho-nitrobenzylphophonate) in 20 mL of AcOH and 20 mL of EtOH was added 1.8 g of Fe powder (32 mmol). The resultant mixture was allowed to reflux at 80 °C overnight. After cooled down to ambient temperature, the resulting mixture was filtrated with a pad of Celite. The filtrate was diluted with 50 mL of water and washed with 3 × 10 mL dichloromethane. The resulting organic phase was washed with 40 mL of brine and dried over Na$_2$SO$_4$. After filtration, the filtrate was concentrated in *vacuo*. Purification of the reaction mixture using MPLC afforded the product.

**B. Synthesis of ortho-Amino-Substituted Styrenes.**

**Styrene s18.** The general procedure of Horner–Wadsworth–Emmons reaction was followed using 1.09 g of ortho-nitrobenzylphosphonate$^6$ (4.0 mmol), 0.45 mL of cyclobutanone (6.0 mmol) and LDA (4.4 mmol) in 6 mL of THF. After work-up, the representative pathway of nitro-group reduction was followed by using 1.79 g of Fe (32.0 mmol), in 20.0 mL of AcOH and 20.0 mL of EtOH. Purification by MPLC (1:100 – 20:80 EtOAc: hexanes) afforded the product as a light yellow oil (0.25 g, 39% two steps): $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.16 – 7.19 (m, 1H), 7.07 – 7.11 (m, 1H), 6.72 (d, $J$ = 8.0 Hz, 1H), 6.79 – 6.83 (m, 1H), 6.11 (s, 1H), 3.71 (s, 2H), 2.92 – 2.99 (m, 4H), 2.10 – 2.16 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 145.2 (C), 143.5 (C), 128.2 (CH), 127.3 (CH), 123.4 (C), 118.5 (CH), 115.8 (CH), 115.7 (CH), 32.6 (CH$_2$), 32.3 (CH$_2$), 18.2 (CH$_3$); IR (thin film): 3451, 3366, 2948, 1614, 1488 1297, 1263, 744 cm$^{-1}$. HRMS (EI) $m$/z calcd for C$_{11}$H$_{13}$N (M)$^+$ 159.10480, found 159.10560.

**Styrene s19.** The general procedure of Horner–Wadsworth–Emmons reaction was followed using 1.09 g of ortho-nitrobenzylphosphonate$^6$ (4.0 mmol), 0.55 mL of tetrahydro-4H-pyran-4-one (6.0 mmol) and LDA (4.4 mmol) in 6 mL of THF. After work-up, the representative pathway of nitro-group reduction was followed by using 1.79 g of Fe (32.0 mmol), in 20.0 mL of AcOH and 20.0 mL of EtOH. Purification by MPLC (1:100 – 20:80 EtOAc: hexanes) afforded the product as a light yellow oil (0.50 g, 66% two steps): $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.07 (t, $J$ = 8.0 Hz, 1H), 6.99 (d, $J$ = 7.5 Hz, 1H), 6.69 – 6.75 (m, 2H), 6.14 (s, 1H), 3.80 (t, $J$ = 5.5 Hz, 2H), 3.69 (s, 2H), 3.66 (t, $J$ = 5.5 Hz, 2H), 2.43 (t, $J$ = 5.5 Hz, 2H), 2.36 (t, $J$ = 5.5 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 144.2 (C), 139.8 (C), 130.1 (CH), 127.9 (CH), 122.9 (C), 119.6 (CH), 118.1 (CH), 115.1 (CH), 69.7 (CH$_2$), 69.0 (CH$_2$), 37.0 (CH$_2$), 31.0 (CH$_2$); IR (thin film): 3459, 3355, 1613, 1489, 1452, 1229, 1093, 995, 746 cm$^{-1}$. HRMS (EI) $m$/z calcd for C$_{12}$H$_{15}$ON (M)$^+$ 189.11537, found 189.11613.
Styrene s20. The general procedure of Horner–Wadsworth–Emmons reaction was followed using 1.09 g of ortho-nitrobenzylphosphonate\textsuperscript{6} (4.0 mmol), 0.83 g of 4-acetylbenzotrifluoride (4.4 mmol) and LDA (4.4 mmol) in 6 mL of THF. After work-up, the representative pathway of nitro-group reduction was followed by using 1.79 g of Fe (32.0 mmol), in 20.0 mL of AcOH and 20.0 mL of EtOH. Purification by MPLC (1:100 – 20:80 EtOAc: hexanes) afforded the crude product as a brown oil (0.34 g, 31% two steps). The aniline was carried on to the azidation reaction without further purification.

C. General Procedure for the Azidation Reaction.
Following the procedure of Tor and co-workers,\textsuperscript{7} the aniline group was transformed into an azide (s5). Yields were not optimized.

To a solution of aniline (3 mmol) in 5 mL of CH\textsubscript{2}Cl\textsubscript{2} was added subsequently 24 mg of CuSO\textsubscript{4}, 1.2 mL of Et\textsubscript{3}N, freshly prepared triflyl azide (9 mmol) in 15 mL of CH\textsubscript{2}Cl\textsubscript{2}, 1 mL of water and 2 mL of MeOH. The resulting mixture was allowed to react at room temperature overnight. Then, the reaction mixture was taken up by 15 mL dichloromethane, neutralized with a saturated aq. soln. of NaHCO\textsubscript{3} and washed with 3 \times 10 mL of CH\textsubscript{2}Cl\textsubscript{2}. The resulting organic phase was washed with 20 mL of brine and dried over Na\textsubscript{2}SO\textsubscript{4}. After filtration, the filtrate was concentrated \textit{in vacuo}. Purification of the reaction mixture using MPLC afforded the product.

D. Synthesis of Styryl Azides.

Styryl Azide 14f. The general procedure for azidation was followed using 0.31 g of aniline s20 (1.1 mmol), 0.01 g of CuSO\textsubscript{4}, freshly prepared dichloromethane solution of TfN\textsubscript{3} (from 3.0 mmol of Tf\textsubscript{2}O), and 0.4 mL of Et\textsubscript{3}N (3.0 mmol) in 4 mL CH\textsubscript{2}Cl\textsubscript{2}, 2 mL of MeOH and 1 mL of H\textsubscript{2}O. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a light yellow solid (0.22 g, 66%): mp 62 - 65 °C; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \textit{d} 7.51 (d, \textit{J} = 8.0 Hz, 2H), 7.28 (d, \textit{J} = 8.0 Hz, 2H), 7.17 – 7.20 (m, 1H), 7.12 (dd, \textit{J} = 1.0 Hz, 8.0 Hz, 1H), 6.80 – 6.83 (m, 1H), 6.74 (d, \textit{J} = 7.5 Hz, 1H), 6.65 (s, 1H), 2.29 (s, 3H); \textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) \textit{d} 145.3 (C), 138.6 (C), 138.1 (C), 131.1 (CH), 129.076 (q, \textit{J}_{CF} = 32.6 Hz, C), 129.075 (C), 128.7 (CH), 128.1 (CH), 125.2 (q, \textit{J}_{CF} = 3.5 Hz, CH), 124.3 (CH), 124.2 (q, \textit{J}_{CF} = 271 Hz, C), 123.5 (CH), 118.2 (CH), 23.0 (CH\textsubscript{3}); \textsuperscript{19}F NMR (CDCl\textsubscript{3}, 282 MHz) \textit{d} –63.04; IR (thin film): 2122, 1615, 1482, 1323, 1123, 738 cm\textsuperscript{–1}. HRMS (EI) \textit{m} / \textit{z} calcd for C\textsubscript{16}H\textsubscript{12}N\textsubscript{3}F\textsubscript{3} (M\textsuperscript{+}) 303.09833, found 303.09697.
Styryl Azide 17a. The general procedure for azidation was followed using 0.23 g of aniline \( s18 \) (1.44 mmol), 0.02 g of \( \text{CuSO}_4 \), freshly prepared dichloromethane solution of \( \text{TfN}_3 \) (from 4.5 mmol of \( \text{Tf}_2\text{O} \)), and 0.6 mL of \( \text{Et}_3\text{N} \) (4.5 mmol) in 6 mL \( \text{CH}_2\text{Cl}_2 \), 3 mL of \( \text{MeOH} \) and 2 mL of \( \text{H}_2\text{O} \). Purification by MPLC (100% hexanes) afforded the product as a light yellow oil (0.14 g, 54%): \( ^1\text{H NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) 7.30 (d, \( J = 8.0 \text{ Hz}, 1\text{H} \)), 7.23 (t, \( J = 8.0 \text{ Hz}, 1\text{H} \)), 7.11 (t, \( J = 7.5 \text{ Hz}, 1\text{H} \)), 6.35 (s, 1H), 3.01 – 3.04 (m, 2H), 2.92 – 2.95 (m, 2H), 2.12 – 2.16 (m, 2H); \( ^13\text{C NMR} \) (125 MHz, CDCl\(_3\)) \( \delta \) 146.5 (C), 136.5 (C), 129.5 (C), 127.9 (CH), 127.1 (CH), 124.5 (CH), 118.3 (CH), 115.1 (CH), 32.9 (CH\(_2\)), 32.7 (CH\(_2\)), 18.4 (CH\(_2\)); IR (thin film): 2951, 2113, 1482, 1285, 1099, 743, 665 cm\(^{-1}\). HRMS (EI) \( m/z \) calcld for \( \text{C}_{11}\text{H}_{11}\text{N}_3 \) (M\(^+\)) 185.09530, found 185.09451.

Styryl Azide 17h. The general procedure for azidation was followed using 0.43 g of aniline \( s19 \) (2.28 mmol), 0.02 g of \( \text{CuSO}_4 \), freshly prepared dichloromethane solution of \( \text{TfN}_3 \) (from 9.0 mmol of \( \text{Tf}_2\text{O} \)), and 1.3 mL of \( \text{Et}_3\text{N} \) (9.0 mmol) in 6 mL \( \text{CH}_2\text{Cl}_2 \), 3 mL of \( \text{MeOH} \) and 2 mL of \( \text{H}_2\text{O} \). Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a light yellow oil (0.31 g, 63%): \( ^1\text{H NMR} \) (500 MHz, CDCl\(_3\)) 7.22 – 7.25 (m, 1H), 7.10 – 7.15 (m, 2H), 7.07 (t, \( J = 7.5 \text{ Hz}, 1\text{H} \)), 6.24 (s, 1H), 3.77 (t, \( J = 5.5 \text{ Hz}, 2\text{H} \)), 3.64 (t, \( J = 5.5 \text{ Hz}, 2\text{H} \)), 2.37 – 2.41 (m, 4H); \( ^13\text{C NMR} \) (125 MHz, CDCl\(_3\)) \( \delta \) 139.3 (C), 138.1 (C), 130.8 (CH), 129.1 (C), 128.0 (CH), 124.3 (CH), 119.3 (CH), 118.4 (CH), 69.4 (CH\(_2\)), 68.6 (CH\(_2\)), 37.2 (CH\(_2\)), 30.9 (CH\(_2\)); IR (thin film): 2115, 2082, 1482, 1279, 1230, 1097, 997, 748, 665 cm\(^{-1}\). HRMS (EI) \( m/z \) calcld for \( \text{C}_{12}\text{H}_{13}\text{ON}_3 \) (M\(^+\)) 215.10587, found 215.10709.

III. Preparation of Substrates using a Suzuki Reaction.

General Procedure for the Arylboronic Acid Pinacol Ester Syntheses.

To a mixture of 0.85 g of 2-bromo-aniline (5.0 mmol), 2.09 mL of \( \text{Et}_3\text{N} \) (20.0 mmol), 0.185 g of \( \text{(dppf)PdCl}_2 \) (0.25 mmol) in 15 mL 1,4-dioxane, was added dropwise 2.20 mL 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15.0 mmol). The resultant mixture was heated to 100 °C. After 12h, the mixture was cooled to room temperature and diluted with 20 mL of \( \text{NH}_3\text{Cl} \). The resulting aqueous phase was extracted with an additional 2 \times 20 mL of \( \text{CH}_2\text{Cl}_2 \). The combined organic phases were washed with \( 1 \times 30 \text{ mL of brine} \). The resulting organic phase was dried over \( \text{Na}_2\text{SO}_4 \), and was concentrated \textit{in vacuo}. Purification via MPLC afforded the product.
A. Syntheses of Arylboronic Acid Pinacol Esters.

**Aniline s21.** The general procedure was followed using 3.4 g of 2-bromo-aniline (20.0 mmol), 8.7 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (60.0 mmol), 0.82 g of (dppf)PdCl₂ (1.0 mmol), and 8.4 mL of Et₃N (80.0 mmol) in 100 mL of 1,4-dioxane. Purification by MPLC (2:100 – 10:90 EtOAc: hexanes) afforded the product as a light yellow solid (3.02 g, 69%): mp 62-64 °C; The spectral data matched that reported by Driver and co-workers: ¹H NMR (500 MHz, CDCl₃) δ 7.64 (d, J = 7.5 Hz, 1H), 7.24 (t, J = 7.0 Hz, 1H), 6.70 (t, J = 7.0 Hz, 1H), 6.61 (d, J = 8.5 Hz, 1H), 4.76 (s, 2H), 1.36 (s, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 153.7 (C), 136.8 (CH), 132.8 (CH), 116.9 (CH), 114.8 (CH), 83.5 (C), 25.0 (CH₃); IR (thin film): 3486, 3380, 1624, 1605, 1352, 1311, 1244, 1135, 1086, 847, 758, 654 cm⁻¹.

**Aniline s22.** The general procedure was followed using 2.65 g of 2-bromo-4-(trifluoromethyl)aniline (10.0 mmol), 4.4 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30.0 mmol), 0.41 g of (dppf)PdCl₂ (0.5 mmol), and 4.2 mL of Et₃N (40.0 mmol) in 50 mL of 1,4-dioxane. Purification by MPLC (2:100 – 10:90 EtOAc: hexanes) afforded the product as a brown solid (1.81 g, 63%): mp 107-109 °C. The spectral data matched that reported by Driver and co-workers: ¹H NMR (500 MHz, CDCl₃) δ 7.86 (s, 1H), 7.41 (d, J = 8.5 Hz, 1H), 6.59 (d, J = 8.5 Hz, 1H), 5.08 (s, 2H), 1.35 (s, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 156.1 (C), 134.3 (q, JCF = 3.8 Hz, CH), 129.5 (q, JCF = 3.8 Hz, CH), 125.0 (q, JCF = 268.8 Hz, C), 118.5 (q, JCF = 32.5 Hz, C), 84.0 (C) 114.2 (CH), 24.9 (CH₃); ¹⁹F NMR (CDCl₃, 282 MHz) δ –61.64; IR (thin film): 3472, 3375, 1625, 1370, 1304, 1256, 1140, 1097, 832.9 cm⁻¹.

**Aniline s23.** The general procedure was followed using 2.02 g of 2-bromo-4-methoxyaniline (10.0 mmol), 4.4 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30.0 mmol), 0.41 g of (dppf)PdCl₂ (0.5 mmol), and 4.2 mL of Et₃N (40.0 mmol) in 50 mL of 1,4-dioxane. Purification by MPLC (5:100 – 10:90 EtOAc: hexanes) afforded the product as a brown liquid (1.52 g, 61%). The spectral data matched that reported by Driver and co-workers: ¹H NMR (500 MHz, CDCl₃) δ 7.16 (d, J = 3.5 Hz, 1H), 6.85 (dd, J = 3.0 Hz, 8.5 Hz, 1H), 6.58 (d, J = 8.5 Hz, 1H), 4.48 (s, 2H), 3.76 (s, 3H), 1.34 (s, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 151.3 (C), 147.9 (C), 120.7 (CH), 119.5 (CH), 116.5 (CH), 83.6 (C), 56.0 (CH₃), 25.0 (CH₃); IR (thin film): 3452, 3375, 1625, 1370, 1304, 1256, 1140, 1097, 832.9 cm⁻¹. HRMS (EI) m/z calcd for C₁₃H₂₀O₃NB (M)+ 249.1536, found 249.1540.
B. General Procedure for the Triflate Formation.

\[
\begin{align*}
\text{CH}_3 & \text{O} \quad \text{THF} \quad \text{OTi} \\
\text{O} & \text{H} \\
\text{t-Bu} & \text{N} \quad \text{t-Bu}
\end{align*}
\]

To a mixture of 10.0 mmol of cyclopentanecarboxaldehyde and 2.65 mL 2,6-di-tert-butylpyridine (12.0 mmol) in 40 mL of 1,2-dichloroethane was added 1.85 mL of triflic anhydride (11.0 mmol). The resultant mixture was heated to 70 °C. After 2h, the mixture was cooled to room temperature and diluted with 40 mL CH$_2$Cl$_2$. The resulting aqueous phase was extracted with an additional $2 \times 30$ mL of CH$_2$Cl$_2$. The combined organic phases were washed with $1 \times 30$ mL of brine. The resulting organic phase was dried over Na$_2$SO$_4$, and was concentrated in vacuo to afford crude triflate.

C. General Procedure for the Suzuki Reaction.

Following the procedure of Driver and co-workers, was aniline s6 treated with vinyl triflate s7 in the presence of (dppf)PdCl$_2$ to produce the desired aniline (s8). Yields were not optimized.

\[
\begin{align*}
\text{R-O} & \text{Me} \quad \text{Me} \\
\text{O} & \text{Me} \\
\text{Me} & \text{O}
\end{align*}
\]

To a mixture of 0.919 g of boronic ether s6 (3.2 mmol), 0.261 g of (dppf)PdCl$_2$ (0.32 mmol) in 40 mL 1,4-dioxane was added 8 mL of a 3M solution of NaOH in water followed by 1.36 g of crude triflate s7 (5.12 mmol). The resultant mixture was heated to 80 °C. After 12 h, the mixture was cooled to room temperature and filtrated through a pad of Celite. The filtrate was diluted with 20 mL saturated NH$_4$Cl and extracted with an additional $2 \times 30$ mL of CH$_2$Cl$_2$. The combined organic phases were washed with $1 \times 30$ mL of brine. The resulting organic phase was dried over Na$_2$SO$_4$, and was concentrated in vacuo. Purification via MPLC afforded the product.

D. Synthesis of Anilines.

Aniline s24. The general procedure was followed using 1.10 g of boronic ester s6 (5.0 mmol), crude vinyl triflate (derived from 10.0 mmol of cyclohexanecarboxaldehyde), 0.82 g of (dppf)PdCl$_2$ (1.0 mmol), and 1.8 g of NaOH (45.0 mmol) in 75 mL of 1,4-dioxane and 15 mL of water. Purification by MPLC (2:100 – 10:90 EtOAc: hexanes) afforded the product as a light yellow oil (0.74 g, 79%): $^1$H NMR (500 MHz, CDCl$_3$) δ 7.09 (t, $J$ = 6.0 Hz, 1H), 7.04 (d, $J$ = 7.5 Hz, 1H), 6.77 (t, $J$ = 7.5 Hz, 1H), 6.72 (d, $J$ = 8.0 Hz, 1H), 6.05 (s, 1H), 3.70 (s, 2H), 2.33 (t, $J$ = 6.0 Hz, 2H), 2.24 (t, $J$ = 6.0 Hz, 2H), 1.56 – 1.70 (m, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 145.4 (C), 144.3 (C), 130.3 (CH), 127.5 (CH), 124.0 (C), 118.0 (CH), 117.8 (CH), 115.0 (CH), 37.2 (CH$_3$), 30.0
(CH₂), 28.9 (CH₂), 28.1 (CH₂), 26.8 (CH₂); IR (thin film): 3466, 3368, 1161, 1489, 1448, 1297, 1265, 745 cm⁻¹. HRMS (EI) m/z calcld for C₁₃H₁₇N (M)+ 187.13610, found 187.13596.

Aniline s²⁵. The general procedure was followed using 2.19 g of boronic ester s⁶ (10.0 mmol), crude vinyl triflate (derived from 15.0 mmol of cyclopentanecarboxaldehyde), 0.82 g of (dppf)PdCl₂ (1.0 mmol), and 3.6 g of NaOH (90.0 mmol) in 100 mL of 1, 4-dioxane and 30 mL of water. Purification by MPLC (2:100 – 10:90 EtOAc: hexanes) afforded the product as a light yellow oil (1.54 g, 89%): ¹H NMR (500 MHz, CDCl₃) δ 7.16 (d, J = 7.5 Hz, 1H), 7.05 (dt, J = 1.5 Hz, 7.5 Hz, 1H), 6.76 (t, J = 7.5 Hz, 1H), 6.70 (d, J = 7.5 Hz, 1H), 6.23 (s, 1H), 3.67 (s, 2H), 2.49 (s, 2H), 2.39 (s, 2H), 1.70 – 1.73 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 148.6 (C), 143.7 (C), 129.1 (CH), 127.3 (CH), 124.9 (C), 118.2 (CH), 115.7 (CH), 115.2 (CH), 34.6 (CH₂), 30.7 (CH₂), 26.7 (CH₂), 25.8 (CH₂); IR (thin film): 3452, 3368, 1613, 1488, 1453, 1295, 1263, 1155, 871, 744 cm⁻¹. HRMS (EI) m/z calcld for C₁₂H₁₅N (M)+ 173.1164, found 173.1204.

Aniline s²⁶. The general procedure was followed using 0.76 g of boronic ester s⁶ (3.5 mmol), crude vinyl triflate (derived from 10.0 mmol of cycloheptanecarboxaldehyde), 0.25 g of (dppf)PdCl₂ (0.3 mmol), and 1.2 g of NaOH (30.0 mmol) in 40 mL of 1, 4-dioxane and 10 mL of water. Purification by MPLC (2:100 – 10:90 EtOAc: hexanes) afforded the product as a light yellow oil (0.25 g, 35%): ¹H NMR (500 MHz, CDCl₃) δ 7.07 (dt, J = 1.5 Hz, 7.5 Hz, 1H), 7.03 (d, J = 7.5 Hz, 1H), 6.74 (dt, J = 1.0 Hz, 7.5 Hz, 1H), 6.71 (dd, J = 1.5 Hz, 7.5 Hz, 1H), 6.10 (s, 1H), 3.68 (s, 2H), 2.43 – 2.45 (m, 2H), 2.31 – 2.33 (m, 2H) 1.68 – 1.72 (m, 2H), 1.52 – 1.62 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 147.5 (C), 144.0 (C), 130.0 (CH), 127.4 (CH), 124.5 (C), 121.0 (CH), 118.0 (CH), 37.8 (CH₂), 31.2 (CH₂), 29.9 (CH₃), 29.5 (CH₂), 29.37 (CH₂), 27.3 (CH₂); IR (thin film): 3464, 3372, 2918, 2849, 1611, 1489, 1451, 745 cm⁻¹. HRMS (EI) m/z calcld for C₁₄H₁₉N (M)+ 201.15175 found 201.15198.

Aniline s²⁷. The general procedure was followed using 1.69 g of boronic ester s⁶ (6.8 mmol), crude vinyl triflate (derived from 10.0 mmol of cyclopentanecarboxaldehyde), 0.57 g of (dppf)PdCl₂ (0.68 mmol), and 1.44 g of NaOH (36.0 mmol) in 40 mL of 1, 4-dioxane and 12 mL of water. Purification by MPLC (2:100 – 20:80 EtOAc: hexanes) afforded the product as a brown oil (0.97 g, 70%): ¹H NMR (500 MHz, CDCl₃) δ 6.77 (d, J = 1.8 Hz, 1H), 6.64 – 6.64 (m, 2H), 6.23 (t, J = 2.3 Hz, 1H), 3.75 (s, 3H), 3.44 (s, 2H), 2.48 (ddd, J = 7.7, 5.5, 1.9 Hz, 2H), 2.42-2.40 (m, 2H), 1.71 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 152.4 (C), 148.8 (C), 137.5 (C), 126.2 (C), 116.4 (CH), 115.9 (CH), 114.6 (CH), 112.9 (CH), 55.8 (CH₃), 34.7 (CH₂), 30.8 (CH₂), 26.7 (CH₂), 25.8 (CH₂); IR (thin film): 3437, 3357, 2947, 1604, 1494, 1281, 1040, 904, 813 cm⁻¹. HRMS (EI) m/z calcld for C₁₃H₁₇ON (M)+ 203.13102, found 203.13075.
Aniline s28. The general procedure was followed using 1.44 g of boronic ester s6 (5.8 mmol), crude vinyl triflate (derived from 9.0 mmol of cyclohexanecarboxaldehyde), 0.57 g of (dppf)PdCl₂ (0.68 mmol), and 1.20 g of NaOH (30.0 mmol) in 40 mL of 1, 4-dioxane and 10 mL of water. Purification by MPLC (2:100 – 20:80 EtOAc: hexanes) afforded the product as a brown oil (0.21 g, 17%): 1H NMR (500 MHz, CDCl₃): 6.60 – 6.68 (m, 3H), 6.01 (s, 1H), 3.74 (s, 3H), 3.13 (s, 2H), 2.29 (t, J = 6.0 Hz, 2H), 2.21 (t, J = 6.5 Hz, 2H), 1.52 – 1.66 (m, 6H); 13C NMR (125 MHz, CDCl₃) δ 152.2 (C), 145.6 (C), 138.0 (C), 125.3 (C), 117.7 (CH), 116.1 (CH), 115.7 (CH), 113.1 (CH), 55.8 (CH₃), 37.2 (CH₂), 30.0 (CH₂), 28.8 (CH₂), 28.0 (CH₂), 26.7 (CH₂); IR (thin film): 3438, 3358, 1494, 1276, 1216, 1159, 1039, 811 cm⁻¹. HRMS (EI) m/z calcd for C₁₄H₁₉ON (M)⁺ 217.1467, found 217.1466.

Aniline s29. The general procedure was followed using 3.01 g of boronic ester s6 (10.5 mmol), crude vinyl triflate (derived from 15.0 mmol corresponding aldehyde), 0.87 g of (dppf)PdCl₂ (1.05 mmol), and 3.60 g of NaOH (90.0 mmol) in 110 mL of 1, 4-dioxane and 30 mL of water. Purification by MPLC (2:100 – 10:90 EtOAc: hexanes) afforded the product as a brown liquid (1.82 g, 62%): 1H NMR (500 MHz, CDCl₃) δ 7.30 (d, J = 8.5 Hz, 1H), 7.26 (s, 1H), 6.69 (d, J = 8.5 Hz, 1H), 5.98 (s, 1H), 4.01 (s, 2H), 2.32 (t, J = 5.5 Hz, 2H), 2.18 (t, J = 6.5 Hz, 2H), 1.54 – 1.71 (m, 6H); 13C NMR (125 MHz, CDCl₃) δ 147.3 (C), 147.1 (C), 127.3 (q, J_FC = 3.8 Hz, CH), 125.1 (q, J_FC = 268.8 Hz, C), 124.6 (q, J_CF = 3.8 Hz, CH), 123.3 (C), 119.5 (q, J_CF = 31.3 Hz, C), 116.4 (CH), 114.1 (CH), 37.1 (CH₂), 30.0 (CH₂), 28.8 (CH₂), 28.0 (CH₂), 26.6 (CH₂); 19F NMR (CDCl₃, 282 MHz) δ –61.47; IR (thin film): 3492, 3398, 1620, 1323, 1142, 1103, 1071, 820 cm⁻¹. HRMS (EI) m/z calcd for C₁₄H₁₆NF₃ (M)⁺ 255.1235, found 255.1239.

Aniline s30. The general procedure was followed using 1.75 g of boronic ester s6 (8.0 mmol), crude vinyl triflate (derived from 15.0 mmol corresponding aldehyde), 0.66 g of (dppf)PdCl₂ (0.8 mmol), and 3.60 g of NaOH (90.0 mmol) in 110 mL of 1,4-dioxane and 30 mL of water. Purification by MPLC (1:100 – 10:90 EtOAc: hexanes) afforded the product as a light yellow oil, as a 69:31 mixture of Z- and E-isomers (1.41 g, 84%): Rf = 0.45 (18:82 EtOAc: hexane). Selected spectral data for the major (Z) isomer: 1H NMR (500 MHz, CDCl₃) δ 7.11 – 7.23 (m, 5H), 6.97 (t, J = 8.0 Hz, 1H), 6.72 – 6.76 (m, 1H), 6.62 (d, J = 8.0 Hz, 1H), 6.52 (t, J = 7.5 Hz, 1H), 6.41 (s, 1H), 3.70 (br, 2H), 2.28 (s, 3H); 13C NMR (125 MHz, CDCl₃) δ 144.0 (C), 141.2 (C), 139.5 (C), 130.0 (CH), 128.1 (CH), 127.5 (CH), 127.0 (CH), 123.98 (C), 123.1 (CH), 118.3 (CH), 115.3 (CH), 25.7 (CH₃) one overlapping aromatic C not distinguishable; Selected spectral data for the minor (E) isomer: 1H NMR (500 MHz, CDCl₃) δ 7.57 – 7.58 (m, 2H), 7.38 – 7.41 (m, 2H), 7.31 – 7.34 (m, 1H), 7.11– 7.23 (m, 2H), 6.81 (t, J = 7.5 Hz, 1H), 6.72 – 6.76 (m, 2H), 3.70 (br s, 2H), 2.17 (s, 3H); 13C NMR (125 MHz, CDCl₃) δ 144.4 (C), 142.9 (C), 139.1 (C), 130.5 (CH), 128.4 (CH), 128.1 (CH), 127.4 (CH), 124.01 (C), 123.9 (CH), 123.5 (CH), 118.2 (CH), 115.2 (CH), 17.2 (CH₃); Selected spectral data for the mixture: δ IR (thin film): 3464, 3374, 1613, 1489, 1454, 1275, 1264 cm⁻¹. HRMS (EI) m/z calcd for C₁₅H₁₅N (M)⁺ 209.12045, found 209.12206.
E. General Procedure for Styryl Azides Syntheses.

Following the procedure of Tor and co-workers, the aniline group was transformed into an azide (s5). Yields were not optimized.

To a solution of aniline (3 mmol) in 5 mL of CH₂Cl₂ was added subsequently 24 mg of CuSO₄, 1.2 mL of Et₃N, freshly prepared triflyl azide (9 mmol) in 15 mL of CH₂Cl₂, 1 mL of water and 2 mL of MeOH. The resulting mixture was allowed to react at room temperature overnight. Then, the reaction mixture was taken up by 15 mL dichloromethane, neutralized with a saturated aq. soln. of NaHCO₃ and washed with 3 × 10 mL of CH₂Cl₂. The resulting organic phase was washed with 20 mL of brine and dried over Na₂SO₄. After filtration, the filtrate was concentrated in vacuo. Purification of the reaction mixture using MPLC afforded the product.

F. Synthesis of Styryl Azides.

Styryl Azide 17b. The general procedure for azidation was followed using 0.95 g of aniline s39 (5.5 mmol), 0.05 g of CuSO₄, freshly prepared dichloromethane solution of TfN₃ (from 18.0 mmol of Tf₂O), and 2.5 mL of Et₃N (18.0 mmol) in 6 mL of CH₂Cl₂, 4 mL of MeOH and 2 mL of H₂O. Purification by MPLC (1:100 EtOAc: hexanes) afforded the product as a light yellow oil, as a 72:28 mixture of Z- and E-isomers (0.68 g, 62%): Selected spectral data for the major (Z) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.21 – 7.32 (m, 6H), 7.13 – 7.15 (d, J = 8.5 Hz, 1H), 6.80 – 6.84 (m, 2H), 6.62 (s, 1H), 2.33 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 141.5 (C), 140.3 (C), 137.9 (C), 131.2 (CH), 129.8 (C), 128.4 (CH), 127.7 (CH), 127.1 (CH), 124.2 (CH), 121.9 (CH), 118.1 (CH), 26.5 (CH₃); Selected spectral data for the minor (E) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.64 (dd, J = 1.0 Hz, 8.5 Hz, 2H), 7.36 – 7.47 (m, 5H), 7.18 (dd, J = 2.0 Hz, 6.0 Hz, 2H), 6.92 (s, 1H), 2.72 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 143.3 (C), 138.7 (C), 138.5 (C), 130.8 (CH), 130.2 (C), 128.5 (CH), 128.2 (CH), 127.5 (CH), 126.1 (CH), 124.4 (CH), 123.1 (CH), 118.5 (CH), 17.5 (CH₃); Selected spectral data for the mixture: δ IR (thin film): 2116, 2083, 1479, 1443, 1278, 759 cm⁻¹. HRMS (El) m/z calcd for C₁₂H₁₃N₃ (M⁺) 199.1109, found 119.1112.

Styryl Azide 14e.⁹ The general procedure for azidation was followed using 0.65 g of aniline s30 (3.1 mmol), 0.02 g of CuSO₄, freshly prepared dichloromethane solution of TfN₃ (from 9.0 mmol of Tf₂O), and 1.3 mL of Et₃N (9.0 mmol) in 4 mL of CH₂Cl₂, 2 mL of MeOH and 1 mL of H₂O. Purification by MPLC (1:100 – 20:80 EtOAc: hexanes) afforded the product as a light yellow oil, as a 72:28 mixture of Z- and E-isomers (0.59 g, 81%): Selected spectral data for the major (Z) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.21 – 7.32 (m, 6H), 7.13 – 7.15 (d, J = 8.5 Hz, 1H), 6.80 – 6.84 (m, 2H), 6.62 (s, 1H), 2.33 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 141.5 (C), 140.3 (C), 137.9 (C), 131.2 (CH), 129.8 (C), 128.4 (CH), 127.7 (CH), 127.1 (CH), 124.2 (CH), 121.9 (CH), 118.1 (CH), 26.5 (CH₃) one overlapping aromatic C not distinguishable; Selected spectral data for the minor (E) isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.64 (dd, J = 1.0 Hz, 8.5 Hz, 2H), 7.36 – 7.47 (m, 5H), 7.18 (dd, J = 2.0 Hz, 6.0 Hz, 2H), 6.92 (s, 1H), 2.72 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 143.3 (C), 138.7 (C), 138.5 (C), 130.8 (CH), 130.2 (C), 128.5 (CH), 128.2 (CH), 127.5 (CH), 126.1 (CH), 124.4 (CH), 123.1 (CH), 118.5 (CH), 17.5 (CH₃); Selected spectral data for the mixture: δ IR (thin film): 2116, 2083, 1479, 1443, 1278, 759 cm⁻¹. HRMS (El) m/z calcd for C₁₂H₁₃N₃ (M⁺) 199.1109, found 119.1112.
Hz, 6.0 Hz, 2H), 6.92 (s, 1H), 2.72 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 143.3 (C), 138.7 (C), 138.5 (C), 130.8 (CH), 130.2 (C), 128.5 (CH), 128.2 (CH), 127.5 (CH), 126.1 (CH), 124.4 (CH), 123.1 (CH), 118.5 (CH), 17.5 (CH₃); Selected spectral data for the mixture: δ IR (thin film): 2116, 2083, 1479, 1443, 1278, 759 cm⁻¹. HRMS (EI) m/z calcd for C₁₅H₁₃N₃ (M)+ 235.11095, found 235.11230.

**Styryl Azide 17c.** The general procedure for azidation was followed using 1.42 g of aniline s39 (7.6 mmol), 0.06 g of CuSO₄, freshly prepared dichloromethane solution of TfN₃ from 22.8 mmol of Tf₂O, and 3.2 mL of Et₃N (22.8 mmol) in 10 mL of CH₂Cl₂, 5 mL of MeOH and 3 mL of H₂O. Purification by MPLC (100% hexane) afforded the product as a light yellow oil (1.36 g, 84%): ¹H NMR (500 MHz, CDCl₃) δ 7.23 – 7.27 (m, 1H), 7.17 (d, J = 7.5 Hz, 1H), 7.13 (dd, J = 1.0 Hz, 8.0 Hz, 1H), 7.07 – 7.10 (m, 1H), 6.14 (s, 1H), 2.30 (t, J = 5.5 Hz, 2H), 2.25 (t, J = 5.5 Hz, 2H), 1.55 – 1.68 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 145.0 (C), 138.0 (C), 131.0 (CH), 130.2 (C), 127.5 (CH), 124.3 (CH), 118.3 (CH), 117.3 (CH), 37.5 (CH₂), 29.8 (CH₂), 28.6 (CH₂), 27.9 (CH₂), 26.7 (CH₃); IR (thin film): 2112, 2080, 1482, 1444, 1281, 746, 836, 746, 725, 671 cm⁻¹. HRMS (EI) m/z calcd for C₁₃H₁₅N₃ (M)+ 213.12660, found 213.12686.

**Styryl Azide 17d.** The general procedure for azidation was followed using 0.21 g of aniline s39 (1.1 mmol), 0.01 g of CuSO₄, freshly prepared dichloromethane solution of TfN₃ from 3.0 mmol of Tf₂O, and 0.4 mL of Et₃N (3.0 mmol) in 4 mL of CH₂Cl₂, 2 mL of MeOH and 1 mL of H₂O. Purification by MPLC (100% hexane) afforded the product as a light yellow oil (0.18 g, 76%): ¹H NMR (500 MHz, CDCl₃) δ 7.19 – 7.26 (m, 2H), 7.08 – 7.14 (m, 2H), 6.25 (s, 1H), 2.45 (t, J = 6.0 Hz, 2H), 2.37 (t, J = 6.0 Hz, 2H), 1.58 – 1.70 (m, 8H); ¹³C NMR (125 MHz, CDCl₃) δ 146.8 (C), 137.8 (C), 130.6 (CH), 127.4 (CH), 124.3 (CH), 120.6 (CH), 118.3 (CH), 38.3 (CH₂), 31.3 (CH₂), 29.8 (CH₂), 29.3 (CH₂), 29.1 (CH₂), 27.3 (CH₂); IR (thin film): 2919, 2113, 2079, 1572, 1480, 1443, 1281, 1085, 746 cm⁻¹. HRMS (EI) m/z calcd for C₁₄H₁₇N₃ (M)+ 227.14225, found 227.14169.

**Styryl Azide 17e.** The general procedure for azidation was followed using 0.97 g of aniline s39 (4.8 mmol), 0.02 g of CuSO₄, freshly prepared dichloromethane solution of TfN₃ from 14.4 mmol of Tf₂O, and 2.0 mL of Et₃N (14.4 mmol) in 6 mL CH₂Cl₂, 3 mL of MeOH and 2 mL of H₂O. Purification by MPLC (100% hexane) afforded the product as a light yellow oil (0.80 g, 73%): ¹H NMR (500 MHz, CDCl₃) δ 7.04 (d, J = 8.7 Hz, 1H), 6.93 (d, J = 2.8 Hz, 1H), 6.77 (dd, J = 8.7, 2.9 Hz, 1H), 6.43 (s, 1H), 3.80 (s, 3H), 2.46 – 2.52 (m, 4H), 1.71 – 1.78 (m, 2H), 1.71 – 1.66 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 156.4 (C), 149.3 (C), 131.6 (C), 129.8 (C), 119.1 (CH), 115.3 (CH), 114.6 (CH), 112.5 (CH), 55.5 (CH₃), 35.5 (CH₂), 31.2 (CH₂), 27.0 (CH₂), 25.6 (CH₂); IR (thin film): 2953, 2115, 2080, 1480, 1446, 744 cm⁻¹. HRMS (EI) m/z calcd for C₁₃H₁₅ON₃ (M)+ 229.12152, found 229.12192.
Styryl Azide 17f. The general procedure for azidation was followed using 0.21 g of aniline (1.0 mmol), 0.01 g of CuSO₄, freshly prepared dichloromethane solution of TfN₃ (from 3.0 mmol of Tf₂O), and 1.3 mL of Et₃N (3.0 mmol) in 3 mL of CH₂Cl₂, 2 mL of MeOH and 1 mL of H₂O. Purification by MPLC (100% hexane) afforded the product as a light yellow oil (0.41 g, 43%): ¹H NMR (500 MHz, CDCl₃) δ 7.04 (d, J = 9.0 Hz, 1H), 6.80 (dd, J = 3.0 Hz, 8.5 Hz, 1H), 6.72 (d, J = 3.0 Hz, 1H), 6.12 (s, 1H), 3.79 (s, 3H), 2.26 – 2.31 (m, 4H), 1.56 – 1.67 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 156.3 (C), 145.3 (C), 131.3 (C), 130.6 (C), 119.3 (CH), 117.4 (CH), 116.4 (CH), 112.8 (CH), 55.5 (CH₃), 37.4 (CH₂), 29.9 (CH₂), 28.6 (CH₂), 27.8 (CH₂), 26.6 (CH₂); IR (thin film): 2106, 2084, 1486, 1284, 1239, 1165, 1035, 798, 732 cm⁻¹. HRMS (EI) m/z calcd for C₁₄H₁₇ON₃ (M⁺) 243.1372, found 243.1372.

Styryl Azide 17g. The general procedure for azidation was followed using 1.60 g of aniline (6.3 mmol), 0.04 g of CuSO₄, freshly prepared dichloromethane solution of TfN₃ (from 18.8 mmol of Tf₂O), and 2.6 mL of Et₃N (18.8 mmol) in 8 mL of CH₂Cl₂, 4 mL of MeOH and 3 mL of H₂O. Purification by MPLC (100% hexane) afforded the product as a light yellow oil (0.04 g, 3%): ¹H NMR (500 MHz, CDCl₃) δ 7.49 (dd, J = 8.5 Hz, 2.0 Hz, 1H), 7.40 (s, 1H), 7.20 (d, J = 7.0 Hz, 1H), 6.11 (s, 1H), 2.30 (t, J = 5.5 Hz, 2H), 2.22 (t, J = 5.5 Hz, 2H), 1.54 – 1.70 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 146.7 (C), 141.5 (C), 130.6 (C), 128.2 (q, J_CF = 3.6 Hz, CH), 126.4 (q, J_CF = 31.4 Hz, C), 124.4 (q, J_CF = 3.4 Hz, CH), 124.0 (q, J_CF = 270.1 Hz, C), 118.5 (CH), 116.3 (CH), 37.4 (CH₂), 29.8 (CH₂), 28.5 (CH₂), 27.8 (CH₂), 26.5 (CH₂); ¹⁹F NMR (CDCl₃, 282 MHz) δ –61.62; IR (thin film): 2929, 2120, 2088, 1329, 1289, 1106, 817 cm⁻¹. HRMS (EI) m/z calcd for C₁₄H₁₄NF₃ (M – N₂)⁺ 255.1000, found 255.1000.

IV. Development of Rhodium-Catalyzed Migration Reaction.

A. General Procedure for the Screening of Catalysts to Promote the Migration.

To a mixture of 0.026 g of aryl azide 8 (0.1 mmol), 0-100 % w/w of crushed 4 Å mol sieves, and metal salt (0 – 5 mol %) in Schlenk tube was added 0.50 mL of solvent. The resulting mixture was heated and, after 16 h, the heterogenous mixture was filtered through a short pad of Al₂O₃. The filtrate was concentrated in vacuo. The resulting solid (oil) was dissolved in 1.5 mL of CDCl₃ and 0.007 mL of dibromomethane (0.1 mmol) was added. The areas of the C–H peak on the carbon 6 position in 9 and carbon 10 in 10 were compared to the area of CH₂Br₂ to derive a yield.
Table s1. Optimization of Migration Process\textsuperscript{a,b}

| Entry | metal salt | Mol %  | solvent | wt %, 4 Å MS | T (°C) | yield, %\textsuperscript{c} | 6:7   |
|-------|------------|--------|---------|-------------|--------|-----------------|------|
| 1     | none       | n.a.   | xylenes | 0           | 170    | xx:xx           |      |
| 2     | Rh\textsubscript{2}(O\textsubscript{2}C\textsubscript{2}H\textsubscript{3})\textsubscript{4} | 5      | PhMe    | 100         | 70     | 8 n.a.          |      |
| 3     | Rh\textsubscript{2}(O\textsubscript{2}CCF\textsubscript{3})\textsubscript{4} | 5      | PhMe    | 100         | 70     | 86 100:0        |      |
| 4     | Rh\textsubscript{2}(O\textsubscript{2}CC\textsubscript{2}F\textsubscript{7})\textsubscript{4} | 5      | PhMe    | 100         | 70     | 95 100:0        |      |
| 5     | Rh\textsubscript{2}(O\textsubscript{2}CC\textsubscript{2}H\textsubscript{15})\textsubscript{4} | 5      | PhMe    | 100         | 70     | 93 95:100       |      |
| 6     | Rh\textsubscript{2}(O\textsubscript{2}CC\textsubscript{2}H\textsubscript{15})\textsubscript{4} | 3      | PhMe    | 100         | 70     | 80\textsuperscript{d} 96:4 |      |
| 7     | Rh\textsubscript{2}(O\textsubscript{2}CC\textsubscript{7}H\textsubscript{15})\textsubscript{4} | 3      | PhMe    | 100         | 60     | 88\textsuperscript{e} 96:4 |      |
| 8     | Rh\textsubscript{2}(O\textsubscript{2}CC\textsubscript{7}H\textsubscript{15})\textsubscript{4} | 5      | PhMe    | 100         | 70     | 95 96:4         |      |
| 9     | Rh\textsubscript{2}(O\textsubscript{2}CC\textsubscript{7}H\textsubscript{15})\textsubscript{4} | 5      | DCE     | 100         | 60     | 74\textsuperscript{f} 96:4 |      |
| 10    | Rh\textsubscript{2}(O\textsubscript{2}CC\textsubscript{7}H\textsubscript{15})\textsubscript{4} | 5      | DCE     | 100         | 70     | 94 98:2         |      |
| 11    | Rh\textsubscript{2}(O\textsubscript{2}CC\textsubscript{7}H\textsubscript{15})\textsubscript{4} | 5      | DCE     | 100         | 80     | 88 96:4         |      |
| 12    | Rh\textsubscript{2}(esp)\textsubscript{2} | 5      | PhMe    | 100         | 70     | 98 >98:2        |      |
| 13    | RhCl\textsubscript{3} | 5      | PhMe    | 100         | 70     | 0 n.a.          |      |
| 14    | (Ph\textsubscript{3}P)\textsubscript{3}RuCl | 5      | PhMe    | 100         | 70     | trace n.a.      |      |
| 15    | Cu(OTf)\textsubscript{2} | 5      | PhMe    | 100         | 70     | 0 n.a.          |      |
| 16    | Ru(TPFPP)CO | 5      | IPAC    | 0           | 48     | 48 100:0        |      |

\textsuperscript{a}Reaction performed in conical vial. \textsuperscript{b}16 hour reaction time. \textsuperscript{c}Isolated yield after Al\textsubscript{2}O\textsubscript{3} chromatography.

B. Optimized General Procedure.

To a mixture of 0.026 g of aryl azide 5 (0.1 mmol), 100 % w/w of crushed 4 Å mol sieves, and metal salt (Rh\textsubscript{2}(esp)\textsubscript{4} or Rh\textsubscript{2}(hpfb)\textsubscript{4}, 5 mol %) in Schlenk tube was added 0.50 mL of PhMe. The resulting mixture was heated at 70 °C for 16 h, then, the heterogenous mixture was filtered through a short pad of Al\textsubscript{2}O\textsubscript{3}. The filtrate was concentrated \textit{in vacuo} to afford analytically pure indole. In some cases, purification by MPLC is required.

C. Effect of Aryl Azide Substitution on Rhodium-Catalyzed Migration Selectivity.

\textbf{Indole 9.} The general procedure was followed using 0.027 g of styryl azide 8 (0.102 mmol) and 0.005 g of Rh\textsubscript{2}(hpfb)\textsubscript{4} (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al\textsubscript{2}O\textsubscript{3} afforded analytically pure compound 9 (0.025, 95%). mp 125 – 127 °C; \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \textdelta 7.94 – 7.96 (m, 2H), 7.87 (d, J = 7.5 Hz, 1H), 7.34 –
7.40 (m, 2H), 7.30 (d, \( J = 7.5 \) Hz, 1H), 7.18 – 7.24 (m, 3H), 2.94 (t, \( J = 7.5 \) Hz, 2H), 2.76 – 2.78 (m, 2H), 2.23 – 2.29 (m, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 141.0 (C), 136.9 (C), 135.7 (C), 135.1 (C), 129.3 (CH), 127.9 (CH), 127.3 (C), 126.3 (CH), 125.3 (CH), 121.6 (CH), 120.1 (CH), 119.2 (CH), 112.8 (C), 110.6 (CH), 33.5 (CH\(_2\)), 30.1 (CH\(_2\)), 26.5 (CH\(_2\)); IR (thin film): 3396, 1599, 1492, 1459, 1275, 906, 745 cm\(^{-1}\). HRMS (EI) \( m/z \) calcd for C\(_{17}\)H\(_{15}\)N (M\(^+\)) 233.12054, found 233.11957.

**Indoles 12a.** The general procedure was followed using 0.0291 g of styryl azide 11a (0.100 mmol) and 0.0053 g of Rh\(_2\)(hpfb), (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al\(_2\)O\(_3\) afforded analytically pure compound 12a (0.0252 g, 96%) as a colorless oil. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 8.31 (br, 1H), 7.88 (dd, \( J = 1.0 \) Hz, 7.5 Hz, 1H), 7.57 (d, \( J = 8.0 \) Hz, 1H), 7.38 (dt, \( J = 1.5 \) Hz, 7.5 Hz, 1H), 7.30 (dd, \( J = 1.0 \) Hz, 7.5 Hz, 1H), 7.21 (dt, \( J = 1.5 \) Hz, 7.5 Hz, 1H), 7.13 (t, \( J = 8.0 \) Hz, 1H), 6.71 (d, \( J = 8.0 \) Hz, 1H), 4.02 (s, 3H), 2.97 (t, \( J = 7.5 \) Hz, 2H), 2.79 – 2.76 (m, 2H), 2.30 – 2.25 (m, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 164.0 (C), 145.8 (C), 141.0 (C), 136.5 (C), 135.4 (C), 129.3 (CH), 128.6 (C), 128.0 (CH), 126.3 (CH), 125.2 (CH), 120.5 (CH), 113.3 (C), 112.2 (CH), 101.8 (CH), 55.4 (CH\(_2\)), 33.6 (CH\(_2\)), 30.2 (CH\(_2\)), 26.4 (CH\(_2\)); IR (thin film): 3443, 2941, 1497, 1264, 733 cm\(^{-1}\). HRMS (EI) \( m/z \) calcd for C\(_{18}\)H\(_{17}\)ON (M\(^+\)) 263.13102, found 263.13028.

**Indoles 12b.** The general procedure was followed using 0.0291 g of styryl azide 11b (0.100 mmol) and 0.0053 g of Rh\(_2\)(hpfb), (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al\(_2\)O\(_3\) afforded analytically pure compound 12b (0.0254 g, 97%) as a white solid; mp 164 – 166 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.85 – 7.83 (m, 2H), 7.81 (d, \( J = 7.5 \) Hz, 1H), 7.35 (dt, \( J = 1.5 \) Hz, 7.5 Hz, 1H), 7.27 (dd, \( J = 1.0 \) Hz, 7.5 Hz, 1H), 7.21 (dt, \( J = 1.0 \) Hz, 7.5 Hz, 1H), 6.85 (dd, \( J = 2.5 \) Hz, 8.5 Hz, 1H), 6.82 (d, \( J = 1.5 \) Hz, 1H), 3.85 (s, 3H), 2.91 (t, \( J = 7.5 \) Hz, 2H), 2.77 – 2.75 (m, 2H), 2.23 – 2.17 (m, 2H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 156.0 (C), 141.1 (C), 136.6 (C), 135.6 (C), 135.0 (C), 129.3 (CH), 127.8 (CH), 126.3 (CH), 125.2 (CH), 121.7 (C), 120.0 (CH), 112.5 (C), 109.3 (CH), 94.7 (CH), 55.8 (CH\(_3\)), 33.7 (CH\(_2\)), 29.5 (CH\(_2\)), 26.8 (CH\(_2\)); IR (thin film): 3399, 2937, 1461, 1264, 738 cm\(^{-1}\). HRMS (EI) \( m/z \) calcd for C\(_{18}\)H\(_{17}\)ON (M\(^+\)) 263.13102, found 263.13140.
**Indoles 12c.** The general procedure was followed using 0.0295 g of styryl azide 11c (0.100 mmol) and 0.0053 g of Rh₂(hpfb)₄ (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound 12c (0.0264 g, 99%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.92 (br, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 7.79 (dd, *J* = 1.5 Hz, 7.5 Hz, 1H), 7.37 (dt, *J* = 1.5 Hz, 7.5 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.21 (dt, *J* = 1.5 Hz, 6.5 Hz, 1H), 7.14 (dd, *J* = 2.0 Hz, 6.5 Hz, 1H), 2.91 (t, *J* = 7.5 Hz, 2H), 2.78 – 2.74 (m, 2H), 2.26 – 2.21 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 141.1 (C), 137.5 (C), 136.1 (C), 134.5 (C), 129.4 (CH), 127.8 (CH), 127.3 (C), 126.4 (CH), 126.0 (C), 125.6 (CH), 120.7 (CH), 120.1 (CH), 112.9 (C), 110.5 (CH), 33.5 (CH₂), 29.8 (CH₂), 26.6 (CH₂); IR (thin film): 3401, 2929, 1462, 1275, 749 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₇H₁₄NCl (M)⁺ 267.08147, found 267.08182.

**Indoles 12d.** The general procedure was followed using 0.0319 g of styryl azide 11d (0.100 mmol) and 0.0053 g of Rh₂(esp)₂ (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound 12d (0.0274 g, 94%) as a white solid; mp 203 – 205 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.55 (br, 1H), 8.11 (d, *J* = 1.5 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.85 (dd, *J* = 1.5 Hz, 8.5 Hz, 1H), 7.79 (dd, *J* = 1.0 Hz, 8.0 Hz, 1H), 7.37 (dt, *J* = 1.5 Hz, 7.5 Hz, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.20 (dt, *J* = 1.5 Hz, 7.5 Hz, 1H), 3.96 (s, 3H), 2.97 (t, *J* = 7.5 Hz, 2H), 2.75 – 2.72 (m, 2H), 2.30 – 2.25 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 168.4 (C), 140.9 (C), 140.8 (C), 135.0 (C), 134.5 (C), 130.9 (C), 129.4 (CH), 127.9 (CH), 126.4 (CH), 125.7 (CH), 122.9 (C), 121.3 (CH), 118.6 (CH), 113.5 (C), 112.9 (CH), 52.0 (CH₃), 33.3 (CH₂), 30.2 (CH₂), 26.4 (CH₂); IR (thin film): 3656, 2950, 1690, 1503, 1217, 1062, 911 cm⁻¹. HRMS (EI) *m/z* calcd for C₁₉H₁₇O₂N (M)⁺ 291.12593, found 291.12593.

**Indole 12e.** The general procedure was followed using 0.046 g of styryl azide 11e (0.140 mmol) and 0.007 g of Rh₂(hpfb)₄ (0.007 mmol) in 0.6 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound 12e (0.038 g, 90%). ¹H NMR (500 MHz, CDCl₃): 8.18 (s, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.80 (d, *J* = 7.5 Hz, 1H), 7.06 (s, 1H), 7.38 – 7.42 (m, 2H), 7.31 – 7.32 (m, 1H), 7.22 – 7.26 (m, 1H), 2.95 (t, 7.5 Hz, 2H), 2.73 – 2.76 (m, 2H), 2.24 – 2.30 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): 141.0 (C), 139.7 (C), 134.6 (C), 134.3 (C), 129.6 (C), 129.5 (CH), 127.9 (CH), 126.5 (CH), 125.8 (CH), 125.3 (q, *J* = 269.9 Hz, C), 123.5 (q, *J* = 31.8 Hz, C), 119.4 (CH), 116.8 (q, *J* = 3.5 Hz, CH), 113.2 (C), 108.1 (q, *J* = 4.8 Hz, CH), 33.3 (CH₂), 30.1 (CH₂), 26.4 (CH₂); ¹⁹F
NMR (CDCl₃, 282 MHz); IR (thin film): 3401, 2940, 1740, 1728, 1333, 1217, 1111, 1057 cm⁻¹. HRMS (EI) m/z calcd for C₁₈H₁₄NF₃ (M)+ 301.10783, found 301.10748.

**Indoles 12f.** The general procedure was followed using 0.0339 g of styryl azide 11f (0.100 mmol) and 0.0053 g of Rh₂(hpfb)₄ (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound 12f (0.0295 g, 95%) as a white solid; mp 159 – 161 °C. ¹H NMR (500 MHz, CDCl₃) δ 9.23 (br, 1H), 8.11 (d, J = 1.0 Hz, 1H), 7.97 (d, J = 8.5 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.65 (dd, J = 1.0 Hz, 8.5 Hz, 1H), 7.36 (dt, J = 1.0 Hz, 7.5 Hz, 1H), 7.29 (d, J = 7.5 Hz, 1H), 7.21 (dt, J = 1.0 Hz, 7.5 Hz, 1H), 3.13 (s, 3H), 2.99 (t, J = 7.5 Hz, 2H), 2.71 (t, J = 6.0 Hz, 2H), 2.29 – 2.24 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 142.4 (C), 140.9 (C), 134.5 (C), 134.1 (C), 132.0 (C), 131.0 (C), 129.1 (CH), 127.8 (CH), 126.5 (CH), 126.0 (CH), 119.6 (CH), 118.2 (CH), 113.4 (C), 111.0 (CH), 45.3 (CH₂), 33.2 (CH₂), 30.2 (CH₂), 26.2 (CH₂); IR (thin film): 3411, 2936, 1469, 1264, 740 cm⁻¹. HRMS (EI) m/z calcd for C₁₇H₁₄O₂NS (M)+ 311.09800, found 311.09821.

**Indoles 12g.** The general procedure was followed using 0.0340 g of styryl azide 11g (0.100 mmol) and 0.0053 g of Rh₂(hpfb)₄ (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound 12g (0.0295 g, 95%) as a white solid; mp 146 – 148 °C. ¹H NMR (500 MHz, CDCl₃) δ 8.03 (d, J = 1.5 Hz, 1H), 8.00 (br, 1H), 7.76 (d, J = 7.5 Hz, 1H), 7.37 (dt, J = 1.5 Hz, 7.5 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.21 (dt, J = 1.0 Hz, 6.5 Hz, 1H), 7.19 (d, J = 8.5 Hz, 1H), 2.92 (t, J = 7.5 Hz, 2H), 2.74 – 2.72 (m, 2H), 2.27 – 2.22 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 140.9 (C), 138.2 (C), 134.4 (C), 134.3 (C), 129.4 (CH), 129.0 (C), 127.8 (CH), 126.5 (CH), 125.7 (CH), 124.3 (CH), 121.6 (CH), 113.5 (C), 112.6 (C), 111.9 (CH), 33.4 (CH₂), 30.1 (CH₂), 26.4 (CH₂); IR (thin film): 3411, 2936, 1469, 1264, 740 cm⁻¹. HRMS (EI) m/z calcd for C₁₇H₁₄NBr (M)+ 313.02891, found 313.03030.

**Indole 12h.** The general procedure was followed using 0.0319 g of styryl azide 11h (0.100 mmol) and 0.0053 g of Rh₂(esp)₂ (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound 12h (0.0276 g, 95%) as a white solid; mp 244 – 246 °C. ¹H NMR (500 MHz, acetone-d₆) δ 10.65 (br, 1H), 8.57 (s, 1H), 7.82 (dd, J = 1.0 Hz, 8.5 Hz, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.46 (d, J = 8.5 Hz, 1H), 7.37 (dt, J = 1.5 Hz,
7.5 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.17 (dt, J = 1.5 Hz, 7.5 Hz, 1H), 3.87 (s, 3H), 3.04 (t, J = 7.5 Hz, 2H), 2.74 – 2.72 (m, 2H), 2.24 – 2.19 (m, 2H); $^{13}$C NMR (125 MHz, acetone-$d_6$) $\delta$ 167.5 (C), 141.2 (C), 139.3 (C), 139.0 (C), 134.6 (C), 129.3 (CH), 127.7 (CH), 126.8 (C), 126.3 (CH), 125.4 (CH), 122.4 (CH), 121.6 (C), 121.2 (CH), 112.9 (C), 110.6 (CH), 51.0 (CH$_3$), 33.3 (CH$_2$), 29.6 (CH$_3$), 26.1 (CH$_2$); IR (thin film): 3643, 2951, 1737, 1231, 1062, 913, 857 cm$^{-1}$. HRMS (EI) $m/z$ calcd for C$_{19}$H$_{17}$O$_2$N (M)$^+$ 291.12593, found 291.12504.

D. Effect of Migrating Group Identity on Rhodium-Catalyzed Migration Selectivity.

Indole 15a. $^{10}$ The general procedure was followed using 0.041 g of styryl azide 14a (0.17 mmol) and 0.006 g of Rh$_2$(esp)$_4$ (0.008 mmol) in 0.7 mL of PhMe. Filtration by Al$_2$O$_3$ afforded a 98:2 mixture of compound 12a and 12b; Purification by MPLC (10:100 EtOAc: hexanes) afforded compound 15a as a white powder (0.032 g, 88%); Indole 15a was previously reported by Katritzky and Wang: $^{10}$ $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.05 (d, J = 7.5 Hz, 1H), 7.95 (s, 1H), 7.88 (d, J = 7.5 Hz, 1H), 7.31 – 7.36 (m, 2H), 7.19 – 7.27 (m, 3H), 7.09 – 7.12 (m, 1H), 3.05 – 3.08 (t, J = 7.5 Hz, 2H), 2.93 – 2.96 (t, J = 7.5 Hz, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 137.2 (C), 136.2 (C), 133.9 (C), 133.3 (C), 128.0 (CH), 127.0 (CH), 125.0 (C), 124.3 (CH), 122.3 (CH), 121.5 (CH), 120.6 (CH), 119.5 (CH), 111.1 (CH), 110.8 (C), 29.5 (CH$_3$), 22.5 (CH$_2$); IR (thin film): 3396, 1601, 1497, 1456, 1255, 908, 767, 731 cm$^{-1}$. HRMS (EI) $m/z$ calcd for C$_{19}$H$_{17}$O$_2$N (M)$^+$ 291.12593, found 291.12504.

Indole 15b. The general procedure was followed using 0.050 g of styryl azide 14b (0.16 mmol) and 0.006 g of Rh$_2$(esp)$_4$ (0.008 mmol) in 0.6 mL of PhMe. Filtration by Al$_2$O$_3$ afforded a 95:5 mixture of compound 15b and 16b; Purification by MPLC (10:100 EtOAc: hexanes) afforded compound 15b as a light yellow powder (0.031 g, 78%); mp 227 - 230 °C; $^1$H NMR (500 MHz, DMSO) $\delta$ 8.03 (d, J = 7.5 Hz, 1H), 7.93 – 7.95 (m, 1H), 7.37 – 7.45 (m, 3H), 7.11 – 7.13 (m, 2H), 3.10 (t, J = 7.5 Hz, 2H), 2.98 (t, J = 8.0 Hz, 2H); N-H peak not available; $^{13}$C NMR (125 MHz, DMSO) $\delta$ 139.2 (C), 136.9 (C), 136.4 (C), 131.6 (C), 127.53 (CH), 127.49 (q, J$_{CF} = 27.8$ Hz, C), 126.0 (CH), 125.3 (q, J$_{CF} = 272.0$ Hz, C), 124.6, 121.5 (CH), 120.9 (q, J$_{CF} = 5.5$ Hz, CH), 120.6 (CH), 119.1 (CH), 112.2 (CH), 108.3 (C), 25.5 (CH$_3$), 21.5 (CH$_2$); IR (thin film): 3406, 1601, 1557, 1452, 1311, 1162, 1108, 749 cm$^{-1}$. HRMS (EI) $m/z$ calcd for C$_{17}$H$_{12}$NF$_3$ (M)$^+$ 287.09218, found 287.09182.
**Indole 15c.** The general procedure was followed using 0.041 g of styryl azide 14c (0.141 mmol) and 0.005 g of Rh₂(esp)₄ (0.007 mmol) in 0.5 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound 15c (0.034 g, 92%). ¹H NMR (500 MHz, CDCl₃) δ 7.99 (s, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.23 (t, J = 7.5 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 6.82 – 6.85 (m, 2H), 3.86 (s, 3H), 3.11 (t, J = 7.0 Hz, 2H), 2.89 – 2.91 (m, 2H), 2.15 – 2.19 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 158.7 (C), 144.0 (C), 136.1 (C), 132.7 (C), 130.2 (C), 126.4 (CH), 124.6 (C), 122.4 (CH), 119.5 (CH), 118.4 (CH), 115.5 (CH), 113.1 (C), 111.5 (CH), 110.5 (CH), 55.3 (CH₂), 35.6 (CH₂), 26.7 (CH₂), 26.0 (CH₂); IR (thin film): 3414, 2926, 2834, 1605, 1461, 1433, 1260, 1243, 810, 735 cm⁻¹. HRMS (EI) m/z calcd for C₁₈H₁₇ON (M)⁺ 263.13102, found 263.13192.

**Indole 15d.** The general procedure was followed using 0.052 g of styryl azide 14d (0.198 mmol) and 0.008 g of Rh₂(esp)₄ (0.010 mmol) in 0.7 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound 15d (0.044 g, 94%). mp 175 -177 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.14 (d, J = 7.5 Hz, 1H), 8.10 (d, J = 7.5 Hz, 1H), 8.04 (s, 1H), 7.31 – 7.32 (m, 1H), 7.12 – 7.26 (m, 5H), 4.39 (t, J = 6.0 Hz, 2H), 3.32 (t, J = 6.0 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 158.7 (C), 136.5 (C), 134.8 (C), 128.4 (CH), 127.3 (C), 127.0 (C), 125.9 (CH), 123.8 (CH), 122.1 (CH), 121.1 (CH), 120.3 (CH), 120.2 (CH), 110.6 (CH), 109.7 (C), 70.0 (CH₂), 31.0 (CH₂); IR (thin film): 3348, 1492, 1459, 1441, 1196, 905, 748 cm⁻¹. HRMS (EI) m/z calcd for C₁₆H₁₃ON (M)⁺ 235.09972, found 235.10055.

**Indole 15e.**¹¹ The general procedure was followed using 0.044 g of styryl azide 14e (0.187 mmol) and 0.007 g of Rh₂(esp)₄ (0.009 mmol) in 0.6 mL of PhMe (reaction is set up at 80 °C). Filtration by Al₂O₃ afforded analytically pure compound 15e (0.035 g, 91%). Spectral data for 15e matched that reported by Tan and Hartwig:¹¹ ¹H NMR (500 MHz, CDCl₃) δ 7.93 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.53 – 7.55 (m, 2H), 7.47 – 7.50 (m, 2H), 7.31 – 7.35 (m, 2H), 7.17 – 7.20 (m, 1H), 7.12 – 7.15 (m, 1H), 2.52 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 135.5 (C), 135.3 (C), 131.4 (C), 129.5 (CH), 128.5 (CH), 127.9 (C), 125.8 (CH), 121.6 (CH), 120.0 (CH), 118.8 (CH), 114.6 (C), 110.3 (CH), 12.6 (CH₃); IR (thin film): 3401, 1603, 1496, 1459, 1258, 908, 748, 702 cm⁻¹.
Indole 15f. The general procedure was followed using 0.036 g of styryl azide 14f (0.117 mmol) and 0.005 g of Rh₂(esp)₄ (0.006 mmol) in 0.5 mL of PhMe (reaction is set up at 80 °C). Filtration by Al₂O₃ afforded analytically pure compound 15f (0.030 g, 93%). Indole 15f was previously reported by Chiba and co-workers.

Spectral data for 15f: ¹H NMR (500 MHz, CDCl₃) δ 8.02 (s, 1H), 7.73 (d, J = 8.5 Hz, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.22 (dt, J = 1.0 Hz, 8.0 Hz, 1H), 7.16 (dt, J = 1.0 Hz, 7.5 Hz, 1H), 2.53 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 139.4 (C), 135.3 (C), 132.2 (C), 129.4 (CH), 127.7 (q, J_CF = 32.8 Hz, C), 127.5 (C), 125.5 (q, J_CF = 3.5 Hz, CH), 124.5 (q, J_CF = 269.9 Hz, C), 122.0 (CH), 120.4 (CH), 118.5 (CH), 113.4 (C), 110.5 (CH), 12.6 (CH₃); IR (thin film): 3397, 1615, 1459, 1234, 1163, 1109, 1068, 747 cm⁻¹.

E. Effect of Ring Size on Rhodium-Catalyzed Migration.

1. General Procedure for the Optimization of Conditions to Promote the Migration.

To a mixture of 0.1 mmol of aryl azide 17c (0.1 mmol), 0-100 % w/w of crushed 4 Å mol sieves, and metal salt (0 – 5 mol %) in Schlenk tube was added 0.50 mL of solvent. The resulting mixture was heated and, after 16 h, the heterogenous mixture was filtered through a short pad of Al₂O₃. The filtrate was concentrated in vacuo. The resulting solid (oil) was dissolved in 1.5 mL of CDCl₃ and 0.007 mL of dibromomethane (0.1 mmol) was added. The areas of the C–H peak on the carbon 13 position in 17c and carbon 13 in 18c were compared to derive a yield.
Table s2. Optimization of Migration Process

| entry | metal salt | mol % | wt %, 4 Å MS | temp (°C) | yield, % |
|-------|------------|-------|--------------|-----------|----------|
| 1     | None       | n.a.  | 0            | 150       | >95      |
| 2     | Rh$_2$(O$_2$CC$_7$H$_{15}$)$_4$ | 5      | 100          | 55        | 33       |
| 3     | Rh$_2$(O$_2$CC$_7$H$_{15}$)$_4$ | 5      | 100          | 65        | 63       |
| 4     | Rh$_2$(O$_2$CC$_7$H$_{15}$)$_4$ | 5      | 0           | 65        | 53       |
| 5     | Rh$_2$(O$_2$CC$_7$H$_{15}$)$_4$ | 3      | 100          | 65        | 39       |
| 6     | Rh$_2$(O$_2$CC$_7$H$_{15}$)$_4$ | 5      | 100          | 80        | 90       |
| 7     | [Ir(cod)OMe]$_2$ | 5      | 100          | 80        | 0        |
| 8     | Rh$_2$(esp)$_2$ | 5      | 100          | 80        | 20       |
| 9     | RhCl(PPh$_3$)$_3$ | 5      | 100          | 80        | 0        |
| 10    | Rh$_2$(O$_2$CC$_3$F$_7$)$_4$ | 5      | 100          | 80        | 66       |
| 11    | RhCl$_3$    | 5      | 100          | 80        | 0        |
| 12    | Rh$_2$(O$_2$CC$_3$)$_4$ | 5      | 100          | 80        | 0        |
| 13    | Rh$_2$(O$_2$CCF$_3$)$_4$ | 5      | 100          | 80        | 34       |
| 14    | RuCl$_3$•xH$_2$O | 5      | 100          | 65        | trace    |
| 15    | RuCl$_3$•xH$_2$O | 5      | 0           | 65        | trace    |
| 16    | Rh octanoate | 5      | 100          | 65(40h)   | 90       |
| 17    | Co TPP      | 5      | 100          | 65        | 0        |
| 18    | Ag(OTf)$_2$ | 5      | 100          | 65        | 0        |
| 19    | Cu(OTf)$_2$ | 5      | 100          | 65        | 0        |
| 20    | Rh octanoate (cyclopentane) | 5      | 100          | 75        | 59       |
| 21    | ZnI$_2$     | 10     | 100          | 65        | 0        |
| 22    | FeBr$_2$    | 20     | 100          | 65        | 0        |
| 23    | AuCl        | 10     | 100          | 65        | 0        |

*a Isolated yield after Al$_2$O$_3$ chromatography.

2. Optimization of Solvent.

![Diagram](SI1-29)

| Solvent | PhMe | 1,2-DCE | 1,4-dioxane | DME | DMF |
|---------|------|---------|-------------|-----|-----|
| Yield, % | 63%  | 66%     | 0           | 0   | 0   |

*a Isolated yield after Al$_2$O$_3$ chromatography.

3. Optimized Procedure for Ring Expansion.

![Diagram](SI1-29)

To a mixture of 0.026 g of aryl azide 17 (0.1 mmol), 100 % w/w of crushed 4 Å mol sieves, and metal salt (Rh$_2$(O$_2$CC$_7$H$_{15}$)$_4$, 5 mol %) in Schlenk tube was added 0.50 mL of PhMe. The resulting mixture was heated at
80 °C for 16 h, then, the heterogeneous mixture was filtered through a short pad of Al₂O₃. The filtrate was concentrated in vacuo to afford analytically pure indole.

4. Scope and Limitations of Ring Expansion.

**Indole 18a.** The general procedure was followed using 0.035 g of styryl azide 17a (0.189 mmol) and 0.007 g of Rh₂(O₂CC₇H₁₅)₄ (0.009 mmol) in 0.6 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound 18a (0.029 g, 98%). Indole 18a was previously reported by Tan and Hartwig. mp 58 - 61 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.74 (s, 1H), 7.47 – 7.49 (m, 1H), 7.29 – 7.31 (m, 1H), 7.12 – 7.14 (m, 2H), 2.86 -2.89 (m, 4H), 2.56 – 2.59 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 143.8 (C), 141.0 (C), 124.8 (C), 120.5 (CH), 119.8 (C), 119.5 (CH), 118.5 (CH), 111.4 (CH), 28.7 (CH₂), 25.9 (CH₂), 24.5 (CH₂); IR (thin film): 3400, 2951, 2853, 1467, 1313, 913, 736 cm⁻¹.

**Indole 18b.** The general procedure was followed using 0.055 g of styryl azide 17b (0.276 mmol) and 0.011 g of Rh₂(O₂CC₇H₁₅)₄ (0.014 mmol) in 0.7 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound 18b (0.044 g, 93%). The spectral data for 18b matched that reported by Leogane and Lebel: ¹H NMR (500 MHz, CDCl₃) δ 7.64 (s, 1H), 7.48 (d, J = 7.5 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 7.08 – 7.15 (m, 2H), 2.73 (t, J = 6.0 Hz, 4H), 1.87 – 1.96 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 135.7 (C), 134.1 (C), 127.9 (C), 121.0 (CH), 119.1 (CH), 117.7 (CH), 110.4 (CH), 110.2 (C), 23.34 (CH₂), 23.26 (CH₂), 21.0 (CH₂) one overlapping aliphatic C not distinguishable; IR (thin film): 3397, 1667, 1603, 1497, 1456, 1276, 911, 749 cm⁻¹.

**Indole 18c.** The general procedure was followed using 0.051 g of styryl azide 17c (0.239 mmol) and 0.009 g of Rh₂(O₂CC₇H₁₅)₄ (0.012 mmol) in 0.6 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound 18c (0.041 g, 93%). The spectral data for 18c matched that reported by Banwell and co-workers: mp 140 - 142 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.61 (s, 1H), 7.15 – 7.53 (m, 1H), 7.26 – 7.27 (m, 1H), 7.11 – 7.15 (m, 2H), 2.82 -2.87 (m, 4H), 1.91 – 1.94 (m, 2H), 1.81 – 1.83 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 137.5 (C), 134.3 (C), 129.3 (C), 120.6 (CH), 119.1 (CH), 117.7 (CH), 113.8 (C), 110.3 (CH), 31.9 (CH₂), 29.6 (CH₂), 28.8 (CH₂), 27.6 (CH₂), 24.7 (CH₂); IR (thin film): 3391, 2914, 2844, 1465, 1438, 913, 743 cm⁻¹.
Indole 18d. The general procedure was followed using 0.046 g of styryl azide 17d (0.203 mmol) and 0.008 g of Rh₂(O₂CC₇H₁₅)₄ (0.010 mmol) in 0.6 mL of PhMe. Analysis of the reaction progress using ¹H NMR spectroscopy revealed that 18% of indole 18d formed and 35% starting of aryl azide 17d remained.

![Indole 18d](image)

Indole 18e. The general procedure was followed using 0.061 g of styryl azide 17e (0.266 mmol) and 0.010 g of Rh₂(O₂CC₇H₁₅)₄ (0.013 mmol) in 0.7 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound 18e (0.054 g, 100%). Spectral data for 18e: ¹H NMR (500 MHz, CDCl₃) δ 7.56 (s, 1H), 7.16 (d, J = 9.0 Hz, 1H), 6.97 (d, J = 2.5 Hz, 1H), 6.81 (dd, J = 2.5 Hz, 9.0 Hz, 1H), 3.89 (s, 3H), 2.70 – 2.72 (m, 4H), 1.89 – 1.95 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 153.9 (C), 135.2 (C), 130.8 (C), 128.2 (C), 111.0 (CH), 110.5 (CH), 110.0 (C), 100.4 (CH), 56.0 (CH₃), 23.38 (CH₂), 23.27 (CH₂), 21.0 (CH₂) one overlapping aliphatic carbon signal not distinguishable; IR (thin film): 3281, 2936, 1659, 1492, 1274, 1214, 1030, 732 cm⁻¹. HRMS (EI) m/z calcd for C₁₃H₁₅ON (M)+ 201.11537, found 201.11616.

![Indole 18e](image)

Indole 18f. The general procedure was followed using 0.045 g of styryl azide 17f (0.201 mmol) and 0.008 g of Rh₂(O₂CC₇H₁₅)₄ (0.013 mmol) in 0.5 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound 18f (0.039 g, 100%). mp 42 - 46 °C; Spectral data for 18f: ¹H NMR (500 MHz, CDCl₃) δ 7.58 (s, 1H), 7.14 (d, J = 8.5 Hz, 1H), 6.97 (d, J = 2.5 Hz, 1H), 6.79 (dd, J = 2.5 Hz, 8.5 Hz, 1H), 3.89 (s, 3H), 2.79 – 2.81 (m, 4H), 1.90 – 1.92 (m, 2H), 1.79 – 1.81 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 153.9 (C), 138.6 (C), 129.6 (C), 129.4 (C), 113.6 (C), 110.9 (C), 110.4 (CH), 100.1 (CH), 56.0 (CH₃), 31.9 (CH₂), 29.7 (CH₂), 28.8 (CH₂), 27.6 (CH₂), 24.8 (CH₂); IR (thin film): 3401, 2916, 1625, 1483, 1452, 913, 745 cm⁻¹. HRMS (EI) m/z calcd for C₁₄H₁₇ON (M)+ 215.13102, found 215.13248.

![Indole 18f](image)

Indole 18g. The general procedure was followed using 0.027 g of styryl azide 17g (0.009 mmol) and 0.004 g of Rh₂(O₂CC₇H₁₅)₄ (0.005 mmol) in 0.5 mL of PhMe. Filtration by Al₂O₃ afforded analytically pure compound 18g (0.021 g, 88%). Spectral data for 18g: ¹H NMR (500 MHz, CDCl₃) δ 7.89 (s, 1H), 7.76 (s, 1H), 7.29 – 7.34 (m, 2H), 2.82 – 2.86 (m, 4H), 1.90 – 1.94 (m, 2H), 1.76 – 1.82 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 139.3 (C), 135.6 (C), 128.7 (C), 125.6 (q, J_CF = 270.1 Hz, C), 121.4 (q, J_CF = 31.3 Hz, C), 117.4 (q, J_CF = 3.6 Hz, CH), 115.4 (q, J_CF = 3.5 Hz, CH), 114.7 (C), 110.2 (CH), 31.6 (CH₂), 29.6 (CH₂), 28.5 (CH₂), 27.4 (CH₂), 24.6 (CH₂);
Indole 18h. The general procedure was followed using 0.057 g of styryl azide 17h (0.265 mmol) and 0.010 g of Rh$_2$(O$_2$CC$_7$H$_{15}$)$_4$ (0.013 mmol) in 0.6 mL of PhMe. Filtration by Al$_2$O$_3$ afforded analytically pure compound 18h (0.048 g, 97%). mp 116 - 119 °C; Spectral data for 18h: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.85 (s, 1H), 7.49 (d, $J$ = 7.5 Hz, 1H), 7.12 – 7.18 (m, 2H), 3.97 – 4.02 (m, 4H), 3.00 – 3.03 (m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 135.5 (C), 134.8 (C), 128.9 (C), 121.2 (CH), 119.4 (CH), 111.8 (CH), 112.4 (C), 110.4 (CH), 73.1 (CH$_2$), 70.7 (CH$_2$), 32.2 (CH$_2$), 27.6 (CH$_2$); IR (thin film): 3400, 3294, 2936, 1464, 1113, 913 cm$^{-1}$. HRMS (EI) m / z calcd for C$_{12}$H$_{13}$ON (M)$^+$ 187.09972, found 187.10060.

V. Mechanistic Experiments

A. Synthesis of Aryl Azides 27.

Styrene s31. To a solution of 10.4 g of the phosphonium salt (19.3 mmol) in 100 mL of THF at –78 °C, was added 8.5 mL of $n$-BuLi (2.5 M in hexanes, 21.2 mmol) dropwise. After stirring for 1 h at –78 °C, the mixture was warmed to room temperature and stirred additional half an hour. Then 2.65 g of 2-nitrobenzaldehyde (17.5 mmol) was added, and the mixture was heated to reflux. After 16 h, the reaction mixture was diluted with 50 mL of water and extracted with CH$_2$Cl$_2$ (3 × 30 mL). The resulting organic phase was washed with 60 mL of brine and dried over Na$_2$SO$_4$. The mixture was filtered and the filtrate was concentrated in vacuo to afford styrene s31, which was carried on to the subsequent Fe-mediated reduction without any additional purification.

Aniline s32. To a solution of nitro-substituted styrene s31 in 40 mL of AcOH and 40 mL of EtOH was added 8.6 g of Fe powder (154.4 mmol). The resultant mixture was heated to reflux at 80 °C. After 16 h, the reaction mixture was cooled down to ambient temperature. Once cool, the resulting mixture was filtered through a pad of Celite. The filtrate was diluted with 80 mL of water and washed with 3 × 30 mL of dichloromethane. The resulting organic phase was washed with 50 mL of brine and dried over Na$_2$SO$_4$. The resulting mixture was filtered, and the filtrate was concentrated in vacuo to afford styrene s31, which was carried on to the subsequent Fe-mediated reduction without any additional purification.
6.50 (t, J = 7.5 Hz, 1H), 3.84 (s, 3H); N-H peak not available; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 144.6 (C), 140.3 (C), 136.0 (C), 130.51 (CH), 130.43 (CH), 129.3 (CH), 127.8 (CH), 127.4 (CH), 122.8 (CH), 118.2 (CH), 115.4 (CH), 55.4 (CH\(_3\)). These are the only visible peaks.

**Aryl Azide 27a.** To a solution of 0.82 g of aniline s32 (2.7 mmol) in 5 mL of CH\(_2\)Cl\(_2\) was added subsequently 24 mg of CuSO\(_4\), 1.2 mL of Et\(_3\)N, freshly prepared triflyl azide (9 mmol) in 15 mL of CH\(_2\)Cl\(_2\), 1 mL of water and 2 mL of MeOH. The resulting mixture was stirred at room temperature. After 16 h, the reaction mixture was diluted with 15 mL of CH\(_2\)Cl\(_2\), and the resulting mixture was neutralized by the addition of a saturated aq. soln. of NaHCO\(_3\). Once pH 7 was reached, the resulting mixture was washed with 3 \(\times\) 10 mL of CH\(_2\)Cl\(_2\). The resulting organic phase was washed with 20 mL of brine and dried over Na\(_2\)SO\(_4\). After filtration, the filtrate was concentrated in vacuo. Purification by MPLC (10:1 hexane:EtOAc) afforded the product as a yellow viscous oil as a 69:31 mixture of E- and Z-isomers (0.42 g, 48%): Selected spectral data for the major (E) isomer: 1H NMR (500 MHz, CDCl\(_3\)) \(\delta\): 7.27 – 7.36 (m, 4H), 7.12 – 7.17 (m, 2H), 7.08 (d, J = 9.0 Hz, 2H), 6.87 – 6.88 (m, 2H), 6.80 – 6.83 (m, 3H), 3.82 (s, 3H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\): 159.0 (C), 143.8 (C), 143.5 (C), 138.6 (C), 132.2 (C), 129.8 (C), 131.8 (CH), 130.7 (CH), 129.2 (CH), 128.37 (CH), 128.18 (CH), 128.11 (CH), 127.7 (CH), 124.1 (CH), 118.2 (CH), 113.8 (CH), 55.2 (CH\(_3\)).

**Styrene s33.** To a solution of 10.8 g of the phosphonium salt (19.1 mmol) in 60 mL of THF at \(-78\) °C, was added 8.4 mL of n-BuLi (2.5 M in hexanes, 21.01 mmol) dropwise. After stirring for 1 h at \(-78\) °C, the mixture was warmed to room temperature and stirred additional half an hour. Then 2.69 g of 2-nitrobenzaldehyde (19.1 mmol) was added, and the mixture was heated to reflux. After 16 h, the reaction mixture was diluted with 50 mL of water and extracted with CH\(_2\)Cl\(_2\) (3 \(\times\) 30 mL). The resulting organic phase was washed with 60 mL of brine and dried over Na\(_2\)SO\(_4\). The mixture was filtered and the filtrate was concentrated in vacuo to afford styrene s35, which was carried on to the subsequent Fe-mediated reduction without any additional purification.

**Aniline s34.** To a solution of nitro-substituted styrene s33 in 40 mL of AcOH and 40 mL of EtOH was added 8.6 g of Fe powder (152.8 mmol). The resultant mixture was heated to reflux at 80 °C. After 16 h, the reaction mixture was cooled down to ambient temperature. Once cool, the resulting mixture was filtered through a pad of Celite. The filtrate was diluted with 80 mL of water and washed with 3 \(\times\) 30 mL of dichloromethane. The resulting organic phase was washed with 50 mL of brine and dried over Na\(_2\)SO\(_4\). The resulting mixture was
filtered, and the filtrate was concentrated in vacuo. Purification by MPLC (10:1 hexanes:EtOAc) afforded the product as a yellow solid (1.5 g, 24%, two steps); Spectral data for the major isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.37 – 7.39 (m, 2H), 7.31 – 7.33 (m, 2H), 7.25 – 7.27 (m, 3H), 7.19 – 7.21 (m, 2H), 6.97 – 7.00 (m, 1H), 6.84 (s, 1H), 6.65 (d, J = 8.0 Hz, 1H), 6.51 (t, J = 7.5 Hz, 1H), 3.74 (br, 2H), 1.37 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 150.8 (C), 144.7 (C), 143.9 (C), 140.4 (C), 140.2 (C), 130.53 (CH), 130.43 (CH), 128.2 (CH), 127.9 (CH), 127.7 (CH), 125.2 (CH), 123.7 (CH), 118.2 (CH), 115.4 (CH), 34.6 (C), 31.4 (CH₃); IR (thin film): 3379, 1617, 1246, 905, 726, 701, 649 cm⁻¹.

**Aryl Azide 27b.** To a solution of 1.2 g of aniline s34 (3.8 mmol) in 5 mL of CH₂Cl₂ was added subsequently 32 mg of CuSO₄, 1.6 mL of Et₃N, freshly prepared triflyl azide (12 mmol) in 15 mL of CH₂Cl₂, 1 mL of water and 2 mL of MeOH. The resulting mixture was stirred at room temperature. After 16 h, the reaction mixture was diluted with 15 mL of CH₂Cl₂, and the resulting mixture was neutralized by the addition of a saturated aq. soln. of NaHCO₃. Once pH 7 was reached, the resulting mixture was washed with 3 × 10 mL of CH₂Cl₂. The resulting organic phase was washed with 20 mL of brine and dried over Na₂SO₄. After filtration, the filtrate was concentrated in vacuo. Purification by MPLC (100:1 hexane:EtOAc) afforded the product as a yellow solid as an 1:1 mixture of E- and Z-isomers (0.88 g, 66%): Spectral data for E- and Z-isomers: ¹H NMR (500 MHz, CDCl₃) δ 7.27 – 7.36 (m, 14H), 7.11 – 7.17 (m, 6H), 7.06 – 7.07 (m, 2H), 7.02 (s, 2H), 6.76 – 6.82 (m, 4H), 1.33 – 1.34 (m, 18H); ¹³C NMR (125 MHz, CDCl₃) δ 150.9 (C), 143.4 (C), 140.1 (C), 138.6 (C), 136.8 (C), 130.78 (CH), 130.73 (CH), 130.56 (CH), 130.1 (CH), 129.70 (C), 129.63 (C), 128.35 (CH), 128.15 (CH), 128.08 (CH), 127.93 (CH), 127.90 (CH), 127.67 (CH), 127.55 (CH), 127.39 (CH), 125.20 (CH), 125.14 (CH), 124.01 (CH), 123.98 (CH), 122.7 (CH), 122.3 (CH), 118.1 (CH), 34.6 (CH₃), 31.4 (CH₃); IR (thin film): 2117, 2085, 1796, 1730, 1287, 908, 733 cm⁻¹. HRMS (EI) m / z calcd for C₂₄H₂₃N₃ (M)+ 353.18920, found 353.19017.

**Styrene s35.** To a solution of 9.6 g of the phosphonium salt (16.4 mmol) in 60 mL of THF at –78 °C, was added 7.2 mL of n-BuLi (2.5 M in hexanes, 18.1 mmol) dropwise. After stirring for 1 h at –78 °C, the mixture was warmed to room temperature and stirred additional half an hour. Then 2.48 g of 2-nitrobenzaldehyde (16.4 mmol) was added, and the mixture was heated to reflux. After 16 h, the reaction mixture was diluted with 50 mL of water and extracted with CH₂Cl₂ (3 × 30 mL). The resulting organic phase was washed with 60 mL of brine and dried over Na₂SO₄. The mixture was filtered and the filtrate was concentrated in vacuo to afford styrene s33, which was carried on to the subsequent Fe-mediated reduction without any additional purification.

**Aniline s36.** To a solution of nitro-substituted styrene s35 in 30 mL of AcOH and 30 mL of EtOH was added 7.3 g of Fe powder (131.2 mmol). The resultant mixture was heated to reflux at 80 °C. After 16 h, the reaction
The mixture was cooled down to ambient temperature. Once cool, the resulting mixture was filtered through a pad of Celite. The filtrate was diluted with 70 mL of water and washed with 3 × 30 mL of dichloromethane. The resulting organic phase was washed with 50 mL of brine and dried over Na₂SO₄. The resulting mixture was filtered, and the filtrate was concentrated in vacuo. Purification by MPLC (10:1 hexanes:EtOAc) afforded the product as a yellow solid (602 mg, 11%, two steps); Spectral data for the major isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.63 – 7.70 (m, 4H), 7.47 – 7.56 (m, 5H), 7.27 – 7.34 (m, 1H), 6.93 (s, 1H), 6.86 (d, J = 7.5 Hz, 1H), 6.70 – 6.71 (m, 1H), 6.65 – 6.66 (m, 1H), 3.92 (br, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 144.8 (C), 143.7 (C), 143.2 (C), 142.1 (C), 140.7 (C), 140.6 (C), 140.5 (C), 131.1 (CH), 130.56 (C), 130.5 (C), 130.38 (CH), 129.53, 129.46, 128.9 (CH), 128.6 (CH), 128.20 (CH), 127.6 (CH), 127.71 (CH), 127.01 (CH), 124.4 (CH), 123.7 (C), 118.3 (CH), 115.6 (CH); IR (thin film): 3457, 1738, 1486, 1454, 1366, 1216, 905 cm⁻¹.

**Aryl Azide 27c.** To a solution of 0.55 g of aniline s36 (1.6 mmol) in 5 mL of CH₂Cl₂ was added subsequently 16 mg of CuSO₄, 0.8 mL of Et₃N, freshly prepared triflyl azide (6 mmol) in 15 mL of CH₂Cl₂, 1 mL of water and 2 mL of MeOH. The resulting mixture was stirred at room temperature. After 16 h, the reaction mixture was diluted with 15 mL of CH₂Cl₂, and the resulting mixture was neutralized by the addition of a saturated aq. soln. of NaHCO₃. Once pH 7 was reached, the resulting mixture was washed with 3 × 10 mL of CH₂Cl₂. The resulting organic phase was washed with 20 mL of brine and dried over Na₂SO₄. After filtration, the filtrate was concentrated in vacuo. Purification by MPLC (100:1 hexane:EtOAc) afforded the product as a pale solid (0.26 g, 43%). Spectral data for E- and Z isomer mixture: ¹H NMR (500 MHz, CDCl₃) δ 7.63 – 7.66 (m, 4H), 7.54 – 7.59 (m, 4H), 7.10 – 7.49 (m, 25H), 7.06 (s, 1H), 6.91 – 6.93 (m, 1H), 6.78 – 6.84 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 143.8 (C), 143.7 (C), 143.2 (C), 142.1 (C), 140.7 (C), 140.6 (C), 140.5 (C), 131.1 (CH), 130.84 (CH), 130.84 (CH), 130.76 (CH), 130.6 (CH), 129.53, 129.46, 128.8 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.2 (CH), 127.9 (CH), 127.6 (CH), 127.4 (CH), 127.4 (CH), 127.1 (CH), 126.99 (CH), 126.54 (CH), 124.2 (CH), 124.1 (CH), 123.3 (CH), 123.0 (CH), 118.2 (CH), 118.2 (CH) only distinguishable peaks; IR (thin film): 2117, 2085, 1738, 1604, 1509, 1289, 1246, 1176, 1034, 751 cm⁻¹. HRMS (EI) m/z calcd for C₂₆H₁₉N₃ (M)+ 373.15790, found 373.15891.

**Styrene s37.** To a solution of 8.5 g of the phosphonium salt (15.7 mmol) in 50 mL of THF at −78 °C, was added 6.9 mL of n-BuLi (2.5 M in hexanes, 17.3 mmol) dropwise. After stirring for 1 h at −78 °C, the mixture was warmed to room temperature and stirred additional half an hour. Then 2.4 g of 2-nitrobenzaldehyde (15.7 mmol) was added, and the mixture was heated to reflux. After 16 h, the reaction mixture was diluted with 50 mL of water and extracted with CH₂Cl₂ (3 × 30 mL). The resulting organic phase was washed with 60 mL of brine and dried over Na₂SO₄. The mixture was filtered and the filtrate was concentrated in vacuo to afford styrene s37, which was carried on to the subsequent Fe-mediated reduction without any additional purification.
Aniline s38. To a solution of nitro-substituted styrene s37 in 40 mL of AcOH and 40 mL of EtOH was added 7.1 g of Fe powder (125.6 mmol). The resultant mixture was heated to reflux at 80 °C. After 16 h, the reaction mixture was cooled down to ambient temperature. Once cool, the resulting mixture was filtered through a pad of Celite. The filtrate was diluted with 80 mL of water and washed with 3 × 30 mL of dichloromethane. The resulting organic phase was washed with 50 mL of brine and dried over Na₂SO₄. The resulting mixture was filtered, and the filtrate was concentrated in vacuo. Purification by MPLC (10:1 hexanes:EtOAc) afforded the product as a pale solid (1024 mg, 21%, two steps); Spectral data for the major isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.12 – 7.36 (m, 9H), 6.98 – 7.04 (m, 1H), 6.81 – 6.84 (m, 1H), 6.77 – 6.78 (m, 1H), 6.66 – 6.68 (m, 1H), 6.50 – 6.56 (m, 1H), 3.76 (br, 2H); spectral data for both the E- and Z-isomer: ¹³C NMR (125 MHz, CDCl₃) δ 144.74 (C), 144.71 (C), 143.9 (C), 143.02 (C), 142.96 (C), 141.9 (C), 139.6 (C), 138.5 (C), 133.5 (C), 133.2 (C), 131.9 (CH), 130.45 (CH), 130.35 (CH), 130.29 (CH), 129.4 (CH), 128.52 (CH), 128.38 (CH), 128.36 (CH), 128.30 (CH), 127.9 (CH), 127.6 (CH), 125.0 (CH), 124.8 (CH), 118.34 (CH), 118.28 (CH), 115.59 (CH), 115.54 (CH); IR (thin film): 3463, 3378, 1614, 1485, 1089, 728 cm⁻¹.

Aryl Azide 27d. To a solution of 0.90 g of aniline s38 (3.0 mmol) in 5 mL of CH₂Cl₂ was added subsequently 24 mg of CuSO₄, 1.2 mL of Et₃N, freshly prepared triflyl azide (9 mmol) in 15 mL of CH₂Cl₂, 1 mL of water and 2 mL of MeOH. The resulting mixture was stirred at room temperature. After 16 h, the reaction mixture was diluted with 15 mL of CH₂Cl₂, and the resulting mixture was neutralized by the addition of a saturated aq. soln. of NaHCO₃. Once pH 7 was reached, the resulting mixture was washed with 3 × 10 mL of CH₂Cl₂. The resulting organic phase was washed with 20 mL of brine and dried over Na₂SO₄. After filtration, the filtrate was concentrated in vacuo. Purification by MPLC (100:1 hexane:EtOAc) afforded the product as a yellow viscous oil (0.44 g, 45%): Spectral data for the mixture: ¹H NMR (500 MHz, CDCl₃) δ 7.10 – 7.37 (m, 22H), 6.96 – 7.04 (m, 2H), 6.75 – 6.84 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 143.0 (C), 142.7 (C), 141.6 (C), 139.6 (C), 138.78 (C), 138.74 (C), 138.5 (C), 133.7 (C), 133.4 (C), 132.0 (CH), 130.7 (CH), 130.51 (CH), 130.41 (CH), 130.1 (CH), 129.25 (CH), 129.17 (CH), 128.69 (CH), 128.55 (CH), 128.41 (CH), 128.36 (CH), 128.31 (CH), 128.0 (CH), 127.7 (CH), 126.6 (CH), 125.6 (CH), 124.24 (CH), 124.09 (CH), 123.8 (CH), 123.4 (CH), 118.30 (CH), 118.27 (CH), 118.18 (CH); IR (thin film): 2117, 2085, 1738, 1604, 1509, 1289, 1246, 1176, 1034, 751 cm⁻¹. HRMS (El) m/z calcd for C₂₀H₁₄N₃Cl (M)⁺ 331.08762, found 331.08665.
Styrene s39. To a solution of 3.46 g of the phosphonium salt (6 mmol) in 60 mL of THF at –78 °C, was added 2.4 mL of n-BuLi (2.5 M in hexanes, 6 mmol) dropwise. After stirring for 1 h at –78 °C, the mixture was warmed to room temperature and stirred additional half an hour. Then 0.91 g of 2-nitrobenzaldehyde (6 mmol) was added, and the mixture was heated to reflux. After 16 h, the reaction mixture was diluted with 50 mL of water and extracted with CH₂Cl₂ (3 × 30 mL). The resulting organic phase was washed with 60 mL of brine and dried over Na₂SO₄. The mixture was filtered and the filtrate was concentrated in vacuo to afford styrene s31, which was carried on to the subsequent Fe-mediated reduction without any additional purification.

Aniline s40. To a solution of nitro-substituted styrene s39 in 15 mL of AcOH and 15 mL of EtOH was added 2.7 g of Fe powder (48 mmol). The resultant mixture was heated to reflux at 80 °C. After 16 h, the reaction mixture was cooled down to ambient temperature. Once cool, the reaction mixture was filtered through a pad of Celite. The filtrate was diluted with 20 mL of water and washed with 3 × 10 mL of dichloromethane. The resulting organic phase was washed with 20 mL of brine and dried over Na₂SO₄. The resulting mixture was filtered, and the filtrate was concentrated in vacuo. Purification by MPLC (10:1 hexanes:EtoAc) afforded the product as a yellow solid (190 mg, 12%, two steps); ¹H NMR (500 MHz; CDCl₃) δ 7.69 (d, J = 8.5 Hz, 2.4H), 7.61 (d, J = 8.0 Hz, 1.6H), 7.57 (d, J = 8.5 Hz, 2.4H), 7.45 (s, 4H), 7.42 (d, J = 8.0 Hz, 1.6H), 7.38 – 7.37 (m, 3.6H), 7.30 – 7.29 (m, 2.4H), 7.11 (t, J = 7.5 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H); 6.92 (d, J = 8.0 Hz, 1.2H), 6.84 (d, J = 8.0 Hz, 0.8H), 6.67 (dd, J = 8.0, 3.5 Hz, 3H), 6.62 (t, J = 8.0 Hz, 2H), 5.83 (br, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 147.2 (C), 145.1 (C), 145.0 (C), 144.1 (C), 142.9 (C), 142.8 (C), 139.5 (C), 131.1 (CH), 130.6 (CH), 130.5 (CH), 130.4 (CH), 128.7 (CH), 128.6 (CH), 128.6 (CH), 128.5 (CH), 128.2 (CH), 128.2 (CH), 128.0 (CH), 126.4 (CH), 125.9 (CH), 125.3 (q, JCF = 3.5 Hz, CF₃), 123.4 (C), 123.3 (C), 123.2 (C), 123.0 (C), 118.4 (CH), 118.4 (CH), 115.8 (CH), 115.7 (CH); only distinguishable peaks. HRMS (EI) m/z calcd for C₂₁H₁₆F₃N (M)+ 339.12348, found 339.12435.

Aryl Azide 27e. To a solution of 0.17 g of aniline s40 (0.5 mmol) in 5 mL of CH₂Cl₂ was added subsequently 6 mg of CuSO₄, 0.3 mL of Et₃N, freshly prepared triflyl azide (2 mmol) in 5 mL of CH₂Cl₂, 1 mL of water and 2 mL of MeOH. The resulting mixture was stirred at room temperature. After 16 h, the reaction mixture was diluted with 10 mL of CH₂Cl₂, and the resulting mixture was neutralized by the addition of a saturated aq. soln. of NaHCO₃. Once pH 7 was reached, the resulting mixture was washed with 3 × 10 mL of CH₂Cl₂. The resulting organic phase was washed with 20 mL of brine and dried over Na₂SO₄. After filtration, the filtrate was concentrated in vacuo. Purification by MPLC (100:1 hexane:EtoAc) afforded the product as a yellow viscous oil (0.076 g, 42%); ¹H NMR (500 MHz; CDCl₃) δ 7.59 (d, J = 8.0 Hz, 2.4H), 7.54 (d, J = 8.0 Hz, 1.6H), 7.46 (s, 2.4H), 7.44 (s, 1.6H), 7.36 – 7.28 (m, 8H), 7.23 – 7.10 (m, 8H), 6.81 – 6.77 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 146.7 (C), 144.0 (C), 142.8 (C), 142.4 (C), 139.3 (C), 138.9 (C), 131.0 (CH), 130.7 (CH), 130.5 (CH),
130.5 (C), 128.9 (C), 128.6 (CH), 128.6 (CH), 128.4 (CH), 128.2 (CH), 128.1 (CH), 128.0 (CH), 127.9 (CH), 125.3 (q, $J = 3.5$ Hz, CF$_3$), 125.2 (q, $J_{CF} = 3.5$ Hz, CF$_3$), 124.9 (CH), 124.5 (CH), 124.3 (CH), 124.1 (CH), 118.3 (CH), 118.2 (CH) only distinguishable peaks. IR (thin film): 1752, 1727, 1368, 1228, 1216, 750 cm$^{-1}$.

B. Syntheses of 2,3-Diarylindoles

2-Phenyl-3-arylindoles were synthesized from alkynyltrifluoroacetanilide $s41$ following the method reported by Cacchi and co-workers.$^{15}$

\[
\text{Ph} \quad + \quad \text{t-Bu} \quad \xrightarrow{\text{Pd(PPh$_3$)$_4$, Cs$_2$CO$_3$, MeCN, 100 °C}} \quad \text{Ph} \quad (s25)
\]

**Indole 28b.$^{15}$** To a solution of 0.59 g of acetylene (2.0 mmol) in 15 mL of MeCN was added subsequently 1.43 g of Cs$_2$CO$_3$, 0.1 mol of Pd(PPh$_3$)$_4$ (5 mol %), 1.14 g of 4-tert-butyliodobenzene (4.4 mmol). The resulting mixture was stirred at 100 °C until complete conversion (2h). After this time, the reaction mixture was cooled to room temperature, diluted with 30 mL of water and extracted with CH$_2$Cl$_2$ (3 $\times$ 20 mL). The resulting organic phase was washed with 60 mL of brine and dried over Na$_2$SO$_4$. Purification by MPLC (30:1 hexane:EtOAc) afforded the product 28b as a yellow solid (0.59 g, 91%). The spectral data matched that reported by Cacchi and co-workers:$^{15}$ $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.18 (br, 1H), 7.76 (d, $J = 8.0$ Hz, 1H), 7.40 – 7.48 (m, 7H), 7.26 – 7.36 (m, 4H), 7.17 – 7.20 (m, 1H) 1.49 (s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 149.0 (C), 136.0 (C), 134.0 (C), 133.0 (C), 132.0 (C), 129.7 (CH), 129.0 (C), 128.7 (CH), 128.3 (CH), 127.6 (CH), 125.5 (CH), 122.7 (CH), 120.3 (CH), 120.0 (CH), 115.0 (C), 110.9 (CH), 34.6 (C), 31.5 (CH$_3$); IR (thin film): 3457, 1761, 1442, 1378, 1223, 732 cm$^{-1}$. HRMS (EI) $m/z$ calcld for C$_{24}$H$_{23}$N (M)$^+$ 325.18404, found 325.18305.

\[
\text{NHCOCF$_3$} \quad + \quad \text{Ph} \quad + \quad \text{Ph} \quad \xrightarrow{\text{Pd(PPh$_3$)$_4$, Cs$_2$CO$_3$, MeCN, 100 °C}} \quad \text{Ph} \quad (s26)
\]

**Indole 28c.$^{15}$** To a solution of 0.59 g of acetylene (2.0 mmol) in 15 mL of MeCN was added subsequently 1.43 g of Cs$_2$CO$_3$, 0.1 mol of Pd(PPh$_3$)$_4$ (5 mol %), 1.03 g of 4-bromobiphenyl (4.4 mmol). The resulting mixture was stirred at 100 °C until complete conversion (2h). After this time, the reaction mixture was cooled to room temperature, diluted with 30 mL of water and extracted with CH$_2$Cl$_2$ (3 $\times$ 20 mL). The resulting organic phase was washed with 60 mL of brine and dried over Na$_2$SO$_4$. Purification by MPLC (30:1 hexane:EtOAc) afforded the product 28c as a yellow solid (0.54 g, 78%). The spectral data matched that reported by Cacchi and co-workers:$^{15}$ $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.25 (br, 1H), 7.78 (d, $J = 7.5$ Hz, 1H), 7.69 (d, $J = 8.0$ Hz, 2H), 7.65 (d, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 7.5$ Hz, 2H), 7.45 – 7.55 (m, 5H), 7.22 – 7.39 (m, 5H), 7.19 – 7.22 (m, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 141.0 (C), 138.8 (C), 136.0 (C), 134.29 (C), 134.20 (C), 132.8 (C), 130.5 (CH),...
128.81 (CH), 128.76 (CH), 128.3 (CH), 127.8 (CH), 127.23 (CH), 127.18 (CH), 126.99 (CH), 122.8 (CH),
120.6 (CH), 119.8 (CH), 114.6 (C), 111.0 (CH); IR (thin film): 3415, 1770, 1455, 1248, 903, 725, 698, 649 cm
1. HRMS (EI) m / z calcld for C_{26}H_{19}N (M)+ 345.15175, found 345.25258.

Indole 28d.15 To a solution of 0.59 g of acetylene (2.0 mmol) in 15 mL of MeCN was added subsequently 1.43
g of Cs\textsubscript{2}CO\textsubscript{3}, 0.1 mol of Pd(PPh\textsubscript{3})\textsubscript{4} (5 mol %), 1.05 g of 1-chloro-4-iodobenzene (4.4 mmol). The resulting
mixture was stirred at 100 °C until complete conversion (2h). After this time, the reaction mixture was cooled to
room temperature, diluted with 30 mL of water and extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 × 20 mL). The resulting organic
phase was washed with 60 mL of brine and dried over Na\textsubscript{2}SO\textsubscript{4}. Purification by MPLC (30:1 hexane:EtOAc)
afforded the product 28d as a yellow solid (0.53 g, 88%). The spectral data matched that reported by Cacchi
and co-workers:15 1H NMR (500 MHz, CDCl\textsubscript{3}) δ 8.23 (br, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.34 -7.45 (m, 10H),
7.29 (t, J = 7.5 Hz, 1H), 7.20 – 7.23 (m, 1H); 13C NMR (125 MHz, CDCl\textsubscript{3}) δ 135.9 (C), 134.4 (C), 133.7 (C),
132.4 (C), 131.2 (C), 131.4 (CH), 128.88 (CH), 128.84 (CH), 128.5 (CH), 128.3 (CH), 128.0 (CH), 122.9 (CH),
120.7 (CH), 119.5 (CH), 113.8 (C), 111.1 (CH); IR (thin film): 3411, 1770, 1601, 1500, 1248, 1091, 1014, 905,
728 cm\textsuperscript{-1}. HRMS (EI) m / z calcld for C\textsubscript{20}H\textsubscript{14}NCl (M)+ 303.08147, found 303.08070.

Indole 28e.16 To a solution of 0.59 g of acetylene (2.0 mmol) in 15 mL of MeCN was added subsequently 1.43
g of Cs\textsubscript{2}CO\textsubscript{3}, 0.1 mol of Pd(PPh\textsubscript{3})\textsubscript{4} (5 mol %), 0.97 g of 4-trifluromethyliodobenzene (4.4 mmol). The resulting
mixture was stirred at 100 °C until complete conversion (2h). After this time, the reaction mixture was cooled to
room temperature, diluted with 30 mL of water and extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 × 20 mL). The resulting organic
phase was washed with 60 mL of brine and dried over Na\textsubscript{2}SO\textsubscript{4}. Purification by MPLC (30:1 hexane:EtOAc)
afforded the product 28e as a yellow solid (0.63 g, 94%). The spectral data matched that reported by Wang and
co-workers:16 1H NMR (500 MHz, CDCl\textsubscript{3}) δ 8.29 (br, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 8.0 Hz, 2H),
7.57 (d, J = 8.0 Hz, 2H), 7.36 – 7.47 (m, 6H), 7.29 – 7.32 (m, 1H), 7.20 – 7.24 (m, 1H); 13C NMR (125 MHz, CDCl\textsubscript{3}) δ 139.1 (C), 136.0 (C), 135.0 (C), 132.2 (C), 130.2 (CH), 129.0 (CH), 128.4 (CH), 128.2 (CH), 128.1 (d, J\textsubscript{CF} = 38.5 Hz, CH), 125.5 (d, J\textsubscript{CF} = 3.6 Hz, CH), 124.5 (d, J\textsubscript{CF} = 270.0 Hz, C), 123.1 (C), 121.3 (C), 120.9
(CH), 119.3 (CH), 113.6 (C), 111.2 (CH); IR (thin film): 3405, 1770, 1614, 1448, 1321, 1108, 1065, 905, 850 cm\textsuperscript{-1}. HRMS (EI) m / z calcld for C\textsubscript{20}H\textsubscript{14}NF\textsubscript{3} (M)+ 337.10783, found 337.10868.
C. Intramolecular Competition Experiments.

To a mixture of 0.023 g of aryl azide 27a (0.07 mmol), 0.023 g of crushed 4 Å mol sieves, and 0.004 g of Rh$_2$(O$_2$CC$_3$F$_7$)$_4$ (0.004 mol) in Schlenk tube was added 0.50 mL of PhMe. The resulting mixture was heated at 80 °C, after 16 h, the heterogenous mixture was filtered through a short pad of Al$_2$O$_3$. The filtrate was concentrated in vacuo to afford 0.021 g of a mixture of 28a and 29a (78:22). The resulting solid was dissolved in 1.5 mL of CDCl$_3$. The areas of the C–H peak on the methoxy position were compared to derive a ratio (78:22). The products were identified by comparison with published $^1$H NMR spectra of 28a.\textsuperscript{17}

To a mixture of 0.058 g of aryl azide 27b (0.16 mmol), 0.058 g of crushed 4 Å mol sieves, and 0.009 g of Rh$_2$(O$_2$CC$_3$F$_7$)$_4$ (0.008 mol) in Schlenk tube was added 0.50 mL of PhMe. The resulting mixture was heated at 80 °C, after 16 h, the heterogenous mixture was filtered through a short pad of Al$_2$O$_3$. The filtrate was concentrated in vacuo to afford 0.053 g of a mixture of 28b and 29b (73:27). The resulting solid was dissolved in 1.5 mL of CDCl$_3$. The areas of the C–H peak on the aromatic region were compared to derive a ratio (73:27). The products were identified by comparison with $^1$H NMR spectra of 28b.

To a mixture of 0.060 g of aryl azide 27c (0.16 mmol), 0.060 g of crushed 4 Å mol sieves, and 0.009 g of Rh$_2$(O$_2$CC$_3$F$_7$)$_4$ (0.008 mol) in Schlenk tube was added 0.50 mL of PhMe. The resulting mixture was heated at 80 °C, after 16 h, the heterogenous mixture was filtered through a short pad of Al$_2$O$_3$. The filtrate was concentrated in vacuo to afford 0.054 g of a mixture of 28c and 29c (60:40). The resulting solid was dissolved in 1.5 mL of CDCl$_3$. The areas of the C–H peak on the aromatic region were compared to derive a ratio (60:40). The products were identified by comparison with $^1$H NMR spectra of 28c.
To a mixture of 0.043 g of aryl azide 27d (0.13 mmol), 0.043 g of crushed 4 Å mol sieves, and 0.007 g of Rh$_2$(O$_2$CC$_3$F$_7$)$_4$ (0.006 mol) in Schlenk tube was added 0.50 mL of PhMe. The resulting mixture was heated at 80 °C, after 16 h, the heterogenous mixture was filtered through a short pad of Al$_2$O$_3$. The filtrate was concentrated *in vacuo* to afford 0.039 g of a mixture of 28d and 29d (34:66). The resulting solid was dissolved in 1.5 mL of CDCl$_3$. The areas of the C–H peak on the aromatic region were compared to derive a ratio (34:66). The products were identified by comparison with $^1$H NMR spectra of 28d.

To a mixture of 0.040 g of aryl azide 27e (0.11 mmol), 0.040 g of crushed 4 Å mol sieves, and 0.006 g of Rh$_2$(O$_2$CC$_3$F$_7$)$_4$ (0.005 mol) in Schlenk tube was added 0.50 mL of PhMe. The resulting mixture was heated at 80 °C, after 16 h, the heterogenous mixture was filtered through a short pad of Al$_2$O$_3$. The filtrate was concentrated *in vacuo* to afford 0.032 g of a mixture of 28e and 29e (21:79). The resulting solid was dissolved in 1.5 mL of CDCl$_3$. The areas of the C–H peak on the aromatic region were compared to derive a ratio (21:79). The products were identified by comparison with $^1$H NMR spectra of 28e.

**D. Correlation of Product Ratio with Hammett Plot.**

The log of the product ratios were correlated with Hammett $\sigma$-values to ascertain the existence of any linear free energy relationships.
**Figure s1.** Correlation of Product Ratios with Hammett $\sigma^+$-Values.

**Figure s2.** Correlation of Product Ratios with Hammett $\sigma_{para}$-Values.
D. Intermolecular Competition Experiment.

To a mixture of 0.013 g of styryl azide 11a (0.05 mmol) and 0.0145 g of styryl azide 8 (0.05 mmol), 100% w/w of crushed 4 Å mol sieves, and Rh$_2$(hpfb)$_4$ (5 mol %) in Schlenk tube was added 0.50 mL of PhMe. The resulting mixture was heated at 70 °C. After 30 min, the heterogenous mixture was filtered through a short pad of Al$_2$O$_3$. The filtrate was concentrated in vacuo to afford analytically pure indoles. Analysis of the $^1$H NMR spectrum showed 98% conversion of the styryl azide 11a into 12a and 23% conversion of the styryl azide 8 into indole 9. $^1$H NMR (500 MHz, CDCl$_3$) δ 4.02 (s, 3 H) vs 3.94 (s, 0.0734 H) vs 7.07 – 7.08 (m, 0.774 H) = 12a vs 11a vs 8.

D. Examination of Rates of Reaction of E- and Z-Isomers.

To a mixture of 0.043 g of aryl azide 8 (0.16 mmol), 0.043 g of crushed 4 Å mol sieves, and 0.009 g of Rh$_2$(O$_2$CC$_3$F$_7$)$_4$ (0.008 mol) in Schlenk tube was added 0.60 mL of PhMe. The resulting mixture was heated at 70 °C, after 30 min, the heterogenous mixture was filtered through a short pad of Al$_2$O$_3$. The filtrate was concentrated in vacuo. The resulting solid (oil) was dissolved in 1.5 mL of CDCl$_3$. The areas of the C–H peak on the carbon 9 in starting material aryl azide 8 was compared to derive a E:Z ratio.
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MeO$_2$C-$_7$CHO

s17
SI2-26

The diagram shows the structure of compound 11c, which contains a chlorine (Cl) and a nitrogen triazole (N₃) group. The spectrum indicates the presence of various chemical shifts, with peaks at specific ppm values indicated for each atom.

- **Cl**: 140.550, 139.302, 135.841
- **N₃**: 77.407, 77.155
- **C**: 34.938, 30.289, 28.179, 24.127, 23.713

These chemical shifts correspond to the molecular structure, providing insights into the bonding and electronic properties of the compound.
\[ \text{NH}_2 \]

\[ \text{O} \]

\[ \text{B} \]

\[ \text{O} \]

\[ s21 \]

\[ \text{ppm} \]

\[ 163.952 \]

\[ 153.709 \]

\[ 136.830 \]

\[ 132.791 \]

\[ 116.896 \]

\[ 114.809 \]

\[ 83.548 \]

\[ 77.396 \]

\[ 77.143 \]

\[ 76.892 \]

\[ 24.986 \]
NH$_2$

s24
s26

\[ \text{NH}_2 \]
SI2-83
The image contains a chemical structure with resonances labeled with their corresponding ppm values. The structure is labeled as 12d.
12h
\[ F_3C \]

18g
27b
$\text{N}_3$ \quad \text{Cl}

27d
28e
Intramolecular Competition Experiment

$$\text{Rh}_2(O_2CC_3F_7)_4 \quad (5 \text{ mol } \%)$$

$4 \text{ Å MS} \quad (100 \text{ wt } \%)$

PhMe, 80 °C, 16h quant.

$$\text{OMe}$$

$$\text{78:22}$$

$$\text{27a} \quad 28a \quad 29a$$
Intramolecular Competition Experiment

\[
\text{Rh}_2(O_2C\text{C}_3\text{F}_7)_4 \quad (5 \text{ mol %})
\]
\[
\text{PhMe, 80 °C, 16h quant.}
\]

73:27
Intramolecular Competition Experiment

\[ \text{H} \quad \text{Ph} \quad \text{N}_3 \quad \text{Ph} \quad \text{Rh}_2(O_2C_3F_7)_4 \quad (5 \text{ mol} \%) \quad 4 \text{ Å MS (100 wt %)} \quad \text{PhMe}, 80 \, ^\circ \text{C}, 16 \text{h quant.} \quad \]

\[ \begin{align*}
\text{60:40} \\
\text{ppm} & \quad 11 & \quad 10 & \quad 9 & \quad 8 & \quad 7 & \quad 6 & \quad 5 & \quad 4 & \quad 3 & \quad 2 & \quad 1 & \quad 0
\end{align*} \]

\[ \psi \quad 0.297 \quad \psi \quad 0.49 \]
Intramolecular Competition Experiment

$$\text{Rh}_2(O_2CCF_7)_4$$ (5 mol %) in 4 Å MS (100 wt %) in PhMe, 80 °C, 16h quant. 34:66
Intramolecular Competition Experiment

\[
\begin{align*}
\text{A} & : 1^1H + B 1^1H \\
\text{H} & : 2^1H & B
\end{align*}
\]

\[
\begin{align*}
\text{Rh}_2(O_2CCF_3)_4 & \quad \text{(5 mol %)} \\
4 \text{ Å MS (100 wt %)} & \quad \text{PhMe, 80 °C, 16h} \\
\text{quant.} & \quad 21:79
\end{align*}
\]
Intermolecular Competition Experiment

5 vs 8a

R=H, OMe

5 mol% \text{Rh}_2(\text{hpfb})_4

100 \text{ wt\% 4A MS, toluene, 70 }^\circ\text{C}

0.5 \text{ h}

ppm 11 10 9 8 7 6 5 4 3 2 1 0
Examination of Rates of Reaction of E- and Z-Isomers

E : Z = 5.3 : 1

Rh$_2$(O$_2$CC$_3$F$_7$)$_4$ 5 M%
30 min, PhMe,
M.S. 70 °C
conversion 35%

E : Z = 5.4 : 1

SI2-139