Rh_2(II)-Catalyzed Intramolecular Aliphatic C–H Bond Amination Reactions using Aryl Azides as the *N*-Atom Source.

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Supporting Information 1

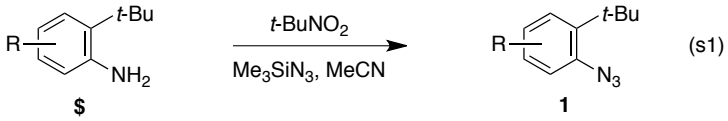
Contents:

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 δ 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_2O, and CH_2Cl_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 Substituted *ortho-tert*-Butyl-Substituted Aryl Azides.

A. General Procedure for the Azidation reaction

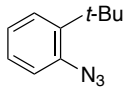
Following the procedure of Zhang and Moses,[2] the 2-*tert*-butyl aryl azides were prepared. Yields were not optimized.



$ **1**

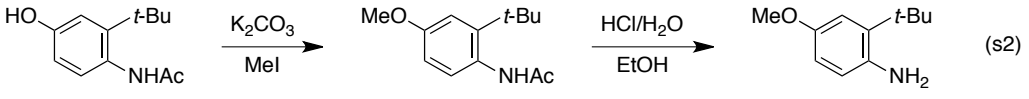
To a cooled solution of aniline in MeCN (0.2 M) was added dropwise *t*-$BuNO_2$ (4 equiv) and Me_3SiN_3 (3 equiv) dropwise. The resulting solution was warmed to room temperature. After 1h, visualization of the reaction progress using TLC indicated the consumption of the starting material. De–ionized water was added to the reaction mixture. The mixture then was extracted with 2 × 30 mL of CH_2Cl_2. The combined organic phases were washed with 20 mL of brine. The resulting organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. Purification of the residue by MPLC (0:100 – 5:95 EtOAc: hexanes) afforded azide.

B. Synthesis of *ortho-tert*-Butyl-Substituted Aryl Azides.



1a

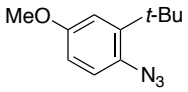
1-Azido-2-*tert*-butylbenzene 1a.[3] The general procedure was followed using 0.298 g of 2-*tert*-butylaniline (2 mmol) in 10 mL of MeCN, 0.951 mL of *t*-$BuNO_2$ and 0.842 mL of Me_3SiN_3. Purification by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded the product as a yellow oil (0.287 g, 84%). This azide was previously reported by Smith and co-workers.[3] ^{1}H NMR (500MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 1.42 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.0 (C), 137.9 (C), 127.3 (CH), 127.2 (CH), 124.7 (CH), 119.5 (CH), 35.1 (C), 29.9 (CH_3). ATR-FTIR (thin film): 3067, 2995, 2956, 2118, 2081, 1575, 1484, 1439, 1283, 1150, 1056, 747, 646 cm^{-1}.



s1 **s2** **s3**

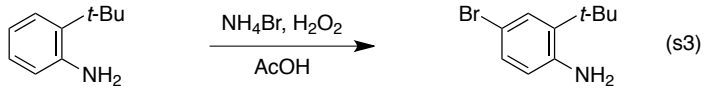
2-*tert*-Butyl-4-methoxyaniline s3.[4] To a solution of 2.07 g of acetamide **s1** (10.0 mmol) and 6.9 g K_2CO_3 (50.0 mmol) in 40 mL of acetone was added 5.3 mL of MeI (80.0 mmol), after refluxing for 6 hours, the mixture was cooled to room temperature and diluted with 20 mL of H_2O. The resulting aqueous phase was extracted with additional 3 × 20 mL of Et_2O. The resulting organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. Without further purification, to the crude product **s2** in 100 mL of H_2O was added 30 mL of EtOH and 30 mL of HCl. After stirring at 100 °C overnight, the resulting mixture was neutralized with Na_2CO_3, and extract with 3 × 30 mL of CH_2Cl_2. The organic phase was concentrated *in vacuo*. Purification by MPLC (5:95 – 20:80 EtOAc:hexanes) afford aniline **s3** as brown solid (0.587 g, 33%). The spectral data matched that reported by Glorius and co-workers.[4] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.5 Hz, 1H), 6.94 (d, *J* = 1.5 Hz, 1H), 6.79 (dd, *J* = 1.5, 8.5 Hz, 1H), 3.81 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ

156.6 (C), 142.6 (C), 130.4 (C), 120.4 (CH), 114.5 (CH), 111.0 (CH), 55.5 (CH_3), 35.2 (C), 29.9 (CH_3); ATR-FTIR (thin film): 2998, 2955, 2912, 2105, 1602, 1483, 1416, 1260, 1225, 1048, 876, 799, 637 cm^{-1}.



1b

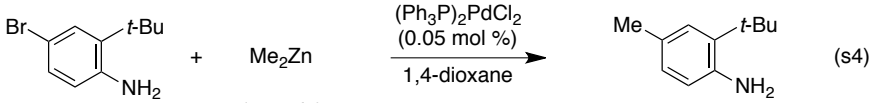
1-Azido-2-*tert*-butyl-4-methoxybenzene 1b. The general procedure was followed using 0.358 g of 2-*tert*-butyl-4-methoxyaniline **s3** (2 mmol) in 10 mL of MeCN, 0.951 mL of *t*-$BuNO_2$ and 0.842 mL of Me_3SiN_3. Purification by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded the product as a yellow oil (352 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.5 Hz, 1H), 6.94 (d, *J* = 1.5 Hz, 1H), 6.79 (dd, *J* = 1.5, 8.5 Hz, 1H), 3.81 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.6 (C), 142.6 (C), 130.4 (C), 120.4 (CH), 114.5 (CH), 111.0 (CH), 55.5 (CH_3), 35.2 (C), 29.9 (CH_3); ATR-FTIR (thin film): 2998, 2955, 2912, 2105, 1602, 1483, 1416, 1260, 1225, 1048, 876, 799, 637cm^{-1}; HRMS (EI) *m/z* calculated for $C_{11}H_{15}N_3O$ $(M)^+$: 205.1215, found: 205.1207.



(s3)

s4

4-Bromo-2-*tert*-butylaniline s4. In the round-bottom flask were placed 1.79 g of 2-*tert*-butylaniline (12.03 mmol), 1.29 g of NH_4Br (13.23 mmol, 1.1 equiv) and 24 mL of glacial acetic acid. 1.36 mL of H_2O_2 was added dropwise via a syringe pump and the reaction mixture was left to stir for 48 hours. The reaction mixture then was neutralized with $NaHCO_3$ and extracted with with an additional 3 × 20.0 mL of CH_2Cl_2. The combined organic phases were washed with 30.0 mL of brine. The resulting organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. Purification using MPLC (0:100 – 50:50 EtOAc: hexanes) afforded the product as a yellow oil (1.64 g, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 2.5 Hz, 1H), 7.12 (dd, *J* = 6.5 Hz, 2.0 Hz, 1H), 6.51 (d, *J* = 8.5 Hz, 1H), 3.82 (s, 2H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7 (C), 135.9 (C), 129.6 (C), 129.5 (CH), 119.2 (CH), 110.7 (CH), 34.4 (C), 29.4 (CH_3). ATR-FTIR (thin film): 3493, 3392, 2963, 2909, 2871, 1619, 1486, 1400, 1249, 1151, 1101, 867, 809 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{10}H_{14}BrN$ $(M)^+$: 227.0310, found: 227.0300.

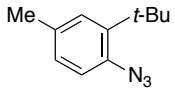


s4 **s5**

(s4)

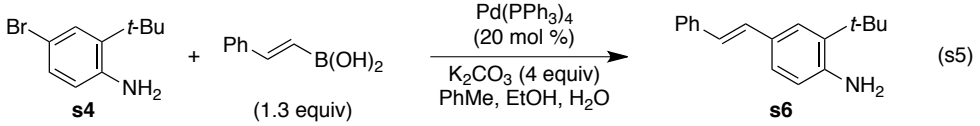
2-*tert*-Butyl-4-methylaniline s5.[5] Following the procedure by Herbert, aniline **s5** was prepared.[6] To the solution of 1.1 g of 2-*tert*-butyl-4-bromo-phenylamine **s4** (5.0 mmol), 0.17 g of $PdCl_2(PPh_3)_2$ (0.25 mmol) in 20 mL of 1,4-dioxane under argon was added 5 mL of Me_2Zn (2M in toluene). After refluxing for 3 hours, the mixture was cooled to room temperature. Then the resulting solution was diluted with 20 mL of MeOH, washed with 20 mL of 1M HCl, and extracted with 3 × 20 mL of Et_2O. The organic phase was collected and concentrated. Purification by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded aniline **s5** as a pale solid (0.530 g, 65%). This aniline was reported recently by Dixon and Burgoyne.[5] ^{1}H NMR (500 MHz, $CDCl_3$ + DMSO) δ 6.75 (m, 2H), 6.53 (dd, *J* = 5.5 Hz, 3.0 Hz, 1H), 3.47 (s, 2H), 1.97 (s, 3H), 1.25 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$ + DMSO) δ 156.3 (C), 148.1 (C), 133.0 (CH), 127.5 (C), 113.7 (CH), 113.2 (CH), 35.0 (C), 31.1 (CH_3), 23.5

(CH_3). ATR-FTIR (thin film): 3287, 2967, 1679, 1601, 1531, 1427, 1365, 1291, 1204, 1141, 1078, 804, 618 cm^{-1}.



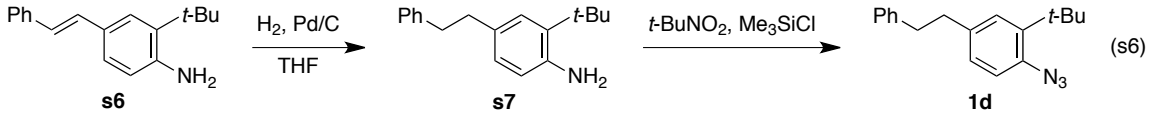
1c

1-Azido-2-*tert*-butyl-4-methoxybenzene 1c. The general procedure was followed using 0.326 g of 2-*tert*-butyl-4-methylaniline (2 mmol) in 10 mL of MeCN, 0.951 mL of *t*-$BuNO_2$ and 0.842 mL of Me_3SiN_3. Purification by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded the product as a yellow oil (318 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.13 (m, 2H), 2.41 (s, 3H), 1.50 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8 (C), 135.1 (C), 134.2 (C), 128.2 (CH), 127.8 (CH), 119.5 (CH), 35.0 (C), 30.1 (CH_3), 21.2 (CH_3). ATR-FTIR (thin film): 2995, 2956, 2912, 2871, 2109, 1574, 1493, 1439, 1361, 1282, 1213, 807, 750 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{11}H_{15}N_3$ $(M)^+$: 189.1266, found: 189.1270.



s4 **s6**

(*E*)-2-*tert*-Butyl-4-styrylaniline s6. To a dry 100 mL round bottom flask equipped with a stir bar were added 2-0.456 g of 2-tert-butyl-4-bromoaniline (2 mmol), 0.429 g of (*E*)-2-phenylvinylboronic acid (2.9 mmol), K_2CO_3 (1.1 g) and 0.105 g of $Pd(PPh_3)_4$ (0.2 equiv). The mixture of toluene:H_2O:EtOH (3:2:1) was added to reaction flask. The resultant mixture was heated to 100 °C. After 16 hours, the mixture was cooled to room temperature and diluted with 20 mL of NH_4Cl. The resulting aqueous phase was extracted with an additional 3 × 20 mL of CH_2Cl_2. The combined organic phases were washed with 30 mL of brine. The resulting organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. Purification by MPLC (0:100 – 50:50 EtOAc: hexanes) afforded the product as a yellow oil (0.366 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 1.5 Hz, 1H), 7.34 – 7.37 (m, 2H), 7.28 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.22 – 7.25 (m, 1H), 7.08 (d, *J* = 16.5 Hz, 1H), 6.95 (d, *J* = 16.5 Hz, 1H), 6.66 (d, *J* = 8.5 Hz, 1H), 3.93 (br, 2H), 1.48 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5 (C), 138.2 (C), 133.6 (C), 129.4 (CH), 128.6 (CH), 127.9 (C), 126.8 (CH), 126.1 (CH), 125.8 (CH), 125.0 (CH), 124.8 (CH), 118.1 (CH), 34.3 (C), 29.6 (CH_3); ATR-FTIR (thin film): 3498, 3388, 3020, 2955, 2871, 1709, 1617, 1592, 1497, 1410, 1277, 1192, 958, 813, 751, 691 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{18}H_{21}N$ $(M)^+$: 251.1674, found: 251.1671.

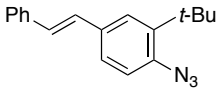


s6 **s7** **1d**

1-Azido-2-*tert*-butyl-4-phenethylbenzene 1d. A mixture of (*E*)-2-*tert*-butyl-4-styrylaniline **s6** and Pd/C (Pd, 10 wt % on carbon powder) in THF were vigorous stirred at room temperature under hydrogen atmosphere. After 20h, visualization of the reaction progress using TLC indicated consumption of the starting material. The mixture then was filtered through a pad of Celite, and the filtrate was concentrated *in vacuo* to afford crude product, which was subjected to the *t*-$BuNO_2$-mediated azidation reaction without purification.

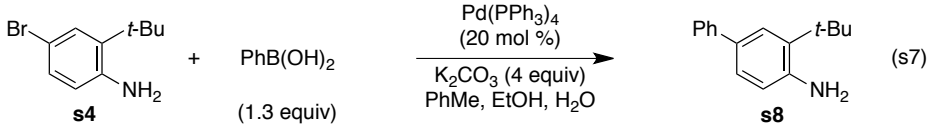
The general azidation procedure was followed using 0.506 g of 2-*tert*-butyl-4-phenethylaniline **s7** (2 mmol) in 10 mL of MeCN, 0.951 mL of *t*-$BuNO_2$ and 0.842 mL of $(CH_3)_3SiN_3$. Purification by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded the product as a yellow oil (0.497 g, 89%).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, *J* =

7.0 Hz, 2H), 7.24 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.11 (m, 2H), 7.09 (s, 1H), 2.94 (s, 4H), 1.41 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.6 (C), 140.7 (C), 138.1 (C), 135.6 (C), 128.6 (CH), 128.4 (CH), 127.8 (CH), 127.1 (CH), 126.0 (CH), 119.5 (CH), 38.1 (CH_2), 37.6(CH_2), 35.0 (C), 30.0 (CH_3); ATR-FTIR (thin film): 3027, 2953, 2863, 2102, 2061, 1602, 1489, 1291, 1076, 809, 745, 697 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{18}H_{21}N_3$ $(M)^+$: 279.1735, found: 279.1742.

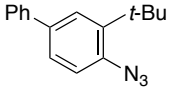


1e

(*E*)-1-Azido-2-*tert*-butyl-4-styrylbenzene 1e. The general azidation procedure was followed using 0.502 g of (*E*)-2-*tert*-butyl-4-styrylaniline **s6** (2 mmol) in 10 mL of MeCN, 0.951 mL of *t*-$BuNO_2$ and 0.842 mL of $(CH_3)_3SiN_3$. Purification by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded the product as a yellow oil (0.432 g, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.5 Hz, 2H), 7.55 (s, 1H), 7.47 (d, *J* = 7.0 Hz, 1H), 7.43 (m, 2H), 7.33 (m, 1H), 7.19 (d, *J* = 8.5, 1H), 7.15 (d, *J* = 16.5 Hz, 1H), 7.11 (d, *J* = 16.5 Hz, 1H), 1.53 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2 (C), 137.4 (C), 137.1 (C), 133.9 (C), 128.8 (CH), 128.35 (CH), 128.3 (CH), 127.7 (CH), 126.6 (CH), 126.0 (CH), 125.1 (CH), 120.0 (CH), 35.2 (C), 30.0 (CH_3); ATR-FTIR (thin film): 2999, 2957, 2863, 2104, 2070, 1591, 1480, 1357, 1289, 1073, 957, 891. 799, 690 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{18}H_{19}N_3$ $(M)^+$: 277.1579, found: 277.1568.



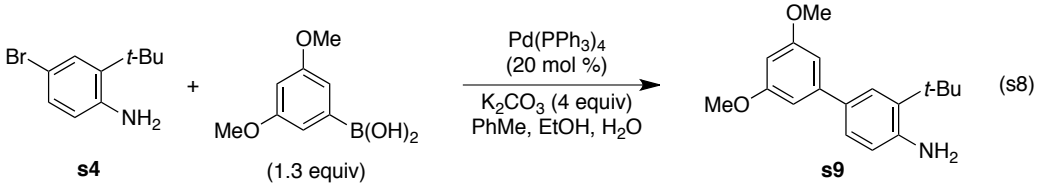
2-*tert*-Butyl-4-phenylaniline s8. To a dry 100 mL round bottom flask equipped with a stir bar were 0.456 g of 2-*tert*-butyl-4-bromoaniline (2 mmol), 0.354 g of phenylboronic acid (2.9 mmol), 1.1 g of K_2CO_3 (4 equiv) and 0.105 g of $Pd(PPh_3)_4$ (0.2 equiv). A mixture of toluene:H_2O:EtOH (3:2:1) was added to reaction flask. The resultant mixture was heated to 100 °C. After 16 hours, the mixture was cooled to room temperature and diluted with 20 mL of NH_4Cl. The resulting aqueous phase was extracted with an additional 3 × 20 mL of CH_2Cl_2. The combined organic phases were washed with 30 mL of brine. The resulting organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. Purification using MPLC (0:100 – 50:50 EtOAc: hexanes) afforded aniline **s8** as a yellow oil (0.283 g, 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.0 Hz, 2H), 7.60 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.40 – 7.35 (m, 2H), 6.79 (d, *J* = 8.0 Hz, 1H), 3.94 (s, 2H), 1.57 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2 (C), 141.9 (C), 133.9 (C), 131.6 (C), 128.8 (CH), 126.7 (CH), 126.3 (CH), 125.7 (CH), 118.3 (CH), 34.5 (C), 29.8 (CH_3) only visible signals; ATR-FTIR (thin film): 3497, 3385, 3028, 2955, 1617, 1483, 1402, 1292, 1240, 1157, 1024, 890, 762, 696 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{19}N$ $(M)^+$: 225.1517, found: 225.1521.



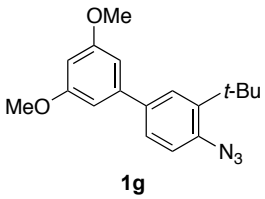
1f

1-Azido-2-*tert*-butyl-4-phenylbenzene 1f. The general azidation procedure was followed using 0.450 g of 2-*tert*-butyl-4-phenylaniline **s7** (2 mmol) in 10 mL of MeCN, 0.951 mL of *t*-$BuNO_2$ and 0.842 mL of $(CH_3)_3SiN_3$. Purification by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded the product as a yellow oil (0.412 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.59 (m, 3H), 7.45 – 7.50 (m, 3H), 7.35 -7.38 (m, 1H), 7.24 (s, 1H), 1.48 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3 (C), 140.9 (C), 137.7 (C), 137.1 (C), 128.8 (CH), 127.2 (CH), 127.0

(CH), 126.3 (CH), 125.9 (CH), 120.0 (CH), 35.3 (C), 30.0 (CH_3); ATR-FTIR (thin film): 3004, 2948, 2903, 2116, 2089, 1600, 1475, 1394, 1290, 1240, 1075, 1023, 894, 811, 756 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{17}N_3$ $(M)^+$: 251.1244, found: 251.1431.

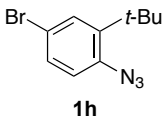


3-*tert*-Butyl-3',5'-dimethoxybiphenyl-4-amine s9. To a dry 100 mL round bottom flask equipped with a stir bar were added 0.456 g of 2-*tert*-butyl-4-bromoaniline (2 mmol), 0.548 g of 3,5-dimethoxyphenylboronic acid (2.9 mmol), 1.1 g of K_2CO_3 (4 equiv) and 0.105 g of $Pd(PPh_3)_4$ (0.2 equiv). A mixture of toluene:H_2O:EtOH (3:2:1) was added to reaction flask. The resultant mixture was heated to 100 °C. After 16 hours, the mixture was cooled to room temperature and diluted with 20 mL of NH_4Cl. The resulting aqueous phase was extracted with an additional 3 × 20.0 mL of CH_2Cl_2. The combined organic phases were washed with 30.0 mL of brine. The resulting organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. Purification by MPLC (0:100 – 50:50 EtOAc: hexanes) afforded aniline **s9** as a yellow oil (0.416 g, 73%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.0 Hz, 1H), 7.33 (dd, *J* = 6.0 Hz, 2.0 Hz, 1H), 6.76 (d, *J* = 2.0 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 1H), 6.48 (t, *J* = 2.0 Hz, 1H), 3.96 (s, 2H), 3.89 (s, 6H), 1.52 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.1 (C), 157.9 (C), 144.5 (C), 144.2 (C), 133.8 (C), 131.5 (C), 125.7 (CH), 118.1 (CH), 105.1 (CH), 98.2 (CH), 94.3 (CH), 93.1 (CH), 55.4 (CH_3), 34.5 (C), 29.7 (CH_3); ATR-FTIR (thin film): 2975, 2925, 2855, 1685, 1600, 1480, 1455, 1386, 1290, 1245, 1163, 908, 724 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{18}H_{23}NO_2$ $(M)^+$: 285.1729, found: 285.1712.



1g

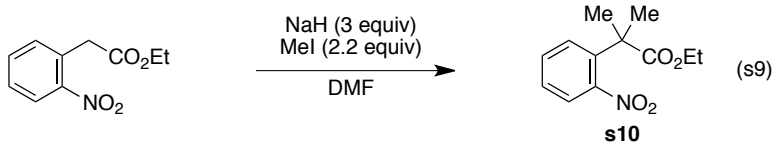
4-Azido-3-*tert*-butyl-3',5'-dimethoxybiphenyl 1g. The general azidation procedure was followed using 0.570 g of 3-*tert*-butyl-3',5'-dimethoxybiphenyl-4-amine **s9** (2 mmol) in 10 mL of MeCN, 0.951 mL of *t*-$BuNO_2$ and 0.842 mL of $(CH_3)_3SiN_3$. Purification by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded the product as a yellow oil (0.566 g, 91%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 6.83 (s, 2H), 6.58 (s, 1H), 3.92 (s, 6H), 1.58 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3 (C), 143.1 (C), 141.3 (C), 137.7 (C), 137.4 (C), 126.4 (CH), 126.0 (CH), 120.0 (CH), 105.5 (CH), 99.1 (CH), 55.4 (CH_3), 35.3 (C), 30.1 (CH_3); ATR-FTIR (thin film): 2995, 2955, 2838, 2117, 2079, 1592, 1495, 1456, 1386, 1285, 1202, 1151, 929, 812 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{18}H_{21}N_3O_2$ $(M)^+$: 311.1634, found: 311.1620.



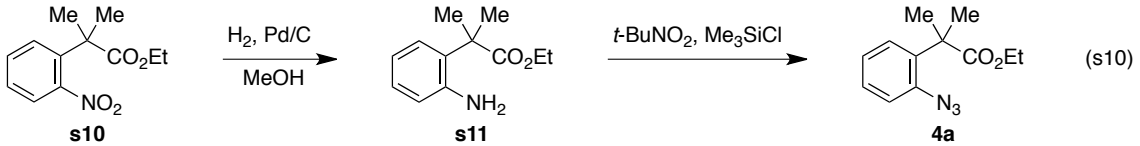
1h

1-Azido-4-bromo-2-*tert*-butylbenzene 1h. The general procedure was followed using 0.454 g of 4-bromo-2-*tert*-butylaniline **s4** (2 mmol) in 10 mL of MeCN, 0.951 mL of *t*-$BuNO_2$ and 0.842 mL of $(CH_3)_3SiN_3$. Purification by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded the product as a yellow oil (0.409 g, 81%). ^1H

NMR (500MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.0 Hz, 1H), 7.37 (dd, *J* = 6.5 Hz, 2.0 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 1.46 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2 (C), 137.2 (C), 130.6 (CH), 130.0 (CH), 121.0 (CH), 117.9 (C), 35.3 (C), 29.7 (CH_3). ATR-FTIR (thin film): 2991, 2956, 2909, 2118, 2088, 1585, 1565, 1481, 1362, 1289, 1077, 805, 583 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{10}H_{12}BrN_3$ $(M)^+$: 253.0215, found: 253.0220.

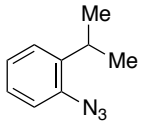


2-Methyl-2-(2-nitrophenyl)proponic acid ethyl ester s10. Following the procedure reported by Glorius and co-workers, methyl ester **s10** was prepared.[4] To a 2.1 g of (2-nitro-phenyl)-acetic acid methyl ester (10.0 mmol), and 2 mL of MeI (22.0 mmol) in 20 mL of DMF at 0 °C was added small amount of NaH (60% in mineral oil) until the mixture turn blue. The rest NaH (total 1.2 g, 30.0 mmol) was added gradually during 30 minutes while the temperature was kept at 0 °C. Then the reaction was warmed to room temperature. After 6 hours, the mixture was diluted with 60 mL of H_2O and extracted with 4 × 30 mL of Et_2O. The organic phase was concentrated. Purification by MPLC (2:98 – 10:90 EtOAc:hexanes) afforded the product as a light yellow solid (1.9 g, 80%). The spectral data matched that reported by Glorius and co-workers [4]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.58 (m, 2H), 7.35 – 7.38 (m, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 1.63 (s, 6H), 1.14 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.1 (C), 148.7 (C), 139.4 (C), 133.2 (CH), 128.1 (CH), 127.7 (CH), 125.5 (CH), 61.0 (CH_2), 46.4 (C), 27.5 (CH_3), 13.9 (CH_3); ATR-FTIR (thin film): 2985, 1722, 1526, 1351, 1227, 1111, 911, 729 cm^{-1}.



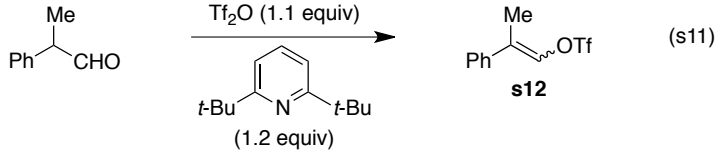
Ethyl 2-(2-azidophenyl)-2-methylpropanoate 4a. Reduction of the nitro group was accomplished by mixing 0.47 g of ethyl ester **s11** and 0.1 g of Pd on activated carbon in 10 mL of MeOH. A balloon of hydrogen was attached. After 4 hours, the balloon was removed, and the reaction mixture was filtered. The resulting filtrate was concentrated *in vacuo* to afford aniline **s11**, which was used in the azidation reaction without further purification.

The general procedure for azidation was followed using 0.41 g of ethyl 2-(2-aminophenyl)-2-methylpropanoate **s11** (2 mmol) in 10 mL of MeCN, 0.951 mL of *t*-$BuNO_2$ and 0.842 mL of $(CH_3)_3SiN_3$. Purification by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded the product as a yellow oil (0.16 g, 34%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 – 7.34 (m, 1H), 7.33 – 7.29 (m, 1H), 7.17 – 7.14 (m, 2H), 4.16 (q, *J* = 7.0 Hz, 2H), 1.54 (s, 6H), 1.19 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 177.1 (C), 137.5 (C), 136.4 (C), 128.0 (CH), 126.4 (CH), 124.9 (CH), 118.6 (CH), 60.8 (CH_2), 45.1 (C), 26.1 (CH_3), 14.1 (CH_3); ATR-FTIR (thin film): 2987, 2931, 2122, 2092, 1729, 1578, 1487, 1445, 1382, 1285, 1140, 858, 748, 672 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{15}N_3O_2$ $(M)^+$: 233.1164, found: 233.1166.

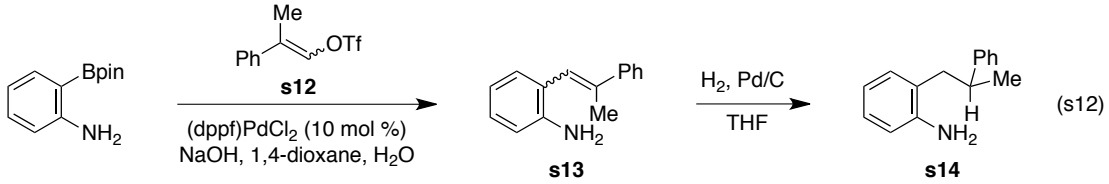


4b

1-Azido-2-isopropylbenzene 4b. [7] The general procedure was followed using 0.270 g of 2-isopropylaniline (2 mmol) in 10 mL of MeCN, 0.951 mL of *t*-$BuNO_2$ and 0.842 mL of $(CH_3)_3SiN_3$. Purification by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded the product as a yellow oil (0.258 g, 80%). The spectral data matched that reported by Fokin and co-workers.[7] ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.25 (m, 2H), 7.17 – 7.13 (m, 2H), 3.26 (m, *J* = 7.0 Hz, 1H), 1.25 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.0 (C), 137.2 (C), 126.9 (CH), 126.6 (CH), 125.0 (CH), 118.1 (CH), 28.0 (CH), 22.9 (CH_3); ATR-FTIR (thin film): 3067, 2963, 2121, 2091, 1580, 1487, 1445, 1290, 1077, 907, 748 cm^{-1}.



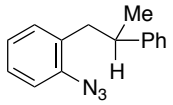
(E)-2-phenylprop-1-enyl trifluoromethanesulfonate s12. To a mixture of 1.32 mL of 2-phenylpropanal (10.0 mmol) and 2.65 mL of 2,6-di-*tert*-butylpyridine (12.0 mmol) in 40 mL of 1,2-dichloroethane was added 1.85 mL of triflic anhydride (11.0 mmol). The resultant mixture was heated to 70 °C. After 2h, the mixture was cooled to room temperature and diluted with 40 mL of CH_2Cl_2. The phases were separated, and the resulting aqueous phase was extracted with an additional 2 × 30 mL of CH_2Cl_2. The combined organic phases were washed with 1 × 30 mL of brine. The resulting organic phase was dried over Na_2SO_4, and was concentrated *in vacuo* to afford 2.53 g of triflate **s12**, which was used in the subsequent Suzuki cross-coupling reaction without further purification.



Aniline s13. To a mixture of 0.7 g of 2-aniline boronic pinacol ester (3.2 mmol), 0.261 g of $(dppf)PdCl_2$ (0.32 mmol) in 40 mL of 1,4-dioxane was added 8 mL of a 3 M solution of NaOH in water followed by 1.36 g of triflate **s12** (5.12 mmol). The resultant mixture was heated to 80 °C. After 12 h, the mixture was cooled to room temperature and filtered through a pad of Celite. The filtrate was diluted with 20 mL of a saturated aqueous solution of NH_4Cl. The phases were separated and the resulting aqueous phase was extracted with an additional 2 × 30 mL of CH_2Cl_2. The combined organic phases were washed with 1 × 30 mL of brine. The resulting organic phase was dried over Na_2SO_4, and was concentrated *in vacuo* to afford 0.627 g of aniline **s14**, which was submitted to the subsequent hydrogenation step without further purification.

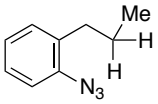
To a mixture of 0.627 g of aniline **s13** and 0.540 g of Pd/C (Pd, 10 wt % on carbon powder) in 40 mL of THF was added a balloon of H_2. After 16 h the balloon was removed, and the reaction mixture was filtered. The resulting filtrate was concentrated *in vacuo*. Purification by MPLC (0:100 – 5:95 EtOAc:hexane) afforded 0.397 g of aniline **s14** as a yellow oil (1.76 mmol, 59% over two steps).). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.35 (m, 2H), 7.23 – 7.26 (m, 3H), 7.05 – 7.08 (m, 1H), 7.0 (d, *J* = 8.0 Hz, 1H), 6.74 (t, *J* = 8.0 Hz, 1H) 6.67 (d, *J* = 8.0 Hz, 1H), 3.44 (br, 2H), 3.09 – 3.15 (m, 1H), 2.85 (dd, *J* = 6.5 Hz, 14.0 Hz, 1H), 2.74 (dd, *J* = 8.0 Hz,

14.0 Hz, 1H), 1.36 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.1 (C), 144.5 (C), 131.0 (CH), 128.5 (CH), 127.2 (CH), 127.0 (CH), 126.3 (CH), 125.3 (C), 118.7 (CH), 115.9 (CH), 40.8 (CH_2), 39.5 (CH), 21.4 (CH_3); ATR-FTIR (thin film): 3451, 3371, 1621, 1490, 1449, 1268, 907 cm^{-1}. HRMS (EI) *m/z* calculated for $C_{15}H_{17}N$ $(M)^+$: 211.1361, found: 211.13080.



4c

Azide 4c. The general azidation procedure was followed using 0.422 g of 2-(2-phenylpropyl)aniline **s15** (2 mmol) in 10 mL of MeCN, 0.951 mL of *t*-$BuNO_2$ and 0.842 mL of $(CH_3)_3SiN_3$. Purification by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded the product as a yellow oil (0.356 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, J = 7.5 Hz, 1H), 7.23 – 7.29 (m, 4H), 7.17 (d, J = 8.0 Hz, 1H), 7.04 (m, 2H), 3.08 – 3.15 (m, 1H), 2.93 (dd, J = 7.0 Hz, 13.0 Hz, 1H), 2.84 (dd, J = 7.0 Hz, 13.0 Hz, 2H), 1.31 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9 (C), 138.3 (C), 132.4 (C), 131.5 (CH), 128.3 (CH), 127.5 (CH), 127.1 (CH), 126.1 (CH), 124.4 (CH), 118.1 (CH), 40.5 (CH_2), 40.3 (CH), 21.0 (CH_3); IR (thin film): 2113, 1578, 1490, 1448, 1281, 1148, 902, 731 cm^{-1}. HRMS (EI) *m/z* calculated for $C_{15}H_{15}N_3$ $(M)^+$: 237.1266, found: 237.1276.



4d

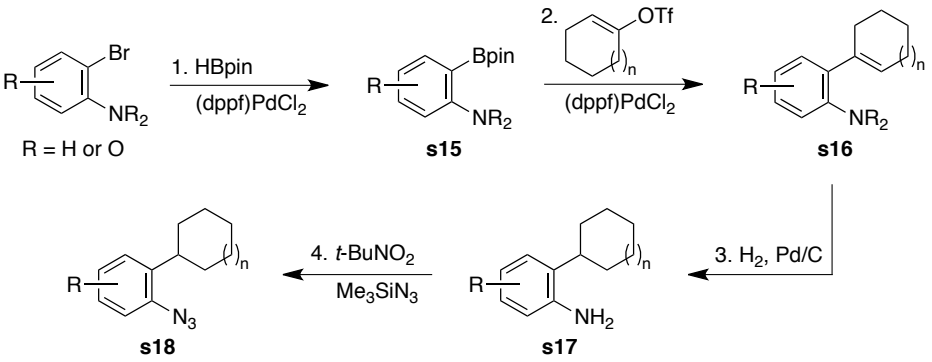
1-Azido-2-*n*-propylbenzene 4d.[8] The general procedure was followed using 0.270 mg of 2-*n*-butylaniline (2 mmol) in 10 mL of MeCN, 0.951 mL of *t*-$BuNO_2$ and 0.842 mL of $(CH_3)_3SiN_3$. Purification by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded the product as a yellow oil (0.264 g, 82%). The spectral data matched that reported by Driver and co-workers.[8] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.28 (m, 1H), 7.15 – 7.20 (m, 2H), 7.08 – 7.11 (m, 1H), 2.59 (t, J= 7.5 Hz, 2H), 1.64 (td, J= 10.Hz, J= 7.5 Hz, 2H), 0.99 (t, J= 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 134.2, 130.5, 127.2, 124.6, 118.1, 33.3, 23.5, 14.0; IR (thin film): 2122, 1582, 1489, 1450, 1285, 1450, 1107, 750, 653 cm^{-1}.

II. Preparation of Substituted *ortho*-cycloalkyl-Substituted Aryl Azides.

A. Route to Substrates.

Substituted *ortho*-azido-cycloalkylbenzenes were synthesized using the route outlined in Scheme s1. Arylboronic pinacol esters **s16** were prepared from corresponding 2-bromoaniline or 2-bromo-1-nitrobenzene. A subsequent Suzuki cross-coupling reaction with a vinyl triflate afforded substituted 2-cycloalkenylanilines **s17**. Hydrogenation of **s17** using the combination of Pd/C and H_2 afforded 2-cycloalkylanilines **s18**. Treatment of the anilines with *tert*-butyl nitrite and azidotrimethylsilane provided the requisite aryl azides.

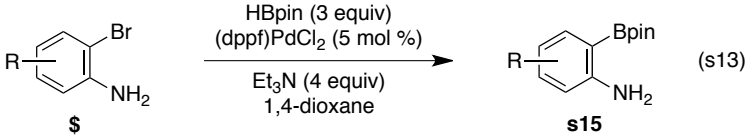
Scheme s1. Synthetic Route to *ortho*-Cyclosubstituted Aryl Azides.



B. Synthesis of Aryl Boronic Pinacol Esters.

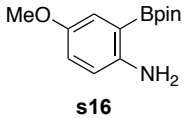
1. General Procedure.

The requisite arylboronic pinacol esters were prepared in one-step from commercially available *ortho*-bromoanilines and HBPin using $(dppf)PdCl_2$ as catalyst. Yields were not optimized.

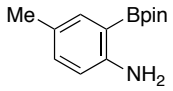


To a mixture of 2-bromo-aniline (5.00 mmol), 0.185 g of $(dppf)PdCl_2$ (0.250 mmol), 2.78 mL of Et_3N (20.0 mmol) in 20.0 mL of 1,4-dioxane, was added dropwise 2.17 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (15.0 mmol). The resultant mixture was heated to 100 °C. After 16h, the mixture was cooled to room temperature and diluted with 20.0 mL of NH_4Cl. The resulting aqueous phase was extracted with an additional 3 × 20.0 mL of CH_2Cl_2. The combined organic phases were washed with 30.0 mL of brine. The resulting organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. Purification using MPLC afforded the product.

2. Syntheses.

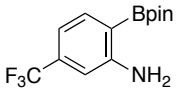


Aryl boronicpinacol ester s16.[9] The general procedure was following using 2.02 g of 2-bromo-4-methoxylaniline (10.0 mmol), 0.401 mg of $(dppf)PdCl_2$ (0.500 mmol), 4.40 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30.0 mmol) and 5.70 mL of Et_3N (40.0 mmol) in 50.0 mL of 1,4-dioxane. Purification by MPLC (5:100 – 10:90 EtOAc: hexanes) afforded the product as a brown liquid (1.53 g, 62%). The spectral data matched that reported by Driver and co-workers.[9] ^1H NMR ($CDCl_3$, 500 MHz) δ 7.15 (s, 1H), 6.85 (dd, J = 8.5, 3.0 Hz, 1H), 6.57 (d, J = 8.5 Hz, 1H), 4.47 (s, 2H), 3.76 (s, 3H), 1.34 (s, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.4 (C), 148.0 (C), 120.6 (CH), 119.6 (CH), 116.5 (CH), 83.6 (C), 56.0 (CH_3), 25.0 (CH_3) only signals visible; ATR-FTIR (thin film): 3456, 3366, 1494, 1421, 1359, 1304, 1226, 1037, 855, 829, 750 cm^{-1}.



s17

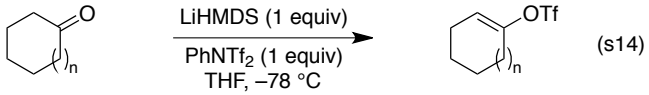
Aryl boronicpinacol ester s17. The general procedure was following using 1.86 g of 2-bromo-4-methylaniline (10.0 mmol), 0.401 g of (dppf)$PdCl_2$ (0.500 mmol), 4.40 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30.0 mmol) and 5.70 mL of Et_3N (40.0 mmol) in 50.0 mL of 1,4-dioxane. Purification by MPLC (1:100 – 10:90 EtOAc: hexanes) afforded the product as a yellow solid (0.840 g, 36%), mp 60 °C, R_f = 0.45 (15:75 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.48 (s, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 4.65 (s, 2H), 2.26 (s, 3H), 1.38 (s, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 151.5 (C), 136.8 (CH), 133.7 (CH), 125.8 (C), 115.1 (CH), 83.5 (C), 67.1 (C), 25.0 (CH_3), 20.3 (CH_3); ATR-FTIR (thin film): 3500, 2980, 2244, 1618, 1576, 1496 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{20}BNO_2$ $(M)^+$: 233.1587, found: 233.1583.



s18

Aryl boronicpinacol ester s18. The general procedure was following using 2.40 g of 2-bromo-5-(trifluoromethyl)aniline (10.0 mmol), 0.401 g of (dppf)$PdCl_2$ (0.500 mmol), 4.40 mL of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (30.0 mmol) and 5.7 mL of Et_3N (40.0 mmol) in 50.0 mL of 1,4-dioxane. Purification by MPLC (1:100 – 10:90 EtOAc: hexanes) afforded the product as a yellow solid (1.83 g, 64%): mp 63-65 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 1H), 6.83 (s, 1H), 5.03 (s, 2H), 1.38 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.9 (C), 137.6 (CH), 134.3 (q, J_{CF} = 32 Hz, C), 124.3 (q, J_{CF} = 272 Hz, CF_3), 112.6 (q, J_{CF} = 3.4 Hz, CH), 110.9 (q, J_{CF} = 4.5 Hz, CH), 84.0 (C), 29.9 (C), 24.8 (CH_3); ^{19}F NMR (282 MHz, $CDCl_3$) δ –63.95. ATR-FTIR (thin film): 3499, 3397, 2980, 2958, 2929, 1622, 1508, 1437, 1333, 1245 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{17}BFNO_2$ $(M)^+$: 287.1304, found: 287.1310.

C. General Procedure for the Synthesis of Vinyl Triflates.



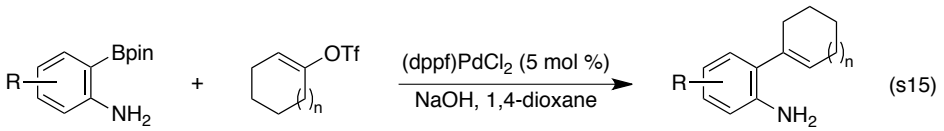
(s14)

To a stirring solution of 1.67 g of LiHMDS (10.0 mmol) in THF (30.0 mL) at –78 °C was added 10.0 mmol of cyclic ketone. The resultant mixture was warmed to room temperature for 1h, then cooled to –78 °C. A solution of 3.57 g of $PhNTf_2$ (10.0 mmol) in THF was added to reaction mixture in one portion, and then the mixture was maintained at –78 °C for 1h. The cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. After 18h at room temperature, the mixture was diluted with 40 mL of CH_2Cl_2. The resulting aqueous phase was extracted with an additional 2 × 30 mL of CH_2Cl_2. The combined organic phases were washed with 30 mL of brine. The resulting organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo* to afford crude triflate.

D. Suzuki Reaction of *ortho*-Bromoanilines.

1. General Procedure.

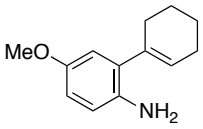
Following the procedure of Driver and co-workers,[9] a series of aryl boronicpinacol esters were treated with cyclic triflates in the presence of (dppf)$PdCl_2$ to produce the desire aniline. Yields were not optimized.



s15 **s16**

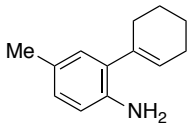
To a mixture of 1.00 mmol of boronic ester **s15**, and 0.037g of (dppf)$PdCl_2$ (0.050 mmol) in 15 mL of 1,4-dioxane was added 3.00 mL of a 3M solution of NaOH in water followed by 1.20 mmol of cycloalkyltriflate. The resultant mixture was heated to 100 °C. After 12 h, the mixture was cooled to room temperature and diluted with 10 mL of a saturated aqueous solution of NH_4Cl. The resulting mixture was separated, and the aqueous phase was extracted with an additional 2 × 30 mL of CH_2Cl_2. The combined organic phases were washed with 30 mL of brine. The resulting organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. Purification of the oily residue using MPLC afforded the product.

2. Syntheses.



s19

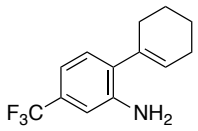
Aniline s19. The general procedure was following using 1.24 g of boronic ester **s17** (5.00 mmol), crude cyclohexyltriflate (derived from 10.0 mmol of cyclohexanone), 0.183 g of (dppf)$PdCl_2$, and 1.80 g of NaOH (45.0 mmol) in 75.0 mL of 1,4-dioxane and 15.0 mL of water. Purification by MPLC (10:90 – 50:50 EtOAc: hexanes) afforded the product as a brown yellow oil (0.741 g, 73%), R_f = 0.78 (50:50 EtOAc:hexanes, visualized by 254 nm UV light): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.65 – 6.62 (m, 3H), 5.78 (t, *J* = 4.0 Hz, 1H), 3.75 (s, 3H), 3.54 (s, 2H), 2.27 (d, *J* = 2.0 Hz, 2H), 2.20 (d, *J* = 3.5 Hz, 2H), 1.79 (d, *J* = 6.0 Hz, 2H), 1.71 (d, *J* = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5 (C), 136.9 (C), 136.6 (C), 131.7 (C), 126.9 (CH), 116.6 (CH), 114.3 (CH), 113.2 (CH), 55.7 (CH_3), 29.3 (CH_2), 25.5 (CH_2), 23.2 (CH_2), 22.2(CH_2). ATR-FTIR (thin film): 3420, 3009, 2929, 2227, 1623, 1521, 1462, 987, 758 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{17}NO$ $(M)^+$: 203.1310, found: 203.1296.



s20

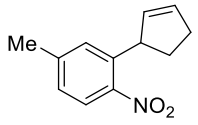
Aniline s20. The general procedure was following using 1.16 g of boronic ester **s17** (5.00 mmol), crude cyclohexyltriflate (derived from 10.0 mmol of cyclohexanone), 0.183 g of (dppf)$PdCl_2$, and 1.80 g of NaOH (45.0 mmol) in 75.0 mL of 1,4-dioxane and 15.0 mL of water. Purification by MPLC (1:100 – 10:90 EtOAc: hexanes) afforded the product as a yellow oil (0.842 g, 90%), R_f = 0.47 (15:75 EtOAc:hexanes, visualized by 254 nm UV light): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (d, *J* = 9.0 Hz, 1H), 6.93 (s, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.86 (t, *J* = 2.0 Hz, 1H), 3.73 (s, 2H), 2.36 (m, 2H), 2.35 (s, 3H), 2.28 (m, 2H), 1.9 (m, 2H), 1.8 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7 (C), 136.8 (C), 130.6 (C), 129.3 (CH), 128.1 (CH), 127.4 (C), 126.7 (CH),

115.7 (CH), 29.6 (CH_2), 25.6 (CH_2), 23.4 (CH_2), 22.4(CH_2), 20.6 (CH_3). ATR-FTIR (thin film): 3444, 2927, 2224, 1618, 1500, 1461, 815 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{17}N$ $(M)^+$: 187.1361, found: 187.1365.



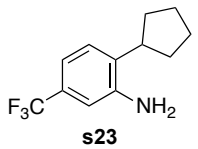
s21

Aniline s21. The general procedure was following using 1.43 g of boronic ester **s18** (5.00 mmol), crude cyclohexyltriflate (derived from 10.0 mmol of cyclohexanone), 0.183 g of (dppf)$PdCl_2$, and 1.80 g of NaOH (45.0 mmol) in 75.0 mL of 1,4-dioxane and 15.0 mL of water. Purification by MPLC (1:100 – 10:90 EtOAc: hexanes) afforded the product as a yellow oil (0.961 g, 80%), R_f = 0.45 (15:75 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.0 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.92 (s, 1H), 5.8 (s, 1H), 3.94 (s, 2H), 2.21 (m, 4H), 1.75 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7 (C), 135.6 (C), 133.5 (C), 129.7 (q, J_{CF} = 31 Hz, CF_3), 129.1 (CH), 127.9 (CH), 124.5 (q, J_{CF} = 270 Hz, C), 114.7 (q, J_{CF} = 3 Hz, C), 111.7 (q, J_{CF} = 3.5 Hz, C), 29.2 (CH_2), 25.4 (CH_2), 23.1 (CH_2), 22.1(CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ –61.06. ATR-FTIR (thin film): 2936, 2240, 1619, 1512, 1433, 1333 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{14}NF_3$ $(M)^+$: 241.1078, found: 241.1081.



s22

2-(cyclopent-2-enyl)-4-methyl-1-nitrobenzene s22. Following the procedure of Larock and co-workers,[10] nitrobenzene **s22** was synthesized using 0.71 mL of 2-iodo-4-methyl-1-nitrobenzene (5 mmol), 1.7 g of cyclopentene (5 equiv), 0.028 g of $Pd(OAc)_2$ (2.5 mol %), 1.39 g of *n*-Bu_4NCl (1 equiv), 0.735 g of KOAc (3 equiv), 0.0328 g of PPh_3 (2.5 mol %) in 10 mL of DMF. Purification by MPLC (1:100 – 10:90 EtOAc: hexanes) afforded the product as a yellow oil (0.457 g, 45%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.16 (s, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 6.05 (t, *J* = 5.0 Hz, 1H), 5.70 (q, *J* = 2.0 Hz, 1H), 4.41 (t, *J* = 4.5 Hz, 1H), 2.66 – 2.60 (m, 1H), 2.51 – 2.47 (m, 2H), 2.41 (s, 3H), 1.74 – 1.70 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.1 (C), 143.9 (C), 141.1 (C), 133.6 (CH), 132.6 (CH), 129.4 (CH), 127.4 (CH), 124.3 (CH), 46.4 (CH), 33.5 (CH_2), 32.3 (CH_2), 21.5 (CH_3). ATR-FTIR (thin film): 3004, 2933, 1614, 1531, 1467, 1331, 1195, 845, 735, 679 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{13}NO_2$ $(M)^+$: 203.0946, found: 203.0934.



s23

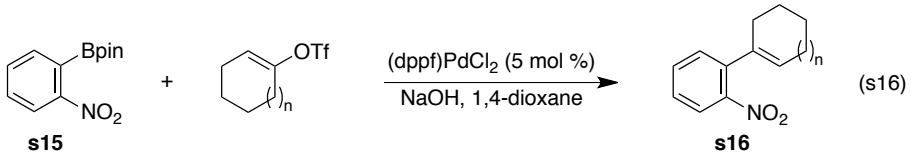
Aniline s23. The general Suzuki cross-coupling procedure was following using 1.43 g of boronic ester **s18** (5.00 mmol), crude cyclopentyltriflate (derived from 10.0 mmol of cyclopentanone), 0.183 g of (dppf)$PdCl_2$, and 1.80 g of NaOH (45.0 mmol) in 75.0 mL of 1,4-dioxane and 15.0 mL of water. Purification by MPLC (1:100 – 10:90 EtOAc: hexanes) afforded the product as a yellow oil, which was immediately submitted to the subsequent hydrogenation step. To a mixture of 0.829 g of aniline and 0.273 g of Pd/C (Pd, 10 wt % on carbon powder) in 20 mL of THF was added a balloon of H_2. After 16 h the balloon was removed, and the reaction mixture was filtered. The resulting filtrate was concentrated *in vacuo*. Purification by MPLC (0:100 – 5:95

EtOAc:hexane) afforded 0.652 g of aniline **s23** as a yellow oil (2.85 mmol, 57% over two steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, J = 8.0 Hz, 1H), 6.98 (d, J = 8.0 Hz, 1H), 6.89 (s, 1H), 3.84 (s, 2H), 2.98 (m, 1H), 2.09 – 2.05 (m, 2H), 1.84 – 1.80 (m, 2H), 1.74 – 1.71 (m, 2H), 1.67 – 1.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4 (C), 133.9 (C), 128.8 (q, J_{CF} = 31 Hz, C), 126.3 (CH), 124.4 (q, J_{CF} = 270 Hz, CF_3), 115.2 (q, J_{CF} = 4.3 Hz, C), 111.9 (q, J_{CF} = 3.6 Hz, C), 39.9 (CH), 32.0 (CH_2), 25.2 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.94. ATR-FTIR (thin film): 3485, 3403, 2956, 2870, 1624, 1513, 1433, 1335, 1256, 1116, 927, 814 cm^{-1}. HRMS (EI) *m/z* calculated for $C_{12}H_{14}NF_3$ $(M)^+$: 229.1078, found: 229.1075.

E. Suzuki Reaction of 2-Bromo-1-Nitrobenzenes.

1. General Procedure.

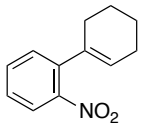
Following the procedure of Driver and co-workers,[9] 2-nitrophenylboronic acid was treated with a cyclic triflate in the presence of (dppf)$PdCl_2$ to produce the desire 2-cycloalkenylnitrobenzenes. Yields were not optimized.



s15 **s16** (s16)

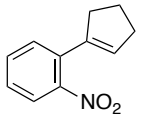
To a mixture of 0.165 g of 2-nitrophenylboronic acid (1.00 mmol), 0.037g of (dppf)$PdCl_2$ (0.050 mmol) in 15 mL of 1,4-dioxane was added 3 mL of a 3M solution of NaOH in water followed by 1.20 mmol of cycloalkenyltriflate. The resultant mixture was heated to 100 °C. After 12 h, the mixture was cooled to room temperature and diluted with 10 mL of saturated aqueous solution of NH_4Cl. The phases were separated, and the aqueous phase was extracted with an additional 2 × 30 mL of CH_2Cl_2. The combined organic phases were washed with 30 mL of brine. The resulting organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. Purification of the oily residue using MPLC afforded the product.

2. Syntheses.



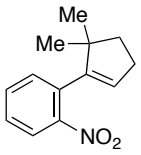
s24

Nitrobenzene s24. The general procedure was following using 0.825 g of boronic acid (5.00 mmol), crude cyclohexenyl triflate (derived from 10.0 mmol of cyclohexanone), 0.183 g of (dppf)$PdCl_2$, 1.80 g of NaOH (45.0 mmol) in 75.0 mL of 1,4-dioxane and 15.0 mL of water. Purification by MPLC (1:100 – 10:90 EtOAc: hexanes) afforded the product as a yellow oil (0.995 g, 98%), R_f = 0.5 (15:75 EtOAc:hexanes, visualized by 254 nm UV light):^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 1H), 7.46 (t, J = 9.0 Hz, 1H), 7.30 (t, J = 7.0 Hz, 1H), 7.23 (d, J = 7.5 Hz, 1H), 5.57 (t, J = 2.0 Hz, 1H), 2.18 (q, J = 2.5 Hz, 2H), 2.09 (q, J = 2.5 Hz, 2H), 1.71 (q, J = 3.5 Hz, 2H), 1.62 (q, J = 6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7 (C), 139.4 (C), 135.9 (C), 132.4 (CH), 130.8 (CH), 127.4 (CH), 126.6 (CH), 123.8 (CH), 29.3 (CH_2), 25.4 (CH_2), 22.8 (CH_2), 21.7 (CH_2). ATR-FTIR (thin film): 2956, 2928, 2859, 2249, 1606, 1571, 1526, 1457, 1264 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{13}NO_2$ $(M)^+$: 203.0946, found: 203.0953.



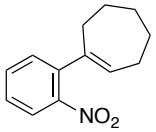
s25

Nitrobenzene s25. The general procedure was following using 0.825 g of boronic acid (5.00 mmol), crude cyclohexyltriflate (derived from 10.0 mmol of cyclohexanone), 0.183 g of (dppf)$PdCl_2$, and 1.80 g of NaOH (45.0 mmol) in 75.0 mL of 1,4-dioxane and 15.0 mL of water. Purification by MPLC (1:100 – 10:90 EtOAc: hexanes) afforded the product as a yellow oil (0.995 g, 98%), R_f = 0.5 (15:75 EtOAc:hexanes, visualized by 254 nm UV light): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.35 – 7.31 (m, 2H), 5.81 (t, *J* = 2.0 Hz, 1H), 2.57 (t, *J* = 7.0 Hz, 2H), 2.47 (t, *J* = 6.5 Hz, 2H), 2.00 (m, *J* = 7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8 (C), 140.0 (C), 133.5 (C), 132.1 (CH), 130.8 (CH), 127.6 (CH), 123.6 (CH), 35.3 (CH_2), 33.5 (CH_2), 24.1 (CH_2) only visible signals. ATR-FTIR (thin film): 2964, 2934, 2849, 2229, 1623, 1573, 1526, 1459, 1265, 987, 783 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{11}H_{11}NO_2$ $(M)^+$: 189.0790, found: 189.0799.



s26

Nitrobenzene s26. The general procedure was following using 0.825 g of boronic acid (5.00 mmol), crude cyclopentyltriflate (derived from 10.0 mmol of 2,2-dimethylcyclopentanone), 0.183 g of (dppf)$PdCl_2$, and 1.80 g of NaOH (45.0 mmol) in 75.0 mL of 1,4-dioxane and 15.0 mL of water. Purification by MPLC (1:100 – 10:90 EtOAc: hexanes) afforded the impure product as a yellow oil. This product was carried on to the next step without any characterization.

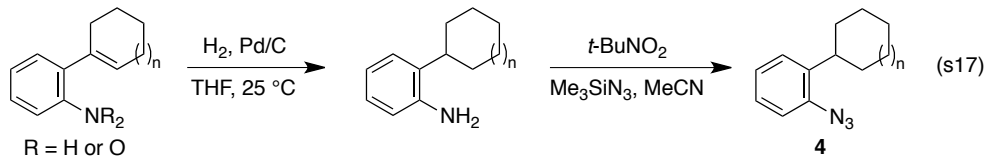


s27

Nitrobenzene s27. The general procedure was following using 0.825 g of boronic acid (5.00 mmol), crude cycloheptyltriflate (derived from 10.0 mmol of cycloheptanone), 0.183 g of (dppf)$PdCl_2$, and 1.80 g of NaOH (45.0 mmol) in 75.0 mL of 1,4-dioxane and 15.0 mL of water. Purification by MPLC (1:100 – 10:90 EtOAc: hexanes) afforded the product as a yellow oil (0.998 g, 92%), R_f = 0.5 (15:75 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 5.79 (t, *J* = 6.5 Hz, 1H), 2.40 (t, *J* = 5.5 Hz, 2H), 2.23 (q, *J* = 6.0 Hz, 2H), 1.78 (m, *J* = 6 Hz, 2H), 1.61 (m, *J* = 6 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0 (C), 142.4 (C), 141.3 (C), 132.5 (CH), 132.0 (CH), 130.9 (CH), 127.2 (CH), 123.9 (CH), 34.6 (CH_2), 32.3 (CH_2), 29.1 (CH_2), 26.8 (CH_2), 26.7 (CH_2). ATR-FTIR (thin film): 2923, 2848, 1713, 1606, 1524, 1350, 904, 783, 725 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{15}NO_2$ $(M)^+$: 217.1103, found: 217.1115.

F. Preparation of the Aryl Azide Substrates through Hydrogenation/Azidation Sequence.

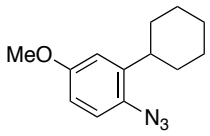
1. General Procedure



A mixture of aniline and Pd/C (Pd, 10 wt % on carbon powder) in THF were vigorous stirred at room temperature under hydrogen atmosphere. After 20h, visualization of the reaction progress using TLC indicated consumption of the starting material. The mixture then was filtered through a pad of Celite, and the filtrate was concentrated *in vacuo* to afford crude 2-cycloalkylaniline, which was subjected to the *t*-$BuNO_2$-mediated azidation reaction without further purification.

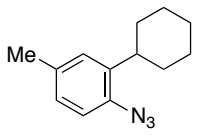
To a cooled solution of aniline in MeCN (0.2 M) was added dropwise *t*-$BuNO_2$ (4 equiv) and Me_3SiN_3 (3 equiv) dropwise. The resulting solution was warmed to room temperature. After 1h, visualization of the reaction progress using TLC indicated the consumption of the starting material. De-ionized H_2O was then added to the reaction mixture. The mixture then was extracted with 2 × 30 mL of CH_2Cl_2. The combined organic phases were washed with 20 mL of brine. The resulting organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. Purification of the residue by MPLC (0:100 – 5:95 EtOAc: hexanes) afforded azide **4**.

2. Syntheses.



4e

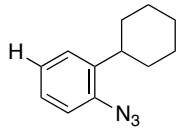
1-Azido-2-cyclohexyl-4-methoxybenzene 4e. The general procedure was following using crude aniline (derived from 2 mmol of aniline **s19**), 0.95 mL of *t*-$BuNO_2$, and 0.84 mL of Me_3SiN_3. Purification by MPLC (0:100 – 10:90 EtOAc: hexanes) afforded the product as a brown yellow oil (0.296 g, 64% from **s19**), R_f = 0.7 (15:75 EtOAc:hexanes, visualized by 254 nm UV light): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (d, *J* = 9 Hz, 1H), 6.84 (s, 1H), 6.78 (d, *J* = 8.5 Hz, 1H), 3.81 (s, 3H), 2.85 (t, *J* = 11.5 Hz, 1H), 1.84 (m, 5H), 1.40 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1 (C), 140.6 (C), 129.7 (C), 118.9 (CH), 113.4 (CH), 111.6 (CH), 55.4 (CH_3), 38.5 (CH), 33.3 (CH_2), 26.9 (CH_2), 26.3 (CH_2). ATR-FTIR (thin film): 2923, 2855, 2110, 1717, 1605, 1493, 1448, 1355, 1287, 1242, 1220, 1036, 796 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{17}N_3O$ $(M)^+$: 231.1372, found: 231.1366.



4f

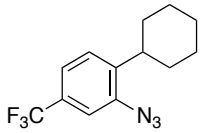
1-Azido-2-cyclohexyl-4-methylbenzene 4f. The general procedure was following using crude aniline (derived from 2 mmol of aniline **s20**), in 10 mL of MeCN, 0.951 mL of *t*-$BuNO_2$ and 0.842 mL of $TMSN_3$. Purification by MPLC (0:100 – 10:90 EtOAc:hexanes) afforded the product as a yellow oil (0.378 g, 88% from **s20**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (s, 1H) , 7.05 (s, 2H), 2.84 (t, *J* = 11.5 Hz, 1H), 2.36 (s, 3H), 1.86 (m, 5H),

1.44 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.9 (C), 134.5 (C), 134.4 (C), 127.9 (CH), 127.5 (CH), 118.0 (CH), 38.3 (CH), 33.4 (CH_3), 27.0 (CH_2), 26.4 (CH_2), 21.1 (CH_2). ATR-FTIR (thin film): 3002, 2971, 2934, 1738, 1567, 1494, 1378, 1288, 1211, 967, 754 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{17}N_3$ $(M)^+$: 215.1422, found: 215.1413.



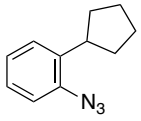
4g

1-Azido-2-cyclohexylbenzene 4g.[11] The general procedure was following using crude aniline (derived from 2 mmol of nitrobenzene **s21**), 0.95 mL of*t*-$BuNO_2$, and 0.84 mL of Me_3SiN_3. Purification by MPLC (0:100 – 10:90 EtOAc: hexanes) afforded the product as a yellow oil (0.209 g, 52% from **s21**), R_f = 0.8 (15:75 EtOAc:hexanes, visualized by 254 nm UV light). Azide **4g** was originally reported by Smolinsky. [11] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 8 Hz, 1H), 7.34 (d, *J* = 9 Hz, 1H), 7.32 (d, *J* = 8 Hz, 1H), 3.15 (t, *J* = 6.5 Hz, 1H), 2.05 (m, 5H), 1.66 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.3 (C), 137.4 (C), 127.2 (CH), 127.0 (CH), 125.0 (CH), 118.1 (CH), 38.4 (CH), 33.5 (CH_2), 27.2 (CH_2), 26.5 (CH_2). ATR-FTIR (thin film): 2924, 2852, 2114, 2082, 1577, 1486, 1447, 1281, 898, 732 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{15}N_3$ $(M)^+$: 201.1266, found: 201.1275.



4h

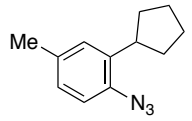
1-Azido-3-triflouromethyl-5-cyclohexylbenzene 4h. The general procedure was following using crude aniline (derived from 2 mmol of nitrobenzene **s22**), 0.95 mL of *t*-$BuNO_2$, and 0.84 mL of Me_3SiN_3. Purification by MPLC (0:100 – 10:90 EtOAc: hexanes) afforded the product as a yellow light oil (0.479 g, 89% from **s22**), R_f = 0.8 (15:75 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.36 (s, 1H), 7.34 (s, 1H), 2.89 (t, *J* = 12 Hz, 1H), 1.84 (m, 5H), 1.41 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.0 (C), 138.1 (C), 129.3 (q, J_{CF} = 33 Hz, C), 127.7 (CH), 123.8 (q, J_{CF} = 271 Hz, CF_3), 121.6 (q, J_{CF} = 3.5 Hz, CH), 114.8 (q, J_{CF} = 3.6 Hz, CH), 38.3 (CH), 33.1 (CH_2), 26.7 (CH_2), 26.1 (CH_2). ^{19}F NMR (282 MHz, $CDCl_3$) δ – 63.06. ATR-FTIR (thin film): 2929, 2859, 2103, 1606, 1500, 1448, 1417, 1324, 1272, 1119, 1085, 872 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{14}N_3F_3$ $(M)^+$: 269.1140, found: 269.1131.



4i

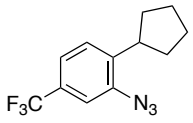
1-Azido-2-cyclopentylbenzene 4i. The general procedure was following using crude aniline (derived from 2 mmol of nitrobenzene **s25**, 0.95 mL of *t*-$BuNO_2$, and 0.84 mL of Me_3SiN_3. Purification by MPLC (0:100 – 10:90 EtOAc: hexanes) afforded the product as a yellow oil (0.161g, 43% from **s25**), R_f = 0.8 (15:75 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 3.29 (m, 1H), 2.08 (m, 2H), 1.86 (m, 2H), 1.74 (m, 2H), 1.60 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9 (C), 137.7 (C), 127.3 (CH), 126.9 (CH), 124.9

(CH), 118.1 (CH), 40.1 (CH), 33.6 (CH_2), 25.6 (CH_2). ATR-FTIR (thin film): 2957, 2870, 2123, 2089, 1580, 1489, 1451, 1292, 903, 725 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{11}H_{13}N_3$ $(M)^+$: 187.1109, found: 187.1105.



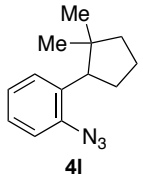
4j

1-Azido-2-cyclopentyl-4-methylbenzene 4j. The general procedure was following using crude aniline (derived from 2 mmol of nitrobenzene **s22**), 0.95 mL of *t*-$BuNO_2$, and 0.84 mL of Me_3SiN_3. Purification by MPLC (0:100 – 10:90 EtOAc: hexanes) afforded the product as a yellow oil (0.346 g, 86% from **s22**), R_f = 0.8 (15:75 EtOAc:hexanes, visualized by 254 nm UV light). ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 (s, 1H), 7.14 (s, 2H), 3.38 (m, 1H), 2.47 (s, 3H), 2.19 (m, 2H), 1.98 (m, 2H); 1.86 (m, 2H), 1.72 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.5 (C), 135.2 (C), 134.5 (C), 128.0 (CH), 127.6 (CH), 118.0 (CH), 40.3 (CH), 33.7 (CH_2), 25.7 (CH_2), 21.1 (CH_3). ATR-FTIR (thin film): 2952, 2867, 2114, 1715, 1608, 1578, 1493, 1452, 1359, 1290, 1218, 881, 804 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{15}N_3$ $(M)^+$: 201.1266, found: 201.1262.



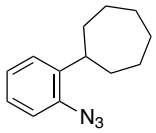
4k

1-Azido-3-trifluoromethyl-5-cyclopentylbenzene 4k. The general procedure was following using crude aniline (derived from 2 mmol of nitrobenzene **s23**), 0.95 mL of *t*-$BuNO_2$, and 0.84 mL of Me_3SiN_3. Purification by MPLC (0:100 – 10:90 EtOAc: hexanes) afforded the product as a brown yellow oil (0.398 g, 78% from **s23**), R_f = 0.8 (15:75 EtOAc:hexanes, visualized by 254 nm UV light). ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (m, 3H), 3.36 (m, 1H), 2.13 (q, *J* = 6.5 Hz, 2H), 1.89 (m, 2H); 1.79 (q, *J* = 5 Hz, 2H), 1.62 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.8 (C), 138.8 (C), 129.5 (q, J_{CF} = 32 Hz, CF_3), 127.6 (CH), 123.9 (q, J_{CF} = 271 Hz, CF_3), 121.5 (q, J_{CF} = 3 Hz, CH), 114.7 (q, J_{CF} = 3.5 Hz, CH), 40.2 (CH), 33.3 (CH_2), 25.5 (CH_2). ^{19}F NMR (282 MHz, $CDCl_3$) δ – 63.06. ATR-FTIR (thin film): 2956, 2873, 2107, 1713, 1612, 1578, 1505, 1417, 1328, 1276, 1122, 872, 826 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{12}H_{12}N_3F_3$ $(M)^+$: 255.0983, found: 255.0969.



4l

1-Azido-2-(2,2-dimethylcyclopentyl)benzene 4l. The general procedure was following using impure aniline **s25** (derived from 0.96 g of nitrobenzene **s26** containing some impurity), 0.95 mL of *t*-$BuNO_2$, and 0.84 mL of Me_3SiN_3. Purification by MPLC (0:100 – 10:90 EtOAc: hexanes) afforded the product as a brown yellow oil (0.370 g, 35% over 3 steps, calculation based on corresponding boronic acid), R_f = 0.8 (15:75 EtOAc:hexanes, visualized by 254 nm UV light). ^1H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.30 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 3.27 (dt, *J* = 1.5 Hz, *J* = 8.5 Hz, 1H), 2.00 – 2.05 (m, 2H), 1.77 – 1.91 (m, 2H), 1.63 – 1.66 (m, 2H), 1.08 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6 (C), 134.6 (C), 129.3 (CH), 127.0 (CH), 124.1 (CH), 118.0 (CH), 48.0 (CH), 43.2 (C), 41.6 (CH_2), 30.9 (CH_2), 28.8 (CH_3), 23.6 (CH_3), 22.0 (CH_2) ATR-FTIR (thin film): 2953, 2118, 2084, 1578, 1445, 1294, 908, 734 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{17}N_3$ $(M)^+$: 215.1422, found: 215.1441.



4m

1-Azido-2-cycloheptylbenzene 4m. The general procedure was following using crude aniline (derived from 2 mmol of nitrobenzene **s27**), 0.95 mL of *t*-$BuNO_2$, and 0.84 mL of Me_3SiN_3. Purification by MPLC (0:100 – 10:90 EtOAc: hexanes) afforded the product as a yellow oil (0.288 g, 67% from **s27**), R_f = 0.8 (15:75 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 8 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 3.07 (m, 1H), 1.88 (m, 4H), 1.79 (m, 2H), 1.66 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2 (C), 136.6 (C), 127.5 (CH), 126.7 (CH), 124.9 (CH), 118.0 (CH), 40.3 (CH), 35.8 (CH_2), 28.0 (CH_2), 27.5 (CH_2). ATR-FTIR (thin film): 2925, 2854, 2118, 1579, 1487, 1446, 1288, 1084, 904, 727 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{17}N_3$ $(M)^+$: 215.1423, found: 215.1428.

III. Rhodium-Catalyzed Formation of Indolines from Aryl Azides.

A. General Procedure for the Screening of Catalysts to Promote the Decomposition of Aryl Azides.

1a **2a** (s18)

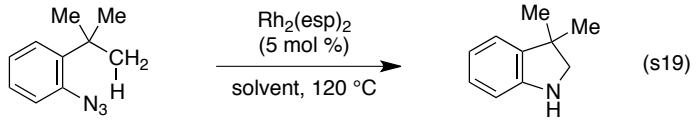
To a mixture of 0.0175 g of 1-azido-2-*tert*-butylbenzene **1a** (0.1 mmol), and a metal salt (0 – 5 mol %) in Schlenk tube was added 0.50 mL of solvent. The resulting mixture was heated, and after 16 h, the heterogenous mixture was filtered through a short pad of Al_2O_3. The filtrate was concentrated *in vacuo*. The resulting oil was dissolved in 1.5 mL of $CDCl_3$ and 0.007 mL of dibromomethane (0.1 mmol) was added. The area of the C6–H peak in **2a** was compared to the area of CH_2Br_2 to derive a yield.

Table s1. Survey of Transition Metal Complexes.

entry	metal salt	mol %	solvent	T (°C)	**2a** yield, %[a]
1	none	n.a.	mesitylene	220	No rxn
2	none	n.a.	PhMe	120	No rxn
3	$[(cod)Ir(OMe)]_2$	5	PhMe	120	No rxn
4	$Ru(cod)Cl_2$	5	PhMe	120	No rxn
5	$[Ru(p\text{-cymene})Cl_2]_2$	5	PhMe	120	No rxn
6	$Ru_3(CO)_{12}$	5	PhMe	120	No rxn
7	$RuBr_3$	5	PhMe	120	No rxn
8	$RuCl_3$	5	PhMe	120	No rxn
9	Ir(cod)(cp')	5	PhMe	120	No rxn
10	$[(cod)Rh(OMe)]_2$	5	PhMe	120	No rxn
11	$RhCl_4$	5	PhMe	120	No rxn
12	$[Rh(cod)_2]SO_3CF_3$	5	PhMe	120	No rxn
13	$[Rh(PPh_3)_3]Cl$	5	PhMe	120	No rxn
14	$[(HO)Rh(cod)]_2$	5	PhMe	120	Aniline formed (10)
15	$Rh(OAc)_4$	5	PhMe	120	No rxn
16	$Rh_2(O_2CC_7H_{15})_4$	5	PhMe	120	35
17	$Rh_2(O_2CC_3F_7)_4$	5	PhMe	120	20
18	$Rh_2(esp)_2$	5	PhMe	120	75
19	$Rh_2(esp)_2$	2	PhMe	120	45
20	$Rh_2(S\text{-PTAD})_4$	5	PhMe	120	No rxn
21	ZnI_2	5	PhMe	120	No rxn
22	$FeBr_2$	5	PhMe	120	Aniline formed (dec)
23	CuBr	5	PhMe	120	No rxn
24	AgOTf	5	PhMe	120	No rxn
25	$Ag(O_2CCF_3)$	5	PhMe	120	No rxn
26	AgOAc	5	PhMe	120	No rxn
27	CoTTP[b]	5	PhMe	120	No rxn

[a]As determined using ^1H NMR spectroscopy. [b]TTP = tetraphenylporphyrin.

Table s2. Survey of Solvents.

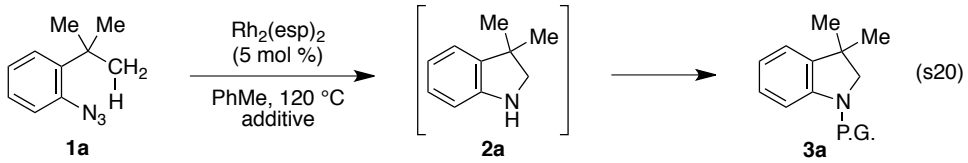


1a **2a** (s19)

entry	metal salt	mol %	solvent	T (°C)	**2a** yield, %[a]
1	$Rh_2(esp)_2$	5	PhMe	120	75
2	$Rh_2(esp)_2$	5	PhH	120	73
3	$Rh_2(esp)_2$	5	PhBr	120	56
4	$Rh_2(esp)_2$	5	PhCl	120	47
5	$Rh_2(esp)_2$	5	1,3-$C_6H_4Cl_2$	120	61
6	$Rh_2(esp)_2$	5	$PhCF_3$	120	31
7	$Rh_2(esp)_2$	5	DCE	120	47

[a]As determined using ^{1}H NMR spectroscopy.

Table s3. Survey of Additives.

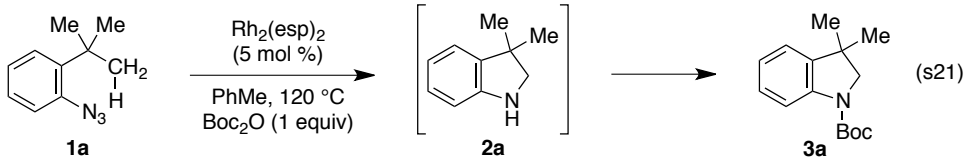


1a **2a** **3a** (s20)

entry	metal salt	mol %	solvent	T (°C)	additives	**2a** yield, %[a]
1	$Rh_2(esp)_2$	5	PhMe	120	TsCl (1 equiv)	20
2	$Rh_2(esp)_2$	5	PhMe	120	TsCl (1 equiv) Et_3N (3 equiv)	No rxn
3[b]	$Rh_2(esp)_2$	5	PhMe	120	TsCl (1 equiv) DTBMP (1 equiv)	No rxn
4	$Rh_2(esp)_2$	5	PhMe	120	TsCl (1 equiv) Cs_2CO_3 (1 equiv)	20
5	$Rh_2(esp)_2$	5	PhMe	120	Boc_2O (1 equiv)	83
6	$Rh_2(esp)_2$	5	PhMe	120	Moc_2O (1 equiv)	45
7	$Rh_2(esp)_2$	5	PhMe	120	Ac_2O (1 equiv)	73
8	$Rh_2(esp)_2$	5	PhMe	120	Bz_2O (1 equiv)	aniline
9	$Rh_2(esp)_2$	5	PhMe	120	$(CF_3CO)_2O$ (1 equiv)	35
10	$Rh_2(esp)_2$	5	PhMe	120	Tf_2O (1 equiv)	20

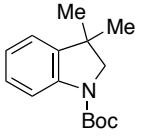
[a]As determined using ^{1}H NMR spectroscopy.[b]DTBMP = 2,6-di-*tert*-butyl-4-methylpyridine.

B. Optimized General Procedure.



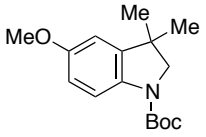
To a mixture of 0.070 g of aryl azide **1a** (0.40 mmol), 0.0870 g of Boc_2O, and 0.0153 g of $Rh_2(esp)_2$ (5 mol%) in Schlenk tube was added 0.80 mL of PhMe. The resulting mixture was heated at 120 °C. After 16 h, the mixture was cooled to room temperature and diluted with 5 mL of a saturated aqueous solution of Na_2CO_3. The phases were separated, and the aqueous phase was extracted with an additional 2 × 5 mL of CH_2Cl_2. The combined organic phases were washed with 10 mL of brine. The resulting organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. Purification of the residue by flash chromatography (0:100 – 10:90 EtOAc: hexanes) with Al_2O_3 afforded the indoline (0.082 g, 84%).

C. Scope and Limitations of Indoline Formation.



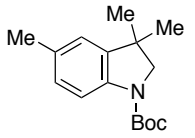
3a

Indoline 3a. [12] The general procedure was followed with 0.0700 g of aryl azide **1a** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product, a brown oil, as a 66:34 mixture of amide rotamers (0.082 g, 84%), R_f = 0.65 (15:75 EtOAc:hexanes, visualized by 254 nm UV light). Indoline **3a** was previously reported by Faul and co-workers.[12] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 20 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 3.72 (s, 2H), 1.58 (s, 9H), 1.33 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.7 (C), 141.7 (C), 140.1 (C), 127.6 (CH), 122.4 (CH), 121.9 (CH), 114.7 (CH), 80.3 (C), 62.3 (CH_2), 39.5 (C), 28.8 (CH_3), 28.5 (CH_3). ATR-FTIR (thin film): 3004, 2963, 2925, 1697, 1602, 1484, 1455, 1381, 1335, 1290, 1159, 1016, 857, 747 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{15}H_{21}NO_2$ $(M)^+$: 247.1572, found: 247.1581.



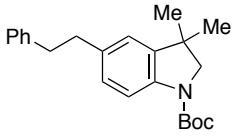
3b

Indoline 3b. The general procedure was followed with 0.0820 g of aryl azide **1b** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product, a red oil, as a 66:34 mixture of amide rotamers (0.0698 g, 63%), R_f = 0.38 (15:75 EtOAc:hexanes, visualized by 254 nm UV light): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 6.69 (d, *J* = 8.5 Hz, 1H), 6.67 (s, 1H), 3.78 (s, 3H), 3.68 (s, 2H), 1.54 (s, 9H), 1.31 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7 (C), 152.6 (C), 141.7 (C), 135.4 (C), 115.1 (CH), 111.8 (CH), 108.8 (CH), 80.1 (C), 62.6 (CH_3), 62.2 (C), 55.7 (CH_3), 39.7 (C), 28.5 (CH_3). ATR-FTIR (thin film): 3026, 2960, 2934, 1685, 1598, 1493, 1394, 1274, 1221, 1143, 1082, 1015, 807, 763 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{23}NO_3$ $(M)^+$: 277.1678, found: 277.1689.



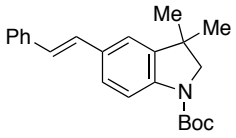
3c

Indoline 3c. The general procedure was followed with 0.0756 g of aryl azide **1c** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product, a yellow oil, as a 65:35 mixture of amide rotamers (0.0564 g, 54%), R_f = 0.55 (15:75 EtOAc:hexanes, visualized by 254 nm UV light): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 6.97 (d, *J* = 7 Hz, 1H), 6.91 (s, 1H), 3.68 (s, 2H), 2.31 (s, 3H), 1.56 (s, 9H), 1.31 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6 (C), 131.8 (CH), 129.7 (C), 128.0 (CH), 124.1 (C), 122.6 (C), 114.4 (CH), 80.2 (C), 62.4 (CH_2), 57.7 (C), 28.7 (CH_3), 28.5 (CH_3), 21.0 (CH_3). ATR-FTIR (thin film): 2977, 2929, 2871, 1689, 1613, 1491, 1470, 1432, 1392, 1338, 1282, 1146, 1021, 860, 817 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{23}NO_2$ $(M)^+$: 261.1729, found: 261.1724.



3d

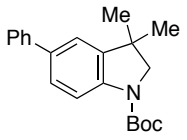
Indoline 3d. The general procedure was followed with 0.1116 g of aryl azide **1d** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product, a brown yellow oil, as 68:32 mixture of amide rotamers (0.0899 g, 64%), R_f = 0.52 (15:75 EtOAc:hexanes, visualized by 254 nm UV light): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.3 (t, *J* = 7.5 Hz, 2H), 7.21 (m, 3H), 7.04 (d, *J* = 8 Hz, 1H), 6.85 (s, 1H), 3.72 (s, 2H), 2.91 (s, 4H), 1.60 (s, 9H), 1.32 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9 (C), 152.7 (C), 141.9 (CH), 135.9 (CH), 128.6 (CH), 128.3 (CH), 127.6 (CH), 125.9 (CH), 122.3 (C), 122.2 (C), 114.5 (CH), 80.2 (C), 62.5 (CH_2), 39.5 (C), 38.4 (CH_2), 37.7 (CH_2), 28.7 (CH_3), 28.6 (CH_3). ATR-FTIR (thin film): 3022, 2975, 2927, 1683, 1489, 1336, 1144, 1021, 907, 818, 728 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{23}H_{29}NO_2$ $(M)^+$: 351.2198, found: 351.2187.



3e

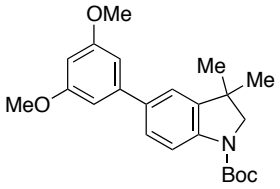
Indoline 3e. The general procedure was followed with 0.1108 g of aryl azide **1e** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product, a brown yellow oil, as a 66:34 mixture of amide rotamers (0.0977 g, 70%), R_f = 0.47 (15:75 EtOAc:hexanes, visualized by 254 nm UV light): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (s, 1H), 7.51 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 3H), 7.29 (s, 1H), 7.25 (t, *J* = 8 Hz, 1H), 7.10 (d, *J* = 16.5 Hz, 1H), 7.02 (d, *J* = 16.5 Hz, 1H), 3.74 (s, 2H), 1.58 (s, 9H), 1.37 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.9 (C), 152.6 (C), 141.5 (C), 140.8 (C), 137.7 (CH), 131.9 (CH), 128.7 (CH), 127.2 (CH), 126.7 (CH), 126.6 (CH), 126.3 (CH), 119.8 (C), 114.7 (CH), 80.6 (C), 62.6 (CH_2), 39.4 (C), 28.8 (CH_3), 28.5 (CH_3). ATR-FTIR (thin film): 3026, 2974, 2931, 1692, 1596, 1488, 1438, 1378,

1335, 1244, 1145, 1019, 960, 816 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{23}H_{27}NO_2$ $(M)^+$: 349.2042, found: 349.2030.



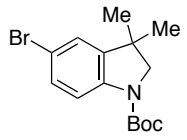
3f

Indoline 3f. The general procedure was followed with 0.1005g of aryl azide **1f** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product, a brown yellow oil, as a 66:34 mixture of amide rotamers (0.0564 g, 54%), R_f = 0.55 (15:75 EtOAc:hexanes, visualized by 254 nm UV light):^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (s, 1H), 6.97 (d, *J* = 7 Hz, 1H), 6.91 (s, 1H), 3.68 (s, 2H), 2.31 (s, 3H), 1.56 (s, 9H), 1.31 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6 (C), 141.3 (C), 135.7 (C), 128.8 (CH), 126.9 (CH), 126.8 (CH), 126.6 (CH), 121.1 (C), 120.9 (C), 120.8 (CH), 114.9 (CH), 80.6 (C), 62.7 (CH_2), 39.6 (C), 28.8 (CH_3), 28.5 (CH_3). ATR-FTIR (thin film): 2977, 2929, 2871, 1689, 1613, 1491, 1470, 1432, 1392, 1338, 1282, 1146, 1021, 860, 817 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{21}H_{25}NO_2$ $(M)^+$: 323.1885, found: 323.1896.



3g

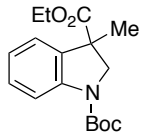
Indoline 3g. The general procedure was followed with 0.1244g of aryl azide **1g** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product, a brown yellow oil, as a 64:36 mixture of amide rotamers (0.0889 g, 58%), R_f = 0.48 (15:75 EtOAc:hexanes, visualized by 254 nm UV light): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.31 (s, 1H), 6.72 (s, 2H), 6.45 (s, 1H), 3.86 (s, 6H), 3.76 (s, 2H), 1.59 (s, 9H), 1.38 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.1 (C), 152.6 (C), 143.5 (C), 141.5 (C), 140.8 (C), 135.6 (CH), 126.6 (CH), 120.8 (C), 114.8 (CH), 105.2 (CH), 98.7 (CH), 80.6 (C), 62.7 (CH_2), 55.5 (CH_3), 39.5 (C), 28.8 (CH_3), 28.5 (CH_3). ATR-FTIR (thin film): 3007, 2962, 2931, 1685, 1594, 1469, 1389, 1369, 1333, 1203, 1146, 1065, 826, 647 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{23}H_{29}NO_4$ $(M)^+$: 383.2097, found: 383.2114.



3h

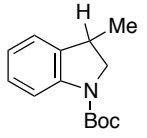
Indoline 3h. The general procedure was followed with 0.1010g of aryl azide **1h** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product as a yellow oil (0.0950 g, 73%), R_f = 0.59 (15:75 EtOAc:hexanes, visualized by 254 nm UV light): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.26 (s, 1H), 7.17 (s, 1H), 3.69 (s, 2H), 1.55 (s, 9H), 1.30 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4 (C), 140.9 (C), 130.4 (CH), 125.3 (CH), 122.4 (C), 116.2 (CH), 114.7 (C), 80.8 (C). 62.4 (CH_2), 39.5 (C), 28.6

(CH_3), 28.5 (CH_3). ATR-FTIR (thin film): 2970, 1694, 1594, 1482, 1378, 1337, 1247, 1147, 1021, 819 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{15}H_{20}BrNO_2$ $(M)^+$: 325.0677, found: 325.0669.



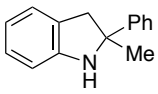
6a

Indoline 6a. The general procedure was followed with 0.0932 g of aryl azide **4a** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product, a yellow oil, as a 66:34 mixture of amide rotamers (0.0854g, 70%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 8 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 4.57 (d, *J* = 11 Hz, 1H), 4.17 (m, 2H), 3.71 (s, 1H), 1.58 (s, 9H), 1.56 (s, 3H), 1.24 (t, *J* = 7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.8 (C), 152.2 (C), 142.1 (C), 133.5 (C), 128.8 (CH), 123.9 (CH), 122.4 (CH), 114.8 (CH), 80.8 (C), 65.9 (C), 61.5 (CH_2), 57.9 (CH_2), 28.5 (CH_3), 25.7 (CH_3), 14.1 (CH_3). ATR-FTIR (thin film): 2976, 2928, 1730, 1702, 1599, 1484, 1389, 1336, 1143, 1016, 858, 750 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{17}H_{23}NO_4$ $(M)^+$: 305.1627, found: 305.1636.



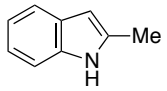
6b

Indoline 6b. The general procedure was followed with 0.0644 g of aryl azide **4b** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product, a brown yellow oil, as 67:33 mixture of amide rotamers (0.0187 mg, 20%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.17 (d, *J* = 8.5 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 4.15 (t, *J* = 8 Hz, 1H), 3.49 (t, *J* = 7 Hz, 1H), 3.39 (m, 1H), 1.57 (s, 9H), 1.32 (d, *J* = 7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.6 (C), 135.9 (C), 127.5 (CH), 123.5 (CH), 122.2 (CH), 116.6 (C), 114.6 (CH), 80.3 (C), 55.7 (CH_2), 34.1 (C), 28.5 (CH_3), 20.3 (CH_3). ATR-FTIR (thin film): 2978, 2931, 1690, 1602, 1484, 1452, 1391, 1171, 1145, 1045, 905, 648 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{14}H_{19}NO_2$ $(M)^+$: 233.1416, found: 233.1411.



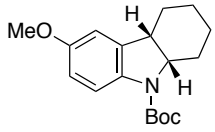
6c

Indoline 6c. The general procedure was followed (without the presence of Boc_2O) with 0.0948g of aryl azide **4c** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product as a yellow oil (0.070 g, 55%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 2H), 7.24 – 7.27 (m, 1H), 7.07 – 7.10 (m, 2H), 6.70 – 6.76 (m, 2H), 4.02 (br, 1H), 4.23 (dd, *J* = 15.5 Hz, *J* = 18.0 Hz, 2H), 1.67 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.0 (C), 148.8 (C), 128.4 (CH), 127.5 (CH), 126.6 (CH), 125.2 (CH), 124.9 (CH), 118.7 (CH), 109.2 (CH), 66.3 (C), 46.0 (CH_2), 29.4 (CH_3); ATR-FTIR (thin film): 3358, 3030, 1609, 1483, 1253, 904, 693 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{15}H_{15}N$ $(M)^+$: 209.2863, found: 209.1218.



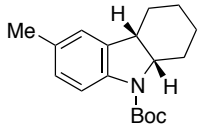
6d

Indoline 6d. The general procedure was followed (without the presence of Boc_2O) with 0.0644 g of aryl azide **4d** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product as a brown yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (br, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.28 – 7.30 (m, 1H), 7.06 – 7.13 (m, 2H), 6.23 (s, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.1 (C), 135.0 (C), 129.1 (C), 121.0 (CH), 119.6 (CH), 110.2 (CH), 100.4 (CH), 13.8 (CH_3) only signals visible; ATR-FTIR (thin film): 3411, 2928, 1727, 1455, 1284, 1047, 904, 721 cm^{-1}.



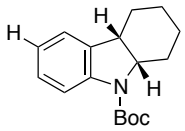
6e

Indoline 6e. The general procedure was followed with 0.0924g of aryl azide **4e** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product as a yellow oil (0.0970 g, 80%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (s, 1H), 6.71 (s, 1H), 6.68 (d, *J* = 9.5 Hz, 1H), 4.33 (s, 1H), 3.78 (s, 3H), 3.39 (t, *J* = 5 Hz, 1H), 2.18 (t, *J* = 14 Hz, 1H), 2.06 (s, 1H), 1.78 (s, 1H), 1.55 (m, 11H), 1.2 (m, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8 (C), 152.2 (C), 115.9 (C), 115.4 (C), 111.3 (CH), 109.7 (CH), 108.3 (CH), 80.8 (C), 60.5 (CH), 55.7 (CH_3), 48.4 (CH), 39.5 (CH_2), 28.5 (CH_3), 24.2 (CH_2), 22.4 (CH_2), 21.1 (CH_2). ATR-FTIR (thin film): 3016, 2915, 2923, 1657, 1604, 1489, 1334, 1291, 1153, 1023, 877, 775 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{18}H_{25}NO_3$ $(M)^+$: 303.1834, found: 303.1821.



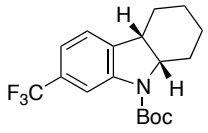
6f

Indoline 6f. The general procedure was followed with 0.0861g of aryl azide **4f** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product as a yellow oil (0.0838 g, 73%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8 Hz, 1H), 6.97 (d, *J* = 8 Hz, 1H), 6.94 (s, 1H), 4.33 (s, 1H), 3.39 (t, *J* = 6.5 Hz, 1H), 2.32 (s, 3H), 2.24 (m, 1H), 2.10 (m, 2H), 1.57 (m, 11H), 1.48 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3 (C), 131.8 (CH), 127.6 (CH), 123.4 (C), 122.1 (C), 115.3 (CH), 114.6 (C), 80.8 (C), 60.5 (CH), 39.3 (CH), 28.5 (CH_3), 27.9 (CH_3), 24.2 (CH_2), 22.4 (CH_2), 21.1 (CH_2) only visible signals. ATR-FTIR (thin film): 3013, 2945, 2956, 1667, 1656, 1434, 1323, 1245, 1023, 845, 767 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{18}H_{25}NO_2$ $(M)^+$: 287.1885, found: 287.1880.



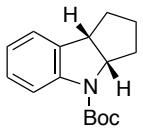
6g

Indoline 6g. [13] The general procedure was followed with 0.0804g of aryl azide **4g** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product as a dark brown oil (0.0765 mg, 70%). Indoline **6g** was previously reported by Gilchrist and co-workers.[13] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7 Hz, 1H), 6.98 (t, *J* = 7 Hz, 1H), 4.34 (s, 1H), 3.42 (t, *J* = 5.5 Hz, 1H), 2.27 (d, *J* = 14.5 Hz, 1H), 2.08 (s, 1H), 1.80 (m, 1H), 1.57 (m, 11H), 1.21 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3 (C), 127.3 (CH), 122.6 (CH), 122.4 (CH), 121.4 (C), 115.5 (CH), 114.8 (C), 81.0 (C), 60.5 (CH), 39.3 (CH), 28.5 (CH_3), 24.1 (CH_2), 22.4 (CH_2), 21.1 (CH_2) only visible signals. ATR-FTIR (thin film): 2969, 2929, 2859, 1691, 1603, 1477, 1460, 1389, 1365, 1168, 1141, 909, 647 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{17}H_{23}NO_2$ $(M)^+$: 273.1729, found: 273.1734.



6h

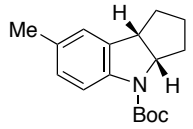
Indoline 6h. The general procedure was followed with 0.1076g of aryl azide **4h** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product as a yellow oil (0.0859 g, 63%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.24 (d, *J* = 8 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 4.38 (s, 2H), 3.44 (s, 1H), 2.26 (d, *J* = 14 Hz, 1H), 2.10 (d, *J* =11 Hz, 1H), 1.85 – 1.80 (m, 1H), 1.57 (m, 11H), 1.20 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1 (C), 142.6 (C), 137.7 (C), 129.8 (q, J_{CF} = 31.4 Hz, C), 124.4 (q, J_{CF} = 271 Hz, CF_3), 122.7 (CH), 119.5 (q, J_{CF} = 3.3 Hz, CH), 112.3 (q, J_{CF} = 4.1 Hz, CH), 81.2 (C), 60.7 (CH), 39.4 (CH), 28.4 (CH3), 27.2 (CH_2), 23.9 (CH_2), 22.1 (CH_2), 21.0 (CH_2); ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.43. ATR-FTIR (thin film): 3004, 2963, 2929, 1696, 1602, 1484, 1335, 1290, 1159, 1016, 857, 747 cm^{-1}. HRMS (EI) *m/z* calculated for $C_{17}H_{22}F_3NO_2$ $(M)^+$: 341.1603, found: 341.1619.



6i

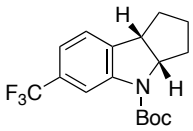
Indoline 6i. The general procedure was followed with 0.0748 g of aryl azide **4i** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product, a dark brown oil, as a 34:66 mixture of amide rotamers (0.0881 g, 85%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (br s, 0.59H), 7.50 (br s, 0.30H), 7.15 (s, 1H), 7.10 (d, *J* = 6.5 Hz, 1H), 6.94 (t, *J* = 7 Hz, 1H), 4.75 – 4.55 (br s, 1H), 3.78 (t, *J* = 8.5 Hz, 1H), 1.96 (m, 3H), 1.84 (m, 1H), 1.58 (m, 10H), 1.39 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ152.5 (C), 143.3 (C), 134.6 (C), 127.5 (CH), 124.1 (CH), 122.4 (CH), 114.4 (CH), 80.2 (C), 64.9 (CH), 44.9 (CH), 35.6 (CH_2), 34.9 (CH_2), 28.5 (CH_3), 23.9 (CH_2). ATR-FTIR (thin film): 2974, 2934, 2869, 1690, 1601, 1482, 1387, 1256, 1147, 1046, 859, 647 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{16}H_{21}NO_2$ $(M)^+$: 259.1575, found: 259.1564. See page SI2 *s*-120 for a ^{1}H NMR spectrum of the crude reaction mixture of indoline **5i**. Diagnostic data for disastereoselectivity

determination: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (d, *J* = 7.0 Hz, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.67 (t, *J* = 7.5 Hz, 1H), 6.53 (d, *J* = 7.5 Hz, 1H), 4.36 (t, *J* = 8.0 Hz, 1H), 3.781 (t, *J* = 7.5 Hz, 1H), 3.9 – 3.7 (br s, 1H), 1.96 (m, 1H), 1.81 – 1.56 (m, 5H).



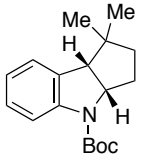
6j

Indoline 6j. The general procedure was followed with 0.0804 g of aryl azide **4j** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product, a yellow oil, as a 65:35 mixture of amide rotamers (0.0798 g, 73%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (br, 1H), 6.95 (s, 1H), 6.92 (s, 1H), 4.65 (br, 1H), 3.74 (t, *J* = 8 Hz, 1H), 2.29 (s, 3H), 1.97 (m, 4H), 1.56 (s, 9H), 1.40 (br, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4 (C), 141.0 (C), 134.7 (C), 131.8 (CH), 127.9 (CH), 124.8 (C), 114.1 (CH), 80.0 (C), 65.1 (CH), 44.9 (CH), 35.6 (CH_2), 34.8 (CH_2), 28.6 (CH_3), 23.9 (CH_3), 20.9 (CH_2). ATR-FTIR (thin film): 2975, 2930, 2845, 1691, 1609, 1585, 1420, 1387, 1257, 1137, 1034, 885, 649 cm^{-1}. HRMS (EI) *m/z* calculated for $C_{17}H_{23}NO_2$ $(M)^+$: 273.1729, found: 273.1734. See page SI2 *s*-124 for a ^{1}H NMR spectrum of the crude reaction mixture of indoline **5j**. Diagnostic data for disastereoselectivity determination: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.45 (t, *J* = 6.0 Hz, 1H), 3.79 (t, *J* = 8.0 Hz, 1H).



6k

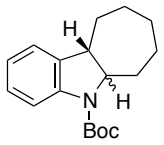
Indoline 6k. The general procedure was followed with 0.1020 g of aryl azide **4k** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product, a yellow oil, as a 68:32 mixture of amide rotamers (0.107 g, 82%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.19 (m, 2H), 4.71 (s, 1H), 3.79 (t, *J* = 8.5 Hz, 1H), 2.02 (m, 3H), 1.98 (m, 1H), 1. 83 (m, 1H), 1.56 (s, 9H), 1.38 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3 (C), 143.8 (C), 138.6 (C), 129.9 (q, J_{CF} = 30.6 Hz, C), 124.4 (q, J_{CF} = 270 Hz, CF_3), 124.2 (q, J_{CF} = 4.5 Hz, CH), 119.4 (CH), 111.3 (q, J_{CF} = 2.8 Hz, CH), 80.9 (C), 65.4 (CH), 44.9 (CH), 35.6 (C), 34.8 (CH_2), 28.4 (CH_3), 23.9 (CH_2). ATR-FTIR (thin film): 2974, 2932, 2867, 1689, 1674, 1580, 1521, 1469, 1345, 1233, 1145, 970, 750 cm^{-1}. HRMS (EI) *m/z* calculated for $C_{17}H_{20}FN_3O_2$ $(M)^+$: 327.1446, found: 327.1456. See page SI2 *s*-126 for a ^{1}H NMR spectrum of the crude reaction mixture of indoline **5k**. Diagnostic data for disastereoselectivity determination: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.45 (t, *J* = 7.5 Hz, 1H), 3.81 (t, *J* = 7.0 Hz, 1H).



6l

Indoline 6l. The general procedure was followed with 0.0860 g of aryl azide **4l** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography

(0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product, a yellow oil, as a 67:33 mixture of amide rotamers (0.101 g, 88%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (br, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 7.13 (d, *J* = 7.0 Hz, 1H), 6.92 (t, *J* = 7.0 Hz, 1H), 4.70 (s, 1H), 3.31 (d, *J* = 9.5 Hz, 1H), 2.33 (s, 1H), 1.90 (s, 1H), 1.56 (s, 9H), 1.45 (t, *J* = 7.5 Hz, 2H), 1.20 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.5 (C), 143.7 (C), 131.3 (C), 127.6 (CH), 125.2 (CH), 121.6 (CH), 114.4 (CH), 80.2 (C), 65.9 (CH), 55.5 (CH), 43.5 (CH_2), 40.0 (CH_2), 33.8 (C), 29.8 (CH_3), 28.5 (CH_3), 24.5 (CH_3). ATR-FTIR (thin film): 2963, 2931, 2864, 1688, 1596, 1483, 1458, 1386, 1344, 1271, 1166, 1141, 908, 724 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{18}H_{25}NO_2$ $(M)^+$: 287.1885, found: 287.1899. See page SI2 *s*-130 for a ^{1}H NMR spectrum of the crude reaction mixture of indoline **5i**. Diagnostic data for disastereoselectivity determination: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.5 Hz, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.64 (t, *J* = 7.5 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 4.48 (td, *J* = 6.5 Hz, 2.5 Hz, 1H), 3.84 (s, 1H), 3.28 (d, *J* = 9.5 Hz, 1H), 2.07 – 2.03 (br s, 1H), 1.75 – 1.71 (m, 1H), 1.60 – 1.56 (m, 1H), 1.46 – 1.42 (m, 1H), 1.15 (s, 3H), 0.87 (s, 3H).

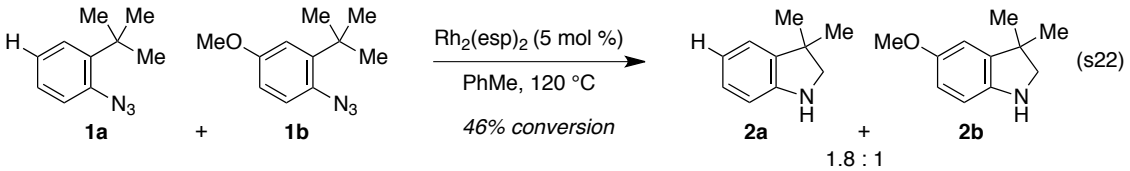


6m

Indoline 6m. The general procedure was followed with 0.0860 g of aryl azide **4m** (0.40 mmol), 0.0872 g of Boc_2O (0.40 mmol) and 0.0153 g of $Rh_2(esp)_2$ (0.02 mmol) in 0.8 mL of toluene. Purification by flash chromatography (0:100 – 10:90 EtOAc: hexanes) using Al_2O_3 afforded the product as an 82:18 mixture of diastereomers (0.0724 g, 63%). Major diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.15 (t, *J* = 8 Hz, 1H), 7.06 (d, *J* = 7 Hz, 1H), 6.95 (t, *J* = 7.5 Hz, 1H), 4.46 (s, 1H), 3.66 (m, 1H), 2.32 (m, 1H), 1.77 (m, 3H), 1.64 (m, 2H), 1.61 (m, 2H), 1.52 (s, 9H), 1.32 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3 (C), 143.4 (C), 133.7 (C), 127.3 (CH), 122.4 (CH), 122.2 (CH), 114.9 (CH), 81.0 (C), 65.9 (CH), 46.0 (CH), 31.1 (CH_2), 30.5 (CH_2), 28.5 (CH_3), 27.8 (CH_2), 27.3 (CH_2), 26.9 (CH_2); Selected data for the minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.99 (m, 1H), 3.21 (m, 1H), 2.81 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.7 (C), 135.6 (C), 133.1 (C), 127.7 (CH), 127.4 (CH), 123.6 (CH), 122.7 (CH), 77.3 (C), 66.6 (CH), 43.9 (CH), 33.5 (CH_2), 30.3 (CH_2), 29.9 (CH_2), 28.4 (CH_3), 26.8 (CH_2), 25.2 (CH_2). Mixture: ATR-FTIR (thin film): 3004, 2966, 2934, 1591, 1505, 1455, 1201, 1151, 901, 819, 724, 648 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{18}H_{25}NO_2$ $(M)^+$: 287.1885, found: 287.1898.

IV. Mechanistic Experiments.

A. Intermolecular Competition Experiment.



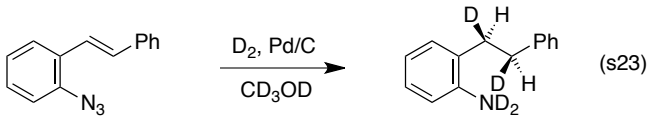
1a + **1b** → **2a** + **2b** (1.8 : 1)

To a mixture of 0.070 g of 1-azido-2-*tert*-butylbenzene **1a** (0.4 mmol), 0.0820 g of 1-azido-2-*tert*-butyl-4-methoxybenzene **1b** (0.4 mmol) and 0.0155 g of $Rh_2(esp)_2$ (5 mol %) in a Schlenk tube was added 0.80 mL of

PhMe. The resulting mixture was heated to 120 °C. After 3 h, the mixture was cooled to room temperature and diluted with 5 mL of a saturated aqueous solution of Na_2CO_3. The phases were separated, and the aqueous phase was extracted with an additional 2 × 5 mL of CH_2Cl_2. The combined organic phases were washed with 10 mL of brine. The resulting organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. Purification of the residue by flash chromatography (0:100 – 10:90 EtOAc: hexanes) recovered 6% azide **1b** and 48% azide **1a**.

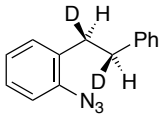
B. Isotope Labeling Studies.

1. Synthesis of Aryl Azide Substrates.



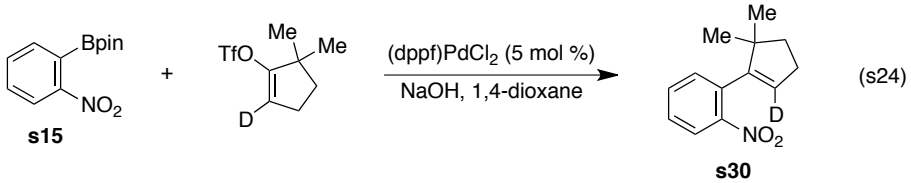
s28 **s29** (s23)

Aniline **s29.** A mixture of azide **s28** and Pd/C (Pd, 10 wt % on carbon powder) in CD_3OD were vigorous stirred at room temperature under deuterium atmosphere. After 3h, visualization of the reaction progress using TLC indicated consumption of the starting material. The balloon of D_2 was removed, and the mixture then was filtered through a pad of Celite, and the filtrate was concentrated *in vacuo* to afford aniline **s29**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (t, J = 7.5 Hz, 2H), 7.66 – 7.60 (m, 3H), 7.49 (q, J = 8.0 Hz, 2H), 7.21 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 3.75 (s, 0.5 H), 3.32 (m, 1H), 3.14 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3 (C), 141.9 (C), 129.5 (CH), 128.6 (CH), 128.5 (CH), 127.3 (CH), 126.2 (CH), 126.1 (C), 119.0 (C), 115.8 (C), 35.0 (q, J_{CD} = 25.9 Hz, CD), 33.1 (q, J_{CD} = 25.6 Hz, CD).



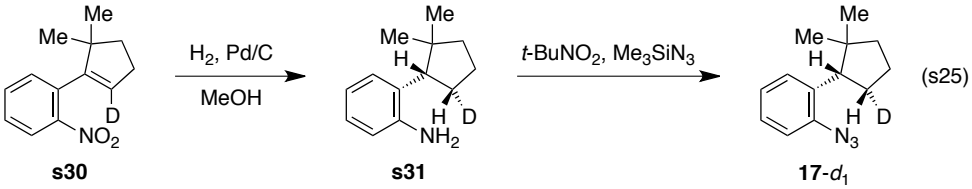
14-d_2

1-Azido-2-phenylethylbenzene 14-d_2. To a cooled solution of aniline in MeCN (0.2 M) was added dropwise *t*-$BuNO_2$ (4 equiv) and Me_3SiN_3 (3 equiv). The resulting solution was warmed to room temperature. After 1h, visualization of the reaction progress using TLC indicated the consumption of the starting material. Deionized H_2O was added to the reaction mixture. The mixture then was extracted with 2 × 30 mL of CH_2Cl_2. The combined organic phases were washed with 20 mL of brine. The resulting organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. Purification of the residue by MPLC (0:100 – 5:95 EtOAc: hexanes) afforded azide **14**-d_2: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (t, J = 7.0 Hz, 2H), 7.52 (m, 4H), 7.40 (m, 2H), 7.34 (t, J = 7.5 Hz, 1H), 3.19 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 130.6 (CH), 128.5 (CH), 128.4 (CH), 127.5 (CH), 126.0 (CH), 124.7 (CH), 118.1 (CH), 36.3 (q, J_{CD} = 25.8 Hz, CD), 33.1 (q, J_{CD} = 23.8 Hz, CD) only visible signals.



s15 **s30** (s24)

1-Nitro-2-dimethylcyclopentylbenzene-d_1 s30. To a mixture of 0.825 g of boronic ester **s15** (5.00 mmol), 1.80 g of NaOH (45.0 mmol) and 0.183 g of (dppf)$PdCl_2$ (0.224 mmol) was added 75 mL of 1,4-dioxane and 15.0 mL of water followed by 1.20 mmol of 2,2-dimethylcyclopentyltriflate-d_1 (prepared from 10.0 mmol of 2,2-dimethylcyclopentanone-d_2, which was prepared following the procedure reported by Shiner and Imhoff.)[14] The resultant mixture was heated to 100 °C. After 12 h, the mixture was cooled to room temperature and diluted with 10 mL of a saturated aqueous solution of NH_4Cl. The resulting mixture was separated, and the aqueous phase was extracted with an additional 2 × 30 mL of CH_2Cl_2. The combined organic phases were washed with 30 mL of brine. The resulting organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. Purification of the oily residue using MPLC (1:100 – 10:90 EtOAc: hexanes) afforded the 0.96 g of the impure nitrobenzene **s30**, which was submitted to the hydrogenation reaction without further purification.

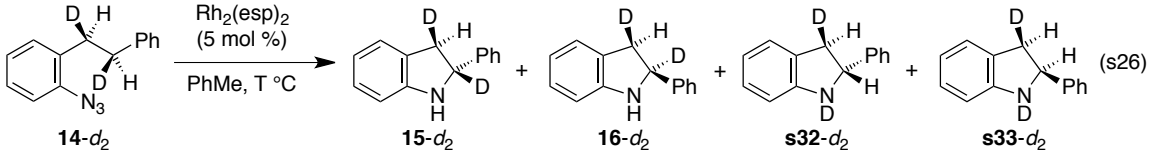


s30 **s31** **17-d_1**

Aryl Azide 17-d_1. A mixture of nitrobenzene **s30**-d_1 (0.96 g) and Pd/C (Pd, 10 wt % on carbon powder) in MeOH were vigorous stirred at room temperature under hydrogen atmosphere. After 3h, visualization of the reaction progress using TLC indicated consumption of the starting material. The mixture then was filtered through a pad of Celite, and the filtrate was concentrated *in vacuo* to afford crude aniline **s31**-d_1, which was subjected to the *t*-$BuNO_2$-mediated azidation reaction without further purification.

To a cooled solution of aniline in MeCN (0.2 M) was added dropwise 0.95 mL of *t*-$BuNO_2$ (4 equiv) and 0.84 mL of Me_3SiN_3 (3 equiv). The resulting solution was warmed to room temperature. After 1h, visualization of the reaction progress using TLC indicated the consumption of the starting material. De-ionized H_2O was then added to the reaction mixture. The mixture then was extracted with 2 × 30 mL of CH_2Cl_2. The combined organic phases were washed with 20 mL of brine. The resulting organic phase was dried over Na_2SO_4, filtered, and the filtrate was concentrated *in vacuo*. Purification of the residue by MPLC (0:100 – 5:95 EtOAc: hexanes) afforded azide **17**-d_1 as a single diastereomer (0.370 g, 35% from boronic acid **s15**), R_f = 0.8 (15:75 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.27 (m, 2H), 7.16 – 7.18 (m, 1H), 7.10 – 7.13 (m, 1H), 3.23 (d, J = 8.0 Hz, 1H), 1.95 – 2.00 (m, 1H), 1.74 – 1.87 (m, 2H), 1.59 – 1.65 (m, 2H), 1.95 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.6 (C), 134.5 (C), 129.3 (CH), 127.0 (CH), 124.1 (CH), 118.0 (CH), 47.9 (CH), 43.2, 41.5 (CH_2), 30.5 (t, J_{CD} = 18.9 Hz, CH), 28.8 (CH_3), 23.6 (CH_3), 21.9 (CH_2); ATR-FTIR (thin film): 2951, 2118, 2084, 1487, 1281, 1151, 746 cm^{-1}; HRMS (EI) *m/z* calculated for $C_{13}H_{16}DN_3$ $(M)^+$: 216.1500, found: 216.1499.

2. C–H Bond Amination Experiments.



14-d_2 **15-d_2** **16-d_2** **s32-d_2** **s33-d_2**

To a mixture of 0.0225 g of azide **14-d_2** (0.1 mmol) and 0.0038 g of $Rh_2(esp)_2$ (5 mol %) in a Schlenk tube was added 0.50 mL of toluene. The resulting mixture was heated to three different temperatures (120 °C, 100 °C and 80 °C) and after 16 h, the heterogenous mixture was filtered through a short pad of Al_2O_3. The filtrate was concentrated *in vacuo*, and the reaction progress was analyzed using ^{1}H NMR spectroscopy. The kinetic

isotope effect at each temperature was determined from the ratio of **s32-d_2** and **15-d_2**, which was determined by comparing the areas of the peaks at 4.16 ppm and 4.97 ppm. The ratio of **15**-d_2 and **16**-d_2 was determined by comparing the areas of the peaks at 3.01 and 3.46 ppm. The ^{1}H NMR spectra for these isotopic experiments can be found on pages S141-S143 in Supporting Information 2.

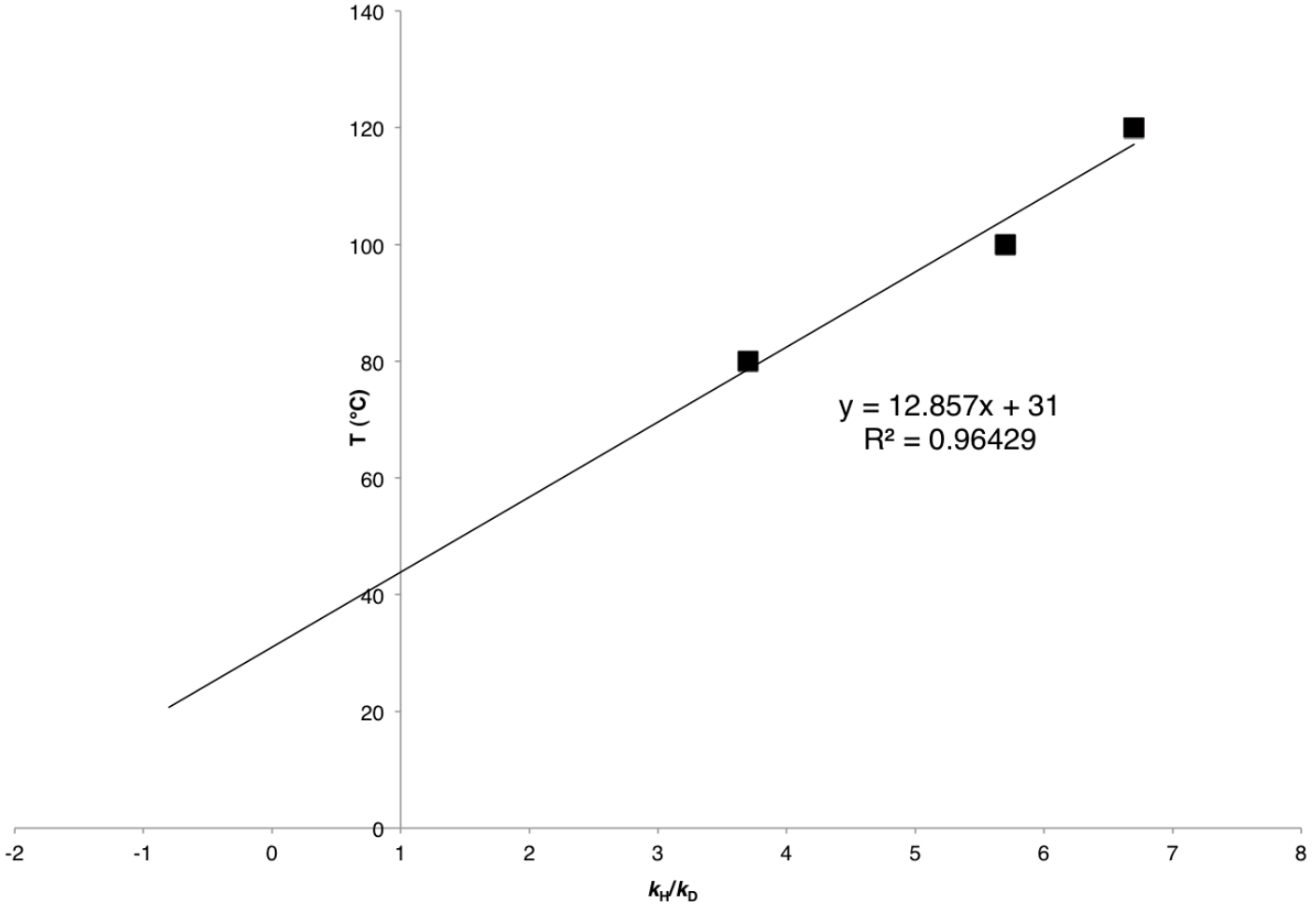
Table s4. Observed Kinetic Isotope Effects.

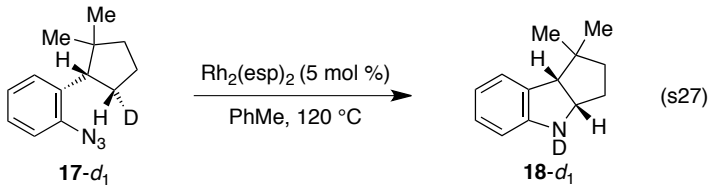
entry	T (°C)	k_H/k_D[a]
1	80	3.7
2	100	5.7
3	120	6.7

[a] As determined using ^{1}H NMR spectroscopy.

From these data, the isokinetic temperature was calculated to be approximately 43 °C (Figure s1), indicating that the reaction is under entropic control.

Figure s1. Temperature Dependence of k_H/k_D.





17-d_1 **18**-d_1

To a mixture of 0.0215 g of azide **17**-d_1 (0.1 mmol) and 0.0038 g of $Rh_2(esp)_2$ (5 mol %) in a Schlenk tube was added 0.50 mL of toluene-d_8. The resulting mixture was heated to 120 °C and after 16 h, the reaction progress was analyzed using ^{1}H NMR spectroscopy. The reaction conversion was determined to be 64.6% by comparison the pick C5 – H of azide **17**-d_1 with the C5 – H pick of indoline **18**-d_1. Only the formation of a single diastereomer of **18** was observed. No change in the diastereomeric ratio of **17** was observed.

V. References.

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