Rh_2(II)-Catalyzed Nitro Migration Reactions: Selective Synthesis of 3-Nitroindoles from β-Nitro Styryl Azides

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Supporting Information 1

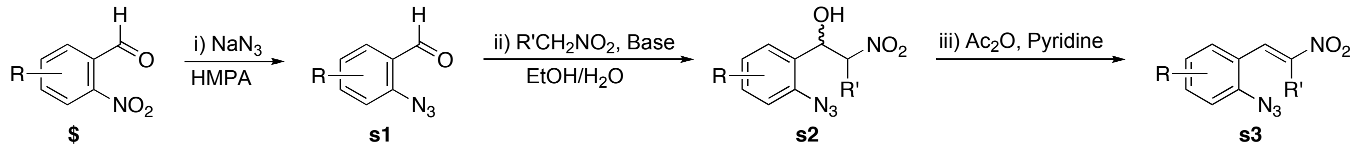
Contents

Full reference 4a: Bernotas, R. C.; Antane, S.; Shenoy, R.; Le, V.-D.; Chen, P.; Harrison, B. L.; Robichaud, A. J.; Zhang, G. M.; Smith, D.; Schechter, L. E. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 1657.

General. ^{1}H NMR, ^{13}C NMR, ^{13}C DEPT-135 NMR, ^{19}F NMR, and ^{31}P NMR spectra were recorded at ambient temperature using 500 MHz Bruker or 300 MHz Varian spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane or undeuterated solvent on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. Raw FIDs for all samples are available upon request. High resolution mass spectra were were obtained by peak matching. Melting points are reported uncorrected. Infared 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 medium pressure liquid chromatography (MPLC) to force flow the indicated solvent system down columns that had been packed with 60 Å (40 – 60 μm) mesh silica gel (SiO_2) unless otherwise noted. All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. 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 *ortho*-Azido-β-Nitrostyrenes

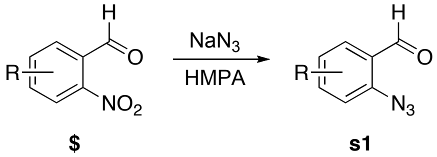
Scheme s1. Synthetic Route to *ortho*-Azido-β-Nitrostyrenes.



ortho-Azido-β-nitrostyrenes were synthesized using the route outlined in Scheme s1. Nucleophilic aromatic substitution of 2-azidobenzaldehydes using NaN_3 gave 2-azidobenzaldehydes **s1**. Subsequent nitroaldol (Henry) reaction afforded *ortho*-azido alcohols **s2**, which were subsequently hydrolyzed using Ac_2O and pyridine to give *ortho*-azidonitrostyrenes **s3**.

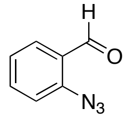
A. General Procedure for the Preparation of *ortho*-Azidobenzaldehydes

The requisite *ortho*-azidobenzaldehydes were prepared in one step using the reaction of commercially available *ortho*-nitrobenzaldehydes with sodium azide in HMPA as reported by Spagnolo and coworkers (eq. s1).[2] Yields were not optimized.

 (s1)

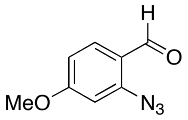
To a stirring solution of 2-nitrobenzaldehyde (5.00 g, 32 mmol) in HMPA (93 mL) was added sodium azide (4.34 g, 67 mmol) at 0 °C. The water bath was allowed to warm to ambient temperature and the reaction was stirred overnight. The mixture was poured over ice (200 g) and extracted with methyl *tert*-butyl ether (200 mL). The organic phase was washed with water (2 × 200 mL), concentrated *in vacuo*, taken up in CH_2Cl_2 and dried over Na_2SO_4. After decanting and reconcentration, the crude product was taken up in a portion of CH_2Cl_2 and concentrated onto neutral alumina and purified by MPLC (0:100 – 30:70 EtOAc:hexanes on SiO_2) to give pure product.

B. *ortho*-Azidobenzaldehyde Synthesis



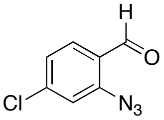
s4

***ortho*-Azidobenzaldehyde s4.**[3] The general procedure was followed using 5.00 g of 2-nitrobenzaldehyde (32 mmol), 4.34 g of sodium azide (67 mmol), and 93 mL of HMPA. MPLC (0:100 – 30:70 EtOAc:hexanes on SiO_2) afforded analytically pure **s4** as a low-melting solid (4.45 g, 93%), R_f = 0.58 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). The spectral data matched that reported by Driver and coworkers.[3] ^1H NMR ($CDCl_3$, 500 MHz): δ 10.36 (s, 1H), 7.89 (dd, J = 8.0, 2.0 Hz, 1H), 7.63 (m, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 188.6 (C), 143.0 (C), 135.5 (CH), 129.1 (CH), 127.0 (C), 124.9 (CH), 119.1 (CH); ATR-FTIR (thin film): 3076, 2882, 2120, 2100, 1685, 1592, 1475, 1273, 1196 cm^{-1}.



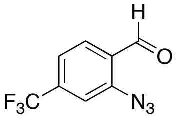
s5

***ortho*-Azidobenzaldehyde s5.**[3] The general procedure was followed using 1.00 g of 4-methoxy-2-nitrobenzaldehyde (5.4 mmol), 0.714 g of sodium azide (11 mmol), and 15 mL of HMPA. Workup afforded analytically pure **s5** as a white powder (0.927 g, 98%), mp 70 °C, $R_f = 0.60$ (30:70 EtOAc:hexanes, visualized by 254 nm UV light). The spectral data matched that reported by Driver and coworkers.[3] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.18 (s, 1H), 7.85 (d, $J = 8.5$ Hz, 1H), 6.74 (ddd, $J = 9.0, 2.5, 1.0$ Hz, 1H), 6.69 (d, $J = 2.0$ Hz, 1H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 187.3 (CH), 165.4 (C), 144.9 (C), 131.2 (CH), 121.1 (C), 111.1 (CH), 104.0 (CH), 55.8 (CH_3); ATR-FTIR (thin film): 3038, 2993, 2950, 2895, 2843, 2105, 1675, 1598, 1570, 1503, 1301, 1236, 1180, 1086, 1033 cm^{-1}.



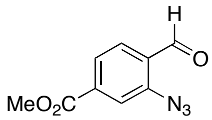
s6

***ortho*-Azidobenzaldehyde s6.** The general procedure was followed using 1.00 g of 4-chloro-2-nitrobenzaldehyde (5.3 mmol), 0.703 g of sodium azide (11 mmol), and 15 mL of HMPA. MPLC (0:100 – 50:50 benzene:hexanes on SiO_2) afforded analytically pure **s6** as off-white plates (0.210 g, 22%), mp 65 °C, $R_f = 0.67$ (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.27 (s, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.27-7.24 (m, 1H), 7.23-7.18 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 187.4 (CH), 144.0 (C), 141.7 (C), 130.2 (CH), 125.5 (CH), 125.4 (C), 119.2 (CH); ATR-FTIR (thin film): 3093, 2875, 2129, 1682, 1590, 1569, 1477, 1406, 1389, 1267, 1198, 1139, 1079 cm^{-1}; HRMS (EI) m / z calculated for C_7H_4NOCl $(M – N_2)^+$: 152.99814, found: 152.99737.



s7

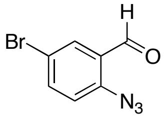
***ortho*-Azidobenzaldehyde s7.**[3] The general procedure was followed using 0.240 g of 2-nitro-4-(trifluoromethyl)benzaldehyde (1.1 mmol), 0.143 g of sodium azide (2.2 mmol), and 3.0 mL of HMPA. Workup afforded analytically pure **s7** as tan powder (0.205 g, 90%), mp 92 °C, $R_f = 0.64$ (20:80 EtOAc:hexanes, visualized by 254 nm UV light). The spectral data matched that reported by Driver and coworkers.[3] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.39 (s, 1H), 8.00 (d, $J = 8.5$ Hz, 1H), 7.50 (s, 1H), 7.48 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 187.7 (CH), 143.6 (C), 136.9 (q, $J_{C–F} = 33.0$ Hz, C), 129.9 (CH), 129.0 (C), 123.0 (q, $J_{C–F} = 271.4$ Hz, C) 121.7 (q, $J_{C–F} = 3.5$ Hz, CH), 116.3 (q, $J_{C–F} = 3.5$ Hz, CH); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –64.1; IR (thin film): 3054, 2876, 2120, 1688, 1418, 1328, 1167, 1129, 1071 cm^{-1}.



s8

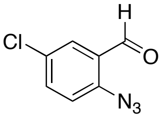
***ortho*-Azidobenzaldehyde s8.** The general procedure was followed using 2.09 g of methyl 4-formyl-3-nitrobenzoate (10 mmol), 1.31 g of sodium azide (20 mmol), and 50 mL of HMPA. MPLC (0:100 – 5:95 EtOAc:hexanes on SiO_2) afforded analytically pure **s8** as white solid (1.95 g, 95 %); mp 112 – 114 °C. ^{1}H

NMR ($CDCl_3$, 500 MHz): δ 10.38 (s, 1H), 7.94 – 7.92 (m, 2H), 7.85 – 7.83 (m, 1H), 3.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 188.1 (CH), 165.3 (C), 143.1 (C), 136.2 (C), 129.4 (C), 129.1 (CH), 125.6 (CH), 120.3 (C), 52.9 (CH_3); ATR-FTIR (thin film): 3458, 3015, 2970, 2122, 1738, 1366, 1216 cm^{-1}; HRMS (EI) *m / z* calculated for $C_9H_7O_3N_3$ $(M)^+$ 205.04875, found 205.04990.



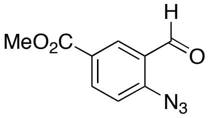
s9

***ortho*-Azidobenzaldehyde s9.**[4] The general procedure was followed using 5.00 g of 5-bromo-2-fluorobenzaldehyde (24 mmol), 3.15 g of sodium azide (48 mmol), and 48 mL of HMPA. Workup afforded analytically pure **s9** as yellow solid (5.05 g, 93%), mp 88 °C, R_f = 0.68 (15:85 EtOAc:hexanes, visualized by 254 nm UV light). The spectral data matched that reported by Hartley and coworkers.[4] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.26 (s, 1H), 7.98 (d, *J* = 2.5 Hz, 1H), 7.71 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 187.2 (CH), 141.9 (C), 138.1 (CH), 131.7 (CH), 128.0 (C), 120.8 (CH), 118.3 (C); ATR-FTIR (thin film): 2877, 2759, 2129, 1670 cm^{-1}.



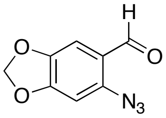
s10

***ortho*-Azidobenzaldehyde s10.** The general procedure was followed using 0.906 g of 5-chloro-2-nitrobenzaldehyde (4.8 mmol), 0.590 g of sodium azide (10 mmol), and 13 mL of HMPA. MPLC (0:100 – 50:50 benzene:hexanes on SiO_2) afforded analytically pure **s10** as off-white plates (0.407 g, 47%), mp 95 °C, R_f = 0.47 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.27 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.27-7.24 (m, 1H), 7.23-7.18 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 187.4 (CH), 144.0 (C), 141.7 (C), 130.2 (CH), 125.5 (CH), 125.4 (C), 119.2 (CH); ATR-FTIR (thin film): 3343, 3073, 3033, 2891, 2098, 1678, 1613, 1599, 1573, 1484, 1426, 1390, 1294, 1243, 1193, 1127, 1074, 1001 cm^{-1}; HRMS (EI) *m / z* calculated for C_7H_4NOCl: 152.99814, found: 152.99884.



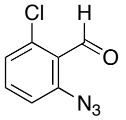
s11

***ortho*-Azidobenzaldehyde s11.** The general procedure was followed using 2.09 g of methyl 3-formyl-4-nitrobenzoate (10 mmol), 1.31 g of sodium azide (20 mmol), and 50 mL of HMPA. MPLC (0:100 – 3:97 EtOAc:hexanes on SiO_2) afforded analytically pure **s11** as white solid (1.97 g, 96%), mp 118 – 120 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.31 (s, 1H), 8.49 (d, *J* = 2.0 Hz, 1H), 8.23 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 187.7 (CH), 165.4 (C), 146.8 (C), 136.0 (CH), 130.8 (CH), 127.0 (C), 127.6 (C), 119.2 (CH), 52.5 (CH_3); ATR-FTIR (thin film): 3458, 3015, 2970, 2122, 1738, 1366, 1216 cm^{-1}; HRMS (EI) *m / z* calculated for $C_9H_7O_3N_3$ $(M)^+$ 205.04875, found 205.04980.



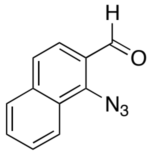
s12

***ortho*-Azidobenzaldehyde s12.** The general procedure was followed using 1.95 g of 6-nitrobenzo[*d*][1,3]dioxole-5-carbaldehyde (10 mmol), 1.31 g of sodium azide (20 mmol), and 50 mL of HMPA. MPLC (0:100 – 5:95 EtOAc:hexanes on SiO_2) afforded analytically pure **s12** as white solid (1.64 g, 86% yield), mp 111 – 113 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.17 (s, 1H), 7.29 (s, 1H), 6.72 (s, 1H), 6.07 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 186.6 (CH), 154.0 (C), 145.8 (C), 139.9 (C), 121.7 (C), 106.6 (CH), 102.7 (CH_2), 99.2 (CH); ATR-FTIR (thin film): 3040, 2110, 1670, 1614, 1491, 1252, 1033 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_5O_3N_3$ $(M)^+$ 191.03310, found 191.03398.



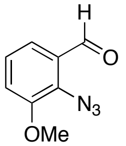
s13

***ortho*-Azidobenzaldehyde s13.** The general procedure was followed using 1.85 g of 6-chloro-2-nitrobenzaldehyde (10 mmol), 0.98 g of sodium azide (15 mmol), and 50 mL of HMPA. MPLC (0:100 – 1:40 EtOAc:hexanes on SiO_2) afforded analytically pure **s13** as white solid (0.83 g, 46% yield), mp 80 °C, $R_f = 0.59$ (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.46 (s, 1H), 7.48 (t, *J* = 8.5 Hz, 1H), 7.24 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.19 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (DMSO, 125 MHz): δ 188.9 (C), 135.5 (CH), 135.2 (C), 127.5 (CH), 124.3 (C), 124.0 (C), 120.2 (CH); ATR-FTIR (thin film): 3078, 2962, 2880, 2788, 2163, 2111, 1689, 1577, 1446, 1411, 1296, 1273, 1211, 1162, 1120, 1080, 1020 cm^{-1}; HRMS (EI) *m* / *z* calculated for C_7H_4NOCl $(M - N_2)^+$: 152.99814, found: 152.99775.



s14

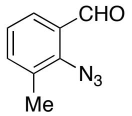
***ortho*-Azidobenzaldehyde s14.**[5] The general procedure was followed using 2.01 g of 1-nitro-2-naphthaldehyde (10 mmol), 1.31 g of sodium azide (20 mmol), and 50 mL of HMPA. MPLC (0:100 – 2:98 EtOAc:hexanes on SiO_2) afforded **s14** as white solid (1.80 g, 91%), mp 46 – 48 °C. The spectral data matched that reported by Boswell and coworkers.[5] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.53 (s, 1H), 8.37 (d, *J* = 8.5 Hz, 1H), 7.89 – 7.86 (m, 2H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.69 – 7.63 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 189.7 (CH), 140.3 (C), 137.0 (C), 129.7 (CH), 128.6 (CH), 127.9 (C), 127.6 (CH), 126.4 (CH), 125.4 (C), 124.9 (CH), 123.9 (CH); ATR-FTIR (thin film): 2361, 2341, 2111, 1733, 1693, 1334, 1264 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{11}H_7ON_3$ $(M)^+$: 197.05892, found: 197.05963.



s15

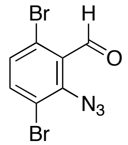
***ortho*-Azidobenzaldehyde s15.** The general procedure was followed using 1.81 g of 3-methoxy-2-nitrobenzaldehyde (10 mmol), 1.31 g of sodium azide (20 mmol), and 50 mL of HMPA. MPLC (0:100 – 30:70 EtOAc:hexanes on SiO_2) afforded analytically pure **s15** as white solid (1.61 g, 91% yield), mp 54 – 56 °C. ^{1}H

NMR ($CDCl_3$, 500 MHz): δ 10.15 (s, 1H), 7.82 (d, *J* = 8.5 Hz, 1H), 6.72 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.67 (d, *J* = 2.5 Hz, 1H), 3.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 187.2 (CH), 165.3 (C), 144.9 (C), 131.1 (CH), 121.0 (C), 111.1 (CH), 103.9 (CH), 55.8 (CH_3); ATR-FTIR (thin film): 2359, 2341, 2110, 1723, 1264 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_7O_2N_3$ $(M)^+$ 177.05383, found 177.05529.



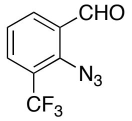
s16

***ortho*-Azidobenzaldehyde s16.** The general procedure was followed using 1.65 g of 3-methyl-2-nitrobenzaldehyde (10 mmol), 1.31 g of sodium azide (20 mmol), and 50 mL of HMPA. MPLC (0:100 – 10:90 EtOAc:hexanes on SiO_2) afforded analytically pure **s16** as colorless oil (1.53 g, 95% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.31 (s, 1H), 7.69 (d, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.0 (CH), 140.1 (C), 137.1 (CH), 133.6 (C), 129.2 (C), 129.0 (CH), 125.8 (CH), 17.9 (CH_3); ATR-FTIR (thin film): 2855, 2741, 2101, 1694, 1291,777 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_7ON_3$ $(M)^+$ 161.05892, found 161.05805.



s17

***ortho*-Azidobenzaldehyde s17.** The general procedure was followed using 3.07 g of 3,6-dibromo-2-nitrobenzaldehyde (10 mmol), 1.31 g of sodium azide (20 mmol), and 50 mL of HMPA. MPLC (0:100 – 30:70 EtOAc:hexanes on SiO_2) afforded analytically pure **s17** as white solid (2.74 g, 90% yield), mp 98 °C, $R_f = 0.66$ (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.39 (s, 1H), 7.61 (d, *J* = 6.5 Hz, 1H), 7.40 (d, *J* = 6.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.2 (C), 150.3 (C), 138.3 (CH), 132.0 (CH), 128.5 (C), 125.6 (C), 119.0 (C); ATR-FTIR: 3099, 3058, 2897, 2125, 1679, 1561, 1538, 1435, 1381, 1319, 1308, 1261, 1190, 1173, 1127 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_7H_3Br_2N_3O$ $(M)^+$: 302.86432, found: 302.86383.

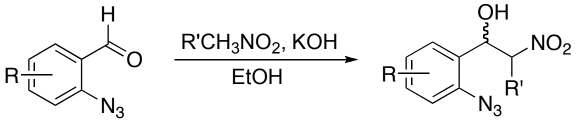


s18

***ortho*-Azidobenzaldehyde s18.** The general procedure was followed using 1.92 g of 2-fluoro-3-(trifluoromethyl)benzaldehyde (10 mmol), 1.31 g of sodium azide (20 mmol), and 50 mL of HMPA. MPLC (0:100 – 10:90 EtOAc:hexanes on SiO_2) afforded analytically pure **s18** as colorless oil (2.00 g, 93% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.37 (s, 1H), 8.06 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.91 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 188.6 (CH), 140.0 (C), 135.2 (CH), 132.5 (q, $J_{C\text{-}F}$ = 5.5 Hz, CH), 130.5 (C), 125.6 (CH), 124.9 (q, $J_{C\text{-}F}$ = 6.2 Hz, C), 122.8 (q, $J_{C\text{-}F}$ = 271.9 Hz, C); ATR-FTIR (thin film): 2871, 2755, 2120, 1701, 1583, 1317, 1128, 803, 661 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_4ON_3F_3$ $(M)^+$ 215.03065, found 215.03136.

C. General Procedure A for the Preparation of *ortho*-Azido-β-Nitro Alcohols

Unless otherwise noted, the requisite *ortho*-azido alcohols were prepared from the KOH-catalyzed condensation reaction of *ortho*-azidobenzaldehydes **s1** with nitromethane in EtOH derived from the KCl-catalyzed procedure by Molina and coworkers[6] as recommended by Gribble and coworkers (eq. s2).[7] Yields were not optimized.



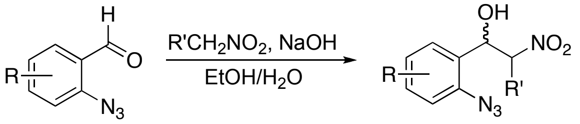
(s2)

s1 **s2**

To a stir bar-equipped flame-dried 50 mL round bottom flask containing a stirring mixture of 2-azidobenzaldehyde **s4** (1.00 g, 6.8 mmol), nitromethane (0.75 mL, 13 mmol, 2 equiv), and ethanol (10 mL) in an ice water bath was added a solution of KOH (0.474 g, 7.5 mmol, 1.1 equiv) in anhydrous ethanol (10 mL), dropwise. After stirring for 1 h, the reaction mixture was quenched with AcOH (3.4 mL) and water (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The comined organic layers were dried over Na_2SO_4 and concentrated to afford an oil. The crude product was taken up in a small amount of CH_2Cl_2 and added to silica gel, and the mixture was evaporated to dryness. The resulting powder was purified on a dry-packed MPLC column (0:100 – 30:70 EtOAc:hexanes on SiO_2) to give the product.

D. General Procedure B for the Preparation of *ortho*-Azido-β-Nitro Alcohols

Unless otherwise noted, the requisite *ortho*-azido alcohols were prepared from the aqueous NaOH-catalyzed condensation reaction of *ortho*-azidobenzaldehydes **s1** with nitromethane in EtOH and H_2O as reported by Muchowski and coworkers (eq. s3).[8] Yields were not optimized.

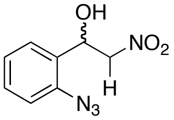


(s3)

s1 **s2**

To a stir bar-equipped flame-dried 25 mL round bottom flask containing a stirring mixture of 2-azidobenzaldehyde **s4** (0.500 g, 1.6 mmol), nitromethane (2.1 mL), water (1.6 mL), and ethanol (1.6 mL) in an ambient temperature water bath was added aqueous sodium hydroxide (0.25 mol L^{-1}, 0.5 mL), dropwise. After stirring overnight, the reaction mixture was poured into aqueous sodium chloride (20 mL) and extracted with CH_2Cl_2 (20 mL). The extract was washed with water (2 × 30 mL), dried over Na_2SO_4, and concentrated to afford an oil. The crude product was taken up in a small amount of CH_2Cl_2 and added to silica gel, and the mixture was evaporated to dryness. The resulting powder was purified on a dry-packed MPLC column (0:100 – 30:70 EtOAc:hexanes on SiO_2) to give the product.

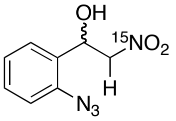
E. *ortho*-Azido-β-Nitro Alcohols Synthesis



s19

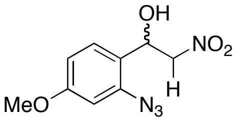
***ortho*-Azido-β-nitro alcohol s19.** General procedure A was followed using 1.00 g of 2-azidobenzaldehyde **s4** (6.8 mmol), 0.75 mL of nitromethane, and 0.474 g of KOH (7.5 mmol) in 20 mL of EtOH. Workup afforded

s19 as a beige oil (1.37 g, 96%), R_f = 0.49 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.56 (dd, J = 8.0, 1.5 Hz, 1H), 7.40 (td, J = 8.0, 1.5 Hz, 1H), 7.21 (td, J = 7.5, 1.0 Hz, 1H), 7.18 (dd, J = 8.0, 1.0 Hz, 1H), 5.64 (dd, J = 9.5, 3.0 Hz, 1H), 4.63 (dd, J = 8.5, 2.5 Hz, 1H), 4.50 (dd, J = 13.0, 9.5 Hz, 1H), 2.15 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.7 (C), 130.0 (CH), 128.9 (C), 127.6 (CH), 125.4 (CH), 118.1 (CH), 79.7 (CH_2), 66.9 (CH); ATR-FTIR (thin film): 2124, 1709, 1553, 1483, 1287 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_8N_4O_3$ $(M)^+$: 208.05954, found: 208.05906.



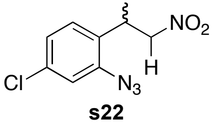
s20

***ortho*-Azido-β-nitro alcohol s20.** General procedure A was followed using 0.250 g of 2-azidobenzaldehyde **s4** (1.7 mmol), 0.215 g of ^{15}N-nitromethane (3.4 mmol), and 0.115 g of KOH (1.8 mmol) in 5.2 mL of EtOH. Workup afforded **s20** as a beige oil (0.310 g, 87%), R_f = 0.49 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.53 (dd, J = 8.0, 1.0 Hz, 1H), 7.39 (td, J = 7.5, 1.0 Hz, 1H), 7.19 (td, J = 7.5, 1.0 Hz, 1H), 7.16 (dd, J = 8.0, 1.0 Hz, 1H), 5.59 (d, J = 9.0 Hz, 1H), 4.59 (ddd, J = 13.0, 2.5, 1.0 Hz, 1H), 4.47 (ddd, J = 13.0, 9.5, 1.0 Hz, 1H), 3.32 (d, J = 4.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 136.6 (C), 129.9 (CH), 129.0 (C), 127.5 (CH), 125.4 (CH), 118.1 (CH), 79.7 (d, $J_{C\text{–}15N}$ = 7.4 Hz, CH_2), 66.9 (CH); ATR-FTIR (thin film): 2125, 1584, 1518, 1487, 1451, 1414, 1358, 1294, 1279, 1106, 1069 cm^{-1}; HRMS: (EI) *m* / *z* calculated for $C_8H_8N_3{}^{15}NO_3$ $(M)^+$: 209.05668, found: 209.05590.



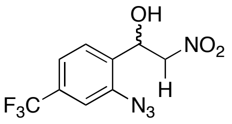
s21

***ortho*-Azido-β-nitro alcohol s21.** General procedure A was followed using 0.896 g of 4-methoxy-2-azidobenzaldehyde **s5** (5.1 mmol), 0.55 mL of nitromethane (10 mmol), and 0.353 g of KOH (5.6 mmol) in 15 mL of EtOH. Workup afforded analytically pure **s21** as a yellow oil (1.162 g, 96%), R_f = 0.79 (60:40 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43 (d, J = 8.5 Hz, 1H), 6.73 (dd, J = 8.5, 2.5 Hz, 1H), 6.69 (d, J = 2.5 Hz, 1H), 5.56 (dd, J = 9.0, 3.0 Hz, 1H), 4.57 (dd, J = 13.0, 3.0 Hz, 1H), 4.50 (dd, J = 13.0, 4.0 Hz, 1H), 3.84 (s, 3H), 2.97 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 160.9 (C), 137.8 (C), 128.7 (CH), 121.2 (C), 110.6 (CH), 104.3 (CH), 79.9 (CH_2), 66.8 (CH), 55.6 (CH_3); HRMS (EI) *m* / *z* calculated for $C_9H_{10}N_4O_4$ $(M)^+$: 238.07020, found: 238.07048.



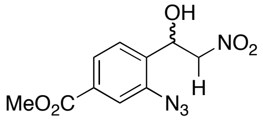
s22

***ortho*-Azido-β-nitro alcohol s22.** General procedure A was followed using 0.150 g of *ortho*-azidobenzaldehyde **s6** (0.83 mmol), 0.90 mL of nitromethane, and 0.059 g of KOH (0.91 mmol) in 2.5 mL of EtOH. Workup afforded analytically pure **s22** as a tan liquid (0.171 g, 85%), mp 68 °C, R_f = 0.23 (15:85 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): 7.50 (d, J = 8.0 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 7.15 (s, 1H), 5.57 (d, J = 9.0 Hz, 1H), 4.59 (ddd, J = 14.0, 3.0, 1.0 Hz, 1H), 4.44 (ddd, J = 14.0, 9.5, 1.0 Hz, 1H), 3.19 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.8 (C), 135.6 (C), 128.7 (CH), 127.4 (C), 125.6 (CH), 118.2 (CH), 79.4 (CH_2), 66.3 (CH); ATR-FTIR (thin film): 3548, 3486, 3032, 2935, 2108, 1548, 1484, 1379, 1282 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_7N_4O_3Cl$ $(M)^+$: 242.02067, found: 242.01981.



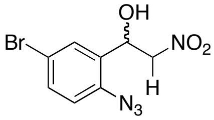
s23

***ortho*-Azido-β-nitro alcohol s23.** General procedure B was followed using 0.676 g of *ortho*-azidobenzaldehyde **s7** (3.1 mmol), 4.0 mL of nitromethane, and 1.0 mL of aqueous NaOH in 3.0 mL of EtOH and 3.0 mL of H_2O. Workup afforded **s23** as an off-white wax (0.866 g, 100%), R_f = 0.31 (20:80 EtOAc:hexanes, visualized by 254 nm UV light). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.76 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.0 Hz, 1H), 7.40 (s, 1H), 5.72-6.65 (m, 1H), 4.67 (dd, J = 14.0, 2.5 Hz, 1H), 4.45 (dd, J = 14.0, 9.5, 1H), 3.11 (d, J = 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.5 (C), 132.5 (C), 132.3 (q, $J_{C–F}$ = 33.3 Hz, C), 128.3 (CH), 125.5 (q, $J_{C–F}$ = 270.1 Hz, C), 122.1 (q, $J_{C–F}$ = 3.6 Hz, CH), 114.9 (q, $J_{C–F}$ = 3.6 Hz, CH), 79.1 (CH_2), 66.3 (CH); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –63.5; ATR-FTIR (thin film): 3325, 2961, 2119, 1553, 1413, 1327, 1287, 1117 cm^{-1}; HRMS (EI) *m / z* calculated for $C_9H_7N_4O_3F_3$ $(M)^+$: 276.04703, found: 276.04730.



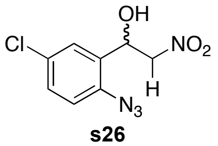
s24

***ortho*-Azido-β-nitro alcohol s24.** General procedure B was followed using 1.03 g of methyl 3-azido-4-formylbenzoate **s8** (5.0 mmol), 6.6 mL of nitromethane, and 1.6 mL of aqueous NaOH in 5.0 mL of EtOH and 5.0 mL of H_2O. MPLC (0:100 – 5:95 EtOAc:hexanes on SiO_2) afforded analytically pure **s24** as a colorless oil (1.22 g, 92%). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.84 (dd, J = 8.0, 1.5 Hz, 1H), 7.81 (d, J = 1.5 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 5.66 (d, J = 9.5 Hz, 1H), 4.65 (dd, J = 14.0, 2.5 Hz, 1H), 4.46 (dd, J = 14.0, 9.0 Hz, 1H), 3.94 (s, 3H), 3.30 (br, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.8 (C), 137.1 (C), 133.6 (C), 131.8 (C), 127.7 (CH), 126.4 (CH), 119.0 (CH), 79.3 (CH_2), 66.5 (CH), 52.6 (CH_3); ATR-FTIR (thin film): 3483, 3056, 2955, 2120, 1556, 1262 cm^{-1}; HRMS (EI) *m / z* calculated for $C_{10}H_{10}O_5N_4$ $(M)^+$: 266.06511, found: 266.06450.



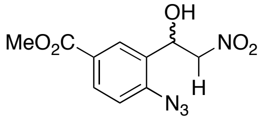
s25

***ortho*-Azido-β-nitro alcohol s25.** General procedure A was followed using 1.00 g of *ortho*-azidobenzaldehyde **s9** (4.4 mmol), 0.48 mL of nitromethane, and 0.287 g of KOH (4.5 mmol) in 13 mL of EtOH. Workup afforded **s25** as a tan powder (1.09 g, 86%), mp 49 °C, R_f = 0.30 (15:85 EtOAc:hexanes, visualized by 254 nm UV light). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.72 (d, J = 2.5 Hz, 1H), 7.50 (dd, J = 8.5, 2.5 Hz, 1H), 7.05 (d, J = 8.5 Hz, 1H), 5.64-5.57 (m, 1H), 4.62 (dd, J = 14.0, 2.5 Hz, 1H), 4.43 (dd, J = 14.0, 9.5 Hz, 1H), 3.15 (dd, J = 5.0, 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 135.7 (C), 132.8 (CH), 130.79 (C), 130.7 (CH), 119.7 (CH), 118.5 (C), 79.3 (CH_2), 66.2 (CH); ATR-FTIR (thin film): 3370, 3108, 2130, 2092, 1777, 1683, 1549, 1477, 1410, 1299, 1182, 1087 cm^{-1}; HRMS (EI) *m / z* calculated for $C_8H_7N_4O_3Br$ $(M)^+$: 285.97015, found: 285.97155.



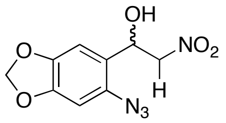
s26

***ortho*-Azido-β-nitro alcohol s26.** General procedure A was followed using 0.150 g of *ortho*-azidobenzaldehyde **s10** (0.83 mmol), 0.09 mL of nitromethane, and 0.059 g of KOH (0.91 mmol) in 2.5 mL of EtOH. Purification by MPLC (0:100 – 30:70 EtOAc:hexanes) afforded analytically pure **s26** as a tan powder (0.192 g, 94%), mp 48 °C, R_f = 0.30 (15:85 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.26 (d, *J* = 2.0 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 1H), 7.03 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.59 (dd, *J* = 9.0, 2.0 Hz, 1H), 4.63 (dd, *J* = 14.0, 2.5 Hz, 1H), 4.43 (dd, *J* = 14.0, 9.0 Hz, 1H), 3.29 (br s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.4 (C), 132.9 (C), 130.7 (C), 120.4 (CH), 119.5 (CH), 118.1 (CH), 79.4 (CH_2), 66.4 (CH); ATR-FTIR (thin film): 3351, 2133, 2103, 1550, 1484, 1414, 1303, 1095 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_7N_4O_3Cl$ $(M)^+$: 242.02067, found: 242.02160.



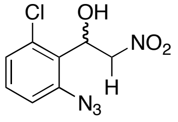
s27

***ortho*-Azido-β-nitro alcohol s27.** General procedure B was followed using 1.03 g of methyl 4-azido-3-formylbenzoate **s11** (5.0 mmol), 6.6 mL of nitromethane, and 1.6 mL of aqueous NaOH in 5.0 mL of EtOH and 5.0 mL of H_2O. MPLC (0:100 – 5:95 EtOAc:hexanes on SiO_2) afforded analytically pure **s27** as a colorless oil (1.24 g, 94%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.21 (d, *J* = 1.0 Hz, 1H), 7.99 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.18 (d, *J* = 8.5 Hz, 1H), 5.62 (d, *J* = 9.0 Hz, 1H), 4.60 (dd, *J* = 14.0, 2.5 Hz, 1H), 4.46 (dd, *J* = 14.0, 9.5 Hz, 1H), 3.87 (s, 3H), 3.71 (br, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.2 (C), 141.2 (C), 131.2 (CH), 129.4 (C), 129.1 (CH), 127.0 (C), 118.1 (CH), 79.5 (CH_2), 66.3 (CH), 52.4 (CH_3); ATR-FTIR (thin film): 3398, 3043, 2955, 2126, 1716, 1551, 1284 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{10}H_{10}O_5N_4$ $(M)^+$: 266.06511, found: 266.06401.



s28

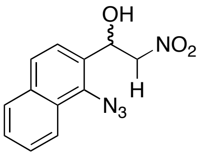
***ortho*-Azido-β-nitro alcohol s28.** General procedure B was followed using 0.955 g of 6-azidobenzo[*d*][1,3]dioxole-5-carbaldehyde **s12** (5.0 mmol), 6.6 mL of nitromethane, and 1.6 mL of aqueous NaOH in 5.0 mL of EtOH and 5.0 mL of H_2O. MPLC (0:100 – 10:90 EtOAc:hexanes on SiO_2) afforded analytically pure **s28** as a white solid (1.02 g, 81%), mp 93 – 95 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.02 (s, 1H), 6.67 (s, 1H), 6.00 (dd, *J* = 6.0, 1.5 Hz, 2H), 5.58 – 5.55 (m, 1H), 4.54 (dd, *J* = 14.0, 2.5 Hz, 1H), 4.43 (dd, *J* = 14.0, 9.5 Hz, 1H), 3.01 (d, *J* = 4.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 148.8 (C), 145.6 (C), 129.9 (C), 122.1 (CH_2), 107.1 (CH), 102.1 (CH_2), 99.2 (CH), 79.7 (CH_2), 66.5 (CH); ATR-FTIR (thin film): 3570, 3054, 2117, 1556, 1484, 1264 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_9H_8O_5N_4$ $(M)^+$: 252.04946, found: 252.05043.



s29

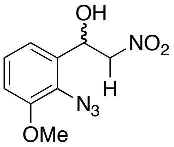
***ortho*-Azido-β-nitro alcohol s29.** General procedure B was followed using 0.081 g of *ortho*-azidobenzaldehyde **s13** (0.45 mmol), 0.58 mL of nitromethane, and 0.14 mL of aqueous NaOH in 0.45 mL of

EtOH and 0.45 mL of H_2O. Workup afforded analytically pure **s29** as a yellow powder (0.107 g, 99%), mp 41 °C, R_f = 0.44 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.34 (t, *J* = 8.0 Hz, 1H), 7.22 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.13 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.00 (td, *J* = 10.0, 3.5 Hz, 1H), 4.96 (dd, *J* = 13.0, 10.0 Hz, 1H), 4.51 (dd, *J* = 13.0, 3.5 Hz, 1H), 3.83 (d, *J* = 10 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 139.8 (C), 134.8 (C), 130.7 (CH), 126.8 (CH), 126.0 (C), 117.6 (CH), 78.7 (CH_2), 68.2 (CH); ATR-FTIR (thin film): 3471, 2113, 1564, 1549, 1456, 1414, 1382, 1312, 1281, 1255, 1185, 1122, 1093, 1072, 1038 cm^{-1}; HRMS (EI) *m / z* calculated for $C_8H_7ClN_4O_3$ $(M)^+$: 242.02067, found: 242.02198.



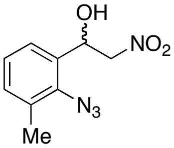
s30

***ortho*-Azido-β-nitro alcohol s30.** General procedure B was followed using 0.985 g of 1-azido-2-naphthaldehyde **s14** (5.0 mmol), 6.6 mL of nitromethane, and 1.6 mL of aqueous NaOH in 5.0 mL of EtOH and 5.0 mL of H_2O. MPLC (0:100 – 5:95 EtOAc:hexanes on SiO_2) afforded analytically pure **s30** as a colorless oil (1.21 g, 94%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.11 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.57 (t, *J* = 6.5 Hz, 1H), 6.00 (s, 1H), 4.60 (m, 2H), 3.45 (br, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 134.4 (C), 132.0 (C), 129.0 (CH), 128.5 (C), 127.9 (C), 127.5 (2 CH), 127.1 (CH), 123.3 (CH), 121.7 (CH), 79.8 (CH_2), 67.2 (CH); ATR-FTIR (thin film): 3432, 3054, 2116, 1628, 1513, 1336, 1263 cm^{-1}; HRMS (EI) *m / z* calculated for $C_{12}H_{10}O_3N_4$ $(M)^+$: 258.07529, found: 238.07628.



s31

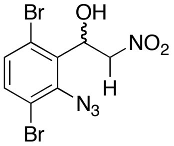
***ortho*-Azido-β-nitro alcohol s31.** General procedure B was followed using 0.885 g of 2-azido-3-methoxybenzaldehyde **s15** (5 mmol), 6.6 mL of nitromethane, and 1.6 mL of aqueous NaOH in 5.0 mL of EtOH and 5.0 mL of H_2O. MPLC (0:100 – 10:90 EtOAc:hexanes on SiO_2) afforded analytically pure **s31** as a colorless oil (1.13 g, 95%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.13 (t, *J* = 8.0 Hz, 1H), 7.08 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.88 (dd, *J* = 8.0, 1.0 Hz, 1H), 5.60 (d, *J* = 8.0 Hz, 1H), 4.58 (dd, *J* = 13.0, 3.0 Hz, 1H), 4.45 (dd, *J* = 13.0, 9.0 Hz, 1H), 3.90 (s, 3H), 3.30 (br, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 153.8 (C), 130.6 (C), 125.8 (CH), 124.6 (C), 118.9 (CH), 112.0 (CH), 79.7 (CH_2), 67.3 (CH), 56.2 (CH_3); ATR-FTIR (thin film): 3581, 3055, 2116, 1552, 1483, 1263 cm^{-1}; HRMS (EI) *m / z* calculated for $C_9H_{10}O_4N_4$ $(M)^+$: 238.07020, found: 238.07097.



s32

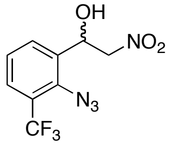
***ortho*-Azido-β-nitro alcohol s32.** General procedure B was followed using 0.805 g of 2-azido-3-methylbenzaldehyde **s16** (5 mmol), 6.6 mL of nitromethane, and 1.6 mL of aqueous NaOH in 5.0 mL of EtOH and 5.0 mL of H_2O. MPLC (0:100 – 30:70 EtOAc:hexanes on SiO_2) afforded analytically pure **s32** as a colorless oil (1.07 g, 96%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.4 – 7.39 (m, 1H), 7.17 – 7.16 (m, 2H), 5.73 (d, *J* =

9.5 Hz, 1H), 4.60 (dd, *J* = 13.5, 2.5 Hz, 1H), 4.49 (dd, *J* = 13.5, 9.5 Hz, 1H), 3.15 (br, 1H), 2.47 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 134.8 (C), 133.0 (C), 132.1 (CH), 131.3 (C), 126.5 (CH), 125.0 (CH), 79.9 (CH_2), 67.4 (CH), 18.0 (CH_3); ATR-FTIR (thin film): 3525, 2920, 2107, 1547, 1288, 780 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_9H_{10}O_3N_4$ $(M)^+$: 222.07529 , found: 222.07615 .



s33

***ortho*-Azido-β-nitro alcohol s33.** General procedure B was followed using 0.500 g of 2-azidobenzaldehyde **s17** (1.6 mmol), 2.1 mL of nitromethane, and 0.50 mL of aqueous NaOH in 1.6 mL of EtOH and 1.6 mL of H_2O. MPLC (0:100 – 30:70 EtOAc:hexanes on SiO_2) afforded analytically pure **s33** as a tan foam (0.583 g, 99%), R_f = 0.62 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43 (d, *J* = 8.5 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 6.05 (m, 1H), 5.02 (dd, *J* = 13.0, 9.5 Hz, 1H), 4.52 (dd, *J* = 13.0, 3.5 Hz, 1H), 3.86 (d, *J* = 3.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 137.9 (C), 135.2 (CH), 132.6 (C), 132.1 (CH), 123.1 (C), 119.5 (C), 78.2 (CH_2), 71.34 (CH); ATR-FTIR (thin film): 2124, 1709, 1553, 1483, 1287 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_4Br_2N_2O_2$ $(M - N_2 - H_2O)^+$: 317.86398, found: 317.86306.

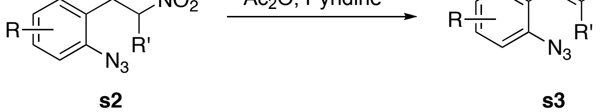


s34

***ortho*-Azido-β-nitro alcohol s34.** General procedure B was followed using 1.08 g of 2-azido-3-methylbenzaldehyde **s18** (5 mmol), 6.6 mL of nitromethane, and 1.6 mL of aqueous NaOH in 5.0 mL of EtOH and 5.0 mL of H_2O. MPLC (0:100 – 30:70 EtOAc:hexanes on SiO_2) afforded analytically pure **s34** as a colorless oil (1.25 g, 91%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 5.85 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.67 (dd, *J* = 13.5, 2.5 Hz, 1H), 4.50 (dd, *J* = 13.5, 9.5 Hz, 1H), 3.19 (br, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 134.7 (C), 133.7 (C), 131.2 (CH), 127.7 (q, $J_{C\text{–}F}$ = 5.5 Hz, CH), 126.2 (CH), 123.3 (q, $J_{C\text{–}F}$ = 270.2 Hz, C), 124.0 (q, $J_{C\text{–}F}$ = 31.4 Hz, C), 79.4 (CH_2), 66.7 (CH); ATR-FTIR (thin film): 3379, 2127, 1558, 1320, 1119, 1096, 647 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_9H_7O_3N_4F_3$ $(M)^+$: 276.04703, found: 276.04794.

F. General Procedure for the Preparation of *ortho*-Azido-β-Nitrostyrenes

The requisite *ortho*-azido-β-nitrostyrenes were prepared from the ambient temperature base-catalyzed hydrolysis reaction of 2-hydroxy-(*ortho*-azidophenyl)nitroethanes in Ac_2O as reported by Molina and coworkers (eq. s4).[6] Yields were not optimized.

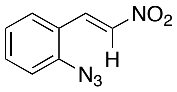


(s4)

s2 **s3**

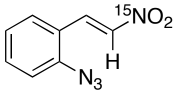
To a stir bar-equipped flame-dried 50 mL round bottom flask was added azido alcohol **s2** (1.37 g, 6.6 mmol), Ac_2O (13 mL), and pyridine (1.3 mL) in an ambient temperature water bath. After stirring overnight, the reaction mixture was poured into water (50 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried over Na_2SO_4 and concentrated to afford an oil. The crude product was taken up in a small amount of CH_2Cl_2 and added to netural alumina, and the mixture was evaporated to dryness. The resulting powder was purified on a dry-packed MPLC column (0:100 – 30:70 EtOAc:hexanes on SiO_2) to give pure product. **Caution:** *ortho*-azido-β-nitrostyrenes are potent skin irritants.

G. *ortho*-Azido-β-nitrostyrene Synthesis



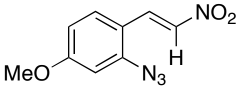
1

***ortho*-Azido-β-nitrostyrene 1.**[6] The general procedure was followed using 1.37 g of azido alcohol **s19** (6.6 mmol), 13 mL of Ac_2O, and 1.3 mL of pyridine. MPLC (0:100 – 30:70 EtOAc:hexanes on SiO_2) afforded analytically pure **1** as a yellow powder (1.01 g, 81%), mp 84 °C, $R_f = 0.80$ (60:40 EtOAc:hexanes, visualized by 254 nm UV light). **Caution:** this compound is a potent skin irritant. The spectral data matched that reported by Molina and coworkers.[6] ^1H NMR ($CDCl_3$, 500 MHz): δ 8.16 (d, $J = 13.5$ Hz, 1H), 7.77 (d, $J = 13.5$ Hz, 1H), 7.55-7.48 (m, 2H), 7.28-7.16 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 140.5 (C), 138.6 (CH), 133.9 (CH), 133.0 (CH), 130.5 (CH), 125.2 (CH), 121.6 (C), 119.1 (CH); ATR-FTIR (thin film): 3104, 2126, 2093, 1634, 1595, 1634, 1595, 1510, 1498, 1451, 1334, 1293, 1196, 1163, 1149, 1085 cm^{-1}.



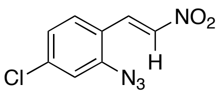
1-^{15}N

***ortho*-Azido-β-nitrostyrene 1-^{15}N.** The general procedure was followed using 0.110 g of azido alcohol **s20** (0.53 mmol), 1.0 mL of Ac_2O, and 0.10 mL of pyridine. MPLC (0:100 – 30:70 EtOAc:hexanes on SiO_2) afforded analytically pure **1**-^{15}N as a yellow powder (0.069 g, 67%), mp 68 °C, $R_f = 0.80$ (60:40 EtOAc:hexanes, visualized by 254 nm UV light). **Caution:** this compound is a potent skin irritant. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.19-8.11 (m, 1H), 7.80-7.73 (m, 1H), 7.55-7.48 (m, 2H), 7.28-7.23 (m, 1H), 7.23-7.17 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 140.5 (C), 138.6 (d, $J_{C\text{-}*N} = 14.8$ Hz, CH), 133.9 (CH), 133.0 (CH), 130.5 (CH), 125.3 (CH), 121.6 (C), 119.2 (CH); ATR-FTIR: 3103, 2108, 1632, 1595, 1464, 1307, 1285, 1206, 1164 cm^{-1}; HRMS: (EI) *m* / *z* calculated for $C_8H_6N_3{}^{15}NO_3$ $(M)^+$: 191.04611, found: 191.04758.



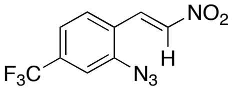
4a

***ortho*-Azido-β-nitrostyrene 4a.** The general procedure was followed using 1.35 g of azido alcohol **s21** (5.7 mmol), 11 mL of Ac_2O, and 1.1 mL of pyridine. MPLC (0:100 – 30:70 EtOAc:hexanes on SiO_2) afforded analytically pure **4a** as a yellow powder (0.855 g, 69%), 67 °C, $R_f = 0.61$ (60:40 EtOAc:hexanes, visualized by 254 nm UV light). **Caution:** this compound is a potent skin irritant. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.08 (d, $J = 14.0$ Hz, 1H), 7.70 (d, $J = 14.0$ Hz, 1H), 7.43 (d, $J = 8.5$ Hz, 1H), 6.73 (d, $J = 8.5$ Hz, 1H), 6.71 (s, 1H), 3.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 163.6 (C), 142.3 (C), 136.4 (CH), 134.0 (CH), 132.3 (CH), 114.4 (C), 111.5 (CH), 104.7 (CH), 55.8 (CH_3); ATR-FTIR (thin film): 3130, 2116, 1600, 1567, 1514, 1504, 1328, 1308, 1296, 1240, 1190, 1090, 1026 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_9H_8N_4O_3$ $(M)^+$: 220.05964, found: 220.06032.



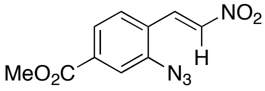
4b

***ortho*-Azido-β-nitrostyrene 4b.** The general procedure was followed using 0.100 g of azido alcohol **s22** (0.41 mmol), 0.82 mL of Ac_2O, and 0.08 mL of pyridine. MPLC (0:100 – 30:70 EtOAc:hexanes on SiO_2) afforded analytically pure **4b** as a yellow powder (0.059 g, 64%), mp 151 °C, R_f = 0.61 (15:85 EtOAc:hexanes, visualized by 254 nm UV light). **Caution:** this compound is a potent skin irritant. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.09 (d, *J* = 14.0 Hz, 1H), 7.75 (d, *J* = 14.0 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.24 (d, *J* = 2.0 Hz, 1H), 7.18 (dd, *J* = 8.5, 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.6 (C), 139.0 (C), 138.8 (CH), 132.9 (CH), 131.5 (CH), 125.7 (CH), 120.1 (C), 119.4 (CH); ATR-FTIR (thin film): 3134, 3046, 2108, 1626, 1508, 1394, 1346, 1303 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_5N_4O_2Cl$ $(M)^+$: 224.01010, found: 224.00915.



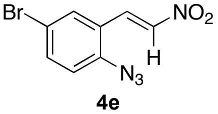
4c

***ortho*-Azido-β-nitrostyrene 4c.** The general procedure was followed using 0.860 g of azido alcohol **s23** (3.1 mmol), 6.5 mL of Ac_2O, and 0.65 mL of pyridine. MPLC (0:100 – 30:70 EtOAc:hexanes on SiO_2) afforded analytically pure **4c** as a faintly yellow powder (0.478 g, 60%), mp 80 °C, R_f = 0.61 (20:80 EtOAc:hexanes, visualized by 254 nm UV light). **Caution:** this compound is a potent skin irritant. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.14 (d, *J* = 14.0 Hz, 1H), 7.79 (d, *J* = 14.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.47 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.1 (C), 140.2 (C), 134.5 (q, J_{C-F} = 33.0 Hz, C), 132.4 (CH), 131.1 (CH), 124.7 (C), 123.0 (q, J_{C-F} = 271.8 Hz, C), 121.8 (CH), 116.1 (q, J_{C-F} = 4.1 Hz, CH); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –63.9; ATR-FTIR (thin film): 2119, 1696, 1511, 1125, 1082 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_9H_5N_4O_2F_3$ $(M)^+$: 258.03646, found: 258.03485.



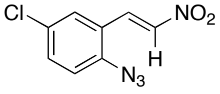
4d

***ortho*-Azido-β-nitrostyrene 4d.** The general procedure was followed using 1.06 g of azido alcohol **s24** (4.0 mmol), 8.0 mL of Ac_2O, and 0.80 mL of pyridine. MPLC (0:100 – 3:97 EtOAc:hexanes on SiO_2) afforded analytically pure **4d** as a yellow solid (0.84 g, 85% yield), mp 137 – 139 °C. **Caution:** this compound is a potent skin irritant. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.13 (d, *J* = 13.5 Hz, 1H), 7.89 (s, 1H), 7.85-7.75 (m, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 3.96 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.2 (C), 140.7 (C), 140.0 (CH), 134.1 (C), 132.8 (CH), 130.5 (CH), 125.9 (CH), 125.4 (C), 120.0 (CH), 52.8 (CH_3); ATR-FTIR (thin film): 3096, 2920, 2121, 1705, 1514, 1411, 1294 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{10}H_8O_4N_4$ $(M)^+$: 248.05455, found: 248.05361.



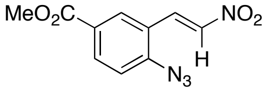
4e

***ortho*-Azido-β-nitrostyrene 4e.** The general procedure was followed using 0.500 g of azido alcohol **s25** (1.7 mmol), 3.5 mL of Ac_2O, and 0.35 mL of pyridine. MPLC (0:100 – 30:70 EtOAc:hexanes on SiO_2) afforded analytically pure **4e** as a faintly yellow powder (0.231 g, 50%), mp 85 °C, R_f = 0.61 (15:85 EtOAc:hexanes, visualized by 254 nm UV light). **Caution:** this compound is a potent skin irritant. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.06 (d, *J* = 14.0 Hz, 1H), 7.73 (d, *J* = 14.0 Hz, 1H), 7.64 (d, *J* = 2.0 Hz, 1H), 7.61 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.14 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 139.5 (C), 139.4 (CH), 135.6 (CH), 132.9 (CH), 132.5 (CH), 123.3 (C), 120.7 (CH), 118.0 (C); ATR-FTIR (thin film): 2126, 1633, 1512, 1287 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_5N_4O_2Br$ (M)$^+$: 267.95958, found: 267.96085.



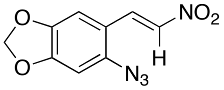
4f

***ortho*-Azido-β-nitrostyrene 4f.** The general procedure was followed using 0.086 g of azido alcohol **s26** (0.35 mmol), 0.71 mL of Ac$_2$O, and 0.07 mL of pyridine. MPLC (0:100 – 30:70 EtOAc:hexanes on SiO$_2$) afforded analytically pure **4f** as a yellow powder (0.053 g, 67%), mp 84 °C, R$_f$ = 0.74 (15:85 EtOAc:hexanes, visualized by 254 nm UV light). **Caution:** this compound is a potent skin irritant. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.10 (d, *J* = 14.0 Hz, 1H), 7.74 (d, *J* = 14.0 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.18 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.12 (d, *J* = 2.5 Hz, 1H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 139.4 (CH), 137.3 (C), 136.9 (C), 133.0 (CH), 123.4 (CH), 122.8 (C), 120.6 (CH), 120.2 (CH); ATR-FTIR (thin film): 3138, 2130, 1633, 1563, 1517, 1338, 1285, 1190 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_5N_4O_2Cl$ (M)$^+$: 224.01010, found: 224.00818.



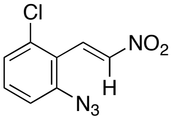
4g

***ortho*-Azido-β-nitrostyrene 4g.** The general procedure was followed using 1.06 g of azido alcohol **s27** (4.0 mmol), 8.0 mL of Ac$_2$O, and 0.80 mL of pyridine. MPLC (0:100 – 3:97 EtOAc:hexanes on SiO$_2$) afforded analytically pure **4g** as a yellow solid (0.910 g, 90% yield), mp 120 – 122 °C. **Caution:** this compound is a potent skin irritant. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.20-8.09 (m, 3H), 7.79 (d, *J* = 14.0 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 165.3 (C), 144.5 (C), 139.3 (CH), 133.7 (CH), 133.0 (CH), 131.8 (CH), 127.1 (C), 121.5 (C), 119.1 (CH), 52.6 (CH$_3$); ATR-FTIR (thin film): 3132, 3030, 2958, 2131, 1716, 1498, 1309, 1259 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{10}H_8O_4N_4$ (M)$^+$: 248.05455, found: 248.05579.



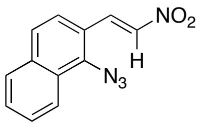
4h

***ortho*-Azido-β-nitrostyrene 4h.** The general procedure was followed using 1.01 g of azido alcohol **s28** (4.0 mmol), 8.0 mL of Ac$_2$O, and 0.80 mL of pyridine. MPLC (0:100 – 5:95 EtOAc:hexanes on SiO$_2$) afforded analytically pure **4h** as a yellow solid (0.790 g, 84% yield), mp 148 – 150 °C. **Caution:** this compound is a potent skin irritant. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.18 (d, *J* = 14.0 Hz, 1H), 7.56 (d, *J* = 14.0 Hz, 1H), 6.92 (s, 1H), 6.73 (s, 1H), 6.08 (s, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 152.4 (C), 145.8 (C), 136.4 (C), 136.4 (CH), 133.5 (CH), 114.7 (C), 107.1 (CH), 102.7 (CH$_2$), 99.8 (CH); ATR-FTIR (thin film): 3112, 2922, 2359, 2118, 1610, 1470, 1237, 1031 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_9H_6O_4N_4$ (M)$^+$: 234.03890, found: 234.03932.



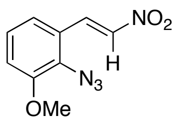
4i

***ortho*-Azido-β-nitrostyrene 4i.** The general procedure was followed using 0.053 g of azido alcohol **s29** (0.22 mmol), 0.44 mL of Ac$_2$O, and 0.04 mL of pyridine. MPLC (0:100 – 30:70 EtOAc:hexanes on SiO$_2$) afforded analytically pure **4i** as a yellow powder (0.037 g, 76%), mp 115 °C, R_f = 0.66 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). **Caution:** this compound is a potent skin irritant. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.32 (d, *J* = 14.0 Hz, 1H), 8.11 (d, *J* = 14.0 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.28 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.1 (CH), 141.7 (C), 138.0 (C), 132.2 (CH), 130.4 (CH), 126.7 (CH), 120.0 (C), 117.6 (CH); ATR-FTIR (thin film): 3140, 2114, 1626, 1583, 1561, 1509, 1455, 1431, 1337, 1306, 1224, 1169, 1131, 1086 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_5N_2O_2Cl$ $(M - N_2)^+$: 196.00396, found: 196.00488.



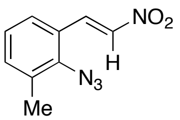
4j

***ortho*-Azido-β-nitrostyrene 4j.** The general procedure was followed using 1.03 g of azido alcohol **s30** (4.0 mmol), 8.0 mL of Ac_2O, and 0.8 mL of pyridine. MPLC (0:100 – 2:98 EtOAc:hexanes on SiO_2) afforded analytically pure **4j** as a yellow solid (0.760 g, 80%), mp 90 – 92 °C. **Caution:** this compound is a potent skin irritant. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.55 (d, *J* = 14.0 Hz, 1H), 8.21 (d, *J* = 9.0 Hz, 1H), 7.88 (d, *J* = 9.5 Hz, 1H), 7.72-7.64 (m, 4H), 7.48 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.5 (CH), 137.5 (C), 135.8 (C), 134.1 (CH), 128.9 (CH), 128.8 (CH), 128.2 (C), 128.0 (CH), 127.3 (CH), 123.4 (CH), 123.0 (CH), 120.8 (C); ATR-FTIR (thin film): 3371, 3111, 2923, 2111, 1625, 1503, 1276 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{12}H_8O_2N_4$ $(M)^+$: 240.06472, found: 240.06530.



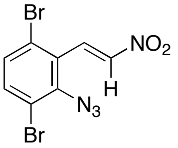
4k

***ortho*-Azido-β-nitrostyrene 4k.** The general procedure was followed using 0.95 g of azido alcohol **s31** (4.0 mmol), 8.0 mL of Ac_2O, and 0.80 mL of pyridine. MPLC (0:100 – 1:50 EtOAc:hexanes on SiO_2) afforded analytically pure **4k** as a yellow solid (0.74 g, 84% yield), mp 100 – 102 °C. **Caution:** this compound is a potent skin irritant. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.15 (d, *J* = 14.0 Hz, 1H), 7.65 (d, *J* = 14.0 Hz, 1H), 7.10 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 3.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.4 (C), 138.4 (CH), 134.5 (CH), 128.8 (C), 125.4 (CH), 122.8 (C), 121.3 (CH), 114.6 (CH), 56.2 (CH_3); ATR-FTIR (thin film): 3112, 2923, 2113, 1625, 1510, 1265 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_9H_8O_3N_4$ $(M)^+$: 230.05964, found: 220.05983.



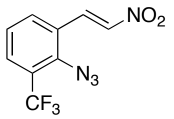
4l

***ortho*-Azido-β-nitrostyrene 4l.** The general procedure was followed using 0.89 g of azido alcohol **s32** (4.0 mmol), 8.0 mL of Ac_2O, and 0.80 mL of pyridine. MPLC (0:100 – 1:90 EtOAc:hexanes on SiO_2) afforded analytically pure **4l** as a yellow solid (0.74 g, 91% yield), mp 50 – 52 °C. **Caution:** this compound is a potent skin irritant. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.32 (d, *J* = 14.0 Hz, 1H), 7.64 (d, *J* = 13.5 Hz, 1H), 7.38 (d, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.5 (CH), 138.4 (C), 135.2 (CH), 134.9 (CH), 133.9 (C), 127.1 (CH), 126.3 (CH), 124.1 (C), 18.1 (CH_3); ATR-FTIR (thin film): 3106, 2921, 2107, 1509, 1334, 962, 784, 640 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_9H_8O_2N_4$ $(M)^+$: 204.06472, found: 204.06554.



4m

***ortho*-Azido-β-nitrostyrene 4m.** The general procedure was followed using 0.282 g of azido alcohol **s33** (0.77 mmol), 1.6 mL of Ac_2O, and 0.16 mL of pyridine. MPLC (0:100 – 30:70 EtOAc:hexanes on SiO_2) afforded analytically pure **4m** as a faintly yellow powder (0.101 g, 38%), mp 84 °C, $R_f = 0.81$ (30:70 EtOAc:hexanes, visualized by 254 nm UV light). **Caution:** this compound is a potent skin irritant. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.21 (d, J = 14.0 Hz, 1H), 7.86 (d, J = 14.0 Hz, 1H), 7.49 (d, J = 8.5 Hz, 1H), 7.41 (d, J = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.0 (CH), 138.2 (C), 136.4 (CH), 133.2 (CH), 131.8 (CH), 126.4 (C), 125.7 (C), 118.5 (C); ATR-FTIR (thin film): 3133, 3097, 3041, 2924, 2850, 2155, 2120, 1630, 1510, 1426, 1393, 1342, 1307, 1190, 1105 cm^{-1}; HRMS (EI) m / z calculated for $C_8H_4BrN_4O_2$ $(M)^+$: 345.87012, found: 345.87087.



4n

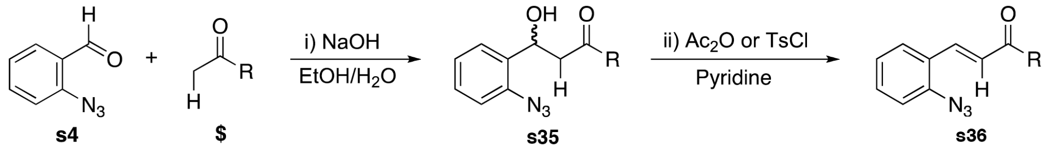
***ortho*-Azido-β-nitrostyrene 4n.** The general procedure was followed using 1.10 g of azido alcohol **s34** (4.0 mmol), 8.0 mL of Ac_2O, and 0.80 mL of pyridine. MPLC (0:100 – 1:90 EtOAc:hexanes on SiO_2) afforded analytically pure **4n** as a yellow solid (0.87 g, 84% yield), mp 73 – 75 °C. **Caution:** this compound is a potent skin irritant. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.36 (d, J = 13.5 Hz, 1H), 7.81 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 7.5 Hz, 1H), 7.63 (d, J = 13.5 Hz, 1H), 7.39 (t, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 139.9 (CH), 138.0 (C), 133.1 (CH), 132.4 (CH), 130.4 (q, J_{C-F} = 7.0 Hz, CH), 126.6 (C), 126.1 (CH), 125.1 (q, J_{C-F} = 31.4 Hz, C), 122.9 (q, J_{C-F} = 271.4 Hz, C); ATR-FTIR (thin film): 3118, 2123, 1632, 1506, 1433, 1346, 1116, 800, 620 cm^{-1}; HRMS (EI) m / z calculated for $C_9H_5O_2N_4F_3$ $(M)^+$: 258.03646, found: 258.03579.

II. Preparation of *ortho*-Azido-β-Acylstyrenes

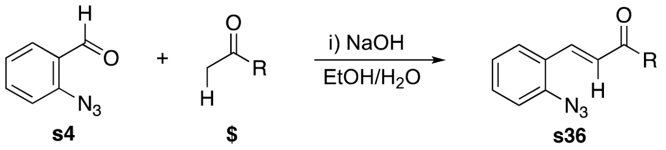
A. Synthetic Routes to *ortho*-Azido-β-Acylstyrenes

Scheme s2. Synthetic Routes to *ortho*-Azido-β-Acylstyrenes.

Sequential Aldol Condensation/Hydrolysis



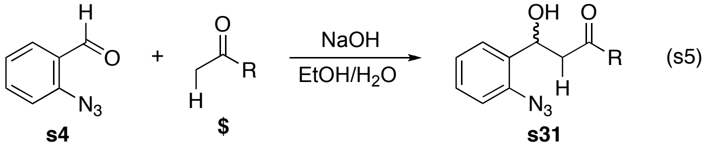
Hydrolytic Aldol Condensation



ortho-Azido-β-acylstyrenes were synthesized using the routes outlined in Scheme s2. Substituted ketones were condensed with 2-azidobenzaldehyde **s4** to afford *ortho*-azido alcohols **s35**, which, if necessary, were subsequently hydrolyzed using Ac_2O and pyridine to give *ortho*-azidoacylstyrenes **s36**.

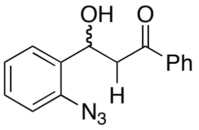
B. General Procedure for the Preparation of *ortho*-Azido-β-Acyl Alcohols

Unless otherwise noted, *ortho*-azido alcohols were prepared from the aqueous NaOH-catalyzed condensation reaction of *ortho*-azidobenzaldehydes with substituted ketones in EtOH and H_2O as reported by Muchowski and coworkers (eq. s5).[8] Yields were not optimized.



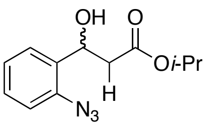
To a stir bar-equipped flame-dried 25 mL round bottom flask containing a stirring mixture of 2-azidobenzaldehyde **s4** (0.433 g, 2.7 mmol), methyl phenyl ketone (3.6 mL), water (2.7 mL), and ethanol (2.7 mL) in an ambient temperature water bath was added aqueous NaOH (0.25 mol L^{-1}, 0.82 mL), dropwise. After stirring overnight, the reaction mixture was poured into aqueous sodium chloride (20 mL) and extracted with CH_2Cl_2 (20 mL). The extract was washed with water (2 × 30 mL), dried over Na_2SO_4, and concentrated to afford an oil. The crude product was taken up in a small amount of CH_2Cl_2 and added to silica gel, and the mixture was evaporated to dryness. The resulting powder was purified on a dry-packed MPLC column (0:100 – 30:70 EtOAc:hexanes on SiO_2) to give the product.

C. *ortho*-Azido-β-Acyl Alcohol Synthesis



s37

***ortho*-Azido-β-acyl alcohol s37.** The general procedure was followed using 0.433 g of *ortho*-azidobenzaldehyde **s4** (2.7 mmol), 3.6 mL of acetophenone, and 0.82 mL of aqueous NaOH in 2.7 mL of EtOH and 2.7 mL of H_2O. Workup afforded analytically pure **s37** as a pink powder (0.609 g, 83%), mp 90 °C, R_f = 0.59 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.99-7.94 (m, 2H), 7.68-7.63 (m, 1H), 7.62-7.57 (m, 1H), 7.50-7.45 (m, 2H), 7.35 (td, J = 7.5, 1.5 Hz, 1H), 7.21 (td, J = 7.5, 1.0 Hz, 1H), 7.17 (dd, J = 7.0, 1.0 Hz, 1H), 5.56-5.50 (m, 1H), 3.74 (d, J = 4.0 Hz, 1H), 3.49 (dd, J = 17.5, 2.5 Hz, 1H), 3.20 (dd, J = 17.5, 9.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 200.3 (C), 136.6 (C), 136.1 (C), 134.1 (C), 133.7 (CH), 128.7 (CH), 128.6 (CH), 128.2 (CH), 127.2 (CH), 125.2 (CH), 117.9 (CH), 65.5 (CH), 45.9 (CH_2); ATR-FTIR (thin film): 3060, 2905, 2122, 2085, 1677, 1581, 1490, 1448, 1296, 1202, 1070, 1023 cm^{-1}; HRMS (EI) m / z calculated for $C_{15}H_{13}NO_2$ $(M)^+$: 239.09463, found: 239.09356.



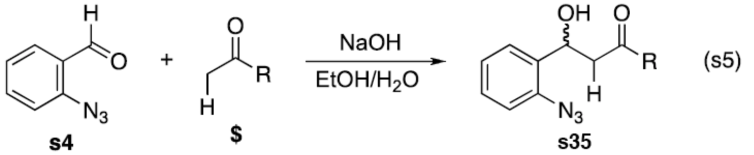
s38

***ortho*-Azido-β-acyl alcohol s38.** The following procedure, adapted from the report by Xu and Yuan,[9] was used to synthesize **s38**. To a solution of 0.38 mL of diisopropyl amine (3.7 mmol) in 4.0 mL of dry THF was added

1.5 mL of a 2.5 M solution of *n*-BuLi in hexanes at –78 °C under nitrogen. The mixture was kept at this temperature for 1 h, then a mixture of 0.43 mL of isopropyl acetate (3.7 mmol) and 2.0 mL of dry THF was added at –78 °C. After the reaction stirred for 1 h at –78 °C, a mixture of 0.453 g of 2-azidobenzaldehyde **s4** (3.1 mmol) and 2.0 mL of dry THF was added. After the mixture was stirred for another 1 h, 50 mL of saturated aqueous NH_4Cl was added and the aqueous layer was extracted with CH_2Cl_2 (3 x 50 mL), the combined extracts were dried over Na_2SO_4 and concentrated to afford an oil that was charged on neutral alumina and concentrated to dryness. MPLC (0:100 – 50:50 EtOAc:hexanes on SiO_2) afforded analytically pure **s38** as a red oil (0.484 g, 63%), R_f = 0.53 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.56-7.52 (m, 1H), 7.35-7.29 (m, 1H0, 7.18-7.12 (m, 2H), 5.32-5.27 (m, 1H), 5.06 (septet, 6.5 Hz, 1H), 3.60-3.55 (m, 1H), 2.78-2.73 (m, 1H), 2.60 (dd, *J* = 16.5, 9.0 Hz, 1H), 1.24 (dd, *J* = 15.0, 6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.1 (C), 136.3 (C), 133.5 (C), 128.8 (CH), 127.1 (CH), 125.1 (CH), 117.9 (CH), 68.5 (CH), 66.0 (CH), 42.0 (CH_2), 21.8 (CH_3); ATR-FTIR (thin film): 3437, 2891, 2123, 1712, 1583, 1486, 1450, 1373, 1294, 1277, 1191, 1107, 1065 cm^{-1}; HRMS (EI) m / z calculated for $C_{12}H_{15}N_3O_3$ $(M)^+$: 249.11135, found: 249.11190.

D. General Procedure A for the Preparation of *ortho*-Azido-β-Acylstyrenes

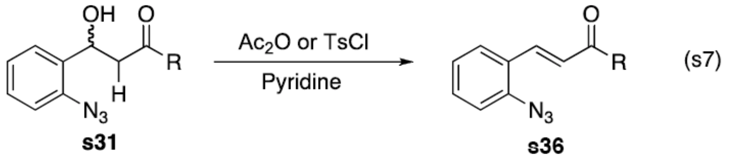
Unless otherwise noted, the requisite *ortho*-azido-β-acylstyrenes were prepared from the aqueous NaOH-catalyzed hydrolytic condensation reaction of *ortho*-azidobenzaldehydes with substituted ketones in EtOH and H_2O as reported by Muchowski and coworkers (eq. s6).[8] Yields were not optimized.



To a stir bar-equipped flame-dried 25 mL round bottom flask containing a stirring mixture of 2-azidobenzaldehyde **s4** (0.500 g, 3.1 mmol), acetone (4.1 mL), water (3.2 mL), and ethanol (3.2 mL) in an ambient temperature water bath was added aqueous NaOH (0.25 mol L^{-1}, 1.0 mL), dropwise. After stirring overnight, the reaction mixture was poured into aqueous sodium chloride (20 mL) and extracted with CH_2Cl_2 (20 mL). The extract was washed with water (2 × 30 mL), dried over Na_2SO_4, and concentrated to afford an oil. The crude product was taken up in a small amount of CH_2Cl_2 and added to silica gel, and the mixture was evaporated to dryness. The resulting powder was purified on a dry-packed MPLC column (0:100 – 30:70 EtOAc:hexanes on SiO_2) to give the product.

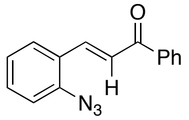
E. General Procedure B for the Preparation of *ortho*-Azido-β-Acylstyrenes

Unless otherwise noted, the requisite *ortho*-azido-β-acylstyrenes were prepared from the ambient temperature base-catalyzed hydrolysis reaction of *ortho*-azidoalcohols **s35** in Ac_2O or TsCl as reported by Molina and coworkers (eq. s7).[6] Yields were not optimized.



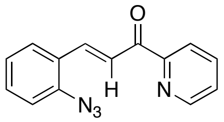
To a spin vane-equipped oven-dried 2.5 mL conical vial was added azido alcohol **s37** (0.605 g, 2.3 mmol), of TsCl (0.437 g, 2.4 mmol), and pyridine (0.45 mL) in an ambient temperature water bath. After stirring overnight, the reaction mixture was poured over ice (25 g) and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were dried over Na_2SO_4 and concentrated to afford an oil. The crude product was taken up in a small amount of CH_2Cl_2 and added to netural alumina, and the mixture was evaporated to dryness. The resulting powder was purified on a dry-packed MPLC column (0:100 – 30:70 EtOAc:hexanes on SiO_2) to give pure product. **Caution:** *ortho*-azido-β-substituted styrenes are potent skin irritants.

F. *ortho*-Azido-β-Acylstyrene Synthesis



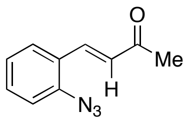
7a

***ortho*-Azido-β-acylstyrene 7a.**[10] General procedure B was followed using 0.605 g of azido alcohol **s37** (2.3 mmol), 0.437 g of TsCl (2.4 mmol), and 0.45 mL of pyridine. MPLC (0:100 – 50:50 EtOAc:hexanes on SiO_2) afforded analytically pure **7a** as a yellow powder (0.231 g, 50%), mp 85 °C, R_f = 0.61 (15:85 EtOAc:hexanes, visualized by 254 nm UV light). **Caution:** *ortho*-azido-β-substituted styrenes are potent skin irritants. The spectral data matched that reported by Sundberg and coworkers.[10] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.04-7.97 (m, 3H), 7.67 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.58-7.52 (m, 2H), 7.51-7.45 (m, 2H), 7.42-7.36 (m, 1H), 7.18-7.12 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 190.5 (C), 139.6 (C), 139.1 (CH), 138.1 (C), 132.8 (CH), 131.5 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 126.5 (C), 125.0 (CH), 123.8 (CH), 118.9 (CH); ATR-FTIR (thin film): 3059, 2123, 1659, 1590, 1570, 1482, 1418, 1308, 1280, 1210, 1178, 1161, 1087, 1013 cm^{-1}.



7b

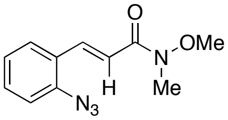
***ortho*-Azido-β-acylstyrene 7b.**[10] General procedure A was followed using 0.200 g of 2-azidobenzaldehyde **s4** (1.5 mmol), 1.8 mL of 2-acetylpyridine (**caution:** stench), and 0.41 mL of aqueous NaOH in 1.4 mL of EtOH and 1.4 mL of H_2O. MPLC (0:100 – 40:60 EtOAc:hexanes on SiO_2) afforded analytically pure **s7b** as yellow plates (0.072 g, 21%), mp 104 °C, R_f = 0.49 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). **Caution:** *ortho*-azido-β-substituted styrenes are potent skin irritants. The spectral data matched that reported by Sundberg and coworkers.[10] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.73 (d, *J* = 4.5 Hz, 1H), 8.29 (d, *J* = 16.0 Hz, 1H), 722-7.15 (m, 2H), 7.89-7.84 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.50-7.45 (m, 1H), 7.44-7.39 (m, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 189.4 (C), 154.2 (C), 148.9 (CH), 139.9 (C), 138.8 (CH), 137.0 (CH), 131.4 (CH), 128.5 (CH), 126.9 (CH), 126.8 (C), 124.9 (CH), 123.0 (CH), 122.3 (CH), 118.9 (CH); ATR-FTIR (thin film): 3327, 3060, 2123, 1671, 1596, 1567, 1484, 1455, 1336, 1312, 1284, 1217, 1089, 1049, 1025 cm^{-1}.



7c

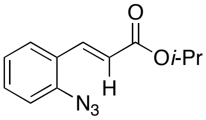
***ortho*-Azido-β-acylstyrene 7c.**[8] General procedure A was followed using 0.500 g of 2-azidobenzaldehyde **s4** (3.1 mmol), 4.1 mL of acetone, and 1.0 mL of aqueous NaOH in 3.2 mL of EtOH and 3.2 mL of H_2O. MPLC

(0:100 – 40:60 EtOAc:hexanes on SiO_2) afforded analytically pure **7c** as a yellow powder (0.792 g, 14%), mp 95 °C, R_f = 0.58 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). The spectral data matched that reported by Muchowski and Maddox.[8] **Caution:** *ortho*-azido-β-substituted styrenes are potent skin irritants. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.78 (d, *J* = 16.5 Hz, 1H), 7.60 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.46-7.41 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 16.5 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 198.7 (C), 139.3 (C), 137.7 (CH), 131.6 (CH), 128.7 (CH), 127.9 (CH), 126.1 (C), 125.1 (CH), 118.8 (CH), 27.2 (CH_3); ATR-FTIR (thin film): 3300, 3066, 3034, 2118, 2086, 1668, 1644, 1621, 1595, 1572, 1484, 1456, 1423, 1358, 1309, 1287, 1252, 1209, 1174, 1087 cm^{-1}.



7d

***ortho*-Azido-β-acylstyrene 7d.** A stirring suspension of sodium hydride (0.264 g, 11 mmol) in anhydrous THF (50 mL) was cooled to 0 °C to which was slowly added diethyl (*N*-methoxy-*N*-methylcarbamoylmethyl)phosphonate (2.39 g, 10 mmol) under N_2 atmosphere. The mixture was stirred for 30 minutes, at which time the reaction temperature was lowered to –10 °C and a solution of 2-azidobenzaldehyde **s4** (2.2 g, 15 mmol) in THF (30 mL) was added with vigorous stirring over 2 minutes. After 30 minutes the solution was allowed to warm to room temperature and stirring continued for 2 h. The reaction was quenched with 1 N HCl (20 mL), extracted with CH_2Cl_2 (3 × 20 mL), and the organic layer was washed with brine (30 ml) and water (2 x 30 ml), and was then dried over $MgSO_4$. The solvent was removed *in vacuo* and the crude material purified by MPLC to afford aryl azide **7d** as a colorless oil (2.16 g, 93%). **Caution:** *ortho*-azido-β-substituted styrenes are potent skin irritants. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.93 (d, *J* = 16.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 16.0 Hz, 1H), 3.76 (s, 3H), 3.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.8 (C), 139.1 (C), 137.9 (CH), 130.8 (CH), 128.3 (CH), 126.9 (C), 124.8 (CH), 118.8 (CH), 117.7 (CH), 61.9 (CH_3), 32.6 (CH_3); ATR-FTIR (thin film): 3068, 2935, 2112, 1650, 1377, 1279 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{11}H_{12}O_2N_4$ $(M)^+$: 232.09602, found: 232.09691.



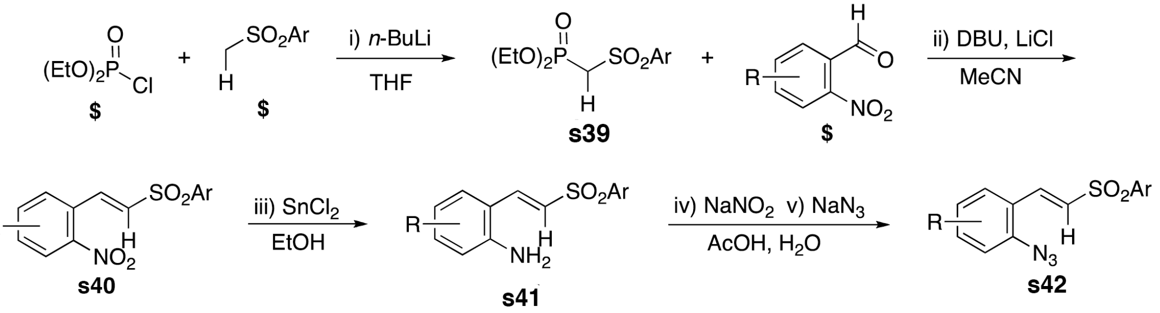
7e

***ortho*-Azido-β-acylstyrene 7e.** The following procedure, adapted from the report by Suri and Marcischak,[11] was used to synthesize **7e**. To a mixture of 0.10 mL of chlorotrimethylsilane (0.95 mmol) and 0.067 g of lithium bromide (0.76 mmol) in dry acetonitrile (0.75 mL) was added 0.095 g of *ortho*-azido-β-hydroxy ester **s38** (0.38 mmol) under nitrogen at room temperature, and the reaction was allowed to stir for 1 h before being taken up in CH_2Cl_2 (20 mL) and washed successively with aqueous sodium bicarbonate, water, and brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated to afford the crude product, which was taken up in a small amount of CH_2Cl_2 and added to neutral alumina. This mixture was evaporated to dryness, and the resulting powder was purified on a dry-packed MPLC column (0:100 – 30:70 EtOAc:hexanes on SiO_2) to give the product.MPLC (0:100 – 50:50 EtOAc:hexanes on SiO_2) afforded analytically pure **7e** as a colorless oil (0.036 g, 41%), R_f = 0.69 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). **Caution:** *ortho*-azido-β-substituted styrenes are potent skin irritants. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.88 (d, *J* = 16.0 Hz, 1H), 7.55 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.42-7.37 (m, 1H), 7.20-7.17 (m, 1H), 7.16-7.11 (m, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 5.14

(septet, *J* = 6.0 Hz, 1H), 1.31 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.4 (C), 139.1 (C), 138.6 (CH), 131.1 (CH), 128.2 (CH), 126.2 (C), 124.9 (CH), 120.5 (CH), 118.8 (CH), 67.9 (CH), 22.0 (CH_3); ATR-FTIR (thin film): 2979, 2934, 2122, 2091, 1706, 1633, 1596, 1574, 1483, 1452, 1273, 1176, 1107 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{12}H_{13}N_3O_2$ $(M)^+$: 231.10078, found: 231.10139.

III. Preparation of *ortho*-Azido-β-Sulfonylstyrenes

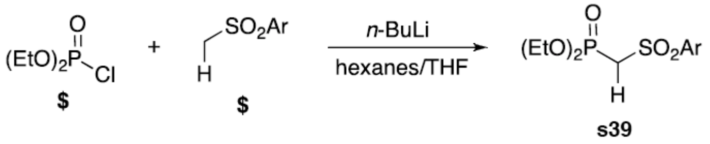
Scheme s3. Synthetic Route to *ortho*-Azido-β-Sulfonylstyrenes.



ortho-Azido-β-sulfonylstyrenes were synthesized using the route outlined in Scheme s3. Aryl methyl sulfones were condensed with diethylchlorophosphate to afford aryl methanesulfonylphosphates **s39**, which was subsequently coupled to 2-nitrobenzaldehyde in the presence of LiCl under basic conditions to give *ortho*-nitrosulfonylstyrene **s40**. Tin(II) chloride reduction afforded *ortho*-anilinosulfonylstyrene **s41**. Diazotization followed by nucleophilic substitution with sodium azide afforded *ortho*-azidosulfonylstyrene **s42**.

A. General Procedure for the Preparation of Methanesulfonylphosphates

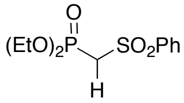
The requisite aryl methanesulfonylphosphates were prepared in one step from the condensation of commerically available diethylchlorophosphate with aryl methylsulfones using a solution of *n*-BuLi in hexanes and additional anhydrous THF as reported by Carter and coworkers (eq. s8).[12] Yields were not optimized.



(s8)

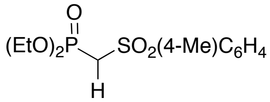
To a stirring solution of methyl phenyl sulfone (4.24 g, 27 mmol) in 25 mL of THF was added a 2.5 M solution of *n*-BuLi in hexanes (24 mL, 60 mmol) at 0 °C. After 0.5 h, diethylchlorophosphate (4.7 mL, 32 mmol) was added dropwise. After 1 h, the reaction was quenched with saturated aqueous NH_4Cl (5 mL). The organic volatiles were removed *in vacuo* and the residue was extracted with CH_2Cl_2 (2 × 50 mL). The organic layer was dried over Na_2SO_4 and concentrated to afford an oil, which was taken up in a portion of CH_2Cl_2 and concentrated onto neutral alumina and purified by MPLC (50:50 – 100:0 EtOAc:hexanes on SiO_2) to give the product.

B. Methanesulfonylphosphate Synthesis



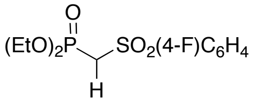
s43

Phosphonate s43.[13] The general procedure was followed using 4.24 g of methylphenylsulfone (27 mmol), 24 mL of a 2.5 M solution of *n*-BuLi in hexanes (60 mmol), and 4.7 mL of diethylchlorophosphate (32 mmol) in 25 mL of THF. Purification by MPLC (30:70 – 70:30 EtOAc:hexanes on SiO_2) afforded phosphonate **s43** as a white solid (6.61 g, 85%), mp 47 °C, $R_f = 0.17$ (60:40 EtOAc:hexanes, visualized by 254 nm UV light). The spectral data matched that reported by Bray and de Faveri.[13] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.93 (dd, J = 8.5, 1.0 Hz, 2H), 7.62 (tt, J = 7.5, 1.0 Hz, 1H), 7.52 (t, J = 7.5 Hz, 2H), 4.13-4.05 (m, 4H), 3.73 (d, J = 17.0 Hz, 2H), 1.22 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 139.9 (C), 134.1 (CH), 129.1 (CH), 128.3 (CH), 63.4 (d, J_{C-P} = 5.5 Hz, CH_2), 53.7 (d, J_{C-P} = 136.4 Hz, CH_2), 16.2 (d, J_{C-P} 5.6 Hz, CH_3); ATR-FTIR (thin film): 2981, 2903, 1447, 1397, 1308, 1251, 1152 cm^{-1}.



s44

Phosphonate s44.[14] The general procedure was followed using 5.06 g of methyl tolylsulfone (29 mmol), 25 mL of a 2.5 M solution of *n*-BuLi in hexanes (63 mmol), and 5.1 mL of diethylchlorophosphate (35 mmol) in 29 mL of THF. Purification by MPLC (30:70 – 70:30 EtOAc:hexanes on SiO_2) afforded phosphonate **s44** as a white solid (4.85 g, 55%), mp 59 °C, $R_f = 0.30$ (60:40 EtOAc:hexanes visualized by 254 nm UV light). The spectral data matched that reported by Mieloszynski and coworkers.[14] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.84 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 4.18-4.10 (m, 4H), 3.72 (d, J = 17.0 Hz, 2H), 2.43 (s, 3H), 1.27 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.2 (C), 137.1 (C), 129.7 (CH), 128.4 (CH), 63.37 (d, J_{C-P} = 5.6 Hz, CH_2), 53.8 (d, J_{C-P} = 136.9 Hz, CH_2), 21.7 (CH_3), 16.2 (d, J_{C-P} = 7.1 Hz, CH_3); ^{31}P NMR ($CDCl_3$, 202 MHz): δ 9.8; ATR-FTIR (thin film): 2958, 2884, 1598, 1308, 1253, 1152 cm^{-1}.

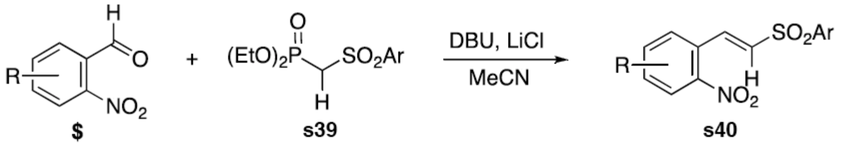


s45

Phosphonate s45. The general procedure was followed using 4.79 g of methyl (4-fluorophenyl)sulfone (27 mmol), 24 mL of a 2.5 M solution of *n*-BuLi in hexanes (59 mmol), and 4.7 mL of diethylchlorophosphate (32 mmol) in 27 mL of THF. Purification by MPLC (30:70 – 70:30 EtOAc:hexanes on SiO_2) afforded phosphonate **s45** as a white solid (4.60 g, 56%), mp 74 °C, $R_f = 0.18$ (60:40 EtOAc:hexanes visualized by 254 nm UV light). This compound was previously reported by Posner and Brunelle.[15] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.03-7.97 (m, 2H), 7.25-7.18 (m, 2H), 4.17-7.09 (m, 4H), 3.74 (d, J = 16.5 Hz, 2H), 1.26 (t, J = 7.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.1 (d, J_{C-F} = 255.4 Hz, C), 135.9 (C), 131.5 (d, J_{C-F} = 10.8 Hz, CH), 116.4 (d, J_{C-F} = 22.8 Hz, CH), 63.4 (d, J_{C-P} = 7.1 Hz, CH_2), 54.0 (d, J_{C-P} = 136.6 Hz, CH_2), 16.3 (d, J_{C-P} = 6.3 Hz, CH_3); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –103.1; ^{31}P NMR ($CDCl_3$, 202 MHz): δ 9.5; ATR-FTIR (thin film): 2896, 1767, 1681, 1589, 1494, 1395, 1316, 1253, 1150, 1012 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{11}H_{17}O_5SFP$ $(M)^+$: 311.05183, found: 311.05219.

C. General Procedure for the Preparation of *ortho*-Nitro-β-Sulfonylstyrenes

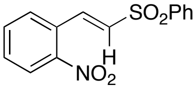
The requisite *ortho*-nitro-β-sulfonylstyrenes were prepared in one step from the Masamune-Roush-modified Horner-Wadsworth-Emmons reaction between aryl methanesulfonylphosphates and commercially available 2-nitrobenzaldehydes using DBU and LiCl in CH_3CN as reported by Carter and coworkers (eq. s9).[12] Yields were not optimized.



(s9)

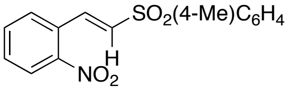
To a stirring suspension of LiCl (0.300 g, 4.51 mmol) in anhydrous CH_3CN (38 mL) was added a solution of **s43** (1.36 g, 6.77 mmol) in CH_3CN (2.0 mL). An additional portion of CH_3CN (3 × 1.0 mL) was used to wash the phosphonate flask. After promptly adding DBU (0.58 mL, 3.76 mmol), 2-nitrobenzaldehyde (0.580 g, 3.76 mmol) in CH_3CN (2.0 mL) was added dropwise. An additional portion of CH_3CN (3 × 1.0 mL) was added to wash the aldehyde flask. The resulting mixture was stirred for 2 h, then quenched with saturated aqueous NH_4Cl (15 mL), and concentrated *in vacuo* to remove CH_3CN. The residue was extracted with CH_2Cl_2 (4 × 50 mL), dried over Na_2SO_4, and concentrated. The residue was taken up in a portion of CH_2Cl_2 and concentrated onto neutral alumina and purified by MPLC (50:50 – 100:0 EtOAc:hexanes on SiO_2) to give the product.

D. *ortho*-Nitro-β-Sulfonylstyrene Synthesis



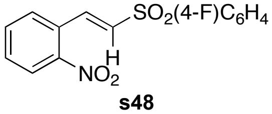
s46

***ortho*-Nitro-β-sulfonylstyrene s46.** The general procedure was followed using 0.580 g of 2-nitrobenzaldehyde (3.76 mmol), 1.36 g of aryl methanesulfonylphosphate **s43** (6.77 mmol), 0.300 g of LiCl (4.51 mmol), and 0.58 mL of DBU (3.76 mmol) in 48 mL of CH_3CN. Purification by MPLC (20:80 – 50:50 EtOAc:hexanes on SiO_2) afforded sulfone **s46** as a pale yellow solid (0.353 g, 32%), mp 99 °C, R_f = 0.23 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^1H NMR ($CDCl_3$, 500 MHz): δ 8.11 (d, *J* = 15.5 Hz, 1H), 8.05 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.96-7.94 (m, 2H), 7.66-7.60 (m, 2H), 7.57-7.51 (m, 4H), 6.81 (d, *J* = 15.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 147.9 (C), 139.8 (C), 139.0 (CH), 134.1 (CH), 133.9 (CH), 132.1 (CH), 131.3 (CH), 129.6 (CH), 129.5 (CH), 128.4 (C), 127.9 (CH), 125.2 (CH); ATR-FTIR (thin film): 3096, 2847, 1517, 1443, 1309, 1138, 1080 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{14}H_{12}NO_4S$ (M^+): 290.0487, found: 290.0487.



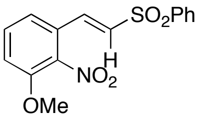
s47

***ortho*-Nitro-β-sulfonylstyrene s47.** The general procedure was followed using 0.580 g of 2-nitrobenzaldehyde (3.8 mmol), 1.36 g of aryl methanesulfonylphosphate **s44** (6.8 mmol), 0.300 g of LiCl (4.5 mmol), and 0.58 mL of DBU (3.8 mmol) in 48 mL of CH_3CN. Purification by MPLC (20:80 – 50:50 EtOAc:hexanes on SiO_2) afforded sulfone **s47** as a pale yellow solid (0.353 g, 32%), mp 99 °C, R_f = 0.23 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). The compound was previously reported by Baliah and Seshapathirao.[16] ^1H NMR ($CDCl_3$, 500 MHz): δ 8.12 (d, *J* = 15.5 Hz, 1H), 8.11 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.99-7.96 (m, 2H), 7.68-7.63 (m, 1H), 7.60-7.55 (m, 1H), 7.55-7.52 (m, 1H), 7.39-7.35 (m, 2H), 6.77 (d, *J* = 15.5 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 147.9 (C), 144.9 (C), 138.6 (CH), 136.8 (C), 134.0 (CH), 132.6 (CH), 131.0 (CH), 130.1 (CH), 129.6 (CH), 129.2 (C), 128.1 (CH), 125.2 (CH), 21.7 (CH_3); IR (thin film): 3096, 2847, 1517, 1443, 1309, 1138, 1080 cm^{-1}; HRMS (EI) *m / z* calculated for $C_{14}H_{12}NO_4S$ (M)$^+$: 290.0487, found: 290.0487.



s48

***ortho*-Nitro-β-sulfonylstyrene s48.** The general procedure was followed using 0.331 g of 2-nitrobenzaldehyde (2.2 mmol), 1.36 g of aryl methanesulfonylphosphate **s45** (3.2 mmol), 0.110 g of LiCl (2.6 mmol), and 0.39 mL of DBU (2.6 mmol) in 11 mL of CH_3CN. Purification by MPLC (20:80 – 50:50 EtOAc:hexanes on SiO_2) afforded sulfone **s48** as a white solid (0.497 g, 75%), mp 133 °C, R_f = 0.22 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.16 (d, J = 15.5 Hz, 1H), 8.12 (dd, J = 8.0, 1.0 Hz, 1H), 8.03-7.98 (m, 2H), 7.70-7.65 (m, 1H), 7.62-7.57 (m, 1H), 7.56-7.52 (m, 1H), 7.28-7.22 (m, 2H), 6.77 (d, J = 15.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.9 (d, J_{C-F} = 255.3 Hz, C), 147.9 (C), 139.6 (CH), 135.9 (C) 134.1 (CH) 132.0 (CH), 131.2 (CH), 130.9 (d, J_{C-F} = 10.4 Hz, CH), 129.6 (CH), 129.0 (C), 125.3 (CH), 116.9 (d, J_{C-F} = 22.4 Hz, CH); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –103.5; IR (thin film): 2923, 2852, 1737, 1589, 1524, 1342, 1136 cm^{-1}; HRMS (EI) *m / z* calculated for $C_{14}H_{11}NO_4SF$ (M)$^+$: 308.03928, found: 308.03946.

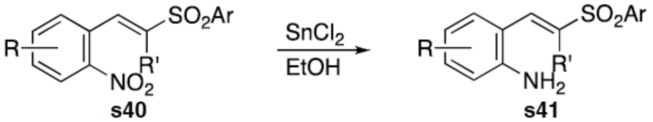


s49

***ortho*-Nitro-β-sulfonylstyrene s49.** The general procedure was followed using 0.425 g of 3-methoxy-2-nitrobenzaldehyde (2.3 mmol), 1.00 g of phenyl methanesulfonylphosphate **s43** (3.4 mmol), 0.117 g of LiCl (2.7 mmol), and 0.42 mL of DBU (2.7 mmol) in 15 mL of CH_3CN. Purification to the best of our ability by MPLC (25:75 – 75:25 EtOAc:hexanes on SiO_2) afforded sulfone **s49** as a white powder (0.065 g, 9%), mp 189 °C, R_f = 0.05 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR (DMSO, 500 MHz): δ 7.92-7.89 (m, 2H), 7.87 (d, J = 15.0 Hz, 1H), 7.78-7.72 (m, 1H), 7.69-7.64 (m, 2H), 7.60 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 15.0 Hz, 1H), 3.89 (s, 3H); ^{13}C NMR (DMSO, 125 MHz): δ 151.0 (C), 140.8 (C), 139.9 (C), 134.6 (CH), 134.0 (CH), 133.6 (CH), 132.7 (CH), 130.4 (CH), 128.0 (CH), 125.5 (C), 119.8 (CH), 116.6 (CH), 57.5 (CH_3); IR (thin film): 3040, 2910, 1576, 1518, 1476, 1363, 1289, 1220, 1152, 1063 cm^{-1}; HRMS (EI) *m / z* calculated for $C_{15}H_{13}NO_5S$ (M)$^+$: 319.05144, found: 319.05083.

E. General Procedure for the Preparation of *ortho*-Amino-β-Sulfonylstyrenes

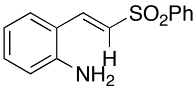
The requisite *ortho*-amino-β-sulfonylstyrenes were prepared in one step from the $SnCl_2$-promoted reduction of *ortho*-nitro-β-sulfonylstyrenes in anhydrous EtOH as reported by Bellamy and Ou (eq. s10).[17] Yields were not optimized.



(s10)

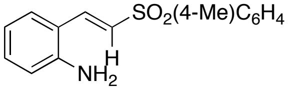
A stirring mixture of *ortho*-nitro-β-sulfonylstyrene **s40** (0.198 g, 0.68 mmol) and $SnCl_2$ (0.662 g, 3.4 mmol) in EtOH (1.5 mL) in a conical vial was heated at 40 °C for 1 h. The solution was allowed to cool to room temperature, poured over ice (10 g), and basified with 5% aqueous sodium bicarbonate. The resulting mixture was extracted with CH_2Cl_2 (3 × 10 mL), dried over Na_2SO_4, and concentrated. The residue was taken up in a portion of CH_2Cl_2 and concentrated onto neutral alumina and purified by MPLC (05:00:95 – 05:30:65 Et_3N:EtOAc:hexanes on SiO_2) to give the product, which decomposes upon contact with SiO_2.

F. *ortho*-Amino-β-Sulfonylstyrene Synthesis



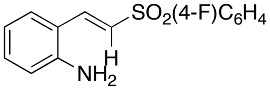
s50

***ortho*-Amino-β-sulfonylstyrene s50.** The general procedure was followed using 0.198 g of *ortho*-nitro-β-sulfonylstyrene **s46** (0.68 mmol) and 0.662 g of $SnCl_2$ (3.4 mmol) in 1.5 mL of anhydrous EtOH. Purification by MPLC (05:00:95 – 05:30:65 Et_3N:EtOAc:hexanes) afforded sulfone **s50** as a yellow powder (0.170 g, 96%), mp 111 °C, R_f = 0.08 (30:70 EtOAc:hexanes on an Et_3N-treated TLC plate, visualized by 254 nm or 365 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.96-7.94 (m, 2H), 7.86 (d, J = 15.0 Hz, 1H), 7.61-7.56 (m, 1H), 7.54-7.48 (m, 2H), 7.23 (dd, J = 8.0, 1.5 Hz, 1H), 7.16-7.12 (m, 1H), 6.80 (d, J = 15.0 Hz, 1H), 6.70-6.67 (m, 2H), 4.20 (br s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.6 (C), 140.9 (C), 138.4 (CH), 133.4 (CH), 132.4 (CH), 129.4 (CH), 128.6 (CH), 127.6 (CH), 126.0 (CH), 118.9 (CH), 117.4 (C), 117.3 (CH); ATR-FTIR (thin film): 3377, 1644, 1596, 1446, 1286, 1140, 1080, 965, 749, 683, 574, 552 cm^{-1}; HRMS (EI) m / z calculated for $C_{14}H_{13}NO_2S$ (M^+): 259.0667, found: 259.0665.



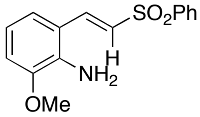
s51

***ortho*-Amino-β-sulfonylstyrene s51.** The general procedure was followed using 0.468 g of *ortho*-amino-β-sulfonylstyrene **s47** (1.5 mmol) and 1.49 g of $SnCl_2$ (7.7 mmol) in 3.0 mL of anhydrous EtOH. Purification by MPLC (05:00:95 – 05:30:65 Et_3N:EtOAc:hexanes) afforded sulfone **s51** as a yellow powder (0.351 g, 83%), mp 110 °C, R_f = 0.12 (30:70 EtOAc:hexanes on an Et_3N-treated TLC plate, visualized by 254 nm or 365 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.84-7.79 (m, 3H), 7.30 (d, J = 8.0 Hz, 2H), 7.23 (dd, J = 8.0, 1.0 Hz, 1H), 7.16-7.10 (m, 1H), 6.79 (d, J = 15.0 Hz, 1H), 6.71-6.66 (m, 2H), 4.17 (s, 2H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.5 (C), 144.3 (C), 138.0 (C), 137.8 (CH), 132.3 (CH), 130.0 (CH), 128.5 (CH), 127.6 (CH), 126.5 (CH), 118.9 (CH), 117.5 (C), 117.2 (CH), 21.7 (CH_3); ATR-FTIR (thin film): 3473, 3386, 3271, 3046, 1643, 1590, 1459, 1281, 1139, 1081 cm^{-1}; HRMS (EI) m / z calculated for $C_{14}H_{13}NO_2S$ $(M)^+$: 259.0667, found: 259.0665.



s52

***ortho*-Amino-β-sulfonylstyrene s52.** The general procedure was followed using 0.483 g of *ortho*-amino-β-sulfonylstyrene **s48** (1.6 mmol) and 1.52 g of $SnCl_2$ (7.9 mmol) in 3.0 mL of anhydrous EtOH. Purification by MPLC (05:00:95 – 05:30:65 Et_3N:EtOAc:hexanes) afforded sulfone **s52** as a yellow powder (0.423 g, 97%), R_f = 0.12 (30:70 EtOAc:hexanes on an Et_3N-treated TLC plate, visualized by 254 nm or 365 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.98-7.92 (m, 2H), 7.82 (d, J = 15.5 Hz, 1H), 7.27 (dd, J = 8.0, 1.0 Hz, 1H), 7.23-7.15 (m, 3H), 6.78 (d, J = 15.5 Hz, 1H), 6.75-6.68 (m, 2H), 4.09 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.5 (d, $J_{C–F}$ = 253.4 Hz, C), 146.3 (C), 138.4 (CH), 137.0 (C), 132.5 (CH), 130.4 (d, $J_{C–F}$ = 9.3 Hz, CH), 128.6 (CH), 126.2 (CH), 119.1 (CH), 117.4 (C), 117.3 (CH), 116.6 (d, $J_{C–F}$ = 22.1 Hz, CH); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –104.5; HRMS (EI) m / z calculated for $C_{14}H_{12}NO_2SF$ $(M)^+$: 277.0573, found: 277.0571.

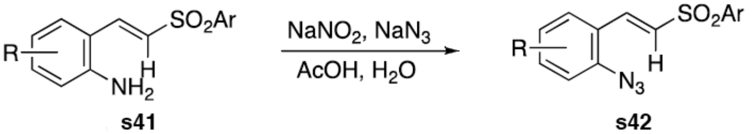


s53

***ortho*-Amino-β-sulfonylstyrene s53.** The general procedure was followed using 0.063 g of *ortho*-amino-β-sulfonylstyrene **s49** (0.20 mmol) and 0.190 g of $SnCl_2$ (0.98 mmol) in 0.40 mL of anhydrous EtOH. Purification by MPLC (05:00:95 – 05:30:65 Et_3N:EtOAc:hexanes) afforded sulfone **s53** as a yellow powder (0.018 g, 32%), mp 61 °C, $R_f = 0.40$ (50:50 EtOAc:hexanes on an Et_3N-treated TLC plate, visualized by 254 nm or 365 nm UV light). ^1H NMR ($CDCl_3$, 500 MHz): δ 7.97-7.92 (m, 2H), 7.83 (d, *J* = 15.5 Hz, 1H), 7.63-7.57 (m, 1H), 7.57-7.51 (m, 2H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.82-6.76 (m, 2H), 6.68 (t, *J* = 8.0 Hz, 1H), 4.28 (s, 2H), 3.86 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 147.8 (C), 141.0 (C), 138.0 (CH), 136.9 (C), 133.2 (CH), 129.3 (CH), 127.6 (CH), 126.4 (CH), 120.1 (CH), 118.0 (CH), 117.3 (C), 111.9 (CH), 55.8 (CH_3); ATR-FTIR (thin film): 3400, 3324, 3056, 2924, 1607, 1444, 1250, 1140, 1084 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{15}H_{15}NO_3S$ $(M)^+$: 289.07727, found: 289.07688.

G. General Procedure for the Preparation of *ortho*-Azido-β-Sulfonylstyrenes

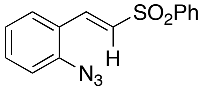
The requisite *ortho*-azido-β-sulfonylstyrenes were prepared in one step from substituted *ortho*-amino-β-sulfonylstyrenes following the procedure of Driver and coworkers (eq. s11).[18] Yields were not optimized.



(s11)

To a cold (0 °C) solution of substituted *ortho*-amino-β-sulfonylstyrene **s50** (0.148 g, 0.57 mmol) in acetic acid (4.0 mL) and water (2.0 mL) was added sodium nitrite (0.107 g, 1.6 mmol). After stirring for 1 h, sodium azide (0.118 g, 1.7 mmol) was added gradually, after which the mixture was allowed to warm to ambient temperature. After an additional h of stirring, the resulting mixture was neutralized with saturated aqueous Na_2CO_3 and extracted with 3 × 20 mL of CH_2Cl_2. The resulting organic phase was dried over Na_2SO_4 and concentrated. The residue was taken up in a portion of CH_2Cl_2 and concentrated onto neutral alumina and purified by MPLC (0:100 – 40:60 EtOAc:hexanes on SiO_2) to give the product. **Caution:** *ortho*-azido-β-substituted styrenes are potent skin irritants.

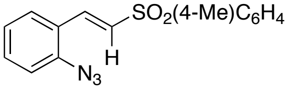
H. *ortho*-Azido-β-Sulfonylstyrene Synthesis



7f

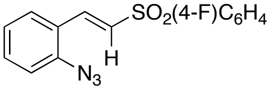
***ortho*-Azido-β-sulfonylstyrene 7f.** The general procedure was followed using 0.148 g of *ortho*-amino-β-sulfonylstyrene **s50** (0.57 mmol), 0.107 g of $NaNO_2$ (1.6 mmol), and 0.118 g of NaN_3 (1.7 mmol) in 4.0 mL of AcOH and 2.0 mL of H_2O. Purification by MPLC (0:100 – 40:60 EtOAc:hexanes) afforded *ortho*-azido-β-sulfonylstyrene **7f** as a white powder (0.074 g, 45%), mp 111 °C, $R_f = 0.43$ (30:70 EtOAc:hexanes, visualized by 254 nm UV light). **Caution:** *ortho*-azido-β-substituted styrenes are potent skin irritants. ^1H NMR ($CDCl_3$, 500 MHz): δ 7.96-7.94 (m, 2H), 7.85 (d, *J* = 15.5 Hz, 1H), 7.61 (tt, *J* = 7.5, 1.5 Hz, 1H), 7.56-7.52 (m, 2H), 7.46-7.40 (m, 2H), 7.18 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.14-7.11 (m, 1H), 7.03 (d, *J* = 15.5 Hz, 1H); ^{13}C NMR

($CDCl_3$, 125 MHz): δ 140.7 (C), 139.7 (C), 137.1 (CH), 133.5 (CH), 132.2 (CH), 129.6 (CH), 129.4 (CH), 129.1 (CH), 127.7 (CH), 125.0 (CH), 123.8 (C), 119.0 (CH); ATR-FTIR (thin film): 3050, 2922, 2852, 2118, 1610, 1446, 1303, 1143, 1083 cm^{-1}; HRMS (EI) *m / z* calculated for $C_{14}H_{11}N_3O_2S$ (M^+): 285.0572, found: 285.0572.



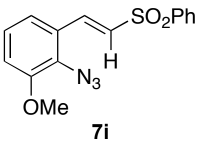
7g

***ortho*-Azido-β-sulfonylstyrene 7g.** The general procedure was followed using 0.341 g of *ortho*-amino-β-sulfonylstyrene **s51** (1.3 mmol), 0.117 g of $NaNO_2$ (1.7 mmol), and 0.130 g of NaN_3 (1.9 mmol) in 8.0 mL of AcOH and 4.0 mL of H_2O. Purification by MPLC (0:100 – 50:50 EtOAc:hexanes) afforded *ortho*-azido-β-sulfonylstyrene **7g** as colorless needles (0.214 g, 57%), mp 110 °C, R_f = 0.42 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). **Caution:** *ortho*-azido-β-substituted styrenes are potent skin irritants. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.84-7.78 (m, 3H), 7.45-7.38 (m, 2H), 7.35-7.30 (m, 2H), 7.16 (dd, J = 8.0, 1.0 Hz, 1H), 7.14-7.09 (m, 1 H), 7.01 (d, J = 15.5 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 144.5 (C), 139.6 (C), 137.7 (C), 136.5 (CH), 132.1 (CH), 130.0 (CH), 129.6 (CH), 129.5 (CH), 127.8 (CH), 125.0 (CH), 123.8 (C), 119.0 (CH), 21.7 (CH_3); ATR-FTIR (thin film): 3067, 2120, 1608, 1479, 1291, 1140, 1081 cm^{-1}; HRMS (EI) *m / z* calculated for $C_{15}H_{13}N_3O_2S$ $(M)^+$: 299.0728, found: 299.0731.



7h

***ortho*-Azido-β-sulfonylstyrene 7h.** The general procedure was followed using 0.421 g of *ortho*-amino-β-sulfonylstyrene **s52** (1.5 mmol), 0.151 g of $NaNO_2$ (2.1 mmol), and 0.148 g of NaN_3 (2.3 mmol) in 8.0 mL of AcOH and 4.0 mL of H_2O. Purification by MPLC (0:100 – 50:50 EtOAc:hexanes) afforded *ortho*-azido-β-sulfonylstyrene **7h** as a white solid (0.249 g, 54%), mp 125 °C, R_f = 0.38 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). **Caution:** *ortho*-azido-β-substituted styrenes are potent skin irritants. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.98-7.91 (m, 2H), 7.81 (d, J = 15.5 Hz, 1H), 7.46-7.37 (m, 2H), 7.23-7.13 (m, 3H), 7.10 (t, J = 7.5 Hz, 1H), 7.02 (d, J = 15.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.6 (d, J_{C-F} = 254.5 Hz, C), 139.7 (C), 137.2 (CH), 136.8 (C), 132.4 (CH), 130.6 (d, J_{C-F} = 9.1 Hz, CH), 129.7 (CH), 128.9 (CH), 125.1 (CH), 123.6 (C), 119.0 (CH), 116.7 (d, J_{C-F} = 23.3 Hz, CH); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –104.3; ATR-FTIR (thin film): 3098, 3064, 2117, 1606, 1484, 1284, 1223, 1141, 1081 cm^{-1}; HRMS (EI) *m / z* calculated for $C_{14}H_{10}N_3O_2SF$ $(M)^+$: 303.0478, found: 303.0482.



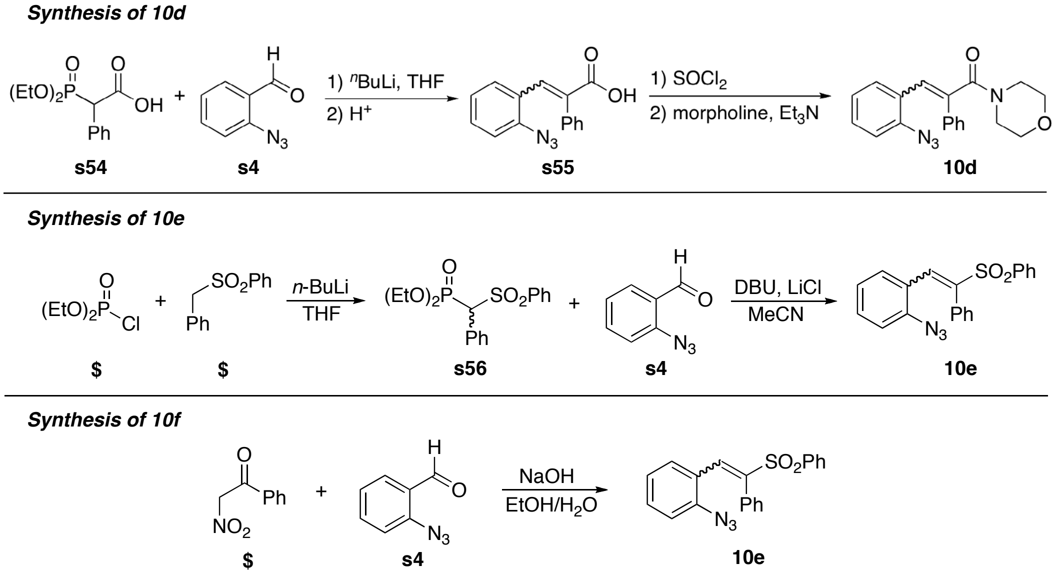
7i

***ortho*-Azido-β-sulfonylstyrene 7i.** The general procedure was followed using 0.014 g of *ortho*-amino-β-sulfonylstyrene **s53** (0.05 mmol), 0.005 g of $NaNO_2$ (0.07 mmol), and 0.005 g of NaN_3 (0.07 mmol) in 1.0 mL of AcOH and 0.50 mL of H_2O. Purification by MPLC (5:20:75 – 5:70:25 Et_3N:EtOAc:hexanes) afforded *ortho*-azido-β-sulfonylstyrene **7i** as a white solid (0.010 g, 65%), mp 125 °C, R_f = 0.36 (50:50 EtOAc:hexanes on an Et_3N-treated TLC plate, visualized by 254 nm UV light). **Caution:** *ortho*-azido-β-substituted styrenes are potent skin irritants. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.98-7.92 (m, 3H), 7.65-7.59 (m, 1H), 7.58-7.52 (m, 2H), 7.09-7.00 (m, 2H), 6.97 (d, J = 15.5 Hz, 1H), 6.91 (dd, J = 7.5, 1.5 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 154.3 (C), 140.7 (C), 137.8 (CH), 133.4 (CH), 129.4 (CH), 129.1 (CH), 128.2 (C), 127.8 (CH), 125.2

(C), 125.1 (CH), 120.7 (CH), 113.7 (CH), 56.2 (CH_3); ATR-FTIR (thin film): 3054, 2920, 2850, 2110, 1781, 1694, 1574, 1448, 1302, 1263 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{15}H_{13}N_3O_3S$ $(M)^+$: 315.0678, found: 315.0680.

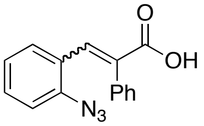
IV. Preparation of *ortho*-Azido-β-Disubstituted Styrenes

Scheme s4. Synthetic Routes to *ortho*-azido-*β*-disubstituted Styrenes **10d-f**



Compound **10d** was synthesized by a two steps sequence (Scheme s4) consisting of 1) condensation of diethylchlorophosphate with benzyl phenyl sulfone using *n*-BuLi, to give phosphonate **s56** and 2) Masamune-Roush-modified Horner-Wadsworth-Emmons reaction between phosphonate **s56** and *ortho*-azidobenzaldehyde **s4**. Compound **10e** was synthesized by the NaOH-catalyzed hydrolytic nitroaldol (Henry) reaction between **s4** and benzoyl nitromethane. Compound **10d** was synthesized according to the procedure described in Scheme s4. 1) **s54** was activated by 2 eqvi. of *n*-BuLi, and then it was undergoing a Horner-Wadsworth-Emmons reaction with **s4** to give the acid **s55**. 2) The acid s52 was converted to acid chloride by using $SOCl_2$. The acid chloride was then reacted with morpholine with the help of Et_3N to give amide **10d**.

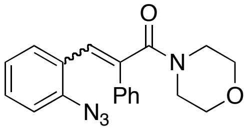
A. Synthesis of 3-(2-azidophenyl)-2-phenylacrylic acid s55



s55

Acid s55. A 2.5 M solution of n-BuLi in hexane (2.5 mL, 6.3 mmol) was added to THF (30 mL) at -60 °C followed by the dropwise addition of **s54** (816 mg, 3 mmol) in THF (5 mL). After 30 min stirring at this temperature, a solution of **s4** (441 mg, 3 mmol) in THF (5 mL) was added dropwise. Kept stirring for 1 hr, the reaction mixture was then allowed to warm to room temperature. After an additional 3 hrs stirring, the reaction was acidified with 1M HCl. The aqueous layer was separated, and the organic layer was extracted once with 1M HCl. The combined aqueous layer was basified with NaOH(aq), and extracted with EA for three times. The combined organic layer was wash with brine and dried with Na_2SO_4. Filter and removed the solvent to provide the acid **s55** as a white solid, which is used directly without further purification.

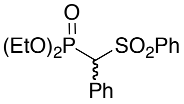
B. Synthesis of 3-(2-azidophenyl)-1-morpholino-2-phenylprop-2-en-1-one 10d



10d

Amide s56. To a solution of acid **s55** (800 mg, 3 mmol) in 30 mL of DCM was added thionyl chloride (714 mg, 6 mmol) dropwise. The mixture was refluxed with stirring for 3 hrs and was concentrated under reduced pressure to give a residue as yellow oil. This residue acid chloride was diluted with DCM (10 mL), and was carefully added dropwise to a solution of morpholine (287 mg, 3.3 mmol), Et_3N (400mg, 4 mmol) and 30 mL DCM at 0 °C. After addition, the reaction was warm to room temperature and reacted for 1h. The solvent was removed under reduced pressure and the reaction was quenched with 1M NaOH(aq) and extracted with EtOAc (3 × 15 mL). The combined organic layers were dried over sodium sulfate and concentrated. The crude material was then purified by MPLC (2:8:90 – 2:49:49 Et_3N:EtOAc:hexanes) to afford the amide **s56** as a yellow oil (0.43 g, two steps 43%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.23–7.20 (m, 5H), 7.12 (d, J = 8.0 Hz, 1H), 6.92 (d, J = 8.0 Hz, 1H), 6.81 (t, J = 8.0 Hz, 1H), 6.77 (s, 1H), 3.67-3.47 (m, 8H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 170 (C), 138.7 (C), 138.0 (C), 134.9 (C), 130.7 (CH), 129.2 (CH), 128.7 (4CH), 128.2 (CH), 127.1 (C), 125.9 (CH), 124.3 (CH), 118.2 (CH), 66.7 (2CH_2), 47.5 (CH_2), 42.3 (CH_2); ATR-FTIR (thin film): 3049, 2962, 2853, 2117, 1629, 1427, 1276, 1115, 732 cm^{-1}; HRMS (EI) m / z calculated for $C_{19}H_{18}O_2N_4$ $(M)^+$: 334.14297, found: 334.14371.

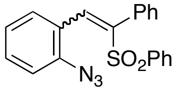
C. Synthesis of Benzylsulfonylphosphate s56



s56

Phosphonate s56. The general procedure was followed using 2.00 g of benzyl phenyl sulfone (8.0 mmol), 7.4 mL of a 2.5 M solution of n-BuLi in hexanes (19 mmol), and 1.5 mL of diethylchlorophosphate (10 mmol) in 8.0 mL of THF. Purification by MPLC (30:70 – 70:30 EtOAc:hexanes on SiO_2) afforded phosphonate **s56** as a white solid (1.567 g, 53%), mp 74 °C, R_f = 0.17 (60:40 EtOAc:hexanes on an Et_3N-treated TLC plate, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.61 (d, J = 7.5 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 2H), 7.32-7.26 (m, 3H), 7.25-7.20 (m, 2H), 4.67 (d, J = 16.0 Hz, 1H), 4.26 (quintet, J = 7.0 Hz, 2H), 4.13-4.01 (m, 1H), 3.93-3.83 (m, 1H), 1.31 (t, J = 7.0 Hz, 3H), 1.09 (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 138.0 (C), 133.8 (CH), 131.1 (d, J_{C-P} = 6.9 Hz, CH), 129.4 (CH), 129.1 (CH), 128.6 (CH), 128.6 (CH), 128.5 (CH), 128.1 (d, J_{C-P} = 4.1 Hz, C), 70.5 (d, J_{C-P} = 137.6 Hz, CH), 63.9 (d, J_{C-P} = 7.0 Hz, CH_2), 16.4 (d, J_{C-P} = 5.5 Hz, CH_3), 16.1 (d, J_{C-P} = 5.6 Hz, CH_3); ^{31}P NMR ($CDCl_3$, 202 MHz): δ 11.1; ATR-FTIR (thin film): 2981, 2922, 1446, 1271, 1146, 1022 cm^{-1}; HRMS (EI) m / z calculated for $C_{17}H_{21}O_5PS$ $(M)^+$: 368.0847, found: 368.0850.

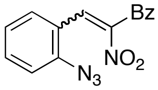
B. Synthesis of *ortho*-Azido-β-Disubstituted Styrene 10e



10e

Styryl azide 10e. The following procedure, adapted from the report by Carter and coworkers,[12] was followed. To a stirring suspension of 0.035 g of LiCl (0.82 mmol) in 3.0 mL of anhydrous CH_3CN was added 0.375 g of a solution of phosphonate **s56** (1.0 mmol) in 0.50 mL CH_3CN. An additional portion of CH_3CN (3 x 0.25 mL) was used to wash the phosphonate flask. After promptly adding 0.13 mL of DBU (0.83 mmol), 0.100 g of 2-azidobenzaldehyde (0.68 mmol) in 0.50 mL of CH_3CN was added dropwise. An additional portion of CH_3CN (3 x 0.25 mL) was added to wash the aldehyde flask. The resulting mixture was stirred overnight, then quenched with saturated aqueous NH_4Cl (20 mL), and concentrated *in vacuo* to remove CH_3CN. The residue was extracted with CH_2Cl_2 (4 × 20 mL), dried over Na_2SO_4, and concentrated. The residue was taken up in a portion of CH_2Cl_2 and concentrated onto neutral alumina and purified by MPLC (20:80 – 50:50 EtOAc:hexanes on SiO_2) to afford **10e** as a white solid (0.034 g, 14%), mp 171 °C, $R_f = 0.55$ (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^1H NMR ($CDCl_3$, 500 MHz): δ 8.22 (s, 1H), 7.65 (d, $J = 7.5$ Hz, 2H), 7.52 (t, $J = 7.5$ Hz, 1H), 7.39 (t, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.29-7.21 (m, 3H), 7.15 (d, $J = 7.5$ Hz, 1H), 7.03 (d, $J = 7.5$ Hz, 2H), 6.77-6.69 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 142.6 (C), 138.7 (C), 133.2 (CH), 132.4 (CH), 131.0 (CH), 130.8 (CH), 130.2 (CH), 129.9 (CH), 129.2 (CH), 128.8 (C), 128.7 (CH), 128.6 (CH), 128.3 (C), 124.5 (C), 124.2 (CH), 118.4 (CH); ATR-FTIR (thin film): 3065, 2927, 2125, 2102, 1630, 1595, 1573, 1479, 1447, 1306, 1292, 1144, 1084, 1000 cm^{-1}; HRMS (EI) *m / z* calculated for $C_{20}H_{15}NO_2S$ $(M - N_2)^+$: 333.08235, found: 333.08318.

C. Synthesis of *ortho*-Azido-β-Disubstituted Styrene 10f

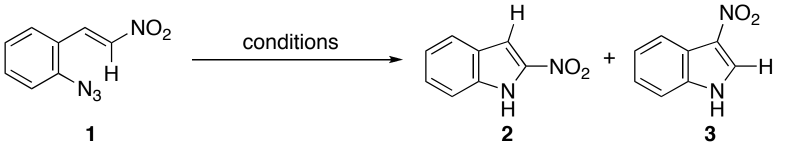


10f

Stryrl azide 10f. The following procedure, adapted from the report by Sagitullin and coworkers,[19] was used to synthesize **10f**: a mixture of 0.120 g of nitroacetophenone (0.71 mmol), 0.100 g of 2-azidobenzaldehyde **s4** (0.68 mmol), 0.006 g of β-alanine (0.07 mmol), 0.100 g of powdered 4 Å molecular sieves, and 0.11 mL of glacial acetic acid in 1.1 mL of benzene was stirred for 3 h at 25 °C. The reaction mixture was taken up in CH_2Cl_2 (5 mL), filtered, and washed with water (3 × 5 ml), dried over Na_2SO_4, and concentrated *in vacuo*. Purification by MPLC (0:100 – 50:50 EtOAc:hexanes on SiO_2) afforded **10f** as a yellow solid (0.199 g, 99%), mp 149 °C, $R_f = 0.57$ (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^1H NMR ($CDCl_3$, 500 MHz): δ 8.58 (s, 1H), 7.91 (d, $J = 7.0$ Hz, 2H), 7.61 (t, $J = 7.5$ Hz, 1H), 7.47 (t, $J = 7.5$ Hz, 2H), 7.45-7.38 (m, 1H), 7.27-7.23 (m, 1H), 7.19 (d, $J = 8.0$ Hz, 1H), 6.97 (t, $J = 7.5$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 187.9 (C), 145.7 (C), 140.9 (C), 135.1 (C), 135.9 (CH), 133.3 (CH), 132.0 (CH), 130.6 (CH), 129.2 (CH), 129.1 (CH), 125.1 (CH), 120.7 (C), 118.9 (CH); ATR-FTIR (thin film): 3068, 3032, 2925, 2851, 2093, 1677, 1632, 1595, 1514, 1482, 1449, 1333, 1309, 1287, 1229, 1171 cm^{-1}; HRMS (EI) *m / z* calculated for $C_{15}H_{10}N_2O_3$ $(M - N_2)^+$: 266.06915, found: 266.06861.

V. Rh(II)-Catalyzed Synthesis of Substituted Indoles from Aryl Azides

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



(s12)

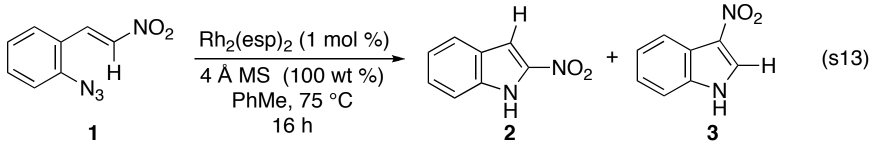
To a conical vial equipped with spin vane was added 0.005 g of aryl azide **1** (0.026 mmol), 0-100% w/w of powdered 4 Å molecular sieves, and metal salt (0 – 5 mol%) and 0.07 mL of solvent. The reaction was sealed with a PTFE-lined screw-top cap and heated and stirred for 1h with stirring. After cooling to room temperature, the mixture had evolved N_2 gas which was released upon opening, and the mixture was filtered through Celite using EtOAc and concentrated *in vacuo*. The concentrate was dissolved in 1.5 mL of DMSO and 0.007 mL of CH_2Br_2 (0.10 mmol). The areas of the C–H peaks at C4 in **2** and C2 in **3** were compared to the area of CH_2Br_2 to calculate conversion and yield.

Table s1. Optimization of Migration Reaction [a,b]

entry	metal salt	mol %	solvent	wt %, 4 Å MS	T (°C)	conv., % [c]	yield, % [c]	**3 : 2**
1	none	n.a.	PhMe	100	75	0	0	n.a.
2	$Rh_2(OAc)_4$	5	PhMe	100	75	0	0	n.a.
3	$Rh_2(O_2CC_7H_{15})_4$	5	PhMe	100	75	95	89	100 : 0
4	Rh_2(S-DOSP)$_4$	5	PhMe	100	75	100	92	100 : 0
5	Rh_2(S-PTAD)$_4$	5	PhMe	100	75	92	82	100 : 0
6	$Rh_2(esp)_2$	5	PhMe	100	75	99	95	100 : 0
7	$Rh_2(esp)_2$	5	PhMe	0	75	100	92	100 : 0
8	$Rh_2(O_2CCF_3)_4$	5	PhMe	100	75	66	61	99 : 1
9	$Rh_2(O_2CC_3F_7)_4$	5	PhMe	100	75	66	61	99 : 1
10	$RuCl_3•xH_2O$	5	DME	100	75	89	67	99 : 1
11	$RuCl_3•xH_2O$	5	PhMe	0	75	0	0	n.a.
12	$[(cod)IrOMe]_2$	5	PhMe	100	75	29	trace	0 : 100
13	CoTPP	5	PhMe	100	75	17	4	57 : 43
14	$[(cymene)RuCl_2]_2$	5	PhMe	100	75	0	0	n.a.
15	CuCl	5	PhMe	100	75	0	0	n.a.
16	$CuCl_2$	5	PhMe	100	75	0	0	n.a.
17	CuOTf	5	PhMe	100	75	0	0	n.a.
18	$Cu(OTf)_2$	5	PhMe	100	75	0	0	n.a.
19	$FeBr_2$	5	PhMe	100	75	0	0	n.a.

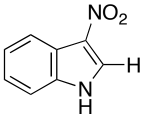
[a] Reaction performed in conical vial. [b] 16 hour reaction time. [c] As determined using ^{1}H NMR spectroscopy.

B. Optimized General Procedure



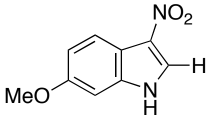
To a mixture of *ortho*-azido-β-nitrostyrene **1** (0.100 g, 0.50 mmol), powdered 4 Å molecular sieves (0.100 g, 100% w/w), and $Rh_2(esp)_2$ (0.004 g, 0.005 mmol) in a spin vane-equipped conical vial was added toluene (0.90 mL). The resulting mixture was sealed with a PTFE-lined screw-top cap and heated at 75 °C for 16 h with stirring. After cooling to room temperature, the mixture had evolved N_2 gas, which was released upon opening, and the mixture was filtered through Celite using EtOAc. The filtrate was concentrated *in vacuo* and purified by MPLC to afford the product. Addition of a small amount of Et_3N (0.5% v/v) during MPLC column packing can prevent coelution of $Rh_2(esp)_2$ and product. The products are have characteristic ^{1}H NMR shifts: C3–H of 2-nitroindoles including **2**: ~7.5 ppm in (DMSO or $CDCl_3$; C2–H of 3-nitroindoles including **3**: ~8.6 ppm.

C. Scope and Limitations of Substituted Indole Formation



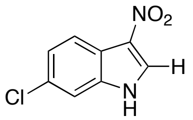
3

Indole 3.[20] The general procedure was followed using 0.100 g of aryl azide **1** (0.50 mmol), 0.004 g of $Rh_2(esp)_2$ (0.005 mmol), and 0.100 g of powdered 4 Å molecular sieves in 0.90 mL of toluene. Purification by MPLC (30:70 – 70:30 EtOAc:hexanes) afforded **3** as a yellow powder (0.081 g, 95%), mp 207 °C, R_f = 0.28 (60:40 EtOAc:hexanes, visualized by 254 nm UV light). The spectral data matched that reported by Gribble and coworkers.[20] ^{1}H NMR (DMSO, 500 MHz): δ 12.65 (br s, 1H), 8.63 (s, 1H), 8.10-8.05 (m, 1H), 7.58-7.52 (m, 1H), 7.35-7.28 (m, 2H); ^{13}C NMR (DMSO, 125 MHz): δ 135.5 (C), 131.0 (CH), 128.9 (C), 124.6 (CH), 124.2 (CH), 120.3 (C), 119.9 (CH), 113.9 (CH); ATR-FTIR (thin film): 3216, 3125, 2924, 1441, 1378, 1321, 1200, 1123 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_6N_2O_2$ (M)$^+$: 162.04293, found: 162.04309.



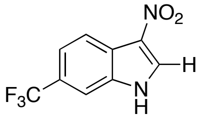
5a

Indole 5a. The general procedure was followed using 0.100 g of aryl azide **4a** (0.45 mmol), 0.004 g of $Rh_2(esp)_2$ (0.005 mmol), and 0.100 g of powdered 4 Å molecular sieves in 1.0 mL of toluene. Purification by MPLC (30:70 – 70:30 EtOAc:hexanes) afforded **5a** as a yellow powder (0.079 g, 91%), mp 234 °C, R_f = 0.10 (60:40 EtOAc:hexanes, visualized by 254 nm UV light). **5a** was previously reported by Barret and coworkers.[21] ^{1}H NMR (DMSO, 500 MHz): δ 12.40 (br s, 1H), 8.49 (s, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.01 (s, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 3.79 (s, 3H); ^{13}C NMR (DMSO, 125 MHz): δ 157.7 (C), 136.6 (C), 129.8 (CH), 129.1 (C), 120.7 (CH), 114.3 (C), 114.0 (CH), 96.6 (CH), 55.8 (CH_3); ATR-FTIR (thin film): 3269, 3114, 2955, 2920, 2850, 2836, 1624, 1518, 1508, 1454, 1439, 1407, 1362, 1351, 1307, 1290, 1213, 1190, 1154, 1110, 1022 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_9H_8N_2O_3$ (M)$^+$: 192.05350, found: 192.05445.



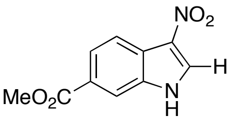
5b

Indole 5b. The general procedure was followed using 0.030 g of aryl azide **4b** (0.13 mmol), 0.001 g of $Rh_2(esp)_2$ (0.001 mmol), and 0.030 g of powdered 4 Å molecular sieves in 0.30 mL of toluene. Purification by MPLC (30:70 – 70:30 EtOAc:hexanes) afforded **5b** as a yellow powder (0.021 g, 79%), mp 235 °C, $R_f = 0.47$ (60:40 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR (DMSO, 500 MHz): δ 12.73 (br s, 1H), 8.67 (s, 1H), 8.05 (d, J = 8.5 Hz, 1H), 7.61 (d, J = 1.5 Hz, 1H), 7.37 (dd, J = 8.5, 1.5 Hz, 1H); ^{13}C NMR (DMSO, 125 MHz): δ 135.9 (C), 131.9 (CH), 129.2 (C), 128.9 (C), 124.5 (CH), 121.3 (CH), 119.1 (C), 113.6 (CH); ATR-FTIR (thin film): 3145, 1372, 1202 cm^{-1}; HRMS (EI) m / z calculated for $C_8H_5O_2N_2Cl$ $(M)^+$: 196.00396, found: 196.00448.



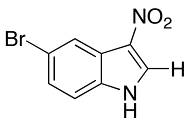
5c

Indole 5c. To a flame-dried round-bottomed flask was added 0.572 g of aryl azide **4c** (2.2 mmol), 0.002 g of $Rh_2(esp)_2$ (0.002 mmol), and 0.572 g of powdered 4 Å molecular sieves in 6.0 mL of toluene. The flask was fitted with a reflux condenser and heated to 75 °C for 16 h with stirring and venting. The mixture was allowed to cool to room temperature, then was filtered through Celite using EtOAc and partially concentrated. A portion of neutral alumina was added and the mixture was evaporated to dryness. The resulting powder was purified on a dry-packed MPLC column (20:80 – 80:20 EtOAc:hexanes) to afford **5c** as a white powder (0.490 g, 96%), mp 229 °C, $R_f = 0.14$ (20:80 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR (DMSO, 500 MHz): δ 13.00 (br s, 1H), 8.85 (s, 1H), 8.27 (d, J = 8.5 Hz, 1H), 7.90 (s, 1H), 7.67 (d, J = 8.5 Hz, 1H); ^{13}C NMR (DMSO, 125 MHz): δ 134.5 (C), 133.5 (CH), 128.9 (C), 125.1 (q, J_{C-F} = 270.0 Hz, C), 124.9 (q, J_{C-F} = 31.4 Hz, C), 122.8 (C), 120.9 (CH), 120.4 (CH), 111.3 (q, J_{C-F} = 3.4 Hz, CH); ^{19}F NMR (DMSO, 282 MHz): δ –60.3; ATR-FTIR (thin film): 3290, 3140, 1528, 1479, 1445, 1375, 1355, 1314, 1264, 1230, 1207, 1173, 1128, 1058 cm^{-1}; HRMS (EI) m / z calculated for $C_9H_5O_2N_2F_3$ $(M)^+$: 230.03032, found: 230.02916.



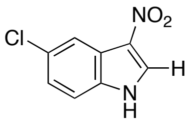
5d

Indole 5d. The general procedure was followed using 0.0248 g of aryl azide **4d** (0.10 mmol), 0.001 g of $Rh_2(esp)_2$ (0.001 mmol), and 0.0238 g of powdered 4 Å molecular sieves in 0.50 mL of toluene. Purification by MPLC (pure EtOAc) afforded **5d** as a pale yellow solid (0.0211 g, 96%), mp > 300 °C. ^{1}H NMR (DMSO, 500 MHz): δ 8.79 (s, 1H), 8.18 (s, 1H), 8.12 (d, J = 8.5 Hz, 1H), 7.89 (d, J = 8.5 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (DMSO, 125 MHz): δ 166.8 (C), 135.3 (C), 133.8 (CH), 128.8 (C), 125.5 (C), 124.5 (CH), 123.7 (C), 119.8 (CH), 115.7 (CH), 52.7 (CH_3); ATR-FTIR (thin film): 3453, 3259, 2388, 1715, 1291 cm^{-1}; HRMS (EI) m / z calculated for $C_{10}H_8O_4N_2$ $(M)^+$: 220.04841, found: 220.04857.



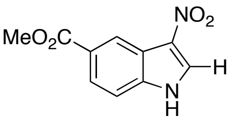
5e

Indole 5e. The general procedure was followed using 0.030 g of aryl azide **4e** (0.11 mmol), 0.001 g of $Rh_2(esp)_2$ (0.001 mmol), and 0.030 g of powdered 4 Å molecular sieves in 0.30 mL of toluene. Purification by MPLC (30:70 – 80:20 EtOAc:hexanes) afforded **5e** as a yellow powder (0.023 g, 87%), mp 92 °C, $R_f = 0.33$ (60:40 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR (DMSO, 500 MHz): δ 12.82 (br s, 1H), 8.69 (s, 1H), 8.17 (d, J = 1.5 Hz, 1H), 7.53 (d, J = 8.5 Hz, 1H), 7.47 (dd, J = 8.5, 2.0 Hz, 1H); ^{13}C NMR (DMSO, 125 MHz): δ 134.3 (C), 132.1 (CH), 128.2 (C), 127.4 (CH), 122.0 (CH), 121.9 (C), 117.0 (C), 116.0 (CH); ATR-FTIR (thin film): 3186, 3131, 1509, 1436, 1364, 1271, 1206 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_5O_2N_2Br$ $(M)^+$: 239.95344, found: 239.95434.



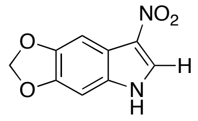
5f

Indole 5f. The general procedure was followed using 0.030 g of aryl azide **4f** (0.13 mmol), 0.001 g of $Rh_2(esp)_2$ (0.001 mmol), and 0.030 g of powdered 4 Å molecular sieves in 0.30 mL of toluene. Purification by MPLC (30:70 – 70:30 EtOAc:hexanes) afforded **5f** as a pale yellow powder (0.024 g, 90%), mp >240 °C, $R_f = 0.28$ (60:40 EtOAc:hexanes, visualized by 254 nm UV light). **5f** was previously reported by Jain and coworkers.[22] ^{1}H NMR (DMSO, 500 MHz): δ 12.81 (br s, 1H), 8.69 (s, 1H), 8.03-8.00 (m, 1H), 7.59-7.55 (m, 1H), 7.37-7.32 (m, 1H); ^{13}C NMR (DMSO, 125 MHz): δ 134.1 (C), 132.2 (CH), 129.0 (C), 128.4 (C), 124.8 (CH), 121.4 (C), 119.0 (CH), 115.7 (CH); ATR-FTIR (thin film): 3256, 3241, 3137, 1582, 1512, 1438, 1326, 1271, 1184, 1085 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_5N_2O_2Cl$ $(M)^+$: 196.00396, found: 196.00380.



5g

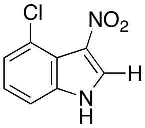
Indole 5g. The general procedure was followed using 0.0248 g of aryl azide **4g** (0.10 mmol), 0.001 mg of $Rh_2(esp)_2$ (0.001 mmol), and 0.0234 g of powdered 4 Å molecular sieves in 0.50 mL of toluene. Purification by MPLC (100% EtOAc) afforded **5g** as a pale yellow solid (0.0208 g, 95%), mp >300 °C. ^{1}H NMR (DMSO, 500 MHz): δ 8.75 (d, J = 1.5 Hz, 1H), 8.67 (s, 1H), 7.89 (d, J = 8.5 Hz, 1H), 7.62 (d, J = 8.5 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (DMSO, 125 MHz): δ 166.9 (C), 138.0 (C), 132.8 (CH), 132.7 (C), 129.5 (C), 125.3 (CH), 121.9 (CH), 119.9 (C), 114.1 (CH), 52.6 (CH_3); ATR-FTIR (thin film): 3613, 2556, 1714, 1376, 1220 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{10}H_8O_4N_2$ $(M)^+$: 220.04841, found: 220.04986.



5h

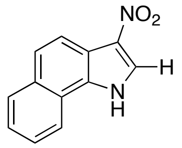
Indole 5h. The general procedure was followed using 0.0234 g of aryl azide **4h** (0.10 mmol), 0.001 g of $Rh_2(esp)_2$ (0.001 mmol), and 0.0234 g of powdered 4 Å molecular sieves in 0.50 mL of toluene. Purification by MPLC (100% EtOAc) afforded **5h** as a pale yellow solid (0.0191 g, 93%), mp >300 °C. ^{1}H NMR (DMSO, 500 MHz): δ 8.37 (s, 1H), 7.71 (s, 1H), 7.08 (s, 1H), 6.05 (s, 2H); ^{13}C NMR (DMSO, 125 MHz): δ 146.3 (C), 146.1

(C), 130.6 (C), 129.2 (C), 128.6 (CH), 114.6 (C), 101.8 (CH_2), 98.5 (CH), 94.4 (CH); ATR-FTIR (thin film): 3461, 3258, 1716, 1462, 1316, 1151 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_9H_6O_4N_2$ $(M)^+$: 206.03276, found: 206.03181.

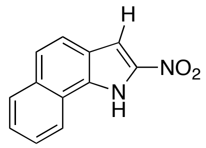


5i

Indole 5i. The general procedure was followed using 0.033 g of aryl azide **4i** (0.15 mmol), 0.001 g of $Rh_2(esp)_2$ (0.002 mmol), and 0.033 g of powdered 4 Å molecular sieves in 0.30 mL of toluene. Purification by MPLC (00:100 – 50:50 EtOAc:hexanes) afforded **5i** as a yellow powder (0.028 g, 95%), mp 191 °C, R_f = 0.59 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR (DMSO, 500 MHz): δ 12.83 (br s, 1H), 8.68 (s, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (DMSO, 125 MHz): δ 137.6 (C), 132.6 (CH), 125.5 (CH), 125.3 (CH), 124.4 (C), 116.9 (C), 115.4 (C), 113.0 (CH); ATR-FTIR (thin film): 3215, 2923, 1470, 1368, 1335, 1314, 1273, 1221, 1196, 1112, 1037 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_5O_2N_2Cl$ $(M)^+$: 196.00396, found: 196.00343.

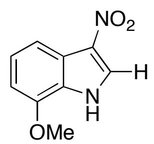


5j

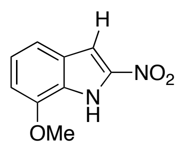


6j

Indole 5j and indole 6j. The general procedure was followed using 0.024 g of aryl azide **4j** (0.10 mmol), 0.001 g of $Rh_2(esp)_2$ (0.001 mmol), and 0.024 g of powdered 4 Å molecular sieves in 0.50 mL of toluene. Purification by MPLC (0:100 – 70:30 EtOAc:hexanes) afforded **5j** as a pale yellow solid (9.1 mg, 46%), mp 226 – 228 °C, and **6j** as a yellow solid (10.2 mg, 48% yield), mp 170 – 172 °C. Spectral data for **5j**: ^{1}H NMR (DMSO, 500 MHz): δ 8.70 (s, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 131.0 (C), 130.6 (C), 130.4 (C), 129.1 (CH), 128.2 (CH), 127.3 (CH), 125.9 (CH), 124.9 (CH), 122.1 (C), 121.3 (CH), 118.8 (CH), 116.7 (C); ATR-FTIR (thin film): 3463, 3253, 2979, 1716, 1472, 1377 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{12}H_8O_2N_2$ $(M)^+$: 212.05858, found: 212.05989. Spectral data for **6j**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 10.0 (br s, 1H), 8.11 (d, *J* = 7.5 Hz, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.66 – 7.58 (m, 4H), 7.54 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 133.1 (C), 131.6 (C), 129.3 (CH), 129.3 (C), 127.3 (CH), 126.9 (CH), 124.1 (CH), 122.8 (C), 121.2 (C), 121.1 (CH), 120.7 (CH), 105.8 (CH); ATR-FTIR (thin film): 3374, 2920, 2850, 1723, 1421, 1359, 1279 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{12}H_8O_2N_2$ $(M)^+$: 212.05858, found: 212.05960.



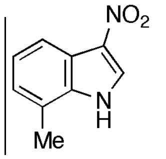
5k



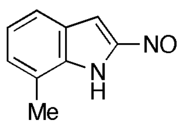
6k

Indole 5k and indole 6k. The general procedure was followed using 0.022 g of aryl azide **4k** (0.10 mmol), 0.001 g of $Rh_2(esp)_2$ (0.001 mmol), and 0.022 g of powdered 4 Å molecular sieves in 0.50 mL of toluene. Purification by MPLC (0:100 – 70:30 EtOAc:hexanes) afforded **5k** as a pale yellow solid (0.0046 g, 24%), mp 171 – 173 °C, and **6k** as a yellow solid (0.0137 g, 71%), mp 90 – 92 °C. Spectral data for **5k**: ^{1}H NMR (DMSO, 500 MHz): δ 12.87 (br s, 1H), 8.47 (s, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 8.0 Hz, 1H), 6.90 (d, *J*

= 8.0 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (DMSO, 125 MHz): δ 147.2 (C), 130.0 (CH), 129.4 (C), 125.6 (C), 125.2 (CH), 121.8 (C), 112.2 (CH), 105.3 (CH), 55.6 (CH$_3$); ATR-FTIR (thin film): 3355, 3130, 2929, 2841, 1970, 1593, 1462, 1380, 1339 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_9H_8O_3N_2$ (M)+: 192.05350, found: 192.05426. Spectral data for **6k**: ^{1}H NMR (CDCl$_3$, 500 MHz): δ 9.37 (br s, 1H), 7.38 (s, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 7.5 Hz, 1H), 3.99 (s, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 146.5 (C), 126.9 (C), 126.4 (C), 122.9 (CH), 122.9 (C), 115.6 (CH), 106.5 (CH), 104.2 (CH), 55.6 (CH$_3$); ATR-FTIR (thin film): 3512, 3179, 3130, 2922, 2359, 2152, 1960, 1352, 1251 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_9H_8O_3N_2$ (M)$^+$: 192.05350, found: 192.05352.

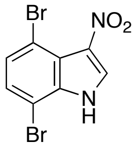


5l

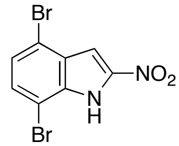


6l

Indole 5l and indole 6l. The general procedure was followed using 0.0204 g of aryl azide **4l** (0.10 mmol), 0.001 g of Rh$_2$(esp)$_2$ (0.001 mmol), and 0.0204 g of powdered 4 Å molecular sieves in 0.50 mL of toluene. Purification by MPLC (0:100 – 70:30 EtOAc:hexanes) afforded **5l** as a pale yellow solid (0.0051 g, 29%), mp 193 – 195 °C, and **6l** as a yellow solid (0.012 g, 68%), mp 96 – 98 °C. Spectral data for **5l**: ^{1}H NMR (DMSO, 500 MHz): δ 12.67 (br, 1H), 8.63 (s, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 6.5 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (DMSO, 125 MHz): δ 135.0 (C), 130.6 (CH), 129.3 (C), 125.2 (CH), 124.4 (CH), 123.4 (C), 120.2 (C), 117.4 (CH), 16.8 (CH$_3$); ATR-FTIR (thin film): 3219, 2364, 1463, 1376,1196, 1132, 741, 588 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_9H_8O_2N_2$ (M)$^+$: 176.05858, found: 176.05951. Spectral data for **6l**: ^{1}H NMR (CDCl$_3$, 500 MHz): δ 9.05 (br, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 2.0 Hz, 1H), 7.26 (t, *J* = 4.0 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 134.9 (C), 128.4 (CH), 128.4 (C), 125.6 (C), 122.8 (CH), 121.7 (C), 121.5 (CH), 104.8 (CH), 16.5 (CH$_3$); ATR-FTIR (thin film): 3275, 2387, 1476, 1268, 1040, 732 cm^{-1}; HRMS (EI) *m* / *z* calculated $C_9H_8O_2N_2$ (M)$^+$: 176.05858, found: 176.05960.

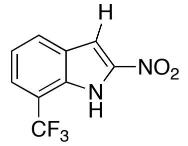


5m



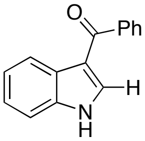
6m

Indole 5m and indole 6m. The general procedure was followed using 0.098 g of aryl azide **4m** (0.28 mmol), 0.002 g of Rh$_2$(esp)$_2$ (0.003 mmol), and 0.098 g of powdered 4 Å molecular sieves in 0.73 mL of toluene. The crude reaction mixture showed an 8:92 ratio of **5m**:**6m** by ^{1}H NMR (DMSO, 500 MHz). Purification by MPLC (0:100 – 50:50 EtOAc:hexanes) afforded **6m** as a yellow powder (0.060 g, 71%), mp 175 °C, R_f = 0.49 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). Selected spectral data for minor product **5m**: ^{1}H NMR (DMSO, 500 MHz): δ 8.67 (s, 1H). Spectral data for major product **6m**: ^{1}H NMR (DMSO, 500 MHz): δ 13.57 (br s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.44 (s, 1H), 7.36 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (DMSO, 125 MHz): δ 143.1 (C), 134.9 (C), 131.3 (CH), 127.5 (C), 126.1 (CH), 115.7 (C), 105.5 (C), 104.3 (CH); ATR-FTIR (thin film): 3383, 3131, 2922, 2851, 1612, 1532, 1504, 1480, 1424, 1387, 1317, 1269, 1168, 1121, 1108, 1085, 1054 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_8H_4O_2N_2Br_2$ (M)$^+$: 317.86398, found: 317.86459.



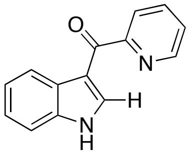
6n

Indole 6n. The general procedure was followed using 0.0258 g of aryl azide **4n** (0.10 mmol), 0.001 g of $Rh_2(esp)_2$ (0.001 mmol), and 0.0258 g of powdered 4 Å molecular sieves in 0.50 mL of toluene. Purification by MPLC (0:100 – 70:30 EtOAc:hexanes) afforded **6n** as a pale yellow solid (0.0227 g, 99%), mp 85 – 87 °C. Spectral data for **6n**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.40 (br, 1H), 7.95 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 7.5 Hz, 1H), 7.50 (d, J = 2.0 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.7 (C), 130.1 (C), 128.0 (CH), 127.2 (C), 125.5 (q, J_{C-F} = 5.4 Hz, CH), 124.0 (q, J_{C-F} = 269.9 Hz, C), 121.9 (CH), 115.0 (q, J_{C-F} = 32.9 Hz, C), 103.8 (CH); ATR-FTIR (thin film): 3464, 3144, 2364, 1509, 1307, 1099, 732 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_9H_5O_2N_2F_3$ $(M)^+$: 230.03032, found: 230.03095.



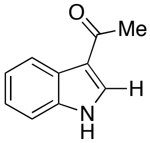
8a

Indole 8a.[23] The general procedure was followed using 0.102 g of aryl azide **7a** (0.40 mmol), 0.003 g of $Rh_2(esp)_2$ (0.004 mmol), and 0.102 g of powdered 4 Å molecular sieves in 1.0 mL of toluene. Purification by MPLC (30:70 – 80:20 EtOAc:hexanes) afforded **8a** as a beige powder (0.085 g, 93%), mp >240 °C, R_f = 0.28 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). The spectral data matched that reported by Yang and coworkers.[23] ^{1}H NMR (DMSO, 500 MHz): δ 12.07 (br s, 1H), 8.27 (d, J = 7.0 Hz, 1H), 7.93 (s, 1H), 7.78 (d, J = 7.0 Hz, 2H), 7.61-7.47 (m, 4H), 7.28-7.19 (m, 2H); ^{13}C NMR (DMSO, 125 MHz): δ 190.5 (C), 141.0 (C), 137.2 (C), 136.3 (CH), 131.5 (CH), 128.9 (CH), 128.8 (CH), 126.7 (C), 123.6 (CH), 122.4 (CH), 122.0 (CH), 115.5 (C), 112.7 (CH); ATR-FTIR (thin film): 2921, 1739, 1594, 1426, 1211 cm^{-1}.



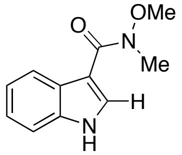
8b

Indole 8b.[24] The general procedure was followed using 0.020 g of aryl azide **7b** (0.080 mmol), 0.002 g of $Rh_2(esp)_2$ (0.003 mmol), and 0.020 g of powdered 4 Å molecular sieves in 0.20 mL of toluene. Purification by MPLC (30:70 – 80:20 EtOAc:hexanes) afforded **8b** as a white powder (0.012 g, 66%), mp 174 °C, R_f = 0.15 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). The spectral data matched that reported by Katritzky and coworkers.[24] ^{1}H NMR (DMSO, 500 MHz): δ 12.07 (br s, 1H), 8.81 (s, 1H), 8.77-8.71 (d, J = 4.0 Hz, 1H), 8.41-8.34 (m, 1H), 8.05-7.98 (m, 2H), 7.63-7.57 (m, 1H), 7.55-7.48 (m, 1H), 7.27-7.19 (m, 2H); ^{13}C NMR (DMSO, 125 MHz): δ 186.6 (C), 156.7 (C), 149.0 (CH), 138.4 (CH), 137.9 (CH), 136.6 (C), 127.4 (C), 126.6 (CH), 123.5 (CH), 123.4 (CH), 122.6 (CH), 122.2 (CH), 114.2 (C), 112.7 (CH); ATR-FTIR (thin film): 3145, 3053, 2922, 1593, 1574, 1558, 1510, 1488, 1440, 1421, 1375, 1343, 1315, 1285, 1238, 1220, 1132, 1116, 1091, 1040, 1011 cm^{-1}.

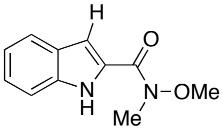


8c

Indole 8c.[23] The general procedure was followed using 0.030 g of aryl azide **7c** (0.16 mmol), 0.006 g of $Rh_2(esp)_2$ (0.008 mmol), and 0.030 g of powdered 4 Å molecular sieves in 0.50 mL of toluene. Purification by MPLC (30:70 – 80:20 EtOAc:hexanes) afforded **8c** as (0.017 g, 65%), mp 170 – 172 °C, R_f = 0.10 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). The spectral data matched that reported by Yang and coworkers.[23] ^{1}H NMR (DMSO, 500 MHz): δ 11.90 (br s, 1H), 8.28 (s, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.21-7.12 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (DMSO, 125 MHz): δ 193.1 (C), 137.1 (C), 134.8 (C), 125.8 (C), 123.2 (CH), 122.1 (CH), 121.8 (CH), 117.2 (C), 112.5 (CH), 22.7 (CH_3); ATR-FTIR (thin film): 3123, 2922, 1609, 1577, 1525, 1493, 1431, 1419, 1383, 1315, 1242, 1177, 1028, 1009 cm^{-1}.

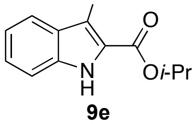


8d



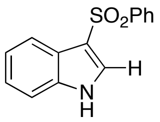
9d

Indole 8d and indole 9d.[25] The general procedure was followed using 0.232 g of aryl azide **7d** (0.10 mmol), 0.008 g of $Rh_2(esp)_2$ (0.001 mmol), and 0.220 g of powdered 4 Å molecular sieves in 0.50 mL of toluene. Purification by MPLC (0:100 – 70:30 EtOAc:hexanes) afforded **8d** as a pale yellow solid (0.045 g, 22%), mp 177 – 179 °C, and **9d** as a yellow solid (0.146 g, 72%), mp 129 – 131 °C. Spectral data for **8d**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.86 (br, 1H), 8.40 (t, *J* = 4.5 Hz, 1H), 7.94 (d, *J* = 2.5 Hz, 1H), 7.39 (d, *J* = 4.5 Hz, 1H), 7.25 (s, 1H), 7.24 (d, *J* = 3.5 Hz, 1H), 3.69 (s, 3H), 3.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.9 (C), 135.3 (C), 129.6 (CH), 127.6 (C), 123.1 (CH), 122.4 (CH), 121.7 (CH), 111.1 (CH), 108.8 (C), 60.8 (CH_3), 33.3 (CH_3); ATR-FTIR (thin film): 3148, 2936, 2818, 2006, 1561, 1438, 1236 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{11}H_{12}O_2N_2$ $(M)^+$: 204.08988, found: 204.09055. The spectral data for **9d** matched that reported by Wulff and coworkers:[25] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.56 (br, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.25 (s, 1H), 7.14 (t, *J* = 8.0 Hz, 1H), 3.86 (s, 3H), 3.45 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.7 (C), 135.8 (C), 128.3 (C), 128.0 (C), 124.9 (CH), 122.6 (CH), 120.5 (CH), 111.8 (CH), 108.0 (CH), 61.4 (CH_3), 33.3 (CH_3); ATR-FTIR (thin film): 3455, 3295, 2935, 2251, 1611, 1344, 1136 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{11}H_{12}O_2N_2$ $(M)^+$: 204.08988, found: 204.08995.

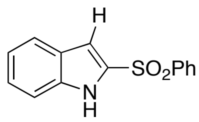


9e

Indole 9e. The general procedure was followed using 0.024 g of aryl azide **7e** (0.10 mmol), 0.001 g of $Rh_2(esp)_2$ (0.001 mmol), and 0.024 g of powdered 4 Å molecular sieves in 0.25 mL of toluene. Purification by MPLC (30:70 – 80:20 EtOAc:hexanes) afforded **9e** as a white powder (0.020 g, 98%), mp 112 °C, R_f = 0.30 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.04 (br s, 1H), 7.69 (d *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.35-7.30 (m, 1H), 7.25-7.22 (m, 1H), 7.18-7.13 (m, 1H), 5.35-5.26 (m, 1H), 1.41 (d, *J* = 6.0 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 161.6 (C), 136.8 (C), 127.9 (C), 127.5 (C), 125.3 (CH), 122.6 (CH), 120.8 (CH), 111.9 (CH), 108.5 (CH), 68.7 (CH), 22.1 (CH_3); ATR-FTIR (thin film): 3303, 2983, 2944, 1687, 1621, 1526, 1434, 1391, 1371, 1342, 1308, 1254, 1204, 1147, 1105 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{12}H_{13}O_2N$: 203.09463, found: 203.09540.

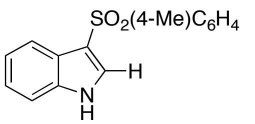


8f

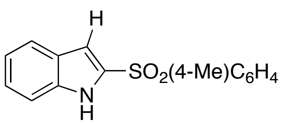


9f

Indole 8f and indole 9f. The general procedure was followed using 0.100 g of aryl azide **7f** (0.35 mmol), 0.003 g of $Rh_2(esp)_2$ (0.004 mmol), and 0.100 g of powdered 4 Å molecular sieves in 0.88 mL of toluene. Purification by MPLC (30:70 – 90:10 EtOAc:hexanes) afforded 3-sulfonylindole **8f** as a white powder (0.079 g, 88%), mp 128 °C, R_f = 0.08 (30:70 EtOAc:hexanes, visualized by 254 nm UV light) and 2-sulfonylindole **9f** as a tan wax (0.007 g, 8%), mp 160 °C, R_f = 0.36 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). The spectral data for major product **8f** matched that reported by Zecchi and coworkers.[26]: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.29 (br s, 1H), 8.05-8.00 (m, 2H), 7.94-7.90 (m, 1H), 7.89 (d, *J* = 2.5 Hz, 1H), 7.53-7.39 (m, 4H), 7.30-7.22 (m, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.1 (C), 136.3 (C), 132.6 (CH), 130.0 (CH), 129.1 (CH), 126.7 (CH), 124.0 (CH), 123.5 (C), 122.6 (CH), 119.6 (CH), 116.8 (C), 112.2 (CH); ATR-FTIR (thin film): 3270, 3143, 2920, 2850, 1508, 1459, 1423, 1287, 1245, 1139, 1107, 1082, 1013 cm^{-1}. Spectral data for minor product **9f**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.99 (br s, 1H), 8.03-7.99 (m, 2H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.60-7.55 (m, 1H), 7.54-7.48 (m, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.37-7.32 (m, 1H), 7.22-7.16 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 145.5 (C), 137.1 (C), 134.2 (C), 133.5 (CH), 129.4 (CH), 127.3 (CH), 127.2 (C), 126.1 (CH), 122.7 (CH), 121.6 (CH), 112.3 (CH), 109.3 (CH); ATR-FTIR (thin film): 3317, 2922, 1510, 1446, 1307, 1143, 1096 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{14}H_{11}O_2NS$: 257.05105, found: 257.05190.

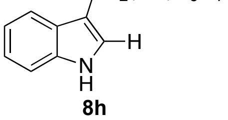


8g

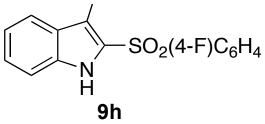


9g

Indole 8g and indole 9g.[27] The general procedure was followed using 0.109 g of aryl azide **7g** (0.36 mmol), 0.009 g of $Rh_2(esp)_2$ (0.011 mmol), and 0.109 g of powdered 4 Å molecular sieves in 0.73 mL of toluene. Purification by MPLC (30:70 – 90:10 EtOAc:hexanes) afforded 3-sulfonylindole **8g** as a white powder (0.068 g, 69%), mp 172 °C, R_f = 0.14 (60:40 EtOAc:hexanes on an Et_3N-treated SiO_2 TLC plate, visualized by 254 nm UV light) and 2-sulfonylindole **9g** as a white solid (0.009 g, 9%), R_f = 0.43 (60:40 EtOAc:hexanes on an Et_3N-treated SiO_2 TLC plate, visualized by 254 nm UV light). Major product **8g** was previously reported by Jadav and coworkers.[28]. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.74 (br s, 1H), 7.92-7.86 (m, 3H), 7.83 (s, 1H), 7.41-7.36 (m, 1H), 7.25-7.19 (m, 4H), 2.34 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 143.6 (C), 140.1 (C), 136.5 (C), 130.1 (CH), 129.7 (CH), 126.7 (CH), 123.9 (CH), 123.4 (C), 122.4 (CH), 119.3 (CH), 116.4 (C), 112.5 (CH), 21.5 (CH_3); ATR-FTIR (thin film): 3278, 3111, 2919, 2852, 1502, 1422, 1285, 1139, 1082 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{15}H_{13}O_2NS$ $(M)^+$: 271.06670, found: 271.06705. The spectral data for minor product **9g** matched that reported by Caddick and coworkers.[27] Selected spectral data for minor product **9g**: ^{1}H NMR ($CDCl_3$, 300 MHz): δ 9.22 (br s, 1H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.47-7.35 (m, 4H), 7.31-7.24 (m, 1H), 2.49 (s, 3H).

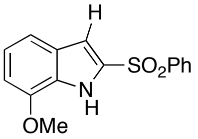


8h



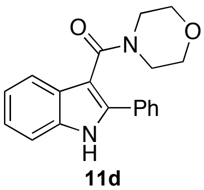
9h

Indole 8h and indole 9h. The general procedure was followed using 0.100 g of aryl azide **7h** (0.33 mmol), 0.003 g of $Rh_2(esp)_2$ (0.003 mmol), and 0.100 g of powdered 4 Å molecular sieves in 0.83 mL of toluene. Purification by MPLC (30:70 – 90:10 EtOAc:hexanes) afforded 3-sulfonylindole **8h** as a white solid (0.083 g, 90%), mp 98 °C, $R_f = 0.10$ (60:40 EtOAc:hexanes on an Et_3N-treated SiO_2 TLC plate, visualized by 254 nm UV light), and 2-sulfonylindole **9h** as a white solid (0.010 g, 10%), mp 155 °C, $R_f = 0.41$ (60:40 EtOAc:hexanes on an Et_3N-treated SiO_2 TLC plate, visualized by 254 nm UV light). Spectral data for major product **8h**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.89 (br s, 1H), 8.05-7.97 (m, 2H), 7.90-7.84 (m, 2H), 7.43-7.38 (m, 1H), 7.25-7.20 (m, 2H), 7.13-7.07 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.1 (d, J_{C-F}= 253.4 Hz, C), 139.0 (C), 136.5 (C), 130.5 (CH), 129.4 (d, J_{C-F} = 9.3 Hz, CH), 124.1 (CH), 123.3 (C), 122.7 (CH), 119.0 (CH), 116.4 (d, J_{C-F} = 22.4 Hz, CH), 115.7 (C), 112.7 (CH); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –105.4; ATR-FTIR (thin film): 3288, 3109, 3072, 2920, 2852, 1587, 1492, 1421, 1285, 1224 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{14}H_{10}O_2NSF$ $(M)^+$: 275.0416, found: 275.0417. Spectral data for minor product **9h**: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.11 (br s, 1H), 8.05-7.99 (m, 2H), 7.69-7.65 (m, 1H), 7.45-7.41 (m, 1H), 7.37-7.32 (m, 1H), 7.21-7.15 (m, 4H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.6 (d, J_{C-F} = 253.8 Hz, C), 137.6 (C), 137.2 (C), 133.9 (C), 130.2 (d, J_{C-F} = 10.5 Hz, CH), 127.1 (C), 126.3 (CH), 122.8 (CH), 121.7 (CH), 116.7 (d, J_{C-F} = 23.6 Hz, CH), 112.3 (CH), 109.3 (CH); ^{19}F NMR ($CDCl_3$, 282 MHz): δ –103.9; ATR-FTIR (thin film): 3373, 3315, 1583, 1489, 1288, 1142 cm^{-1}; HRMS (EI) *m* / *z* calculated for $C_{14}H_{10}O_2NSF$ $(M)^+$: 275.0416, found: 275.0420.



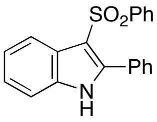
9i

Indole 9i. The general procedure was followed using 0.007 g of aryl azide **7i** (0.02 mmol), 0.0002 g of $Rh_2(esp)_2$ (0.0002 mmol), and 0.007 g of powdered 4 Å molecular sieves in 0.05 mL of toluene. Purification by MPLC (5:0:95 – 5:45:50 Et_3N:EtOAc:hexanes) afforded **9i** as a yellow powder (0.006 g, 98%), mp 111 °C, R_f = 0.31 (50:50 EtOAc:hexanes on an Et_3N-treated TLC plate, visualized by 254 nm UV light). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.97 (br s, 1H), 7.99 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.17 (s, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 7.5 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 146.6 (C), 141.6 (C), 133.8 (C), 133.4 (CH), 129.3 (CH), 128.4 (C), 128.3 (C), 127.3 (CH), 122.1 (CH), 114.8 (CH), 109.4 (CH), 104.8 (CH), 55.5 (CH_3); ATR-FTIR (thin film): 3064, 2919, 2849, 1580, 1524, 1446, 1411, 1316, 1257, 1146, 1109, 1078 cm^{-1}; HRMS: (EI) *m* / *z* calculated for $C_{15}H_{13}O_3NS$ $(M)^+$: 287.06162, found: 287.06265.



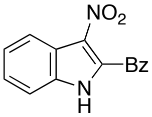
11d

Indole 11d.[29] The general procedure was followed using 33.4 mg of aryl azide **10d** (0.10 mmol), 0.001 mg of $Rh_2(esp)_2$ (0.001 mmol), and 33.4 mg of powdered 4 Å molecular sieves in 1.0 mL of toluene. Purification to the best of our ability by gradient MPLC (EtOAc) afforded **11d** as a white solid (27.8 mg, 91%). The spectral data matched that reported by Skrydstrup and co-workers:[29] ^{1}H NMR ($CDCl_3$, 500 MHz): δ 9.45 (br, 1H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.44–7.42 (m, 2H), 7.29–7.24 (m, 4H), 7.17–7.12 (m, 1H), 3.79–3.19 (m, 8H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 167.3 (C), 136.7 (C), 136.0 (C), 131.5 (C), 128.9 (2CH), 128.6 (CH), 127.5 (2CH), 127.5 (C), 123.0 (CH), 121.0 (CH), 119.5 (CH), 111.5 (CH), 107.5 (C), 66.6 ($2CH_2$), 47.6 (CH_2), 42.5 (CH_2); ATR-FTIR (thin film): 3225, 2860, 2240, 1600, 1437, 1218, 1115, 909, 730 cm^{-1}.



11e

Indole 11e. The general procedure was followed using 0.027 g of aryl azide **10e** (0.07 mmol), 0.003 g of Rh$_2$(esp)$_2$ (0.004 mmol), and 0.027 g of powdered 4 Å molecular sieves in 0.20 mL of toluene. Purification to the best of our ability by gradient MPLC (0:100 – 50:50 EtOAc:hexanes) afforded **11e** as a beige solid (0.011 g, 49%), R_f = 0.31 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.83 (br s, 1H), 8.30-8.26 (m, 1H), 7.70-7.66 (m, 2H), 7.58-7.55 (m, 2H), 7.52-7.47 (m, 1H), 7.47-7.44 (m, 2H), 7.42-7.37 (m, 2H), 7.33-7.27 (m, 4H); ^{13}C NMR (CDCl$_3$, 125 MHz): δ 143.9 (C), 142.7 (C), 134.5 (C), 132.3 (CH), 130.2 (CH), 130.1 (C), 129.9 (CH), 128.7 (CH), 128.2 (CH), 126.4 (CH), 125.9 (C), 124.0 (CH), 122.7 (CH), 120.9 (CH), 113.1 (C), 111.3 (CH); ATR-FTIR (thin film): 3057, 3028, 2922, 2852, 1630, 1489, 1444, 1298, 1142, 1084, 1028 cm^{-1}; HRMS (EI) *m / z* calculated for $C_{20}H_{15}NO_2S$ (M)$^+$: 333.08235, found: 333.08327.

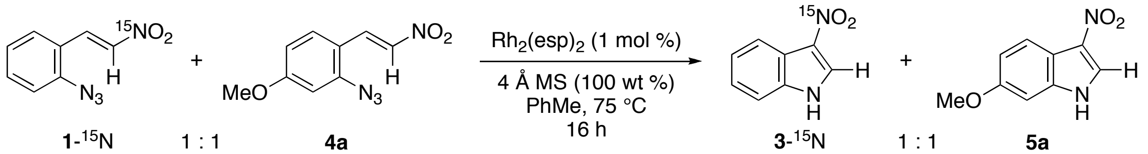


11f

Indole 11f. The general procedure was followed using 0.020 g of aryl azide **10f** (0.07 mmol), 0.001 g of Rh$_2$(esp)$_2$ (0.001 mmol), and 0.020 g of powdered 4 Å molecular sieves in 0.22 mL of toluene. Purification by gradient MPLC (0:100 – 50:50 EtOAc:hexanes) afforded **11f** as a vibrant yellow powder (0.008 g, 41%), mp 174 °C, R_f = 0.32 (30:70 EtOAc:hexanes, visualized by 254 nm UV light). ^{1}H NMR (DMSO, 500 MHz): δ 13.42 (br s, 1H), 8.17-8.13 (m, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.65-7.61 (m, 1H), 7.57 (t, *J* = 7.5 Hz, 2H), 7.49-7.43 (m, 2H); ^{13}C NMR (DMSO, 125 MHz): δ 188.3 (C), 137.8 (C), 135.7 (C), 135.4 (CH), 134.5 (C), 129.8 (CH), 129.6 (CH), 127.2 (C), 126.0 (CH), 125.3 (CH), 120.4 (CH), 120.0 (C), 114.3 (CH); ATR-FTIR (thin film): 3252, 2921, 2848, 1668, 1597, 1469, 1447, 1415, 1366, 1330, 1291, 1252, 1216, 1174 cm^{-1}; HRMS (EI) *m / z* calculated for $C_{15}H_{10}N_2O_3$ (M)$^+$: 266.06915, found: 266.06839.

VI. Mechanistic Experiments

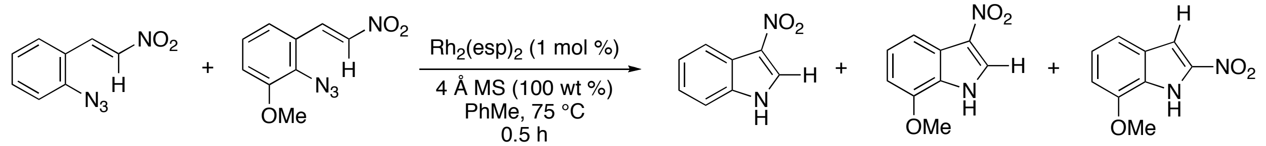
A. Crossover Experiment



(s14)

To a conical vial equipped with spin vane was added 0.024 g of aryl azide **4a** (0.11 mmol), 0.020 g of ^{15}N-labeled aryl azide **1**-^{15}N (0.11 mmol), 0.044 g of powdered 4 Å molecular sieves, and 0.50 mL of toluene. The reaction was sealed with a PTFE-lined screw-top cap and heated at 75 °C for 16 h with stirring. After cooling to room temperature, the mixture had evolved N$_2$ gas, which was released upon opening, and the mixture was filtered through Celite using EtOAc. ^{1}H NMR spectroscopy (DMSO, 125 MHz) of the crude reaction mixture showed a 50:50 mixture of **3**-^{15}N:**5a**. A single carbon corresponding to C-3 of 3-nitroindole (δ 128.9 (C)) showed C-^{15}N splitting (27.4 Hz). No evidence of ^{15}N-labeled **5a** was observed. See p. 171 of Supporting Information 2 for the corresponding assigned NMR spectrum.

B. Relative Rate Experiment



(s15)

1 **4m** **3** **5k** **6k**

1 : 1

2.3 : 1.0 : 3.9

32 : 14 : 54

To a conical vial equipped with spin vane was added 0.010 g of aryl azide **1** (0.05 mmol), 0.012 g of aryl azide **4m** (0.05 mmol), 0.022 g of powdered 4 Å molecular sieves, and 0.50 mL of toluene. The reaction was sealed with a PTFE-lined screw-top cap and heated at 75 °C for 0.5 h with stirring. After cooling to room temperature, the mixture had evolved N_2 gas, which was released upon opening, and the mixture was filtered through Celite using EtOAc. ^{1}H NMR spectroscopy (DMSO, 125 MHz) of the crude reaction mixture showed 46% coversion of aryl azide **1** and 91% conversion of aryl azide **4m** to a 32:14:56 mixture of **3**:**5k**:**6k** (CH_2Br_2 was used as internal standard). See p. 172 of Supporting Information 2 for the corresponding assigned NMR spectrum.

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