

ZnBr₂/Oxone-Mediated *ipso*-Cyclization of *N*-(3-Phenylprop-2-yn-1-yl)aniline

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Supporting Information

1. General procedures
2. Typical procedure for the copper-catalyzed synthesis of aryldiazo sulfones
3. Characterization of the products

1. General procedures

The solvents were distilled from standard drying agents. Unless otherwise stated, commercial reagents purchased from Alfa Aesar, Acros and Aldrich chemical companies were used without further purification. Purification of reaction products was carried out by flash chromatography using Qing Dao Sea Chemical Reagent silica gel (200–300 mesh). ¹H NMR spectra were recorded on a Bruker Avance III 400 (400 MHz) spectrometer and referenced internally to the residual proton resonance in CDCl₃ (δ = 7.26 ppm), or with tetramethylsilane (TMS, δ = 0.00 ppm) as the internal standard. Chemical shifts were reported as parts per million (ppm) in the δ scale downfield from TMS. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Analytical TLC was performed using EM separations percolated silica gel 0.2 mm layer UV 254 fluorescent sheets.

2. Typical procedure for the copper-catalyzed synthesis of aryldiazo sulfones

N-(3-phenylprop-2-yn-1-yl)aniline **1** (0.2 mmol), ZnBr₂ (1 equiv), Oxone (2.0 equiv) were added to a test tube, and then solvent MeCN:H₂O (v/v = 4:1, 2.0 mL) was added. The mixture was stirred at room temperature overnight. After the disappearance of substrate as indicated by TLC, the mixture was filtrated and the resulting filtrate was extracted by DCM (3*2 mL). The organic layers was combined and dried by Na₂SO₄. Then filtration again, evaporation of the solvent and purification by flash column chromatography provided the desired product **3**.

3. Characterization of the products

4-(4-Acetyl-phenyl)-3-bromo-6-iodo-1-(toluene-4-sulfonyl)-1-aza-spiro[4.5]deca-3,6,9-trien-8-one (**3a**)¹: 87 mg, 70% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.27 - 7.21 (m, 2H), 6.98 - 6.88 (m, 2H), 6.31 (d, *J* = 9.9 Hz, 1H), 4.56 (d, *J* = 8.1 Hz, 2H), 2.56 (s, 3H), 2.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 197.2, 181.0, 144.9, 144.7, 141.5, 137.6, 137.0, 136.0, 134.1, 129.9, 129.5, 129.0, 128.3, 127.8, 126.4, 119.4, 78.1, 59.3, 26.6, 21.6

4-[3-Bromo-6-iodo-8-oxo-1-(toluene-4-sulfonyl)-1-aza-spiro[4.5]deca-3,6,9-trien-4-yl]-benzoic acid methyl ester (**3b**)²: 103 mg, 81% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.97 - 7.90 (m, 2H), 7.75 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.24 - 7.17 (m, 2H), 6.97 - 6.86 (m, 2H), 6.30 (d, *J* = 9.7 Hz, 1H), 4.62 - 4.48 (m, 2H), 3.87 (s, 3H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 181.0, 166.2, 144.9, 144.6, 141.5, 137.0, 136.0, 134.0, 131.0, 130.0, 129.9, 129.5, 129.2, 129.0, 127.8, 119.3, 78.1, 59.2, 52.3, 21.6

4-[3-Bromo-6-iodo-8-oxo-1-(toluene-4-sulfonyl)-1-aza-spiro[4.5]deca-3,6,9-trien-4-yl]-benzotrile (**3c**) : 87 mg, 72% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.80 - 7.73 (m, 2H), 7.63 - 7.56 (m, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 6.98 - 6.90 (m, 2H), 6.33 (d, *J* = 9.8 Hz, 1H), 4.57 (d, *J* = 3.5 Hz, 2H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 180.8, 144.8, 144.6, 141.7, 136.3, 135.9, 134.2, 132.2, 130.0, 129.9, 129.5, 129.2, 127.8, 120.2, 117.9, 113.6, 77.9, 59.3, 21.6; HRMS (ESI) calcd for C₂₃H₁₇BrIN₂O₃S⁺: 606.9182 (M⁺+H), found: 606.9189

3-Bromo-4-(4-fluoro-phenyl)-6-iodo-1-(toluene-4-sulfonyl)-1-aza-spiro[4.5]deca-3,6,9-trien-8-one (**3d**) : 90 mg, 75% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 4H), 7.02 - 6.89 (m, 2H), 6.31 (d, *J* = 9.9 Hz, 1H), 4.61 - 4.47 (m, 2H), 2.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 181.1, 163.4 (*¹J_{CF}* = 250 Hz), 145.1, 131.1 (*J* = 8.4 Hz), 137.0, 136.0, 131.1, 131.0, 130.2, 129.8, 129.0, 127.8, 125.3 (*J* = 3.6 Hz), 119.0, 115.7 (*J* = 21.8 Hz), 78.1, 59.1, 21.6; HRMS (ESI) calcd for C₂₂H₁₇BrFINO₃S⁺: 599.9136 (M⁺+H), found: 599.9142

3-Bromo-4-(4-bromo-phenyl)-6-iodo-1-(toluene-4-sulfonyl)-1-aza-spiro[4.5]deca-3,6,9-trien-8-one (**3e**) : 92 mg, 70% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.03 - 6.97 (m, 2H), 6.94 - 6.88 (m, 2H), 6.31 (d, *J* = 9.9 Hz, 1H), 4.60 - 4.46 (m, 2H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 181.1, 145.0, 144.6, 141.5, 136.8, 136.0, 131.7, 130.7, 130.1, 129.9, 129.0, 128.3, 127.8, 124.1, 119.2, 104.9, 77.9, 59.1, 21.7; HRMS (ESI) calcd for C₂₂H₁₇Br₂INO₃S⁺: 659.8335 (M⁺+H), found: 659.8337

4-Biphenyl-4-yl-3-bromo-6-iodo-1-(toluene-4-sulfonyl)-1-aza-spiro[4.5]deca-3,6,9-trien-8-one (**3f**) : 89 mg, 68% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.58 - 7.47 (m, 4H), 7.45 - 7.32 (m, 5H), 7.21 (d, *J* = 8.2 Hz, 2H), 7.00 - 6.92 (m, 2H), 6.34 (d, *J* = 9.9 Hz, 1H), 4.65 - 4.51 (m, 2H), 2.47 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 181.3, 145.3, 144.5, 142.2, 141.6, 139.9, 137.7, 136.1, 130.3, 129.8, 129.4, 129.0, 128.8, 128.2, 127.8, 127.7, 127.0, 127.0, 118.5, 78.1, 59.2, 21.6; HRMS (ESI) calcd for C₂₈H₂₂BrINO₃S⁺: 657.9543 (M⁺+H), found: 657.9525

3-Bromo-6-iodo-1-(toluene-4-sulfonyl)-4-p-tolyl-1-aza-spiro[4.5]deca-3,6,9-trien-8-one (**3g**) : 92 mg, 77% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.80 - 7.72 (m, 2H), 7.34 (d, *J* = 8.5, 2H), 7.07 (d, *J* = 7.4 Hz, 2H), 7.02 - 6.97 (m, 2H), 6.93 - 6.87 (m, 2H), 6.29 (d, *J* = 10.1, 1H), 4.53 (d, *J* = 10.1, 2H), 2.45 (s, 3H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 181.3, 145.3, 144.5, 141.4, 139.6, 137.9, 136.1, 130.5, 129.8, 129.1, 128.9, 127.8, 126.4, 118.1, 104.9, 78.1, 59.1, 21.6, 21.3; HRMS (ESI) calcd for C₂₃H₂₀BrINO₃S⁺: 595.9386 (M⁺+H), found: 595.9376

3-Bromo-6-iodo-4-phenyl-1-(toluene-4-sulfonyl)-1-aza-spiro[4.5]deca-3,6,9-trien-8-one (**3h**) : 90 mg, 77% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.82 - 7.72 (m, 2H), 7.39 - 7.25 (m, 5H), 7.15 - 7.08 (m, 2H), 6.97 - 6.87 (m, 2H), 6.29 (d, *J* = 9.9 Hz, 1H), 4.71 - 4.42 (m, 2H), 2.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 181.2, 145.2, 144.5, 141.4, 137.9, 136.1, 130.4, 129.8, 129.5, 129.4, 129.1, 128.9, 128.3, 127.8, 118.4, 78.2, 59.1, 21.6; HRMS (ESI) calcd for C₂₂H₁₈BrINO₃S⁺: 581.9230 (M⁺+H), found: 581.9218

4-[3-Bromo-6-iodo-9-methyl-8-oxo-1-(toluene-4-sulfonyl)-1-aza-spiro[4.5]deca-3,6,9-trien-4-yl]-benzoic acid methyl ester (**3j**) : 86 mg, 65% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.96 - 7.89 (m, 2H), 7.74 - 7.67 (m, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.20 - 7.13 (m, 2H), 6.85 (s, 1H), 6.57 (d, 1H), 4.62 (d, *J* = 13.4 Hz, 1H), 4.50 (d, *J* = 13.5 Hz, 1H), 3.87 (s, 3H), 2.44 (s, 3H), 1.81 (d, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 181.7, 166.2, 144.5, 141.0, 140.1, 137.6, 136.3, 134.2, 130.9, 129.9, 129.79, 129.5, 129.1, 127.7, 118.6, 78.3, 59.2, 52.3, 21.6, 15.2; HRMS (ESI) calcd for C₂₅H₂₂BrINO₅S⁺: 653.9441 (M⁺+H), found: 653.9435

4-[3-Bromo-9-chloro-6-iodo-8-oxo-1-(toluene-4-sulfonyl)-1-aza-spiro[4.5]deca-3,6,9-trien-4-yl]-benzoic acid methyl ester (**3k**) : 84 mg, 62% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.01 - 7.94 (m, 2H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 6.94 (d, *J* = 3.9 Hz, 2H), 4.75 - 4.63 (m, 1H), 4.49 (d, *J* = 13.9 Hz, 1H), 3.89 (s, 3H), 2.47 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 174.4, 166.1, 144.8, 140.6, 139.6, 136.7, 135.8, 133.5, 133.4, 131.3, 130.9, 130.1, 129.7, 129.1, 127.7, 119.7, 79.2, 59.2, 52.3, 21.6; HRMS (ESI) calcd for C₂₄H₁₉BrClINO₅S⁺: 673.8895 (M⁺+H), found: 673.8895

4-[3-Bromo-7-chloro-6-iodo-8-oxo-1-(toluene-4-sulfonyl)-1-aza-spiro[4.5]deca-3,6,9-trien-4-yl]-benzoic acid methyl ester (**3l**) : 68 mg, 50% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.99 - 7.90 (m, 2H), 7.73 (d, $J = 7.9$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 7.8$ Hz, 2H), 7.06 (d, $J = 9.9$ Hz, 1H), 6.34 (d, $J = 9.9$ Hz, 1H), 4.63 - 4.54 (m, 2H), 3.89 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 173.2, 166.1, 146.1, 144.8, 141.8, 137.4, 135.8, 133.7, 131.2, 130.7, 129.9, 129.7, 129.0, 127.8, 127.6, 119.4, 80.1, 59.3, 52.3, 21.6; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{19}\text{BrClINO}_5\text{S}^+$: 673.8895 (M^+H), found: 673.8877

4-[3,6-Dibromo-8-oxo-1-(toluene-4-sulfonyl)-1-aza-spiro[4.5]deca-3,6,9-trien-4-yl]-benzoic acid methyl ester (**3m**) : 89 mg, 75% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.98 - 7.91 (m, 2H), 7.77 - 7.70 (m, 2H), 7.33 (d, $J = 8.0$ Hz, 2H), 7.20 - 7.12 (m, 2H), 6.87 (d, $J = 9.9$ Hz, 1H), 6.58 (d, 1H), 6.24 (d, $J = 9.9$, 1H), 4.56 (s, 2H), 3.87 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 182.2, 166.2, 147.6, 145.5, 144.6, 136.6, 135.9, 134.2, 134.0, 131.1, 129.8, 129.6, 129.1, 128.9, 127.6, 119.4, 76.6, 59.3, 52.3, 21.6; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{20}\text{Br}_2\text{NO}_5\text{S}^+$: 591.9423 (M^+H), found: 591.9415

4-[3-Bromo-6-methyl-8-oxo-1-(toluene-4-sulfonyl)-1-aza-spiro[4.5]deca-3,6,9-trien-4-yl]-benzoic acid methyl ester; compound with methane (**3n**)²: 72 mg, 68% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.97 - 7.86 (m, 2H), 7.71 (d, $J = 8.3$ Hz, 2H), 7.33 (d, $J = 7.9$ Hz, 2H), 7.09 - 7.02 (m, 2H), 6.51 (d, $J = 9.8$ Hz, 1H), 6.20 - 6.12 (m, 1H), 6.08 - 6.01 (m, 1H), 4.70 - 4.45 (m, 2H), 3.87 (s, 3H), 2.44 (s, 3H), 2.05 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 184.5, 166.1, 156.4, 145.3, 144.5, 137.6, 136.0, 134.5, 130.9, 129.9, 129.8, 129.5, 129.2, 128.7, 127.6, 117.4, 75.4, 59.1, 52.3, 21.6, 19.1;

4-[3-Bromo-1-(4-bromo-benzenesulfonyl)-6-iodo-8-oxo-1-aza-spiro[4.5]deca-3,6,9-trien-4-yl]-benzoic acid methyl ester (**3o**) : 102 mg, 72% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.99 - 7.94 (m, 2H), 7.73 (q, $J = 8.8$ Hz, 4H), 7.21 (d, $J = 8.4$ Hz, 2H), 6.98 - 6.89 (m, 2H), 6.32 (d, $J = 9.8$ Hz, 1H), 4.64 - 4.49 (m, 2H), 3.89 (d, $J = 2.0$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 180.8, 144.7, 141.8, 138.0, 137.2, 133.8, 132.6, 131.2, 129.6, 129.2, 129.2, 129.1, 129.0, 128.8, 119.1, 104.9, 78.2, 59.3, 52.3; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{17}\text{Br}_2\text{INO}_5\text{S}^+$: 703.8233 (M^+H), found: 703.8250

3-Bromo-6-iodo-1-(naphthalene-2-sulfonyl)-4-phenyl-1-aza-spiro[4.5]deca-3,6,9-trien-8-one (**3p**) : 92 mg, 68% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.43 (d, $J = 2.0$ Hz, 1H), 8.00 (t, $J = 7.9$ Hz, 2H), 7.98 - 7.86 (m, 2H), 7.74 - 7.60 (m, 2H), 7.35 - 7.25 (m, 2H), 7.14 - 7.07 (m, 2H), 6.93 (d, $J = 9.5$ Hz, 2H), 6.31 (d, $J = 9.9$ Hz, 1H), 4.70 - 4.54 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 181.2, 145.3, 141.5, 138.0, 135.9, 135.1, 132.0, 130.1, 129.5, 129.4, 129.3, 129.3, 129.0, 128.9, 128.3, 127.9, 127.8, 122.7, 118.4, 104.9, 78.3, 59.3; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{18}\text{BrINO}_3\text{S}^+$: 617.9230 (M^+H), found: 617.9233

3-Bromo-6-iodo-4-naphthalen-2-yl-1-(thiophene-2-sulfonyl)-1-aza-spiro[4.5]deca-3,6,9-trien-8-one (**3q**) : 76 mg, 61% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.84 (d, $J = 6.8$, Hz, 2H), 7.69 (d, $J = 9.1$, Hz, 2H), 7.61 - 7.51 (m, 1H), 7.55 - 7.43 (m, 2H), 7.43 - 7.33 (m, 2H), 7.17 (t, $J = 4.7$ Hz, 1H), 7.07 - 6.93 (m, 2H), 6.10 - 5.51 (m, 1H), 4.79 (d, $J = 1.5$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 180.97, 144.72, 142.16, 140.12, 136.03, 133.54, 132.95, 130.73, 130.37, 130.30, 129.34, 129.08, 128.33, 127.70, 126.93, 126.82, 126.07, 124.82, 124.29, 120.98, 104.99, 79.89, 59.55; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{16}\text{BrINO}_3\text{S}_2^+$: 623.8794 (M^+H), found: 623.8796

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