Supporting Information

Efficient Synthesis of N-(9-Xanthyl)-p-Toluenesulfonamides Enabled by an Addition-Cyclization Cascade of Arynes

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General experimental information: THF was distilled over Na/benzophenone, and dichloromethane, MeCN was distilled over CaH₂. Powdered CsF, TBAT, KF and TBAF (1 M in THF solution) were used as received and stored in a desiccator. Flash column chromatography was performed using 200–300 mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel 60 F254 plates and visualized by exposure to UV light (254 nm). ¹H NMR and ¹³C NMR spectra were recorded on a 400 MHz spectrometer in CDCl₃ solution. ¹H and ¹³C chemical shifts are reported relative to the corresponding residual solvent signal (CDCl₃: δH 7.26 ppm; δC 77.23 ppm). Data for ¹H NMR spectra are reported as follows: chemical shifts, multiplicity (s, singlet; d, doublet; t, triplet; dd, doublet of doublets; m, multiplet and br, broad singlet), coupling constants (Hz) and integration. High-resolution mass spectra were recorded using electron spray ionization (ESI). Melting points were reported uncorrected.

Experimental procedure
General procedure: To a solution of salicyl N-tosylimine¹ (0.38 mmol, 1.0 equiv) and triflate (0.49 mmol, 1.3 equiv) in acetonitrile (5 mL) was added CsF (0.95 mmol, 2.5 equiv) in one portion. After stirring at room temperature for the indicated time (Table 2 in manuscript), the reaction mixture was poured into aq. Na₂CO₃ (10%, 5 mL). The resulting mixture was extracted with ethyl acetate (5 mL × 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give a crude product, which was purified by silica gel column chromatography using elution with ethyl acetate-petroleum ether to afford 9H-xanthene 9-amines.

The procedure for gram-scale preparation of 3a
To a solution of salicyl N-tosylimine 2a (1.05 g, 1.0 equiv) and triflate 1a² (1.47 g, 1.3 equiv) in acetonitrile (30 mL) was added CsF (1.44 g, 2.5 equiv) in one portion. After stirring for 11 h at room temperature, the reaction mixture was poured into aq. Na₂CO₃ (10%, 30 mL). The resulting mixture was extracted with ethyl acetate (30 mL × 3). The combined extracts were dried over sodium sulfate, filtered, and evaporated to give a white solid, which was recrystallized from ethyl acetate-petroleum ether to afford 3a (1.32 g, 99%).

Product Characterization Data

N-(9-xanthyl)-4-toluensulfonamide (3a)
Using salicyl N-tosylimine 2a (105 mg, 0.38 mmol), silylaryl triflate 1a (146 mg, 0.49 mmol) and CsF (144 mg, 0.95 mmol) afforded the title compound 3a (122 mg, 92 % yield) as a white solid: mp 196–198 °C (lit.³ mp 197–197.5 °C); Rf = 0.40 (petroleum ether:EtOAc = 3:1); ¹H NMR (400 MHz, CDCl₃): δ = 7.80 (d, J = 8.1 Hz, 2H), 7.37–7.20 (m, 4H), 7.15 (d, J = 7.8 Hz, 2H), 7.08 (d, J = 8.2 Hz, 2H), 6.99 (t, J = 7.5 Hz, 2H), 5.77 (d, J = 8.6 Hz, 1H), 4.87 (d, J = 8.6 Hz, 1H), 2.47 (s, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 151.5, 143.8, 138.8 , 130.0, 129.7 (overlap, 2C), 127.4, 123.8, 120.6, 116.9, 49.4, 21.8. ESI-HRMS: m/z calcd for C₂₀H₁₇NO₃SNa [M + Na]⁺: 374.0821; found: 374.0825

N-(4-chloro-9H-xanthen-9-yl)-4-methylbenzenesulfonamide (3b)
Using salicyl N-tosylimine 2b (118 mg, 0.38 mmol), silylaryl triflate 1a (146 mg, 0.49 mmol) and CsF (144 mg, 0.95 mmol) afforded the title compound 3b (132 mg, 90 % yield) as a white solid: mp 205–207 °C; Rf = 0.52 (petroleum ether:EtOAc = 3:1); ¹H NMR (400 MHz, CDCl₃): δ = 7.80
Using salicyl N-tosylimine 2c (116 mg, 0.38 mmol) and CsF (144 mg, 0.95 mmol) afforded the title compound 3c (122 mg, 84% yield) as a white solid: mp 173–176 °C; \( R_f = 0.43 \) (petroleum ether:EtOAc = 3:1); \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.81 \) (d, \( J = 8.2 \) Hz, 2H), 7.34 (d, \( J = 8.3 \) Hz, 2H), 7.29–7.23 (m, 1H), 7.16 (d, \( J = 7.8 \) Hz, 1H), 7.09–6.97 (m, 3H), 6.61–6.56 (m, 2H), 5.73 (d, \( J = 8.5 \) Hz, 1H), 4.83 (d, \( J = 8.5 \) Hz, 1H), 3.80 (s, 3H), 2.48 (s, 3H). \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)): \( \delta = 151.2, 147.5, 144.0, 138.7, 130.3, 130.07, 129.92, 129.4, 128.2, 127.3, 124.5, 123.8, 122.5, 122.0, 120.3, 117.4, 49.5, 21.9. 

ESI-HRMS: \( m/z \) calcd for C\(_{20}\)H\(_{16}\)ClNO\(_3\)SNa [M + Na\(^+\)]: 408.0432; found: 408.0437.

**N-(3-methoxy-9H-xanthen-9-yl)-4-methylbenzenesulfonamide (3e)**

Using salicyl N-tosylimine 2e (135 mg, 0.38 mmol), silylaryl triflate 1a (146 mg, 0.49 mmol) and CsF (144 mg, 0.95 mmol) afforded the title compound 3e (96 mg, 59% yield) as a white solid: mp 172–174 °C; \( R_f = 0.32 \) (petroleum ether:EtOAc = 3:1); \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.79 \) (d, \( J = 8.0 \) Hz, 2H), 7.35 (d, \( J = 8.0 \) Hz, 2H), 7.32–7.27 (m, 2H), 7.14–6.97 (m, 5H), 5.72 (d, \( J = 8.6 \) Hz, 1H), 4.90 (d, \( J = 8.3 \) Hz, 1H), 2.48 (s, 3H). \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)): \( \delta = 151.9, 151.0, 144.0, 138.6, 134.9, 130.8, 130.1, 129.9, 129.5, 127.3, 124.2, 124.1, 120.1, 119.2, 117.1, 117.0, 48.8, 21.8. 

ESI-HRMS: \( m/z \) calcd for C\(_{20}\)H\(_{16}\)ClNO\(_3\)SNa [M + Na\(^+\)]: 451.9926; found: 451.9924.

**4-methyl-N-(2-methyl-9H-xanthen-9-yl)benzenesulfonamide (3f)**

Using salicyl N-tosylimine 2f (110 mg, 0.38 mmol), silylaryl triflate 1a (146 mg, 0.49 mmol) and CsF (144 mg, 0.95 mmol) afforded the title compound 3f (104 mg, 75% yield) as a white solid: mp 234–237 °C; \( R_f = 0.38 \) (petroleum ether:EtOAc = 3:1); \( ^1H \) NMR (400 MHz, CDCl\(_3\)): \( \delta = 7.82 \) (d, \( J = 8.2 \) Hz, 2H), 7.36 (d, \( J = 8.2 \) Hz, 2H), 7.29–7.26 (m, 2H), 7.15–6.94 (m, 4H), 6.63 (s, 1H), 5.72 (d, \( J = 8.7 \) Hz, 1H), 4.85 (d, \( J = 8.6 \) Hz, 1H), 2.48 (s, 3H), 2.13 (s, 3H). \( ^{13}C \) NMR (101 MHz, CDCl\(_3\)): \( \delta = 151.6, 149.4, 143.8, 139.0, 133.1, 130.4, 130.0, 129.9, 129.6 (overlap, 2C), 127.5, 123.7, 120.6, 112.0, 116.8, 116.7, 49.5, 21.8, 20.7. 

ESI-HRMS: \( m/z \) calcd for C\(_{21}\)H\(_{16}\)BrNO\(_3\)SNa [M + Na\(^+\)]: 451.9926; found: 451.9924.
1H NMR (400 MHz, CDCl 3): \( \delta = 7.83 \) (d, \( J = 8.2 \) Hz, 2H), 7.39 (d, \( J = 8.2 \) Hz, 2H), 7.36–7.28 (m, 3H), 7.11–7.05 (m, 2H), 6.96 (d, \( J = 8.7 \) Hz, 1H), 6.81 (d, \( J = 2.3 \) Hz, 1H), 5.70 (d, \( J = 8.7 \) Hz, 1H), 4.91 (d, \( J = 8.6 \) Hz, 1H), 2.50 (s, 3H).

13C NMR (101 MHz, CDCl 3): \( \delta = 151.0, 150.4, 144.4, 138.5, 132.7, 132.1, 130.3, 130.0, 129.9, 127.3, 124.3, 122.3, 112.0, 118.8, 116.9, 115.7, 48.9, 21.8. ESI-HRMS: m/z calcd for C20H16BrNO3SNa [M + Na]**: 451.9926; found: 451.9927.

**N-(12H-benzo[a]xanthen-12-yl)-4-methylbenzenesulfonamide (3i)**

Using salicyl N-tosylimine \( 2i \) (124 mg, 0.38 mmol), silylaryl triflate \( 1a \) (146 mg, 0.49 mmol) and CsF (144 mg, 0.95 mmol) afforded the title compound 3i (127 mg, 83% yield) as a white solid:

mp 205–208 °C; \( R_f = 0.28 \) (petroleum ether:EtOAc = 3:1); 1H NMR (400 MHz, CDCl 3): \( \delta = 8.08 \) (d, \( J = 8.2 \) Hz, 1H), 7.81 (d, \( J = 8.8 \) Hz, 2H), 7.55 (d, \( J = 8.2 \) Hz, 2H), 7.35–7.27 (m, 3H), 7.20 (d, \( J = 8.2 \) Hz, 1H), 7.11 (d, \( J = 8.0 \) Hz, 2H), 7.01 (t, \( J = 7.6 \) Hz, 1H), 6.53 (d, \( J = 7.3 \) Hz, 1H), 4.62 (d, \( J = 7.4 \) Hz, 1H), 2.37 (s, 3H). 13C NMR (101 MHz, CDCl 3): \( \delta = 151.7, 151.0, 143.2, 138.8, 131.1, 130.9, 130.8, 130.2, 129.5, 129.4, 128.7, 127.6, 127.1, 124.9, 123.9, 122.6, 120.8, 118.0, 116.9, 112.2, 47.3, 21.7. ESI-HRMS: m/z calcd for C24H19NO3SNa [M + Na]**: 424.0978; found: 424.0988.

**N-(10H-[1,3]dioxolo[4,5-b]xanthen-10-yl)-4-methylbenzenesulfonamide (3j)**

Using salicyl N-tosylimine \( 2a \) (105 mg, 0.38 mmol), silylaryl triflate \( 1b \) (161 mg, 0.49 mmol) and CsF (144 mg, 0.95 mmol) afforded the title compound 3j (125 mg, 83% yield) as a white solid:

mp 191–194 °C; \( R_f = 0.19 \) (petroleum ether:EtOAc = 3:1); 1H NMR (400 MHz, CDCl 3): \( \delta = 7.81 \) (d, \( J = 8.2 \) Hz, 2H), 7.35 (d, \( J = 8.2 \) Hz, 2H), 7.28–7.21 (m, 1H), 7.12–7.00 (m, 2H), 6.97 (t, \( J = 7.5 \) Hz, 1H), 6.58 (s, 1H), 6.53 (s, 1H), 5.93 (s, 2H), 5.67 (d, \( J = 8.5 \) Hz, 1H), 4.80 (d, \( J = 8.5 \) Hz, 1H), 2.48 (s, 3H). 13C NMR (101 MHz, CDCl 3): \( \delta = 151.5, 148.6, 146.6, 144.1, 143.9, 138.8, 130.1, 129.6, 129.5, 127.3, 123.7, 119.9, 116.8, 112.2, 107.7, 101.7, 98.2, 49.9, 21.8. ESI-HRMS: m/z calcd for C21H17NO5SNa [M + Na]**: 418.0720; found: 418.0719.

**N-(1-methoxy-9H-xanthen-9-yl)-4-methylbenzenesulfonamide (3k)**

Using salicyl N-tosylimine \( 2a \) (105 mg, 0.38 mmol), silylaryl triflate \( 1c \) (161 mg, 0.49 mmol) and CsF (144 mg, 0.95 mmol) afforded the title compound 3k (128 mg, 88% yield) as a white solid:

mp 182–185 °C; \( R_f = 0.26 \) (petroleum ether:EtOAc = 3:1); 1H NMR (400 MHz, CDCl 3): \( \delta = 7.51 \) (d, \( J = 7.2 \) Hz, 3H), 7.29–7.00 (m, 6H), 6.74 (d, \( J = 8.2 \) Hz, 1H), 6.43 (d, \( J = 7.9 \) Hz, 1H), 5.94 (d, \( J = 6.2 \) Hz, 1H), 4.92 (d, \( J = 5.3 \) Hz, 1H), 3.55 (s, 3H), 2.38 (s, 3H). 13C NMR (101 MHz, CDCl 3): \( \delta = 157.4, 153.2, 152.1, 142.6, 139.4, 130.5, 129.8, 129.4, 129.2, 126.9, 123.7, 120.4, 116.7, 109.4, 109.3, 104.4, 55.4, 45.8, 21.7. ESI-HRMS: m/z calcd for C21H19NO4SNa [M + Na]**: 404.0927; found: 404.0928.

**4-methyl-N-(3-methyl-9H-xanthen-9-yl)benzenesulfonamide and 4-methyl-N-(2-methyl-9H-xanthen-9-yl)benzenesulfonamide (3l+3l')**
Using salicyl N-tosylamine 2a (105 mg, 0.38 mmol), silylaryl triflate 1d\(^7\) (153 mg, 0.49 mmol) and CsF (144 mg, 0.95 mmol) afforded the title compounds 3f+3l (100 mg, 72% yield) as a white solid (3f:3l = 1.5:1; \(R_f = 0.38\) (petroleum ether:EtOAc = 3:1); 3l (major regioisomer): \(1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.81\) (d, \(J = 7.6\) Hz, 2H), 7.33 (d, \(J = 7.6\) Hz, 2H), 7.28–7.24 (m, 1H), 7.17 (d, \(J = 7.6\) Hz, 1H), 7.08–6.96 (m, 3H), 6.91 (s, 1H), 6.79 (d, \(J = 8.0\) Hz, 1H), 5.74 (d, \(J = 8.8\) Hz, 1H), 4.84 (d, \(J = 9.2\) Hz, 1H), 2.48 (s, 3H), 2.32 (s, 3H). \(^{13}C\) NMR (101 MHz, CDCl\(_3\)): \(\delta = 151.5, 151.3, 143.8, 140.1, 138.9, 130.0, 129.8, 129.6, 129.3, 127.4, 124.8, 122.7, 120.7, 117.6, 117.1, 116.9, 49.2, 21.8, 21.4. ESI-HRMS: \(m/z\) calcd for C\(_{24}\)H\(_{19}\)NO\(_3\)SNa [M + Na\(^+\)]: 424.0978; found: 424.0985. 3l' (minor regioisomer) = 3f.

N-(7H-benzo[c]xanthen-7-yl)-4-methylbenzenesulfonamide and N-(12H-benzo[a]xanthen-12-yl)-4-methylbenzenesulfonamide (3m+3m')

Using salicyl N-tosylamine 2a (105 mg, 0.38 mmol), silylaryl triflate 1e\(^7\) (171 mg, 0.49 mmol) and CsF (144 mg, 0.95 mmol) afforded the title compounds 3m+3m' (127 mg, 83% yield) as a white solid (3m:3m' = 1.5:1; \(R_f = 0.28\) (petroleum ether:EtOAc = 3:1); 3m (major regioisomer) = 3i. 3m' (minor regioisomer): \(1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 8.42\) (d, \(J = 8.0\) Hz, 1H), 7.87–7.76 (m, 3H), 7.60–7.24 (m, 8H), 7.16 (d, \(J = 8.2\) Hz, 1H), 7.06 (t, \(J = 7.4\) Hz, 1H), 5.94 (d, \(J = 8.6\) Hz, 1H), 4.93 (d, \(J = 8.5\) Hz, 1H), 2.49 (s, 3H). \(^{13}C\) NMR (101 MHz, CDCl\(_3\)): \(\delta = 152.0, 151.8, 151.1, 150.7, 150.3, 148.7, 143.8, 138.9, 134.2, 130.2, 129.9, 129.6, 127.7, 127.4, 127.3, 126.5, 126.2, 124.2, 124.1, 123.5, 122.0, 120.5, 117.1, 114.1, 49.7, 21.8. ESI-HRMS: \(m/z\) calcd for C\(_{25}\)H\(_{20}\)NO\(_3\)SNa [M + Na\(^+\)]: 424.0978; found: 424.0986.

(S\(_3\))-N-(3-bromo-9H-xanthen-9-yl)-2-methylpropane-2-sulfinamide 5

To a solution of tBS-imine 4\(^b\) (110 mg, 0.36 mmol), and silylaryl triflate 1a (140 mg, 0.47 mmol) in acetonitrile (5 mL) was added CsF (137 mg, 0.90 mmol) in one portion. After stirring for 6h at room temperature, the reaction mixture was poured into aq. Na\(_2\)CO\(_3\) (10%, 5 mL). The resulting mixture was extracted with ethyl acetate (5 mL) was added CsF (144 mg, 0.95 mmol) afforded the title compounds 5 (97 mg, 71% yield) and 6 (25 mg, 18% yield) as white solids. 5: mp 147–149 °C; \(R_f = 0.13\) (petroleum ether:EtOAc = 3:1); \(1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.76\) (d, \(J = 7.4\) Hz, 1H, minor isomer), 7.68 (d, \(J = 8.4\) Hz, 1H, major isomer), 7.44 (d, \(J = 7.7\) Hz, 1H, minor), 7.36–7.11 (m, 5H, minor), 7.36–7.11 (m, 6H, major), 5.66 (d, \(J = 7.4\) Hz, 1H, minor), 5.66 (d, \(J = 7.4\) Hz, 1H, major), 3.68 (d, \(J = 7.4\) Hz, 1H, minor), 3.68 (d, \(J = 7.4\) Hz, 1H, major), 1.20 (s, 6H, major), 1.19 (s, 6H, minor). \(^{13}C\) NMR (101 MHz, CDCl\(_3\)): \(\delta = 152.0\) (major isomer), 151.8 (minor isomer), 151.1 (major), 150.7 (major), 150.3, 132.0, 131.2, 130.6, 129.92, 129.89, 129.7, 127.3, 126.6, 124.5, 123.9, 122.8, 122.5, 121.7, 121.2, 121.2, 120.7, 120.2, 117.03, 116.96, 56.8 (major), 56.7 (minor), 52.1 (major), 51.9 (minor), 22.97 (major), 22.95 (minor). ESI-HRMS: \(m/z\) calcd for C\(_{17}\)H\(_{18}\)BrNO\(_2\)SNa [M + Na\(^+\)]: 402.0134; found: 402.0138.
References