Intermolecular C-N Addition of Amides and S-N Addition of Sulfinamides to Arynes

Zhijian Liu and Richard C. Larock *

Department of Chemistry, Iowa State University, Ames, Iowa 50011

Supporting Information

General. The ^1H , ^{19}F and ^{13}C NMR spectra were recorded at 300 and 75.5 MHz or 400 and 100 MHz respectively. All melting points are uncorrected. High resolution mass spectra were recorded on a Kratos MS50TC double focusing magnetic sector mass spectrometer using EI at 70 eV. All reagents were used directly as obtained commercially unless otherwise noted. All yields reported represent an average of at least two independent runs. The silylaryl triflate **1a**, CsF and acetonitrile were purchased from Sigma-Aldrich Co. The substituted silylaryl triflates **1b**, **1c**, **1d** and **1e** were prepared according to a literature procedure.¹

Preparation of the starting materials. All the *N*-aryltrifluoroacetamides were either commercially available or easily prepared from commercially available materials.

***N*-(2-Iodophenyl),*N*-phenyltrifluoroacetamide.** To a solution of 1.48 g of *N*-phenyl-2-iodoaniline² (5 mmol) and 1.01 g of triethylamine (10 mmol) in 15 mL of CH_2Cl_2 at 0 °C was added 2.1 g of trifluoroacetic anhydride (10 mmol). The reaction mixture was stirred at room temperature of 1 d. The resulting solution was washed with brine (20 mL) and extracted with CH_2Cl_2 (20 mL). The combined CH_2Cl_2 fractions were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford 1.66 g of the desired product (85% yield) as

a white solid: mp 93-94 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.00-7.62 (m, 8H), 7.94 (d, J = 7.8 Hz, 1H); ^{19}F NMR: -68.0; IR (CDCl_3 , cm^{-1}) 3064, 1711, 1593; Anal Calcd. for $\text{C}_{12}\text{H}_9\text{F}_3\text{INO}$: C, 42.99; H, 2.32; N, 3.58. Found: C, 42.97; H, 2.58; N, 3.65; HRMS m/z 391.9687 (calcd $\text{C}_{12}\text{H}_9\text{F}_3\text{INO}$, 391.9680).

All of the *N*-aryltrifluoromethanesulfinamides have been prepared by the following procedure. To a solution of 1.56 g (10 mmol) of sodium trifluoromethanesulfinate (purity 97 %) in 10 mL of ethyl acetate was added at room temperature 0.467 mL of phosphoryl chloride. The resulting mixture was stirred for 5 min, then 5 mmol of aryl amine was added dropwise and the reaction mixture was stirred for an additional 30 min. The reaction mixture was then washed with brine (20 mL) and extracted with ethyl acetate (20 mL). The combined ethyl acetate fractions were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.

***N*-Phenyltrifluoromethanesulfinamide.** The indicated compound was obtained in an 82% yield as a white solid: mp 63-64 °C (lit.³ mp 64 °C). The ^1H , ^{19}F and ^{13}C NMR spectra match the literature data.³ ^1H NMR (300 MHz, CDCl_3) δ 6.81 (s, 1H), 7.09 (d, J = 7.8, 2H), 7.18 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 138.1, 129.9, 125.4, 123.7, 123.7 (q, J = 333.4 Hz), 120.3; ^{19}F NMR: -78.1.

***N*-(4-Iodophenyl)trifluoromethanesulfinamide.** The indicated compound was obtained in an 86% yield as a white solid: mp 94-95 °C; ^1H NMR (400 MHz, CDCl_3) δ 6.83 (td, J = 8.8, 2.8 Hz, 2H), 7.24 (s, 1H), 7.61 (td, J = 8.8, 2.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.9, 138.4, 123.7 (q, J = 331.4 Hz), 121.8, 88.9; ^{19}F NMR: -77.7; IR (CDCl_3 , cm^{-1}) 3210, 3172, 3023, 2903, 1587, 1487, 1188; HRMS m/z 335.9142 (calcd $\text{C}_7\text{H}_5\text{F}_3\text{INOS}$, 335.9136).

***N*-(4-Methoxyphenyl)trifluoromethanesulfonamide.** The indicated compound was obtained in an 84% yield as a white solid: mp 84-85 °C; ^1H NMR (300 MHz, CDCl_3) δ 3.79 (s, 3H), 6.61 (s, 1H), 6.86 (td, $J = 9.0, 2.4$ Hz, 2H), 7.08 (td, $J = 9.0, 2.4$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 158.3, 130.6, 124.4, 123.8 (q, $J = 331.9$ Hz), 115.1; ^{19}F NMR: -78.1; IR (CDCl_3 , cm^{-1}) 3174, 2966, 2916, 2846, 1511, 1183; HRMS m/z 239.0231 (calcd $\text{C}_8\text{H}_8\text{F}_3\text{NO}_2\text{S}$ 239.0227).

***N*-[3-(2-Methyl-4-thiazolyl)phenyl]trifluoromethanesulfonamide.** The indicated compound was obtained in an 80% yield as a white solid: mp 73-74 °C; ^1H NMR (300 MHz, CDCl_3) δ 2.67 (s, 3H), 6.98 (dd, $J = 7.8, 2.1$ Hz, 1H), 7.21-7.24 (m, 2H), 7.54 (d, $J = 7.8$ Hz, 1H), 7.63 (t, $J = 1.8$ Hz, 1H), 8.16 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.7, 154.1, 139.4, 136.1, 130.3, 124.1 (q, $J = 331.9$ Hz), 122.9, 119.4, 118.2, 113.6, 19.2; ^{19}F NMR: -77.4; IR (CDCl_3 , cm^{-1}) 3207, 3113, 2926, 2828, 2759, 1607, 1587; HRMS m/z 306.0114 (calcd $\text{C}_{11}\text{H}_9\text{F}_3\text{N}_2\text{OS}_2$, 306.0108).

***N*-(4-Bromophenyl)trifluoromethanesulfonamide.** The indicated compound was obtained in an 89% yield as a white solid: mp 96-97 °C; ^1H NMR (300 MHz, CDCl_3) δ 6.97 (td, $J = 8.8, 2.8$ Hz, 2H), 7.02 (s, 1H), 7.44 (td, $J = 8.8, 2.8$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 137.5, 133.0, 123.7 (q, $J = 331.6$ Hz), 121.9, 118.6; ^{19}F NMR: -77.8; IR (CDCl_3 , cm^{-1}) 3214, 3030, 2914, 1490, 1208; HRMS m/z 289.9231 (calcd $\text{C}_7\text{H}_5\text{BrF}_3\text{NOS}$, 286.9227).

***N*-(4-Chlorophenyl)trifluoromethanesulfonamide.** The indicated compound was obtained in a 91% yield as a white solid: mp 89-90 °C; ^1H NMR (300 MHz, CDCl_3) δ 7.02 (td, J = 8.8, 2.8 Hz, 2H), 7.15 (s, 1H), 7.28 (td, J = 8.8, 2.8 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 137.0, 131.1, 130.0, 123.8 (q, J = 331.8 Hz), 121.7; ^{19}F NMR: -77.8; IR (CDCl_3 , cm^{-1}) 3213, 2916, 2848, 1494, 1209; HRMS m/z 242.9737 (calcd $\text{C}_7\text{H}_5\text{ClF}_3\text{NOS}$, 242.9732).

***N*-[4-(Trifluoroacetamido)phenyl]-2,2,2-trifluoromethanesulfonamide.** The indicated compound was obtained in a 61% yield as a white solid: mp 160-162 °C; ^1H NMR (300 MHz, acetone- d_6) δ 7.30 (dt, J = 9.0, 2.8 Hz, 2H), 7.75 (dt, J = 9.0, 2.8 Hz, 2H), 9.01 (s, 1H), 10.30 (s, 1H); ^{13}C NMR (100 MHz, acetone- d_6) δ 155.0 (q, J = 35.2 Hz), 124.3 (q, J = 333.0 Hz), 122.4, 120.7, 116.2 (q, J = 286.0 Hz); ^{19}F NMR: -76.5, -78.4; IR (CDCl_3 , cm^{-1}) 3288, 3220, 3094, 1695, 1547; HRMS m/z 320.0058 (calcd $\text{C}_9\text{H}_6\text{F}_6\text{N}_2\text{O}_2\text{S}$, 320.0059).

***N*-Benzyltrifluoromethanesulfonamide** The indicated compound was obtained in a 92% yield as white solid: mp 26-27 °C; ^1H NMR (300 MHz, CDCl_3) δ 4.27-4.34 (m, 1H), 4.43-4.50 (m, 1H), 4.69 (s, 1H), 7.29-7.40 (m, 7H); ^{13}C NMR (75 MHz, CDCl_3) δ 136.7, 129.2, 128.5, 128.3, 123.9 (q, J = 331.8 Hz), 46.6 (q, J = 0.9 Hz); ^{19}F NMR: -77.1; IR (CDCl_3 , cm^{-1}) 3234, 3093, 3071, 3037, 2881, 1457; HRMS m/z 233.0237 (calcd $\text{C}_7\text{H}_5\text{ClF}_3\text{NOS}$, 233.0233).

General procedure for the intermolecular C-N addition of amides to arynes.

To a solution of the *N*-aryltrifluoroacetamide (0.5 mmol) and silylaryl triflate (0.6 mmol) in acetonitrile (6 mL) was added CsF (1.0 mmol). The solution was allowed to stir at room temperature for 4 h. The resulting solution was washed with brine (20 mL)

and extracted with diethyl ether (20 mL). The combined ether fractions were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.

1-[2-(Phenylamino)phenyl]trifluoroethanone. The indicated compound was obtained in a 77% yield (102 mg) as a yellow solid: mp 70-72 °C; ^1H NMR (300 MHz, CDCl_3) δ 6.76 (dt, $J = 7.8, 1.2$ Hz, 1H), 7.18-7.27 (m, 4H), 7.35-7.42 (m, 3H), 7.83-7.87 (m, 1H), 10.24 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 181.2 (q, $J = 33.2$ Hz), 151.5, 139.1, 137.1, 132.2 (q, $J = 4.1$ Hz), 129.9, 125.8, 124.6, 117.4 (q, $J = 289.6$ Hz), 117.1, 114.7, 112.1; ^{19}F NMR: -69.4; IR (CDCl_3 , cm^{-1}) 3306, 3088, 3040, 1658. HRMS m/z 265.0720 (calcd $\text{C}_{14}\text{H}_{10}\text{F}_3\text{NO}$, 265.0714).

1-[2-(4-Chlorophenylamino)phenyl]trifluoroethanone. The indicated compound was obtained in an 86% yield (128 mg) as a yellow solid: mp 76-77 °C; ^1H NMR (300 MHz, CDCl_3) δ 6.79 (dt, $J = 7.8, 1.2$ Hz, 1H), 7.13-7.25 (m, 3H), 7.33-7.44 (m, 3H), 7.84-7.88 (m, 1H), 10.15 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 181.4 (q, $J = 33.3$ Hz), 151.1, 137.7, 137.2, 132.3 (q, $J = 4.0$ Hz), 130.9, 129.9, 125.8, 117.6, 117.3 (q, $J = 289.5$ Hz), 114.6, 112.4; ^{19}F NMR: -69.5; IR (CDCl_3 , cm^{-1}) 3295, 3089, 1650, 1568; HRMS m/z 299.0329 (calcd $\text{C}_{14}\text{H}_9\text{ClF}_3\text{NO}$, 299.0329).

1-[2-(4-Methoxyphenylamino)phenyl]trifluoroethanone. The indicated compound was obtained in a 78% yield (115 mg) as a yellow solid: mp 77-78 °C; ^1H NMR (300 MHz, CDCl_3) δ 3.84 (s, 3H), 6.72 (t, $J = 7.8$ Hz, 1H), 6.92-7.00 (m, 3H), 7.16-7.20 (m, 2H), 7.35 (t, $J = 7.8$ Hz, 1H), 7.81-7.85 (m, 1H), 10.14 (s, 1H); ^{13}C NMR (75 MHz,

CDCl₃) δ 181.0 (q, J = 33.1 Hz), 158.0, 152.8, 137.1, 132.0 (q, J = 4.0 Hz), 131.6, 127.1, 117.5 (q, J = 289.5 Hz), 116.5, 115.1, 114.4, 111.4, 55.7; ¹⁹F NMR: -69.4 IR (CDCl₃, cm⁻¹) 3307, 3071, 3045, 2959, 2913, 2843, 1656, 1139. HRMS m/z 295.0823 (calcd C₁₅H₁₂F₃NO₂, 295.0820).

Methyl 4-[2-(trifluoroacetyl)phenylamino]benzoate. The indicated compound was obtained in a 60% yield (97 mg) as a yellow solid: mp 82-83 °C; ¹H NMR (300 MHz, CDCl₃) δ 3.92 (s, 3H), 6.72 (td, J = 7.2, 1.5 Hz, 1H), 7.3 (dt, J = 8.7, 1.8 Hz, 2H), 7.41-7.52 (m, 2H), 7.88-7.92 (m, 1H), 8.05 (dt, J = 8.7, 1.5 Hz, 2H), 10.26 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 181.7 (q, J = 33.6 Hz), 166.6, 149.2, 143.9, 137.2, 132.4 (q, J = 4.1 Hz), 131.5, 126.0, 121.6, 118.7, 117.1 (q, J = 289.5 Hz), 115.6, 113.6, 52.3; ¹⁹F NMR: -69.6; IR (CDCl₃, cm⁻¹) 3308, 2999, 2952, 2844, 1721, 1669, 1592; HRMS m/z 323.0774 (calcd C₁₆H₁₂F₃NO₃, 323.0769).

1-[2-(2,4,6-Trimethylphenylamino)phenyl]trifluoroethanone. The indicated compound was obtained in a 69% yield (106 mg) as a yellow solid: mp 96-97 °C; ¹H NMR (300 MHz, CDCl₃) δ 2.17 (s, 6H), 2.36 (s, 3H), 6.37 (d, J = 8.7 Hz, 1H), 6.71 (td, J = 7.8, 0.6 Hz, 1H), 7.01 (s, 2H), 7.32 (td, J = 7.8, 0.6 Hz, 1H), 7.86-7.90 (m, 1H), 9.88 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 181.2 (q, J = 32.9 Hz), 153.3, 137.4, 137.3, 136.4, 133.2, 132.1 (q, J = 4.1 Hz), 129.6, 119.5, 117.5 (q, J = 289.5 Hz), 113.9, 110.9, 21.2, 18.3; ¹⁹F NMR: -69.3; IR (CDCl₃, cm⁻¹) 3307, 3015, 2944, 2915, 2856, 1647, 1568; HRMS m/z 307.1188 (calcd C₁₇H₁₆F₃NO, 307.1184).

1-[2-(4-Iodophenylamino)-6-methoxyphenyl]trifluoroethanone. The indicated compound was obtained in an 88% yield (185 mg) as a yellow solid: mp 99-100 °C; ^1H NMR (300 MHz, CDCl_3) δ 3.87 (s, 3H), 6.35 (d, $J = 8.1$ Hz, 1H), 6.80 (d, $J = 8.4$ Hz, 1H), 6.95 (dt, $J = 8.7, 2.7$ Hz, 2H), 7.29 (t, $J = 8.4$ Hz, 1H), 7.61 (dt, $J = 8.7, 2.7$ Hz, 2H), 8.85 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 184.6 (q, $J = 36.4$ Hz), 161.9, 148.2, 140.0, 138.6, 136.6, 124.4, 116.8 (q, $J = 283.4$ Hz), 108.8, 108.2, 101.4, 87.3, 56.0; ^{19}F NMR: -74.1; IR (CDCl_3 , cm^{-1}) 3360, 3015, 2978, 2945, 2841, 1668, 1579; HRMS m/z 420.9791 (calcd $\text{C}_{15}\text{H}_{11}\text{F}_3\text{INO}_2$, 420.9786).

1-[2-(2,5-Dichlorophenylamino)-6-methoxyphenyl]trifluoroethanone. The indicated compound was obtained in an 87% yield (158 mg) as a yellow solid: mp 95-96 °C; ^1H NMR (300 MHz, CDCl_3) δ 3.91 (s, 3H), 6.52 (d, $J = 8.1$ Hz, 1H), 6.92-6.97 (m, 2H), 7.33 (d, $J = 8.4$ Hz, 1H), 7.38-7.44 (m, 2H), 8.71 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 184.9 (q, $J = 36.9$ Hz), 161.6, 145.5, 138.8, 136.3, 133.2, 131.1, 123.8, 123.6, 120.1, 116.5 (q, $J = 288.0$ Hz), 109.9, 109.6, 103.3, 56.1; ^{19}F NMR: -74.1; IR (CDCl_3 , cm^{-1}) 3364, 3053, 2985, 2919, 2856, 1580, 1474; HRMS m/z 363.0198 (calcd $\text{C}_{15}\text{H}_{10}\text{Cl}_2\text{F}_3\text{NO}_2$, 363.0194).

1-[2-(4-Methylphenylamino)-4,5-dimethoxyphenyl]trifluoroethanone. The indicated compound was obtained in a 70% yield (118 mg) as a yellow solid: mp 105-106 °C; ^1H NMR (300 MHz, CDCl_3) δ 2.37 (s, 3H), 3.77 (s, 3H), 3.85 (s, 3H), 6.59 (s, 1H), 7.14-7.23 (m, 5H), 10.51 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 178.0 (q, $J = 32.5$ Hz),

158.1, 150.6, 141.1, 136.6, 135.5, 130.5, 124.6, 117.8 (q, $J = 289.3$ Hz), 116.6 (q, $J = 3.5$ Hz), 104.4, 95.9, 56.5, 56.1, 21.2; ^{19}F NMR: -69.5; IR (CDCl_3 , cm^{-1}) 3260, 2997, 2969, 2939, 2836, 1633, 1517; HRMS m/z 339.1086 (calcd $\text{C}_{17}\text{H}_{17}\text{F}_3\text{NO}_3$, 339.1082).

1-[2-(4-Methylphenylamino)-4,5-dimethylphenyl]trifluoroethanone. The indicated compound was obtained in a 58% yield (89 mg) as a yellow solid: mp 85-86 °C; ^1H NMR (300 MHz, CDCl_3) δ 2.18 (s, 3H), 2.19 (s, 3H), 2.37 (s, 3H), 6.95 (s, 1H), 7.13 (d, $J = 8.4$, 2H), 7.20 (d, $J = 8.4$, 2H), 7.53 (d, $J = 1.8$, 1H), 10.09 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 180.2 (q, $J = 32.8$ Hz), 150.6, 148.3, 136.7, 135.2, 131.5 (q, $J = 3.9$ Hz), 130.4, 135.6, 124.7, 117.6 (q, $J = 289.2$ Hz), 114.9, 110.2, 21.2, 19.2; ^{19}F NMR: -69.3; IR (CDCl_3 , cm^{-1}) 3287, 2943, 2922, 1646, 1516; HRMS m/z 307.1188 (calcd $\text{C}_{17}\text{H}_{16}\text{F}_3\text{NO}$, 307.1184).

1-[2-(4-Methylphenylamino)-6-methoxyphenyl]-2-chloro-2,2-difluoroethanone. The indicated compound was obtained in a 66% yield (107 mg) as a yellow solid: mp 72-73 °C; ^1H NMR (300 MHz, CDCl_3) δ 2.33 (s, 3H), 3.85 (s, 3H), 6.28 (d, $J = 8.1$ Hz, 1H), 6.74 (d, $J = 8.4$ Hz, 1H), 7.07 (d, $J = 8.4$ Hz, 2H), 7.14 (d, $J = 8.4$ Hz, 2H), 7.23 (t, $J = 8.4$ Hz, 1H), 8.55 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 186.3 (t, $J = 30.4$ Hz), 161.4, 149.3, 137.5, 136.0, 134.4, 130.2, 123.3, 121.0 (t, $J = 320.7$ Hz), 108.1, 107.7, 100.3, 55.6, 21.1; ^{19}F NMR: -62.2; IR (CDCl_3 , cm^{-1}) 3369, 3028, 2942, 2842, 1657; HRMS m/z 326.0762 (calcd $\text{C}_{16}\text{H}_{14}\text{ClF}_2\text{NO}_2$, 326.0759).

1-(2-phenylamino-5-methoxyphenyl)trifluoroethanone. The indicated compound was obtained in a 35% yield (51 mg) as a yellow solid: mp 77-79 °C; ^1H NMR (300 MHz, CDCl_3) δ 3.79 (s, 3H), 7.08-7.22 (m, 6H), 7.37 (td, J = 8.1, 1.8, 2H), 10.03 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 180.5 (q, J = 33.3 Hz), 150.7, 146.6, 139.7, 129.8, 127.3, 125.1, 123.8, 117.4 (q, J = 289.6 Hz), 116.7, 112.4 (q, J = 4.3 Hz), 111.9, 55.9; ^{19}F NMR: -69.7; IR (CDCl_3 , cm^{-1}) 3310, 3002, 2933, 2855, 1657, 1520; HRMS m/z 295.0823 (calcd $\text{C}_{15}\text{H}_{12}\text{F}_3\text{NO}_2$, 295.0820).

1-(2-phenylamino-4-methoxyphenyl)trifluoroethanone. The indicated compound was obtained in a 38% yield (56 mg) as a yellow solid: mp 80-82 °C; ^1H NMR (300 MHz, CDCl_3) δ 3.75 (s, 3H), 6.34 (dd, J = 9.3, 2.7 Hz, 1H), 6.57 (d, J = 2.4 Hz, 1H), 7.20-7.30 (m, 3H), 7.41 (td, J = 8.1, 1.8, 2H), 7.77 (dd, J = 9.0, 2.1 Hz, 1H), 10.48 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 179.2 (q, J = 32.8 Hz), 166.7, 154.3, 139.1, 134.4 (q, J = 4.3 Hz), 129.9, 125.8, 124.8, 117.6 (q, J = 289.4 Hz), 106.7, 106.6, 96.4, 55.6; ^{19}F NMR: -69.22; IR (CDCl_3 , cm^{-1}) 3288, 3024, 2967, 2940, 1643, 1618; HRMS m/z 295.0823 (calcd $\text{C}_{15}\text{H}_{12}\text{F}_3\text{NO}_2$, 295.0820).

1,1'-[1,4-Phenylenebis(imino-2,1-phenylene)]bistrifluoroethanone. The indicated compound was obtained in a 48% yield (109 mg) as a yellow solid: mp 186-188 °C; ^1H NMR (300 MHz, CDCl_3) δ 6.80 (t, J = 7.5 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 7.31 (s, 4H), 7.43 (t, J = 7.2 Hz, 2H), 7.86-7.89 (m, 2H), 10.23 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 181.3 (q, J = 33.4 Hz), 161.4, 137.2, 136.4, 132.3 (q, J = 4.2 Hz), 125.7, 117.4,

117.3 (q, $J = 289.6$ Hz), 114.7, 112.2; ^{19}F NMR: -69.47 ; IR (CDCl_3 , cm^{-1}) 3306, 2956, 2918, 2856, 1648, 1572, 1145; HRMS m/z 452.0966 (calcd $\text{C}_{22}\text{H}_{14}\text{F}_6\text{N}_2\text{O}_2$, 452.0959).

General procedure for the intermolecular S-N addition of sulfinamides to arynes.

To a solution of the *N*-aryltrifluoromethanesulfinamide (0.5 mmol) and silylaryl triflate (0.75 mmol) in THF (6 mL) was slowly added tetra-*n*-butylammonium fluoride (TBAF, 0.9 mmol). The solution was allowed to stir at room temperature for 30 min and was then washed with brine (20 mL) and extracted with diethyl ether (20 mL). The combined ether fractions were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product.

(2-Phenylamino)phenyl trifluoromethyl sulfoxide. The indicated compound was obtained in an 80% yield (114 mg) as a light yellow oil: ^1H NMR (300 MHz, CDCl_3) δ 6.88 (td, $J = 7.8$, 0.9 Hz, 1H), 7.09 (t, $J = 7.2$ Hz, 1H), 7.17 (d, $J = 7.5$ Hz, 2H), 7.24-7.42 (m, 5H), 8.17 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.4, 140.5, 135.1, 129.8, 129.7 (q, $J = 1.0$ Hz), 125.9 (q, $J = 336.1$ Hz) 124.1, 121.9, 118.9, 116.5, 115.7 (q, $J = 1.6$ Hz); ^{19}F NMR: -71.9 ; IR (CDCl_3 , cm^{-1}) 3325, 3059, 3043, 1590, 1472; HRMS m/z 285.0440 (calcd $\text{C}_{13}\text{H}_{10}\text{F}_3\text{NOS}$, 285.0435).

[2-(4-Iodophenylamino)]phenyl trifluoromethyl sulfoxide. The indicated compound was obtained in an 81% yield (166 mg) as a light green oil: ^1H NMR (400 MHz, CDCl_3) δ 6.92-9.95 (m, 3H), 7.29 (d, $J = 8.4$ Hz, 1H), 7.39-7.45 (m, 2H), 7.61 (d, $J = 8.8$ Hz, 2H), 8.19 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.6, 140.4, 138.6, 135.1, 129.8 (q, $J = 1.0$ Hz), 125.7 (q, $J = 335.6$ Hz), 123.1, 119.8, 116.9, 116.4 (q, $J = 1.8$ Hz), 86.4; ^{19}F NMR: -71.7 ; IR (CDCl_3 , cm^{-1}) 3318, 3060, 3028, 2921, 2850, 1583, 1515; HRMS m/z 410.9410 (calcd $\text{C}_{13}\text{H}_9\text{F}_3\text{INOS}$, 410.9402).

[2-(4-Methoxyphenylamino)]phenyl trifluoromethyl sulfoxide. The indicated compound was obtained in a 91% yield (143 mg) as a light yellow oil: ^1H NMR (300 MHz, CDCl_3) δ 3.81 (s, 3H), 6.78 (td, $J = 7.8, 0.9$ Hz, 1H), 6.90 (dt, $J = 9.0, 3.6$ Hz, 2H), 7.00 (d, $J = 8.7$ Hz, 1H), 7.12 (dt, $J = 8.7, 3.3$ Hz, 2H), 7.30-7.35 (m, 2H), 8.07 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 157.3, 150.1, 135.1, 132.8, 129.5, (q, $J = 1.1$ Hz), 126.0 (q, $J = 336.3$ Hz), 125.7, 117.7, 115.2, 115.0, 113.7 (q, $J = 1.6$ Hz), 55.7; ^{19}F NMR: -71.8; IR (CDCl_3 , cm^{-1}) 3332, 3003, 2959, 2909, 2836, 1595, 1512; HRMS m/z 315.0546 (calcd $\text{C}_{14}\text{H}_{12}\text{F}_3\text{NO}_2\text{S}$, 315.0541).

2-[3-(2-Methyl-4-thiazolyl)phenylamino]phenyl trifluoromethyl sulfoxide. The indicated compound was obtained in a 75% yield (143 mg) as a light yellow solid: mp 97-98 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 2.75 (s, 3H), 6.89 (td, $J = 7.5, 1.2$ Hz, 1H), 7.14 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.30 (s, 1H), 7.32-7.43 (m, 4H), 7.58 (d, $J = 7.8$ Hz, 1H), 7.70 (t, $J = 1.8$ Hz, 1H), 8.21 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.2, 154.7, 148.2, 140.9, 136.3, 135.1, 130.0, 129.7, 125.9 (q, $J = 336.0$ Hz), 122.0, 121.1, 119.9, 119.2, 116.7, 115.9, 113.1, 19.5; ^{19}F NMR: -71.7; IR (CDCl_3 , cm^{-1}) 3323, 3109, 3062, 2924, 1587, 1501; HRMS m/z 382.0426 (calcd $\text{C}_{17}\text{H}_{13}\text{F}_3\text{N}_2\text{OS}_2$, 382.0421).

[2-(4-Bromophenylamino)-4,5-dimethoxy]phenyl trifluoromethyl sulfoxide. The indicated compound was obtained in a 72% yield (152 mg) as a white solid: mp 132-133 $^{\circ}\text{C}$; ^1H NMR (300 MHz, CDCl_3) δ 3.82 (s, 3H), 3.88 (s, 3H), 6.81 (s, 1H), 6.92 (d, $J =$

9.0 Hz, 2H), 7.01 (s, 1H), 7.19 (s, 1H), 7.90 (d, $J = 9.0$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 154.9, 144.8, 141.5, 141.1, 132.7, 125.6 (q, $J = 336.0$ Hz), 120.7, 114.7, 111.4 (q, $J = 1.6$ Hz), 110.3, 103.4, 56.8, 56.4; ^{19}F NMR: -72.8; IR (CDCl_3 , cm^{-1}) 3332, 3065, 3007, 2963, 2911, 2835, 1590, 1489; HRMS m/z 423.9756 (calcd $\text{C}_{15}\text{H}_{13}\text{BrF}_3\text{NO}_3\text{S}$, 423.9751).

[2-(4-Chlorophenylamino)-4,5-dimethyl]phenyl trifluoromethyl sulfoxide. The indicated compound was obtained in a 55% yield (96 mg) as a white solid: mp 69-71 °C; ^1H NMR (300 MHz, CDCl_3) δ 2.22 (s, 3H), 2.23 (s, 3H), 7.03-7.08 (m, 3H), 7.16 (s, 1H), 7.25-7.28 (m, 2H), 7.81 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.3, 145.2, 129.8 (q, $J = 1.0$ Hz), 129.7, 129.0, 127.9, 125.7 (q, $J = 335.9$ Hz), 121.9, 118.6, 114.2 (q, $J = 1.5$ Hz), 20.7, 19.1; ^{19}F NMR: -72.1; IR (CDCl_3 , cm^{-1}) 3324, 2972, 2860, 1593, 1492; HRMS m/z 347.0362 (calcd $\text{C}_{15}\text{H}_{13}\text{ClF}_3\text{NOS}$, 347.0358).

[2-(4-Trifluoroacetamidophenylamino)]phenyl trifluoromethyl sulfoxide. The indicated compound was obtained in a 58% yield (114 mg) as a light yellow solid: mp 101-103 °C; ^1H NMR (300 MHz, CDCl_3) δ 6.93 (t, $J = 7.2$ Hz, 1H), 7.18 (d, $J = 8.7$ Hz, 2H), 7.28 (d, $J = 8.1$ Hz, 1H), 7.42 (q, $J = 6.9$ Hz, 2H), 7.54 (d, $J = 8.7$ Hz, 2H), 8.06 (s, 1H), 8.24 (s, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 154.9 (q, $J = 47.1$ Hz), 147.9, 138.7, 135.2, 130.9, 129.8 (q, $J = 1.0$ Hz), 125.7 (q, $J = 335.8$ Hz), 122.3, 122.2, 119.5, 117.9, 116.0 (q, $J = 286.9$ Hz), 115.9 (q, $J = 1.6$ Hz); ^{19}F NMR: -71.7, -76.0; IR (CDCl_3 , cm^{-1}); HRMS m/z 396.0373 (calcd $\text{C}_{15}\text{H}_{10}\text{F}_6\text{N}_2\text{O}_2\text{S}$, 396.0367).

(2-Benzylamino)phenyl trifluoromethyl sulfoxide. The indicated compound was obtained in a 41 % yield as a slightly yellow oil; ^1H NMR (300 MHz, CDCl_3) δ 4.41 (d, J = 5.4 Hz, 2H), 6.63-6.73 (m, 2H), 7.06 (s, 1H), 7.24-7.36 (m, 7H); ^{13}C NMR (75 MHz, CDCl_3) δ 151.2, 138.3, 135.4, 129.6 (q, J = 1.0 Hz), 129.0, 127.6, 127.1, 126.2 (q, J = 336.3 Hz), 116.1, 112.4, 112.4 (q, J = 1.7 Hz), 47.3; ^{19}F NMR: -71.8; IR (CDCl_3 , cm^{-1}) 3375, 3086, 3067, 3034, 2856, 1605, 1527; HRMS m/z 299.0596 (calcd $\text{C}_{14}\text{H}_{12}\text{F}_3\text{NOS}$, 299.0591).

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