



Supporting Information

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Copper(II)-catalyzed Aza Friedel-Crafts Reaction of *N*-(2-pyridyl)sulfonyl Aldimines: Synthesis of Unsymmetrical Diarylamines and Triarylmethanes

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General methods.

Melting points were taken in open-end capillary tubes. NMR spectra were recorded [300 MHz (^1H), 75 MHz (^{13}C)] at room temperature in CDCl_3 calibrated at 7.26 ppm (^1H) or 77.0 ppm (^{13}C) for fluoro containing compounds the observed list of peaks is given as the ^{13}C NMR data. Mass spectra (MS) were determined at an ionizing voltage of 70 eV. All the reactions were carried out in anhydrous solvents and under argon atmosphere. CH_2Cl_2 and CH_3CN were dried and stored over microwave-activated 4Å molecular sieves. Flash column chromatography was performed using silica gel (230-400 mesh).

Typical procedure for the preparation of (2-pyridylsulfonyl)aldimines:

2-Pyridinesulfonamide, *N*-(phenylmethylene) (1e). A mixture of benzaldehyde (479 μL , 4.7 mmol), 2-pyridylsulfonamide¹ (744 mg, 4.7 mmol), activated MS 4A and catalytic amount of Amberlist-

¹ S. Diltz, G. Aguirre, F. Ortega, P. J. Walsh, *Tetrahedron: Asymmetry* **1997**, 8, 3559.

15 in dry toluene (15 mL) was heated in a sealed tube for 12 h. The mixture was filtered through Celite and concentrated. The resulting yellow solid was triturated with diethyl ether, filtered and dried to afford the pure sulfonylimine **1e** (1.0 g, 87%) as a white solid. Mp 173-174 °C; ¹H NMR (300 MHz, CDCl₃): δ 9.24 (s, 1H), 8.70 (ddd, *J* = 4.6, *J* = 1.6 and *J* = 0.8 Hz, 1H), 8.24 (dt, *J* = 1.7, 8.6 Hz, 1H), 8.02-7.93 (m, 3H), 7.64 (m, 1H), 7.60-7.45(m, 2H). ¹³C NMR (75 MHz, CDCl₃): 174.3, 155.9, 150.4, 138.1, 135.4, 132.3.

Typical procedure for the Cu(II)-catalyzed mono Aza Friedel-Crafts reaction to *N*-sulfonyl imines:

(1-Methyl-1*H*-indol-3-yl)(phenyl)-*N*-[(2-pyridyl)sulfonyl]-methanamine(2e**).** A solution of Cu(OTf)₂ (3.6 mg, 0.01 mmol) and (±)-BINAP (6.8 mg, 0.011 mmol) in dry CH₂Cl₂ (0.5 mL) was stirred at rt for 20 min, then a solution of sulfonyl imine **1e** (24.6 mg, 0.1 mmol) in dry CH₂Cl₂ (0.5 mL) was added. The mixture was stirred at rt for 5 min, and then 1-methylindole (12.5 μL, 0.12 mmol) was added. Once the reaction reach completion (TLC monitoring), saturated aqueous NH₄Cl (15 mL) was added. The mixture was extracted with CH₂Cl₂ (3 x 20 mL), and the combined organic phase was dried (Na₂SO₄) and concentrated. The residue was purified by flash chromatography (*n*-hexane-EtOAc 2:1) to afford **2e** (27.2 mg, 72%) as a yellow solid (similar yield was obtained in a 5 mmol scale). Mp 202-204 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.24 (ddd, *J* = 4.6, *J* = 1.6

and $J = 0.8$ Hz, 1H), 7.65 (m, 1H), 7.58-7.42 (m, 2H), 7.31-7.10 (m, 8H), 7.05 (m, 1H), 6.61 (s, 1H), 6.51 (s, 1H), 6.24 (d, $J = 7.0$ Hz, 1H), 6.03 (d, $J = 7.0$ Hz, 1H), 3.59 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): 157.7, 149.5, 140.0, 137.2, 137.1, 127.5, 128.2, 127.3, 126.0, 125.8, 122.1, 122.0, 119.6, 119.5, 114.4, 109.2, 55.5, 32.6. MS (FAB+) m/z 337.1 (M^+ , 53), 235.1 ($\text{M}^+ - \text{SO}_2(2\text{-Py})$, 100). FAB+ HRMS for $\text{C}_{21}\text{H}_{19}\text{O}_2\text{N}_3\text{S}$ (M^+): Calcd: 377.11980. Found: 377.11934

(1-Methyl-1H-indol-3-yl)(phenyl)-N-(p-Tolylsulfonyl)-

methanamine (2a). Yield: 41%; white solid; Mp 169-171 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.55 (d, $J = 8.3$ Hz, 2H), 7.30-7.20 (m, 8H), 7.09 (d, $J = 8.3$ Hz, 2H), 7.00 (m, 1H), 6.51 (s, 1H), 5.85 (d, $J = 7.0$ Hz, 1H), 5.20 (d, $J = 7.0$ Hz, 1H), 3.62 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): 142.9, 140.5, 137.6, 129.2, 128.4, 128.3, 127.3, 127.2, 125.8, 122.1, 119.5, 119.3, 114.7, 109.3, 55.0, 32.6, 21.4.

(1-Methyl-1H-indol-3-yl)(phenyl)-N-(p-nitrophenylsulfonyl)-

methanamine (2b). Yield: 47%; yellow solid; Mp 182-184 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.99 (d, $J = 8.8$ Hz, 2H), 7.51 (d, $J = 8.3$ Hz, 2H), 7.42 (d, $J = 8.5$ Hz, 2H), 7.20-7.00 (m, 5H), 6.92 (m, 1H), 6.35 (s, 1H), 5.81 (d, $J = 6.2$ Hz, 1H), 5.26 (d, $J = 6.2$ Hz, 1H), 3.54 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): 148.1, 143.7, 137.3, 137.0, 129.7, 129.5, 128.3, 128.1, 127.3, 126.4, 125.3, 123.5, 122.6, 119.5, 118.7, 113.3, 109.7, 59.2, 32.7.

(1-Methyl-1H-indol-3-yl)(phenyl)-N-[(2-thiophenyl)sulfonyl]-

methanamine (2c). Yield: 50%; yellow solid; Mp 165-167 °C; ^1H

NMR (300 MHz, CDCl₃): δ 7.45 (dd, J = 5.1 and J = 1.3 Hz, 1H), 7.40-7.20 (m, 9H), 7.03 (m, 1H), 6.89 (dd, J = 4.8 and J = 3.8 Hz, 1H), 6.51 (s, 1H), 5.95 (d, J = 7.0 Hz, 1H), 5.28 (d, J = 7.0 Hz, 1H), 3.65 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 141.7, 140.2, 137.9, 132.4, 131.6, 128.5, 128.4, 127.5, 127.1, 127.0, 125.8, 122.2, 119.7, 119.3, 114.6, 109.4, 55.3, 32.7.

(1-Methyl-1*H*-indol-3-yl)(phenyl)-*N*-[(*N,N*-dimethylamino)-sulfonyl]methanamine (2d). Yield: 45%; white solid; Mp 135-136 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.65 (d, J = 8.0 Hz, 1H), 7.40 (m, 1H), 7.35-7.15 (m, 6H), 7.06 (m, 1H), 6.53 (s, 1H), 5.84 (d, J = 6.0 Hz, 1H), 4.74 (d, J = 6.0 Hz, 1H), 3.62 (s, 3H), 2.47 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): 141.8, 137.5, 128.5, 128.2, 127.6, 127.4, 126.0, 122.3, 119.8, 119.6, 115.6, 109.4, 55.3, 37.6, 32.8.

(4-Fluorophenyl)(1-methyl-1*H*-indol-3-yl)-*N*-[(2-pyridyl)-sulfonyl]methanamine (11e). Yield: 90%; white solid; Mp 200-202 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.16 (ddd, J = 4.6, J = 1.6 and J = 0.8 Hz, 1H), 7.57 (m, 1H), 7.49 (m, 1H), 7.36 (d, J = 7.9 Hz, 1H), 7.22-7.06 (m, 6H), 6.98 (m, 1H), 6.77 (m, 2H), 6.52 (s, 1H), 6.24 (d, J = 7.9 Hz, 1H), 5.94 (d, J = 7.9 Hz, 1H), 3.51 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 163.5, 160.3, 157.6, 149.5, 137.2, 137.1, 135.9, 135.8, 129.2, 129.0, 128.5, 125.9, 122.2, 122.0, 119.6, 119.5, 115.1, 114.8, 114.1, 109.3, 54.8, 32.7.

(4-Methoxyphenyl)(1-methyl-1*H*-indol-3-yl)-*N*-[(2-pyridyl)-sulfonyl]methanamine (12e). Yield: 70%; white solid; Mp 182-

184 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.23 (ddd, J= 4.6, J= 1.6 and J= 0.8 Hz, 1H), 7.57 (m, 1H), 7.49 (m, 1H), 7.35 (d, J= 7.9 Hz, 1H), 7.15-7.05 (m, 6H), 6.94 (m, 1H), 6.67 (m, 3H), 5.98 (d, J= 8.1 Hz, 1H), 5.87 (d, J= 8.1 Hz, 1H), 3.65 (s, 3H), 3.51 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 158.7, 157.7, 149.5, 137.2, 137.1, 132.1, 128.6, 128.5, 126.0, 125.8, 122.1, 122.0, 119.7, 119.4, 114.5, 113.5, 109.2, 55.2, 55.0, 32.66. MS (FAB+) m/z 407.2 (M⁺, 100), FAB+ HRMS for C₂₂H₂₁N₃O₃S (M⁺): Calcd: 407.13036. Found: 407.13215.

(3-Fluorophenyl)(1-methyl-1H-indol-3-yl)-N-[(2-pyridyl)-sulfonyl]methanamine (13e). Yield: 70%; white solid; Mp 164-165 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.16 (ddd, J= 4.6, J= 1.6 and J= 0.8 Hz, 1H), 7.59 (m, 1H), 7.49 (m, 1H), 7.34 (d, J= 7.9 Hz, 1H), 7.13-6.88 (m, 7H), 6.75 (m, 1H), 6.53 (s, 1H), 6.25 (d, J= 8.0 Hz, 1H), 5.94 (d, J= 8.0 Hz, 1H), 3.51 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 164.2, 161.0, 157.6, 149.5, 142.9, 142.8, 137.2, 137.1, 129.8, 129.6, 128.5, 126.0, 125.9, 123.1, 123.0, 122.2, 122.0, 119.6, 119.4, 114.6, 114.3, 114.0, 113.8, 109.3, 54.9, 32.6

(1-Methyl-1H-indol-3-yl)(3-methylphenyl)-N-[(2-pyridyl)sulfonyl]methanamine (14e). Yield: 73%; white solid; Mp 74-75 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.23 (ddd, J= 4.6, J= 1.6 and J= 0.8 Hz, 1H), 7.58 (m, 1H), 7.47 (m, 1H), 7.39 (d, J= 7.9 Hz, 1H), 7.15-7.08 (m, 3H), 6.99-6.91 (m, 3H), 6.75 (m, 1H), 6.53 (s, 1H), 5.89 (m, 2H), 3.52 (s, 3H), 2.12 (s, 3H). ¹³C NMR (75

MHz, CDCl₃): 157.7, 149.5, 139.9, 137.8, 137.3, 137.0, 128.5, 128.2, 128.1, 126.1, 125.8, 124.5, 122.1, 122.0, 119.7, 119.5, 114.5, 109.2, 55.5, 32.7, 21.33. MS (FAB+) m/z 391.2 (M⁺, 100), FAB+ HRMS for C₂₂H₂₁N₃O₂S (M⁺): Calcd: 391.13545. Found: 391.13447.

(2-Bromophenyl)(1-methyl-1H-indol-3-yl)-N-[(2-pyridyl)-sulfonyl]methanamine (15e). Yield: 78%, white solid; Mp 173-174 °C; ¹H NMR (300 MHz, DMSO-D₆): δ 8.90 (bs, 1H), 8.45 (ddd, J= 4.6, J= 1.6 and J= 0.8 Hz, 1H), 7.85 (m, 1H), 7.77 (m, 1H), 7.61 (dd, J= 7.7 and J= 1.4 Hz, 1H), 7.52-7.32 (m, 5H), 7.25-6.98 (m, 5H), 6.52 (s, 1H), 6.25 (bs, 1H), 3.62 (s, 3H). ¹³C NMR (75 MHz, DMSO-D₆): 157.5, 149.5, 140.2, 137.9, 136.7, 132.0, 129.0, 128.7, 128.5, 127.4, 126.4, 126.0, 122.1, 121.5, 121.4, 118.9, 118.8, 113.2, 109.7, 53.3, 32.3.

(1-Methyl-1H-indol-3-yl)(2-naphtyl)-N-[(2-pyridyl)sulfonyl]-methanamine (16e). Yield: 85%; yellow solid; Mp 100-102 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.94 (ddd, J= 4.6, J= 1.6 and J= 0.8 Hz, 1H), 7.68-7.42 (m, 6H), 7.38-7.22 (m, 3H), 7.20-7.02 (m, 3H), 6.96 (m, 1H), 6.77 (m, 1H), 6.69 (d, J= 8.3 Hz, 1H), 6.51 (s, 1H), 6.14 (d, J= 8.3 Hz, 1H), 3.42 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 157.4, 149.2, 137.2, 137.0, 136.8, 132.9, 132.5, 128.7, 127.9, 127.3, 126.1, 125.9, 125.8, 125.5, 125.4, 122.0, 121.9, 121.9, 119.5, 114.1, 109.2, 55.4, 32.5. MS (FAB+) m/z 417.2 (M⁺, 100), FAB+ HRMS for C₂₅H₂₁N₃O₂S (M⁺): Calcd: 417.13545. Found: 417.13605.

Cyclohexyl(1-methyl-1*H*-indol-3-yl)-*N*-[(2-pyridyl)sulfonyl]-

methanamine (17e). Yield: 70%; yellow solid; Mp 132-134 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.15 (ddd, *J* = 4.6, *J* = 1.6 and *J* = 0.8 Hz, 1H), 7.52-7.22 (m, 3H), 7.15-6.90 (m, 4H), 6.66 (s, 1H), 5.72 (d, *J* = 8.9 Hz, 1H), 4.44 (t, *J* = 8.9 Hz, 1H), 3.54 (s, 3H), 2.21-0.80 (m, 12H). ¹³C NMR (75 MHz, CDCl₃): 157.6, 148.7, 136.5, 136.2, 127.5, 126.2, 125.1, 121.7, 121.5, 119.4, 119.0, 113.5, 108.9, 57.2, 42.8, 32.4, 30.3, 29.9, 26.3, 26.0, 25.9.

(1*H*-Indol-3-yl)(phenyl)-*N*-[(2-pyridyl)sulfonyl]methanamine

(18e). Yield: 82%; yellow solid; Mp 185-187 °C; ¹H NMR (300 MHz, Acetone-D₆): δ 8.31 (ddd, *J* = 4.6, *J* = 1.6 and *J* = 0.8 Hz, 1H), 7.65 (m, 2H), 7.31-7.18 (m, 6H), 7.09-6.91 (m, 4H), 6.82-6.76 (m, 2H), 5.91 (d, *J* = 8.8 Hz, 1H). ¹³C NMR (75 MHz, Acetone-D₆): 159.5, 150.4, 142.5, 138.4, 137.9, 128.8, 128.3, 127.7, 126.9, 126.8, 125.0, 122.5, 122.4, 120.2, 119.8, 117.0, 112.2, 56.3.

(5-Methoxy-1*H*-indol-3-yl)(phenyl)-*N*-[(2-pyridyl)sulfonyl]-

methanamine (19e). Yield: 89%; yellow solid; Mp 165-167 °C; ¹H NMR (300 MHz, Acetone-D₆): δ 8.43 (ddd, *J* = 4.6, *J* = 1.6 and *J* = 0.8 Hz, 1H), 7.81 (m, 2H), 7.44-7.34 (m, 4H), 7.28-7.14 (m, 4H), 7.01 (d, *J* = 2.5 Hz, 1H), 6.89 (d, *J* = 2.5 Hz, 1H), 6.77 (dd, *J* = 8.8 and *J* = 2.4 Hz, 1H), 6.30 (d, *J* = 8.8 Hz, 1H), 3.71 (s, 3H). ¹³C NMR (75 MHz, Acetone-D₆): 159.5, 154.7, 150.4, 142.5, 138.4, 132.9, 128.7, 128.3, 127.7, 127.3, 126.9, 125.6, 122.5, 116.5, 112.8, 112.6, 102.2, 56.3, 55.8.

(5-Methoxy-1-methyl-1*H*-indol-3-yl)(phenyl)-*N*-[(2-pyridyl)sulfonyl]methanamine (20e). Yield: 93%; yellow solid; Mp 135-137 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.15 (ddd, *J*= 4.6, *J*= 1.6 and *J*= 0.8 Hz, 1H), 7.54 (m, 1H), 7.42 (m, 1H), 7.18 (m, 2H), 7.10-7.02 (m, 4H), 6.98 (d, *J*= 8.8 Hz, 1H), 6.91 (d, *J*= 2.4 Hz, 1H), 6.74 (dd, *J*= 8.8 and *J*= 2.4 Hz, 1H), 6.46 (s, 1H), 6.21 (d, *J*= 8.2 Hz, 1H), 5.91 (d, *J*= 8.2 Hz, 1H), 3.71 (s, 3H), 3.45 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 157.6, 154.0, 149.2, 140.0, 137.1, 132.5, 129.1, 128.2, 127.4, 127.3, 126.5, 125.8, 122.0, 113.8, 112.4, 110.0, 101.3, 55.9, 55.4, 32.8. MS (FAB+) *m/z* 407.2 (*M*⁺, 18), 250.2 (*M*⁺ - SO₂(2-Py) and - Me, 100). FAB+ HRMS for C₂₂H₂₁O₃N₃S (*M*⁺): Calcd: 407.13007. Found: 407.13036

(2-Methyl-1*H*-indol-3-yl)(phenyl)-*N*-[(2-pyridyl)sulfonyl]-methanamine (21e). Yield: 80%; White solid; Mp 74-76 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.05 (bs, 1H), 7.85 (bs, 1H), 7.50 (m, 1H), 7.42-7.29 (m, 3H), 7.19-7.10 (m, 3H), 7.01-6.85 (m, 4H), 6.76 (m, 1H), 5.93 (d, *J*= 8.1 Hz, 1H), 5.73 (d, *J*= 8.1 Hz, 1H), 2.11 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 159.5, 154.7, 150.4, 142.5, 138.4, 132.9, 128.7, 128.3, 127.7, 127.3, 126.9, 125.6, 122.5, 116.5, 112.8, 112.6, 102.2, 56.3, 55.8.

(2-Phenyl-1*H*-indol-3-yl)(phenyl)-*N*-[(2-pyridyl)sulfonyl]-methanamine (22e). Yield: 70%; White solid; Mp 198-200 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.11 (bs, 1H), 7.92 (d, *J*= 4.6 Hz, 1H), 7.42 (m, 2H), 7.32 (m, 2H), 7.27-7.18 (m, 8H), 7.10 (m, 2H),

7.00 (m, 1H), 6.92 (m, 1H), 6.85 (m, 1H), 6.08 (d, $J = 8.1$ Hz, 1H), 5.71 (d, $J = 8.1$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3): 156.6, 149.2, 140.3, 136.6, 136.3, 136.0, 131.7, 129.1, 128.5, 128.0, 127.5, 127.3, 126.2, 125.7, 122.6, 121.3, 120.2, 120.0, 111.1, 110.7, 54.4. MS (FAB+) m/z 439.1 (M^+ , 22), 297.1 ($\text{M}^+ - \text{SO}_2(2\text{-Py})$, 100). FAB+ HRMS for $\text{C}_{26}\text{H}_{21}\text{N}_3\text{O}_2\text{S}$ (M^+): Calcd: 439.13545. Found: 439.13506.

(3-Methyl-1H-indol-2-yl)(phenyl)-N-[(2-pyridyl)sulfonyl]-methanamine (23e). Yield: 75%; White solid; Mp 152-154 °C; ^1H NMR (300 MHz, CDCl_3): δ 9.33 (d, $J = 8.9$ Hz, 1H), 9.05 (bs, 1H), 7.65 (ddd, $J = 4.6$, $J = 1.6$ and $J = 0.8$ Hz, 1H), 7.54 (d, $J = 7.8$ Hz, 1H), 7.39 (m, 2H), 7.26 (m, 1H), 7.19-7.11 (m, 5H), 7.05 (m, 1H), 6.95 (m, 1H), 6.61 (ddd, $J = 7.6$, $J = 4.7$ and $J = 1.0$ Hz, 1H), 6.13 (d, $J = 8.8$ Hz, 1H), 2.15 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): 155.6, 148.0, 138.3, 136.4, 136.0, 130.5, 128.4, 128.0, 127.8, 127.6, 125.3, 122.1, 121.8, 118.8, 118.2, 111.2, 109.2, 53.75, 8.25.

(1-Methyl-1H-pyrrol-2-yl)(phenyl)-N-[(2-pyridyl)sulfonyl]-methanamine (24e). Yield: 72%; White solid; Mp 165-167 °C; ^1H NMR (300 MHz, CDCl_3): δ 8.35 (ddd, $J = 4.6$, $J = 1.6$ and $J = 0.8$ Hz, 1H), 7.60 (m, 2H), 7.25 (m, 1H), 7.15-7.05 (m, 5H), 6.57 (m, 1H), 6.12 (d, $J = 9.1$ Hz, 1H), 5.89 (dd, $J = 3.6$ and $J = 2.8$ Hz, 1H), 5.82 (d, $J = 9.1$ Hz, 1H), 5.58 (m, 1H), 3.69 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): 157.4, 149.7, 138.2, 137.4, 130.2, 128.1, 127.4, 127.3, 126.1, 123.6, 122.0, 110.0, 106.7, 55.2, 34.3. MS (FAB+) m/z 328.1 (M^+ , 21), 170.1 ($\text{M}^+ - \text{SO}_2(2\text{-Py})$, 100).

FAB+ HRMS for $C_{17}H_{18}N_3O_2S$ (M^+): Calcd: 328.11222. Found: 328.11197.

(5-Methoxythiophen-2-yl)(phenyl)-*N*-[(2-pyridyl)sulfonyl]-methanamine (25e). Yield: 65%; White solid; Mp 153-155 °C; 1H NMR (300 MHz, $CDCl_3$): δ 8.43 (ddd, J = 4.6, J = 1.6 and J = 0.8 Hz, 1H), 7.70-7.59 (m, 2H), 7.26 (ddd, J = 7.3, J = 4.7 and J = 1.4 Hz, 1H), 7.14-7.08 (m, 5H), 6.20 (dd, J = 3.9 and J = 1.1, 1H), 5.84 (d, J = 8.1 Hz, 1H), 5.80 (d, J = 3.9 Hz, 1H), 5.71 (dd, J = 8.1 and J = 1.1 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 166.8, 157.6, 149.8, 139.3, 137.5, 129.9, 128.4, 127.9, 127.2, 126.3, 124.2, 122.0, 103.0, 60.2, 58.3. MS (FAB+) m/z 361.1 (M^+ , 11), FAB+ HRMS for $C_{17}H_{18}N_2O_3S_2$ (M^+): Calcd: 361.06660. Found: 361.06606.

(Furan-2-yl)(phenyl)-*N*-[(2-pyridyl)sulfonyl]methanamine (26e). Yield: 50%; White solid; Mp 140-141°C; 1H NMR (300 MHz, $CDCl_3$): δ 8.43 (ddd, J = 4.6, J = 1.6 and J = 0.8 Hz, 1H), 7.74-7.62 (m, 2H), 7.27 (ddd, J = 7.4, J = 4.6 and J = 1.4 Hz, 1H), 7.16-7.10 (m, 6H), 6.08 (dd, J = 3.3 and J = 1.9 Hz, 1H), 5.93 (d, J = 3.3 Hz, 1H), 5.83 (d, J = 8.3 Hz, 1H), 5.67 (d, J = 8.3 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): 157.5, 152.0, 148.8, 142.6, 138.0, 128.5, 128.0, 127.3, 126.2, 121.9, 110.2, 108.3, 55.8.

(5-Methoxyfuran-2-yl)(phenyl)-*N*-[(2-pyridyl)sulfonyl]-methanamine (27e). Yield: 69%; White solid; Mp 135-137°C; 1H NMR (300 MHz, $CDCl_3$): δ 8.53 (ddd, J = 4.6, J = 1.6 and J = 0.8 Hz, 1H), 7.80-7.69 (m, 2H), 7.35 (ddd, J = 7.4, J = 4.6 and J =

1.4 Hz, 1H), 7.28-7.18 (m, 5H), 6.05 (d, J = 8.3 Hz, 1H), 5.86 (m, 1H), 5.63 (d, J = 8.3 Hz, 1H), 4.88 (dd, J = 3.2 and J = 0.7 Hz, 1H), 3.73 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): 159.8, 155.9, 148.1, 139.9, 136.2, 135.8, 126.8, 126.2, 125.7, 124.5, 120.3, 108.5, 78.3, 56.0, 54.3. MS (FAB+) m/z 345.1 (M^+ , 11), FAB+ HRMS for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_4\text{S}_1$ (M^+): Calcd: 345.09034. Found: 345.09090.

[4-(Dimethylamino)-2-methoxyphenyl](phenyl)-*N*-[(2-pyridyl)-sulfonyl]methanamine (28e). Yield: 73%; White solid; Mp 108-110°C; ^1H NMR (300 MHz, CDCl_3): δ 8.39 (ddd, J = 4.6, J = 1.6 and J = 0.8 Hz, 1H), 7.65 (m, 1H), 7.56 (m, 1H), 7.20-7.08 (m, 7H), 6.69 (d, J = 8.4 Hz, 1H), 6.15 (d, J = 9.4 Hz, 1H), 5.98 (dd, J = 8.4 and J = 2.4 Hz, 1H), 5.90 (d, J = 2.4 Hz, 1H), 5.57 (d, J = 9.4 Hz, 1H), 3.53 (s, 3H), 2.83 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): 157.7, 157.4, 151.6, 148.6, 141.2, 137.1, 130.2, 127.9, 126.7, 125.7, 122.0, 115.6, 104.2, 96.1, 59.2, 55.0, 40.6.

(1-Methoxy2-naphthyl)(phenyl)-*N*-[(2-pyridyl)sulfonyl]-methanamine (29e). Yield: 65%; White solid; Mp 204-205 °C; ^1H NMR (300 MHz, CDCl_3): δ 8.22 (m, 1H), 7.99 (m, 2H), 7.58-7.38 (m, 4H), 7.30-7.05 (m, 7H), 6.84 (d, J = 8.1 Hz, 1H), 6.52 (d, J = 8.1 Hz, 1H), 6.44 (d, J = 8.3 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): 157.4, 155.3, 149.3, 140.1, 137.2, 131.5, 128.3, 127.7, 127.3, 127.1, 127.0, 125.9, 125.1, 123.5, 122.6, 122.0, 102.8, 58.7, 55.5.

(2,4,6-Trimethoxyphenyl)(phenyl)-*N*-[(2-pyridyl)sulfonyl]-methanamine (30e). Yield: 76%; White solid; Mp 166-168°C; ^1H

NMR (300 MHz, CDCl₃): δ 8.26 (ddd, J = 4.6, J = 1.6 and J = 0.8 Hz, 1H), 7.71 (m, 1H), 7.21-7.03 (m, 6H), 6.60 (d, J = 10.7 Hz, 1H), 6.08 (d, J = 10.7 Hz, 1H), 5.76 (s, 2H), 3.64 (s, 3H), 3.52 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 160.7, 157.7, 157.1, 149.4, 140.9, 136.7, 127.7, 126.5, 126.2, 125.7, 121.9, 108.2, 90.3, 55.5, 55.2, 51.5. MS (FAB+) m/z 415.0 (M^+ , 11) 257 (M^+ -SO₂(2-Py), 100), FAB+ HRMS for C₂₁H₂₃N₂O₅S₁ (M^+): Calcd: 415.13353. Found: 415.13276.

Typical procedure for the deprotection of *N*-(2-pyridyl) sulfonyl amines.

(1-Methyl-1*H*-indol-3-yl)(2-naphthyl)methanamine (31). To a suspension of magnesium turnings (22 mg, 10 equiv) in dry MeOH (2 mL) at 0°C, was added a solution of the *N*-(2-pyridyl) sulphonamide **16e** (40 mg, 0.1 mmol) in dry MeOH (0.5 mL). The resulting mixture was stirred at rt for 5 h, then it was filtered over Celite. The filtrate was washed with saturated aqueous NaHCO₃ (15 mL). The organic phase was dried (Na₂SO₄) and concentrated to give the pure amine **31** (22.4 mg, 83%) as a white solid. Mp 122-123 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.89 (s, 1H), 7.80-7.65 (m, 3H), 7.49-7.30 (m, 4H), 7.20-7.02 (m, 2H), 6.94 (m, 1H), 6.82 (s, 1H), 3.62 (s, 3H), 2.21 (bs, 2H). ¹³C NMR (75 MHz, CDCl₃): 136.4, 132.5, 131.7, 127.0, 126.9, 125.6, 125.5, 124.9, 124.7, 124.5, 123.8, 120.7, 118.5, 118.0, 108.2, 31.6, 28.7. MS (FAB+) m/z 286.1 (M^+ , 4) 270 (M^+ -NH₂, 100), FAB+ HRMS for C₂₀H₁₆N (M^+): Calcd: 270.12827. Found: 270.12830.

(2,4,6-Trimethoxyphenyl)(phenyl)methanamine (32). Yield: 83%; white solid; Mp 136-138 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.31-7.25 (m, 2H), 7.20-7.12 (m, 2H), 7.05 (m, 1H), 6.06 (s, 2H), 5.56 (s, 1H), 3.72 (s, 3H), 3.65 (s, 6H), 2.21 (bs, 2H). ¹³C NMR (75 MHz, CDCl₃): 160.0, 158.6, 146.4, 127.7, 126.0, 125.5, 115.0, 91.2, 55.7, 55.3, 49.6.

Typical procedure for the sequential one-pot synthesis of (indolyl)diarylmethanes.

(5-Methoxy-1-methyl-1*H*-indol-3-yl)(1-methyl-1*H*-indol-3-yl)-(phenyl)methane (33). A solution of Cu(OTf)₂ (3.6 mg, 0.01 mmol) and (±)-BINAP (6.8 mg, 0.011 mmol) in dry CH₂Cl₂ (0.5 mL) was stirred at rt for 20 min, then a solution of the sulfonyl imine **1e** (24.6 mg, 0.1 mmol) in dry CH₂Cl₂ (0.5 mL) was added. The mixture was stirred at rt for 5 min, then 1-methylindole (12.5 μL, 0.1 mmol) was added. The mixture was stirred at rt until the starting material was consumed (TLC monitoring), and then 5-Methoxy-1-methylindol (16.1 mg, 0.1 mmol) was added. The reaction mixture was warmed up to 40°C and stirred at 40 °C for 15 min. Saturated aqueous NH₄Cl (15 mL) was added and the mixture was extracted with CH₂Cl₂ (2 x 20 mL). The combined organic phase was dried (Na₂SO₄) and concentrated. The residue was purified by flash chromatography (*n*-hexane-EtOAc 5:1) to afford **33** (24.7 mg, 65%) as a white solid. Mp 163-165 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.31-7.05 (m, 9H), 6.91 (m, 1H), 6.80-6.70 (m, 2H), 6.46 (s, 1H), 6.41 (s, 1H), 5.74 (s, 1H), 3.61

(s, 3H), 3.59 (s, 3H), 3.55 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): 153.5, 144.5, 137.5, 132.9, 128.9, 128.7, 128.3, 128.2, 127.8, 127.5, 126.0, 121.4, 120.1, 118.6, 117.7, 111.5, 109.8, 109.1, 102.1, 56.0, 40.2, 32.8, 32.7. MS (FAB+) m/z 380.2 (M^+ , 62), FAB+ HRMS for $\text{C}_{26}\text{H}_{24}\text{N}_2\text{O}$ (M^+): Calcd: 380.18886. Found: 380.18922.

(1-Methyl-1H-indol-3-yl)(2,4,6-trimethoxyphenyl)(phenyl)-methane (34). Yield: 65%; white solid; Mp 166-168 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.28 (d, J = 8.0 Hz, 1H), 7.20-6.98 (m, 7H), 6.91 (m, 1H), 6.67 (s, 1H), 6.19 (s, 1H), 6.08 (s, 2H), 3.71 (s, 3H), 3.61 (s, 3H), 3.50 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): 159.8, 159.1, 145.0, 136.9, 128.5, 127.3, 124.9, 121.0, 119.9, 118.4, 116.4, 114.8, 108.9, 91.9, 55.9, 55.3, 36.3, 32.7. MS (FAB+) m/z 387.2 (M^+ , 100), FAB+ HRMS for $\text{C}_{25}\text{H}_{25}\text{N}_1\text{O}_3$ (M^+): Calcd: 387.18344. Found: 380.18300.

(4-Fluorophenyl)(1-methyl-1H-indol-3-yl)(5-methoxythiophen-2-yl)methane (35). Yield: 57%; red oil; ^1H NMR (300 MHz, CDCl_3): δ 7.24-7.06 (m, 6H), 6.95-6.85 (m, 3H), 6.56 (s, 1H), 6.24 (dd, J = 3.2 and J = 1.0 Hz, 1H), 5.89 (d, J = 3.7 Hz, 1H), 5.58 (s, 1H), 3.73 (s, 3H), 3.61 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): 165.3, 160.1, 139.6, 137.4, 134.0, 130.0, 129.9, 128.2, 127.0, 122.7, 121.8, 119.7, 119.1, 117.8, 115.3, 115.0, 109.3, 102.7, 60.1, 43.6, 32.7. MS (FAB+) m/z 351.1 (M^+ , 67), FAB+ HRMS for $\text{C}_{21}\text{H}_{18}\text{N}_1\text{O}_1\text{F}_1\text{S}_1$ (M^+): Calcd: 351.10933. Found: 351.10956.

[4-(Dimethylamino)-2-methoxyphenyl](5-methoxy-1-methyl-1H-indol-3-yl)(2-naphthyl)methane (36). Yield: 60%; blue solid;

Mp 75-77 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.75-7.58 (m, 3H), 7.51 (s, 1H), 7.37-7.26 (m, 3H), 7.07 (d, J = 8.7 Hz, 1H), 6.81 (d, J = 8.6 Hz, 1H), 6.75 (dd, J = 8.8 and J = 2.4 Hz, 1H), 6.65 (d, J = 2.4 Hz, 1H), 6.33 (s, 1H), 6.24 (d, J = 2.3 Hz, 1H), 6.15 (dd, J = 8.4 and J = 2.4 Hz, 1H), 5.99 (s, 1H), 3.67 (s, 3H), 3.58 (s, 3H), 3.55 (s, 3H), 2.86 (s, 6H). ^{13}C NMR (75 MHz, CDCl_3): 157.8, 153.4, 150.5, 142.8, 133.5, 133.0, 132.1, 130.5, 129.5, 128.3, 128.0, 127.9, 127.5, 127.3, 126.7, 125.4, 125.0, 121.0, 118.0, 111.3, 109.7, 104.7, 102.5, 96.7, 55.9, 55.7, 40.8, 40.6, 32.8. MS (FAB+) m/z 450.2 (M^+ , 100), FAB+ HRMS for $\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_2$ (M^+): Calcd: 450.23072. Found: 450.23072.

(5-Methoxyfuran-2-yl)(1-methyl-1H-indol-3-yl)(phenyl)methane

(37). Yield: 46%; white solid; Mp 161-163°C; ^1H NMR (300 MHz, CDCl_3): δ 7.36-7.16 (m, 6H), 7.08-6.95 (m, 3H), 6.75 (d, J = 3.3 Hz, 1H), 6.70 (d, J = 3.3 Hz, 1H), 6.30 (s, 1H), 6.43 (s, 1H), 3.73 (s, 3H), 3.59 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): 159.3, 139.6, 137.4, 134.3, 130.4, 129.6, 128.2, 128.0, 122.7, 121.8, 119.7, 119.1, 117.8, 115.3, 115.0, 109.3, 78.3, 55.9, 40.2, 32.8.

(2-Methyl-1H-indol-3-yl)(2,4,6-trimethoxyphenyl)(3-methyl-

phenyl)methane (38). Yield: 63%; white solid; Mp 79-80 °C; ^1H NMR (300 MHz, CDCl_3): δ 7.53 (bs, 1H), 7.15-7.08 (m, 2H), 6.95-6.85 (m, 4H), 6.80 (m, 1H), 6.22 (s, 1H), 6.07 (s, 2H), 3.73 (s, 3H), 3.53 (s, 6H), 2.19 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): 159.7, 159.2, 143.2, 136.9, 134.8, 132.4, 129.6,

129.2, 127.4, 125.8, 125.5, 120.4, 119.9, 118.4, 114.1, 112.7, 109.5, 91.4, 55.6, 55.2, 36.2, 21.5, 12.7. MS (FAB+) m/z 401.2 (M^+ , 100), Electrospray+ HRMS for $C_{26}H_{28}NO_3$ (M^+): Calcd: 402.1991. Found: 402.2005.

(4-Dimethylaminophenyl)(1-methyl-1*H*-indol-3-yl)(phenyl)-methane (39). Yield: 43%; white solid; Mp 135-137°C; 1H NMR (300 MHz, $CDCl_3$): δ 7.38-7.20 (m, 9H), 7.11 (d, J = 8.6 Hz, 2H), 7.00 (m, 1H), 6.70 (d, J = 8.6 Hz, 2H), 6.45 (s, 1H), 5.60 (s, 1H), 3.71 (s, 3H), 2.94 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): 149.1, 144.9, 137.5, 132.4, 129.5, 128.9, 128.6, 128.2, 127.5, 125.9, 121.5, 120.1, 119.0, 118.7, 112.6, 109.0, 47.9, 40.7, 32.6. MS (FAB+) m/z 340.2 (M^+ , 100), Electrospray+ HRMS for $C_{30}H_{30}N_2O_2$ (M^+): Calcd: 450.23072. Found: 341.2008.

(1-Methyl-1*H*-indol-3-yl)(3-methyl-1*H*-indol-2-yl)(phenyl)-methane (40). Yield: 73%; white solid; Mp 103-105 °C; 1H NMR (300 MHz, $CDCl_3$): δ 7.56 (bs, 1H), 7.46 (m, 1H), 7.24-6.98 (m, 12H), 6.90 (m, 1H), 6.44 (s, 1H), 5.84 (s, 1H), 3.61 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 142.3, 137.5, 135.9, 135.0, 129.7, 128.7, 128.6, 128.5, 127.2, 126.6, 122.0, 121.0, 119.8, 119.3, 119.0, 118.3, 115.9, 110.7, 109.3, 107.4, 40.4, 32.8, 8.7.

Typical procedure for the $Sc(OTf)_3$ catalyzed synthesis of unsymmetrical triarylmethanes:

[4-(Dimethylamino)-2-methoxyphenyl](phenyl)(2,4,6-trimethoxyphenyl)methane (41). A solution of $Sc(OTf)_3$ (4.8 mg, 0.01 mmol)

and diarylsulfonamide **28e** (39.7 mg, 0.1 mmol) in dry CH₃CN (1.0 mL) was stirred at rt for 5 min, then 1,3,5-trimethoxybenzene (16.8 mg, 0.1 mmol) was added. The reaction mixture was warmed up to 60 °C and stirred at 60 °C for 12 h. Saturated aqueous NH₄Cl (15 mL) was added and the mixture was extracted with CH₂Cl₂ (2 x 20 mL). The combined organic phase was dried (Na₂SO₄) and concentrated. The residue was purified by flash chromatography (*n*-hexane-EtOAc 5:1) to afford **41** (26.4 mg, 65%) as a yellow solid. Mp 73-75 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.12-7.02 (m, 2H), 7.00-6.92 (m, 3H), 6.87 (d, *J*= 8.3 Hz, 1H), 6.22-6.10 (m, 3H), 6.06 (s, 2H), 3.71 (s, 3H), 3.61 (s, 3H), 3.45 (s, 6H), 2.84 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): 159.6, 159.5, 158.5, 150.3, 145.7, 131.2, 128.4, 127.1, 124.5, 120.4, 114.7, 104.7, 96.9, 92.0, 55.9, 55.8, 55.2, 40.9, 38.5.

[4-(Dimethylamino)-2-methoxyphenyl](4-nitrophenyl)(2,4,6-trimethoxyphenyl)methane (42). Yield: 65%; yellow solid; Mp 74-76 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.91 (d, *J*= 8.9 Hz, 2H), 7.06 (d, *J*= 8.9 Hz, 2H), 6.81 (d, *J*= 8.3 Hz, 1H), 6.25-6.11 (m, 3H), 6.06 (s, 2H), 3.74 (s, 3H), 3.61 (s, 3H), 3.47 (s, 6H), 2.88 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): 160.3, 159.1, 158.3, 155.3, 150.9, 145.2, 130.7, 128.8, 122.3, 117.4, 112.7, 104.5, 96.3, 91.5, 55.6, 55.5, 55.3, 40.7, 38.8. MS (FAB+) *m/z* 452.2 (M⁺, 100), Electrospray+ HRMS for C₂₅H₂₉N₂O₆ (M⁺): Calcd: 450.2020. Found: 453.2005.

[4-(Dimethylamino)-2-methoxyphenyl](5-methoxythiophen-2-yl)-(phenyl)methane (43). Yield: 57%; green oil; ¹H NMR (300 MHz,

CDCl₃): δ 7.32-7.15 (m, 5H), 6.91 (d, J = 8.3 Hz, 1H), 6.39-6.31 (m, 2H), 6.20 (dd, J = 3.9 and J = 1.1, 1H), 5.97 (d, J = 8.1 Hz, 1H), 5.80 (s, 1H), 3.85 (s, 3H), 3.72 (s, 3H), 2.91 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): 164.9, 157.5, 150.8, 144.3, 134.3, 130.1, 128.8, 128.0, 126.0, 123.0, 120.7, 104.5, 102.7, 96.3, 60.0, 55.6, 44.3, 40.7. MS (FAB+) m/z 353.2 (M^+ , 100), Electrospray+ HRMS for C₂₁H₂₄NO₂S (M^+): Calcd: 354.1449. Found: 354.1405.

[4-(Dimethylamino)-2-methoxyphenyl](3-methyl-1*H*-indol-2-yl)

(2-naphthyl)methane (44). Yield: 57%; white solid; Mp 170-172 °C; ¹H NMR (300 MHz, CDCl₃): δ 7.75-7.57 (m, 4H), 7.46 (m, 1H), 7.39 (bs, 1H), 7.33 (m, 2H), 7.22 (dd, J = 8.4 and J = 1.7 Hz, 1H), 7.11 (m, 1H), 7.02 (m, 2H), 6.75 (d, J = 8.3 Hz, 1H), 6.23 (d, J = 2.4 Hz, 1H), 6.18 (dd, J = 8.3 and J = 2.4 Hz, 1H), 6.03 (s, 1H), 3.61 (s, 3H), 2.88 (s, 6H), 2.12 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): 158.0, 151.0, 140.8, 136.0, 135.0, 133.5, 132.2, 130.6, 129.7, 127.9, 127.8, 127.6, 126.5, 125.8, 125.4, 120.8, 118.9, 118.8, 118.2, 110.6, 107.7, 104.8, 96.7, 55.6, 41.9, 40.6, 8.6.

(1-Methoxy-2-naphthyl)(phenyl)(2,4,6-trimethoxyphenyl)methane

(45). Yield: 57%; yellow solid; Mp 169-171 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.19 (d, J = 7.4 Hz, 1H), 7.80 (d, J = 7.6 Hz, 1H), 7.28 (m, 2H), 7.05 (m, 6H), 6.61 (d, J = 8.2 Hz, 1H), 6.47 (s, 1H), 6.07 (s, 2H), 3.86 (s, 3H), 3.69 (s, 3H), 3.41 (s, 6H). ¹³C NMR (75 MHz, CDCl₃): 160.0, 159.4, 153.9, 145.0, 133.2,

131.2, 129.3, 127.5, 126.0, 125.7, 125.2, 124.5, 124.3, 122.3, 114.2, 103.2, 93.0, 92.1, 55.9, 55.4, 55.2, 42.1. MS (FAB+) m/z 414.2 (M^+ , 100), Electrospray+ HRMS for $C_{27}H_{27}O_4$ (M^+): Calcd: 415.1831. Found: 415.1865.

(3,4-Difluorophenyl)(1-methoxy-2-naphthyl)(5-methoxythiophen-2-yl)methane (46). Yield: 44%; red oil; 1H NMR (300 MHz, $CDCl_3$): δ 8.24 (m, 1H), 7.81 (m, 1H), 7.38 (m, 2H), 6.94 (m, 3H), 6.65 (d, J = 8.0 Hz, 1H), 6.11 (d, J = 3.8 Hz, 1H), 6.01 (s, 1H), 5.91 (d, J = 3.8 Hz, 1H), 3.91 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 165.7, 155.0, 150.9, 150.7, 140.8, 132.7, 132.2, 130.7, 129.0, 128.4, 126.9, 126.8, 126.0, 125.0, 124.9, 124.8, 124.7, 124.6, 124.2, 123.4, 122.7, 118.0, 117.8, 117.2, 116.9, 102.9, 102.8, 60.1, 55.5, 47.1.