SUPPORTING INFORMATION

Copper(II) catalyzed C-C/C-N bond formations: Synthesis of pyrrole incorporated triarylmethanes

H. Surya Prakash Rao,* A. Veera Bhadra Rao, Sivakumar Shanmugam[†]

Department of Chemistry, Pondicherry University, Pondicherry - 605 014. India

E.mail: hspr.che@pondiuni.edu.in;

[†] Present Address: Department of Organic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai - 625002. India. E-mail: shivazzen@mkuniversity.org

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General: The progression of all the reactions was monitored by TLC using hexanes (60-80 °C boiling mixture) / ethyl acetate mixture as eluent. Column chromatography was carried on silica gel (100-200 mesh SRL chemicals) using increasing percentage of ethyl acetate in hexanes. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) and DEPT-135 spectra were recorded for $\text{CDCl}_3 + \text{CCl}_4$ (1:1) and $\text{DMSO}-d_6 + \text{CCl}_4$ (1:1) solutions on a Bruker - 400 spectrometer with tetramethylsilane (TMS) as the internal standard; J -values are in Hz. IR spectra were recorded as KBr pellets on a Nicolet-6700 spectrometer. Melting points were recorded using open-ended capillary tubes on VEEGO VMP-DS instrument. High resolution mass spectra were recorded on a Micromass Q-TOF micro mass spectrometer using electro spray ionization mode. Benzimidazole and 2-methylbenzimidazole were prepared according the reported procedures.^[8]

***N,N*-Diethyl-4-((4-(methylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methyl)aniline 3b:** Mp 157 °C; Yield: 86%; R_F = 0.4 (hexanes:EtOAc 8:2); IR (KBr): 3311, 2972, 2923, 1608, 1517, 1312, 1206, 1143, 1082, 804, 706, 604, 521 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CCl}_4$; 1:1): δ 9.85 (s, 1H), 7.95-7.93 (d, J = 8.2 Hz, 2H), 7.26-7.09 (m, 7H), 6.90-6.88 (d, J = 8.5 Hz, 2H), 6.52-6.51 (d, J = 3 Hz, 2H), 5.45 (s, 1H), 3.29-3.27 (m, 4H), 2.39 (s, 3H), 1.76 (s, 3H), 1.13-1.09 (t, J = 8 Hz, 3H); ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CCl}_4$; 1:1) δ 146.4 (C), 146.1 (C), 144.7 (C), 144.0 (C), 139.0 (C), 135.4 (C), 130.5 (C), 129.7 (CH), 129.6 (CH), 129.0 (CH), 128.2 (CH), 127.9 (CH),

126.1 (CH), 121.7 (CH), 119.0 (C), 111.9 (CH), 47.0 (CH), 44.5 (CH₂), 21.8 (CH₃), 20.4 (CH₃), 12.7(CH₃) ppm; HRMS (ESI⁺) calcd for C₂₉H₃₃N₂O₂S₂ (M + H) 505.1983; found 505.1983.

1-((4-(Methylthio)-5-tosyl-1H-pyrrol-3-yl)(phenyl)methyl)naphthalen-2-ol 3c: Mp 144 °C; Yield: 88%; R_F = 0.35 (hexanes:EtOAc 8:2); IR (KBr): 3377, 2923, 2857, 1709, 1624, 1597, 1514, 1492, 1438, 1398, 1299, 1217, 1143, 1083, 1040, 963, 813, 703, 673, 602, 561, 533 cm⁻¹; ¹H NMR (400 MHz, CDCl₃ + CCl₄; 1:1) δ 9.82 (s 1H), 8.01-7.99 (d, *J* = 8.6 Hz, 2H), 7.94-7.92 (d, *J* = 8.2 Hz, 2H), 7.73-7.71 (d, *J* = 8.0 Hz, 1H), 7.67-7.64 (d, *J* = 8.9 Hz, 1H), 7.42-7.14 (m, 11H), 7.03-7.01 (d, *J* = 8.8 Hz, 1H), 6.80-6.79 (d, *J* = 2.0 Hz, 1H), 6.46 (s, 1H), 5.44 (s, 1H), 2.41 (s, 3H), 1.96 (s, 3H); ¹³C NMR (100 MHz, CDCl₃ + CCl₄; 1:1) δ 152.7 (C), 144.5 (C), 144.1 (C), 142.5 (C), 138.9 (C), 133.3 (C), 131.7 (C), 131.6 (C), 129.8 (C), 129.7 (CH), 129.6 (CH), 129.2 (CH), 128.9 (CH), 128.3 (CH), 128.0 (CH), 127.2 (CH), 126.9 (CH), 123.4 (CH), 123.1 (CH), 121.9 (CH), 121.2 (C), 119.9 (CH), 39.5 (CH), 21.8 (CH₃), 20.9 (CH₃); HRMS (ESI⁺) calcd for C₂₉H₂₅NO₃S₂Na (M + Na) 522.1174 found 522.1173.

3-(Methylthio)-4-(phenyl(1H-pyrrol-2-yl)methyl)-2-tosyl-1H-pyrrole 3d: Mp 120 °C; Yield: 81%; R_F = 0.4 (hexanes:EtOAc 8:2); IR (KBr): 3381, 2921, 1595, 1562, 1536, 1492, 1450, 1317, 1218, 1146, 1083, 1027 cm⁻¹; ¹H NMR (400 MHz, CDCl₃ + CCl₄; 1:1) δ 9.89 (s, 1H), 7.95 (d, *J*

= 8.3 Hz, 2H), 7.84 (s, 1H), 7.35-7.10 (m, 7H), 6.64 (d, $J = 3.0$ Hz, 1H), 6.59-6.58 (m, 1H), 6.04-6.02 (m, 1H), 5.76-5.69 (m, 1H), 5.54 (s, 1H), 2.42 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CCl}_4$; 1:1): δ 144.7 (C), 143.0 (C), 138.9 (C), 133.8 (C), 133.3 (C), 131.0 (C), 129.7 (CH), 128.7 (CH), 128.6 (CH), 128.0 (CH), 126.8 (CH), 121.1 (CH), 118.8 (C), 117.0 (CH), 108.6 (CH), 107.5 (CH), 41.7 (CH), 21.9 (CH_3), 20.5 (CH_3); HRMS (ESI^+) calcd for $\text{C}_{23}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_2\text{Na}$ ($\text{M} + \text{Na}$) 445.1020 found 445.1017.

3-((4-(Methylthio)-5-tosyl-1H-pyrrol-3-yl)(phenyl)methyl)-1H-indole 3e: Mp 120 °C; Yield: 84%; $R_F = 0.5$ (hexanes:EtOAc 8:2); IR (KBr): 3394, 1641, 1596, 1516, 1453, 1317, 1217, 1144, 1083, 1041, 738, 700, 674, 600 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CCl}_4$; 1:1) δ 9.53 (s, 1H), 7.97-7.90 (m, 3H), 7.74 (d, $J = 7.1$ Hz, 1H), 7.27 (d, $J = 8.1$ Hz, 3H), 7.25-7.19 (m, 5H), 6.94 (t, $J = 7.5$ Hz, 1H), 6.61-6.44 (m, 2H), 5.71 (s, 1H), 2.41 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CCl}_4$; 1:1) δ 143.9 (C), 139.0 (C), 136.9 (C), 134.5 (C), 130.6 (C), 129.8 (C), 129.7 (CH), 129.6 (C), 128.8 (CH), 128.4 (CH), 127.9 (CH), 126.8 (C), 126.4 (CH), 123.6 (CH), 122.3 (CH), 121.4 (CH), 120.0 (CH), 119.6 (CH), 118.9 (C), 111.2 (CH), 39.8 (CH), 21.8 (CH_3), 20.5 (CH_3); HRMS (ESI^+) calcd for $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_2\text{S}_2\text{Na}$ ($\text{M} + \text{Na}$) 495.1177 found 445.1175.

5-((4-(Methylthio)-5-tosyl-1H-pyrrol-3-yl)(phenyl)methyl)-1H-imidazole 3f: Mp 212 °C; Yield: 92%; R_F = 0.4 (hexanes:EtOAc 8:2); IR (KBr): 3445, 3120, 2924, 2860, 1731, 1595, 1495, 1451, 1325, 1233, 1185, 1148, 1108, 1082, 734, 698, 669, 597 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 11.2 (s, 1H), 7.92 (d, J = 8.3 Hz, 2H), 7.58 (s, 1H), 7.33-7.29 (m, 4H), 7.28 (s, 1H), 7.10 (s, 1H), 7.05-7.02 (m, 2H), 6.86 (s, 1H), 6.63 (s, 1H), 6.59 (s, 1H), 2.39 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.6 (C), 139.1 (C), 138.3 (C), 137.5 (C), 132.4 (C), 129.8 (CH), 129.2 (C), 128.9 (CH), 128.8 (CH), 128.4 (CH), 127.8 (CH), 127.0 (CH), 121.8 (CH), 119.3 (CH), 118.7 (C), 57.4 (CH), 21.7 (CH_3), 20.3 (CH_3); HRMS (ESI^+) calcd for $\text{C}_{22}\text{H}_{21}\text{N}_3\text{O}_2\text{S}_2\text{Na}$ ($M + \text{Na}$) 446.0973 found 446.0973.

1,4-Bis(4-((4-(methylthio)-5-tosyl-1H-pyrrol-3-yl)(phenyl)methyl)phenyl)piperazine 3g: Mp 135 °C; Yield: 78%; R_F = 0.4 (hexanes:EtOAc 8:2); IR (KBr): 2921, 2821, 1734, 1606, 1512, 1449, 1320, 1226, 1083, 1043, 945, 809, 732, 700, 601 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CCl}_4$; 1:1) δ 9.89 (s, 2H), 7.93 (d, J = 7.7 Hz, 4H), 7.28-7.08 (m, 12H), 6.96 (d, J = 7.9 Hz, 4H), 6.79 (d, J = 8.0 Hz, 4H), 6.46 (s, 2H), 5.48 (s, 2H), 3.23 (s, 8H), 2.40 (s, 6H), 1.76 (s, 6H); ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CCl}_4$; 1:1) δ 149.7 (C), 144.3 (C), 144.0 (C), 139.1 (C), 135.3 (C), 135.0 (C), 130.9 (C), 129.79 (CH), 129.70 (CH), 129.1 (CH), 128.4 (CH), 128.0 (CH), 126.3 (CH), 121.6 (CH), 119.0 (C), 116.3 (CH), 49.5 (CH_2), 47.2 (CH), 21.8 (CH_3), 20.5 (CH_3); HRMS (ESI^+) calcd for $\text{C}_{54}\text{H}_{52}\text{N}_4\text{O}_4\text{S}_4\text{Na}$ ($M + \text{Na}$) 971.2769 found 971.2761.

1-((4-(Methylthio)-5-tosyl-1H-pyrrol-3-yl)(phenyl)methyl)-1H-benzo[d]imidazole 3h: Mp 142 °C; Yield: 89%; R_F = 0.3 (hexanes:EtOAc 8:2); IR (KBr): 3317, 3057, 2921, 1595, 1490, 1454, 1324, 1216, 1148, 1084, 699, 600 cm^{-1} ; ^1H NMR (400 MHz, $\text{CDCl}_3 + \text{CCl}_4$; 1:1) δ 10.73 (s, 1H), 7.91 (d, J = 8.3 Hz, 2H), 7.75 (d, J = 5.6 Hz, 2H), 7.30-7.07 (m, 9H), 6.86 (s, 1H), 6.63 (s, 1H), 2.40 (s, 3H), 1.77 (s, 3H); ^{13}C NMR (100 MHz, $\text{CDCl}_3 + \text{CCl}_4$; 1:1); δ 144.4 (C), 142.2 (CH), 138.3 (C), 138.2 (C), 133.5 (C), 132.5 (C), 129.6 (CH), 128.9 (CH), 128.7 (C), 128.3 (CH), 127.7 (CH), 127.0 (CH), 123.1 (CH), 122.5 (CH), 121.8 (CH), 120.0 (CH), 118.8 (C), 115.2 (C), 110.6 (CH), 55.6 (CH), 21.6 (CH_3), 20.3 (CH_3); HRMS (ESI^+) calcd for $\text{C}_{26}\text{H}_{23}\text{N}_3\text{O}_2\text{S}_2\text{Na}$ ($\text{M} + \text{Na}$) 496.1129 found 496.1123.

2-Methyl-1-((4-(methylthio)-5-tosyl-1H-pyrrol-3-yl)(phenyl)methyl)-1H-benzo[d]imidazole 3i: Mp 167 °C; Yield: 83%; R_F = 0.3 (hexanes:EtOAc 8:2); IR (KBr): 3312, 2927, 1585, 1483, 1447, 1335, 1218, 1149, 1073, 702, 603 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO}-d_6 + \text{CCl}_4$) δ 12.73 (s, 1H), 7.82 (d, J = 8.3 Hz, 2H), 7.48 (d, J = 8.0 Hz, 1H), 7.38-7.31 (m, 5H), 7.13-7.04 (m, 3H), 6.94-6.90 (m, 2H), 6.78 (d, J = 8.0 Hz, 1H), 6.53 (d, J = 3.1 Hz, 1H), 2.49 (s, 3H), 2.40 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6 + \text{CCl}_4$) δ 151.7 (C), 143.8 (C), 142.4 (C), 138.7 (C), 138.2 (C), 134.4 (C), 131.3 (C), 129.5 (CH), 128.5 (CH), 127.7 (CH), 127.4 (C), 126.8 (2 ×

CH), 122.5 (CH), 121.3 (CH), 120.9 (CH), 118.4 (CH), 118.1 (C), 111.0 (CH), 55.1 (CH), 21.0 (CH₃), 19.6 (CH₃), 14.5 (CH₃); HRMS (ESI⁺) calcd for C₂₇H₂₆N₃O₂S₂ (M + H) 488.1466 found 488.1462.

¹H NMR (400 MHz, CDCl₃ + CCl₄; 1:1) spectrum of *N,N*-dimethyl-4-((4-(methylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methyl)aniline **3a**.

¹³C NMR (100 MHz, CDCl₃ + CCl₄; 1:1) spectrum of *N,N*-dimethyl-4-((4-(methylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methyl)aniline **3a**.

DEPT-135 spectrum of *N,N*-dimethyl-4-((4-(methylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methyl)aniline **3a**.

HRMS spectrum of *N,N*-dimethyl-4-((4-(methylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methyl)aniline **3a**.

DEPT-135 spectrum of *N,N*-diethyl-4-((4-(methylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methyl)aniline **3b**.

HRMS spectrum of *N,N*-diethyl-4-((4-(methylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methyl)aniline **3b**.

DEPT-135 spectrum of 1-((4-(methylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methyl)naphthalen-2-ol **3c**.

HRMS spectra of 1-((4-(methylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methyl)naphthalen-2-ol **3c**.

DEPT-135 spectrum of 3-(methylthio)-4-(phenyl(1H-pyrrol-2-yl)methyl)-2-tosyl-1H-pyrrole **3d**.

HRMS spectra of 3-(methylthio)-4-(phenyl(1H-pyrrol-2-yl)methyl)-2-tosyl-1H-pyrrole **3d**.

DEPT-135 and HRMS spectrum of 3-((4-(methylthio)-5-tosyl-1H-pyrrol-3-yl)(phenyl)methyl)-1H-indole **3e**.

HRMS spectra of 3-((4-(methylthio)-5-tosyl-1H-pyrrol-3-yl)(phenyl)methyl)-1H-indole **3e**.

¹H NMR (400 MHz, CDCl₃) spectrum of 5-((4-(methylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methyl)-1*H*-imidazole **3f**.

¹³C NMR (100 MHz, CDCl₃) spectrum of 5-((4-(methylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methyl)-1*H*-imidazole **3f**.

DEPT-135 spectrum of 5-((4-(methylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methyl)-1*H*-imidazole **3f**. HRMS spectra of 5-((4-(methylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methyl)-1*H*-imidazole **3f**.

¹H NMR (400 MHz, CDCl₃ + CCl₄; 1:1) spectrum of 1-((4-(methylthio)-5-tosyl-1H-pyrrol-3-yl)(phenyl)methyl)-1H-benzo[d]imidazole **3h**.

¹³C NMR (100 MHz, CDCl₃ + CCl₄; 1:1) spectrum of 1-((4-(methylthio)-5-tosyl-1H-pyrrol-3-yl)(phenyl)methyl)-1H-benzo[d]imidazole **3h**.

DEPT-135 spectrum of 1-((4-(methylthio)-5-tosyl-1H-pyrrol-3-yl)(phenyl)methyl)-1H-benzo[d]imidazole **3h**.

HRMS spectrum of 1-((4-(methylthio)-5-tosyl-1H-pyrrol-3-yl)(phenyl)methyl)-1H-benzo[d]imidazole **3h**.

¹H NMR (400 MHz, CDCl₃) spectrum of 2-methyl-1-((4-(methylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methyl)-1*H*-benzo[*d*]imidazole **3i**.

¹³C NMR (100 MHz, CDCl₃) spectrum of 2-methyl-1-((4-(methylthio)-5-tosyl-1*H*-pyrrol-3-yl)(phenyl)methyl)-1*H*-benzo[*d*]imidazole **3i**.