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Supplementary material

SUPPLEMENTARY MATERIAL TO

Multicomponent synthesis of new bis(pyranopyrazoles) and their antimicrobial–antioxidant evaluations

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ANALYTICAL AND SPECTRAL DATA FOR THE SYNTHESIZED COMPOUNDS

*4,4′-[1,1′-Biphenyl]-4,4′-diylbis(methyleneoxy-4,1-phenylene)]bis(6-amino--3-methyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile)(**3a**)*. Yield: 69 %; brown solid; m.p.: 209–211 °C; Anal. Calcd. for $C_{42}H_{34}N_8O_4$: C, 70.58; H, 4.79; N, 15.68 %. Found: C, 70.30; H, 4.78; N, 15.62 %; IR (KBr, cm^{-1}) 3323, 3150 (N–H), 2974, 2828 (methylene C–H), 2189 (C≡N), 1638 (C=N) & 1233, 1172 (C–O); ^{1}H-NMR (400 MHz, $CDCl_3$, δ / ppm): 12.0 (2H, *bs*, 1-NH), 7.41 (4H, *d*, J_o = 8.1 Hz, H-2″ & H-6″), 7.09 (4H, *d*, J_o = 8.0 Hz, H-3″ & H-5″), 6.89 (4H, *dt*, J_o = 8.0 Hz & J = 10.0 Hz, H-2′ & H-6′), 6.57 (4H, *d*, J_o = 10.0 Hz, H-3′ & H-5′), 6.04 (4H, *bs*, NH_2), 5.35 (4H, *s*, OCH_2), 4.50 (2H, *s*, H-4), 1.80 (6H, *s*, CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 160.56 (C-6), 154.70 (C-3), 131.52 (C-4′), 128.70 (C-7a), 128.32 (C-4″), 128.16 (C-1″), 128.03 (C-2′ & C-6′), 127.97 (C-3″& 5″), 127.83 (C-2″& 6″), 120.70 (C-1′), 113.21 (C≡N), 110.51 (C-3′ & C-5′), 97.56 (C-3a), 67.10 (OCH_2), 57.89 (C-5), 35.59 (C-4), 9.69 (CH_3); ESI-MS (*m*/*z*): 737 (M+Na, 10 %), 715 (M+1, 15 %), 511 (10 %), 489 (15 %), 475 (5 %), 371 (9 %), 294 (13 %), 243 (19 %), 242 (100 %), 215 (7 %), 121 (4 %), 107 (8 %).

*4,4′-[But-2-yne-1,4-diylbis(oxy-4,1-phenylene)]bis(6-amino-3-methyl-1,4--dihydropyrano[2,3-c]pyrazole-5-carbonitrile) (**3b**)*. Yield: 58 %; light yellow solid; m.p.: 98–100 °C; Anal. Calcd. for $C_{32}H_{26}N_8O_4$: C, 65.52; H, 4.47; N, 19.10 %. Found: C, 65.26; H, 4.46; N, 19.03 %; IR (KBr, cm^{-1}) 3471, 3263 (N–H), 2971, 2880 (methylene C–H), 2190 (C≡N), 1600 (C=N) & 1220, 1054 (C–O); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 12.0 (2H, *bs*, 1-NH), 7.09 (4H, *d*, J_o = 7.2 Hz, H-2′ & H-6′), 6.89 (4H, *d*, J_o = 7.5 Hz, H-3′ & H-5′), 6.75 (4H, *bs*, NH_2), 4.81 (4H, *s*, OCH_2) 4.53 (2H, *s*, H-4), 1.79 (6H, *s*, CH_3); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 160.68 (C-6), 155.93 (C-3), 137.15 (C-4′),

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135.41 (C-7a), 128.40 (C-2′ & C-6′), 124.68 (C-3′ & C-5′), 120.41 (C-1′), 114.48 (C≡N), 97.68 (C-3a), 82.38 (C≡C), 57.51 (OCH_2), 55.44 (C-5), 35.51 (C-4), 9.74 (CH_3); ESI-MS (*m*/*z*): 609 (M+Na, 10 %), 587 (M+1, 15 %), 511 (10 %), 489 (15 %), 475 (5 %), 371 (9 %), 294 (13 %), 243 (19 %), 242 (100 %), 215 (7 %), 121 (4 %), 107 (8 %).

*4,4′-[1,2-Phenylenebis(methyleneoxy-4,1-phenylene)]bis(6-amino-3-methyl--1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile) (**3c**)*. Yield: 67 %; grey solid; m.p.: 158–160 °C; Anal. Calcd. for $C_{36}H_{30}N_8O_4$: C, 67.70; H, 4.73; N, 17.54 %. Found: C, 67.43; H, 4.72; N, 17.47 %; IR (KBr, cm^{-1}): 3314–3184 (N–H), 2922, 2871 (methylene C–H), 2190 (C≡N), 1599 (C=N) 1266, 1037 (C–O); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 11.80 (2H, *bs*, 1-NH), 7.53 (2H, *d*, J = 5.4 Hz, H-5″), 7.36 (2H, *dd*, J = 2.1 & J = 3.2 Hz, H-6″), 7.10 (4H, *dd*, J_m=2.0 & J_o=8.3 Hz, H-2′ and H-6′), 6.91 (4H, *d*, J_o = 7.0 Hz, H-3′ & H-5′), 6.38 (4H, *bs*, NH_2), 5.15 (4H, *s*, OCH_2), 4.57 (2H, *s*, H-4), 1.80 (6H, *s*, CH_3); ^{13}C-NMR (100 Mz, DMSO-d_6, δ / ppm): 160.49 (C-6), 156.98 (C-3), 154.73 (C-4′), 136.37 (C-7a), 135.53 (C-1″), 134.90 (C-2′ & C-6′), 128.34 (C-6″), 127.84 (C-5″), 120.68 (C-1′), 118.30 (C≡N), 97.45 (C-3a), 67.30 (OCH_2), 58.25 (C-5), 35.62 (C-4), 9.72 (CH_3); ESI-MS (*m*/*z*): 661 (M+Na, 10 %), 639 (M+1, 15 %), 511 (10 %), 489 (15 %), 475 (5 %), 371 (9 %), 294 (13 %), 243 (19 %), 242 (100 %), 215 (7 %), 121 (4 %), 107 (8 %).

*4,4′-[1,4-Phenylenebis(methyleneoxy-4,1-phenylene)]bis(6-amino-3-methyl--1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile) (**3d**)*. Yield: 64 %; light brown solid; m.p.: 178–180 °C; Anal. Calcd. for $C_{36}H_{30}N_8O_4$: C, 67.70; H, 4.73; N, 17.54 %. Found: C, 67.41; H, 4.70; N, 17.45 %; IR (KBr, cm^{-1}) 3392, 3156 (N–H), 2956, 2880 (methylene C–H), 2189 (C≡N), 1598 & 1256 (C=N), 1018 (C–O); ^{1}H-NMR (400 MHz,$CDCl_3$, δ / ppm): 12.0 (2H, *bs*, 1-NH), 7.49 (4H, *d*, J = 4.1 Hz, H-2″ & H-6″), 6.86 (4H, *dd*, J_o = 7.1 & J_m = 1.1 Hz, H-2′ & H-6′), 6.78 (4H, *d*, J_o = 7.0 Hz, H-3′ & H-5′), 6.65 (4H, *bs*, NH_2), 5.07 (4H, *s*, OCH_2), 4.98 (2H, *s*, H-4), 1.78 (6H, *s*, CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$, δ / ppm): 160.85 (C-6), 154.76 (C-3), 145.82 (C-4′), 129.30 (C-7a), 127.58 (C-1″), 121.47 (C-2′ & C-6′), 120.73 (C-1′), 119.98 (C-2″ & C-6″), 114.11 (C≡N), 112.69 (C-3′ & C-5′), 97.21 (C-3a), 68.95 (OCH_2), 57.41 (C-5), 36.39 (C-4), 9.73 (CH_3); ESI-MS (*m*/*z*): 661 (M+Na, 10 %), 638 (M, 10 %), 489 (15 %), 371 (9 %), 294 (13 %), 243 (19 %), 215 (7 %).

*4,4′-[1,3-Phenylenebis(methyleneoxy-4,1-phenylene)]bis(6-amino-3-methyl--1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile) (**3e**)*. Yield: 70 %; light yellow solid; m.p.: 128–130 °C; Anal. calcd. for $C_{36}H_{30}N_8O_4$: C, 67.70; H, 4.73; N, 17.54 %. Found: C, 67.44; H, 4.71; N, 17.49 %; IR (KBr, cm^{-1}) 3392, 3210––3156 (N–H), 2956, 2888 (methylene C–H), 2169 (C≡N), 1592 & 1256 (C=N), 1018 (C–O); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 11.74 (2H, *bs*, 1-NH), 7.38 (1H, *dt*, J = 4.1 Hz & J = 5.4 Hz, H-5″), 7.09 (2H, *dd*, J =1.6 Hz & J = 6.4

Hz, H-4″ & H-6″), 6.92 (1H, *d*, J_m = 1.8 Hz, H-2″), 6.83 (4H, *dd*, *J* = 4.3 Hz & *J* = 6.8 Hz, H-2′ & H-6′), 6.67 (4H, *d*, *J* = 2.0 Hz & *J* = 3.6 Hz, H-3′ & H-5′), 6.42 (4H, *bs*, NH_2), 4.72 (4H, *s*, OCH_2), 4.51 (2H, *s*, H-4), 1.81 (6H, *s*, CH_3); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 160.83 (C-6), 154.73 (C-3), 139.73 (C-4′), 129.49 (C-7a), 128.35 (C-5″), 128.13 (C-4″ & C-6″), 127.02 (C-2′ & C-6′), 126.76 (C-1″ & C-3″), 120.71 (C-1′), 114.59 (C-2″), 114.29 (C≡N), 113.76 (C-3′ & C-5′), 97.47 (C-3a), 58.16 (C-5), 69.14 (OCH_2), 35.64 (C-4), 9.72 (CH_3); ESI-MS (*m/z*): 639 (M+1, 15 %), 489 (15 %), 371 (9 %), 243 (19 %), 242 (100 %), 215 (7 %), 107 (8 %).

trans-*4,4′-[But-2-ene-1,4-diylbis(oxy-4,1-phenylene)]bis(6-amino-3-methyl--1,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile) (**3f**)*. Yield: 67 %; brown solid; m.p.: 235–237 °C; Anal. Calcd. for $C_{32}H_{28}N_8O_4$: C, 65.30; H, 4.79; N, 19.04 %. Found: C, 65.03; H, 4.77; N, 18.96 %; IR (KBr, cm^{-1}) 3335–3191 (N–H), 2961, 2925 (methylene C–H), 2189 (C≡N), 1607 & 1221 (C=N), 1015 (C–O); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 12.00 (2H, *bs*, 1-NH), 7.08 (4H, *dt*, *J* = 2.0 Hz & *J* = 6.8 Hz, H-2′ & H-6′), 4.81 (4H, *d*, J_o = 8.6 Hz, H-3′ & H-5′), 6.76 (4H, *bs*, NH_2), 6.12 (2H, *t*, J_{vic} = 6.1 Hz, $OCH_2C\mathbf{H}$=), 4.81 (4H, J_{vic} = 6.1 Hz, *s*, OCH_2), 4.52 (2H, *s*, H-4), 1.79 (6H, *s*, CH_3); ^{13}C-NMR (100 MHz, DMSO-d_6, δ / ppm): 160.68 (C-6), 155.94 (C-3), 137.16 (C-4′), 135.42 (C-7a), 128.40 (C-2′ & C-6′), 126.78 ($OCH_2\mathbf{C}H$=), 120.79 (C-1′), 117.67 (C≡N), 114.48 (C-3′ & C-5′), 97.67 (C-3a), 57.50 (OCH_2), 55.45 (C-5), 35.50 (C-4), 9.74 (CH_3); ESI-MS (*m/z*): 611 (M+Na, 10 %), 589 (M+1, 15 %), 511 (10 %), 489 (15 %), 475 (5 %), 371 (9 %), 294 (13 %), 243 (19 %), 242 (100 %), 215 (7 %), 121 (4 %), 107 (8 %).

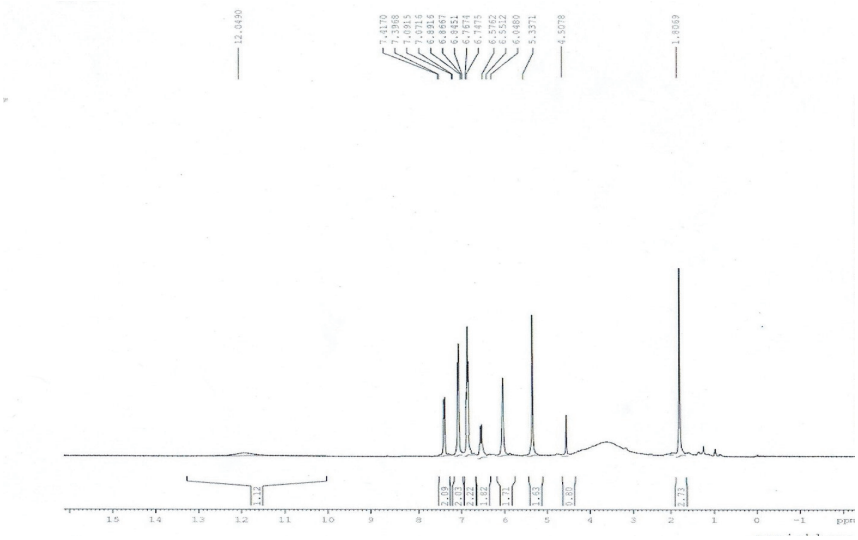

Fig. S-1. ^{1}H-NMR spectrum of **3a**.

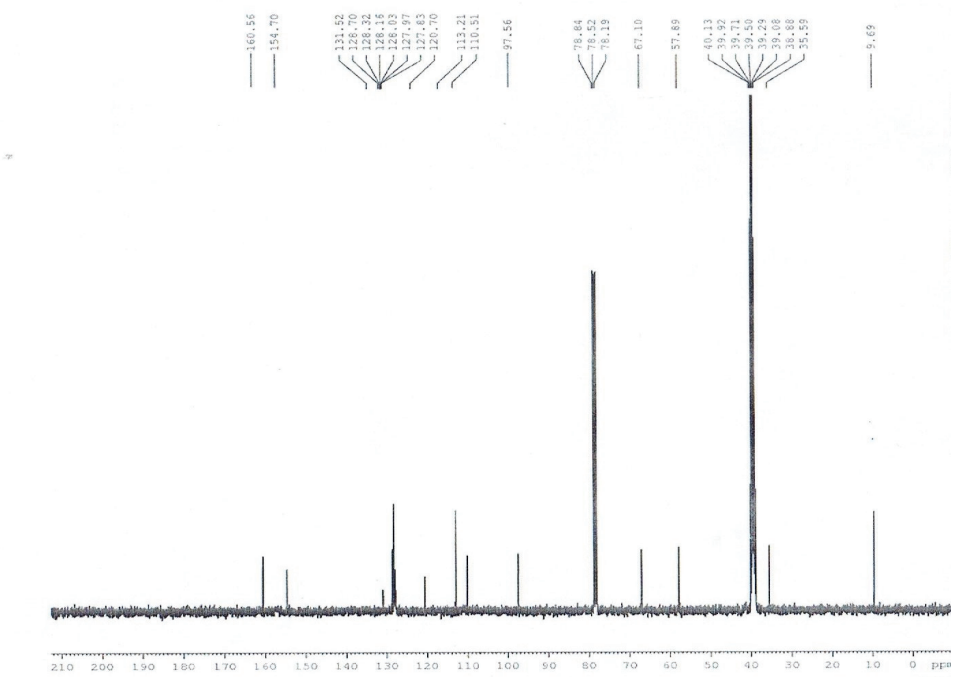

Fig. S-2. ^{13}C-NMR spectrum of **3a**.

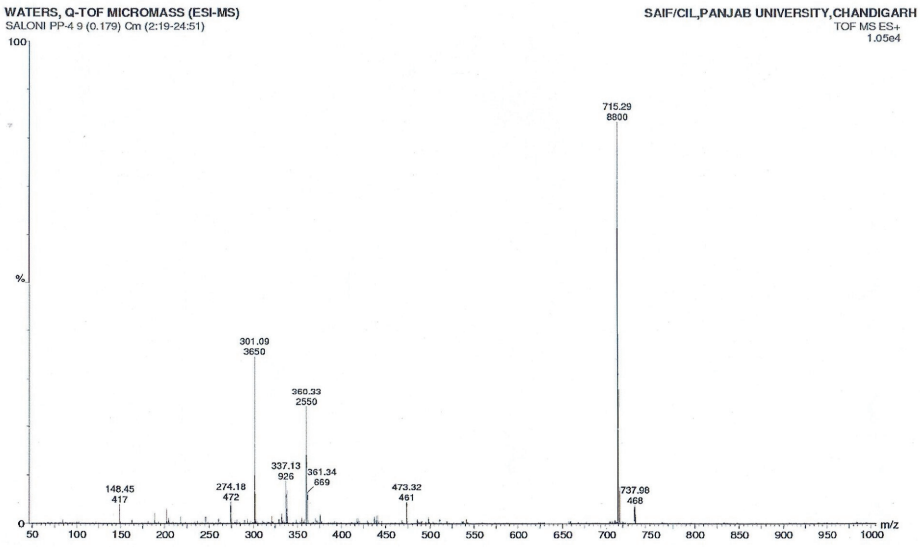

Fig. S-3. ESI-MS spectrum of **3a**.

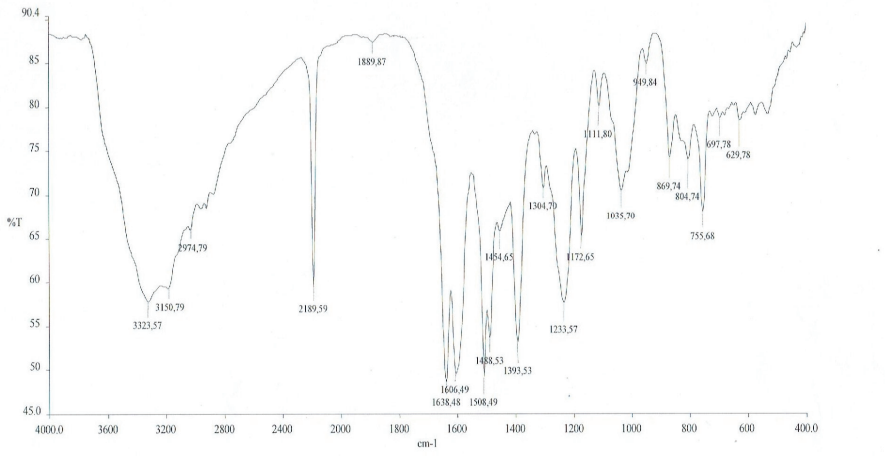

Fig. S-4. IR spectrum of **3a**.