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J. Serb. Chem. Soc. 76 (8) S11–S17 (2011) *Supplementary material*

SUPPLEMENTARY MATERIAL TO

Facile syntheses of Mannich bases of 3-[*p*-(5-arylpyrazolin-3--yl)phenyl]sydnones, as anti-tubercular and anti-microbial agents, under ionic liquid/tetrabutylammonium bromide catalytic conditions

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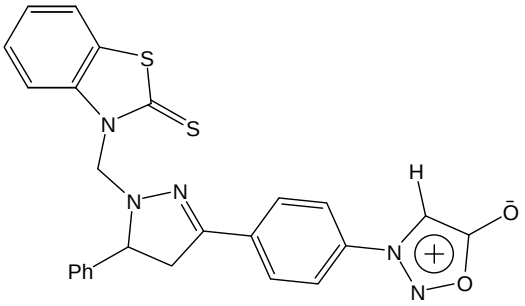
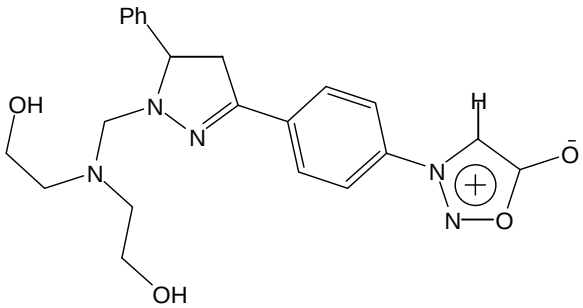
STRUCTURES OF THE PREPARED COMPOUNDS



2a



2b

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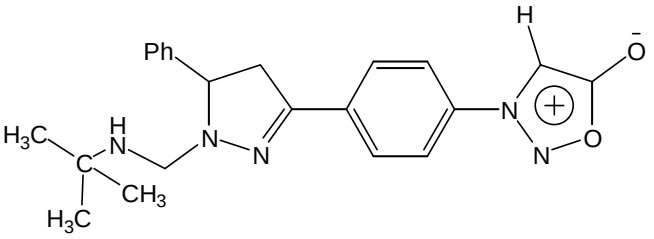

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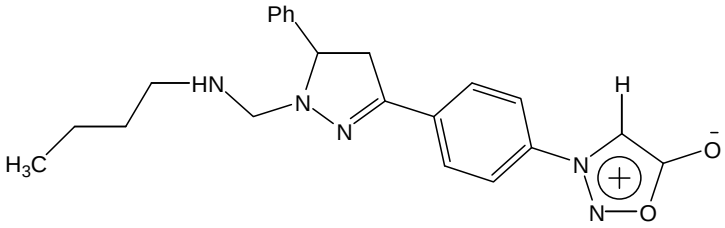

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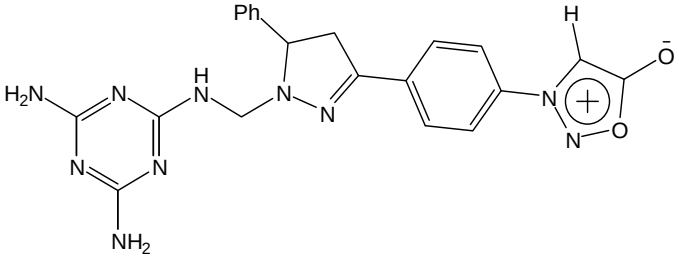

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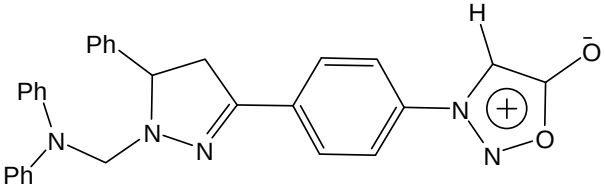

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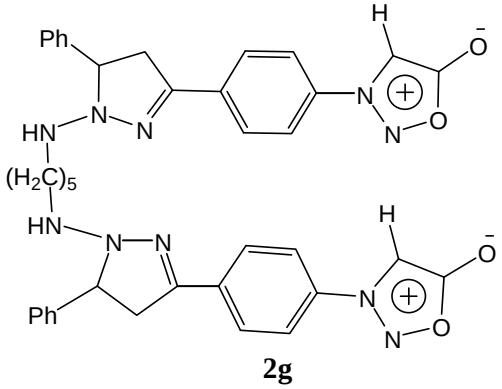

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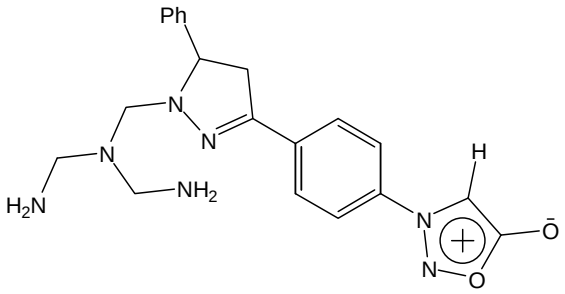

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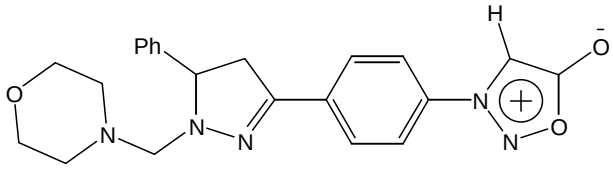
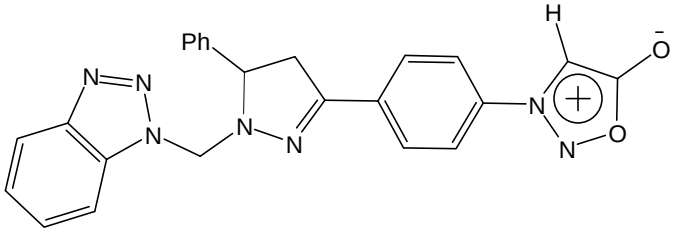


2i



2j

ANALYTICAL AND SPECTRAL DATA OF THE SYNTHESIZED COMPOUNDS **2a**–**j**

*3-{4-[5-Phenyl-1-(2-thioxobenzothiazol-3-ylmethyl)-4,5-dihydro-1*H*-pyrazol-3--yl]phenyl}sydnone (**2a**)*. Yellow amorphous solid (ethanol), R_f 0.88*, m.p. 95–96 °C. Anal. Calcd. for $C_{25}H_{19}N_5O_2S_2$: C, 68.85; H, 3.91; N, 14.43 %. Found: C, 68.84, H, 3.89, N, 14.41 %. IR (KBr, cm^{-1}): 2854 (–CH stretching of sydnone ring), 1754 (–C=O stretching of sydnone ring), 1595 (–C=N stretching of pyrazole ring). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 3.00 (1H, *dd*, $–CH_2$, H_A, J = = 12.05 Hz), 3.45 (2H, s, $–CH_2$, N–CH_2–N), 3.48 (1H, *dd*, $–CH_2$, H_B, J = 12.45 Hz), 4.56 (1H, *dd*, –CH, H_X, J_{XA} = 3Hz, J_{XB} = 9 Hz), 6.65 (1H, *s*, $–C_4$–H of sydnone), 7.32–7.43 (9H, *m*, aromatic), 7.70 (2H, *m*, N_3-aromatic), 7.76 (4H, *d*, N_3-aromatic). ^{13}C-NMR (300 MHz, $CDCl_3$, δ / ppm): 193.9 (C=S), 161 (C=O), 155.6 (C=N), 140.1, 137.2, 131.6, 131.0, 129.9, 129.8, 129.6, 129.5, 129.5, 129.3, 129.2, 128.3, 128.2, 128.1, 128.0, 126.8, 125.6, 125.5, 124.8, 116.7 (CH), 72.7 (CH_2), 48.7 (CH), 40.1 (CH_2). MS (*m*/*z*, (relative abundance, %)): 485 (M^+, 85), 321, 413, 457, 180.8, 161.0, 102.0, 84, 71, 57, 42.

* The eluents used were hexane or ethyl acetate for all compounds.

*3-{4-[1-(Bis(2-hydroxyethyl)aminomethyl)-5-phenyl-4,5-dihydro-1*H*-pyrazol--3-yl]phenyl}sydnone (**2b**)*. Yellow amorphous solid (pet. ether), R_f 0.91, m.p. 85––86 °C. Anal. Calcd. for $C_{22}H_{25}N_5O_4$: C, 62.41; H, 5.91; N, 16.54 %. Found: C, 62.39, H, 5.89, N 16.51 %. IR (KBr, cm^{-1}): 3427 (–OH stretching of CH_2OH), 2922 (–CH stretching of sydnone ring), 1749 (–C=O stretching of sydnone ring), 1594 (–C=N stretching of pyrazole ring). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm.): 3.09 (1H, *dd*, $–CH_2$, H_A, J = 10.88 Hz), 3.53 (1H, *dd*, $–CH_2$, H_B, J = 11.00 Hz), 3.64 (2H, *s*, $–CH_2$, N–CH_2–N), 4.32 (1H, *dd*, –CH, H_X, J_{XA} = 4.38 Hz, J_{XB} = = 11.31 Hz), 4.38 (4H, *t*, $–CH_2N$), 4.83 (4H, *t*, $–CH_2OH$), 5.02 (2H, *s*, –OH, D_2O exchangeable) 6.75 (1H, *s*, $–C_4$–H of sydnone), 7.27–7.81 (9H, *m*, aromatic). ^{13}C-NMR (300 MHz, $CDCl_3$, δ / ppm): 161 (C=O), 155.6 (C=N), 137.2, 131.5, 131.0, 129.8, 129.7, 129.5, 129.4, 128.3, 128.3, 128.1, 128.0, 126.8, 116.7, 73.4, 62.4, 62.4, 54.5, 54.5 (CH_2), 49.0 (CH), 40.1 (CH_2). MS (*m*/*z*, (relative abundance, %)): 424 (M^+, 35), 404, 381, 367, 247, 323, 305, 291, 263, 242, 230, 214, 200, 172, 183, 155, 144,129, 117, 103, 84, 71, 57, 42, 40.

*3-{4-[1-(*t*-Butylaminomethyl)-5-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl]phenyl}--sydnone (**2c**)*. Yellow amorphous solid (chloroform), R_f 0.93, m.p. 76–77 °C. Anal. Calcd. for $C_{22}H_{25}N_5O_2$: C, 67.51; H, 6.39; N, 17.90 %. Found: C, 67.50, H, 6.37, N 17.92 %. IR (KBr, cm^{-1}): 3130 (–NH stretching of secondary amine), 2924 (–CH stretching of sydnone ring), 1748 (–C=O stretching of sydnone ring), 1593 (–C=N stretching of pyrazole ring). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 1.78 (9H, *s*, $(–CH_3)_3C$), 3.09 (1H, *dd*, $–CH_2$, H_A, J = 14.95 Hz), 3.53 (1H, *dd*, $–CH_2$, H_B, J = 15.10 Hz), 3.64 (2H, *s*, $–CH_2$, N–CH_2–N), 4.38 (1H, *dd*, –CH, H_X, J_{XA} = 4.42 Hz, J_{XB} = 11.38 Hz), 5.15 (1H, *s*, –NH, D_2O exchangeable), 6.76 (1H, *s*, $–C_4$–H of sydnone ring), 7.27–7.87 (9H, *m*, aromatic). ^{13}C-NMR (300 MHz, $CDCl_3$, δ / ppm): 161 (C=O), 155.6 (C=N), 137.2, 131.6, 131.0 (C–aromatic), 129.9, 129.6, 129.4, 129.0, 128.3, 128.3, 128.1, 128.0, 126.8 (CH-aromatic), 116.7 (CH), 63.4 (CH_2), 48.7 (CH), 45.4 (**C**–$(CH_3)_3$), 40.1 (CH_2), 31.0 (CH_3). MS (*m*/*z*, (relative abundance, %)): 391 (M^+, 40), 382, 339, 328, 313, 298, 284, 269, 260, 247, 232, 220, 201, 195, 173, 160, 156, 146, 131, 116, 104, 91, 77, 65, 41.

*3-[4-(1-(Butylaminomethyl)-5-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)phenyl]sydnone (**2d**)*. Brown semi-solid (pet ether), R_f 0.90. Anal. Calcd. for $C_{22}H_{25}N_5O_2$: C, 67.51; H, 6.39; N, 17.90 %. Found: C, 67.50, H, 6.37, N, 17.92 %. IR (KBr, cm^{-1}): 3414 (–NH stretching of secondary amine), 2956 ($–CH_2$ stretching of *n*-butyl amine), 2929 (–CH stretching of sydnone ring), 1751 (–C=O stretching of sydnone ring), 1594 (–C=N stretching of pyrazole ring). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 1.05 (3H, *t*, $–CH_3$), 2.70–2.96 (4H, *m*, $–CH_2$) 3.57 (1H, *dd*, $–CH_2$, H_A, J = 12.69 Hz), 3.90 (1H, *dd*, $–CH_2$, H_B, J = 12.89 Hz), 3.94 (2H, *s*, $–CH_2$, N–CH_2–N), 3.92 (2H, *t*, $–CH_2$), 4.11 (2H, *t*, $–CH_2$), 4.23 (1H, *dd*, –CH, H_X, J_{XA} = = 3.60 Hz, J_{XB} = 10.44 Hz), 4.92 (1H, *s*, NH, D_2O exchangeable), 6.77–7.83 (9H,

m, aromatic), 6.75 (1H, *s*, –C_4–H of sydnone). ^{13}C-NMR (300 MHz, $CDCl_3$, δ / ppm): 163.5 (C=O), 155.6 (C=N), 137.2, 132.0, 131.5, 129.7, 129.5, 129.4, 129.0, 128.3, 128.3, 128.1, 128.0, 126.8, 116.7 (CH), 68.7 (CH_2), 48.7 (CH), 46.6, 40.1, 34.1, 20.5, 13.7 (CH_2). MS (*m*/*z*, (relative abundance, %)): 391 (M^+,30), 381, 367, 347, 323, 305, 291, 263, 242, 230, 214, 200, 183, 172, 155, 144, 129, 117, 103, 84, 71, 57, 42.

*3-(4-{1-[(4,6-Diamino-1,3,5-triazin-2-ylamino)methyl]-5-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl}-phenyl)sydnone (**2e**)*. Yellow amorphous solid (chloroform), R_f 0.88, m.p., 89–90 °C. Anal. Calcd. for $C_{21}H_{20}N_{10}O_2$: C, 56.75; H, 4.50; N, 31.53 %. Found: C, 56.77, H, 4.50, N 31.50 %. IR (KBr, cm^{-1}): 3415 (–NH_2 stretching for primary amine), 3106 (–NH stretching for secondary amine), 2921 (–CH_2 stretching), 2852 (–CH stretching for sydnone ring), 1753 (–C=O stretching for sydnone ring), 1560 (–C=N stretching for pyrazole ring). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 3.09 (1H, *dd*, –CH_2, H_A, J = 15.12 Hz), 3.52 (1H, *dd*, –CH_2, H_B, J = 15.35 Hz), 3.71 (2H, *s*, –CH_2, N–CH_2–N), 4.73 (1H, *dd*, –CH, H_X, J_{XA} = = 4.50 Hz, J_{XB} = 10.68 Hz), 4.90 (4H, *d*, –NH_2, D_2O exchangeable), 5.08 (1H, *s*, –NH, D_2O exchangeable), 6.75 (1H, *s*, –C_4–H of sydnone ring), 7.27–7.84 (9H, *m*, aromatic). ^{13}C-NMR (300 MHz, $CDCl_3$, δ / ppm): 164.0 (C=O), 155.6 (C=N), 149.0, 148.3, 145.1, 137.2, 133.0, 131.5, 129.8, 129.6, 129.5, 128.9, 128.3, 128.2, 128.0, 126.8, 116.7, 90.1, 88.9 (CH), 70.8 (CH_2), 48.7 (CH), 40.1 (CH_2). MS (*m*/*z*, (relative abundance, %)): 444 (M^+, 25), 441, 335, 313, 297, 285, 262, 248, 235, 221, 200, 191, 172, 155, 144, 129, 117, 103, 85, 76, 57, 44, 40.

*3-(4-{1-[(Diphenylamino)methyl]-5-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl}phenylsydnone (**2f**)*. Brown semi-solid (pet. ether), R_f 0.928. Anal. Calcd. for $C_{30}H_{25}N_5O_2$: C,73.92; H, 5.11; N, 14.37 %. Found: C, 73.90, H, 5.13, N 14.35 %. IR (KBr, cm^{-1}): 2924 (–CH stretching for sydnone ring), 1749 (–C=O stretching for sydnone ring), 1593 (–C=N stretching of pyrazole ring). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 3.08 (1H, *dd*, –CH_2, H_A, J = 14.89 Hz), 3.52 (1H, *dd*, –CH_2, H_B, J = 15.01 Hz), 3.98 (2H, *s*, –CH_2, N–CH_2–N), 4.42 (1H, *dd*, –CH, H_X, J_{XA} = = 4.80 Hz, J_{XB} = 8.25 Hz), 6.75 (1H, *s*, –C_4–H of sydnone), 7.03–8.21 (19H, *m*, aromatic). ^{13}C-NMR (300 MHz, $CDCl_3$, δ / ppm.): 160.0 (C=O), 155.6 (C=N), 144.0, 143.2, 137.2, 135.0, 131.0, 129.5, 129.4, 129.3, 129.1, 129.0, 128.9, 128.7, 128.6, 128.3, 128.3, 128.1, 128.0, 126.8, 118.0, 118.0, 117.9, 116.7 (CH), 77.6 (CH_2), 49.0 (CH), 40.1 (CH_2). MS (*m*/*z*, (relative abundance, %)): 487 (M^+ 35), 456, 428, 395, 364, 334, 306, 288, 276, 260, 248, 233, 221, 204, 191, 178, 165, 144, 129, 116, 104, 89, 77, 63, 44, 40.

*3,3'-{1,5-Pentanediylbis[imino(5-phenyl-4,5-dihydropyrazole-1,3-diyl)-1,4-phenylene]}bis[sydnone] (**2g**)*. Yellow solid (pet. ether), R_f 0.88, m.p. 99–100 °C. Anal. Calcd. for $C_{22}H_{27}N_7O_2$: C, 69.6; H, 6.07; N, 15.46 %. Found: C, 69.4, H, 6.07, N, 15.44 %. IR (KBr, cm^{-1}): 3150 (–NH stretching for secondary amine), 2930 (–NH stretching for secondary amine), 2922 (–CH stretching for sydnone

ring), 1750 (–C=O stretching for sydnone ring), 1594 (C=N stretching of pyrazole ring); ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 1.34–2.40 (10H, *m*, $–CH_2$), 3.08 (1H, *dd*, $–CH_2$, H_A, J = 15.06 Hz), 3.52 (1H, *dd*, $–CH_2$, H_B, J = 15.68 Hz), 3.98 (2H, *s*, $–CH_2$, N–CH_2–N), 4.42 (1H, *dd*, –CH, H_X, J_{XA} = 3.60 Hz, J_{XB} = = 10.44 Hz), 3.2 (4H, *s*, $–CH_2$), 3.62 (2H, *s*, $–CH_2$), 5.05 (1H, *s*, –NH, D_2O exchangeable), 6.72 (1H, *s*, $–C_4$–H of sydnone), 7.28–7.70 (18H, *m*, aromatic). ^{13}C--NMR (300 MHz, $CDCl_3$, δ / ppm.): 163.0 (C=O), 155.6, 155.6 (C=N), 137.2, 131.6, 131.5, 131.4, 131.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.4, 129.3, 129.2, 128.3, 128.2, 128.1, 128.0, 126.8, 116.7, 116.5 (CH), 68.7 (CH_2), 48.7 (CH), 47.7, 46.9, 42.3, 40.2, 40.1, 34.1, 33.6, 31.6, 24.8, 24.6 (CH_2). MS (*m*/*z*, (relative abundance, %)): 724 (M^+,15), 717, 678, 647, 633, 600, 579, 551, 520, 494, 473, 456, 421, 407, 406, 377, 379, 377, 345, 318, 301, 288, 276, 260, 250, 234, 218, 205, 178, 152, 132, 119, 103, 91, 77, 64, 44, 41.

*3-(4-{1-[Bis(aminomethylamino)methyl]-5-phenyl-4,5-dihydro-1*H*-pyrazol-3--yl}phenyl)sydnone (**2h**)*. Yellow solid (ethanol), R_f 0.89, m.p. 141–142 °C. Anal. Calcd. for $C_{21}H_{22}N_6O_2$: C, 77; H, 3.66; N, 14.0 %. Found: C, 77.01, H, 3.67, N, 14.02. IR (KBr, cm^{-1}): 3140 ($–NH_2$ stretching for primary amine), 2032 (–NH stretching for secondary amine), 2920 (–CH stretching for sydnone ring), 1754 (–C=O stretching for sydnone ring), 1590 (–C=N stretching for pyrazole ring). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 0.88–2.17 (4H, *m*, $–CH_2$), 3.07 (1H, *dd*, $–CH_2$, H_A, J = 12.03 Hz), 3.53 (2H, *s*, $–CH_2$, N–CH_2–N), 3.52 (1H, *dd*, $–CH_2$, H_B, J = 12.46 Hz), 4.64 (1H, *dd*, –CH, H_X, J_{XA} = 4.50 Hz, J_{XB} = 8.70 Hz), 5.04 (1H, *s*, –NH, D_2O exchangeable), 6.74 (1H, *s*, $–C_4$–H of sydnone), 7.28–7.70 (9H, *m*, aromatic). ^{13}C-NMR (300 MHz, $CDCl_3$, δ / ppm): 160.0 (C=O), 155.6 (C=N), 137.2, 132.0, 131.0, 129.9, 129.8, 129.6, 129.5, 128.3, 128.2, 128.1, 128.0, 126.8, 116.7 (CH), 72.8, 55.4 (CH_2), 49.0 (CH), 41.7, 40.1 (CH_2). MS (*m*/*z*, (relative abundance, %)): 422 (M^+, 25), 407, 406, 377, 379, 377, 345, 318, 301, 288, 276, 260, 250, 234, 218, 205, 178, 152, 132, 119, 103, 91, 77, 64, 44, 41.

*3-{4-[1-(Morpholin-4-ylmethyl)-5-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)]-phenyl}sydnone (**2i**)*. Yellow shiny solid (chloroform), R_f 0.85, m.p. 160–161 °C. Anal. Calcd. for $C_{22}H_{23}N_5O_3$: C, 65.18; H, 5.67; N, 11.85 %. Found: C, 65.15, H, 5.65, N, 17.30 %. IR (KBr, cm^{-1}): 2922 (–CH stretching for sydnone ring), 1749 (–C=O stretching for sydnone ring), 1596 (–C=N stretching for pyrazole ring). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm.): 2.45 (2H, *dd*, $–CH_2$), 2.47 (2H, *dd*, $–CH_2$), 2.63 (2H, *s*, $–CH_2$), 3.09 (1H, *dd*, $–CH_2$, H_A, J = 12.13 Hz), 3.55 (1H, *dd*, $–CH_2$, H_B, J = 12.78 Hz), 3.71 (2H, *dd*, $–CH_2$), 3.75 (2H, *dd*, $–CH_2$), 3.94 (2H, *s*, $–CH_2$, N–CH_2–N), 4.39 (1H, *dd*, –CH, H_X, J_{XA} = 4.80 Hz, J_{XB} = 9.00 Hz), 6.74 (1H, *s*, $–C_4$–H of sydnone), 7.28–7.70 (9H, *m*, aromatic). ^{13}C-NMR (300 MHz, $CDCl_3$, δ / ppm): 168.8 (C=O), 144.2 (C=N), 139.79, 128.8, 128.7, 128.5, 128.1, 128.0, 127.7, 127.58, 127.52, 126.85, 126.78, 126.57, 120.9 (CH), 73.83, 67.70, 51.39 (CH_2), 49.0 (CH), 41.0 (CH_2). MS (*m*/*z* (relative abundance, %)): 406 (M^+,

30), 379, 363, 334, 300, 288, 270, 260, 248, 235, 221, 206, 191, 178, 165, 150, 145, 130, 116, 105, 91, 77, 63, 44, 40.

*3-[4-(1-1*H*-Benzotriazol-1-ylmethyl)-5-phenyl-4,5-dihydro-1*H*-pyrazol-3-yl)-phenylsydnone (**2j**)*. Straw colored solid (ethanol), R_f 0.88, m.p. 150–152 °C. Anal. Calcd. for $C_{24}H_{19}N_7O_2$: C, 65.90; H, 4.34; N, 22.42 %. Found: C, 65.87, H, 4.37, N, 22.43 %. IR (KBr, cm^{-1}): 2921 (CH stretching for sydnone ring), 1745.5 (C=O stretching for sydnone ring), 1595 (C=N stretching for sydnone ring). ^{1}H-NMR (300 MHz, $CDCl_3$, δ / ppm): 3.08 (1H, *dd*, CH_2, H_A, J = 11.93 Hz), 3.73 (1H, *dd*, CH_2, H_B, J = 12.87 Hz), 3.75 (2H, *s*, CH_2, N–CH_2–N), 4.52 (1H, *dd*, CH, H_X, J_{XA} = 3.60 Hz, J_{XB} = 8.43 Hz), 6.73 (1H, *s*, C_4–H), 7.28–7.89 (13H, *m*, aromatic). ^{13}C-NMR (300 MHz, $CDCl_3$, δ / ppm): 164.0 (C=O), 155.6 (C=N), 137.2, 134.0, 132.0, 131.0, 130.7, 129.9, 129.8, 129.7, 129.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.0, 126.8, 116.7 (CH), 74.5 (CH_2), 48.7 (CH), 40.1 (CH_2). MS (*m*/*z* (relative abundance, %)): 437 (M^+, 25), 406, 379, 377, 345, 318, 301, 290, 276, 260, 248, 234, 225, 205, 178, 165, 152, 132, 119, 103, 91, 77, 64, 50, 44, 41.