



SUPPLEMENTARY MATERIAL TO
**Synthesis and root growth activity of some new
acetylhydrazinecarbothioamides and 1,2,4-triazoles
substituted with the 5H-dibenzo[a,d][7]annulene moiety**

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ANALYTICAL AND SPECTRAL DATA FOR THE SYNTHESIZED COMPOUNDS

2-(5H-Dibenzo[a,d][7]annulen-5-ylacetyl)hydrazinecarbothioamide (5a). Yield: 87.0 %; m.p.: 146–148 °C; Anal. Calcd. for $C_{18}H_{17}N_3OS$ (FW: 323.24): C, 66.87; H, 5.26; N, 12.99; S, 9.92 %. Found: C, 66.83; H, 5.30; N, 12.98; S, 9.95 %; IR (KBr, cm^{-1}): 3419, 3214, 3184 (N–H stretching), 3068, 3018 (C–H stretching of aromatic ring), 2967, 2859 (CH_2 stretching), 1686 (C=O stretching), 1611, 1532, 1491 (C=C stretching), 1259 (C=S stretching); ¹H-NMR (300 MHz, DMSO-*d*₆, δ / ppm): 10.11, 9.53, 9.06, 8.13 (*s*, NH), 7.87 (2H, *bs*, NH₂), 7.42–7.20 (8H, *m*, aromatic), 7.01 (2H, *s*, CH=CH), 4.60 (1H, *t*, *J* = 7.4 Hz, CH axial isomer), 3.70 (1H, *t*, *J* = 7.4 Hz, CH equatorial isomer), 3.32 (2H, *d*, *J* = 7.4 Hz, CH₂–CO equatorial isomer), 2.52 (2H, *d*, *J* = 7.4 Hz, CH₂–CO axial isomer); ¹³C-NMR (75 MHz, DMSO-*d*₆, δ / ppm): 181.56 (C=S), 169.63 (C=O), 131.19 (CH=CH equatorial isomer), 130.70 (CH=CH axial isomer), 139.79, 139.46, 133.7, 129.54, 129.46, 128.73, 128.71, 127.50, 126.50, 125.78, 125.43 (aromatic ring), 48.85 (CH), 34.29 (CH₂); UV–Vis (CH₃OH) (λ_{max} / nm (log ϵ)): 210.6 (4.34), 227.8 (4.25), 239.2 (4.13), 291.2 (4.04).

2-(5H-Dibenzo[a,d][7]annulen-5-ylacetyl)-N-propylhydrazinecarbothioamide (5b). Yield: 81.1 %; m.p.: 172–173 °C; Anal. Calcd. for $C_{21}H_{23}N_3OS$ (FW: 365.27): C, 69.04; H, 6.30; N, 11.50; S, 8.78 %. Found: C, 69.01; H, 6.34; N, 11.48; S, 8.75 %. IR (KBr, cm^{-1}): 3370, 3201 (N–H stretching), 3070, 3017 (C–H stretching of aromatic ring), 2961, 2867 (CH_3 stretching), 2933, 2847 (CH_2 stretching), 1688 (C=O stretching), 1534 (C=C stretching), 1256 (C=S stretch-

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ing); $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$, δ / ppm): 10.05, 9.46, 9.22, 8.97 (*s*, NH), 7.40–7.18 (8H, *m*, aromatic), 7.07 (2H, *s*, CH=CH), 4.61 (1H, *t*, $J = 7.3$ Hz, CH), 3.30 (2H, *t*, $J = 7.3$ Hz, N–CH₂), 2.54 (2H, *d*, $J = 7.3$ Hz, CH₂–CO), 1.40 (2H, *sx*, $J = 7.3$ Hz, CH₂–CH₃), 0.78 (3H, *t*, $J = 7.3$ Hz, CH₃); $^{13}\text{C-NMR}$ (75 MHz, $\text{DMSO-}d_6$, δ / ppm): 181.84 (C=S), 169.73 (C=O), 131.14 (CH=CH equatorial isomer), 130.70 (CH=CH axial isomer), 139.92, 133.76, 129.46, 129.45, 128.61, 128.35, 127.50, 126.40 (aromatic ring), 48.96 (CH), 45.22 (N–CH₂), 34.76 (CH₂–CO), 21.81 (CH₂–CH₃), 10.92 (CH₃); UV–Vis (CH_3OH) (λ_{max} / nm (log ϵ)): 226.4 (4.42), 239.2 (4.39), 291.2 (4.24).

2-(5H-Dibenzo[a,d][7]annulen-5-ylacetyl)-N-(4-ethylphenyl)hydrazinecarbothioamide (**5c**). Yield: 66.6 %; m.p.: 102–104 °C; Anal. Calcd. for $\text{C}_{26}\text{H}_{25}\text{N}_3\text{OS}$ (FW: 427.32): C, 73.07; H, 5.85; N, 9.83; S, 7.50 %. Found: C, 73.03; H, 5.84; N, 9.82; S, 7.52 %; IR (KBr, cm^{-1}): 3335, 3226 (N–H stretching), 3043, 3019 (C–H stretching of aromatic ring), 2963, 2871 (CH₃ stretching), 2930, 2828 (CH₂ stretching), 1678 (C=O stretching), 1595, 1526 (C=C stretching), 1259 (C=S stretching); $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$, δ / ppm): 10.30, 9.70, 9.60, 9.37 (1H, *s*, NH), 7.45–7.10 (12H, *m*, aromatic), 7.02 (2H, *s*, CH=CH), 4.63 (1H, *t*, $J = 7.3$ Hz, CH axial isomer), 3.75 (1H, *t*, $J = 7.3$ Hz, CH equatorial isomer), 3.42 (2H, *d*, $J = 7.3$ Hz, CH₂–CO equatorial isomer), 2.61 (2H, *d*, $J = 7.3$ Hz, CH₂–CO axial isomer), 2.58 (2H, *q*, $J = 7.3$ Hz, CH₂–CH₃), 1.48 (3H, *t*, $J = 7.3$ Hz, CH₃); $^{13}\text{C-NMR}$ (75 MHz, $\text{DMSO-}d_6$, δ / ppm): 180.95 (C=S), 170.34 (C=O), 131.37 (CH=CH equatorial isomer), 130.90 (CH=CH axial isomer), 140.03, 139.61, 134.95, 133.83, 129.69, 128.89, 128.62, 127.47, 127.25, 126.65 (aromatic ring), 48.81 (CH), 34.65 (CH₂–CO), 27.78 (CH₂–CH₃), 15.74 (CH₃); UV–Vis (CH_3OH) (λ_{max} / nm (log ϵ)): 221.6 (4.45), 280.6 (4.27).

2-(5H-Dibenzo[a,d][7]annulen-5-ylacetyl)-N-(3-nitrophenyl)hydrazinecarbothioamide (**5d**). Yield: 71.6 %; m.p.: 202–203 °C; Anal. Calcd. for $\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}_3\text{S}$ (FW: 444.27): C, 64.88; H, 4.50; N, 12.60; S, 7.22 %. Found: C, 64.89; H, 4.52; N, 12.59; S, 7.23 %; IR (KBr, cm^{-1}): 3334, 3287, 3188 (N–H stretching), 3063, 3021 (C–H stretching of aromatic ring), 2960, 2864 (CH₂ stretching), 1674 (C=O stretching), 1599, 1531, 1494 (C=C stretching), 1599, 1345 (NO₂ stretching), 1258 (C=S stretching); $^1\text{H-NMR}$ (300 MHz, $\text{DMSO-}d_6$, δ / ppm): 9.81, 9.78, 9.70 (*s*, NH), 7.98 (1H, *d*, $J = 8.0$ Hz, CH–nitrophenyl), 7.82 (1H, *dd*, $J = 8.0, 1.7$ Hz, CH–nitrophenyl), 7.59 (1H, *t*, $J = 8.0$, CH–nitrophenyl), 7.50–7.18 (9H, *m*, aromatic), 7.03 (2H, *s*, CH=CH), 4.64 (1H, *t*, $J = 7.3$ Hz, CH), 2.62 (2H, *d*, $J = 7.3$ Hz, CH₂–CO); $^{13}\text{C-NMR}$ (75 MHz, $\text{DMSO-}d_6$, δ / ppm): 181.02 (C=S), 170.47 (C=O), 131.37 (CH=CH equatorial isomer) 130.91 (CH=CH axial isomers), 140.34, 140.04, 139.57, 134.94, 133.83, 129.72, 129.63, 128.90, 128.63, 126.66, 125.66, 123.06 (aromatic ring), 48.68 (CH), 34.64 (CH₂–CO); UV–Vis (CH_3OH) (λ_{max} / nm (log ϵ)): 227.8 (4.56), 274.9 (4.34).

5-(5H-Dibenzo[a,d][7]annulen-5-ylmethyl)-4H-1,2,4-triazole-3-thiol (6a). Yield: 71.5 %; m.p.: 251–253 °C; Anal. Calcd. for C₁₈H₁₅N₃S (FW: 305.24): C, 70.82; H, 4.94; N, 13.78; S, 10.50 %. Found: C, 70.79; H, 4.95; N, 13.76; S, 10.51 %; IR (KBr, cm⁻¹): 3414 (N–H stretching), 3089, 3019 (C–H stretching of aromatic ring), 2848, 2925 (CH₂ stretching), 1592 (C=N stretching of triazole ring), 1492 (C=C stretching), 1213 (C=S stretching); ¹H-NMR (300 MHz, CDCl₃, δ / ppm): 10.85 (1H, s, SH), 9.04 (1H, s, NH), 7.42–7.23 (8H, m, aromatic), 7.03 (2H, s, CH=CH), 4.61 (1H, t, J = 8.0 Hz, CH), 2.89 (2H, d, J = 8.0 Hz, CH₂–C₅-triazole); ¹³C-NMR (75 MHz, CDCl₃, δ / ppm): 165.69 (triazole-C₃), 150.30 (triazole-C₅), 131.16 (CH=CH), 138.78, 133.65, 130.59, 129.73, 129.28, 127.53 (aromatic ring), 50.69 (CH), 25.98 (CH₂–C₅-triazole); UV–Vis (CH₃OH) (λ_{max} / nm (log ε)): 225.5 (4.01), 292.1 (3.90).

5-(5H-Dibenzo[a,d][7]annulen-5-ylmethyl)-4-propyl-4H-1,2,4-triazole-3-thiol (6b). Yield: 62.5 %; m.p.: 153–155 °C, Anal. Calcd. for C₂₁H₂₁N₃S (FW: 347.27): C, 72.63; H, 6.05; N, 12.09; S, 9.23 %. Found: C, 72.59; H, 6.09; N, 12.06; S, 9.20 %; IR (KBr, cm⁻¹): 3119 (N–H stretching), 3093, 3021 (C–H stretching of aromatic ring), 2970, 2875 (CH₃ stretching), 2938 (CH₂ stretching), 1562 (C=N stretching of triazole ring), 1499, 1480 (C=C stretching), 1245 (C=S stretching); ¹H-NMR (300 MHz, CDCl₃, δ / ppm): 11.70 (1H, s, SH), 7.32–7.18 (8H, m, aromatic), 7.01 (2H, s, CH=CH), 4.69 (1H, t, J = 7.7 Hz, CH), 3.52 (2H, t, J = 7.6 Hz, N–CH₂), 3.09 (2H, d, J = 7.7 Hz, CH₂–C₅-triazole), 1.49 (2H, sx, J = 7.6 Hz, CH₂–CH₃), 0.82 (3H, t, J = 7.6 Hz, CH₃); ¹³C-NMR (75 MHz, CDCl₃, δ / ppm): 166.49 (triazole-C₃), 151.03 (triazole-C₅), 130.88 (CH=CH), 138.60, 133.67, 129.87, 129.77, 129.17, 127.14 (aromatic ring), 52.40 (CH), 44.89 (N–CH₂), 26.11 (CH₂–C₅-triazole), 21.51 (CH₂–CH₃), 10.93 (CH₃); UV–Vis (CH₃OH) (λ_{max} / nm (log ε)): 227.3 (4.23), 256.4 (4.16), 290.3 (3.99).

5-(5H-Dibenzo[a,d][7]annulen-5-ylmethyl)-4-(4-ethylphenyl)-4H-1,2,4-triazole-3-thiol (6c). Yield: 68.4 %; m.p.: 219–221 °C; Anal. Calcd. for C₂₆H₂₃N₃S (FW: 409.32): C, 76.28; H, 5.62; N, 10.26; S, 7.83 %. Found: C, 76.31; H, 5.61; N, 10.22; S, 7.87 %; IR (KBr, cm⁻¹): 3410 (N–H stretching), 3069, 3020 (C–H stretching of aromatic ring), 2964, 2873 (CH₃ stretching), 2929 (CH₂ stretching), 1567 (C=N stretching of triazole ring), 1514, 1490 (C=C stretching), 1234 (C=S stretching); ¹H-NMR (300 MHz, CDCl₃, δ / ppm): 10.98 (1H, s, SH), 7.43–7.15 (10H, m, aromatic), 6.81 (2H, d, J = 8.0 Hz, aromatic), 6.62 (2H, s, CH=CH), 4.35 (1H, t, J = 8.0 Hz, CH), 2.98 (2H, d, J = 8.0 Hz, CH₂–C₅-triazole), 2.76 (2H, q, J = 7.8 Hz, CH₂–CH₃), 1.34 (3H, t, J = 7.8 Hz, CH₃); ¹³C-NMR (75 MHz, CDCl₃, δ / ppm): 167.39 (triazole-C₃), 151.57 (triazole-C₅), 130.60 (CH=CH), 146.92, 138.48, 133.79, 130.60, 129.93, 129.41, 128.98, 127.76, 126.98, 125.75 (aromatic ring), 52.58 (CH), 28.64 (CH₂–CH₃), 26.00 (CH₂–C₅-triazole), 15.45 (CH₃); UV–Vis (CH₃OH) (λ_{max} / nm (log ε)): 214.1 (4.40), 266.5 (4.12).

5-(5H-Dibenzo[a,d][7]annulen-5-ylmethyl)-4-(3-nitrophenyl)-4H-1,2,4-triazole-3-thiol (**6d**). Yield: 86.5 %; m.p.: 134–136 °C; Anal. Calcd. for C₂₄H₁₈N₄O₂S (FW: 426.28): C, 67.62; H, 4.22; N, 13.14; S, 7.52 %. Found: C, 67.58; H, 4.25; N, 13.16; S, 7.49 %; IR (KBr, cm⁻¹): 3092 (N–H stretching), 3071, 3022 (C–H stretching of aromatic ring), 2932, 2845 (CH₂ stretching), 1566 (C=N stretching of triazole ring), 1534, 1491 (C=C stretching), 1526, 1350 (NO₂ stretching), 1229 (C=S stretching); ¹H-NMR (300 MHz, CDCl₃, δ / ppm): 11.34 (1H, *s*, SH), 7.67 (1H, *t*, *J* = 2.1 Hz, CH-nitrophenyl), 7.64 (1H, *t*, *J* = 8.3 Hz, CH-nitrophenyl); 7.39 (1H, *ddd*, *J* = 1.0, 2.1, 8.3 Hz, CH-nitrophenyl), 7.32–7.15 (9H, *m*, aromatic), 6.51 (2H, *s*, CH=CH), 4.45 (1H, *t*, *J* = 7.7 Hz, CH), 3.01 (2H, *d*, *J* = 7.7 Hz, CH₂–C₅-triazole); ¹³C-NMR (75 MHz, CDCl₃, δ / ppm): 168.37 (triazole-C₃), 151.23 (triazole-C₅), 130.54 (CH=CH), 148.80, 138.20, 134.18, 133.72, 130.54, 130.25, 129.99, 129.50, 129.27, 127.27, 124.34, 123.81, (aromatic ring), 52.63 (CH), 26.27 (CH₂–C₅-triazole); UV–Vis (CH₃OH) (λ_{max} / nm (log ε)): 215.0 (4.41), 285.0 (4.18).