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SUPPLEMENTARY MATERIAL TO

# Design, synthesis and antimycobacterial evaluation of some new azaheterocycles with the 4,7-phenanthroline skeleton. Part VI

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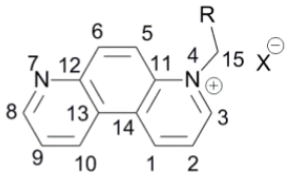
## PHYSICAL AND SPECTRAL DATA FOR THE PREPARED COMPOUNDS




**1.** R =-$COC_6H_4Me$(p), X=Br
**2.** R = -$COC_6H_4OMe$(p), X=Br
**3.** R = -$COC_6H_4NO_2$(p), X=Br
**4.** R = -$COC_6H_4Cl$(p), X=Br
**5.** R = -$COC_6H_4OMe$(m), X=Br
**6.** R= -$CONH_2$, X=I
**7.** R= -CN, X=Br
**8.** R= -COOMe, X=Br

Fig. S-1. The atomic numbering scheme for the 4,7-phenanthrolin-4-ium salts.

*4-(2-Oxo-2-(4-tolylethyl)-4,7-phenanthrolin-4-ium bromide (**1**).* Yield: 67 %; beige powder; m.p.: 246–248 °C; Anal. Calcd. for $C_{21}H_{17}BrN_2O$: C, 64.13; H, 4.36; N, 7.12 %. Found: C, 64.10; H, 4,30; N, 7.20 %; IR (KBr, $cm^{-1}$): 2968 (CH), 1672 (C=O); $^1$H-NMR (500 MHz, DMSO-$d_6$, $\delta$ / ppm): 2.48 (3H, *s*, Me), 7.14 (2H, *s*, H15), 7.52 (2H, *d*, $J$ = 8.5 Hz, 2×Ar-H), 8.06 (1H, *dd*, $J$ = 8.5 and 4.5 Hz, H9), 8.08 (2H, *d*, $J$ = 8.5 Hz, 2×Ar-H), 8.58 (2H, *m*, H2 & H6), 8.63 (1H, *d*, $J$ = 10.0 Hz, H5), 9.27 (1H, *app d*, $J$ = 4.0 Hz, H10), 9.60 (2H, *m*, H1, H8), 10.31 (1H, *app d*, $J$ = 8.5 Hz, H3); $^{13}$C-NMR (125 MHz, DMSO-$d_6$, $\delta$ / ppm): 21.4 ($CH_3$), 63.9 (C15), 129.6 (2×Ar-C), 120.5 (C6), 123.4 (C2), 123.9 (C14), 124.5 (C9), 127.9 (C13), 128.8 (2×Ar-C), 131.1 (Cq-phenyl), 133.0 (C8), 138.2 (C5), 139.5 (C11), 143.1 (C3), 145.6 (Cq-phenyl), 146.2 (C12), 149.3 (C1), 153.3 (C10), 190.2 (CO).

*4-(2-(4-Methoxyphenyl)-2-oxoethyl)-4,7-phenanthrolin-4-ium bromide (**2**).* Yield: 94 %; beige powder; m.p.: 253–255 °C; Anal. Calcd. for $C_{21}H_{17}BrN_2O_2$:

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C, 61.63; H, 4.19; N, 6.84 %. Found: C, 61.64; H 4,10; N, 6.90 %; IR (KBr, $cm^{-1}$): 2940 (CH), 1684 (C=O), 1238, 1179 (CO); $^1$H-NMR (500 MHz, DMSO-$d_6$, $\delta$ / ppm): 3.93 (3H, *s*, $OCH_3$), 7.07 (2H, *s*, H15), 7.23 (2H, *d*, *J* = 8.5 Hz, 2×Ar-H), 8.06 (1H, *dd*, *J* = 8.5 and 4.0 Hz, H9), 8.15 (2H, *d*, *J* = 8.5 Hz, 2×Ar-H), 8.57 (2H, *m*, H2 and H5), 8.64 (1H, *d*, *J* = 10.0 Hz, H6), 9.28 (1H, *app d*, *J* = 4.0 Hz, H10), 9.54 (1H, *app d*, *J* = 6.0 Hz, H1), 9.60 (1H, *app d*, *J* = 4.0 Hz, H8), 10.30 (1H, *app d*, *J* = 8.5 Hz, H3); $^{13}$C-NMR (125 MHz, DMSO-$d_6$, $\delta$ / ppm): 55.9 ($OCH_3$), 63.7 (C15), 114.4 (2×Ar-C), 120.5 (C6), 123.4 (C2), 123.9 (C14), 124.5 (C9), 126.4 (Cq-phenyl), 127.9 (C13), 131.2 (2×Ar-C), 132.9 (C8), 138.3 (C5), 139.5 (C11), 143.0 (C3), 146.2 (C12), 149.3 (C1), 153.4 (C10), 164.5 (Cq-phenyl), 188.8 (CO).

*4-(2-(4-Nitrophenyl)-2-oxoethyl)-4,7-phenanthrolin-4-ium bromide (**3**).* Yield: 91 %; beige powder; m.p.: 235–237 °C; Anal. Calcd. for $C_{20}H_{14}BrN_3O_3$: C, 56.62; H, 3.33; N, 9.90 %. Found: C, 56.70; H, 3,20; N, 9.97 %; IR (KBr, $cm^{-1}$): 3034, 2893 (CH), 1698 (C=O), 1520, 1344 ($NO_2$); $^1$H-NMR (500 MHz, DMSO-$d_6$, $\delta$ / ppm): 7.20 (2H, *s*, H15), 8.06 (1H, *dd*, *J* = 8.5 and 4.5 Hz, H9), 7.40 (2H, *d*, *J* = 8.5 Hz, 2×Ar-H), 8.53 (2H, *d*, *J* = 8.5 Hz, 2×Ar-H), 8.59 (1H, *dd*, *J* = 8.5 and 6.0 Hz, H2), 8.64 (1H, *d*, *J* = 10.0 Hz, H6), 8.73 (1H, *d*, *J* = 10.0 Hz, H5), 9.28 (1H, *app d*, *J* = 3.0 Hz, H10), 9.58 (1H, *app d*, *J* = 6.0 Hz, H1), 9.61(1H, *app d*, *J* = 8.5 Hz, H8), 10.33 (1H, *app d*, *J* = 8.5 Hz, H3); $^{13}$C-NMR (125 MHz, DMSO-$d_6$, $\delta$ / ppm): 64.3 (C15), 120.7 (C6), 123.4 (C2), 123.9 (C14), 124.5 (C9), 128.0 (C13), 124.0 (2×Ar-C), 130.2 (2×Ar-C), 133.0 (C8), 138.2 (C5), 138.3 (Cq-phenyl), 139.6 (C11), 143.4 (C3), 146.2 (C12), 149.3 (C1), 150.7 (C–$NO_2$), 153.4 (C10), 190.1 (CO).

*4-(2-(4-Chlorophenyl)-2-oxoethyl)-4,7-phenanthrolin-4-ium bromide (**4**).* Yield: 74 %; beige powder; m.p.: 242–244 °C; Anal. Calcd. for $C_{20}H_{14}BrClN_2O$: C, 58.07; H, 3.41; N, 6.77 %. Found: C, 58.10; H, 3,29; N, 6.87 %; IR (KBr, $cm^{-1}$): 2951 (CH), 1688 (C=O); $^1$H-NMR (500 MHz, DMSO-$d_6$, $\delta$ / ppm): 7.12 (2H, *s*, H15), 7.81 (2H, *d*, *J* = 8.5 Hz, 2×Ar-H), 8.06 (1H, *dd*, *J* = 8.5 and 4.0 Hz, H9), 8.18 (2H, *d*, *J* = 8.5 Hz, 2×Ar-H), 8.57 (1H, *dd*, *J* = 8.5 and 6.0 Hz, H2), 8.63 (1H, *d*, *J* = 10.0 Hz, H6), 8.65 (1H, *d*, *J* = 10.0 Hz, H5), 9.28 (1H, *dd*, *J* = 4.0 and 1.0 Hz, H10), 9.56 (1H, *app d*, *J* = 6.0 Hz, H1), 9.60 (1H, *app d*, *J* = 4.0 Hz, H8), 10.31 (1H, *app d*, *J* = 8.5 Hz, H3); $^{13}$C-NMR (125 MHz, DMSO-$d_6$, $\delta$ / ppm): 64.0 (C15), 120.6 (C6), 123.4 (C2), 123.9 (C14), 124.5 (C9), 128.0 (C13), 129.2 (2×Ar-C), 130.6 (2×Ar-C), 132.4 (Cq-phenyl), 133.0 (C8), 138.3 (C5), 139.6 (C11), 139.7 (Cq-phenyl), 143.2 (C3), 146.2 (C12), 149.3 (C1), 153.4 (C10), 189.9 (CO).

*4-(2-(3-Methoxyphenyl)-2-oxoethyl)-4,7-phenanthrolin-4-ium bromide (**5**).* Yield: 74 %; beige powder; m.p.: 208–210 °C; Anal. Calcd. for $C_{21}H_{17}BrN_2O_2$: C, 61.63; H, 4.19; N, 6.84 %. Found: C, 61.60; H, 4,12; N, 6.92 %; IR (KBr, $cm^{-1}$): 3006, 2964 (CH), 1684 (C=O), 1238, 1179 (CO); $^1$H-NMR (500 MHz, DMSO-



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-$d_6$, $\delta$ / ppm): 3.89 (3H, *s*, OMe), 7.18 (2H, *s*, H15), 7.41 (1H, *dd*, *J* = 8.50 and 2.0 Hz, Ar-H), 7.64 (2H, *m*, 2×Ar-H), 7.78 (1H, *app d*, *J* = 7.5 Hz, Ar-H), 8.05 (1H, *dd*, *J* = 8.5 and 4.0 Hz, H9), 8.56–8.65 (3H, *m*, H2, H5 and H6), 9.27 (1H, *app d*, *J* = 3.5 Hz, H10), 9.54 (2H, *app d*, H1 and H8), 10.32 (1H, *app d*, *J* = 8.5 Hz, H3); $^{13}$C-NMR (125 MHz, DMSO-$d_6$, $\delta$ / ppm): 55.7 ($OCH_3$), 64.2 (C15), 113.2 (Ar-C), 120.5 (C6), 120.8 (Ar-C), 121.2 (Ar-C), 123.5 (C2), 123.8 (C14), 124.5 (C9), 127.9 (C13), 130.3 (Ar-C), 133.0 (Cq-phenyl), 134.9 (C8), 138.2 (C5), 139.4 (C11), 143.2 (C3), 146.1 (C12), 149.2 (C1), 153.3 (C10), 159.5 (Cq-phenyl), 190.6 (CO).

*4-(2-Amino-2-oxoethyl)-4,7-phenanthrolin-4-ium iodide (**6**).* Yield: 84 %; yellow powder; m.p.: 264–266 °C; Anal. Calcd. for $C_{14}H_{12}IN_3O$: C, 46.05; H, 3.31; N, 11.51 %. Found: C, 46.10; H, 3,29; N, 11.59 %; IR (KBr, $cm^{-1}$): 3351, 3167 (NH), 1673 (C=O); $^1$H-NMR (500 MHz, DMSO-$d_6$, $\delta$ / ppm): 5.27 (2H, *s*, H15), 7.89 (1H, *s*, NH), 8.02 (1H, *dd*, *J* = 8.5 and 3.5 Hz, H9), 8.21 (1H, *s*, NH), 8.44 (1H, *d*, *J* = 10.0 Hz, H5), 8.50 (1H, *dd*, *J* = 8.5 and 6.5 Hz, H2), 8.70 (1H, *d*, *J* = 10.0 Hz, H6), 9.25 (1H, *app d*, *J* = 3.5 Hz, H10), 9.54 (1H, *app d*, *J* = 8.5 Hz, H8), 9.57 (1H, *app d*, *J* = 6.0 Hz, H1),10.22 (1H, *app d*, *J* = 8.5 Hz, H3); $^{13}$C--NMR (125 MHz, DMSO-$d_6$, $\delta$ / ppm): 59.5 (C15), 119.9 (C6), 123.2 (C2), 123.8 (C14), 124.5 (C9), 127.8 (C13), 132.9 (C8), 138.3 (C5), 139.1 (C11), 142.8 (C3), 146.1 (C12), 149.4 (C1), 153.3 (C10), 165.8 (CO).

*4-(Cyanomethyl)-4,7-phenanthrolin-4-ium bromide (**7**).* Yield: 58 %; beige powder; m.p.: 214–216 °C; Anal. Calcd. for $C_{14}H_{10}BrN_3$: C, 56.02; H, 3.36; N, 14.00 %. Found: C, 56.10; H, 3,29; N, 14.09 %; IR (KBr, $cm^{-1}$): 3056 (CH), 2201 (C≡N); $^1$H-NMR (500 MHz, DMSO-$d_6$, $\delta$ / ppm): 6.58 (2H, *s*, H15), 8.08 (1H, *dd*, *J* = 8.5 and 4.0 Hz, H9), 8.55 (1H, *dd*, *J* = 8.5 and 6.0 Hz, H2), 8.80 (1H, *d*, *J* = 10.0 Hz, H5), 8.83 (1H, *d*, *J* = 10.0 Hz, H6), 9.31 (1H, *app d*, *J* = 4.5 Hz, H10), 9.59 (1H, *app d*, *J* = 8.5 Hz, H8), 9.70 (1H, *app d*, *J* = 6.0 Hz, H1), 10.32 (1H, *app d*, *J* = 8.5 Hz, H3); $^{13}$C-NMR (125 MHz, DMSO-$d_6$, $\delta$ / ppm): 45.6 (C15), 114.0 (CN), 119.4 (C6), 123.7 (C2), 124.1 (C14), 124.8 (C9), 128.4 (C13), 133.0 (C8), 138.1 (C5), 139.2 (C11), 144.3 (C3), 146.2 (C12), 149.5 (C1), 153.6 (C10).

*4-(2-Methoxy-2-oxoethyl)-4,7-phenanthrolin-4-ium bromide (**8**).* Yield: 71 %; beige powder; m.p.: 169–170 °C; Anal. Calcd. for $C_{15}H_{13}BrN_2O_2$: C, 54.07; H, 3.93; N, 8.41 %. Found: C, 54.10; H, 3,89; N, 8.49 %; IR (KBr, $cm^{-1}$): 3033, 2977 (CH), 1745 (C=O), 1235 (CO); $^1$H-NMR (500 MHz, DMSO-$d_6$, $\delta$ / ppm): 3.81 (3H, *s*, $CH_3$), 6.35 (2H, *s*, H15), 8.04 (1H, *dd*, *J* = 8.5 and 4.0 Hz, H9), 8.55 (1H, *dd*, *J* = 8.5 and 6.0 Hz, H2), 8.65 (1H, *d*, *J* = 10.0 Hz, H5), 8.68 (1H, *d*, *J* = = 10.0 Hz, H6), 9.26 (1H, *dd*, *J* = 4.0 and 1.0 Hz, H10), 9.58 (1H, *app d*, *J* = 8.5 Hz, H8), 9.66 (1H, *app d*, *J* = 5.5 Hz, H1), 10.31 (1H, *app d*, *J* = 8.5 Hz, H3); $^{13}$C-NMR (125 MHz, DMSO-$d_6$, $\delta$ / ppm): 53.3 ($CH_3$), 58.1 (C15), 120.3 (C6),



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123.4 (C2), 123.8 (C14), 124.5 (C9), 127.9 (C13), 133.0 (C8), 138.4 (C5), 139.1 (C11), 143.6 (C3), 146.1 (C12), 149.5 (C1), 153.4 (C10), 166.6 (C=O).



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