Supporting Information

Functionalisation of Vitamin B_{12} Derivatives with a Cobalt β-Phenyl Ligand Boosters Antimetabolite Activity in Bacteria

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$^1$H-NMR spectrum of 8, β-PhCbl (500 MHz, D$_2$O (presat), 298 K, 3.2 x 10$^{-3}$ M).
Reaction Schemes.

Scheme S1. Synthesis of Co$_p$-cyanocobalamin-c,8-lactam (2).

Scheme S2. Synthesis of Co$_p$-aquacobalamin-c,8-lactam acetate (3).

Scheme S3. Synthesis of Co$_p$-phenylcobalamin-c,8-lactam (4) and its side product Co$_a$-phenylcobalamin-c,8-lactam (4a, not characterized).
Scheme S4. Synthesis of 10-bromo-Coβ-cyanocobalamin (5).

Scheme S5. Synthesis of 10-bromo-Coβ-aquacobalamin tetrafluoroborate (6) from intermediate 10-Bromo-Coβ-phenylethynylcobalamin (reported in ref S4).

Scheme S6. Synthesis of 10-bromo-Coβ-phenylcobalamin (7) from Coβ-phenylcobalamin (reported in ref S3).
Figure S1. Atom numbering of vitamin B$_{12}$ (1) and its analogues. Bottom: Atom numbering of the c,8-lactam ring in derivatives 2 and 4, as well as nomenclature of the phenyl ligand of β-PhCbl, 4 and 7.
NMR and optical Spectra.

Figure S2. $^1$H-NMR spectrum of 2 (500 MHz, D$_2$O (presat), 298 K, 4.1 x 10$^{-3}$ M).

Figure S3. UV/Vis spectrum of 2 (H$_2$O, 4.1 x 10$^{-5}$ M).
Figure S4. $^1$H-NMR spectrum of 3 (500 MHz, CD$_3$OD, 298 K, $7.3 \cdot 10^{-3}$ M).

Figure S5. UV/Vis spectrum of 3 (H$_2$O, $c = 2.2 \cdot 10^{-5}$ M).
Figure S6. $^1$H-NMR spectrum of 4 (500 MHz, D$_2$O (presat), 298 K, $1.2 \times 10^{-2}$ M).

Figure S7. $^{13}$C-NMR spectrum of 4 (126 MHz, D$_2$O, 298 K, $1.2 \times 10^{-2}$ M).
Figure S8. DEPT 135-NMR spectrum of 4 (126 MHz, D$_2$O, 298 K, 1.2 x $10^{-2}$ M).

Figure S9. $^1$H-$^1$H DFQ-COSY spectrum of 4 (500 MHz, D$_2$O, 298 K, 1024 x 2560 p, 12 scans, 1.2 x $10^{-2}$ M).
Figure S10. $^1$H$^1$H NOESY spectrum of 4 (500 MHz, D$_2$O, 298 K, 1024 x 1884 p, 16 scans, $1.2 \times 10^{-2}$ M).

Figure S11. $^1$H$^1$C HSQC spectrum of 4 (500 MHz, 126 MHz, D$_2$O (presat), 298 K, 1024 x 5120 p, 18 scans, $1.2 \times 10^{-2}$ M).
Figure S12. $^1$H-$^{13}$C HMBC spectrum of 4 (500 MHz, 126 MHz, D$_2$O, 298 K, 1024 x 3000 p, 12 scans, 1.2 x 10$^{-2}$ M).

Figure S13. UV/Vis spectrum of 4 (H$_2$O, 3.9 x 10$^{-5}$ M).
Figure S14. $^1$H-NMR spectrum of 5 (500 MHz, D$_2$O (presat), 298 K, 4.9 x 10^{-3} M).

Figure S15. UV/Vis spectrum of 5 (H$_2$O, 4.9 x 10^{-5} M).
Figure S16. $^1$H-NMR spectrum of 7 (500 MHz, CD$_3$OD (presat), 298 K, 8.7 x $10^{-3}$ M).

Figure S17. $^{13}$C-NMR spectrum of 7 (126 MHz, CD$_3$OD (presat), 298 K, 8.7 x $10^{-3}$ M).
Figure S18. $^1$H-$^{13}$C HSQC spectrum of 7 (500 MHz, 126 MHz, CD$_3$OD, 298 K, 1024 x 1024 p, 32 scans, 8.7 x $10^{-3}$ M).

Figure S19. $^1$H-$^{13}$C HMBC spectrum of 7 (500 MHz, 126 MHz, CD$_3$OD, 298 K, 1024 x 2341 p, 12 scans, 8.7 x $10^{-3}$ M).
**Figure S20.** UV/Vis spectrum of 7 (H₂O, 3.5 x 10⁻⁵ M).

**Figure S21.** ¹H-NMR spectrum of 8, β-PhCbl (500 MHz, D₂O (presat), 298 K, 3.2 x 10⁻³ M).
Figure S22. UV/Vis spectrum of 8, β-PhCbl (H₂O, 6.3 x 10⁻⁵ M).