Electronic Supplementary Material (ESI) for Dalton Transactions


# Phenylvinylcobalamin: An alkylcobalamin featuring a ligand with a large trans influence

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# Electronic Supplementary Information

*References in this ESI are given at the end of the document and do not refer to the references in the main text.*

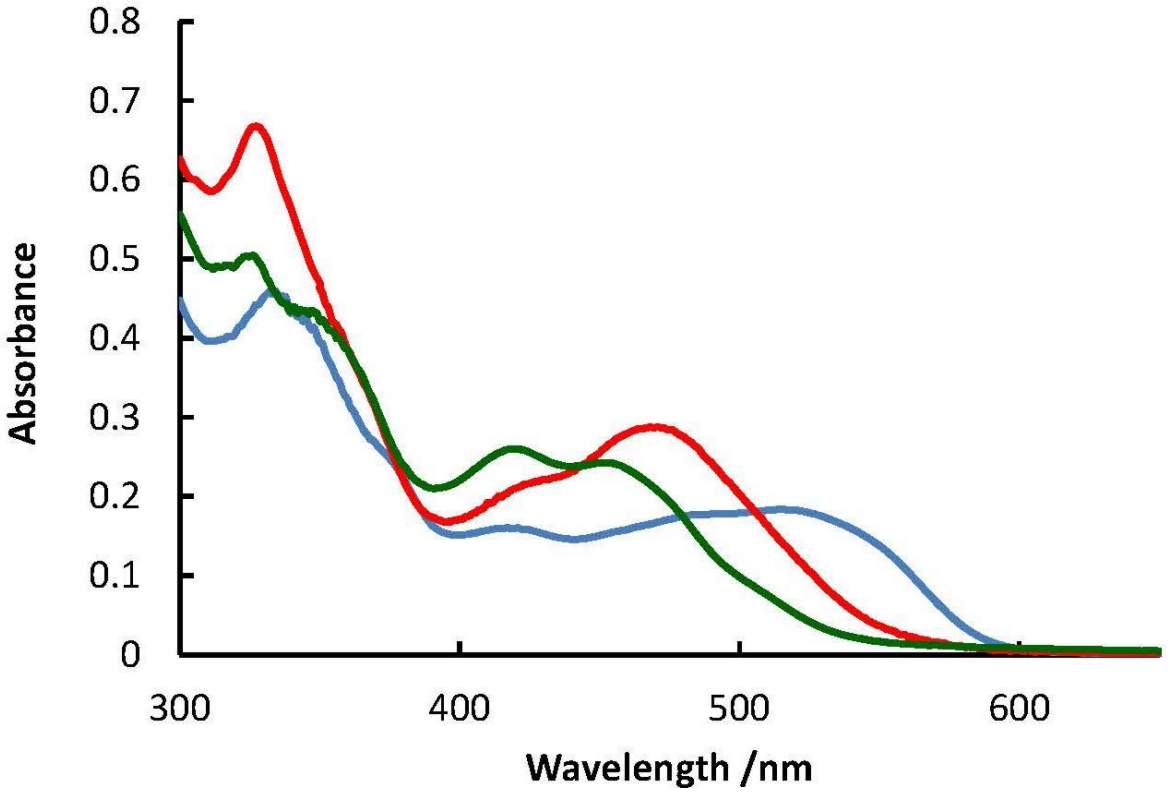


**Fig S1.** The UV-vis spectra of (blue line) *β*-PhVnCbl, pH 7.0 (base-on form); (green line), *β*-PhVnCbl, pH 1.5 (base-off form); and (red line) the putative *α*-PhVnCbl diastereomer. The concentration was determined after photolysis and conversion to dicyanocobalamin ($\varepsilon_{368}$ = 3.04 x $10^4$ $M^{-1}$ $s^{-1}$)[1] on treatment with excess cyanide.

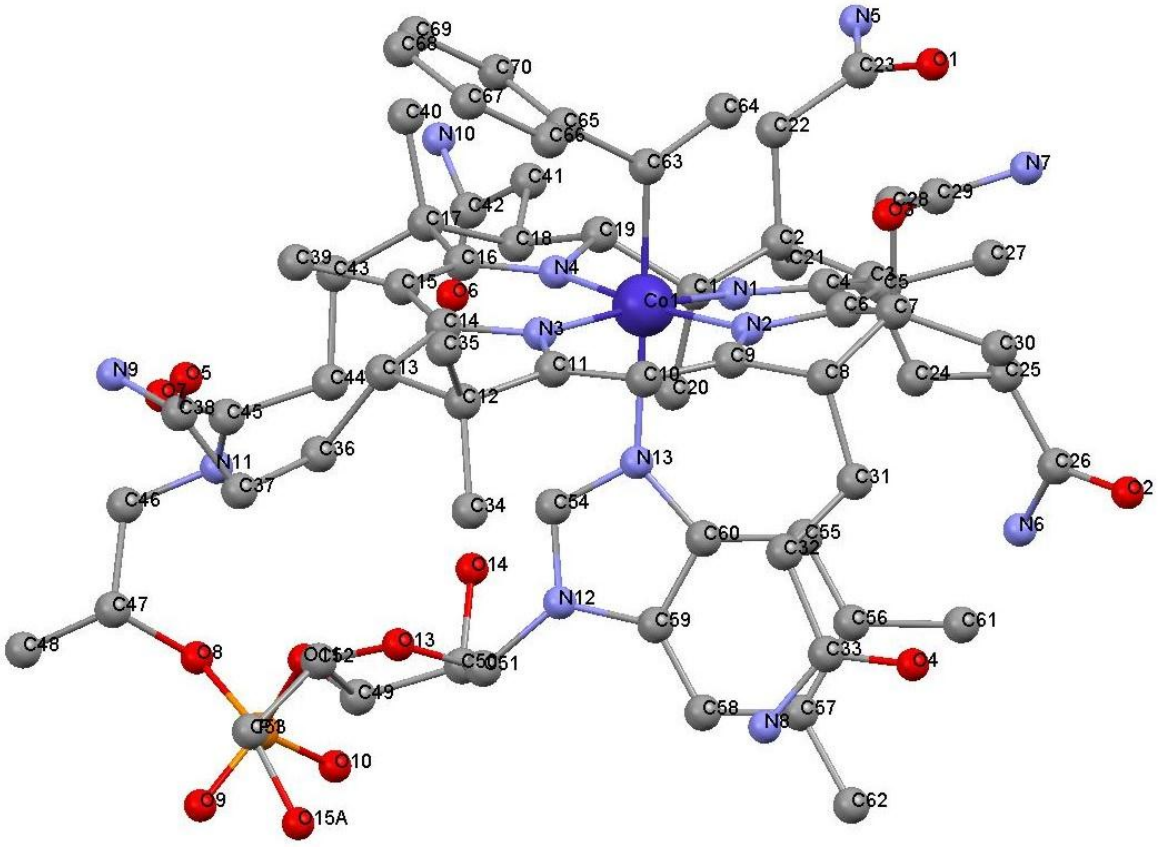


**Fig S2.** Crystallographic numbering scheme for PhVnCbl. There is an acetone solvent molecule in the structure. This, together with solvent water molecules and hydrogen atoms, have been omitted for clarity.

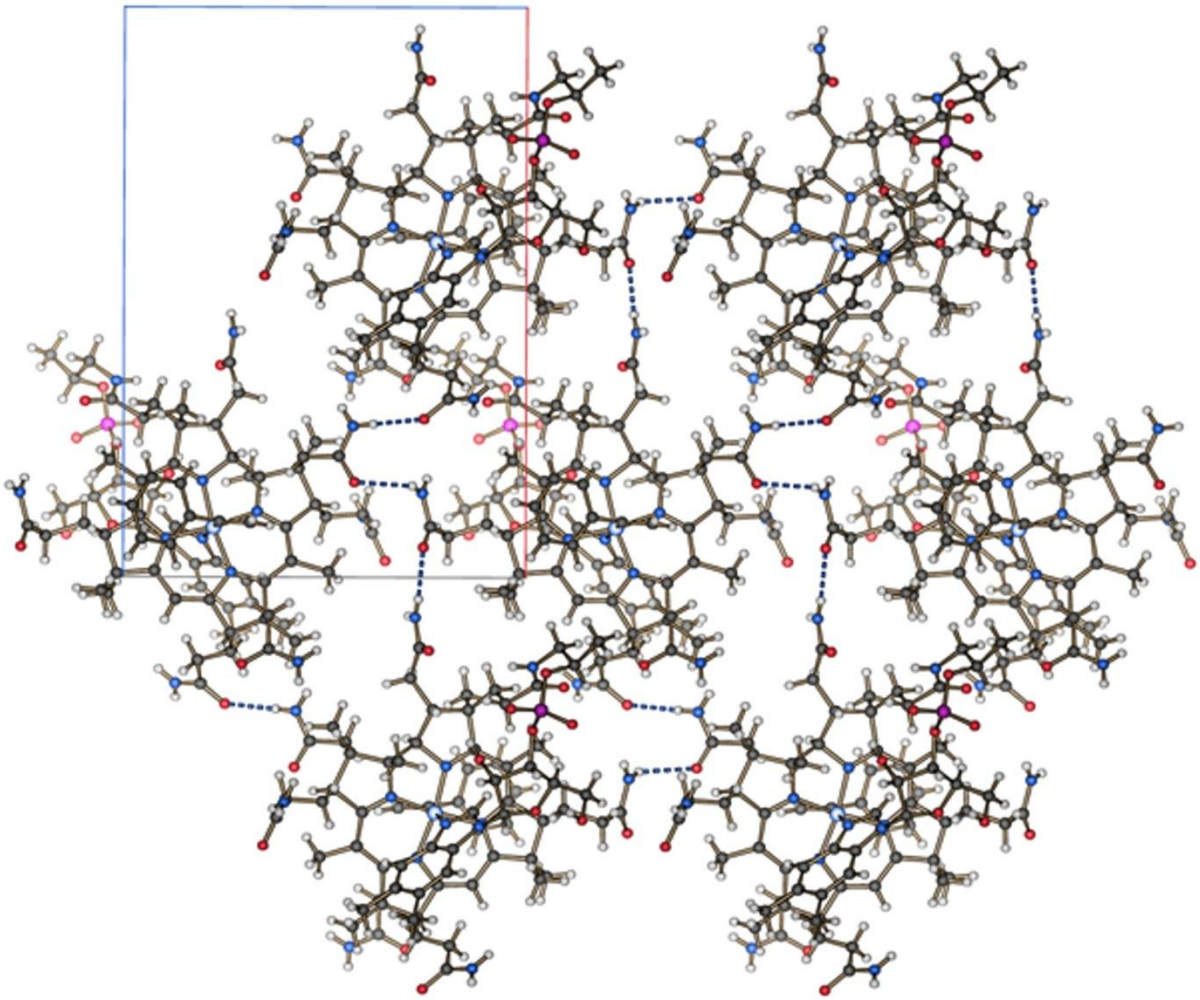

**Fig. S3.** Hydrogen bonding between Cobalamin molecules in the solid state structure of *β*-phenylvinylcobalamin. O1 of the *a* side chain amide hydrogen bonds to N9 of the *e* side chain amide of an neighbouring molecule (O···N = 2.987 Å); N7 of the *c* side chain amide hydrogen bonds to phosphate O10 of a neighbouring molecule (2.995 Å); O4 of the *d* amide is hydrogen bonded to amide N5 of the *a* side chain of a neighbour (2.949 Å); O5 of the amide of the *e* side chain is hydrogen bonded to N10 of a neighbouring *g* side chain amide (2.899 Å); and N6 of the *b* side chain is hydrogen bonded to a neighbouring phosphate O10 (2.964 Å). In addition, there are many hydrogen bonds between solvent water and the ribose OH groups, and the amides of the acetamide and the propionamide side chains of the corrin.

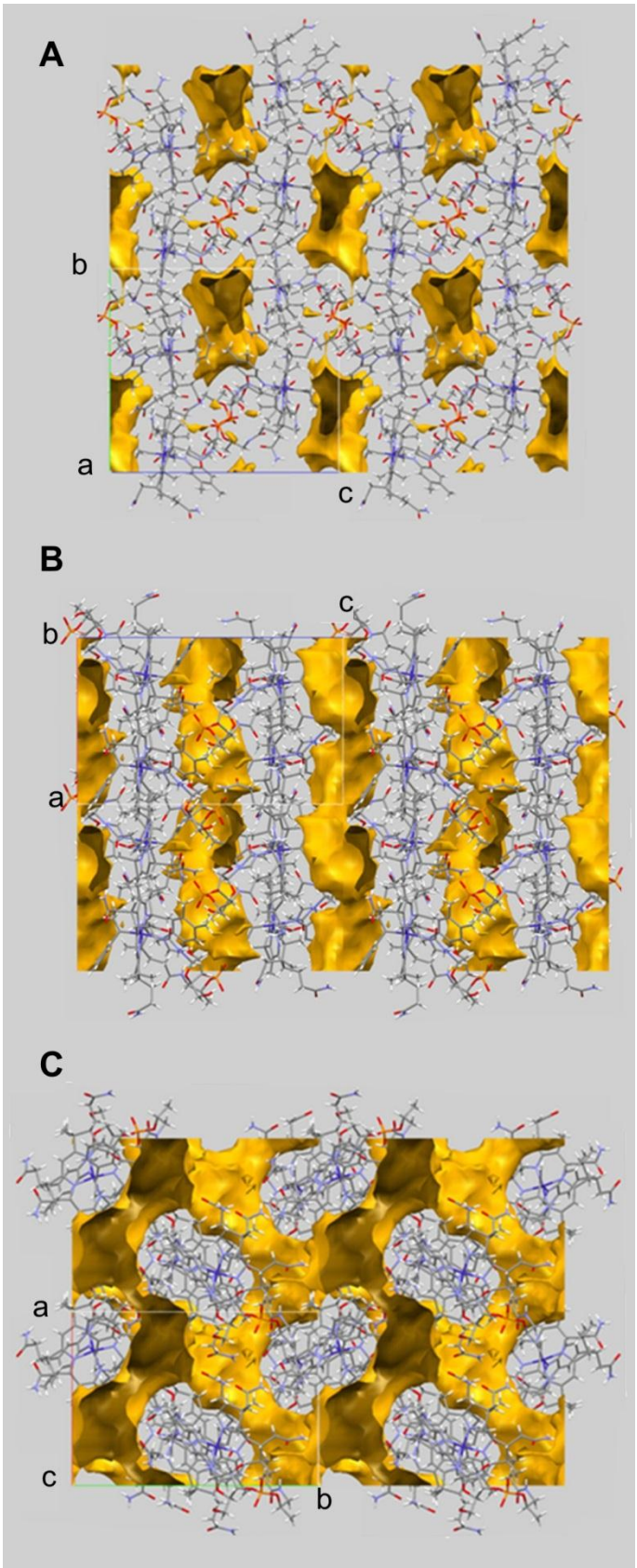


**Fig. S4.** Solvent voids in the structure of *β*-PACbl shown down that (A) *a*, (B) **b** and (C) *c* crystallographic axes.

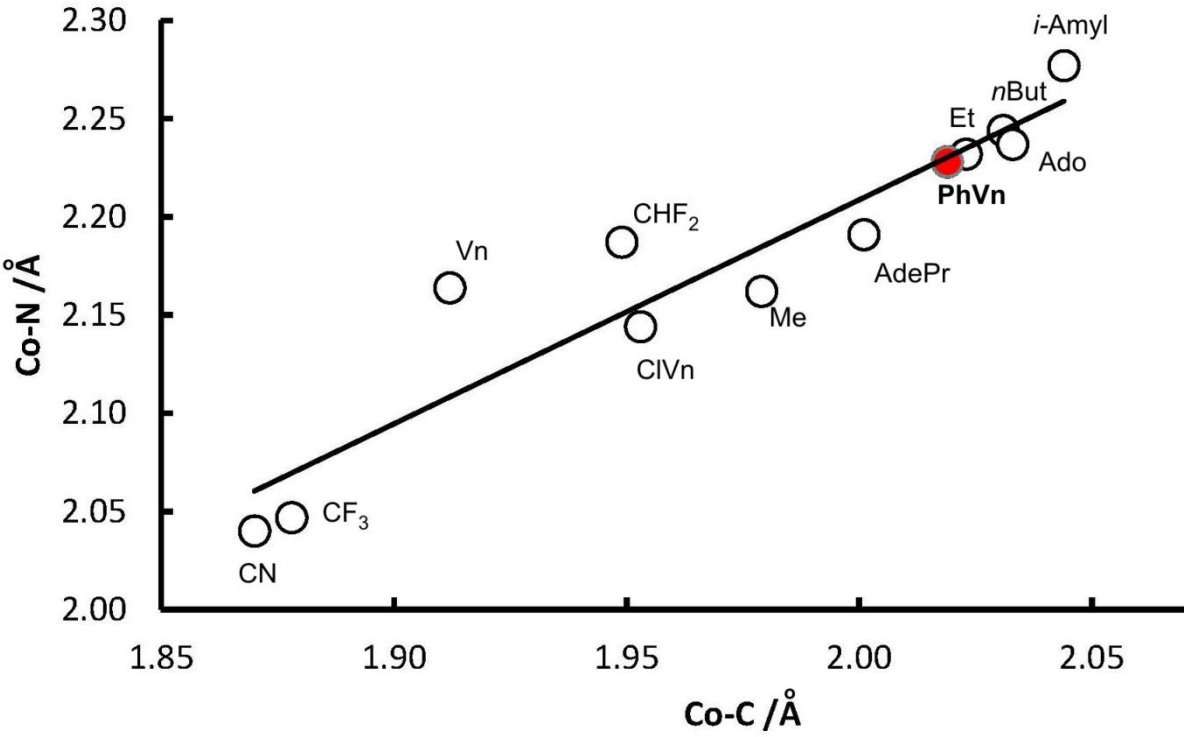


**Fig. S5**. The mutual dependence of the Co–C and the *trans* Co–$N_{dmbzm}$ bond lengths in alkylcobalamins. The data are given in Table S2 of this ESI.

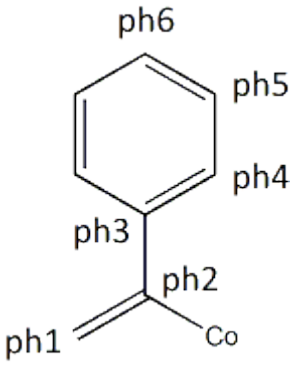


**Fig. S6.** Nomenclature used for the NMR assignments of the $^{1}$H spectrum of the phenylvinyl ligand in *ϑ*-PhVnCbl.

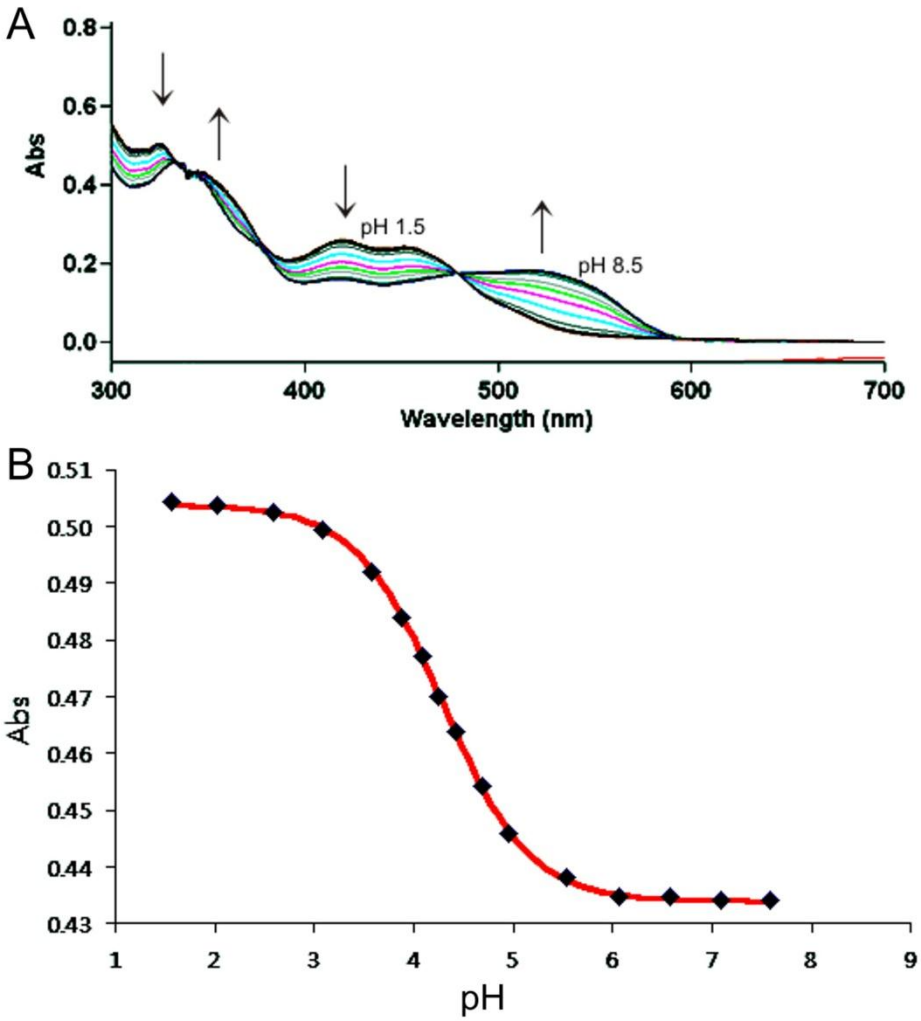


**Fig. S7.** Spectrophotometric titration of *β*–PhVnCbl in aqueous solution (25 mM phosphate, 25 °C). A: Spectroscopic changes observed across the uv-vis spectrum. B: Variation in absorbance at 326 nm as a function of pH. The solid line is a least squares fit to a standard ionisation isotherm $A = \frac{10^{-\mathrm{pH}} A_0 + 10^{-\mathrm{p}K_a} A_1}{10^{-\mathrm{pH}} + 10^{-\mathrm{p}K_a}}$ where $A$, $A_0$ and $A_1$ are the absorbance at intermediate, limiting low and limiting high pH values and p$K_a$ is the acid dissociation constant for the deprotonation of the free dmbzm base and its coordination by Co(III).

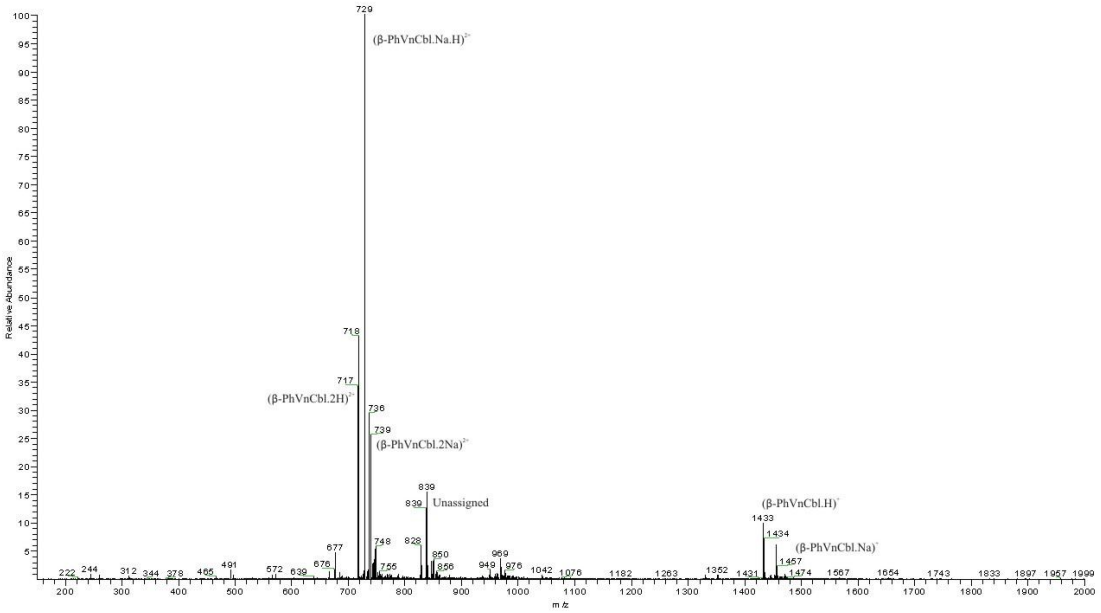


**Figure S8.** ESI-MS (positive mode) of β-PhVnCbl.

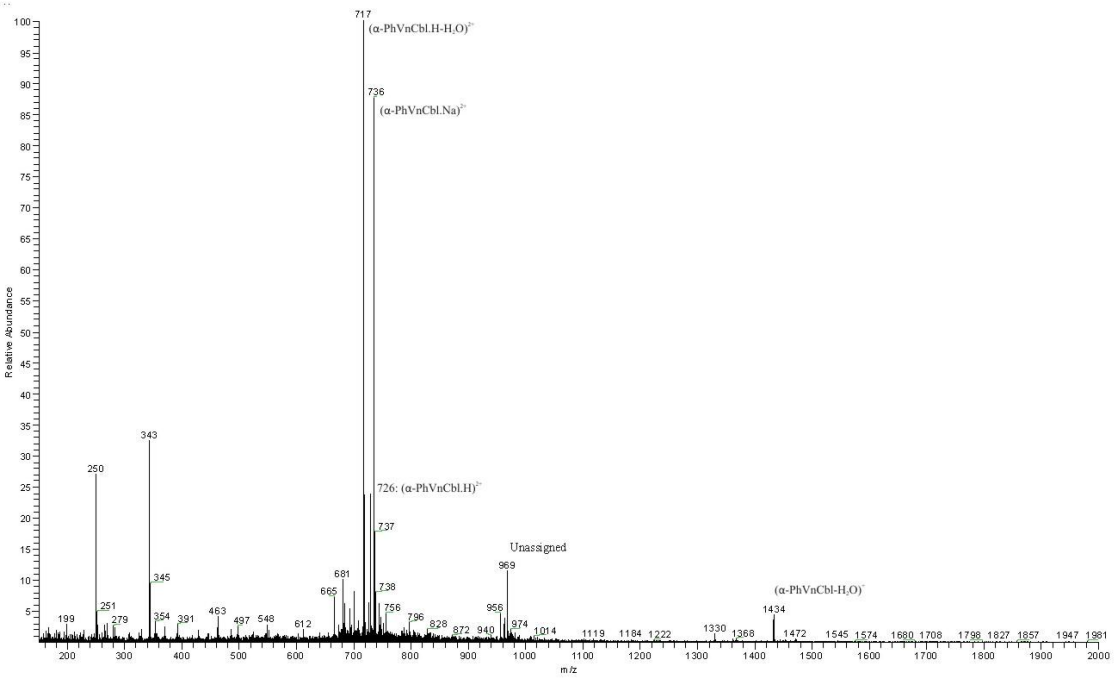


**Figure S9.** ESI-MS (positive mode) of α-PhVnCbl.

**Table S1**. $^{1}$H and $^{13}$C NMR Chemical Shift Assignments for PhVnCbl.[a]

| Atom[b] | $^{1}$H (ppm) | $^{13}$C (ppm) | Atom[b] | $^{1}$H (ppm) | $^{13}$C (ppm) | Atom[b] | $^{1}$H (ppm) | $^{13}$C (ppm) |
|---|---|---|---|---|---|---|---|---|
| C1 | - | 88.39 | C35 | 2.54 | 16.29 | Pr1'' | 3.45 | 46.38 |
| C2 | - | 47.30 | C36 | 1.82 | 19.95 | Pr2 | 4.32 | 73.17 |
| C3 | 4.55 | 56.50 | C37' | 1.72 | 42.99 | Pr3 | 1.18 | 19.99 |
| C4 | - | 178.60 | C37'' | 2.35 | 42.99 | R1 | 6.20 | 87.44 |
| C5 | - | 109.49 | C38 | - | n.a.[c] | R2 | 4.34 | 71.79 |
| C6 | - | 164.85 | C41' | 1.41 | 28.52 | R3 | 4.70 | 75.54 |
| C7 | - | 51.55 | C41'' | 2.01 | 28.52 | R4 | 4.18 | 84.13 |
| C8 | 3.95 | 55.45 | C42' | 1.83 | 33.74 | R5' | 3.69 | 62.49 |
| C9 | - | 173.53 | C42'' | 1.94 | 33.74 | R5'' | 3.78 | 62.49 |
| C10 | 6.50 | 97.82 | C43 | - | n.a.[c] | B2 | 7.61 | 143.24 |
| C11 | - | 177.07 | C46 | 0.94 | 31.37 | B4 | 6.82 | 119.52 |
| C12 | - | 48.17 | C47 | 1.35 | 23.28 | B5 | - | 134.20 |
| C13 | 2.89 | 53.55 | C48' | 2.09 | 34.68 | B6 | - | 132.80 |
| C14 | - | 164.53 | C48'' | 2.18 | 34.68 | B7 | 7.21 | 111.91 |
| C15 | - | 107.32 | C49' | 1.86 | 27.15 | B8 | - | 139.73 |
| C16 | - | 177.72 | C49'' | 2.08 | 27.15 | B9 | - | 132.38 |
| C17 | - | 60.14 | C50 | - | n.a.[c] | B10 | 2.27 | 20.61 |
| C18 | 2.83 | 41.03 | C53 | 2.33 | 16.89 | B11 | 2.25 | 20.43 |
| C19 | 4.40 | 76.10 | C54 | 1.54 | 19.48 | Ph1' | 3.01 | 118.07 |
| C20 | 0.52 | 23.64 | C55' | 1.86 | 33.88 | Ph1'' | 3.06 | 118.07 |
| C25 | 1.30 | 17.80 | C55'' | 2.50 | 33.88 | Ph2 | - | 143.24 |
| C26' | 2.13 | 43.06 | C56' | 1.98 | 32.56 | Ph3 | - | 148.93 |
| C26'' | 2.22 | 43.06 | C56'' | 2.36 | 32.56 | Ph4 | 6.04 | 127.39 |
| C27 | - | n.a.[c] | C57 | - | n.a.[c] | Ph5 | 6.87 | 128.31 |
| C30' | 1.87 | 27.62 | C60' | 2.58 | 33.14 | Ph6 | 7.05 | 127.39 |
| C30'' | 2.02 | 27.62 | C60'' | 2.65 | 33.14 | *f*H | 7.95 | - |
| C31 | 2.40 | 36.40 | C61 | - | n.a.[c] | | | |
| C32 | - | n.a.[c] | Pr1' | 3.06 | 46.38 | | | |

[a]In MeOD, at 25 °C. Chemical shifts are relative to internal TMS. [b]Primes and double primes denote downfield and upfield members, respectively, of pairs of diastereotopic methylene, or in the case of ph1, geminal protons. [c]Not assigned (the carbonyl carbons are clustered in a narrow region between 175 and 180 ppm, making reliable assignments problematic).

**Table S2.** $^{1}H$ and $^{13}C$ assignments and NMR correlations for the phenylvinyl group in PhVnCbl observed by COSY, ROESY, and HMBC spectroscopies[a].

| Resonance | $^{1}H$ (ppm) | $^{13}C$ (ppm) | COSY | ROESY | HMBC |
|---|---|---|---|---|---|
| ph1′ | 3.01 | 118.07 | - | C46, C54, C37′, C26′, C35, ph1′′, C19, C10, ph4 | ph2, ph3 |
| ph1″ | 3.06 | | - | C36, C37′, ph1′, ph4 | |
| ph2 | - | 143.24 | - | - | - |
| ph3 | - | 148.93 | - | - | - |
| ph4 | 6.04 | 127.39 | ph5, ph6 | C46, C54, C37′, C26′, C53, C35, ph1′′, C19, C10, ph5, ph6 | ph5, ph6, ph2 |
| ph5 | 6.87 | 128.31 | ph4, ph6 | C46, C54, C53, ph4, ph6 | ph4, ph6, ph3 |
| ph6 | 7.05 | 127.39 | ph5, ph4 | C46, C37′, ph4, ph5 | ph4, ph5 |

[a]Primes and double primes denote downfield and upfield members, respectively, of pairs of diastereotopic methylene, or in the case of ph1, geminal protons.

**Table S3.** Bond lengths [Å] and angles [°] for PhVnCbl

***Bond Lengths***

| | |
|---|---|
| C(1)-N(1) | 1.472(10) |
| C(1)-C(20) | 1.498(12) |
| C(1)-C(19) | 1.550(11) |
| C(1)-C(2) | 1.576(10) |
| C(2)-C(21) | 1.521(13) |
| C(2)-C(22) | 1.574(12) |
| C(2)-C(3) | 1.585(12) |
| C(3)-C(4) | 1.528(11) |
| C(3)-C(24) | 1.592(14) |
| C(3)-H(3) | 1.0000 |
| C(4)-N(1) | 1.281(9) |
| C(4)-C(5) | 1.443(12) |
| C(5)-C(6) | 1.350(11) |
| C(5)-C(27) | 1.534(11) |
| C(6)-N(2) | 1.375(9) |
| C(6)-C(7) | 1.552(12) |
| C(7)-C(30) | 1.553(11) |
| C(7)-C(8) | 1.558(11) |
| C(7)-C(28) | 1.585(13) |
| C(8)-C(31) | 1.502(12) |
| C(8)-C(9) | 1.521(11) |
| C(8)-H(8) | 1.0000 |
| C(9)-C(10) | 1.351(12) |
| C(9)-N(2) | 1.373(11) |
| C(10)-C(11) | 1.403(12) |
| C(10)-H(10) | 0.9500 |
| C(11)-N(3) | 1.352(11) |
| C(11)-C(12) | 1.483(11) |
| C(12)-C(34) | 1.536(14) |
| C(12)-C(35) | 1.537(13) |
| C(12)-C(13) | 1.575(11) |
| C(13)-C(36) | 1.532(13) |
| C(13)-C(14) | 1.545(10) |
| C(13)-H(13) | 1.0000 |
| C(14)-N(3) | 1.361(10) |
| C(14)-C(15) | 1.373(11) |
| C(15)-C(16) | 1.459(11) |
| C(15)-C(39) | 1.503(12) |
| C(16)-N(4) | 1.304(9) |
| C(16)-C(17) | 1.564(11) |
| C(17)-C(40) | 1.526(13) |
| C(17)-C(18) | 1.542(11) |
| C(17)-C(43) | 1.545(11) |
| C(18)-C(19) | 1.525(11) |
| C(18)-C(41) | 1.541(11) |
| C(18)-H(18) | 1.0000 |
| C(19)-N(4) | 1.488(10) |
| C(19)-H(19) | 1.0000 |
| C(20)-H(20A) | 0.9800 |
| C(20)-H(20B) | 0.9800 |
| C(20)-H(20C) | 0.9800 |
| C(21)-H(21A) | 0.9800 |
| C(21)-H(21B) | 0.9800 |
| C(21)-H(21C) | 0.9800 |
| C(22)-C(23) | 1.505(11) |
| C(22)-H(22A) | 0.9900 |
| C(22)-H(22B) | 0.9900 |
| C(23)-O(1) | 1.240(11) |
| C(23)-N(5) | 1.313(13) |
| C(24)-C(25) | 1.469(13) |
| C(24)-H(24A) | 0.9900 |
| C(24)-H(24B) | 0.9900 |
| C(25)-C(26) | 1.463(18) |
| C(25)-H(25A) | 0.9900 |
| C(25)-H(25B) | 0.9900 |
| C(26)-O(2) | 1.222(14) |
| C(26)-N(6) | 1.338(14) |
| C(27)-H(27A) | 0.9800 |
| C(27)-H(27B) | 0.9800 |
| C(27)-H(27C) | 0.9800 |
| C(28)-C(29) | 1.478(13) |
| C(28)-H(28A) | 0.9900 |
| C(28)-H(28B) | 0.9900 |
| C(29)-O(3) | 1.219(12) |
| C(29)-N(7) | 1.295(11) |
| C(30)-H(30A) | 0.9800 |
| C(30)-H(30B) | 0.9800 |
| C(30)-H(30C) | 0.9800 |
| C(31)-C(32) | 1.484(11) |
| C(31)-H(31A) | 0.9900 |
| C(31)-H(31B) | 0.9900 |
| C(32)-C(33) | 1.511(15) |
| C(32)-H(32A) | 0.9900 |
| C(32)-H(32B) | 0.9900 |
| C(33)-O(4) | 1.234(11) |
| C(33)-N(8) | 1.322(12) |
| C(34)-H(34A) | 0.9800 |
| C(34)-H(34B) | 0.9800 |
| C(34)-H(34C) | 0.9800 |
| C(35)-H(35A) | 0.9800 |
| C(35)-H(35B) | 0.9800 |
| C(35)-H(35C) | 0.9800 |
| C(36)-C(37) | 1.582(11) |
| C(36)-H(36A) | 0.9900 |
| C(36)-H(36B) | 0.9900 |
| C(37)-C(38) | 1.452(15) |
| C(37)-H(37A) | 0.9900 |
| C(37)-H(37B) | 0.9900 |
| C(38)-O(5) | 1.259(13) |
| C(38)-N(9) | 1.366(13) |
| C(39)-H(39A) | 0.9800 |
| C(39)-H(39B) | 0.9800 |
| C(39)-H(39C) | 0.9800 |
| C(40)-H(40A) | 0.9800 |
| C(40)-H(40B) | 0.9800 |
| C(40)-H(40C) | 0.9800 |

| | | | |
|---|---|---|---|
| C(41)-C(42) | 1.498(13) | C(61)-H(61A) | 0.9800 |
| C(41)-H(41A) | 0.9900 | C(61)-H(61B) | 0.9800 |
| C(41)-H(41B) | 0.9900 | C(61)-H(61C) | 0.9800 |
| C(42)-O(6) | 1.217(10) | C(62)-H(62A) | 0.9800 |
| C(42)-N(10) | 1.322(11) | C(62)-H(62B) | 0.9800 |
| C(43)-C(44) | 1.512(12) | C(62)-H(62C) | 0.9800 |
| C(43)-H(43A) | 0.9900 | C(63)-C(64) | 1.333(11) |
| C(43)-H(43B) | 0.9900 | C(63)-C(65) | 1.445(9) |
| C(44)-C(45) | 1.544(12) | C(63)-Co(1) | 2.019(9) |
| C(44)-H(44A) | 0.9900 | C(64)-H(64A) | 0.9500 |
| C(44)-H(44B) | 0.9900 | C(64)-H(64B) | 0.9500 |
| C(45)-O(7) | 1.224(10) | C(65)-C(66) | 1.3900 |
| C(45)-N(11) | 1.322(12) | C(65)-C(70) | 1.3900 |
| C(46)-N(11) | 1.456(11) | C(66)-C(67) | 1.3900 |
| C(46)-C(47) | 1.467(13) | C(66)-H(66) | 0.9500 |
| C(46)-H(46A) | 0.9900 | C(67)-C(68) | 1.3900 |
| C(46)-H(46B) | 0.9900 | C(67)-H(67) | 0.9500 |
| C(47)-O(8) | 1.453(11) | C(68)-C(69) | 1.3900 |
| C(47)-C(48) | 1.539(12) | C(68)-H(68) | 0.9500 |
| C(47)-H(47) | 1.0000 | C(69)-C(70) | 1.3900 |
| C(48)-H(48A) | 0.9800 | C(69)-H(69) | 0.9500 |
| C(48)-H(48B) | 0.9800 | C(70)-H(70) | 0.9500 |
| C(48)-H(48C) | 0.9800 | N(1)-Co(1) | 1.890(5) |
| C(49)-O(11) | 1.417(10) | N(2)-Co(1) | 1.903(6) |
| C(49)-C(50) | 1.509(11) | N(3)-Co(1) | 1.913(6) |
| C(49)-C(52) | 1.507(14) | N(4)-Co(1) | 1.879(6) |
| C(49)-H(49) | 1.0000 | N(5)-H(5A) | 0.8800 |
| C(50)-O(14) | 1.433(10) | N(5)-H(5B) | 0.8800 |
| C(50)-C(51) | 1.512(13) | N(6)-H(6A) | 0.8800 |
| C(50)-H(50) | 1.0000 | N(6)-H(6B) | 0.8800 |
| C(51)-O(13) | 1.393(10) | N(7)-H(7A) | 0.8800 |
| C(51)-N(12) | 1.458(10) | N(7)-H(7B) | 0.8800 |
| C(51)-H(51) | 1.0000 | N(8)-H(8A) | 0.8800 |
| C(52)-O(13) | 1.409(11) | N(8)-H(8B) | 0.8800 |
| C(52)-C(53) | 1.509(14) | N(9)-H(9A) | 0.8800 |
| C(52)-H(52) | 1.0000 | N(9)-H(9B) | 0.8800 |
| C(53)-O(15A) | 1.495(13) | N(10)-H(10A) | 0.8800 |
| C(53)-O(15B) | 1.497(13) | N(10)-H(10B) | 0.8800 |
| C(53)-H(53A) | 0.9900 | N(11)-H(11) | 0.8800 |
| C(53)-H(53B) | 0.9900 | N(13)-Co(1) | 2.224(7) |
| C(53)-H(53C) | 0.9700 | O(8)-P(1) | 1.579(6) |
| C(53)-H(53D) | 0.9700 | O(9)-P(1) | 1.475(7) |
| C(54)-N(13) | 1.302(9) | O(10)-P(1) | 1.457(7) |
| C(54)-N(12) | 1.341(10) | O(11)-P(1) | 1.591(6) |
| C(54)-H(54) | 0.9500 | O(14)-H(14) | 0.8400 |
| C(55)-C(56) | 1.360(13) | O(15A)-H(53C) | 0.7744 |
| C(55)-C(60) | 1.405(11) | O(15A)-H(15A) | 0.8400 |
| C(55)-H(55) | 0.9500 | O(15B)-H(15B) | 0.8200 |
| C(56)-C(57) | 1.442(13) | C(1A)-C(2A) | 1.438(19) |
| C(56)-C(61) | 1.525(13) | C(1A)-H(1A) | 0.9800 |
| C(57)-C(58) | 1.372(12) | C(1A)-H(1B) | 0.9800 |
| C(57)-C(62) | 1.484(14) | C(1A)-H(1C) | 0.9800 |
| C(58)-C(59) | 1.394(12) | C(2A)-O(1A) | 1.247(15) |
| C(58)-H(58) | 0.9500 | C(2A)-C(3A) | 1.44(2) |
| C(59)-C(60) | 1.355(11) | C(3A)-H(3A) | 0.9800 |
| C(59)-N(12) | 1.384(10) | C(3A)-H(3B) | 0.9800 |
| C(60)-N(13) | 1.408(10) | C(3A)-H(3C) | 0.9800 |

***Bond angles***

| | |
|---|---|
| N(1)-C(1)-C(20) | 111.9(7) |
| N(1)-C(1)-C(19) | 102.5(6) |
| C(20)-C(1)-C(19) | 109.8(6) |
| N(1)-C(1)-C(2) | 101.8(6) |
| C(20)-C(1)-C(2) | 112.4(7) |
| C(19)-C(1)-C(2) | 117.7(7) |
| C(21)-C(2)-C(22) | 109.1(7) |
| C(21)-C(2)-C(1) | 119.3(7) |
| C(22)-C(2)-C(1) | 109.0(6) |
| C(21)-C(2)-C(3) | 111.7(7) |
| C(22)-C(2)-C(3) | 105.6(7) |
| C(1)-C(2)-C(3) | 101.2(6) |
| C(4)-C(3)-C(2) | 99.9(6) |
| C(4)-C(3)-C(24) | 109.5(7) |
| C(2)-C(3)-C(24) | 117.0(7) |
| C(4)-C(3)-H(3) | 110.0 |
| C(2)-C(3)-H(3) | 110.0 |
| C(24)-C(3)-H(3) | 110.0 |
| N(1)-C(4)-C(5) | 125.2(7) |
| N(1)-C(4)-C(3) | 112.2(7) |
| C(5)-C(4)-C(3) | 122.6(6) |
| C(6)-C(5)-C(4) | 120.5(6) |
| C(6)-C(5)-C(27) | 123.1(7) |
| C(4)-C(5)-C(27) | 116.4(7) |
| C(5)-C(6)-N(2) | 124.3(7) |
| C(5)-C(6)-C(7) | 127.3(6) |
| N(2)-C(6)-C(7) | 108.4(7) |
| C(30)-C(7)-C(6) | 115.6(7) |
| C(30)-C(7)-C(8) | 111.7(7) |
| C(6)-C(7)-C(8) | 101.4(6) |
| C(30)-C(7)-C(28) | 109.2(7) |
| C(6)-C(7)-C(28) | 106.2(7) |
| C(8)-C(7)-C(28) | 112.6(7) |
| C(31)-C(8)-C(9) | 112.8(7) |
| C(31)-C(8)-C(7) | 114.3(7) |
| C(9)-C(8)-C(7) | 100.7(6) |
| C(31)-C(8)-H(8) | 109.5 |
| C(9)-C(8)-H(8) | 109.5 |
| C(7)-C(8)-H(8) | 109.5 |
| C(10)-C(9)-N(2) | 126.6(8) |
| C(10)-C(9)-C(8) | 122.8(8) |
| N(2)-C(9)-C(8) | 110.5(6) |
| C(9)-C(10)-C(11) | 127.3(8) |
| C(9)-C(10)-H(10) | 116.4 |
| C(11)-C(10)-H(10) | 116.4 |
| N(3)-C(11)-C(10) | 123.4(7) |
| N(3)-C(11)-C(12) | 114.0(7) |
| C(10)-C(11)-C(12) | 122.6(8) |
| C(11)-C(12)-C(34) | 106.8(7) |
| C(11)-C(12)-C(35) | 113.1(7) |
| C(34)-C(12)-C(35) | 110.7(7) |
| C(11)-C(12)-C(13) | 102.6(6) |
| C(34)-C(12)-C(13) | 113.3(8) |
| C(35)-C(12)-C(13) | 110.1(7) |
| C(36)-C(13)-C(14) | 111.3(7) |
| C(36)-C(13)-C(12) | 117.1(7) |
| C(14)-C(13)-C(12) | 102.0(6) |
| C(36)-C(13)-H(13) | 108.7 |
| C(14)-C(13)-H(13) | 108.7 |
| C(12)-C(13)-H(13) | 108.7 |
| N(3)-C(14)-C(15) | 127.2(6) |
| N(3)-C(14)-C(13) | 111.0(6) |
| C(15)-C(14)-C(13) | 121.7(6) |
| C(14)-C(15)-C(16) | 119.6(7) |
| C(14)-C(15)-C(39) | 119.9(7) |
| C(16)-C(15)-C(39) | 120.3(7) |
| N(4)-C(16)-C(15) | 122.7(7) |
| N(4)-C(16)-C(17) | 110.8(6) |
| C(15)-C(16)-C(17) | 126.4(6) |
| C(40)-C(17)-C(18) | 110.8(7) |
| C(40)-C(17)-C(43) | 108.7(7) |
| C(18)-C(17)-C(43) | 112.8(7) |
| C(40)-C(17)-C(16) | 109.5(7) |
| C(18)-C(17)-C(16) | 99.6(6) |
| C(43)-C(17)-C(16) | 115.1(6) |
| C(19)-C(18)-C(41) | 113.2(6) |
| C(19)-C(18)-C(17) | 104.0(6) |
| C(41)-C(18)-C(17) | 117.2(7) |
| C(19)-C(18)-H(18) | 107.3 |
| C(41)-C(18)-H(18) | 107.3 |
| C(17)-C(18)-H(18) | 107.3 |
| N(4)-C(19)-C(18) | 101.8(5) |
| N(4)-C(19)-C(1) | 105.3(6) |
| C(18)-C(19)-C(1) | 121.9(7) |
| N(4)-C(19)-H(19) | 109.0 |
| C(18)-C(19)-H(19) | 109.0 |
| C(1)-C(19)-H(19) | 109.0 |
| C(1)-C(20)-H(20A) | 109.5 |
| C(1)-C(20)-H(20B) | 109.5 |
| H(20A)-C(20)-H(20B) | 109.5 |
| C(1)-C(20)-H(20C) | 109.5 |
| H(20A)-C(20)-H(20C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 |
| C(2)-C(21)-H(21A) | 109.5 |
| C(2)-C(21)-H(21B) | 109.5 |
| H(21A)-C(21)-H(21B) | 109.5 |
| C(2)-C(21)-H(21C) | 109.5 |
| H(21A)-C(21)-H(21C) | 109.5 |
| H(21B)-C(21)-H(21C) | 109.5 |
| C(23)-C(22)-C(2) | 118.5(7) |
| C(23)-C(22)-H(22A) | 107.7 |
| C(2)-C(22)-H(22A) | 107.7 |
| C(23)-C(22)-H(22B) | 107.7 |
| C(2)-C(22)-H(22B) | 107.7 |
| H(22A)-C(22)-H(22B) | 107.1 |
| O(1)-C(23)-N(5) | 120.4(8) |
| O(1)-C(23)-C(22) | 122.4(9) |
| N(5)-C(23)-C(22) | 117.1(9) |
| C(25)-C(24)-C(3) | 115.6(9) |
| C(25)-C(24)-H(24A) | 108.4 |
| C(3)-C(24)-H(24A) | 108.4 |
| C(25)-C(24)-H(24B) | 108.4 |

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| C(3)-C(24)-H(24B) | 108.4 |
| H(24A)-C(24)-H(24B) | 107.4 |
| C(26)-C(25)-C(24) | 113.4(11) |
| C(26)-C(25)-H(25A) | 108.9 |
| C(24)-C(25)-H(25A) | 108.9 |
| C(26)-C(25)-H(25B) | 108.9 |
| C(24)-C(25)-H(25B) | 108.9 |
| H(25A)-C(25)-H(25B) | 107.7 |
| O(2)-C(26)-N(6) | 116.1(11) |
| O(2)-C(26)-C(25) | 128.4(12) |
| N(6)-C(26)-C(25) | 115.6(11) |
| C(5)-C(27)-H(27A) | 109.5 |
| C(5)-C(27)-H(27B) | 109.5 |
| H(27A)-C(27)-H(27B) | 109.5 |
| C(5)-C(27)-H(27C) | 109.5 |
| H(27A)-C(27)-H(27C) | 109.5 |
| H(27B)-C(27)-H(27C) | 109.5 |
| C(29)-C(28)-C(7) | 111.1(8) |
| C(29)-C(28)-H(28A) | 109.4 |
| C(7)-C(28)-H(28A) | 109.4 |
| C(29)-C(28)-H(28B) | 109.4 |
| C(7)-C(28)-H(28B) | 109.4 |
| H(28A)-C(28)-H(28B) | 108.0 |
| O(3)-C(29)-N(7) | 122.6(9) |
| O(3)-C(29)-C(28) | 119.4(9) |
| N(7)-C(29)-C(28) | 117.9(9) |
| C(7)-C(30)-H(30A) | 109.5 |
| C(7)-C(30)-H(30B) | 109.5 |
| H(30A)-C(30)-H(30B) | 109.5 |
| C(7)-C(30)-H(30C) | 109.5 |
| H(30A)-C(30)-H(30C) | 109.5 |
| H(30B)-C(30)-H(30C) | 109.5 |
| C(32)-C(31)-C(8) | 117.3(7) |
| C(32)-C(31)-H(31A) | 108.0 |
| C(8)-C(31)-H(31A) | 108.0 |
| C(32)-C(31)-H(31B) | 108.0 |
| C(8)-C(31)-H(31B) | 108.0 |
| H(31A)-C(31)-H(31B) | 107.2 |
| C(31)-C(32)-C(33) | 113.7(7) |
| C(31)-C(32)-H(32A) | 108.8 |
| C(33)-C(32)-H(32A) | 108.8 |
| C(31)-C(32)-H(32B) | 108.8 |
| C(33)-C(32)-H(32B) | 108.8 |
| H(32A)-C(32)-H(32B) | 107.7 |
| O(4)-C(33)-N(8) | 121.8(10) |
| O(4)-C(33)-C(32) | 120.7(8) |
| N(8)-C(33)-C(32) | 117.5(8) |
| C(12)-C(34)-H(34A) | 109.5 |
| C(12)-C(34)-H(34B) | 109.5 |
| H(34A)-C(34)-H(34B) | 109.5 |
| C(12)-C(34)-H(34C) | 109.5 |
| H(34A)-C(34)-H(34C) | 109.5 |
| H(34B)-C(34)-H(34C) | 109.5 |
| C(12)-C(35)-H(35A) | 109.5 |
| C(12)-C(35)-H(35B) | 109.5 |
| H(35A)-C(35)-H(35B) | 109.5 |
| C(12)-C(35)-H(35C) | 109.5 |
| H(35A)-C(35)-H(35C) | 109.5 |
| H(35B)-C(35)-H(35C) | 109.5 |
| C(13)-C(36)-C(37) | 114.3(8) |
| C(13)-C(36)-H(36A) | 108.7 |
| C(37)-C(36)-H(36A) | 108.7 |
| C(13)-C(36)-H(36B) | 108.7 |
| C(37)-C(36)-H(36B) | 108.7 |
| H(36A)-C(36)-H(36B) | 107.6 |
| C(38)-C(37)-C(36) | 112.8(8) |
| C(38)-C(37)-H(37A) | 109.0 |
| C(36)-C(37)-H(37A) | 109.0 |
| C(38)-C(37)-H(37B) | 109.0 |
| C(36)-C(37)-H(37B) | 109.0 |
| H(37A)-C(37)-H(37B) | 107.8 |
| O(5)-C(38)-N(9) | 119.4(10) |
| O(5)-C(38)-C(37) | 123.5(9) |
| N(9)-C(38)-C(37) | 117.1(11) |
| C(15)-C(39)-H(39A) | 109.5 |
| C(15)-C(39)-H(39B) | 109.5 |
| H(39A)-C(39)-H(39B) | 109.5 |
| C(15)-C(39)-H(39C) | 109.5 |
| H(39A)-C(39)-H(39C) | 109.5 |
| H(39B)-C(39)-H(39C) | 109.5 |
| C(17)-C(40)-H(40A) | 109.5 |
| C(17)-C(40)-H(40B) | 109.5 |
| H(40A)-C(40)-H(40B) | 109.5 |
| C(17)-C(40)-H(40C) | 109.5 |
| H(40A)-C(40)-H(40C) | 109.5 |
| H(40B)-C(40)-H(40C) | 109.5 |
| C(42)-C(41)-C(18) | 115.3(7) |
| C(42)-C(41)-H(41A) | 108.5 |
| C(18)-C(41)-H(41A) | 108.5 |
| C(42)-C(41)-H(41B) | 108.5 |
| C(18)-C(41)-H(41B) | 108.5 |
| H(41A)-C(41)-H(41B) | 107.5 |
| O(6)-C(42)-N(10) | 121.3(9) |
| O(6)-C(42)-C(41) | 121.7(8) |
| N(10)-C(42)-C(41) | 116.8(8) |
| C(44)-C(43)-C(17) | 118.1(7) |
| C(44)-C(43)-H(43A) | 107.8 |
| C(17)-C(43)-H(43A) | 107.8 |
| C(44)-C(43)-H(43B) | 107.8 |
| C(17)-C(43)-H(43B) | 107.8 |
| H(43A)-C(43)-H(43B) | 107.1 |
| C(43)-C(44)-C(45) | 110.0(7) |
| C(43)-C(44)-H(44A) | 109.7 |
| C(45)-C(44)-H(44A) | 109.7 |
| C(43)-C(44)-H(44B) | 109.7 |
| C(45)-C(44)-H(44B) | 109.7 |
| H(44A)-C(44)-H(44B) | 108.2 |
| O(7)-C(45)-N(11) | 125.2(8) |
| O(7)-C(45)-C(44) | 119.3(8) |
| N(11)-C(45)-C(44) | 115.6(7) |
| N(11)-C(46)-C(47) | 113.3(7) |
| N(11)-C(46)-H(46A) | 108.9 |
| C(47)-C(46)-H(46A) | 108.9 |
| N(11)-C(46)-H(46B) | 108.9 |

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| C(47)-C(46)-H(46B) | 108.9 | N(13)-C(54)-H(54) | 123.2 |
| H(46A)-C(46)-H(46B) | 107.7 | N(12)-C(54)-H(54) | 123.2 |
| O(8)-C(47)-C(46) | 107.3(7) | C(56)-C(55)-C(60) | 118.0(8) |
| O(8)-C(47)-C(48) | 107.9(8) | C(56)-C(55)-H(55) | 121.0 |
| C(46)-C(47)-C(48) | 111.4(8) | C(60)-C(55)-H(55) | 121.0 |
| O(8)-C(47)-H(47) | 110.0 | C(55)-C(56)-C(57) | 121.8(8) |
| C(46)-C(47)-H(47) | 110.0 | C(55)-C(56)-C(61) | 120.8(9) |
| C(48)-C(47)-H(47) | 110.0 | C(57)-C(56)-C(61) | 117.4(8) |
| C(47)-C(48)-H(48A) | 109.5 | C(58)-C(57)-C(56) | 118.3(8) |
| C(47)-C(48)-H(48B) | 109.5 | C(58)-C(57)-C(62) | 119.8(8) |
| H(48A)-C(48)-H(48B) | 109.5 | C(56)-C(57)-C(62) | 121.8(8) |
| C(47)-C(48)-H(48C) | 109.5 | C(57)-C(58)-C(59) | 118.5(8) |
| H(48A)-C(48)-H(48C) | 109.5 | C(57)-C(58)-H(58) | 120.7 |
| H(48B)-C(48)-H(48C) | 109.5 | C(59)-C(58)-H(58) | 120.7 |
| O(11)-C(49)-C(50) | 113.8(7) | C(60)-C(59)-N(12) | 106.3(7) |
| O(11)-C(49)-C(52) | 112.6(7) | C(60)-C(59)-C(58) | 122.5(7) |
| C(50)-C(49)-C(52) | 104.0(7) | N(12)-C(59)-C(58) | 131.2(7) |
| O(11)-C(49)-H(49) | 108.7 | C(59)-C(60)-C(55) | 120.2(8) |
| C(50)-C(49)-H(49) | 108.7 | C(59)-C(60)-N(13) | 109.4(7) |
| C(52)-C(49)-H(49) | 108.7 | C(55)-C(60)-N(13) | 130.4(7) |
| O(14)-C(50)-C(51) | 108.6(7) | C(56)-C(61)-H(61A) | 109.5 |
| O(14)-C(50)-C(49) | 110.6(7) | C(56)-C(61)-H(61B) | 109.5 |
| C(51)-C(50)-C(49) | 101.2(6) | H(61A)-C(61)-H(61B) | 109.5 |
| O(14)-C(50)-H(50) | 112.0 | C(56)-C(61)-H(61C) | 109.5 |
| C(51)-C(50)-H(50) | 112.0 | H(61A)-C(61)-H(61C) | 109.5 |
| C(49)-C(50)-H(50) | 112.0 | H(61B)-C(61)-H(61C) | 109.5 |
| O(13)-C(51)-N(12) | 108.9(7) | C(57)-C(62)-H(62A) | 109.5 |
| O(13)-C(51)-C(50) | 107.4(7) | C(57)-C(62)-H(62B) | 109.5 |
| N(12)-C(51)-C(50) | 114.4(7) | H(62A)-C(62)-H(62B) | 109.5 |
| O(13)-C(51)-H(51) | 108.7 | C(57)-C(62)-H(62C) | 109.5 |
| N(12)-C(51)-H(51) | 108.7 | H(62A)-C(62)-H(62C) | 109.5 |
| C(50)-C(51)-H(51) | 108.7 | H(62B)-C(62)-H(62C) | 109.5 |
| O(13)-C(52)-C(53) | 109.4(8) | C(64)-C(63)-C(65) | 118.9(8) |
| O(13)-C(52)-C(49) | 107.6(7) | C(64)-C(63)-Co(1) | 121.6(6) |
| C(53)-C(52)-C(49) | 115.4(8) | C(65)-C(63)-Co(1) | 119.5(5) |
| O(13)-C(52)-H(52) | 108.1 | C(63)-C(64)-H(64A) | 120.0 |
| C(53)-C(52)-H(52) | 108.1 | C(63)-C(64)-H(64B) | 120.0 |
| C(49)-C(52)-H(52) | 108.1 | H(64A)-C(64)-H(64B) | 120.0 |
| O(15A)-C(53)-O(15B) | 130.3(18) | C(66)-C(65)-C(70) | 120.0 |
| O(15A)-C(53)-C(52) | 108.4(7) | C(66)-C(65)-C(63) | 120.9(6) |
| O(15B)-C(53)-C(52) | 108.0(8) | C(70)-C(65)-C(63) | 119.1(5) |
| O(15A)-C(53)-H(53A) | 110.0 | C(65)-C(66)-C(67) | 120.0 |
| C(52)-C(53)-H(53A) | 110.0 | C(65)-C(66)-H(66) | 120.0 |
| O(15A)-C(53)-H(53B) | 110.0 | C(67)-C(66)-H(66) | 120.0 |
| O(15B)-C(53)-H(53B) | 87.6 | C(68)-C(67)-C(66) | 120.0 |
| C(52)-C(53)-H(53B) | 110.0 | C(68)-C(67)-H(67) | 120.0 |
| H(53A)-C(53)-H(53B) | 108.4 | C(66)-C(67)-H(67) | 120.0 |
| O(15B)-C(53)-H(53C) | 106.3 | C(67)-C(68)-C(69) | 120.0 |
| C(52)-C(53)-H(53C) | 111.8 | C(67)-C(68)-H(68) | 120.0 |
| H(53A)-C(53)-H(53C) | 83.9 | C(69)-C(68)-H(68) | 120.0 |
| H(53B)-C(53)-H(53C) | 128.5 | C(70)-C(69)-C(68) | 120.0 |
| O(15A)-C(53)-H(53D) | 87.7 | C(70)-C(69)-H(69) | 120.0 |
| O(15B)-C(53)-H(53D) | 108.6 | C(68)-C(69)-H(69) | 120.0 |
| C(52)-C(53)-H(53D) | 111.9 | C(69)-C(70)-C(65) | 120.0 |
| H(53A)-C(53)-H(53D) | 125.7 | C(69)-C(70)-H(70) | 120.0 |
| H(53C)-C(53)-H(53D) | 110.0 | C(65)-C(70)-H(70) | 120.0 |
| N(13)-C(54)-N(12) | 113.5(7) | C(4)-N(1)-C(1) | 113.4(6) |

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| C(4)-N(1)-Co(1) | 130.0(6) | C(50)-O(14)-H(14) | 109.5 |
| C(1)-N(1)-Co(1) | 116.6(4) | C(53)-O(15A)-H(15A) | 109.5 |
| C(9)-N(2)-C(6) | 110.8(7) | H(53C)-O(15A)-H(15A) | 74.9 |
| C(9)-N(2)-Co(1) | 121.1(5) | C(53)-O(15B)-H(15B) | 103.1 |
| C(6)-N(2)-Co(1) | 127.7(6) | O(10)-P(1)-O(9) | 116.9(4) |
| C(11)-N(3)-C(14) | 109.9(6) | O(10)-P(1)-O(8) | 106.3(4) |
| C(11)-N(3)-Co(1) | 123.3(5) | O(9)-P(1)-O(8) | 112.9(4) |
| C(14)-N(3)-Co(1) | 126.7(5) | O(10)-P(1)-O(11) | 109.9(4) |
| C(16)-N(4)-C(19) | 111.8(6) | O(9)-P(1)-O(11) | 109.5(4) |
| C(16)-N(4)-Co(1) | 132.6(5) | O(8)-P(1)-O(11) | 99.9(3) |
| C(19)-N(4)-Co(1) | 114.8(4) | N(4)-Co(1)-N(1) | 82.9(3) |
| C(23)-N(5)-H(5A) | 120.0 | N(4)-Co(1)-N(2) | 171.6(3) |
| C(23)-N(5)-H(5B) | 120.0 | N(1)-Co(1)-N(2) | 89.4(3) |
| H(5A)-N(5)-H(5B) | 120.0 | N(4)-Co(1)-N(3) | 90.2(3) |
| C(26)-N(6)-H(6A) | 120.0 | N(1)-Co(1)-N(3) | 168.7(3) |
| C(26)-N(6)-H(6B) | 120.0 | N(2)-Co(1)-N(3) | 98.0(3) |
| H(6A)-N(6)-H(6B) | 120.0 | N(4)-Co(1)-C(63) | 89.3(3) |
| C(29)-N(7)-H(7A) | 120.0 | N(1)-Co(1)-C(63) | 96.9(3) |
| C(29)-N(7)-H(7B) | 120.0 | N(2)-Co(1)-C(63) | 88.5(3) |
| H(7A)-N(7)-H(7B) | 120.0 | N(3)-Co(1)-C(63) | 91.9(3) |
| C(33)-N(8)-H(8A) | 120.0 | N(4)-Co(1)-N(13) | 94.3(3) |
| C(33)-N(8)-H(8B) | 120.0 | N(1)-Co(1)-N(13) | 88.8(3) |
| H(8A)-N(8)-H(8B) | 120.0 | N(2)-Co(1)-N(13) | 88.7(3) |
| C(38)-N(9)-H(9A) | 120.0 | N(3)-Co(1)-N(13) | 82.9(3) |
| C(38)-N(9)-H(9B) | 120.0 | C(63)-Co(1)-N(13) | 173.6(3) |
| H(9A)-N(9)-H(9B) | 120.0 | C(2A)-C(1A)-H(1A) | 109.5 |
| C(42)-N(10)-H(10A) | 120.0 | C(2A)-C(1A)-H(1B) | 109.5 |
| C(42)-N(10)-H(10B) | 120.0 | H(1A)-C(1A)-H(1B) | 109.5 |
| H(10A)-N(10)-H(10B) | 120.0 | C(2A)-C(1A)-H(1C) | 109.5 |
| C(45)-N(11)-C(46) | 123.2(7) | H(1A)-C(1A)-H(1C) | 109.5 |
| C(45)-N(11)-H(11) | 118.4 | H(1B)-C(1A)-H(1C) | 109.5 |
| C(46)-N(11)-H(11) | 118.4 | O(1A)-C(2A)-C(1A) | 125(2) |
| C(54)-N(12)-C(59) | 106.4(6) | O(1A)-C(2A)-C(3A) | 114(2) |
| C(54)-N(12)-C(51) | 124.8(7) | C(1A)-C(2A)-C(3A) | 121(2) |
| C(59)-N(12)-C(51) | 127.1(7) | C(2A)-C(3A)-H(3A) | 109.5 |
| C(54)-N(13)-C(60) | 104.4(6) | C(2A)-C(3A)-H(3B) | 109.5 |
| C(54)-N(13)-Co(1) | 120.9(5) | H(3A)-C(3A)-H(3B) | 109.5 |
| C(60)-N(13)-Co(1) | 133.4(5) | C(2A)-C(3A)-H(3C) | 109.5 |
| C(47)-O(8)-P(1) | 121.8(5) | H(3A)-C(3A)-H(3C) | 109.5 |
| C(49)-O(11)-P(1) | 120.5(6) | H(3B)-C(3A)-H(3C) | 109.5 |
| C(51)-O(13)-C(52) | 109.5(6) | | |

**Table S4.** Crystallographic Co–C and Co–$N_{dmbzm}$ bond lengths (Å) in cyanocobalamin and alkylcobalamins

| **β ligand** | **Co–C /Å** | **Co–$N_{dmbzm}$ /Å** | **Ref** |
|---|---|---|---|
| CN (average) | 1.87 | 2.04 | 2-12 |
| $CF_3$ | 1.878 | 2.047 | 13 |
| Vinyl | 1.912 | 2.164 | 14 |
| $CHF_2$ | 1.949 | 2.187 | 15 |
| cis-Chlorovinyl | 1.953 | 2.144 | 14 |
| Me | 1.979 | 2.162 | 12 |
| Adenopropyl | 2.001 | 2.191 | 16 |
| PhVn | 2.008 | 2.228 | This work |
| Et | 2.023 | 2.232 | 17 |
| n-Butyl | 2.031 | 2.244 | 17 |
| Ado | 2.033 | 2.237 | 18 |
| Isoamyl | 2.044 | 2.277 | 19 |

**Table S5.** Available p$K_a$ values for the deprotonation of dmbzm and its coordination by Co(III) in cobalamins

| **β ligand** | **p$K_a$** | **Co–$N_{dmbzm}$** | **Ref** |
|---|---|---|---|
| NO | 5.1 | 2.349(2) | 20 |
| PhVn | 4.60 | 2.228(7) | This work |
| $CH_3CH_2$ | 4.16 | 2.232 (1) | 17 |
| $CH_3CH_2CH_2$ | 4.10 | | 17 |
| Ado | 3.7 | 2.236 (2) | 21 |
| $CH_3$ | 2.90 | 2.17 (2) | 22 |
| AdoPr | 3.31 | 2.212 (8) | 16 |
| $CF_3CH_2$ | 2.60 | | 23 |
| $CH_2$=CH | 2.4 | 2.165 (6) | 14 |
| *cis*-ClCH=CH | 2.30 | 2.144 (5) | 14 |
| $CF_2H$ | 2.15 | 2.187 (7) | 23 |
| $NCCH_2$ | 1.81 | | 24 |
| $CF_3$ | 1.44 | 2.05 (1) | 23 |
| CN | 0.10 | 2.04 (2) | 25 |
| $H_2O$ | -2.13 | 1.925 (2) | 24 |

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