Dataset S1. Summary of intramolecular ^{1}H contacts of the PCB chromophore. Crystal distances of $^{1}H^{\{N21–N24\}}$ – ^{13}C correlations resolved in Fig. 2 (both Pr and Pfr states) are listed according to the *Synechocystis* Cph1 2VEA Pr (6) and *Pseudomonas aeruginosa* PaBphP 3C2W Pfr (14) structures, respectively. The ^{1}H and ^{13}C chemical shifts of the heteronuclear cross-peaks are referenced to our previous 2D homo- and heteronuclear NMR studies on various states of Cph1 phytochrome (3, 4).

	Pr				Pfr			
Cofactor nitrogen	$\sigma^{H\{N21–N24\}}$ (ppm) [3, 4]	Cofactor carbon	σ^{carbon} (ppm) [3, 4]	XRD distance (Å) [6]	$\sigma^{H\{N21–N24\}}$ (ppm) [3, 4]	Cofactor carbon	σ^{carbon} (ppm) [3, 4]	XRD distance (Å) [14]
N21	**11.6**	1	184.1	2.02	**11.7**	1	182.9	1.92
		2	37.1	3.28		2	37.3	2.90
		3	53.3	3.31		3	54.3	2.92
		4	154.0	2.07		4	153.7	1.93
		6	149.3	2.85		6	149.3	2.73
		9	127.9	3.69		9	131.0	3.42
N22	**10.9**	1	184.1	3.69	**11.7**	1	182.9	3.83
		4	154.0	3.05		4	153.7	2.90
		6	149.3	2.14		6	149.3	1.92
		7	125.5	3.37		7	126.3	2.89
		8	145.2	3.32		8	143.6	2.93
		9	127.9	2.12		9	131.0	1.93
		10	112.8	2.95		10	112.4	2.79
		11	127.9	3.37		11	131.0	2.98
N23	**10.9**	9	127.9	3.23	**10.6**	9	131.0	2.90
		10	112.8	2.86		10	112.4	2.76
		11	127.9	2.11		11	131.0	1.92
		12	145.2	3.33		12	145.8	2.92
		13	126.5	3.31		13	130.5	2.88
		14	146.1	2.14		14	152.0	1.92
		15	93.2	2.66		15	91.5	2.72
		16	146.1	4.09		-	-	-
N24	**9.9**	13	126.5	2.76	**9.6**	-	-	-
		13'	11.4	2.10		-	-	-
		14	146.1	3.08		-	-	-
		15	93.2	2.88		15	91.5	2.78
		16	146.1	2.14		16	151.1	1.93
		17	142.1	3.25		17	137.7	2.90
		18	134.2	3.30		18	140.4	2.90
		19	173.7	2.14		19	169.0	1.93