Supporting Information

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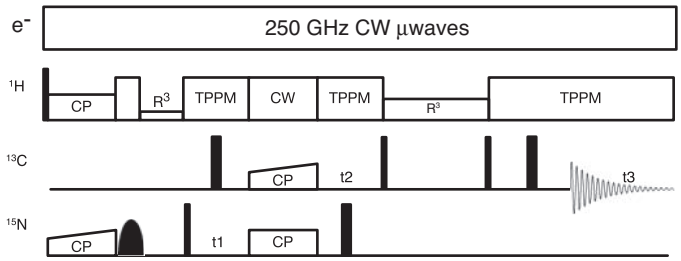

Fig. S1. Pulse sequence for DNP-enhanced multidimensional, band-selective heteronuclear ^{13}C-^{15}N correlation spectroscopy.

Table S1. Chemical shifts (in ppm) of retinal carbons and K216-Nζ in photocycle intermediates of bR

Photostate	bR_{568}	bR_{555}	bR_{555b}	K	Iso-bR	L_{166}	L_{174}	L_{181}	L_{186}	M_o
^{13}C11	135.3	138.5	—	—	—	—	—	—	—	130.0
^{13}C12	133.4	124.9		140.7	—	—	137.0	120.4	121.0	127.2, 125.9
^{13}C13	166.1/.5	—	—	—	—	—	—	—	—	—
^{13}C14	123.1	111.0	—	118.2	—	—	123.3	116.2	116.2	124.5
^{13}C15	160.0	163.2	164.7	160.2	156.3	163	162.9	162.5	162.7	165.4
^{13}C20	13.1	23.5	—	—	—	15.5	—	24.0	24.5	21.5
^{15}N	165.2	171.1	173.8	157.2	164.2	166.0	173.8	181.2	186	317

Here the bR states are identified with subscripts indicating their wavelength of maximum visible absorption, and the L substates are identified with subscripts indicating the ^{15}N chemical shift of the Schiff base. The C15 and Nζ chemical shifts are derived from the spectra shown in Fig. 2, and the other chemical shifts are derived from the spectra shown in Fig. 3.

Table S2. Chemical shifts (in ppm) of the lysine-216 carbons and Nζ in photocycle intermediates of bR

Photostate	bR_{568}	bR_{555}	K	L_{174}	L_{181}	L_{186}	M_o
$^{13}C\varepsilon$	53.5	48.0	50.7	48.2	51.2,49.1	50.0	60.7
$^{13}C\delta$	29.5	30.6	28.0	32.2	29.5,28.2	29.0	—
$^{13}C\gamma$	26.5	27.8	24.3	—	—	23.8	—
$^{13}C\beta$	35.0	—	—	—	—	33.0	—
$^{13}C\alpha$	55.2	—	—	—	—	—	—
$^{15}N\zeta$	165.2	172	156	172	181	186	317

Here the bR states are identified with subscripts indicating their wavelength of maximum visible absorption, and the L substates are identified with subscripts indicating the ^{15}N chemical shift of the Schiff base. These chemical shifts are derived from the spectra shown in Fig. 4.