Photosynthesis is the process converting light energy to chemical potential energy. In phototrophic organisms, chlorophyll (Chl) and bacteriochlorophyll (BChl) pigments are essential for harvesting light energy, migrating excited energy, and transferring electrons. How photosynthesis is emerged on early earth is enigmatic, but pigments are theoretically required first in the ancient phototrophs to absorb light and start photo-induced reactions. A classic question on the evolution of pigment biosynthesis is whether Chl was evolved first or BChl first? Chl molecules mainly absorb visible light wavelength, whereas BChls absorb longer wavelength including near-infrared light region. Therefore, to know which pigment is first evolved is important to know atmospheric environment on early earth. The steps diverging to Chl or BChl in pigment biosynthetic pathways are catalyzed by enzymes similar to nitrogenase. One of the nitrogenase-like enzymes is chlorophyllide oxidoreductase which also catalyzes branching steps toward BChl-a and BChl-b. BChl-b absorbs longest light wavelength among naturally occurring pigments. In my talk, pigment structures and their diversified biosynthetic pathways that we recently revealed will be introduced and experimental approach to solve the evolution of chlorophyllous pigments will be presented.