Blooms of the microalga *Prymnesium parvum* cause devastating fish kills worldwide, which are suspected to be caused by the supersized ladder-frame polyether toxins prymnesin-1 and -2. These toxins have, however, only been detected from *P. parvum* in rare cases since they were originally described two decades ago. Here, we report the isolation and characterization of a novel B-type prymnesin, based on extensive analysis of 2D- and 3D-NMR data of natural as well as 90% 13C enriched material. B-type prymnesins lack a complete 1,6-dioxadecalin core unit, which is replaced by a short acyclic C2 linkage compared to the structure of the original prymnesins. Comparison of the bioactivity of prymnesin-2 with prymnesin-B1 in an RTgill-W1 cell line assay identified both compounds as toxic in the low nanomolar range. Chemical investigations by liquid chromatography high resolution mass spectrometry (LC-HRMS) of 10 strains of *P. parvum* collected worldwide showed that only one strain produced the original prymnesin-1 and -2, whereas four strains produced the novel B-type prymnesin. In total 13 further prymnesin analogues differing in their core backbone and chlorination and glycosylation patterns could be tentatively detected by LC-MS/HRMS, including a likely C-type prymnesin in five strains. Altogether, our work indicates that evolution of prymnesins has yielded a diverse family of fish-killing toxins that occurs around the globe and has significant ecological and economic impact.