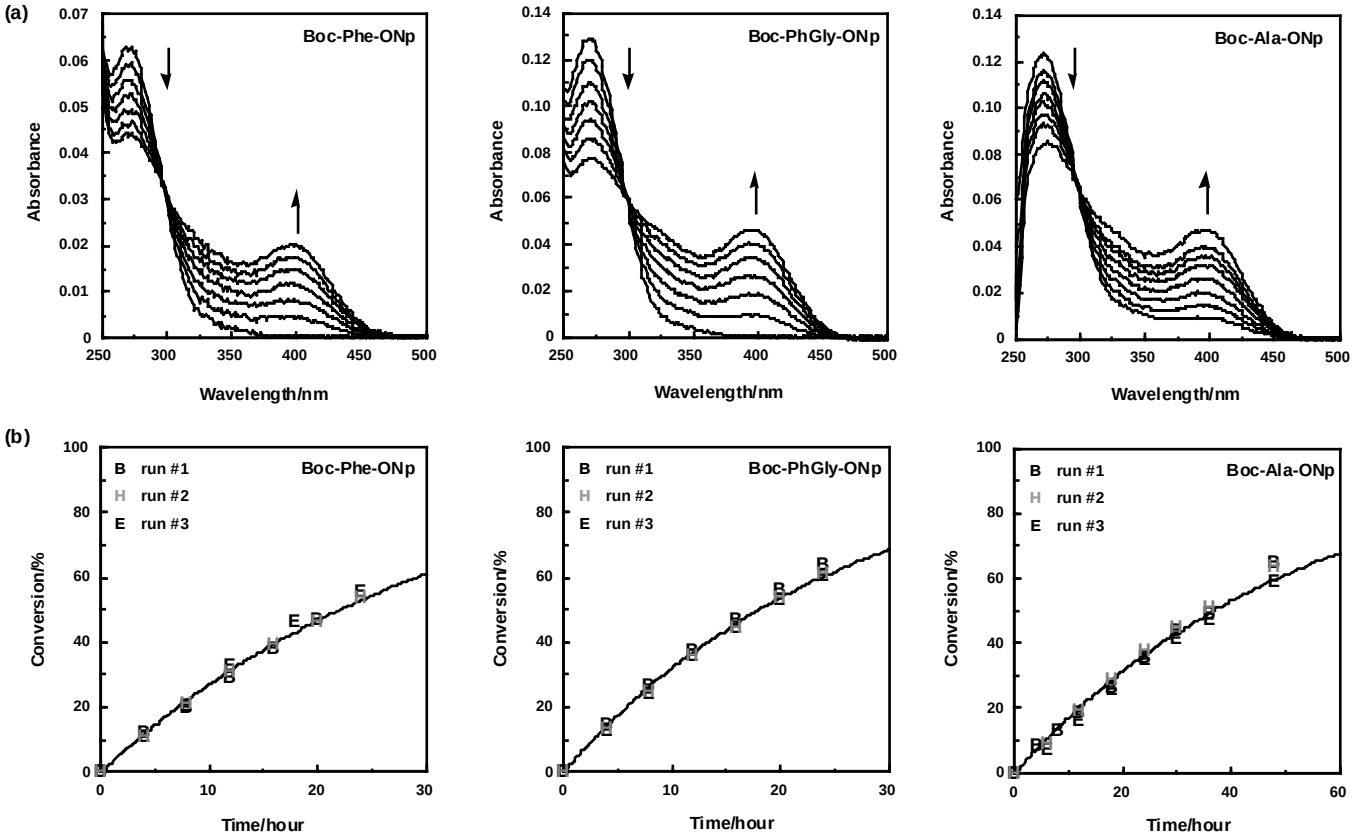
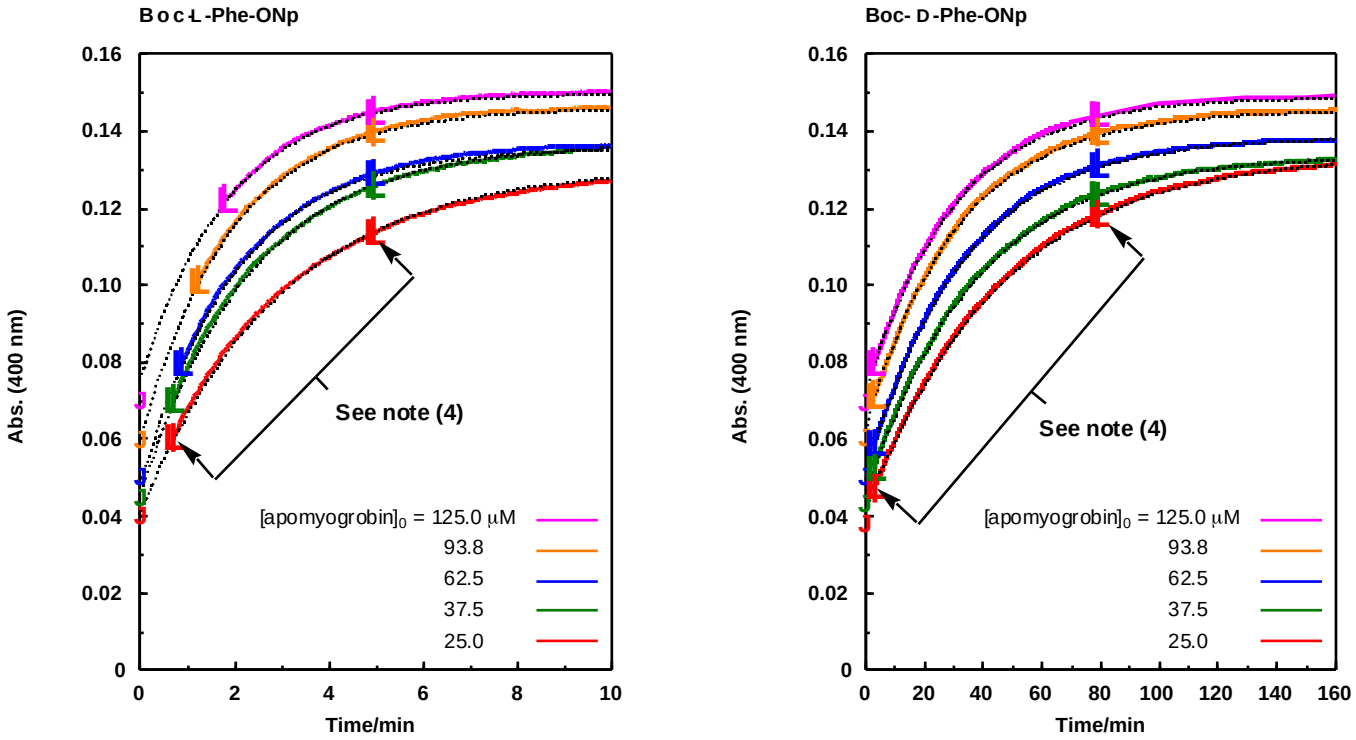
Supporting Information 1



Hydrolysis of Boc-Phe-ONp (6.25 μM), Boc-PhGly-ONp (12.5 μM) and Boc-Ala-ONp (12.5 μM) in the absence of apomyoglobin; (a) absorption spectral changes and (b) time courses of three independent runs.

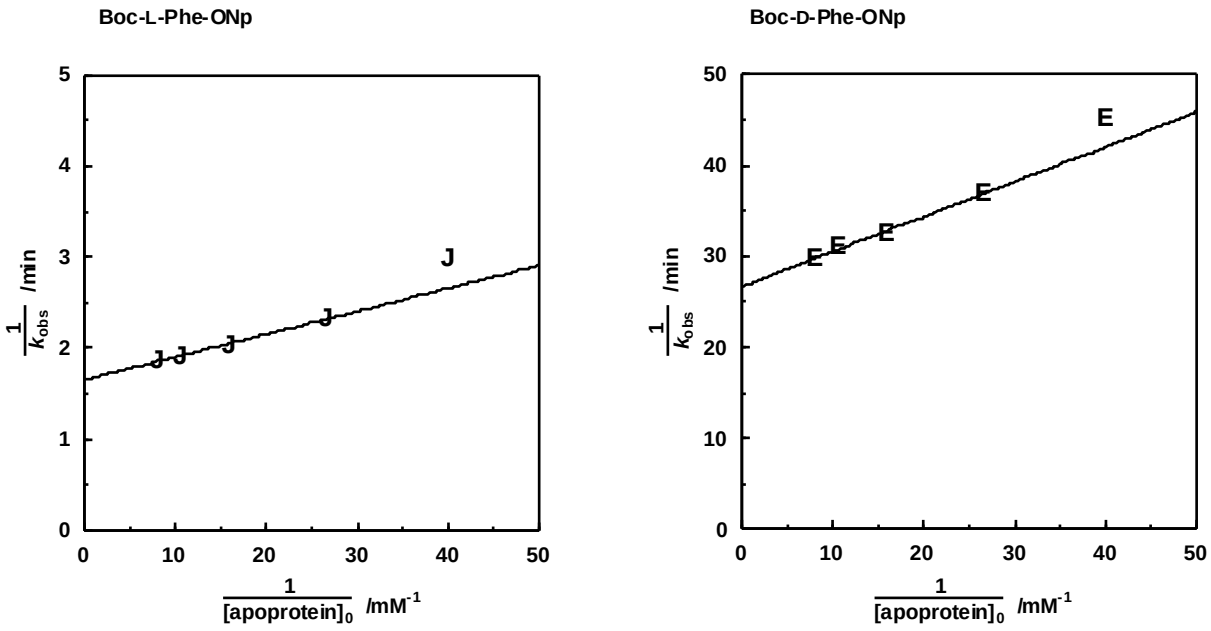
Supporting Information 2



Changes in absorbance at 400 nm upon hydrolysis of Boc-Phe-ONp (12.5 μM) in the presence of apomyoglogin (25–125 μM).

Note:
(1) The solid curves represent changes in absorbance at 400 nm, which were measured every 2 sec for the L-isomer and 10 sec for the D-isomer.
(2) Filled circles (**J**) at $t = 0$ represent the initial absorbances before addition of Boc-Phe-ONp. The apoprotein alone had a very weak absorption at 400 nm, since complete removal of the heme unit from myoglobin (to obtain the apoprotein) is generally impossible.
(3) The broken curves were obtained by curve fitting with a relationship $(1\text{-}[NpO^-]/[\text{Boc-Phe-ONp}]_0) = e^{-kt}$.
(4) The data between the two marks were utilized for the determination of k_{obs}.

Supporting Information 3



Lineweaver-Burk plots for the hydrolysis of Boc-L-Phe-ONp (J; 12.5 μM) and Boc-D-Phe-ONp (E; 12.5 μM) in the presence of apomyoglobin (25–125 μM).

Note: The k_{obs} values at $[apoprotein]_0^{-1} = 40$ mM^{-1} were not used for curve-fitting to determine k_{cat} and K_m, because $[E]_0 >> [S]_0$, a prerequisit for the Michaelis-Menten kinetics, is not satisfied.