SUPPORTING INFORMATION

Captopril as a nucleophile for ester cleavage. Formation of the thiolester S-benzoylcaptopril

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Figure S1. Reaction spectra of PhB hydrolysis at (a)[PhB]=0.20 mM, [OH^-]=0.013 M, scans at 2 min interval; and (b)[PhB]=0.14 mM; $[OH^-]_f$=6.0 mM, and [cap]=0.92 mM; scans at 2 min interval; (c)the same spectra as in (a) showing the expanded scale of the X-axis.

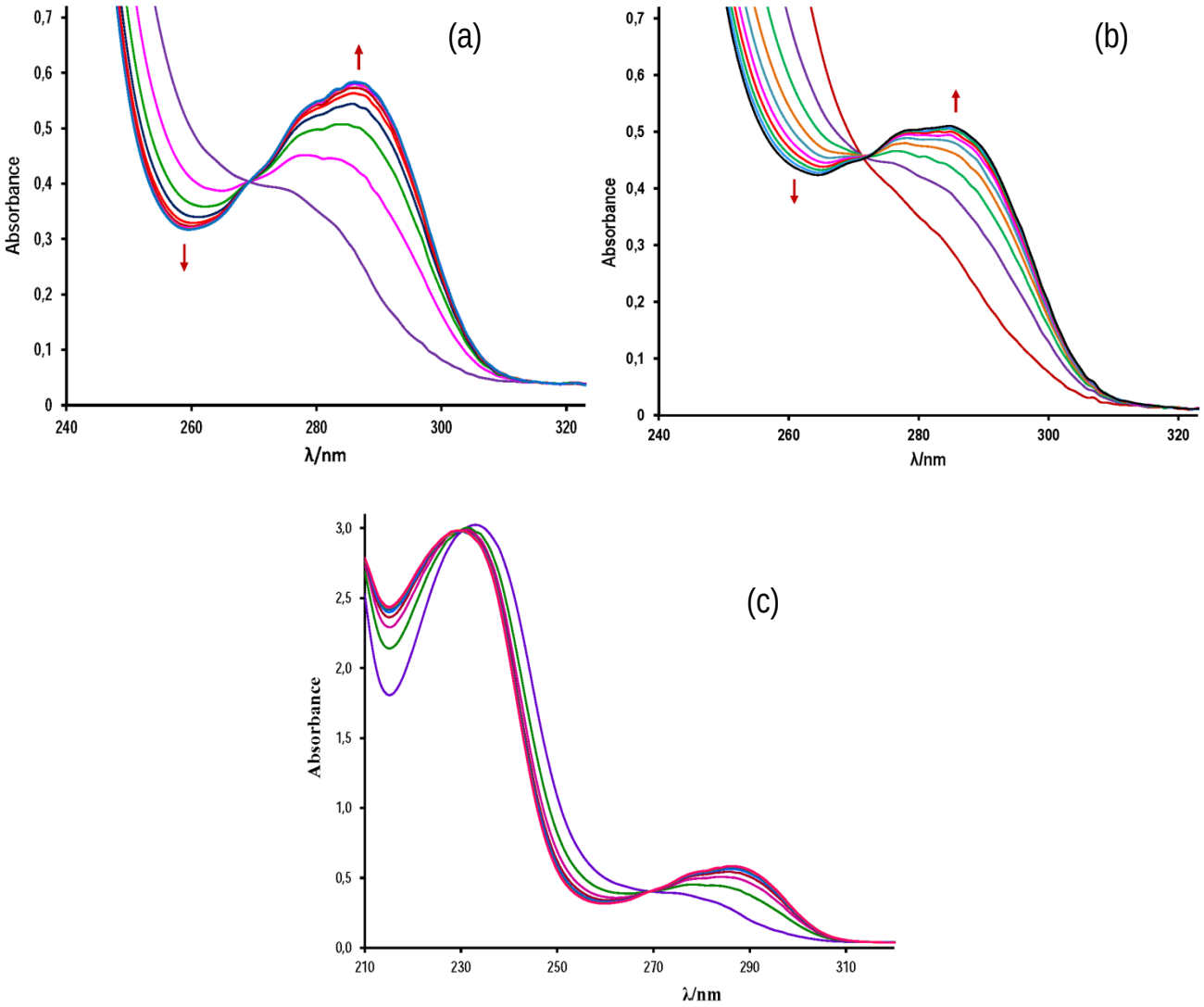

Figure S2. (a)Reaction spectra of ASA hydrolysis at [ASA]=0.23 mM, $[OH^-]$=4.7 mM, scans at 3 min interval, the dashed curve is at infinite time; and (b)reaction spectra of PhA hydrolysis at [PhA]=0.25 mM; $[OH^-]_f$=4.5 m M, and [cap]=3.45 mM; scans at 1.5 min interval, dashed curve is at infinite time.

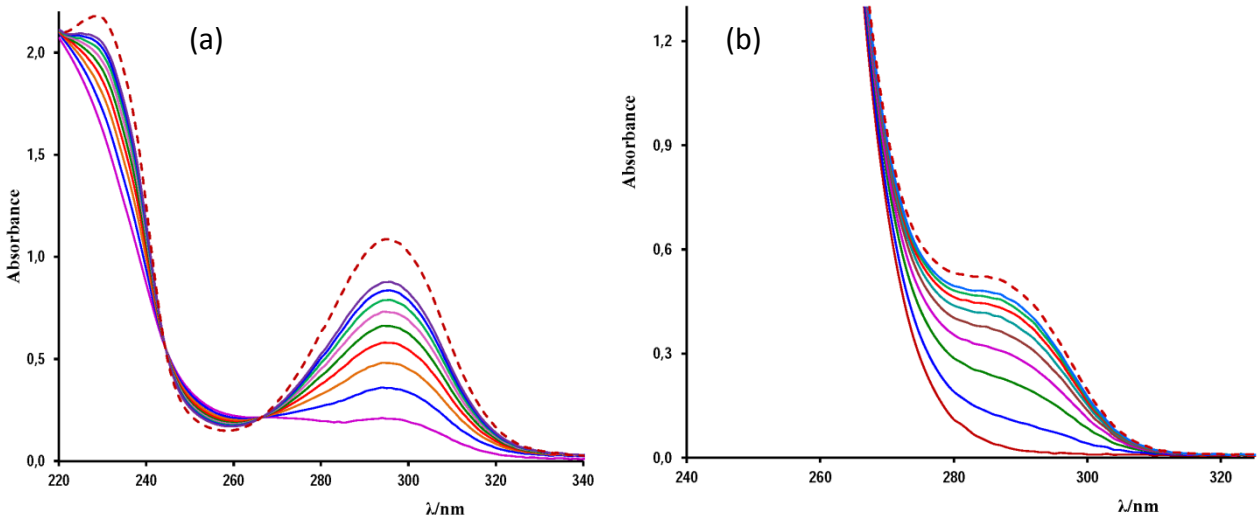

Figure S3. Eyring's plot corresponding to the alkaline hydrolysis of ASA; the datum signed with an arrow was determined in the present study, the others were taken from literature (see Table 1); (◆)not included in the linear correlation.

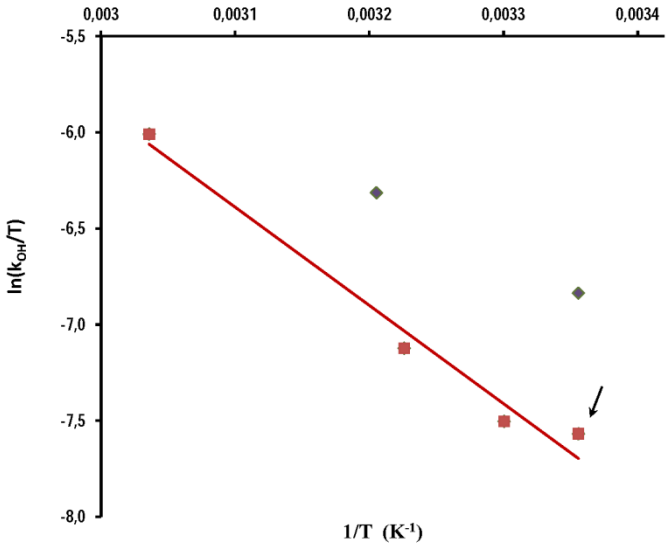

Figure S4. Influence of buffer concentration on the observed rate constant for the ester cleavage of PhB by captopril at pH 9.90 and [cap]=7.13 mM. $k_o/s^{-1}=(7.0\pm0.6)\cdot10^{-4} + (7.5\pm0.3)\cdot10^{-4}$[buffer].

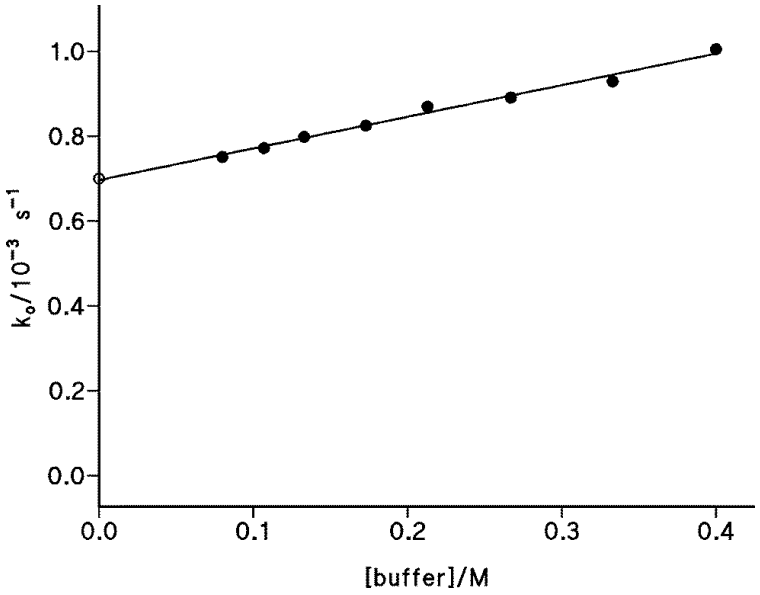

Table S1. Observed rate constants, k_o, obtained as a function of [TTABr] for the thiolysis of PhB by cap at 25 ºC. See text and Figure S5 and Figure S6.

[OH⁻]=6.0 mM; [cap]=4.6 mM; 25 ºC				**[OH⁻]=1.0 mM; [cap]=3.4 mM; 25 ºC**			
[TTABr]/M	k_o/s^{-1}	k^c/s^{-1}	$k^{cc}/M^{-1}s^{-1}$	[TTABr]/M	$k_o/10^{-3}s^{-1}$	$k^c/10^{-3}s^{-1}$	$k^{cc}/M^{-1}s^{-1}$
0,00267	0,00789	0,0113261	1,99082772	0,00267	0,005244	0,00752776	2,18276949
0,00333	0,00921	0,01717205	3,53105314	0,0040	0,00697	0,016031	5,36104186
0,00667	0,010738	0,0433332	12,6284449	0,00533	0,00789	0,02496791	9,30891819
0,010	0,010118	0,0627316	22,6554038	0,0080	0,00782	0,038318	17,0823767
0,0133	0,009044	0,07547218	32,2665518	0,01067	0,006842	0,04540009	23,4869458
0,020	0,007344	0,0932688	52,2936376	0,0133	0,006341	0,05291565	31,1042824
0,0267	0,005661	0,09654836	66,7629037	0,020	0,004537	0,0576199	44,1366205
0,040	0,004172	0,1072204	102,15733	0,0267	0,003614	0,06163677	58,2009373
0,0533	0,003231	0,1109687	134,620354	0,040	0,002433	0,0625281	81,1280981
0,080	0,00216	0,111672	193,685885	0,0533	0,001922	0,06601109	108,998434
0,107	0,001676	0,116063	262,70643	0,080	0,00137	0,070829	167,260995
0,133	0,001294	0,1114781	308,646035	0,1067	0,0010993	0,07591216	233,224048
				0,160	0,000685	0,0710345	318,756719

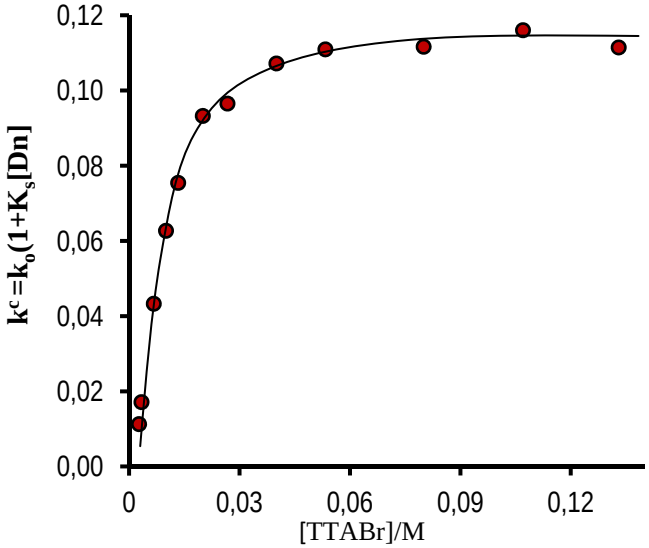

Figure S5. Variation of k^c (=1+K_s[Dn]; with K_s=650 M^{-1} and cmc=2 mM) against [TTABr] for the cap-thiolysis of PhB at [OH^-]=6.0 mM

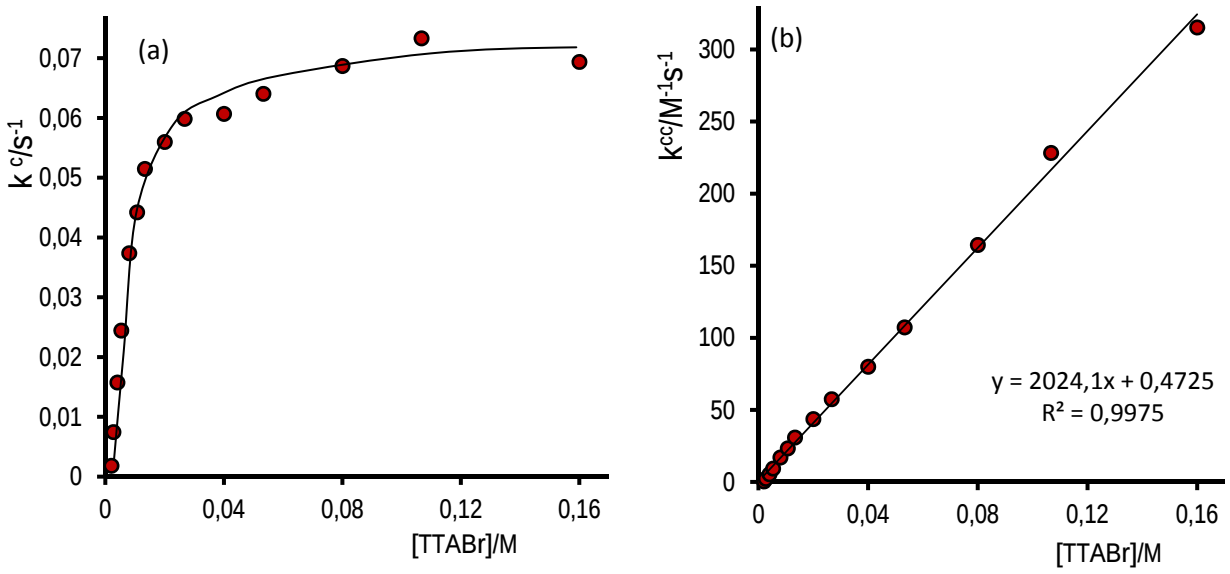

Figure S6. (a) Variation of k^c (=1+K_s[Dn]; with K_s=630 M^{-1} and cmc=2 mM) against [TTABr] and of (b)k^{cc} as a function of [TTABr] for the cap-thiolysis of PhB at [OH^-]=1.0 mM.

Figure S7. Plot of k_o as a function of [cys] for the cleavage of (▲)PhA (●)PhB and (▼)ASA under alkaline conditions of $[OH^-]_f$=1.0 mM