SUPLEMMENTARY MATERIAL

Table S.1. Influence of dioxane and cyclodextrin concentration on k_{obs} for the basic hydrolysis of MNTS at 25.0ºC. [NaOH] = 0.175 M.

$[DIOXANE]_{total}$	**$[\beta\text{-}CD]_{total}$**	k_{obs} **/s^{-1}**
1.56×10^{-2}	0	1.37×10^{-2}
1.56×10^{-2}	5.00×10^{-4}	1.16×10^{-2}
1.56×10^{-2}	1.00×10^{-3}	1.02×10^{-2}
1.56×10^{-2}	2.00×10^{-3}	8.34×10^{-3}
1.56×10^{-2}	3.00×10^{-3}	7.14×10^{-3}
1.56×10^{-2}	4.00×10^{-3}	6.17×10^{-3}
1.56×10^{-2}	5.00×10^{-3}	5.85×10^{-3}
1.56×10^{-2}	6.00×10^{-3}	4.69×10^{-3}
1.56×10^{-2}	7.00×10^{-3}	4.40×10^{-3}
1.56×10^{-2}	8.00×10^{-3}	4.24×10^{-3}
3.90×10^{-2}	0	1.66×10^{-2}
3.90×10^{-2}	5.00×10^{-4}	1.44×10^{-2}
3.90×10^{-2}	1.00×10^{-3}	1.27×10^{-2}
3.90×10^{-2}	2.00×10^{-3}	1.15×10^{-2}
3.90×10^{-2}	3.00×10^{-3}	1.00×10^{-2}
3.90×10^{-2}	4.00×10^{-3}	8.82×10^{-3}
3.90×10^{-2}	5.00×10^{-3}	7.97×10^{-3}
3.90×10^{-2}	6.00×10^{-3}	7.13×10^{-3}
3.90×10^{-2}	7.00×10^{-3}	6.53×10^{-3}
3.90×10^{-2}	8.00×10^{-3}	5.93×10^{-3}
1.17×10^{-1}	0	1.66×10^{-2}
1.17×10^{-1}	5.00×10^{-4}	1.52×10^{-2}
1.17×10^{-1}	1.00×10^{-3}	1.44×10^{-2}
1.17×10^{-1}	2.00×10^{-3}	1.33×10^{-2}
1.17×10^{-1}	3.00×10^{-3}	1.24×10^{-2}
1.17×10^{-1}	4.00×10^{-3}	1.17×10^{-2}
1.17×10^{-1}	5.00×10^{-3}	1.09×10^{-2}
1.17×10^{-1}	6.00×10^{-3}	1.01×10^{-2}
1.17×10^{-1}	7.00×10^{-3}	9.31×10^{-3}

Table S.1.

[DIOXANE]$_{total}$	[β-CD]$_{total}$	k_{obs} /s^{-1}
1.17×10^{-1}	8.00×10^{-3}	8.84×10^{-3}
2.34×10^{-1}	0	1.64×10^{-2}
2.34×10^{-1}	5.00×10^{-4}	1.55×10^{-2}
2.34×10^{-1}	1.00×10^{-3}	1.47×10^{-2}
2.34×10^{-1}	2.00×10^{-3}	1.42×10^{-2}
2.34×10^{-1}	3.00×10^{-3}	1.35×10^{-2}
2.34×10^{-1}	4.00×10^{-3}	1.30×10^{-2}
2.34×10^{-1}	5.00×10^{-3}	1.23×10^{-2}
2.34×10^{-1}	6.00×10^{-3}	1.17×10^{-2}
2.34×10^{-1}	7.00×10^{-3}	1.11×10^{-2}
2.34×10^{-1}	8.00×10^{-3}	1.05×10^{-2}
5.86×10^{-1}	0	1.69×10^{-2}
5.86×10^{-1}	5.00×10^{-4}	1.67×10^{-2}
5.86×10^{-1}	1.00×10^{-3}	1.63×10^{-2}
5.86×10^{-1}	2.00×10^{-3}	1.59×10^{-2}
5.86×10^{-1}	3.00×10^{-3}	1.55×10^{-2}
9.37×10^{-1}	0	1.70×10^{-2}
9.37×10^{-1}	5.00×10^{-4}	1.66×10^{-2}
9.37×10^{-1}	1.00×10^{-3}	1.66×10^{-2}
9.37×10^{-1}	2.00×10^{-3}	1.66×10^{-2}
9.37×10^{-1}	3.00×10^{-3}	1.63×10^{-2}
9.37×10^{-1}	4.00×10^{-3}	1.64×10^{-2}
9.37×10^{-1}	5.00×10^{-3}	1.62×10^{-2}
9.37×10^{-1}	6.00×10^{-3}	1.61×10^{-2}
9.37×10^{-1}	7.00×10^{-3}	1.61×10^{-2}
9.37×10^{-1}	8.00×10^{-3}	1.59×10^{-2}

Table S.2. Influence of dioxane and cyclodextrin concentration on k_{obs} for the acid hydrolysis of MNTS at 25.0ºC. [HCl] = 0.160 M.

$[DIOXANE]_{total}$	$[\beta\text{-CD}]_{total}$	k_{obs} /s^{-1}
$1.95x10^{-2}$	0	$5.03x10^{-3}$
$1.95x10^{-2}$	$5.00x10^{-4}$	$3.02x10^{-3}$
$1.95x10^{-2}$	$1.00x10^{-3}$	$2.34x10^{-3}$
$1.95x10^{-2}$	$2.00x10^{-3}$	$1.59x10^{-3}$
$1.95x10^{-2}$	$4.00x10^{-3}$	$1.03x10^{-3}$
$1.95x10^{-2}$	$6.00x10^{-3}$	$7.11x10^{-4}$
$3.90x10^{-2}$	0	$5.03x10^{-3}$
$3.90x10^{-2}$	$5.00x10^{-4}$	$3.47x10^{-3}$
$3.90x10^{-2}$	$1.00x10^{-3}$	$2.71x10^{-3}$
$3.90x10^{-2}$	$2.00x10^{-3}$	$1.95x10^{-3}$
$3.90x10^{-2}$	$4.00x10^{-3}$	$1.31x10^{-3}$
$3.90x10^{-2}$	$6.00x10^{-3}$	$9.42x10^{-4}$
$7.03x10^{-2}$	0	$4.86x10^{-3}$
$7.03x10^{-2}$	$5.00x10^{-4}$	$3.84x10^{-3}$
$7.03x10^{-2}$	$1.00x10^{-3}$	$2.90x10^{-3}$
$7.03x10^{-2}$	$2.00x10^{-3}$	$2.29x10^{-3}$
$7.03x10^{-2}$	$4.00x10^{-3}$	$1.48x10^{-3}$
$7.03x10^{-2}$	$6.00x10^{-3}$	$1.12x10^{-3}$
$1.17x10^{-1}$	0	$4.73x10^{-3}$
$1.17x10^{-1}$	$5.00x10^{-4}$	$4.01x10^{-3}$
$1.17x10^{-1}$	$1.00x10^{-3}$	$3.42x10^{-3}$
$1.17x10^{-1}$	$2.00x10^{-3}$	$2.71x10^{-3}$
$1.17x10^{-1}$	$4.00x10^{-3}$	$1.90x10^{-3}$
$1.17x10^{-1}$	$6.00x10^{-3}$	$1.43x10^{-3}$
$1.72x10^{-1}$	0	$4.47x10^{-3}$
$1.72x10^{-1}$	$5.00x10^{-4}$	$3.98x10^{-3}$
$1.72x10^{-1}$	$1.00x10^{-3}$	$3.64x10^{-3}$
$1.72x10^{-1}$	$2.00x10^{-3}$	$2.96x10^{-3}$
$1.72x10^{-1}$	$4.00x10^{-3}$	$2.26x10^{-3}$
$1.72x10^{-1}$	$6.00x10^{-3}$	$1.79x10^{-3}$
$2.32x10^{-1}$	0	$4.64x10^{-3}$

Table S.2.		
[DIOXANE]$_{total}$	**[β-CD]$_{total}$**	k_{obs} **/s^{-1}**
2.32x10^{-1}	5.00x10^{-4}	4.13x10^{-3}
2.32x10^{-1}	1.00x10^{-3}	3.72x10^{-3}
2.32x10^{-1}	2.00x10^{-3}	3.11x10^{-3}
2.32x10^{-1}	4.00x10^{-3}	2.43x10^{-3}
2.32x10^{-1}	6.00x10^{-3}	1.98x10^{-3}

Figure S.1. (A) Influence of [β-CD] on k_{obs} for the basic hydrolysis of MNTS in the presence of dioxane at 25.0ºC and [NaOH]=0.175M. (○) [Dioxane]=1.56×10^{-2}M; (●) [Dioxane]=3.90×10^{-2}M; (□) [Dioxane]=0.117M; (■) [Dioxane]=0.234M; (△) [Dioxane]=0.586M; and (▲) [Dioxane]=0.937M. (B) Data fitted according to equation (4).

A **B**

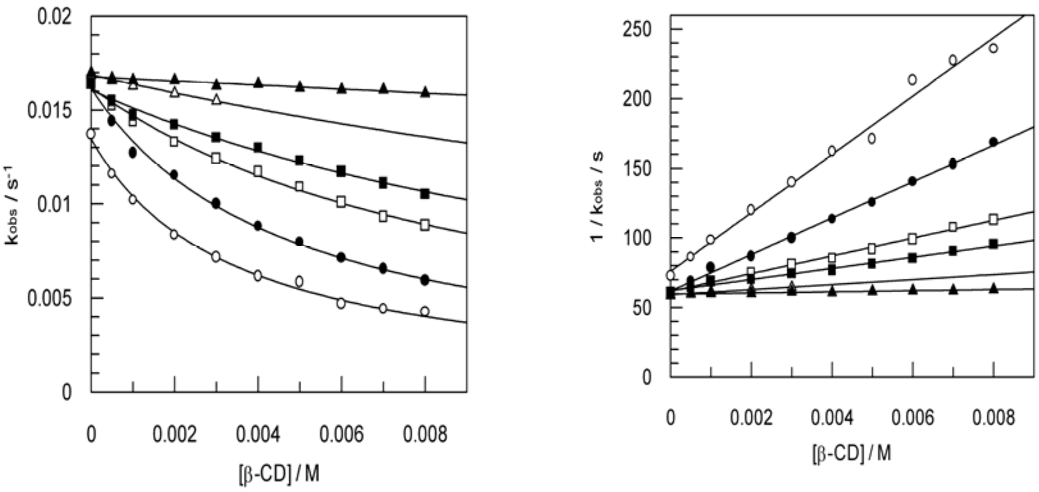


Figure S.2. Influence of $K_{Dioxane}^{\beta-CDH}$ and $K_{Dioxane}^{\beta-CD^-}$ values on the correlation coeffcient for fitting experimental results to equation (9) in the acid (●) and basic (○) hydrolysis of MNTS.

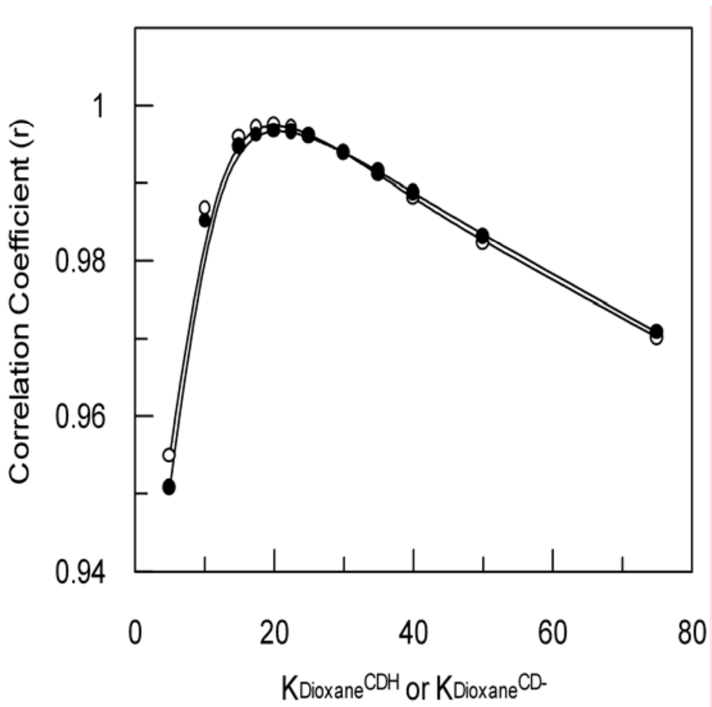


Table S.3. Influence of DMSO and cyclodextrin concentration on k_{obs} for the basic hydrolysis of MNTS at 25.0ºC. [NaOH] = 0.175 M.

$[DMSO]_{total}$	**$[\beta\text{-CD}]_{total}$**	k_{obs} **/s^{-1}**
0.038	0	1.57×10^{-2}
0.038	5.00×10^{-4}	1.21×10^{-2}
0.038	1.00×10^{-3}	9.84×10^{-3}
0.038	2.00×10^{-3}	7.43×10^{-3}
0.038	4.00×10^{-3}	5.37×10^{-3}
0.038	6.00×10^{-3}	4.40×10^{-3}
0.232	0	1.58×10^{-2}
0.232	5.00×10^{-4}	1.29×10^{-2}
0.232	1.00×10^{-3}	1.12×10^{-2}
0.232	2.00×10^{-3}	8.95×10^{-3}
0.232	4.00×10^{-3}	6.66×10^{-3}
0.232	6.00×10^{-3}	5.42×10^{-3}
0.504	0	1.67×10^{-2}
0.504	5.00×10^{-4}	1.52×10^{-2}
0.504	1.00×10^{-3}	1.33×10^{-2}
0.504	2.00×10^{-3}	1.13×10^{-2}
0.504	4.00×10^{-3}	9.43×10^{-3}
0.504	6.00×10^{-3}	7.99×10^{-3}
1.110	0	1.95×10^{-2}
1.110	5.00×10^{-4}	1.93×10^{-2}
1.110	1.00×10^{-3}	1.73×10^{-2}
1.110	2.00×10^{-3}	1.60×10^{-2}
1.110	4.00×10^{-3}	1.30×10^{-2}
1.110	6.00×10^{-3}	1.10×10^{-2}
1.550	0	1.75×10^{-2}
1.550	5.00×10^{-4}	1.69×10^{-2}
1.550	1.00×10^{-3}	1.63×10^{-2}
1.550	2.00×10^{-3}	1.51×10^{-2}
1.550	4.00×10^{-3}	1.35×10^{-2}
1.550	6.00×10^{-3}	1.20×10^{-2}

Table S.4. Influence of DMSO and cyclodextrin concentration on k_{obs} for the acid hydrolysis of MNTS at 25.0ºC. [HCl] = 0.160 M

$[DMSO]_{total}$	$[\beta\text{-CD}]_{total}$	k_{obs} /s^{-1}
0.116	0	3.89×10^{-3}
0.116	5.00×10^{-4}	2.46×10^{-3}
0.116	1.00×10^{-3}	1.72×10^{-3}
0.116	2.00×10^{-3}	1.09×10^{-3}
0.116	4.00×10^{-3}	6.83×10^{-4}
0.116	6.00×10^{-3}	4.33×10^{-4}
0.194	0	4.46×10^{-3}
0.194	5.00×10^{-4}	2.70×10^{-3}
0.194	1.00×10^{-3}	1.94×10^{-3}
0.194	2.00×10^{-3}	1.22×10^{-3}
0.194	4.00×10^{-3}	7.77×10^{-4}
0.194	6.00×10^{-3}	5.87×10^{-4}
0.310	0	3.70×10^{-3}
0.310	5.00×10^{-4}	2.35×10^{-3}
0.310	1.00×10^{-3}	1.68×10^{-3}
0.310	2.00×10^{-3}	1.12×10^{-3}
0.310	4.00×10^{-3}	7.94×10^{-4}
0.310	6.00×10^{-3}	5.75×10^{-4}
0.465	0	4.38×10^{-3}
0.465	5.00×10^{-4}	2.94×10^{-3}
0.465	1.00×10^{-3}	2.26×10^{-3}
0.465	2.00×10^{-3}	1.57×10^{-3}
0.465	4.00×10^{-3}	9.90×10^{-4}
0.465	6.00×10^{-3}	7.55×10^{-4}
0.698	0	4.47×10^{-3}
0.698	5.00×10^{-4}	3.35×10^{-3}
0.698	1.00×10^{-3}	2.73×10^{-3}
0.698	2.00×10^{-3}	2.00×10^{-3}
0.698	4.00×10^{-3}	1.19×10^{-3}
0.698	6.00×10^{-3}	9.96×10^{-4}
1.000	0	3.63×10^{-3}
1.000	5.00×10^{-4}	2.93×10^{-3}
1.000	1.00×10^{-3}	2.47×10^{-3}

Table S.4.		
[DMSO]$_{total}$	**[β-CD]$_{total}$**	k_{obs} **/s^{-1}**
1.000	2.00x10^{-3}	1.82x10^{-3}
1.000	4.00x10^{-3}	1.24x10^{-3}
1.000	6.00x10^{-3}	9.72x10^{-4}
1.474	0	3.35x10^{-3}
1.474	5.00x10^{-4}	2.81x10^{-3}
1.474	1.00x10^{-3}	2.39x10^{-3}
1.474	2.00x10^{-3}	1.35x10^{-3}
1.474	4.00x10^{-3}	1.16x10^{-3}

Table S.5. Kinetic constants obtained by fitting eq. (2) to the experimental results for the acid and basic hydrolysis of MNTS in the presence of β-CD and variable concentrations of DMSO at 25.0ºC.

[NaOH] = 0.170M			[HCl] = 0.160M		
[DMSO]/M	$K_{app}^{\beta-CD^-}$ /M^{-1}	$10^2\,k_w$ /M^{-1}s^{-1}	[DMSO]/M	$K_{app}^{\beta-CDH}$ /M^{-1}	$10^2\,k_w$ /M^{-1}s^{-1}
			0	1690±280	3.21±0.54
0.038	379±23	8.21±0.49	0.116	1405±140	2.55±0.25
0.233	294±10	8.67±0.29	0.194	935±70	2.29±0.17
0.504	172±7	9.40±0.40	0.310	728±55	1.85±0.14
1.110	135±3	11.8±0.30	0.465	725±29	2.40±0.10
1.550	76±1	10.3±0.10	0.698	574±44	2.58±0.20
			1.000	449±11	2.15±0.05
			1.474	306±19	1.93±0.12

Figure S.3. (A) Influence of [β-CD] on k_{obs} for the acid hydrolysis of MNTS in the presence of DMSO at 25.0ºC and [HCl]=0.160M. (○) [DMSO]=0.116M; (●) [DMSO]=0.194M; (□) [DMSO]= 0.310M; (■) [DMSO]=465M; (△) [DMSO]=0.698M; (▲) [DMSO]=1.000M; and (▽) 1.474M (B) Data fitted according to equation (4).

A B

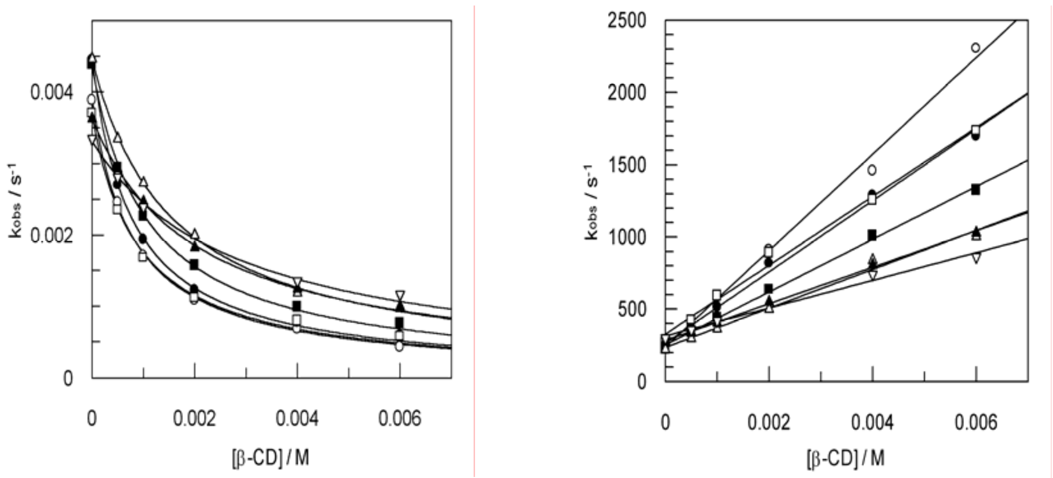


Figure S.4. (A) Influence of [β-CD] on k_{obs} for the Basic hydrolysis of MNTS in the presence of DMSO at 25.0ºC and [NaOH]=0.175M. (○) [DMSO]=3.80x10^{-2}M; (●) [DMSO]=0.233M; (□) [DMSO]= 0.504M; (■) [DMSO]=1.110M; and (△) [DMSO]=1.550M. (B) Data fitted according to equation (4).

A B

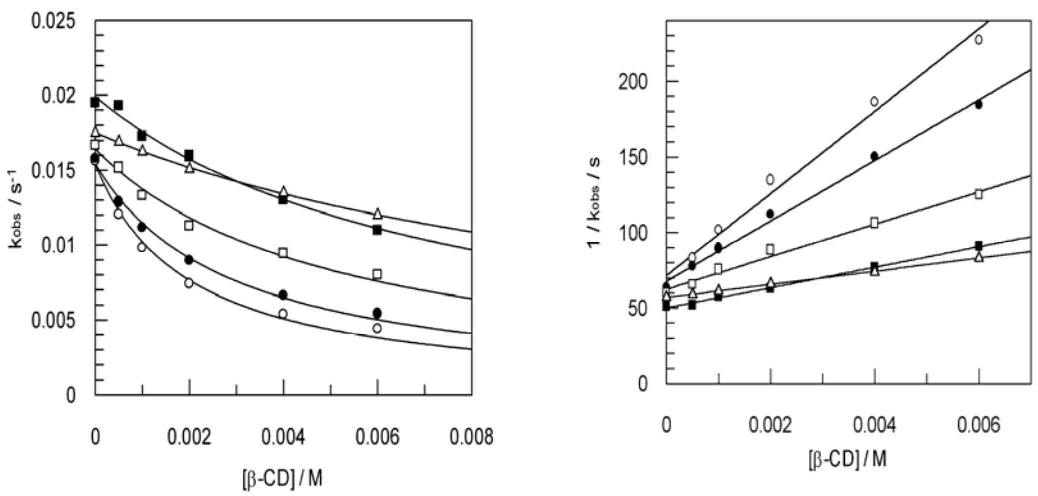


Figure S.5. Influence of [DMSO] on K_{app} (o) for the acid (A) and basic (B) hydrolysis of MNTS in the presence of β-CD. (—) Data fitted according to equation (5).

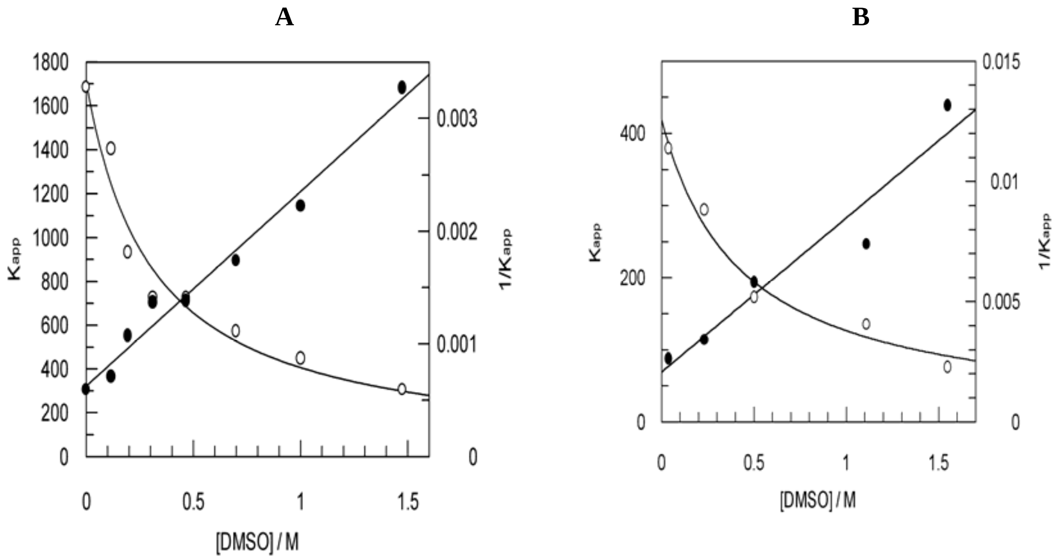


Figure S.6. Influence of $K_{DMSO}^{\beta-CDH}$ and $K_{DMSO}^{\beta-CD^-}$ values on the correlation coeffcient of fitting equation (9) to the experimental results for the acid (●) and basic (○) hydrolysis of MNTS.

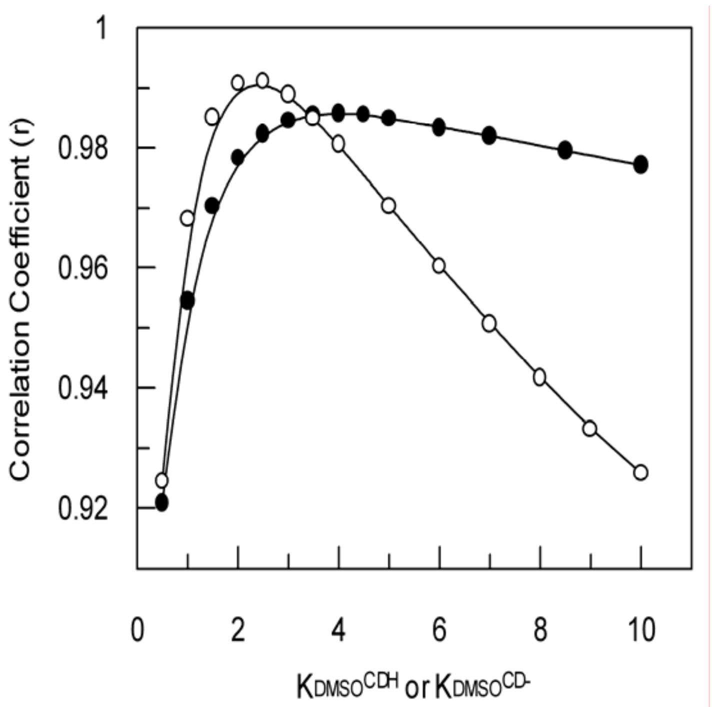


Figure S.7. [A] (o) Influence of the concentration of free β-CD on k_{obs}/k_w for the acid hydrolysis of MNTS in the presence of variable concentrations of DMSO. (•) Fitting of the data to eq. (5). [B] Analysis of the experimental results for the basic hydrolysis of MNTS.

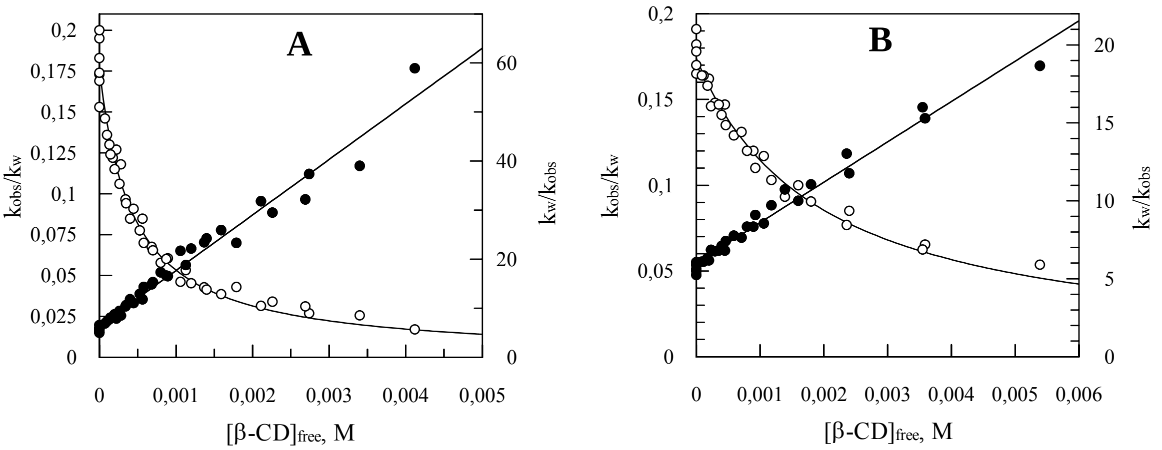


Table S.6. Influence of acetonitrile and cyclodextrin concentration on k_{obs} for the basic hydrolysis of MNTS at 25.0ºC. [NaOH] = 0.175 M.

$[CH_3CN]_{total}$	$[\beta\text{-CD}]_{total}$	k_{obs} /s^{-1}
9.57×10^{-2}	5.00×10^{-4}	1.20×10^{-2}
9.57×10^{-2}	1.00×10^{-3}	1.02×10^{-2}
9.57×10^{-2}	2.00×10^{-3}	8.00×10^{-3}
9.57×10^{-2}	3.00×10^{-3}	6.75×10^{-3}
9.57×10^{-2}	4.00×10^{-3}	5.67×10^{-3}
9.57×10^{-2}	5.00×10^{-3}	5.00×10^{-3}
9.57×10^{-2}	6.00×10^{-3}	4.50×10^{-3}
9.57×10^{-2}	7.00×10^{-3}	4.17×10^{-3}
9.57×10^{-2}	8.00×10^{-3}	3.85×10^{-3}
9.57×10^{-2}	9.00×10^{-3}	3.62×10^{-3}
0.638	5.00×10^{-4}	1.23×10^{-2}
0.638	1.00×10^{-3}	1.10×10^{-2}
0.638	2.00×10^{-3}	8.70×10^{-3}
0.638	3.00×10^{-3}	7.31×10^{-3}
0.638	4.00×10^{-3}	6.54×10^{-3}
0.638	5.00×10^{-3}	5.75×10^{-3}
0.638	6.00×10^{-3}	5.32×10^{-3}
0.638	7.00×10^{-3}	4.75×10^{-3}
0.638	8.00×10^{-3}	4.51×10^{-3}
0.957	5.00×10^{-4}	1.30×10^{-2}
0.957	1.00×10^{-3}	1.16×10^{-2}
0.957	2.00×10^{-3}	9.56×10^{-3}
0.957	3.00×10^{-3}	8.30×10^{-3}
0.957	4.00×10^{-3}	7.15×10^{-3}
0.957	5.00×10^{-3}	6.44×10^{-3}
0.957	6.00×10^{-3}	5.85×10^{-3}
1.910	5.00×10^{-4}	1.44×10^{-2}
1.910	1.00×10^{-3}	1.34×10^{-2}
1.910	2.00×10^{-3}	1.22×10^{-2}
1.910	3.00×10^{-3}	1.07×10^{-2}
1.910	4.00×10^{-3}	9.61×10^{-3}
1.910	5.00×10^{-3}	9.03×10^{-3}
1.910	6.00×10^{-3}	8.18×10^{-3}

Table S.6.		
[CH_3CN]$_{total}$	**[β-CD]$_{total}$**	k_{obs} **/s^{-1}**
1.910	$7.00x10^{-3}$	$7.64x10^{-3}$
1.910	$8.00x10^{-3}$	$7.17x10^{-3}$
1.910	$9.00x10^{-3}$	$6.81x10^{-3}$
2.870	$5.00x10^{-4}$	$1.16x10^{-2}$
2.870	$1.00x10^{-3}$	$1.12x10^{-2}$
2.870	$2.00x10^{-3}$	$1.09x10^{-2}$
2.870	$3.00x10^{-3}$	$1.03x10^{-2}$
2.870	$4.00x10^{-3}$	$9.52x10^{-3}$
2.870	$5.00x10^{-3}$	$9.55x10^{-3}$
2.870	$6.00x10^{-3}$	$9.04x10^{-3}$
2.870	$7.00x10^{-3}$	$8.55x10^{-3}$
2.870	$8.00x10^{-3}$	$8.40x10^{-3}$
2.870	$9.00x10^{-3}$	$8.04x10^{-3}$
3.830	$5.00x10^{-4}$	$9.55x10^{-3}$
3.830	$1.00x10^{-3}$	$9.19x10^{-3}$
3.830	$2.00x10^{-3}$	$9.07x10^{-3}$
3.830	$3.00x10^{-3}$	$8.69x10^{-3}$
3.830	$4.00x10^{-3}$	$8.54x10^{-3}$
3.830	$5.00x10^{-3}$	$8.51x10^{-3}$
3.830	$6.00x10^{-3}$	$8.15x10^{-3}$
3.830	$7.00x10^{-3}$	$7.92x10^{-3}$
3.830	$8.00x10^{-3}$	$7.71x10^{-3}$
3.830	$9.00x10^{-3}$	$7.66x10^{-3}$

Table S.7. Influence of acetonitrile and cyclodextrin concentration on k_{obs} for the acid hydrolysis of MNTS at 25.0ºC. [HCl] = 0.160 M

$[CH_3CN]_{total}$	$[\beta\text{-CD}]_{total}$	k_{obs} /s^{-1}
$6.38x10^{-2}$	0	$4.96x10^{-3}$
$6.38x10^{-2}$	$5.00x10^{-4}$	$2.83x10^{-3}$
$6.38x10^{-2}$	$1.00x10^{-3}$	$1.98x10^{-3}$
$6.38x10^{-2}$	$2.00x10^{-3}$	$1.24x10^{-3}$
$6.38x10^{-2}$	$4.00x10^{-3}$	$7.10x10^{-4}$
$6.38x10^{-2}$	$6.00x10^{-3}$	$5.00x10^{-4}$
0.510	0	$4.85x10^{-3}$
0.510	$5.00x10^{-4}$	$2.77x10^{-3}$
0.510	$1.00x10^{-3}$	$1.98x10^{-3}$
0.510	$2.00x10^{-3}$	$1.32x10^{-3}$
0.510	$4.00x10^{-3}$	$7.60x10^{-4}$
0.510	$6.00x10^{-3}$	$5.50x10^{-4}$
0.957	0	$4.33x10^{-3}$
0.957	$5.00x10^{-4}$	$2.89x10^{-3}$
0.957	$1.00x10^{-3}$	$2.22x10^{-3}$
0.957	$2.00x10^{-3}$	$1.52x10^{-3}$
0.957	$4.00x10^{-3}$	$8.70x10^{-4}$
0.957	$6.00x10^{-3}$	$6.30x10^{-4}$
1.468	0	$3.58x10^{-3}$
1.468	$5.00x10^{-4}$	$2.62x10^{-3}$
1.468	$1.00x10^{-3}$	$2.12x10^{-3}$
1.468	$2.00x10^{-3}$	$1.50x10^{-3}$
1.468	$4.00x10^{-3}$	$9.58x10^{-4}$
1.468	$6.00x10^{-3}$	$7.35x10^{-4}$
1.978	0	$3.16x10^{-3}$
1.978	$5.00x10^{-4}$	$2.71x10^{-3}$
1.978	$1.00x10^{-3}$	$2.20x10^{-3}$
1.978	$2.00x10^{-3}$	$1.65x10^{-3}$
1.978	$4.00x10^{-3}$	$1.13x10^{-3}$
1.978	$6.00x10^{-3}$	$8.40x10^{-4}$
2.872	0	$2.92x10^{-3}$
2.872	$5.00x10^{-4}$	$2.62x10^{-3}$
2.872	$1.00x10^{-3}$	$2.30x10^{-3}$

Table S.7

$[CH_3CN]_{total}$	$[\beta\text{-CD}]_{total}$	k_{obs} /s^{-1}
2.872	2.00x10^{-3}	2.01x10^{-3}
2.872	4.00x10^{-3}	1.48x10^{-3}
2.872	6.00x10^{-3}	1.18x10^{-3}

Figure S.8. (A) Influence of [β-CD] on k_{obs} for the basic hydrolysis of MNTS in the presence of acetonitrile at 25.0ºC and [NaOH]=0.175M. (○) [CH_3CN]=9.57x10^{-2}M; (●) [CH_3CN]=0.638M; (□) [CH_3CN]= 0.957M; (■) [CH_3CN]=1.910M; (△) [CH_3CN]=2.870; and (▲) [CH_3CN]=3.830M. Data fitted according to equation (4).

A B

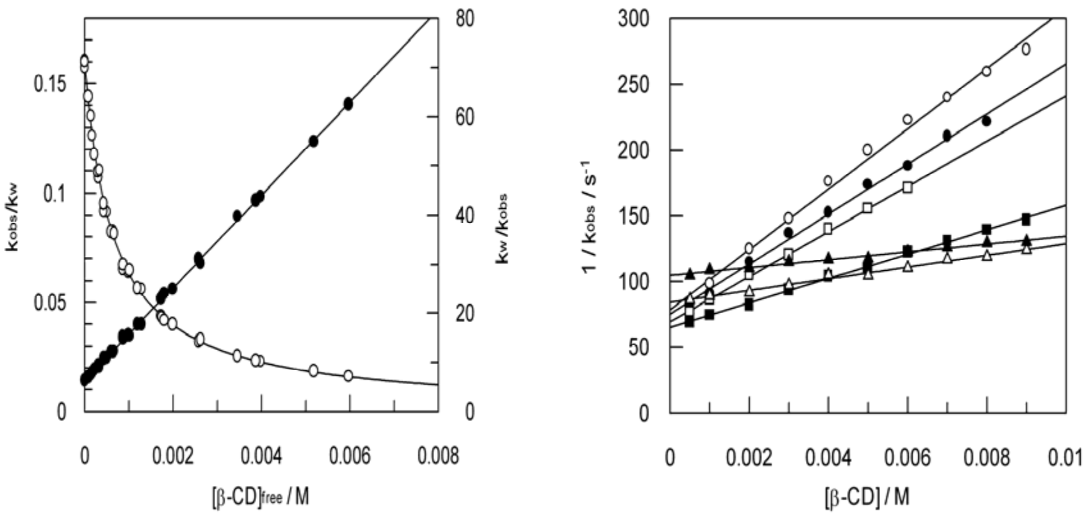


Figure S.9. Influence of $K^{\beta-CDH}_{Acetonitrile}$ and $K^{\beta-CD^-}_{Acetonitrile}$ values on the correlation coeffcient for fitting equation 9 to the experimental results for the acid (●) and basic (○) hydrolysis of MNTS.

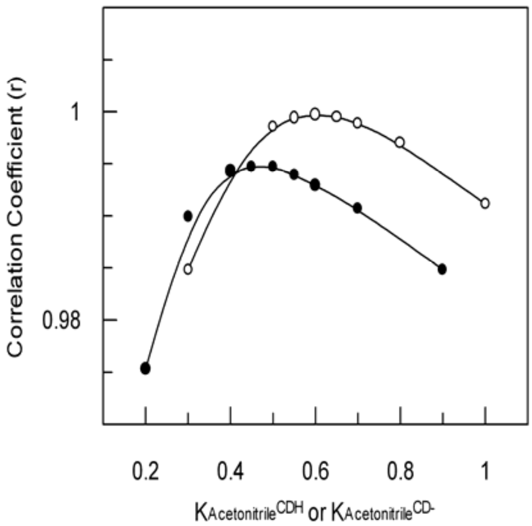


Table S.8. Influence of α–cyclodextrin concentration on k_{obs} for the basic hydrolysis of MNTS at 25.0ºC. [NaOH] = 0.162 M.

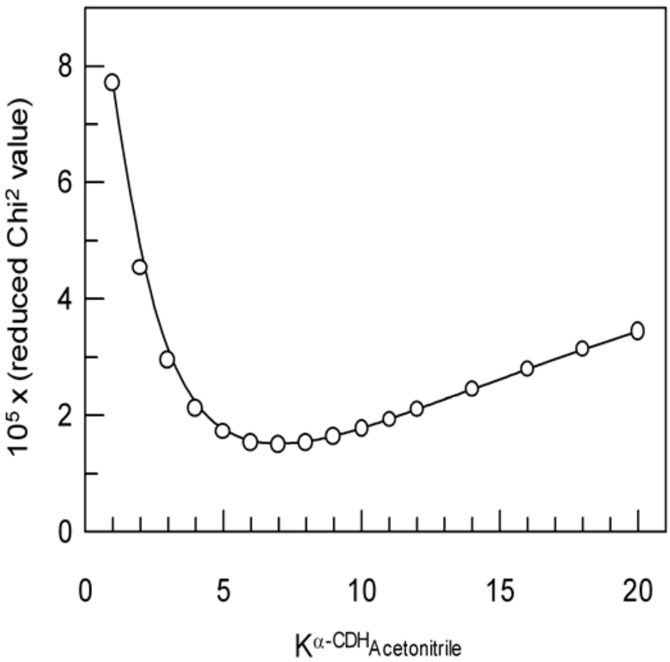
[α-CD]$_{total}$	k_{obs} **/s^{-1}**
0	$1.35x10^{-2}$
$1.06x10^{-2}$	$1.59x10^{-2}$
$2.11x10^{-2}$	$1.77x10^{-2}$
$3.17x10^{-2}$	$1.87x10^{-2}$
$4.23x10^{-2}$	$1.94x10^{-2}$
$5.29x10^{-2}$	$2.00x10^{-2}$
$6.70x10^{-2}$	$2.11x10^{-2}$
$8.46x10^{-2}$	$2.09x10^{-2}$
$9.87x10^{-2}$	$2.13x10^{-2}$
$1.13x10^{-1}$	$2.13x10^{-2}$
$1.27x10^{-1}$	$2.08x10^{-2}$
$1.55x10^{-1}$	$1.98x10^{-2}$
$2.07x10^{-1}$	$1.88x10^{-2}$
$2.58x10^{-1}$	$1.82x10^{-2}$
$3.20x10^{-1}$	$1.70x10^{-2}$
$2.25x10^{-1}$	$1.88x10^{-2}$
$1.75x10^{-1}$	$1.94x10^{-2}$

Table S.9. Influence of acetonitrile and cyclodextrin concentration on k_{obs} for the acid hydrolysis of MNTS at 25.0ºC. [HCl] = 0.160 M

$[CH_3CN]_{total}$	$[\alpha\text{-CD}]_{total}$	k_{obs} /s^{-1}
3.19×10^{-2}	0	4.95×10^{-3}
3.19×10^{-2}	1.66×10^{-2}	3.61×10^{-3}
3.19×10^{-2}	4.75×10^{-2}	2.52×10^{-3}
3.19×10^{-2}	7.13×10^{-2}	2.15×10^{-3}
3.19×10^{-2}	1.09×10^{-1}	1.86×10^{-3}
3.19×10^{-2}	1.35×10^{-1}	1.66×10^{-3}
6.38×10^{-2}	0	5.13×10^{-3}
6.38×10^{-2}	1.66×10^{-2}	3.77×10^{-3}
6.38×10^{-2}	4.75×10^{-2}	2.63×10^{-3}
6.38×10^{-2}	7.13×10^{-2}	2.28×10^{-3}
6.38×10^{-2}	1.09×10^{-1}	1.92×10^{-3}
6.38×10^{-2}	1.35×10^{-1}	1.79×10^{-3}
1.28×10^{-1}	0	4.95×10^{-3}
1.28×10^{-1}	1.66×10^{-2}	3.94×10^{-3}
1.28×10^{-1}	4.75×10^{-2}	2.80×10^{-3}
1.28×10^{-1}	7.13×10^{-2}	2.45×10^{-3}
1.28×10^{-1}	1.09×10^{-1}	2.12×10^{-3}
1.28×10^{-1}	1.35×10^{-1}	1.92×10^{-3}
1.95×10^{-1}	0	4.85×10^{-3}
1.95×10^{-1}	1.66×10^{-2}	3.96×10^{-3}
1.95×10^{-1}	4.75×10^{-2}	2.99×10^{-3}
1.95×10^{-1}	7.13×10^{-2}	2.62×10^{-3}
1.95×10^{-1}	1.09×10^{-1}	2.18×10^{-3}
1.95×10^{-1}	1.35×10^{-1}	1.97×10^{-3}
3.19×10^{-1}	0	4.78×10^{-3}
3.19×10^{-1}	1.66×10^{-2}	4.02×10^{-3}
3.19×10^{-1}	4.75×10^{-2}	3.27×10^{-3}
3.19×10^{-1}	7.13×10^{-2}	2.86×10^{-3}
3.19×10^{-1}	1.09×10^{-1}	2.40×10^{-3}
3.19×10^{-1}	1.35×10^{-1}	2.06×10^{-3}
5.11×10^{-1}	0	4.74×10^{-3}
3.19×10^{-1}	1.66×10^{-2}	4.34×10^{-3}

Table S.9		
$[CH_3CN]_{total}$	**$[\alpha\text{-CD}]_{total}$**	**k_{obs} /s^{-1}**
3.19×10^{-1}	4.75×10^{-2}	3.51×10^{-3}
3.19×10^{-1}	7.13×10^{-2}	3.27×10^{-3}
3.19×10^{-1}	1.09×10^{-1}	2.74×10^{-3}
3.19×10^{-1}	1.35×10^{-1}	2.58×10^{-3}

Figure S.10. Influence of the $K^{\alpha-CDH}_{Acetonitrile}$ values on the Reduced Chi Squared Value for the fitting of equation 20 to the experimental results in the acid hydrolysis of MNTS.



EQUATIONS

From Equation (1) to (2):

Since the total concentration of β-CD will be the combination of those of free and bound cyclodextrin, then[17] $\left[CD\right] = \left[CD\right]_T - \left[Solvent - CD\right]$. By using the binding constant of the cosolvent to β-CD, the following expression for the concentration of free cyclodextrin as a function of the total CD and organic cosolvent concentrations can be obtained:

$$\left[CD\right]_{free} = \frac{\left[CD\right]_T}{1 + K_{Dioxane}^{\beta - CDH}\left[Dioxane\right]_T} \tag{S1}$$

A combination of eqs (1) and (2) yields

$$k_{obs} = \frac{k_w\left[H^+\right]}{1 + K_{MNTS}^{\beta - CDH}\dfrac{\left[CD\right]_T}{1 + K_{Dioxane}^{\beta - CDH}\left[Dioxane\right]_T}} = \frac{k_w\left[H^+\right]}{1 + K_{app}\left[CD\right]_T} \tag{S2}$$

To obtain equation (4):

A general, quantitative analysis can be performed by using the binding mechanism of Scheme 2 and its associated expression for k_{obs} [eq. (1)]. Since the total cyclodextrin concentration will be the combination of the free and bound forms ($\left[\beta - CD\right]_T = \left[\beta - CD\right]_{free} + \left[MNTS - CD\right] + \left[Dioxane - CD\right]$), it can be expressed as function of the binding constants for MNTS ($K_{MNTS}^{\beta - CDH}$) and dioxane ($K_{Dioxane}^{\beta - CDH}$):

$$\left[\beta - CD\right]_T = \left[\beta - CD\right]_{free}\left(1 + \frac{\left[MNTS\right]_T K_{MNTS}^{\beta - CDH}}{1 + K_{MNTS}^{\beta - CDH}\left[\beta - CD\right]_{free}}\right) + \left[Dioxane\right]_T - \frac{\left[Dioxane\right]_T}{1 + K_{Dioxane}^{\beta - CDH}\left[\beta - CD\right]_{free}} \tag{S3}$$

The low concentration of MNTS used in the kinetic tests allows one to assume that

$$1 \gg \frac{\left[MNTS\right]_T K_{MNTS}^{\beta - CDH}}{1 + K_{MNTS}^{\beta - CDH}\left[\beta - CD\right]_{free}}$$

so that eq. (S3) can be reduced to

$$[\beta - CD]_T \approx [\beta - CD]_{free} + [Dioxane]_T - \frac{[Dioxane]_T}{1 + K_{Dioxane}^{\beta - CDH}[\beta - CD]_{free}} = 0 \qquad \text{(S4)}$$

To obtain equation 7:

The mass balances for MNTS, acetonitrile and the cyclodextrin can be expressed as follows:

$$[MNTS]_{total} = [MNTS]_w + [MNTS - CD] \qquad \text{(S5)}$$

$$[\beta - CD]_T = [\beta - CD]_{free} + [MNTS - CD] + [(CH_3CN)_2 - CD] \qquad \text{(S6)}$$

$$[CH_3CN]_T = [CH_3CN]_{free} + 2\ [(CH_3CN)_2 - CD] \qquad \text{(S7)}$$

Based on the mass balance for acetonitrile and the formation equilibrium constant for its complex with β-CD one can write the following second-order equation:

$$2\ K_{CH_3CN}^{\beta - CDH}[\beta - CD]_{free}[CH_3CN]_{free}^2 + [CH_3CN]_{free} - [CH_3CN]_T = 0 \qquad \text{(S8)}$$

Once the concentration of unbound acetonitrile is known, that of free β-CD can be calculated from

$$[\beta - CD]_T = [\beta - CD]_{free} + \frac{[MNTS]_T K_{MNTS}^{\beta - CDH}[\beta - CD]_{free}}{1 + K_{MNTS}^{\beta - CDH}[\beta - CD]_{free}} + \frac{[CH_3CN]_T - [CH_3CN]_{free}}{2} \qquad \text{(S9)}$$

The second term in which can be assumed to be negligible since $[MNTS]_T$ was very low. Therefore:

$$[\beta\text{-CD}]_{free} = [\beta\text{-CD}]_T - \frac{[CH_3CN]_T - [CH_3CN]_{free}}{2} \qquad \text{(S10)}$$