

ELECTRONIC SUPPORTING INFORMATION

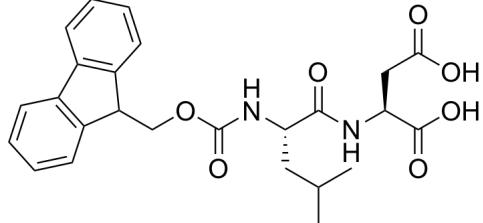
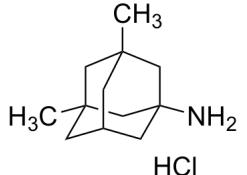
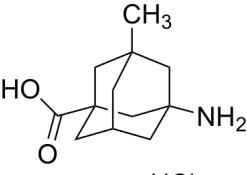
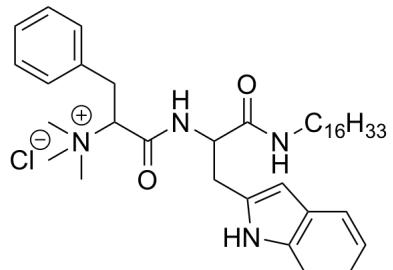
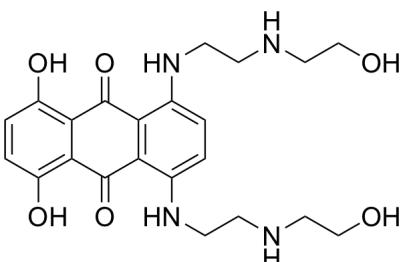
Release of small bioactive molecules from physical gels

Judith Mayr,^a César Saldías^b and David Díaz Díaz*^{a,c}

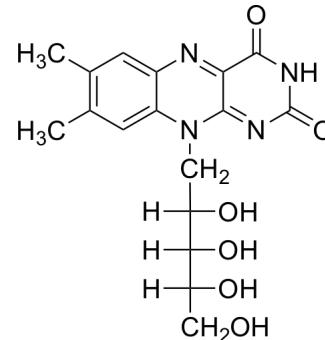
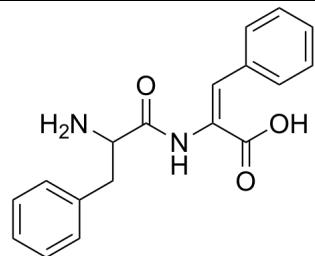
^a*Institut für Organische Chemie, Universität Regensburg, Universitätsstr. 31, 93040 Regensburg, Germany. E-mail: David.Diaz@chemie.uni-regensburg.de; Tel: +49-941-943-4373*

^b*Departamento de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 302, Correo 22, Santiago, Chile*

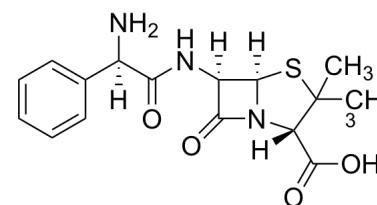
^c*Institute of Advanced Chemistry of Catalonia (IQAC-CSIC), Jordi Girona 18-26, 08034 Barcelona, Spain*

PHYSICAL ENTRAPMENT			
Gelator structure	Drug/vitamin structure	Drug/vitamin name	Reference ^a
Hydrogels			
Peptide			
	 HCl	3,5-dimethyl-1-adamantanamine hydrochloride	71
	 HCl	5-methyl-1-adamantanamine 3-carboxylic acid hydrochloride	
		mitoxantrone	72
	L-cycloserine		

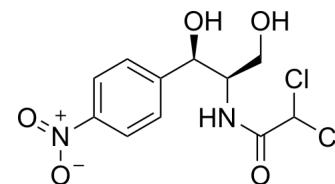
	<p>R = 5'-deoxyadenosyl, Me, OH, CN</p>	vitamin B ₁₂	
	<p>+ vitamin B₁₂</p>	vitamin B ₆	
		ascorbic acid	73



riboflavin

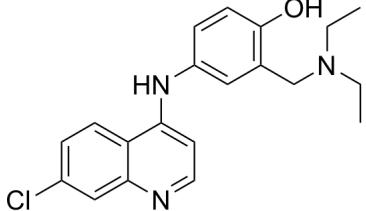
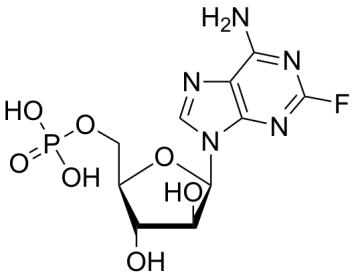
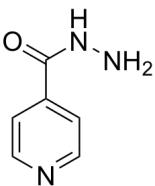
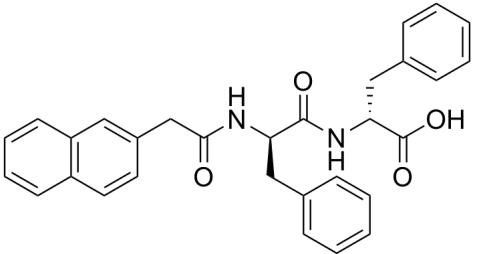
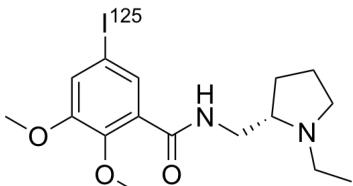


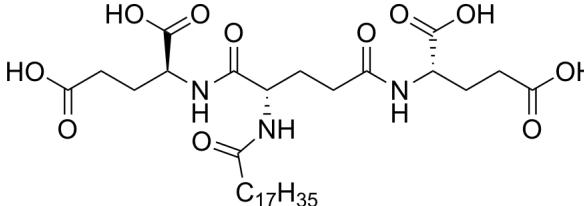
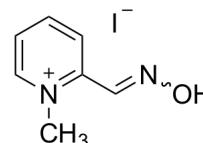
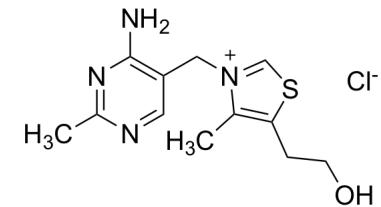
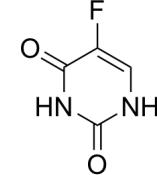
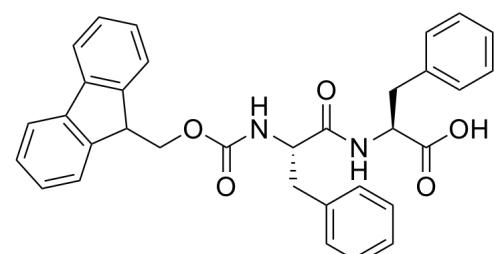
ampicillin



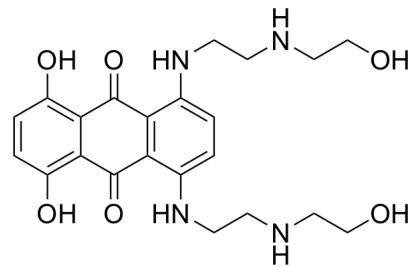
chloramphenicol

amodiaquin

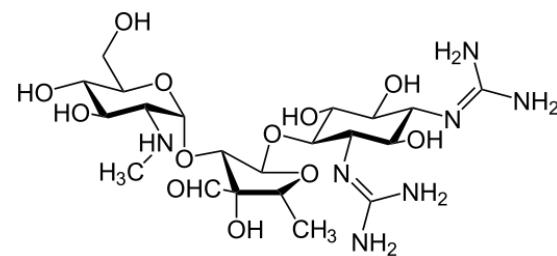
			
		fluradabine	
		isoniazid	
		epidepride	74

		pralidoxime iodine	75
		vitamin B ₁	76
		5-fluorouracil	77
		paclitaxel	

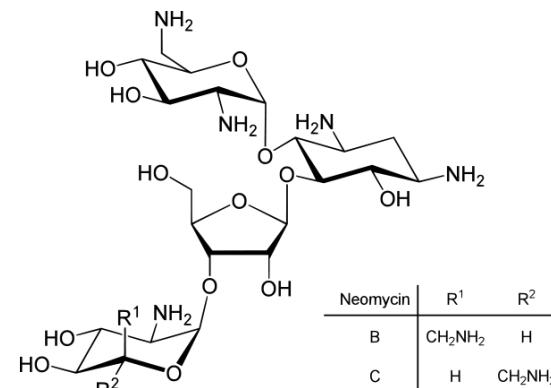
		isoniazid	78
		cisplatin	
		spectinomycin	



mitoxantrone

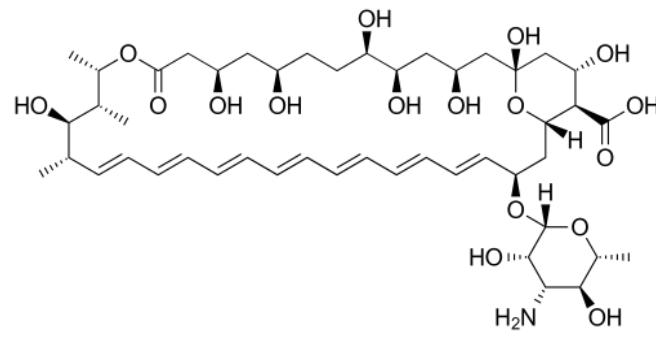
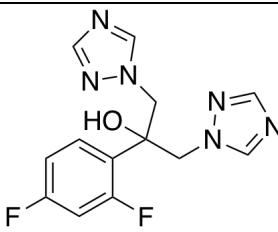


streptomycin

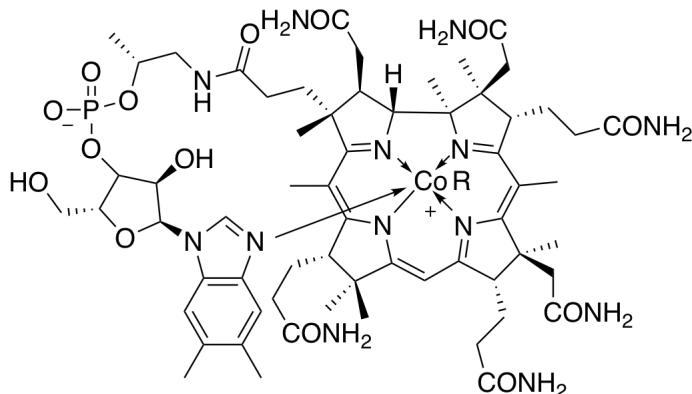


neomycin

fluconazole

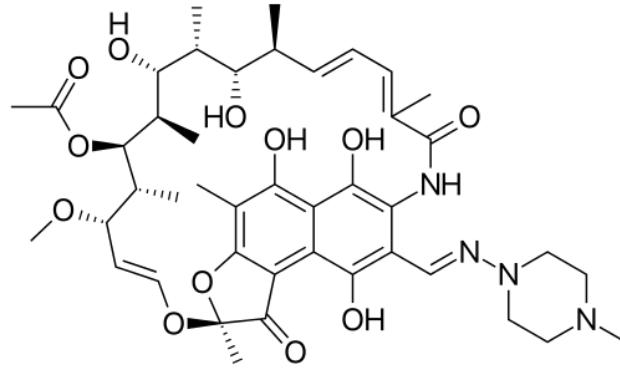


amphotericin B

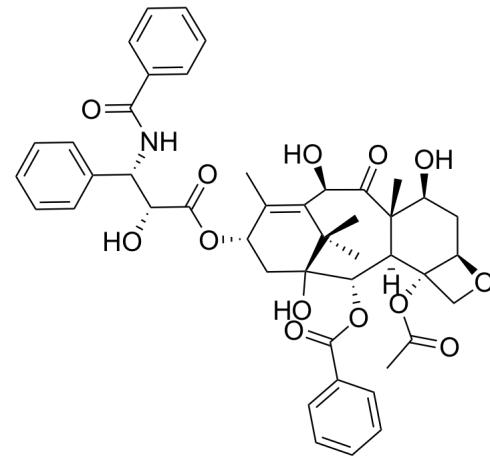


vitamin B12

R = 5'-deoxyadenosyl, Me, OH, CN

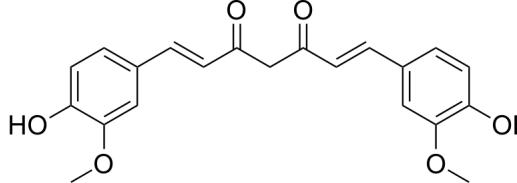
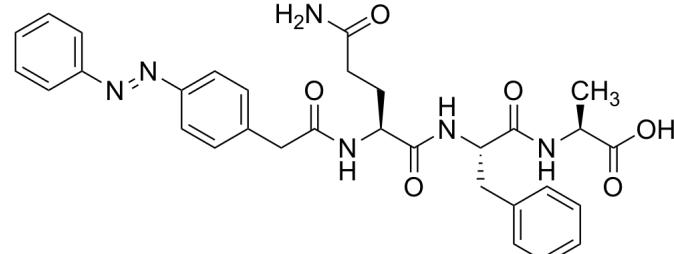
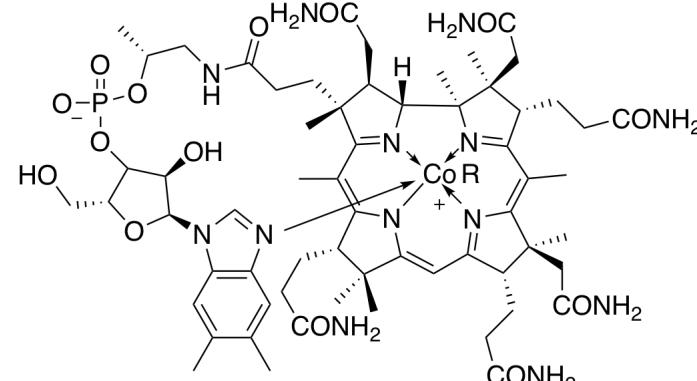
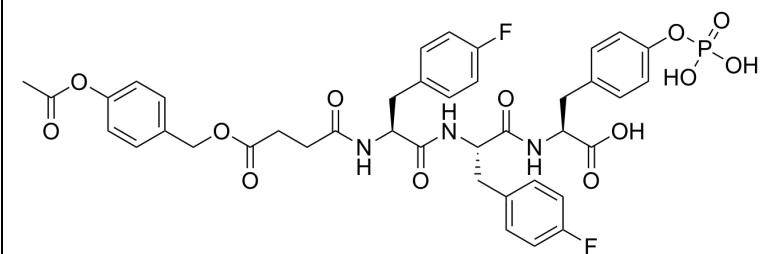
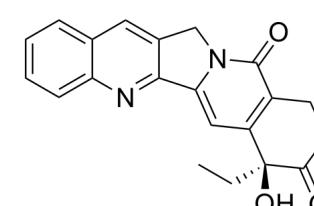


rifampicin

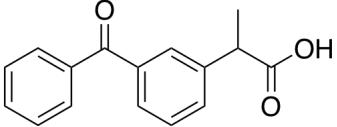
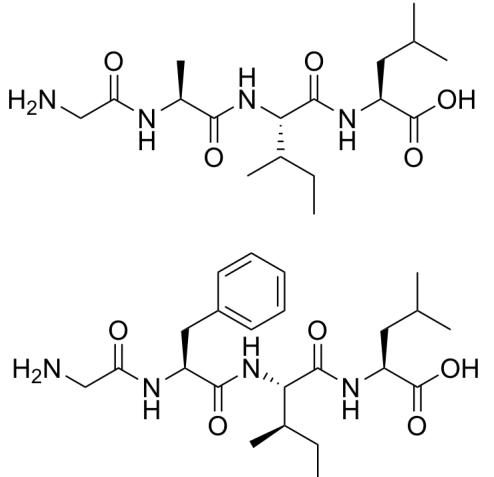
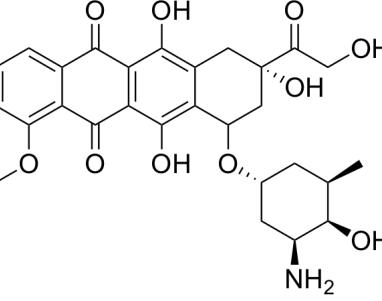
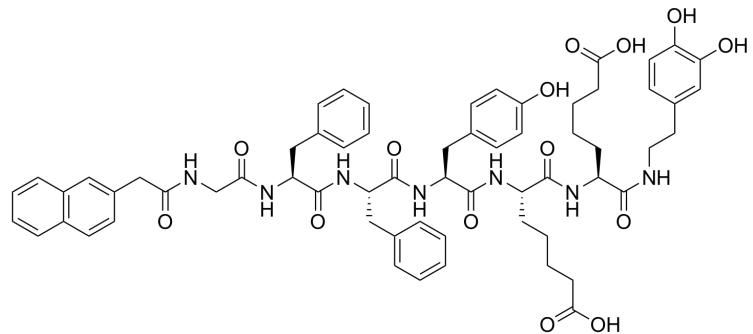
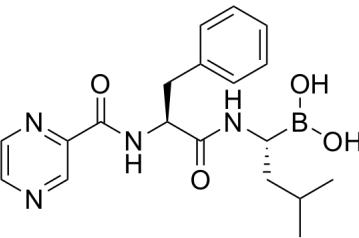


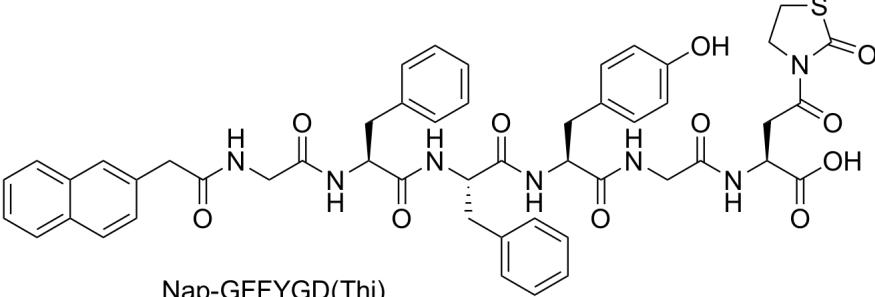
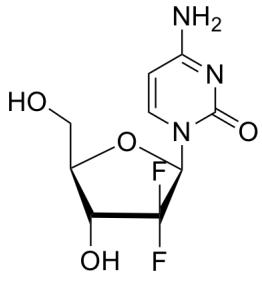
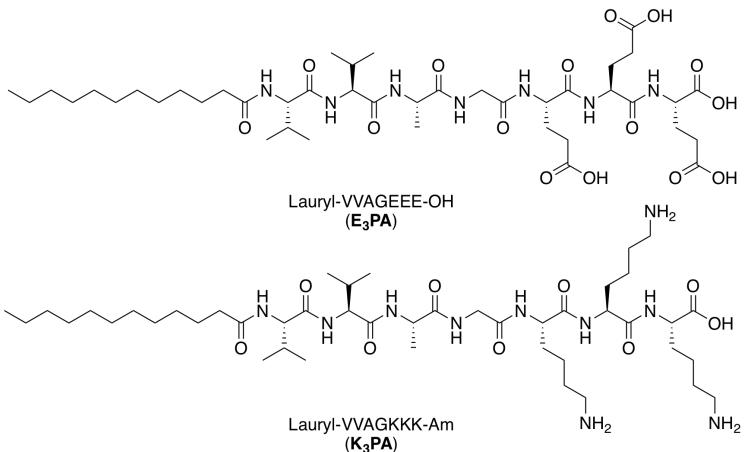
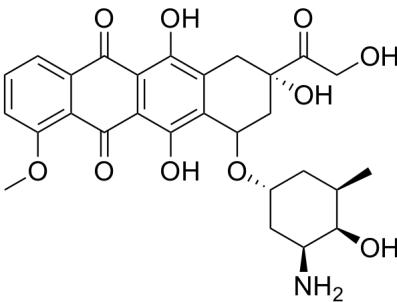
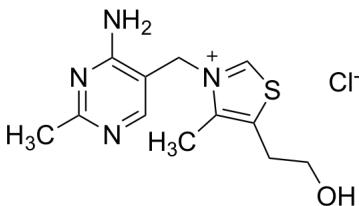
paclitaxel

curcumin

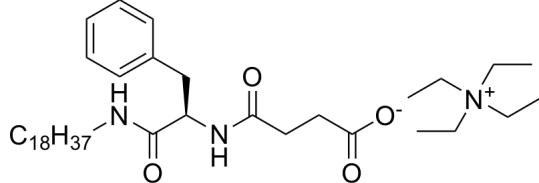
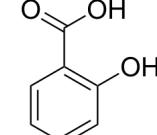
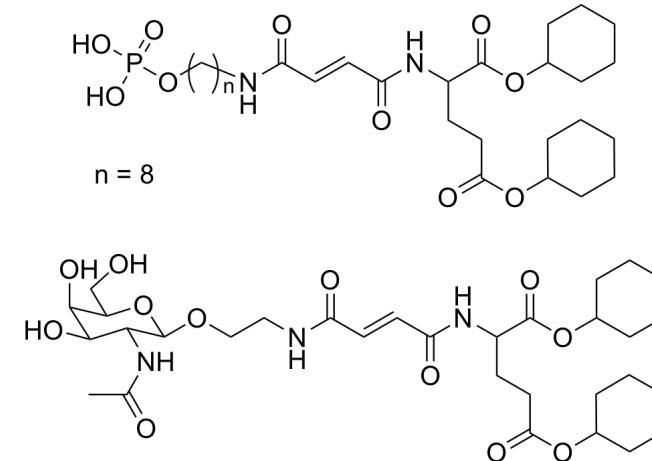
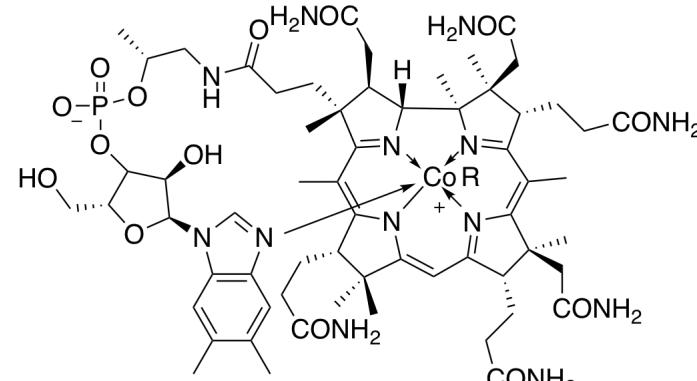
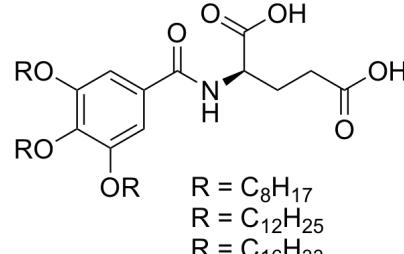
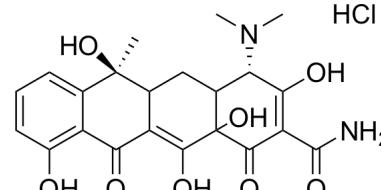
			
	 R = 5'-deoxyadenosyl, Me, OH, CN	vitamin B ₁₂	79
		camptothecin	80
		dexamethasone	81

		doxorubicin	82
		ciprofloxacin	83
		naproxen	

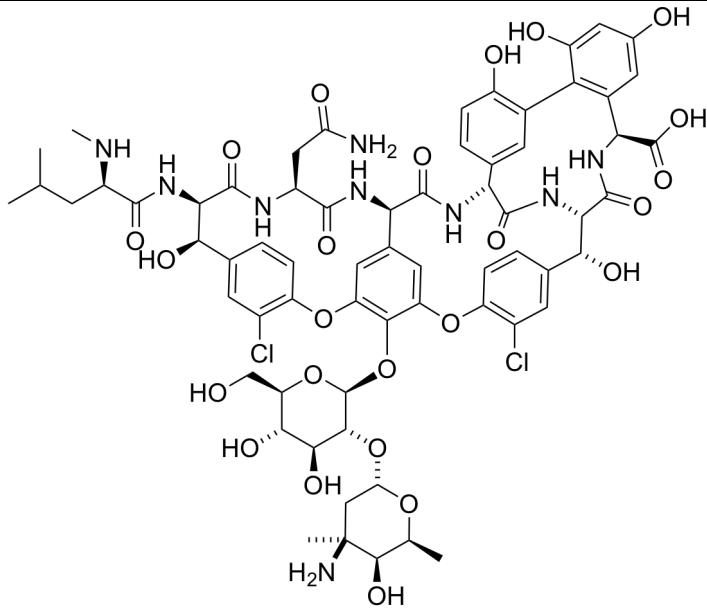
		ketoprofen	
		doxorubicin	84
		bortezomib	85
			86

 <p>Nap-GFFYGD(Thi)</p>	 <p>gemcitabin</p>	naproxen + gemcitabine (not covalently linked)	
 <p>Lauryl-VVAGEEE-OH (E₃PA)</p> <p>Lauryl-VVAGKKK-Am (K₃PA)</p>	 <p>doxorubicin</p>	87	
	 <p>vitamin B₁</p>	89	

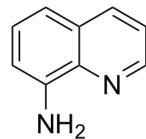
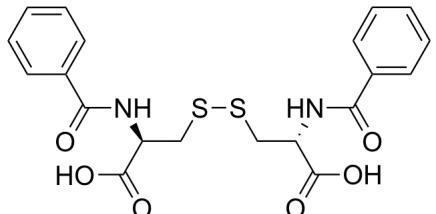
<p>$n = 2$ $n = 6$ $n = 10$</p>		vitamin B ₆	
		vitamin B ₁₂	
Amino acids			
		norleucine	90
		salicylic acid	91

 <p>$C_{18}H_{37}$</p>			
 <p>$n = 8$</p>	 <p>$R = 5'$-deoxyadenosyl, Me, OH, CN</p>	vitamin B ₁₂	92
 <p>$R = C_8H_{17}$ $R = C_{12}H_{25}$ $R = C_{16}H_{33}$</p>		tetracycline hydrochloride	93

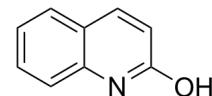
		doxorubicin	94
		caffeine	95
		vancomycin	96



Disulphides

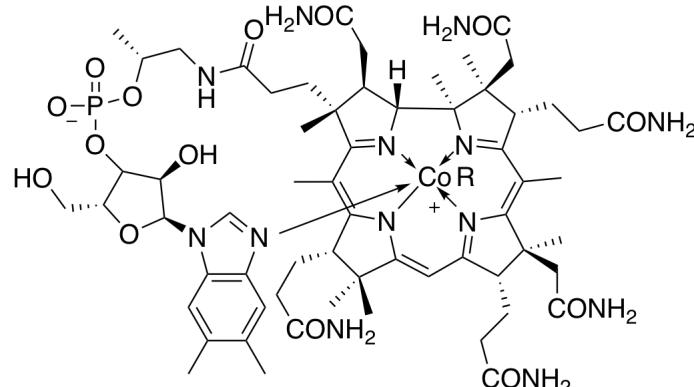
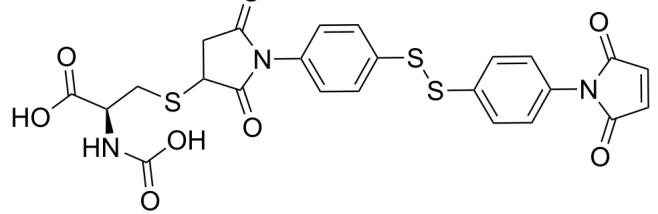


8-amino-
quinoline



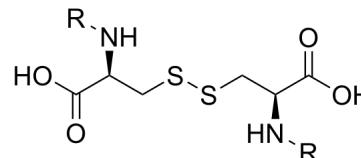
2-hydroxy-
quinoline

97

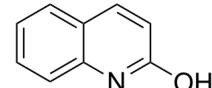


vitamin B₁₂

98



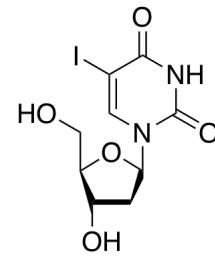
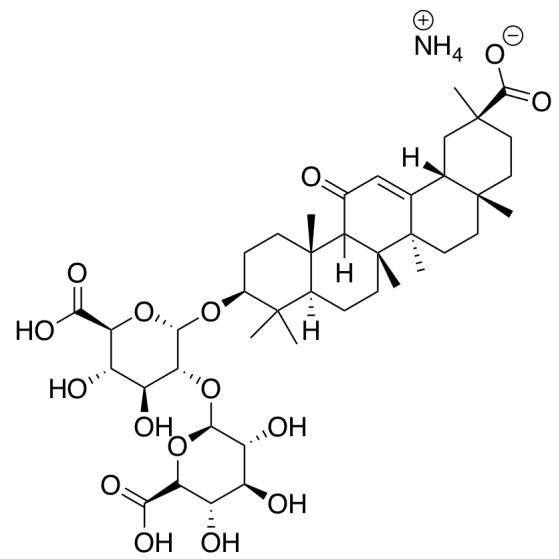
$R = C(O)Ph$
 $R = C(O)p-[CH_2=CH(CH_2)_2]Ph$
 $R = C(O)CH=CH_2$
 $R = C(O)[CH_2]_2CH=CH_2$



2-hydroxy-
quinoline

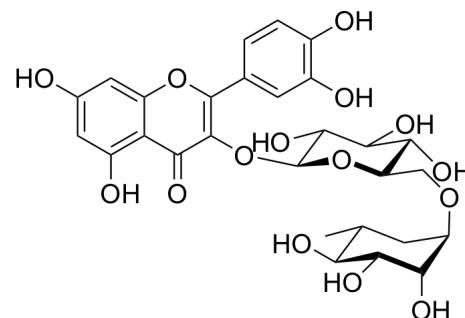
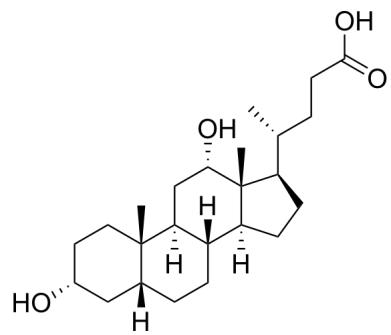
99

Miscellaneous



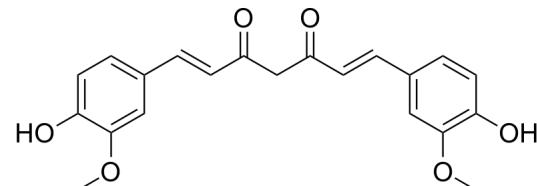
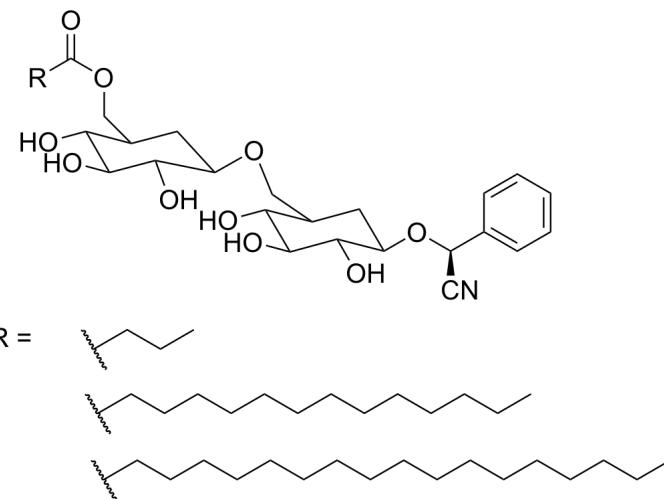
idoxuridine

100



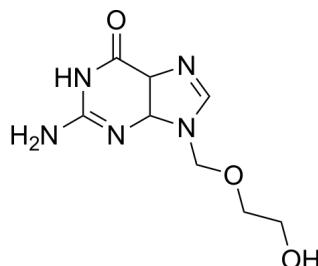
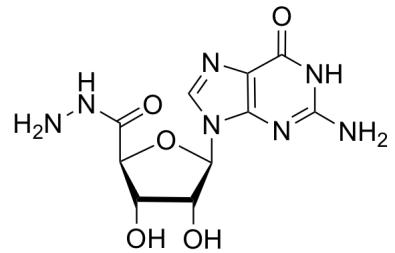
rutin

101



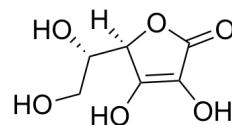
curcumin

102

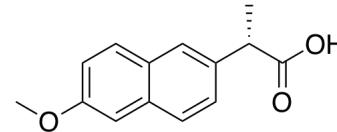
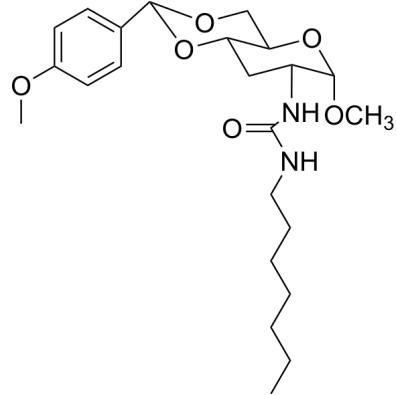


acyclovir

103

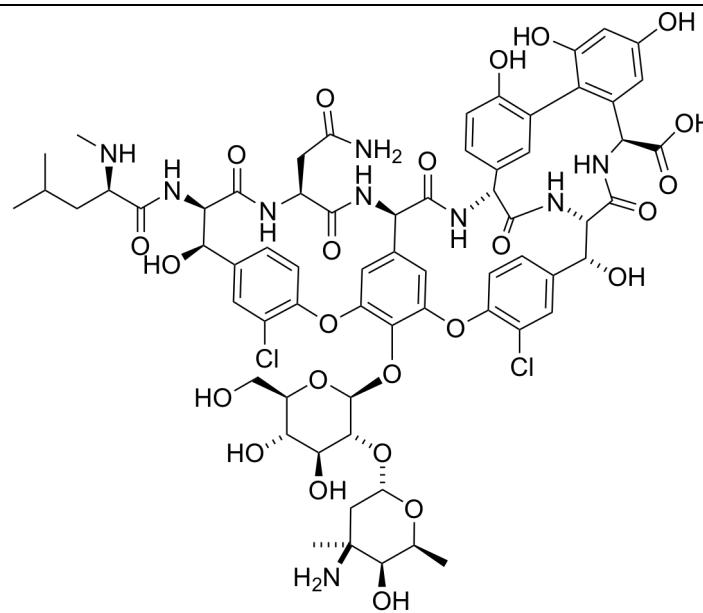


vitamin C

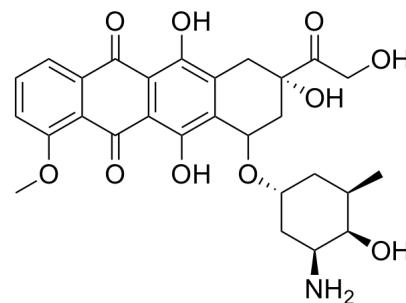
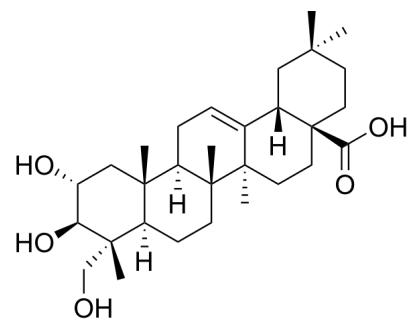


naproxen

104

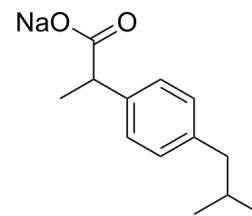
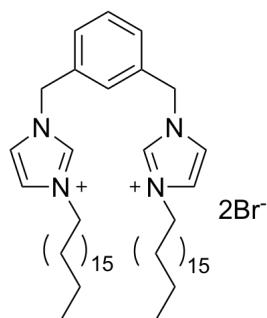


vancomycin



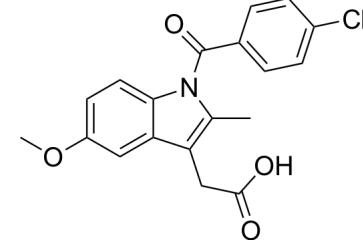
doxorubicin

105



ibuprofen
sodium salt

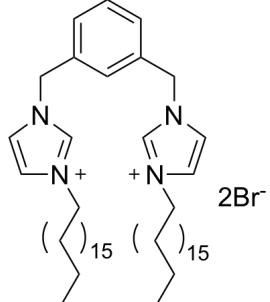
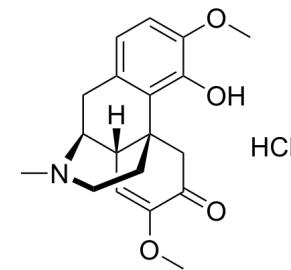
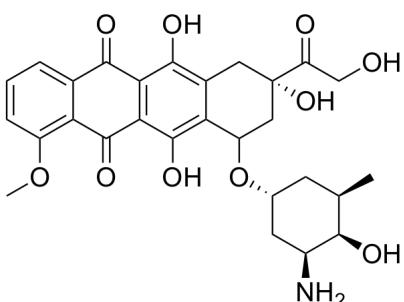
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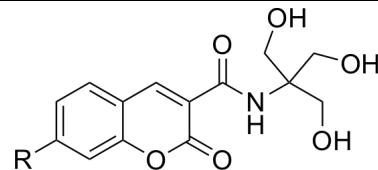


indomethacin

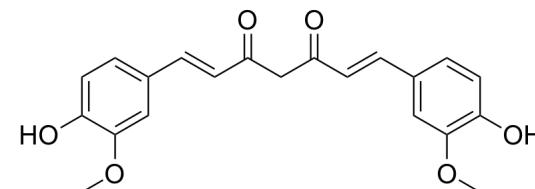
methotrexate
sodium salt

	<p>Chemical structure of a purine nucleoside derivative with a long-chain alkyl side chain.</p>		
<p>Chemical structure of a quaternary ammonium salt with a benzylidene bridge and two long-chain alkyl groups.</p>	<p>Chemical structure of ibuprofen sodium salt.</p>	ibuprofen sodium salt	107
<p>Chemical structure of a quaternary ammonium salt with a benzylidene bridge and two long-chain alkyl groups.</p>	<p>Chemical structure of indomethacin.</p>	indomethacin	

	 AEBSF·HCl	108
	sinomenine hydrochloride	109
	doxorubicin	110

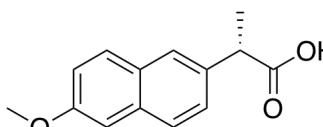
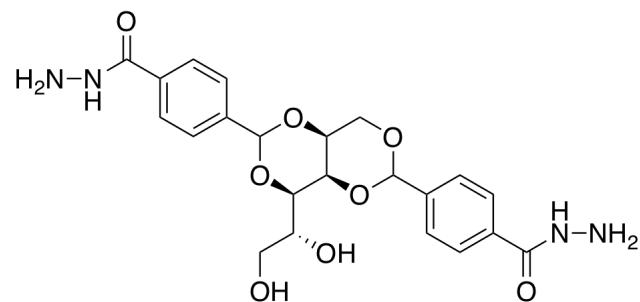


R = 5% 3-n-pentadecyl,
 50% 3-(8Z-pentadecenyl),
 16% 3-(8Z,11Z-pentadecadienyl)
 29% 3-(8Z,11Z,14-pentadecatrienyl)

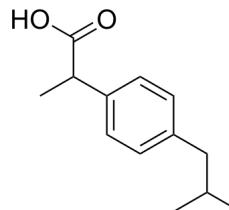


curcum

111

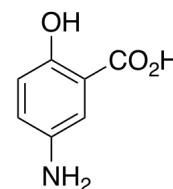


naproxen

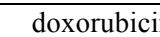


ibuprofen

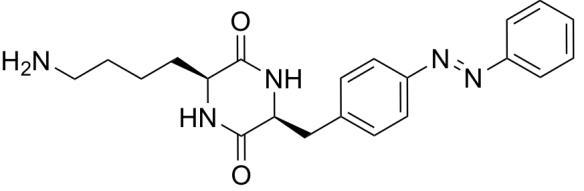
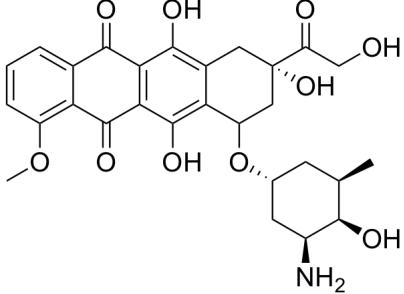
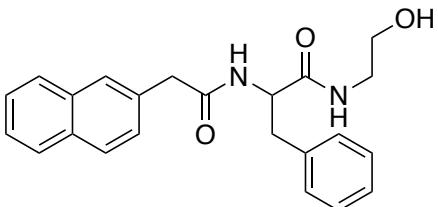
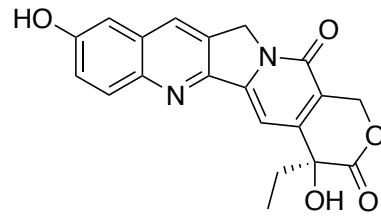
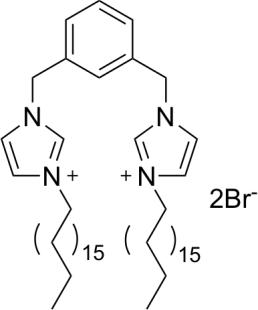
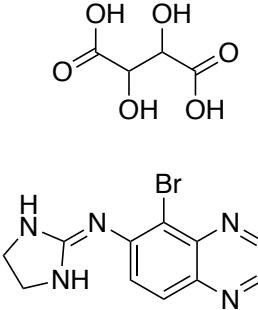
112

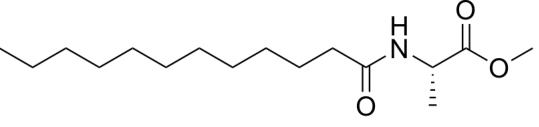
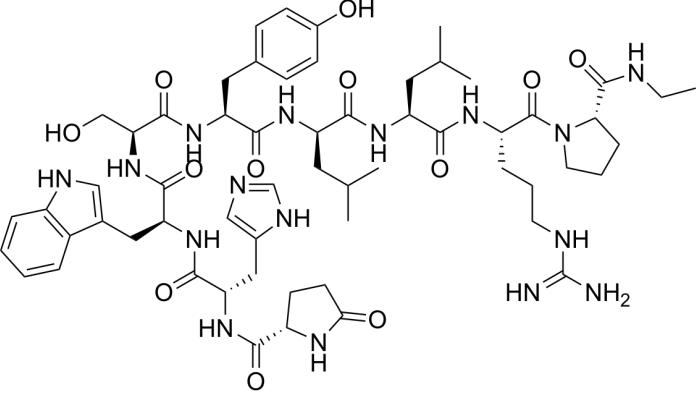
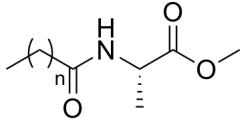
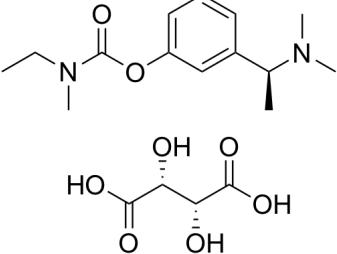
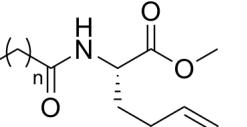
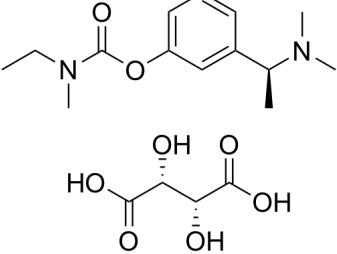


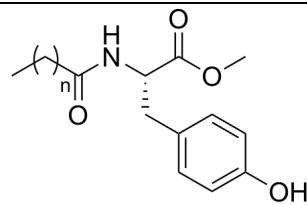
mesalazine



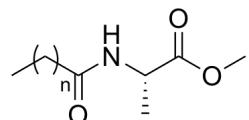
114

			
		10-hydroxy camptothecin	186
		brimonidine tartrate	210
Organogels			
Amino acids		leuprorelin	118

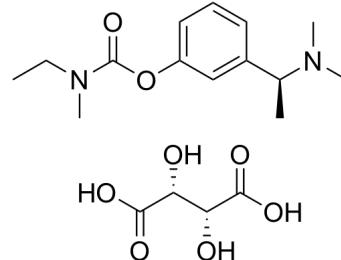
			
 $n = 16 \rightarrow$ stearoyl (S)		rivastigmine tartrate	119
 $n = 16 \rightarrow$ stearoyl (S) $20 \rightarrow$ behenoyl (B)		rivastigmine tartrate	120
		rivastigmine	121



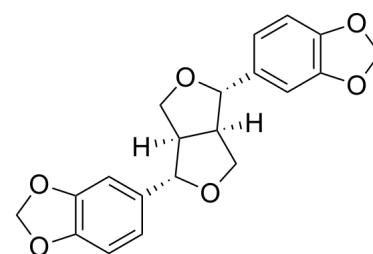
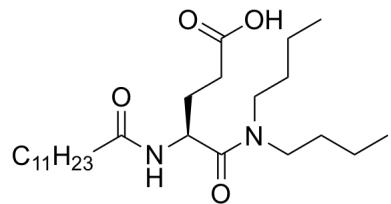
n = 20 -> behenoyl (B)



n = 16 -> stearoyl (S)

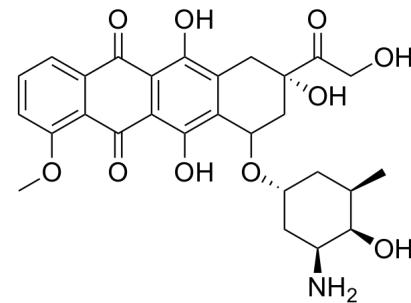


tartrate



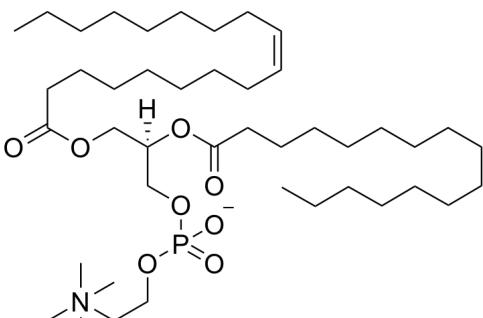
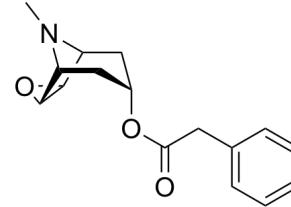
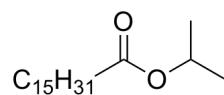
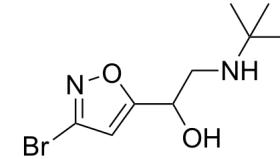
sesamin

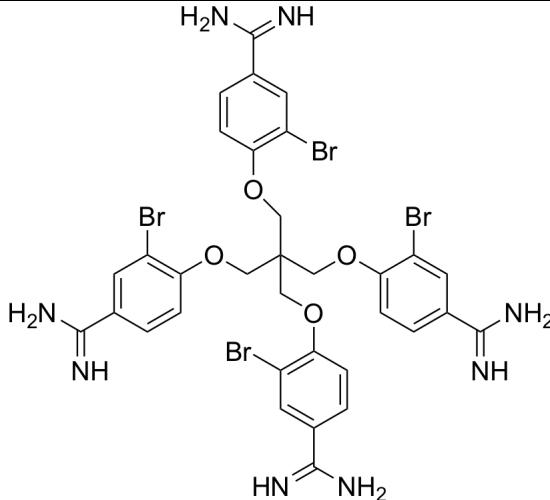
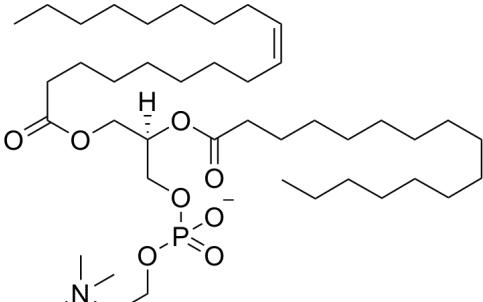
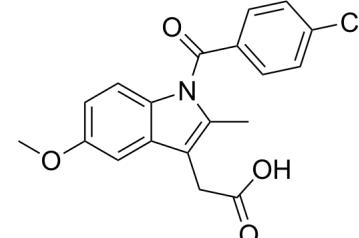
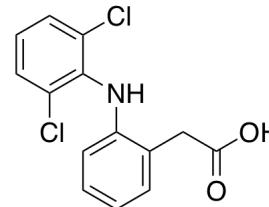
122

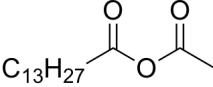
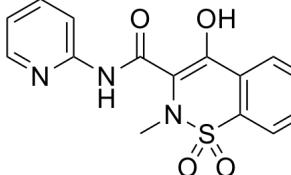
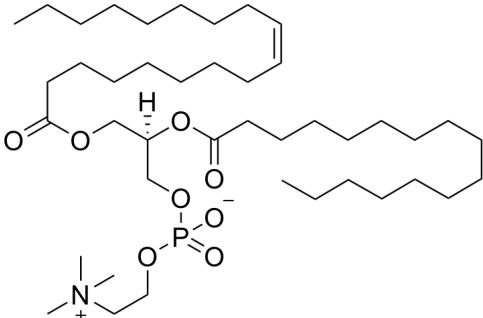
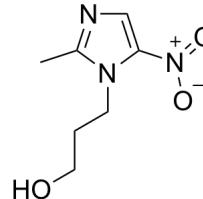
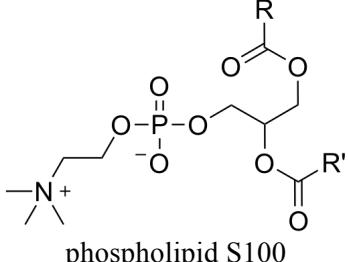
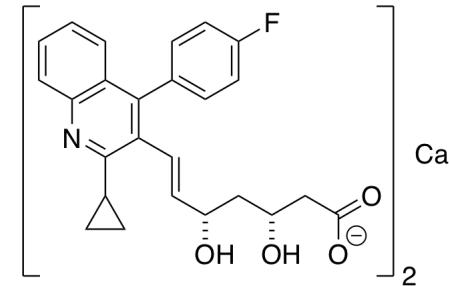


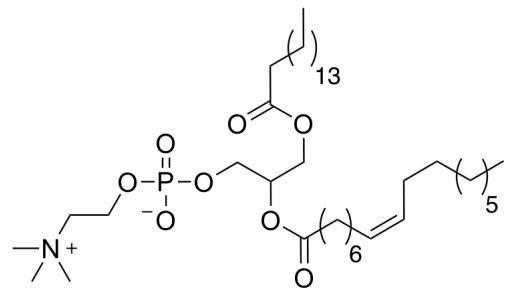
doxorubicin

123

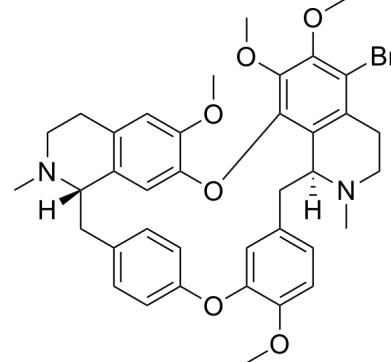
Phospholipids			
 <p>lecithine</p>		scopolamine	128
<p>lecithine +</p> 		broxaterol	

			
 lecithine		indomethacin	130
		diclofenac	
lecithine +		piroxicam	131

 $C_{13}H_{27}$			
 lecithine		metronidazole	132
 phospholipid S100		pitavastin calcium	133

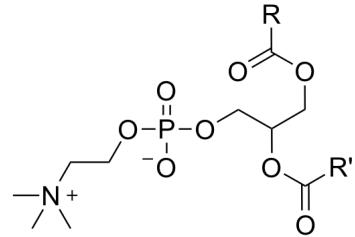


phospholipid E80

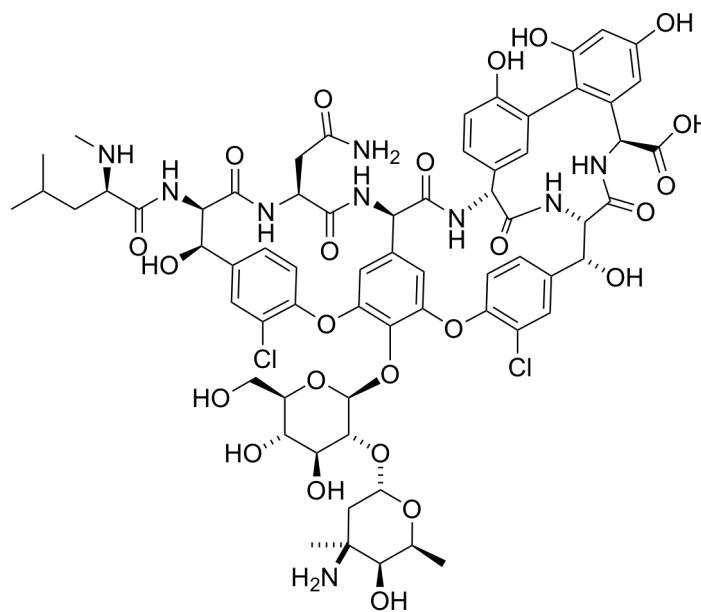


bromo-tetrandrine

134



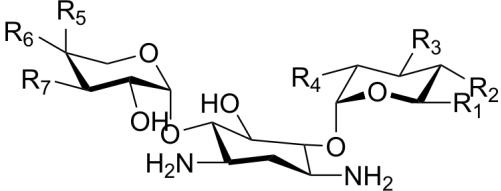
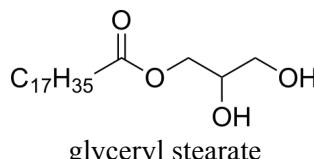
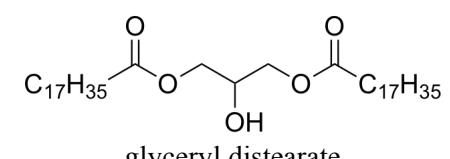
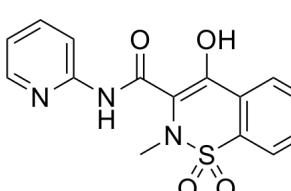
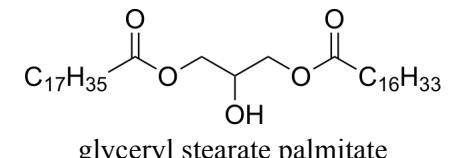
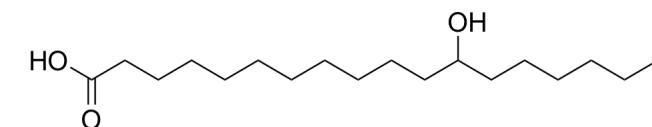
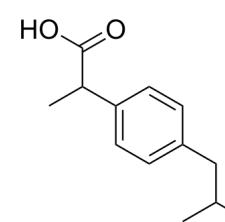
phospholipid S100

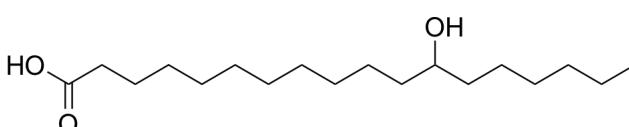
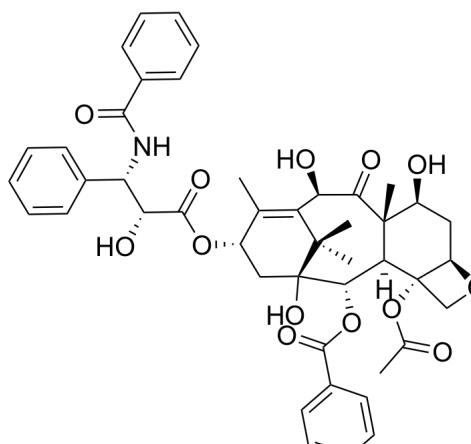
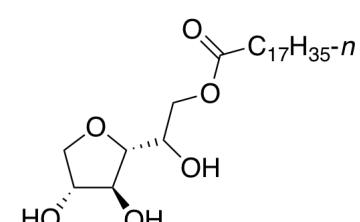
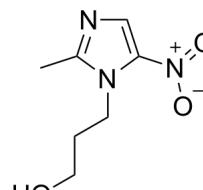
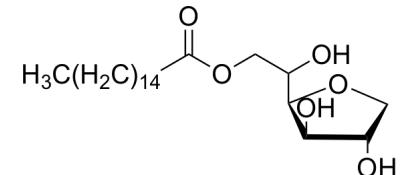
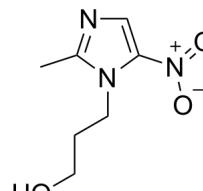


vancomycin

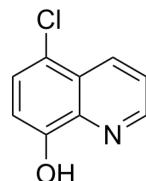
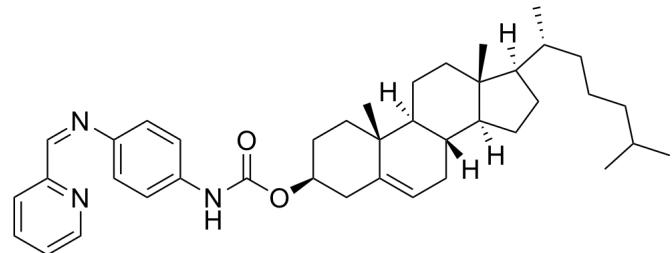
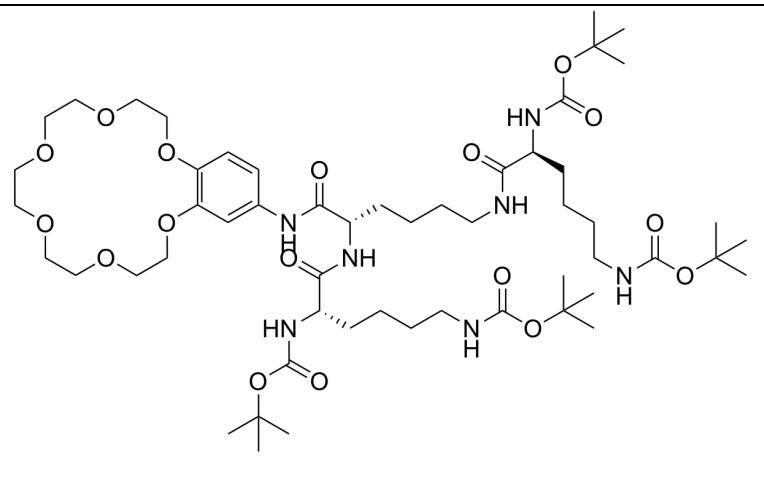
135,136

gentamicin

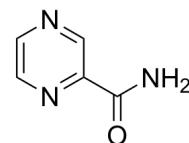
			
Fatty acids			
$\text{C}_{17}\text{H}_{35}$  glyceryl stearate			
$\text{C}_{17}\text{H}_{35}$  glyceryl distearate		piroxicam	137
$\text{C}_{17}\text{H}_{35}$  glyceryl stearate palmitate			
 12-hydroxystearic acid		ibuprofen	138

		paclitaxel	139
		metronidazole	140
		metronidazole	141
		ciprofloxacin	

 12-hydroxystearic acid		efavirenz	142
 12-hydroxystearic acid		flurbiprofen	143
Miscellaneous		dopamine	144



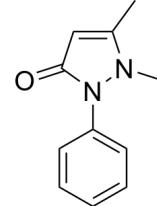
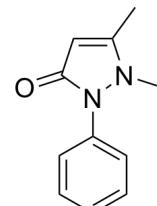
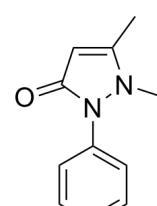
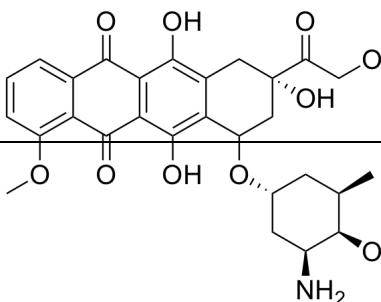
5-chloro-8-
hydroxy-
quinoline



pyrazine-
carboxamide

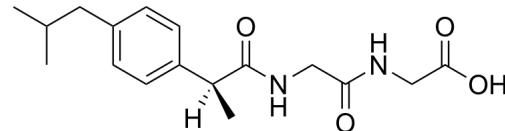
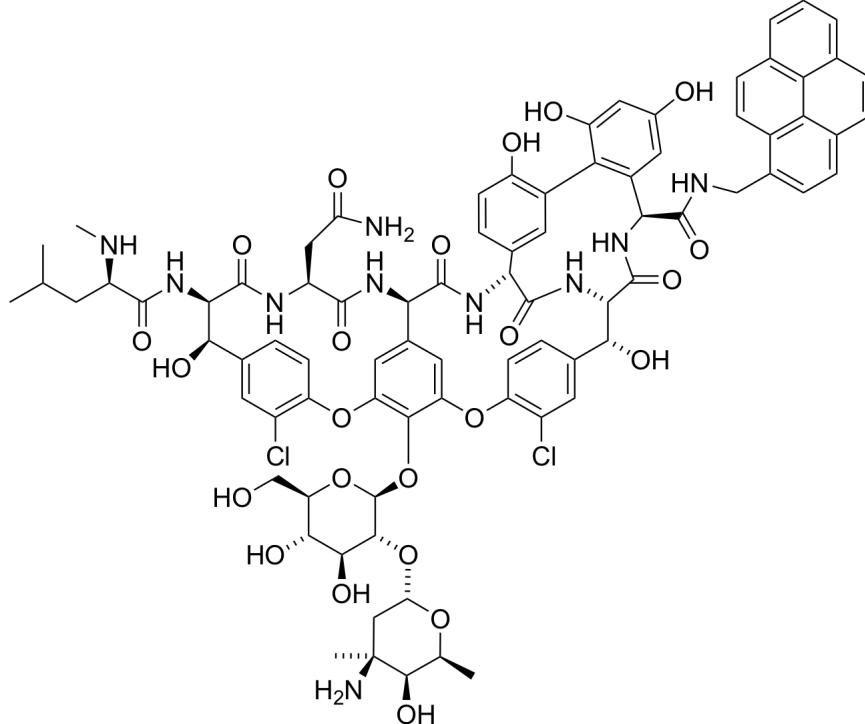
antipyrine

145

			
$\text{R}-\text{C}(=\text{O})-\text{NH}_2$ $\text{R} = \text{C}_8\text{H}_{17}$ $\text{C}_{16}\text{H}_{23}$ $\text{C}_{18}\text{H}_{27}$		antipyrine	146
$\text{C}_{21}\text{H}_{43}-\text{C}(=\text{O})-\text{NH}_2$ behenamide $\text{H}_3\text{C}(\text{H}_2\text{C})_7-\text{HC}=\text{HC}-(\text{H}_2\text{C})_{11}-\text{C}(=\text{O})-\text{NH}_2$ ercamide		antipyrine	147
		doxorubicin	148

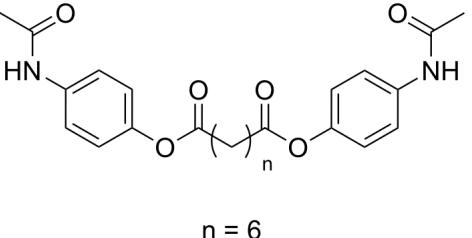
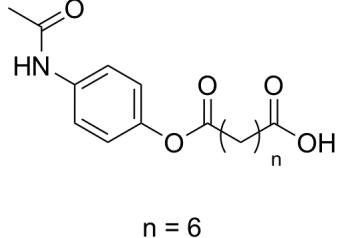
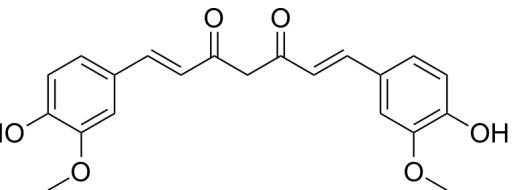
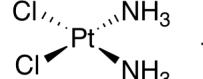
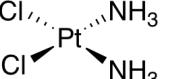
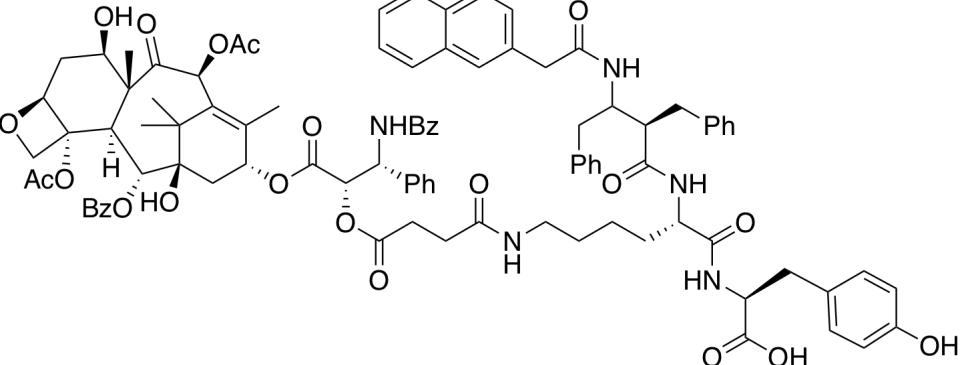
		doxorubicin curcumin	148
		tocopherol	
		candesartan cilexetil	149
		ibuprofen	150

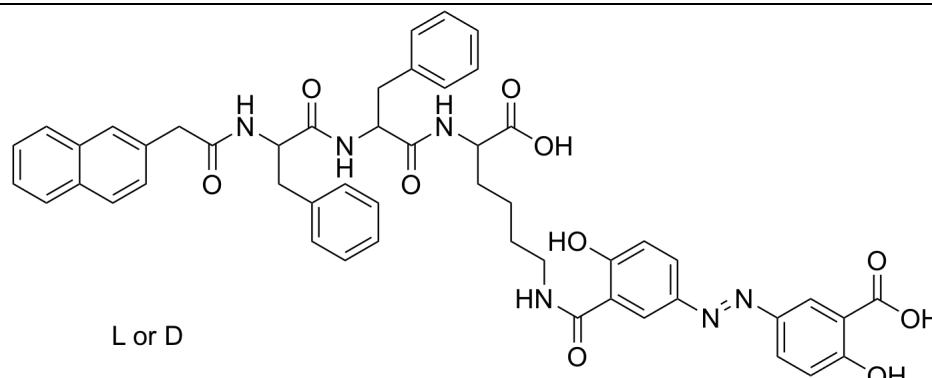
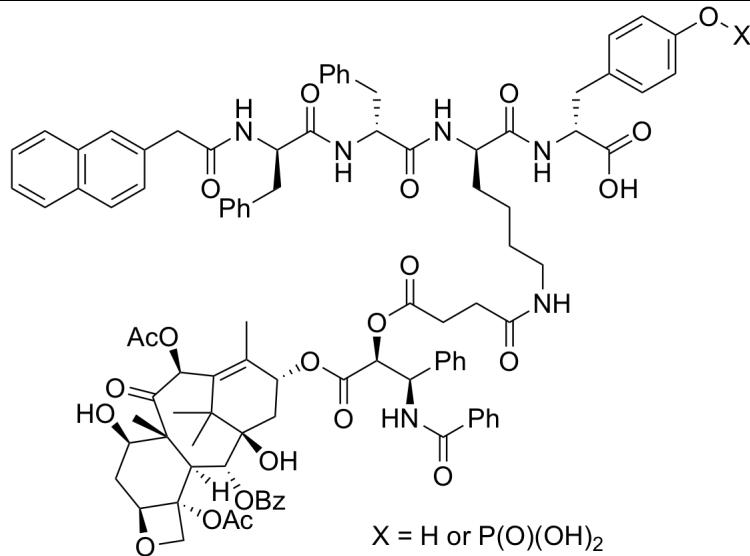
		ibuprofen	150
		ketoconazole	151
+ PVA		indomethacin	
CHEMICAL ENTRAPMENT			
Structure	Drug name	Reference	
Drug-conjugates as hydrogelators			
	vancomycin	152	



ibuprofen 155

acetaminophen
+
curcumin
(not covalently
linked) 156

				
 + <chem>CH3(CH2)14CONHGTAGLIGQRGS-COOH</chem>		cisplatin	157	
		taxol	158	
		taxol	160	

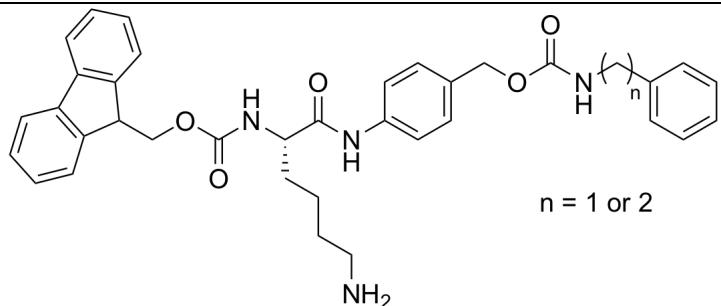


5-aminosalicylic
acid

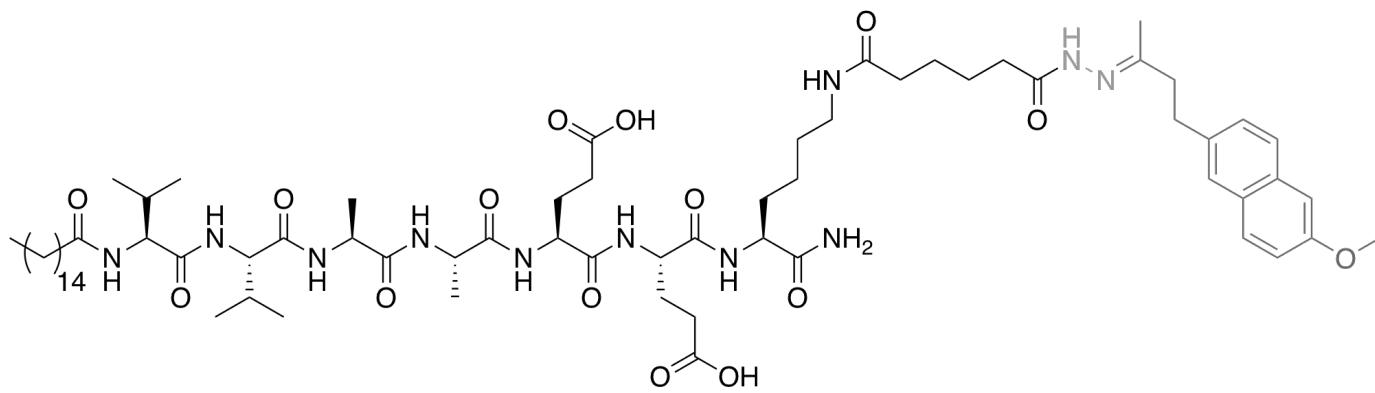
161

phenethylamine

162



$n = 1 \text{ or } 2$

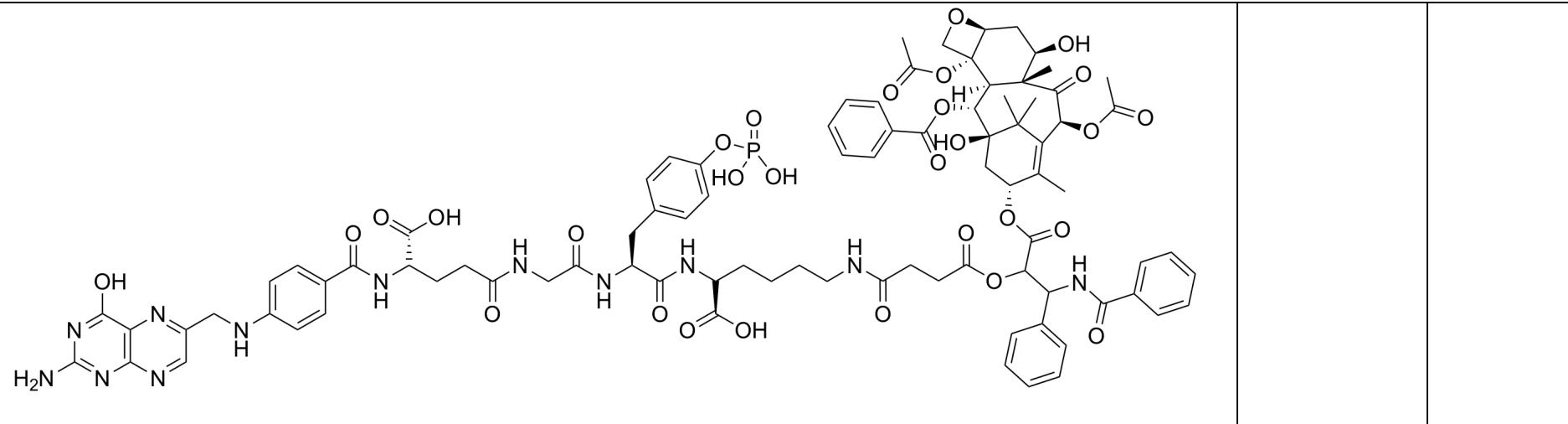


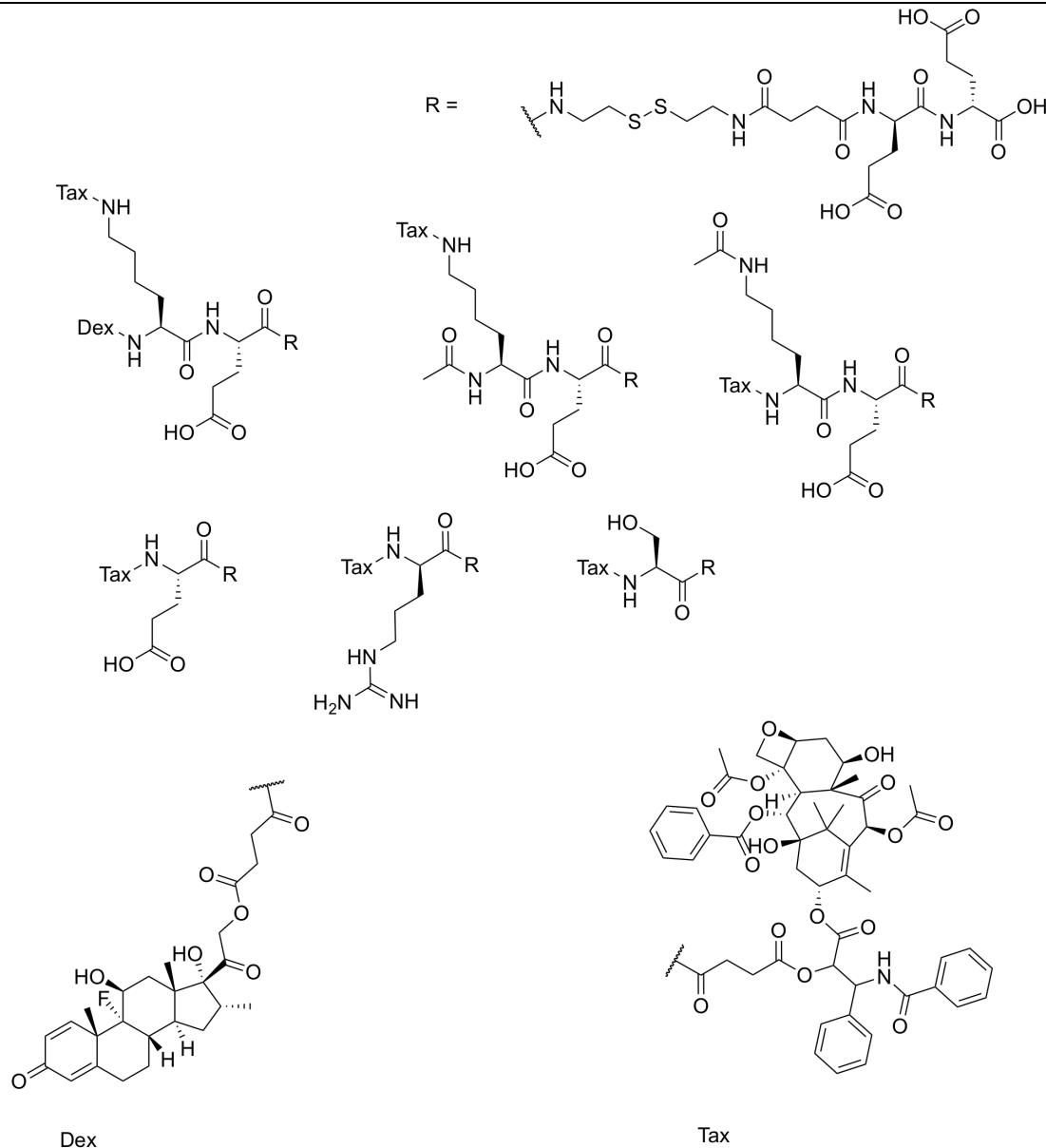
nabumetone

163

taxol

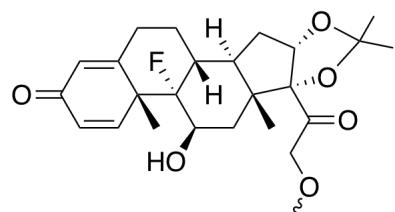
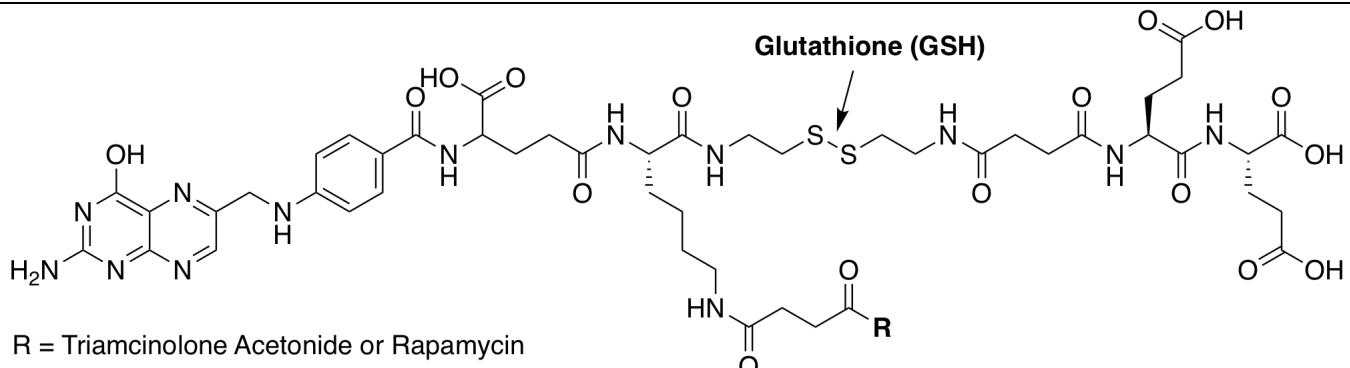
164



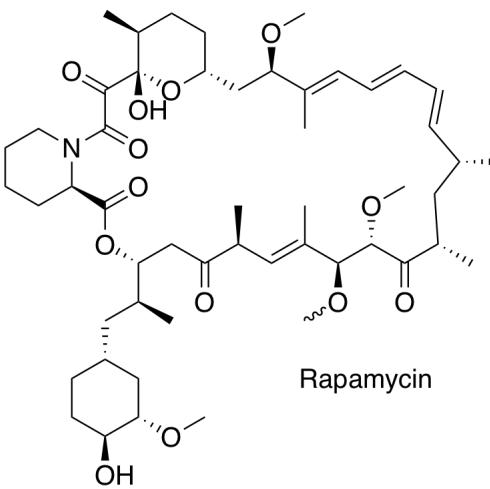


taxol
+
dexamethasone

166



Triamcinolone Acetonide

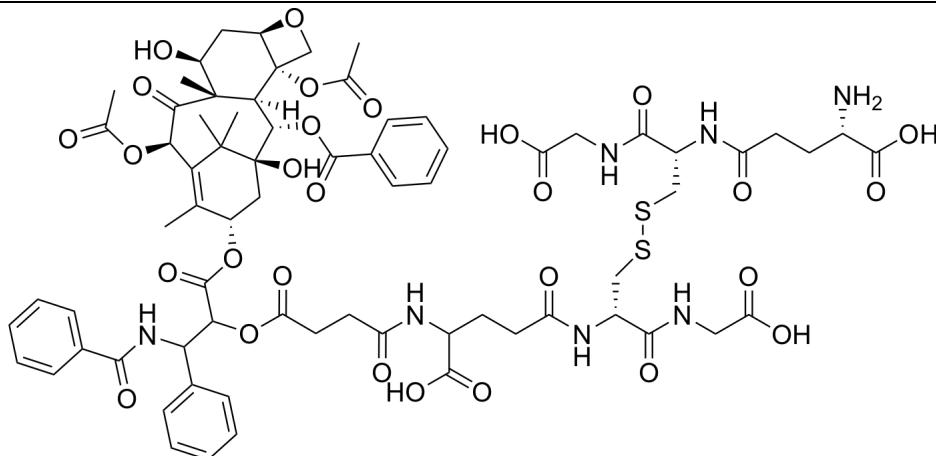


Rapamycin

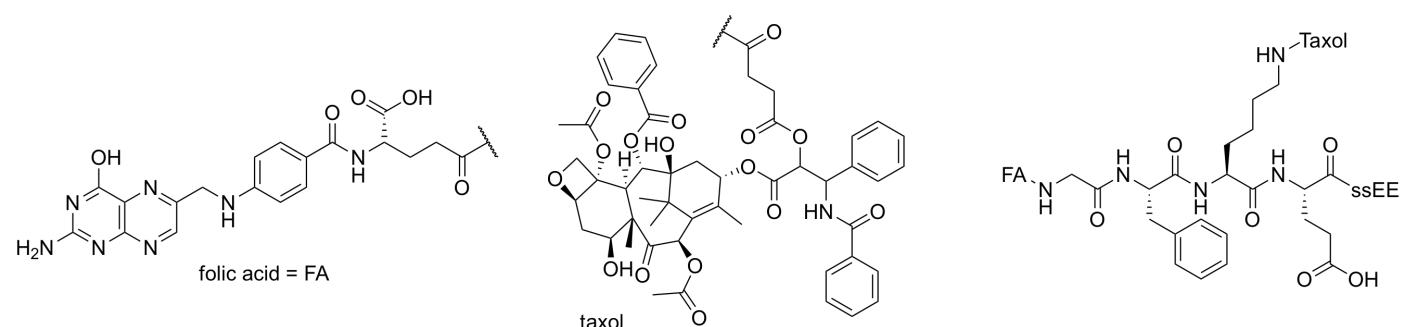
Note: Given as representative example of a precursor of the actual gelator formed upon reduction with GSH

triamcinolone
acetonide,
rapamycin

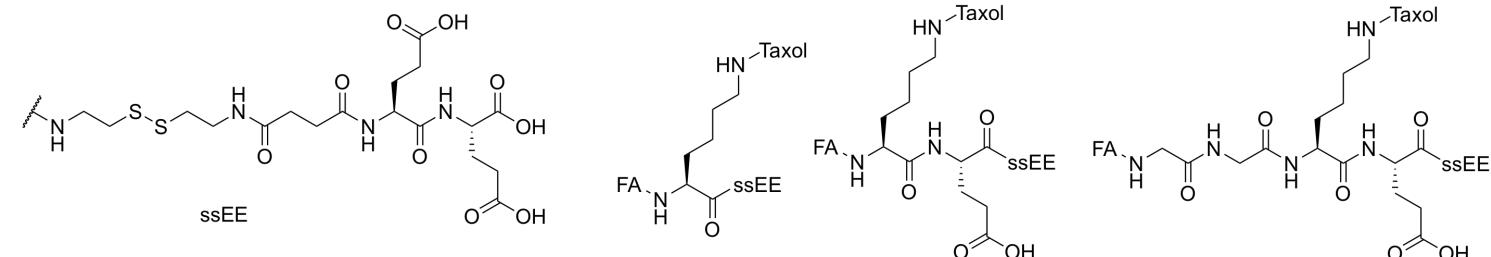
167

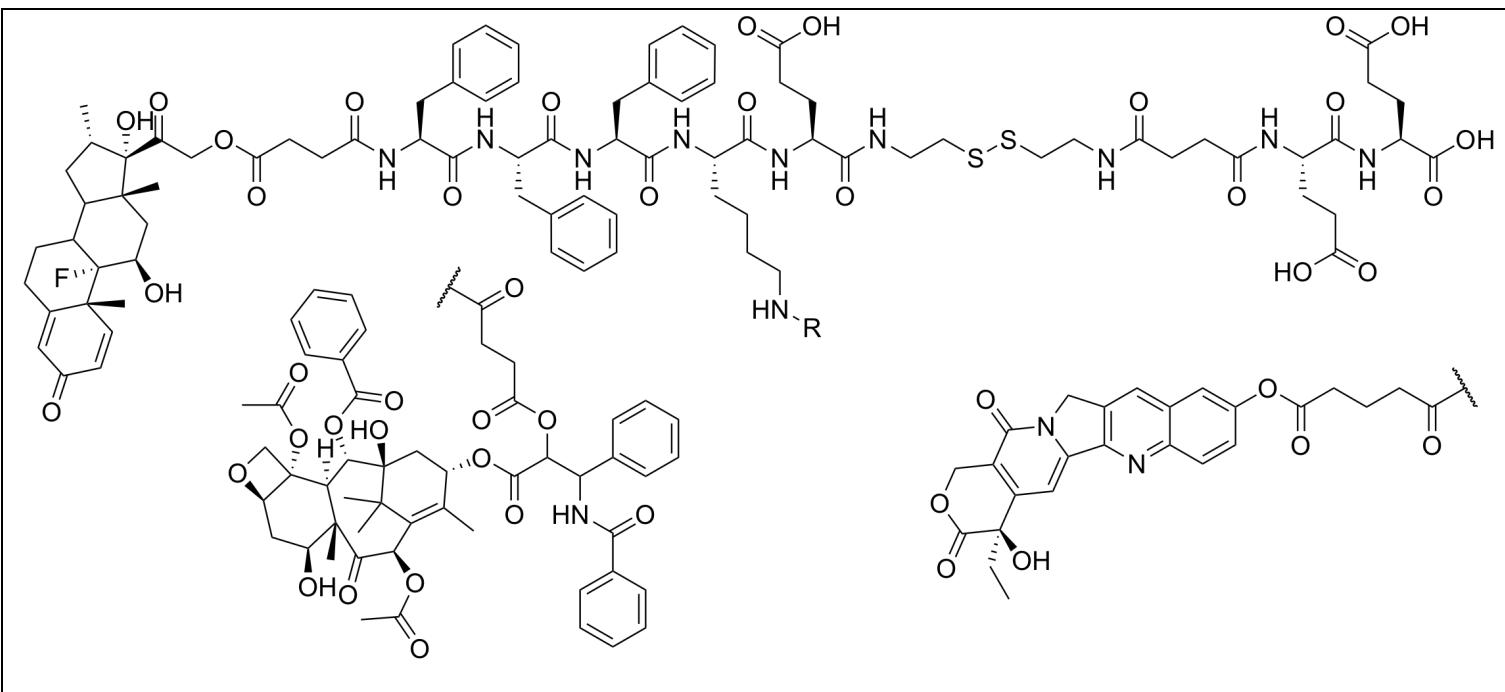
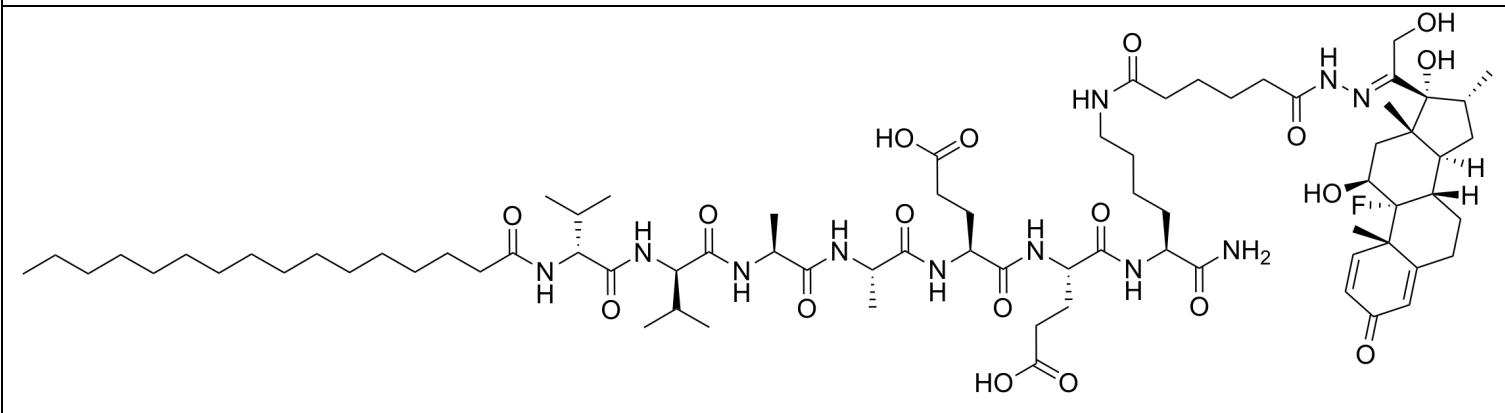


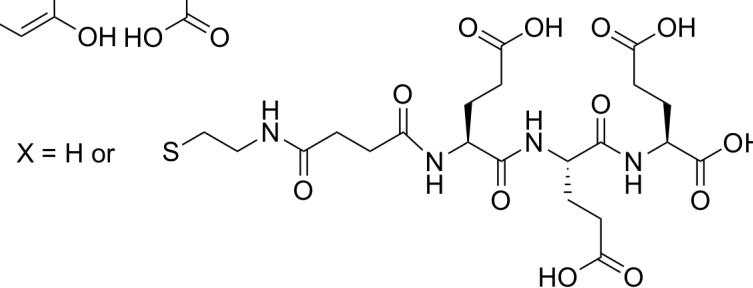
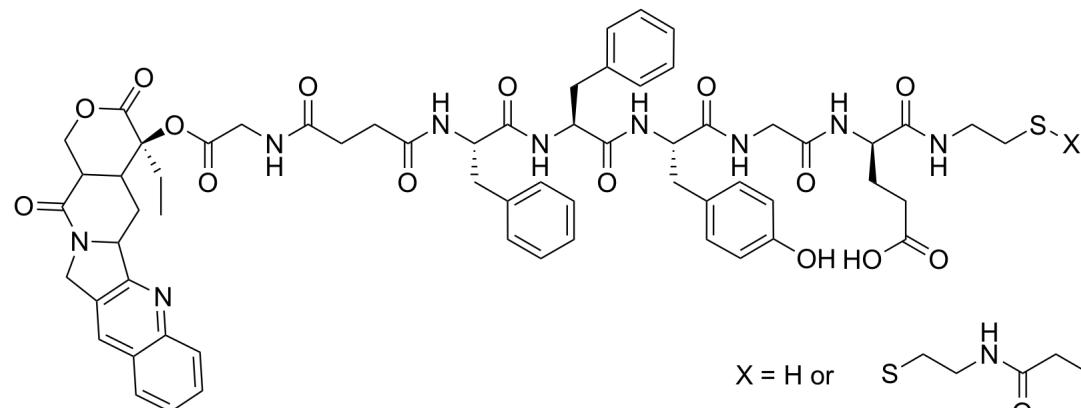
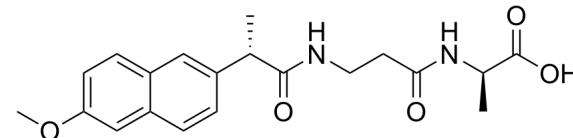
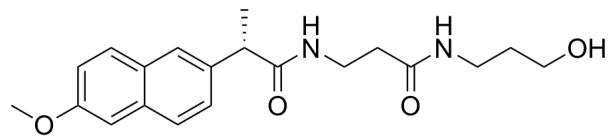
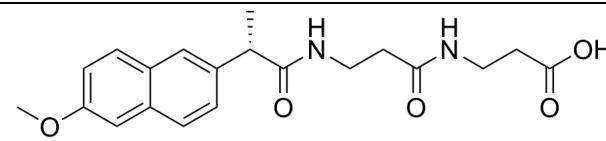
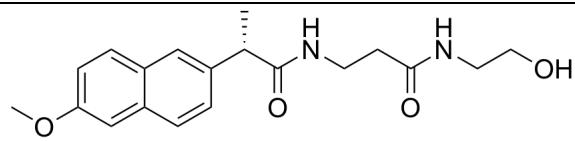
taxol 168



folic acid + taxol 169



	taxol + dexamethasone	170
	dexamethasone	171
	naproxen	172

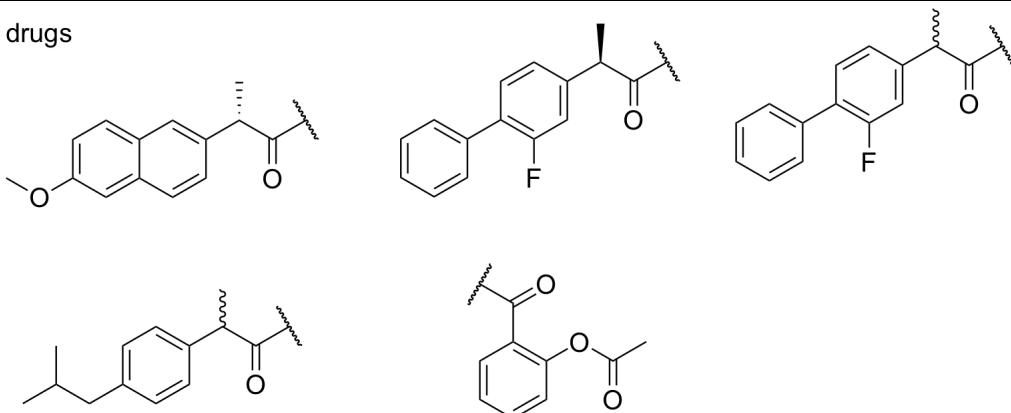
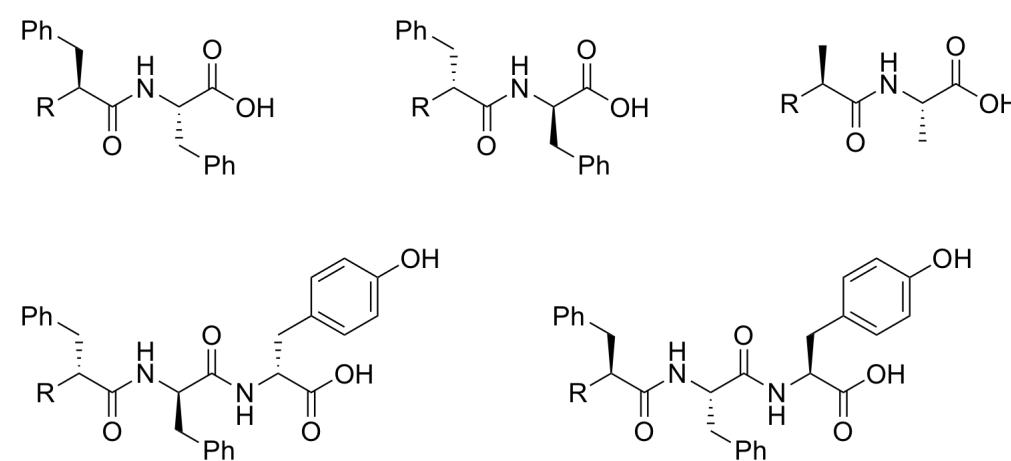


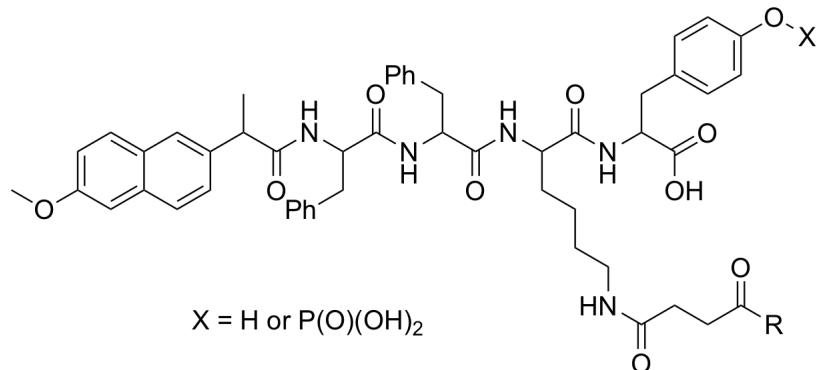
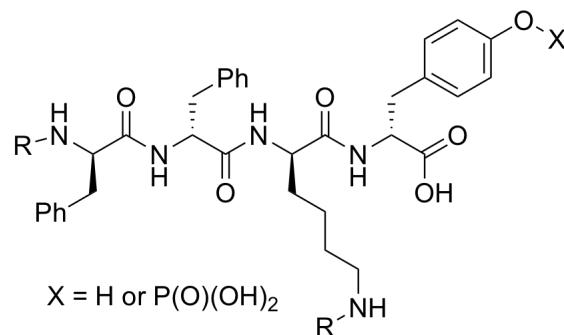
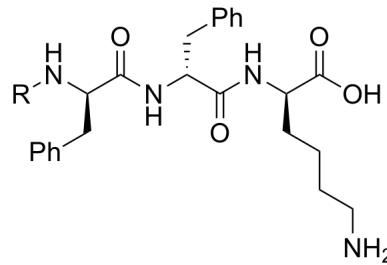
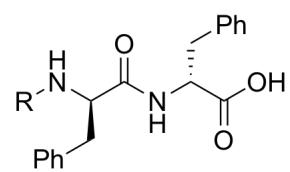
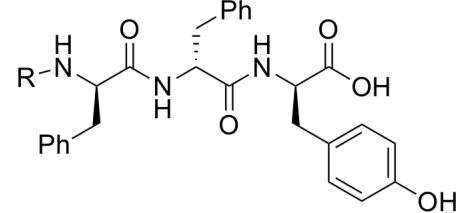
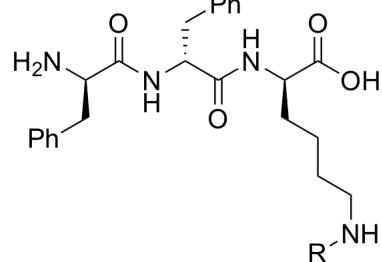
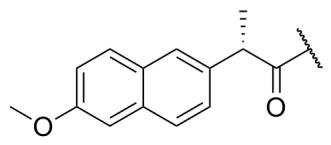
camptothecin

173

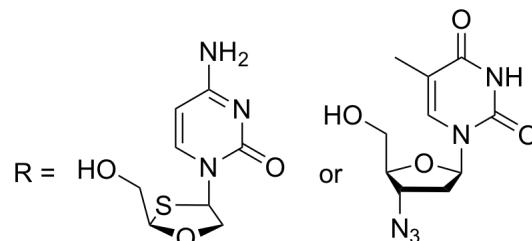
naproxen
+
(R)-flubiprofen
+

174

<p>drugs</p>  <p>small peptides</p> 	<p>(R,S)- flubiprofen + (R,S)-ibuprofen + aspirin</p>	
		naproxen 175



X = H or P(O)(OH)₂

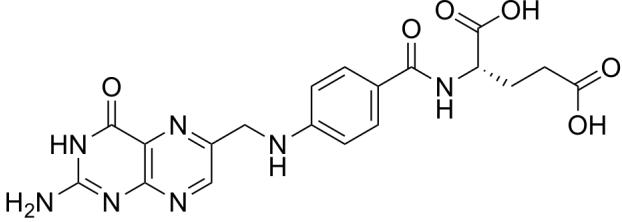
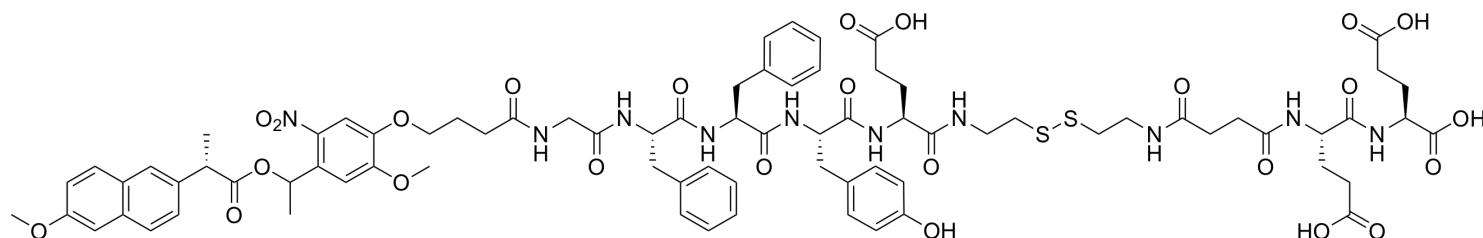
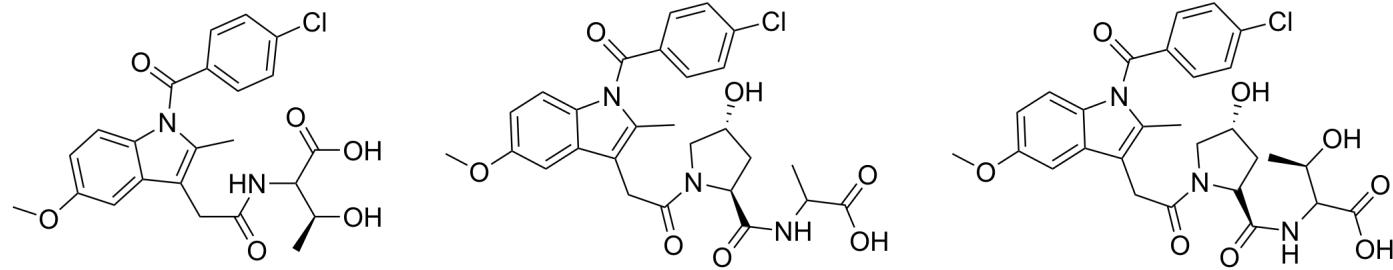


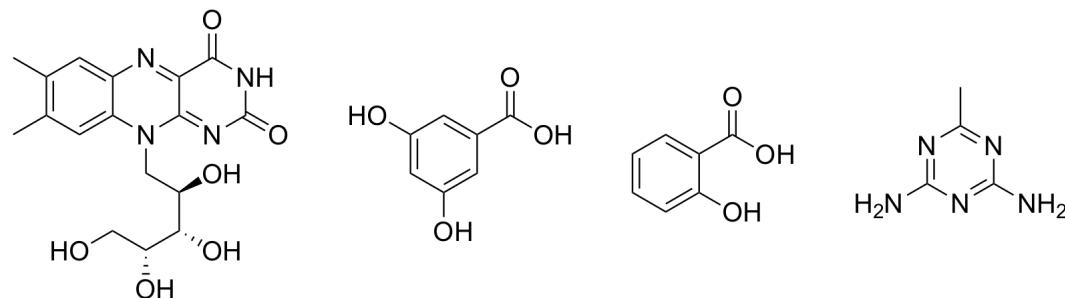
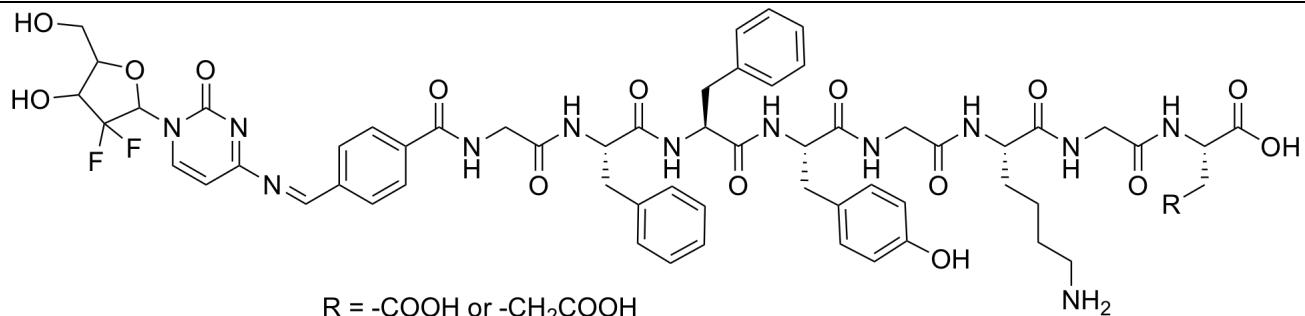
naproxen
+
lamivudine
+
zidovudine

176

folic acid

177

		
	naproxen	178
	indomethacin	179
	gemcitabine	180

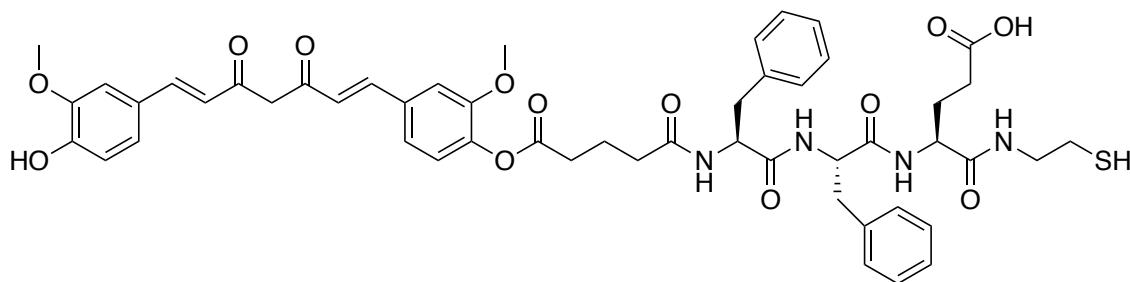
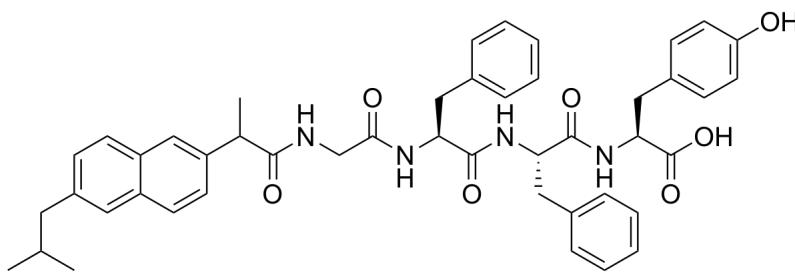
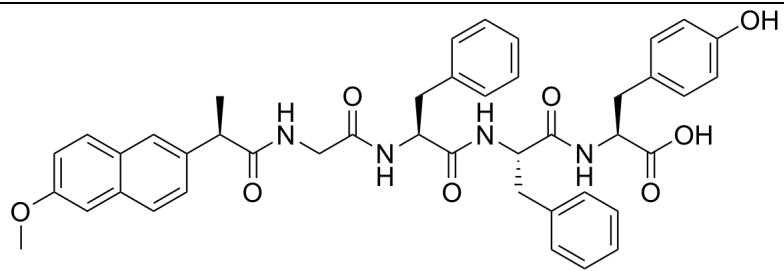


riboflavin
conjugates with
aceto-
guanamine
or
salicylic acid
or
3,5-dihydroxy-
benzoic acid

181

naproxen
+
ibuprofen

182

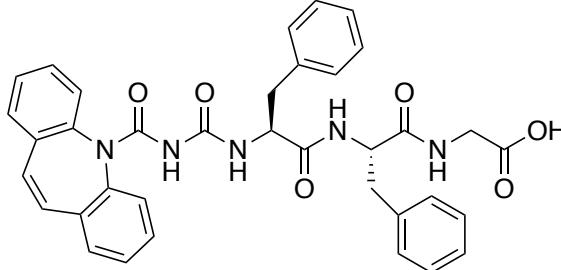
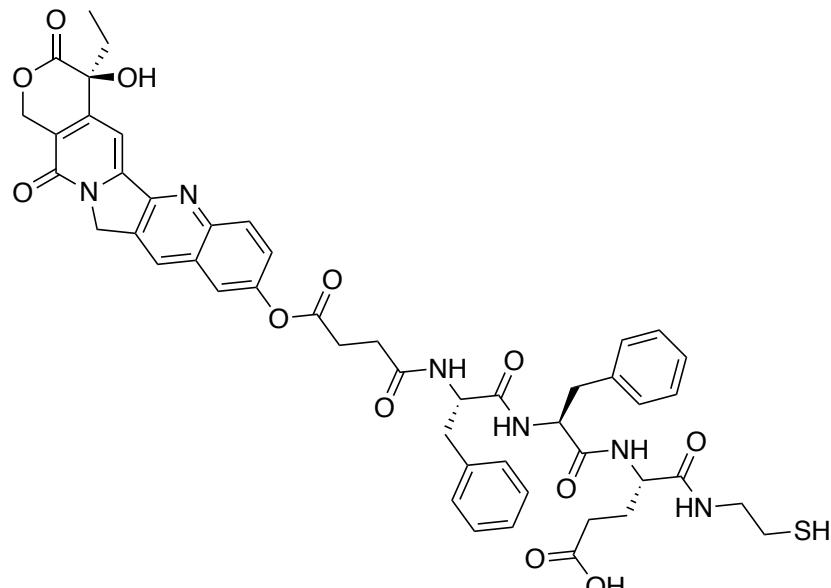


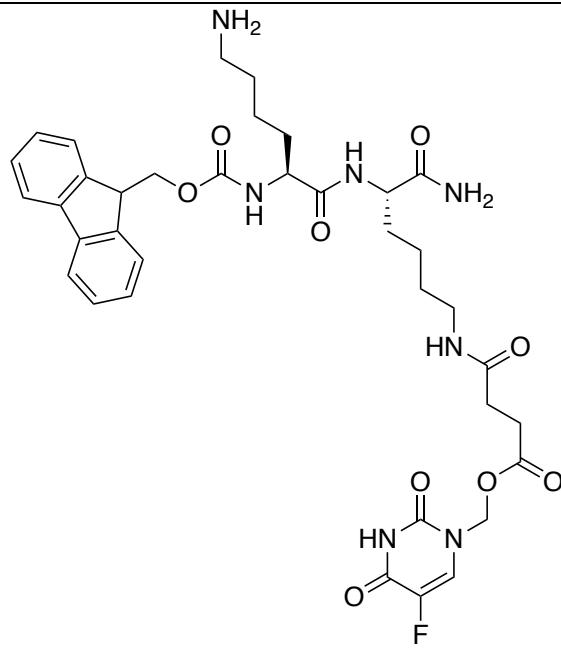
Curcumin

183

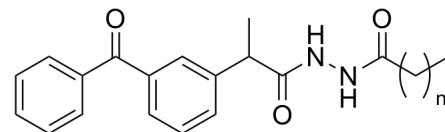


184

	Carbamazepine	
	10-hydroxy camptothecin	185
	5-fluorouracil	187



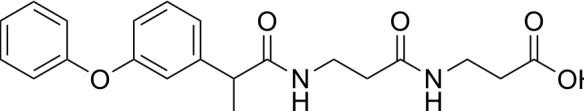
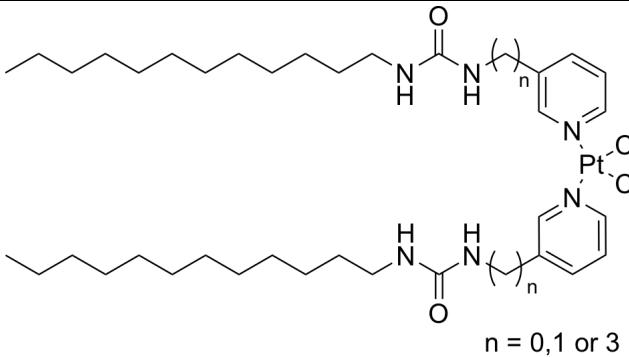
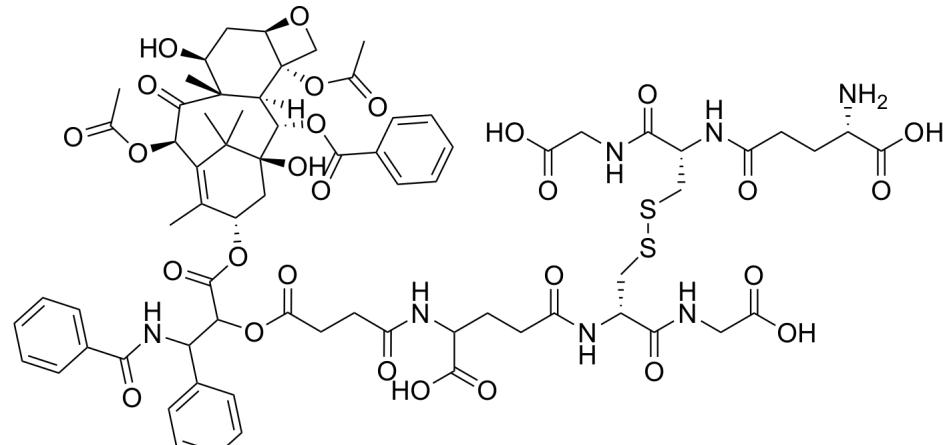
Drug-conjugates as organogelators

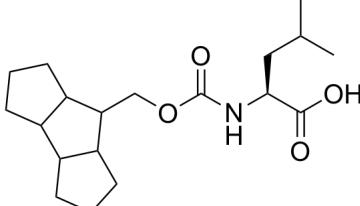
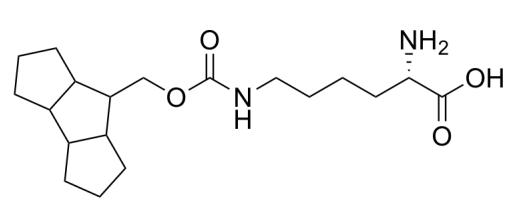
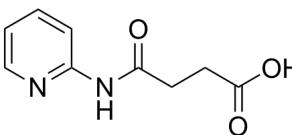
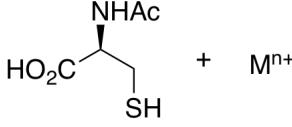
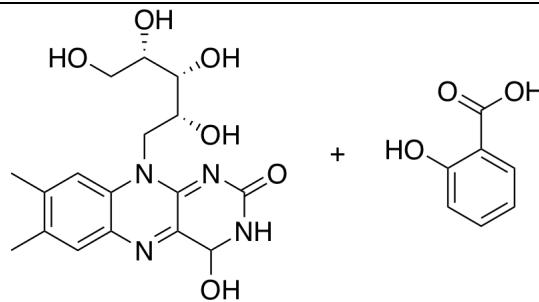


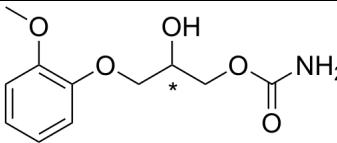
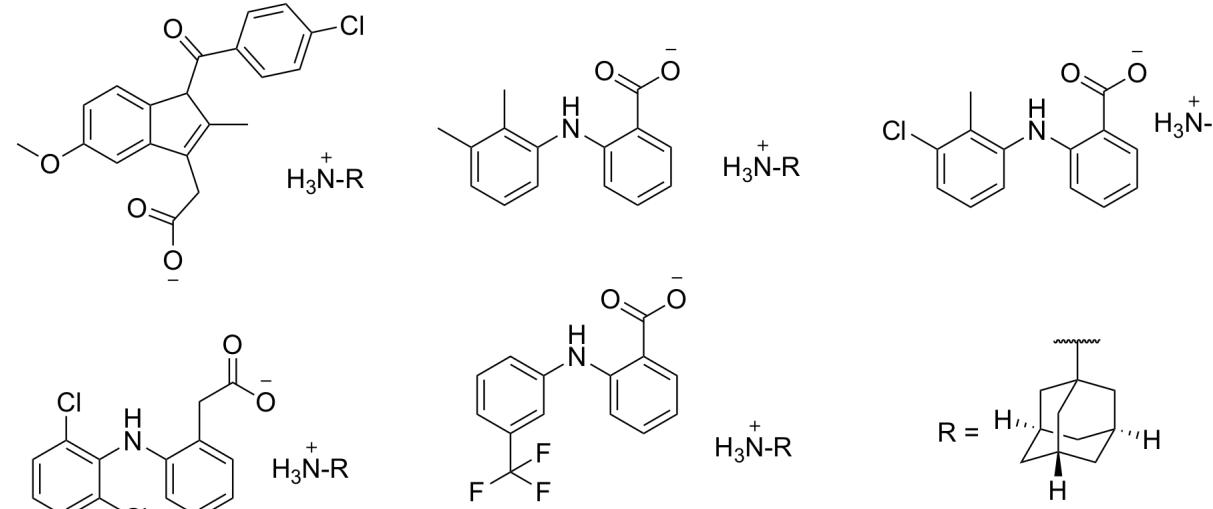
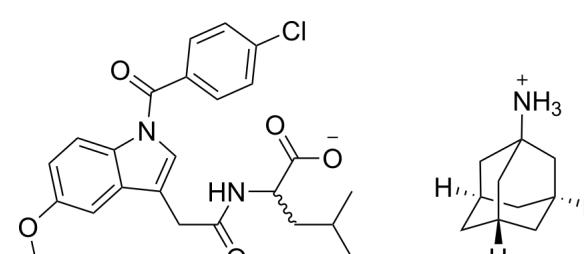
$n = 10, 12, 14 \text{ or } 16$

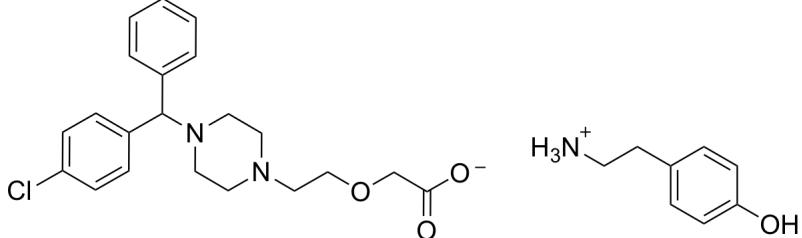
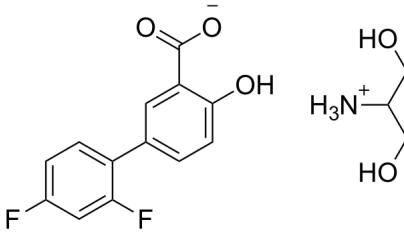
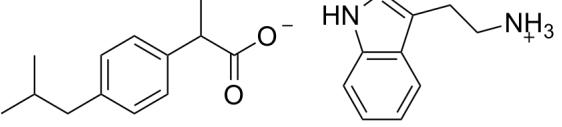
ketoprofen 188

naproxen 189

	fenoprofen	190
	cisplatin	191
GEL-FORMING DRUGS		
	lanreotide	193
	NPC 15199	194

		Fmoc-L-lysine^+	
	4-oxo-4-(2-pyridinylamino)butanoic acid	195	
His-Ser-Gln-Thr-Phe-Thr-Ser-Asp-Tyr-Ser-Lys-Tyr-Leu.Asp-Ser-Arg-Arg-Ala-Glc-Asp-Phe-Val-Gln-Trp-Leu-Met-Asn-Thr	glycagon	196	
 $M^{n+} = Cu^{2+}, Ag^+, Au^{3+}$	<i>N</i> -acetyl-L-cysteine	197	
	salicilic acid	198	
	methocarbamol	199	

			
	 <p>indomethacin + mefenamic acid + diclofenac + tolafenamic acid + flufenamic acid</p>		200
	 <p>indomethacin + amantadine (cation)</p>		201
cetirizine			202

		
	diflunisal + serinol	203
	ibuprofen	204

^a The table has been prepared following the same order given in the main text. References numbers are equivalent to those given in the main text.

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