

Natural disesquiterpenoids: an update

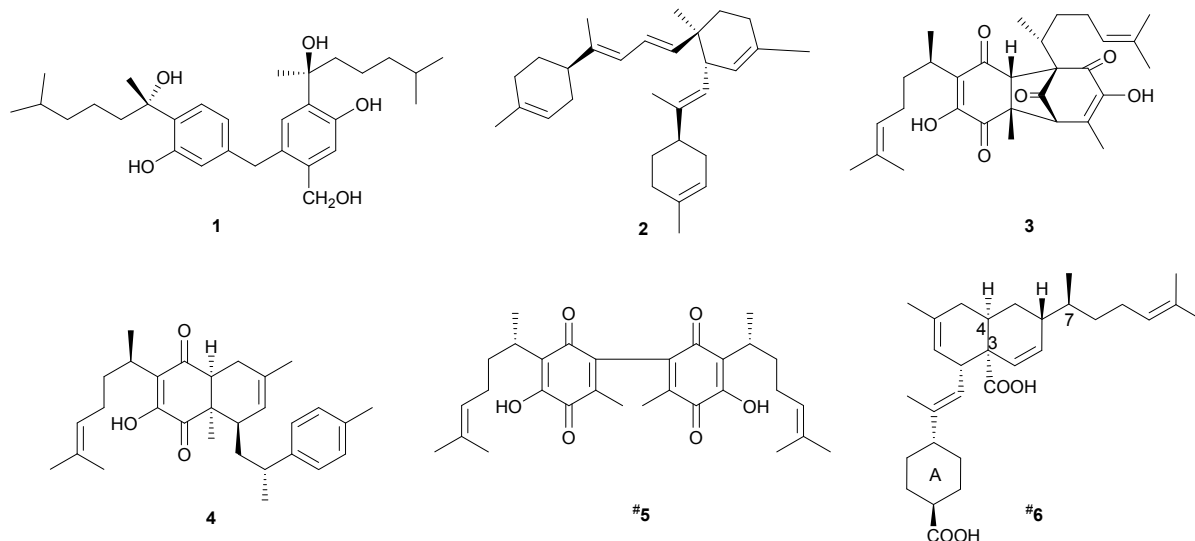
Supplementary Information

Lie-Feng Ma, Yi-Li Chen, Wei-Guang Shan, and Zha-Jun Zhan*

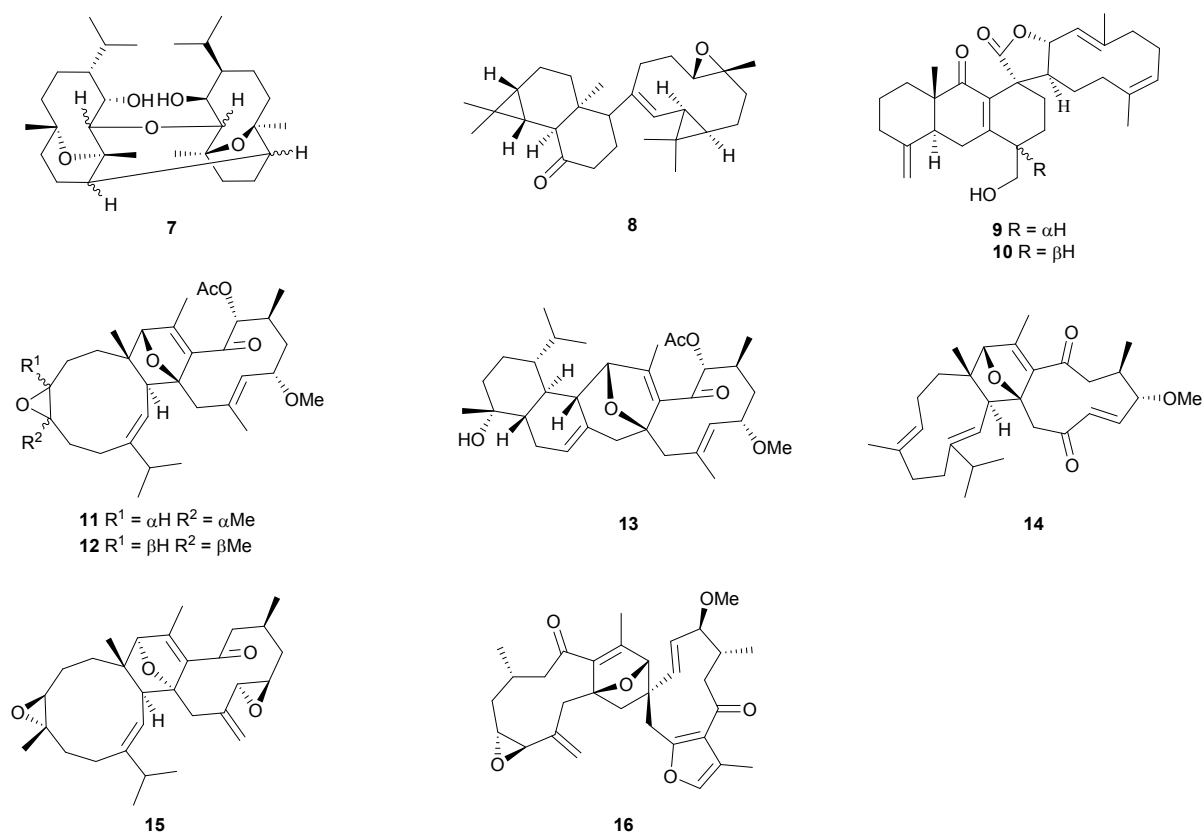
2 True-disesquiterpenoids	2
2.1 Bisabolane sesquiterpenoid dimers (compounds 1–6)	2
2.2 Germacrane sesquiterpenoid dimers (compounds 7–16)	2
2.3 Xanthane sesquiterpenoid dimers (compounds 17–35)	3
2.4 Guaiane and pseudoguaiane sesquiterpenoid dimers (compounds 36–181)	5
2.5 Eremophilane and nardosinane sesquiterpenoid dimers (compounds 182–206)	13
2.6 Cadinane sesquiterpenoid dimers (compounds 207–222)	15
2.7 Eudesmane and elemene sesquiterpenoid dimers (compounds 223–250)	16
2.8 Lindenane sesquiterpenoid dimers (compounds 251–341)	18
2.9 Cuparane, laurane and cyclolaurane sesquiterpenoid dimers (compounds 342–345)	23
2.10 Sesquiterpenoid alkaloid dimers (compounds 346–347)	23
2.11 Miscellaneous sesquiterpenoid dimers (compounds 348–366)	24
3 Pseudo-disesquiterpenoids	25
3.1 Ester linkage (compounds 367–401)	25
3.2 <i>O</i> -ether linkage (compounds 402–416)	28
3.3 Nitrogen and urea linkage (compounds 417–427)	29
3.4 Isocitric acid linkage (compounds 428–437)	30
3.5 Others (compounds 438–447)	31
4 Merosesquiterpenoid dimers	32

2 True-disesquiterpenoids

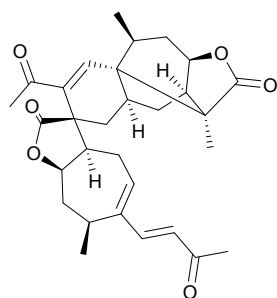
2.1 Bisabolane sesquiterpenoid dimers (compounds 1–6)



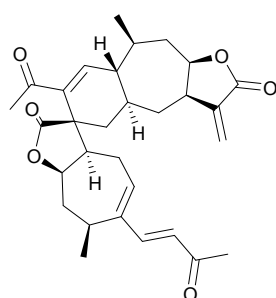
2.2 Germacrane sesquiterpenoid dimers (compounds 7–16)



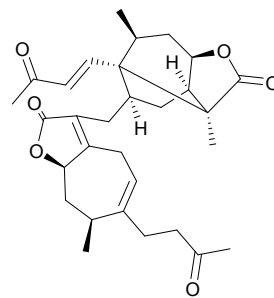
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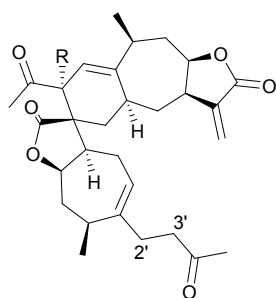
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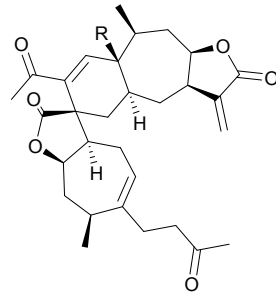
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20 R = H

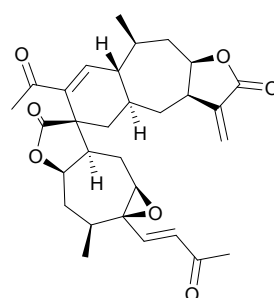
21 R = OH $\Delta^{2'(3')}$

22 R = OH

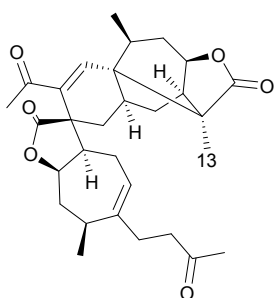


23 R = OAc

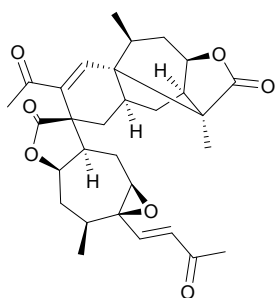
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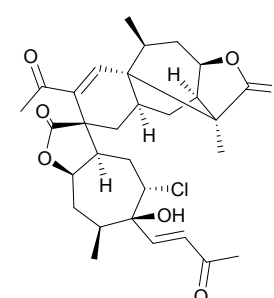
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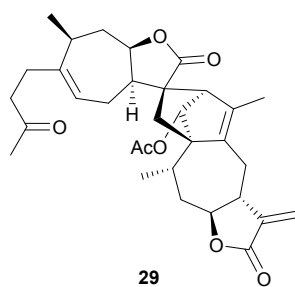
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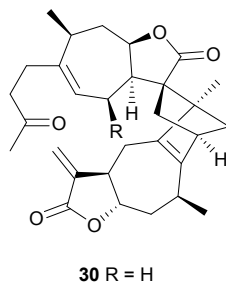
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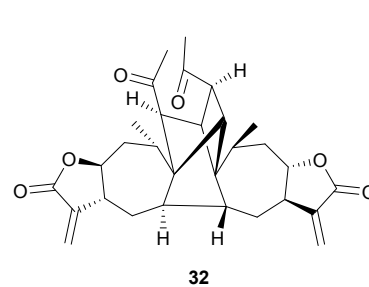


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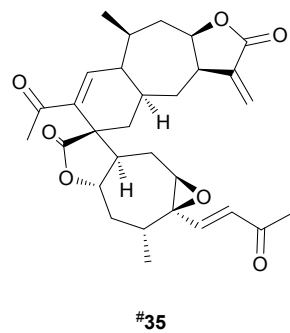
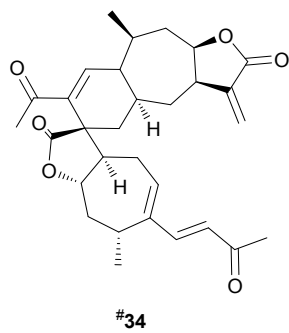
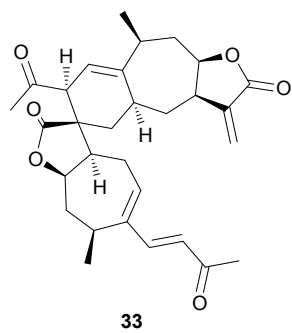


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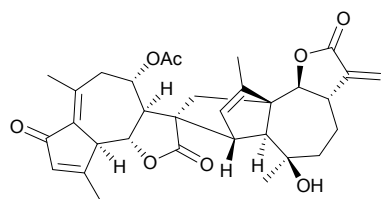
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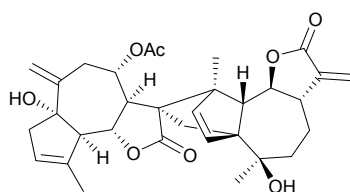
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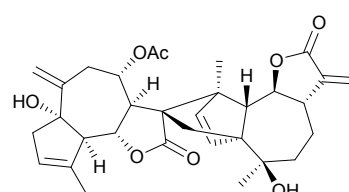
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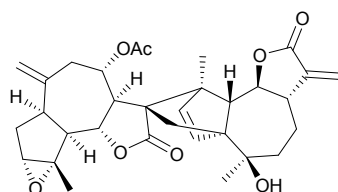
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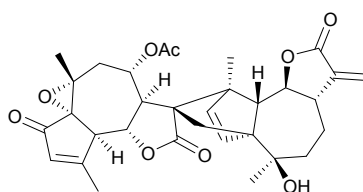
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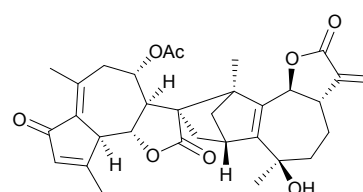
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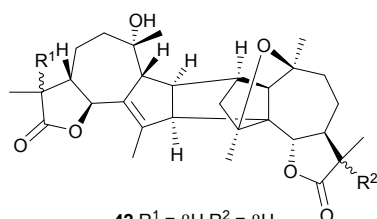
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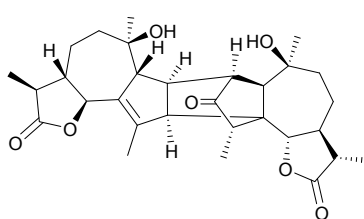


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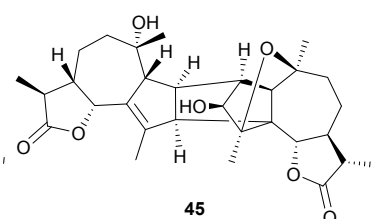


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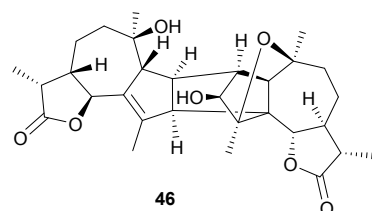
43 R¹ = α H R² = α H



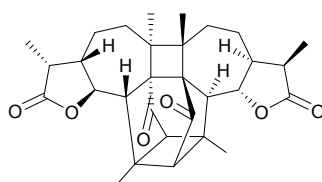
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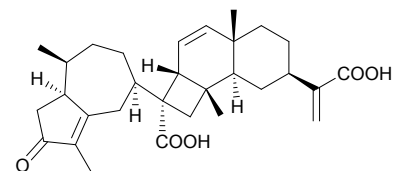
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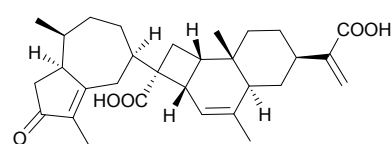
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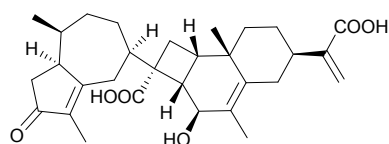
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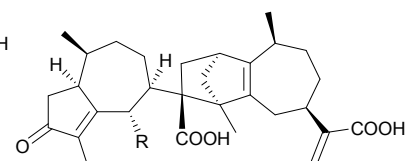
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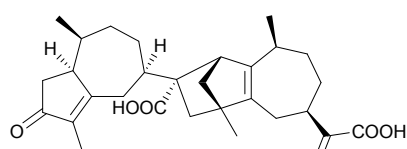
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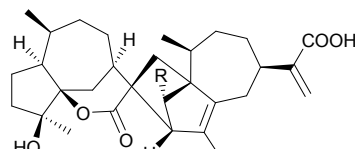
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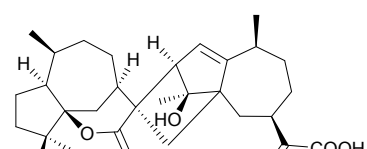
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55 R = OH



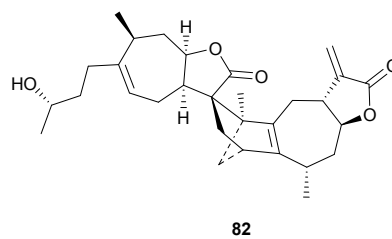
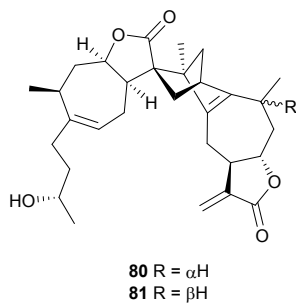
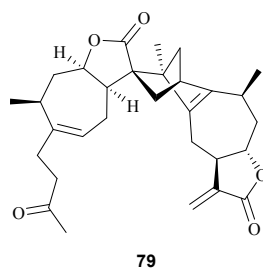
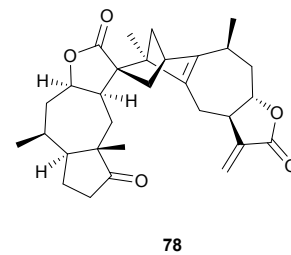
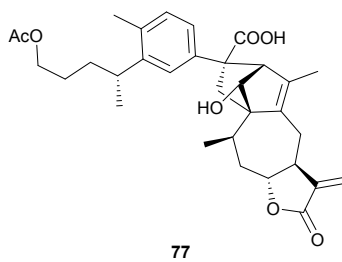
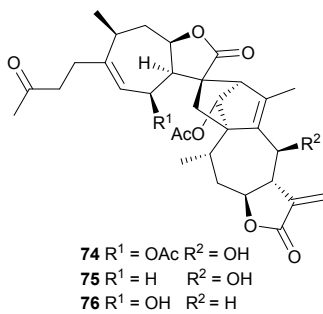
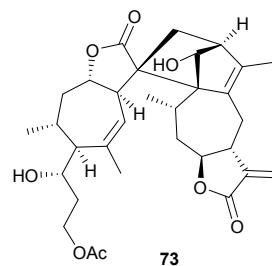
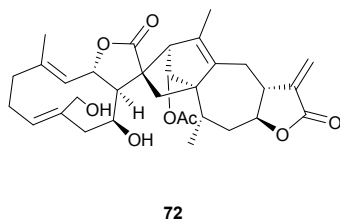
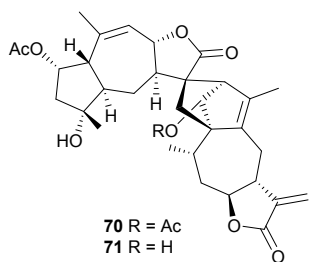
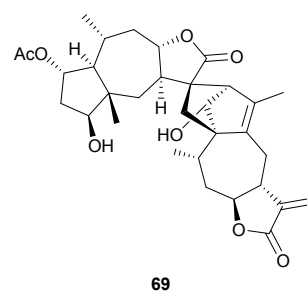
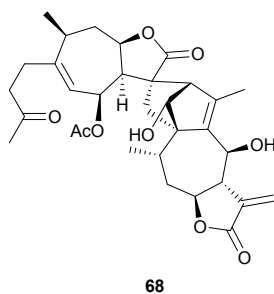
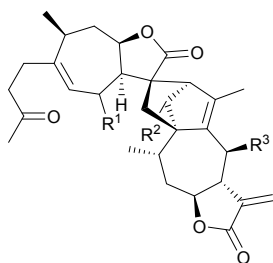
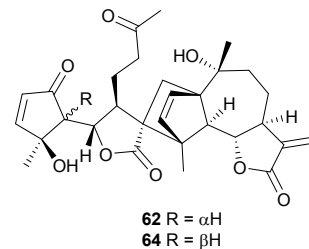
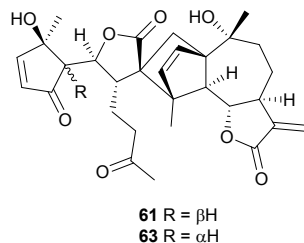
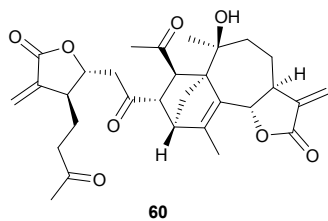
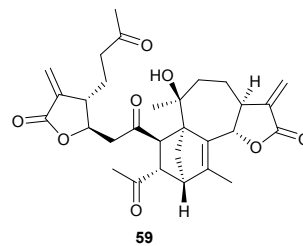
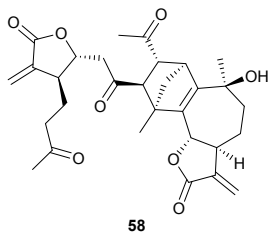
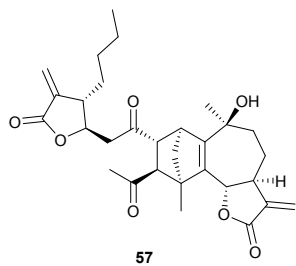
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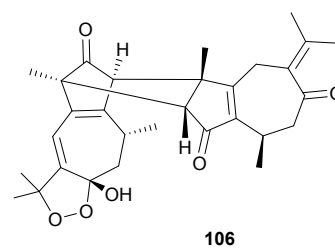
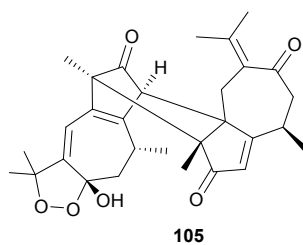
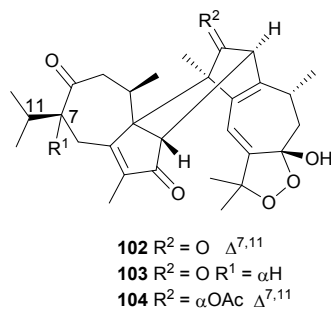
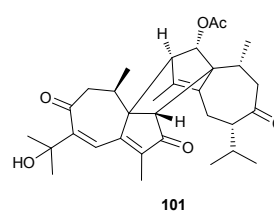
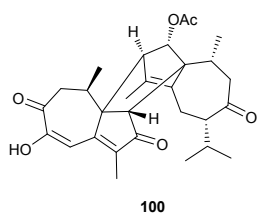
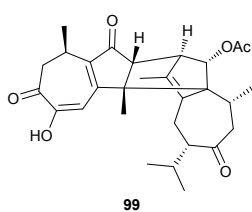
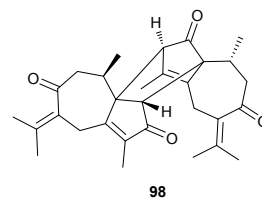
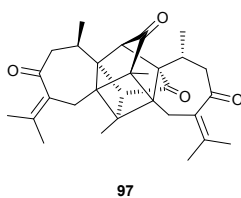
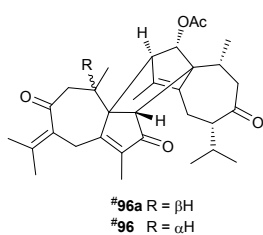
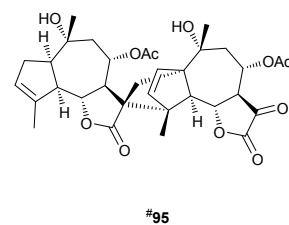
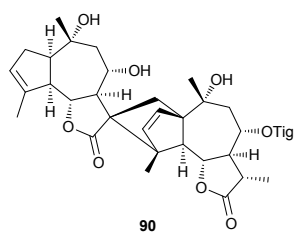
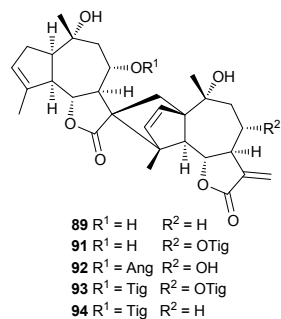
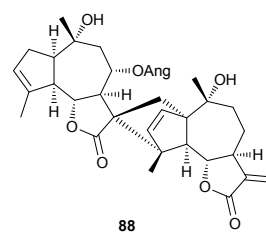
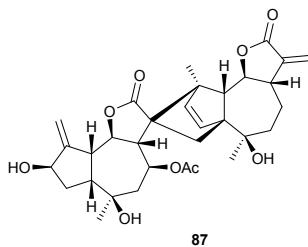
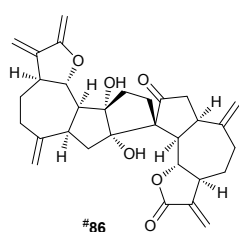
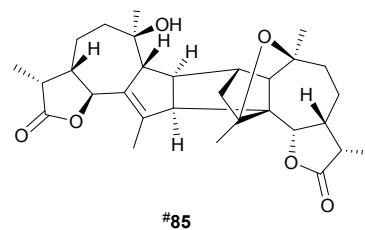
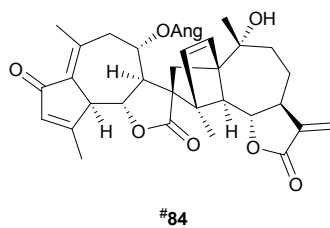
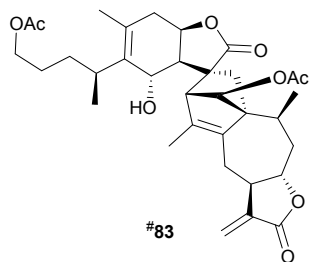


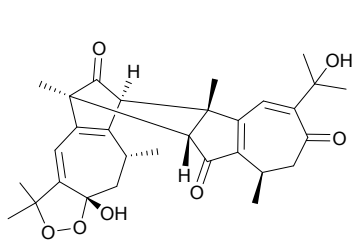
53 R = H
56 R = OH



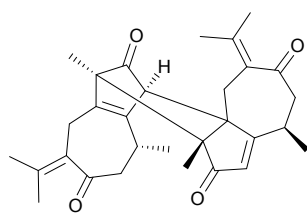
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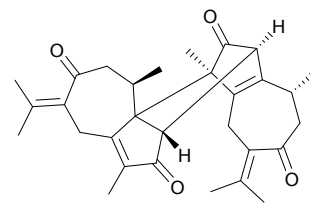




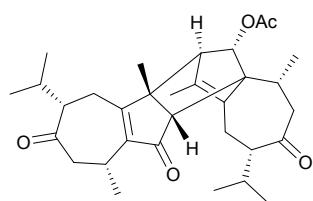
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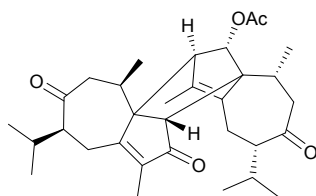
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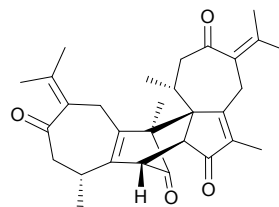
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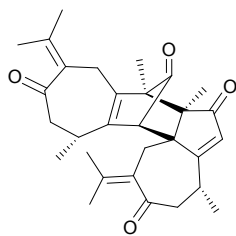
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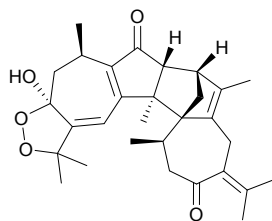
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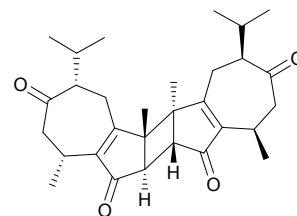
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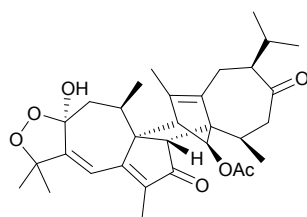
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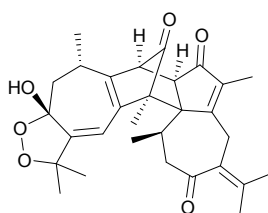
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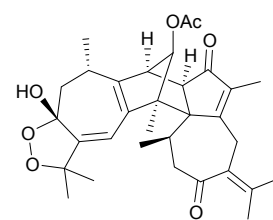
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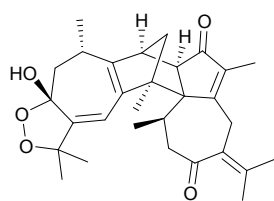
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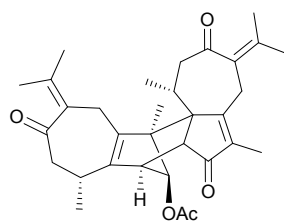
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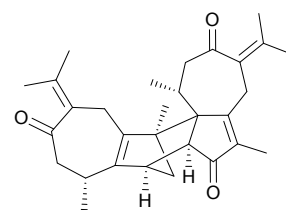
118



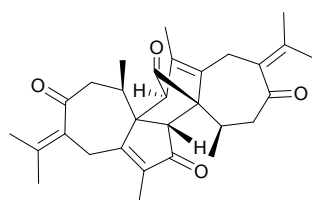
119



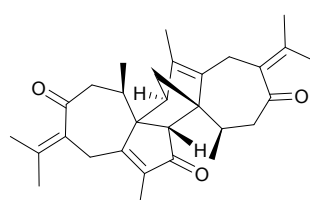
120



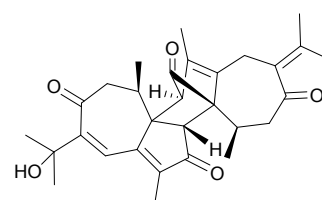
121



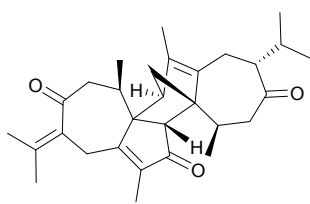
122



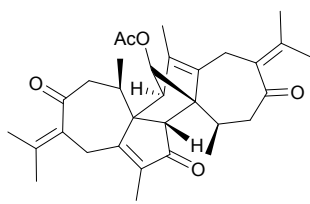
123



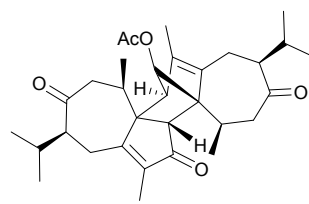
124



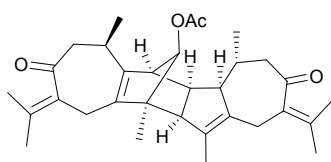
125



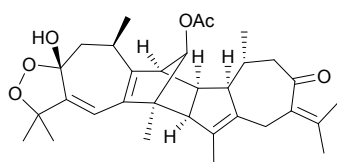
126



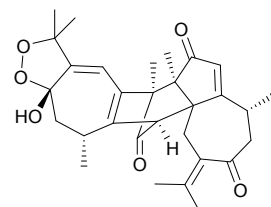
127



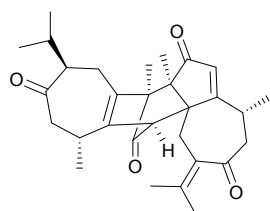
128



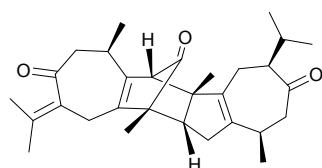
129



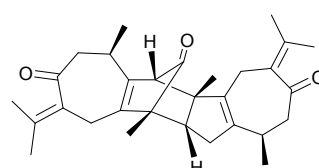
130



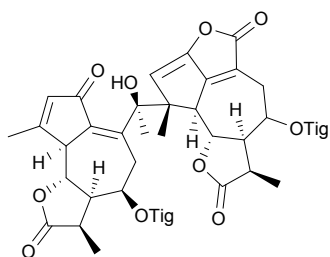
131



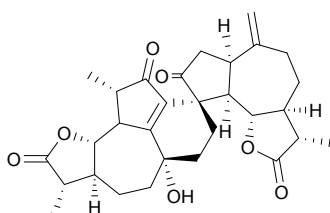
132



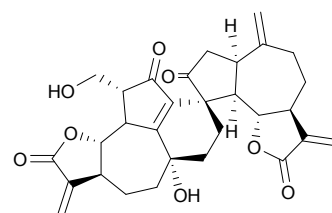
133



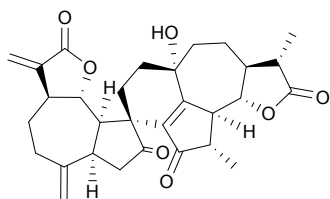
134



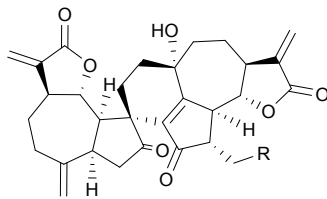
135



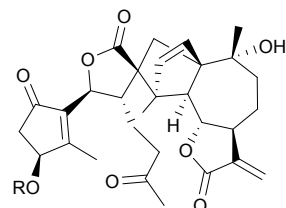
136



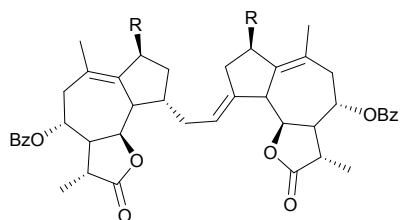
137



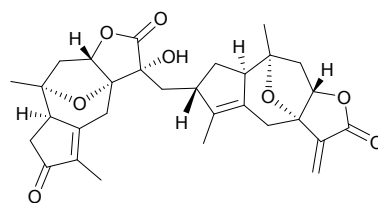
138 R = OMe
139 R = OEt
140 R = H



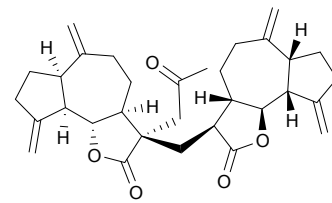
141 R = Me
142 R = H



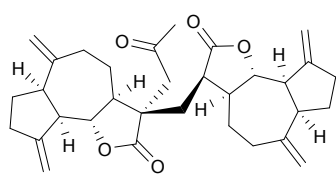
143 R = OAc
144 R = H



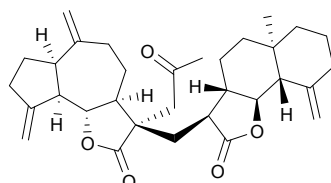
145



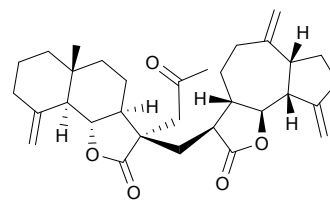
146



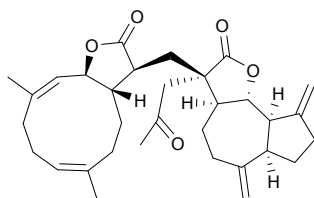
147



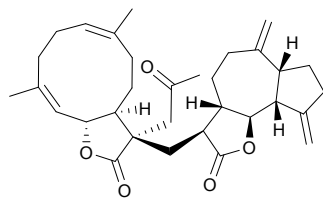
148



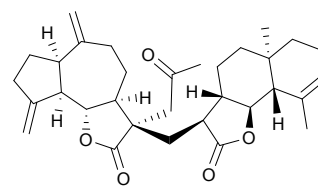
149



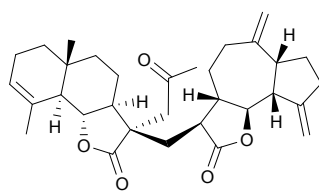
150



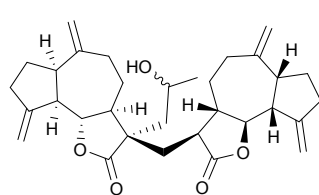
151



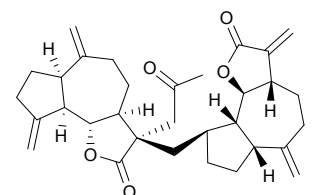
152



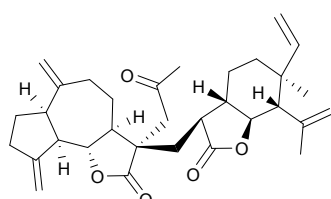
153



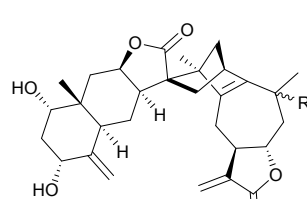
154



155

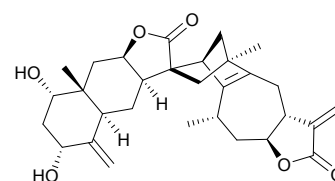


156

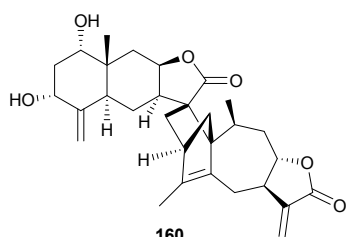


157 R = α H

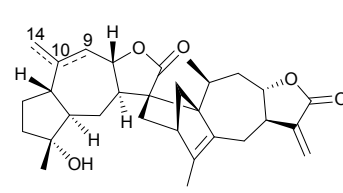
158 R = β H



159

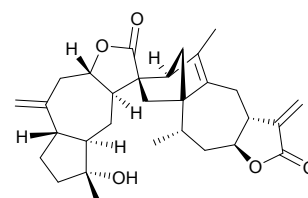


160

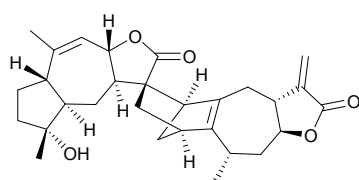


161 $\Delta^{10,14}$

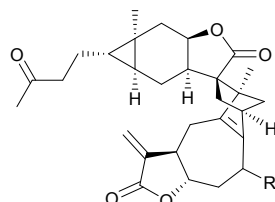
163 $\Delta^{9,10}$



162

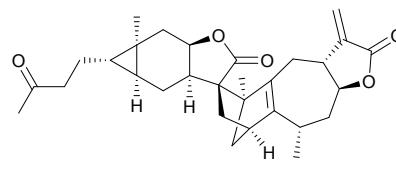


164

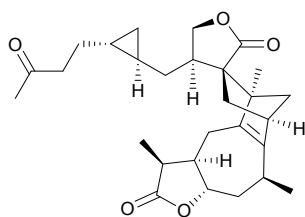


165 R = β Me

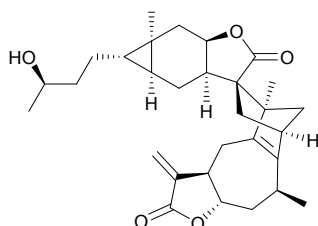
167 R = α Me



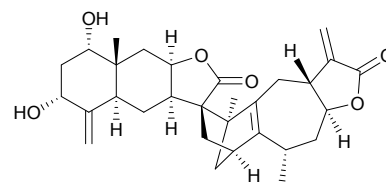
166



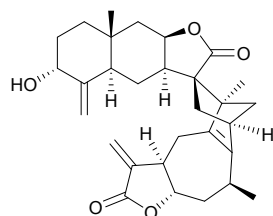
168



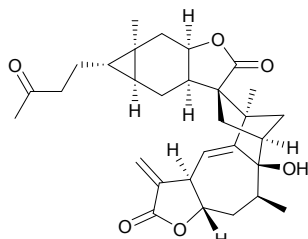
169



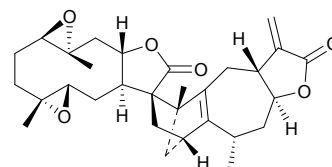
170



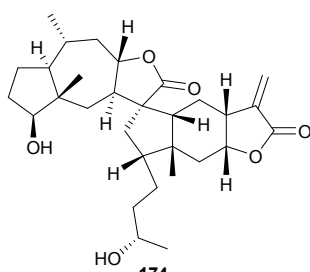
171



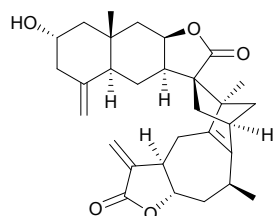
172



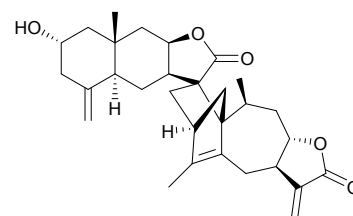
173



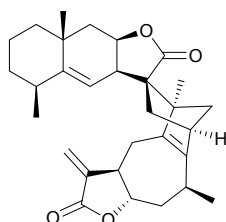
174



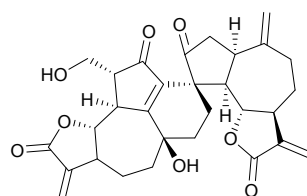
175



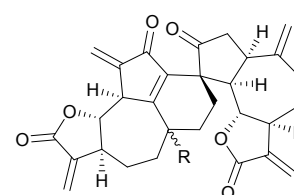
176



177



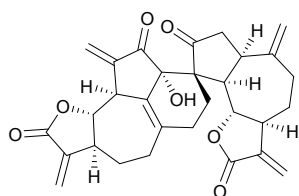
#178



#179 R = α OH

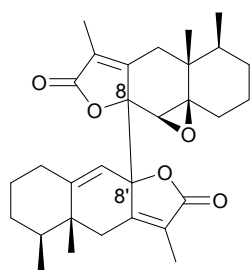
#180 R = β OH

#181 R = α H

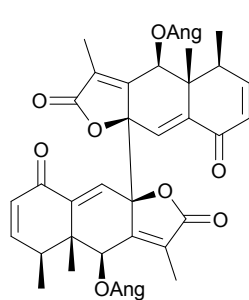


#180a

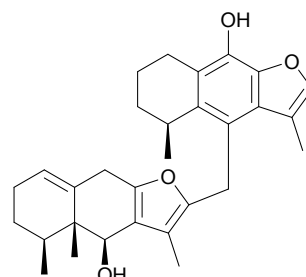
2.5 Eremophilane and nardosinane sesquiterpenoid dimers (compounds 182–206)



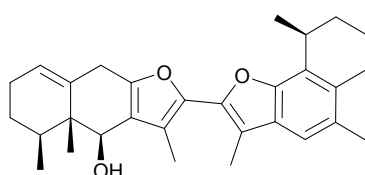
182 8(*R*), 8'(*S*)
183 8(*S*), 8'(*R*)



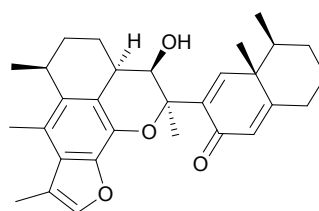
184



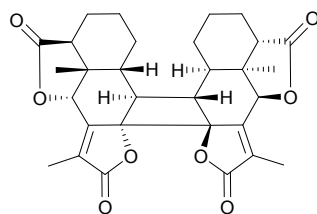
185



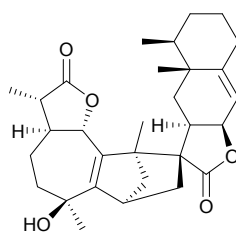
186



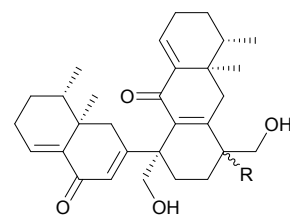
187



188



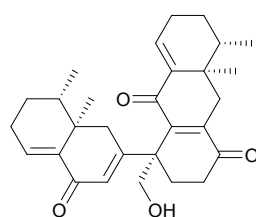
189



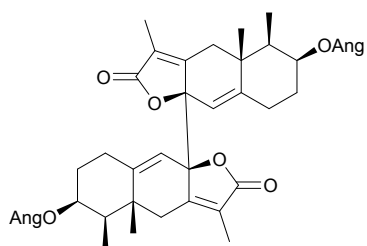
190 R = α OH

191 R = β OH

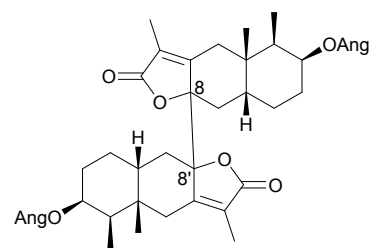
192 R = α H



193

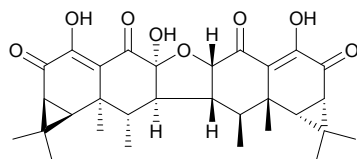


194

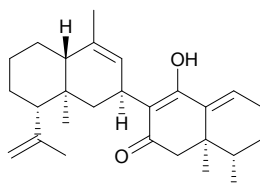


195 8(*S*), 8'(*R*)

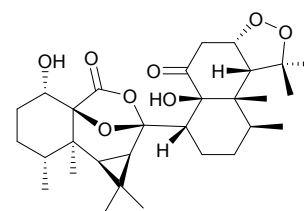
196 8(*R*), 8'(*S*)



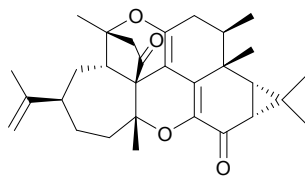
197



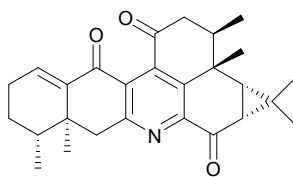
198



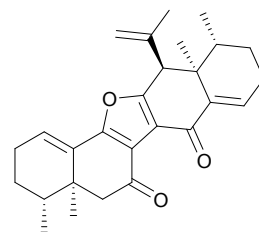
199



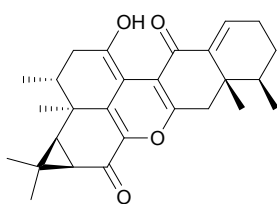
200



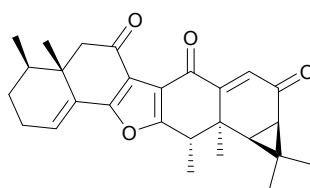
201



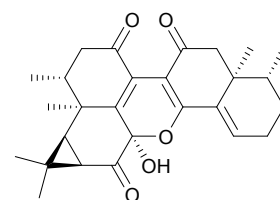
202



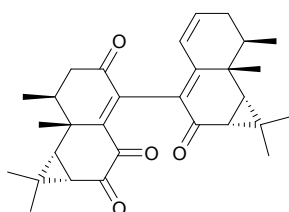
203



204

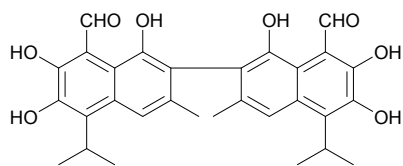


205

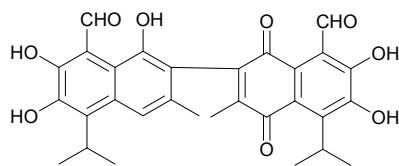


206

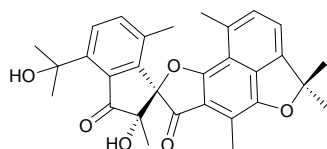
2.6 Cadinane sesquiterpenoid dimers (compounds 207–222)



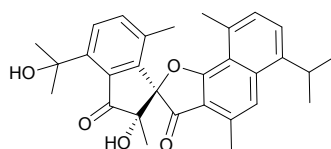
#207



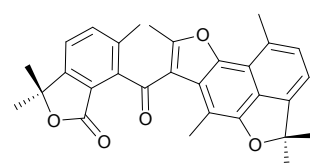
208



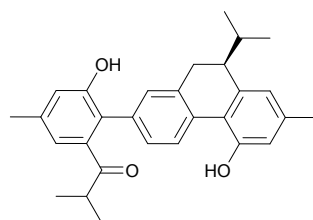
209



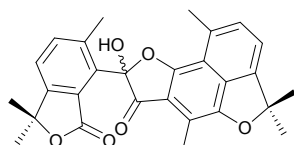
210



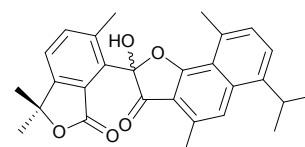
211



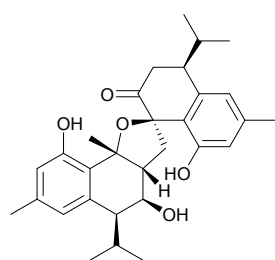
212



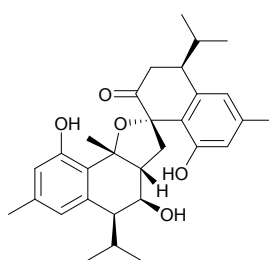
213



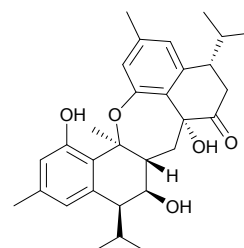
214



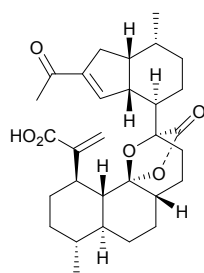
215



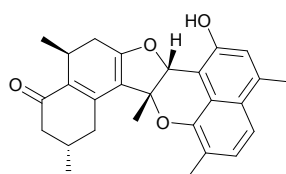
216



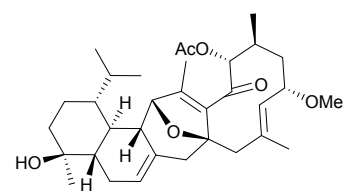
217



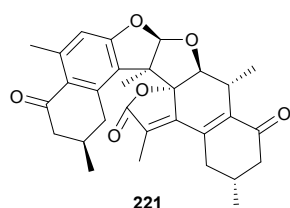
218



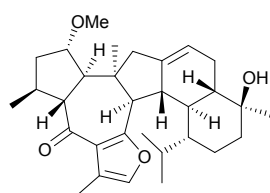
219



220

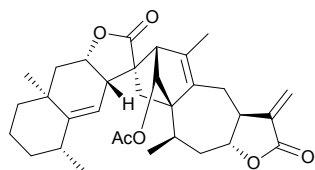


221

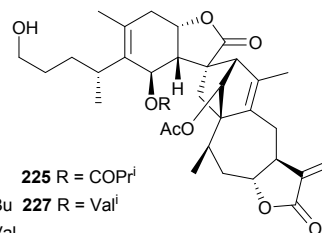


222

2.7 Eudesmane and elemene sesquiterpenoid dimers (compounds 223–250)



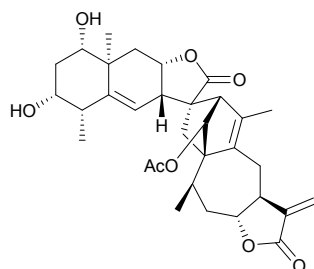
#223



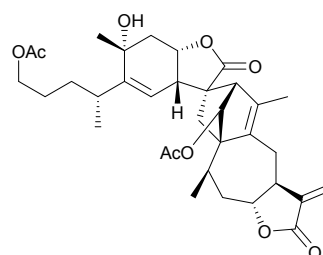
224 R = Ac 225 R = COPriⁱ

226 R = MeBu 227 R = Valⁱ

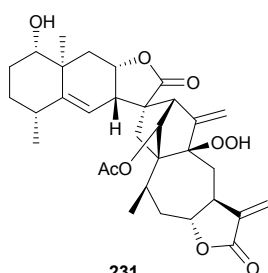
228 R = MeVal



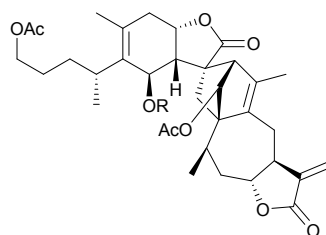
229



230

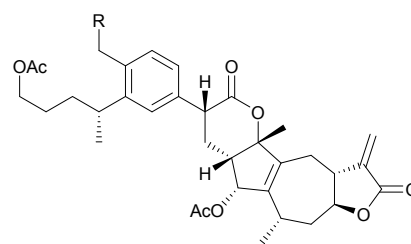


231



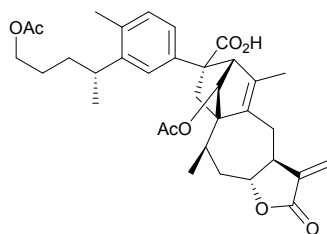
232 R = COPriⁱ

233 R = MeVal

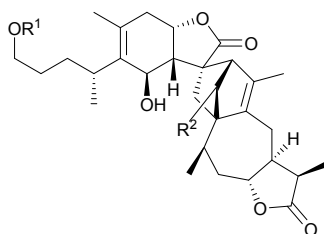


234 R = OH

235 R = H



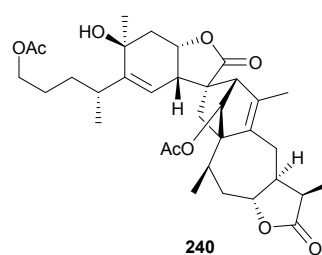
236



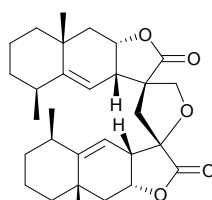
237 R¹ = Ac R² = OAc

238 R¹ = H R² = OAc

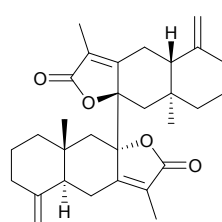
239 R¹ = Ac R² = H



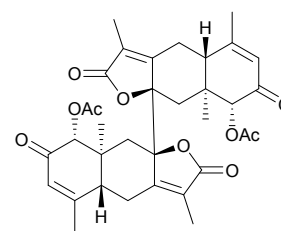
240



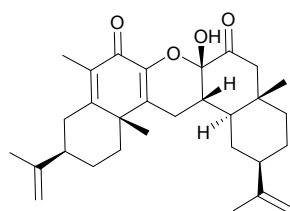
241



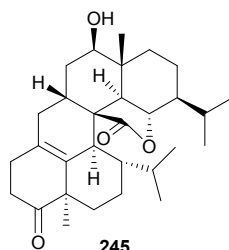
#242



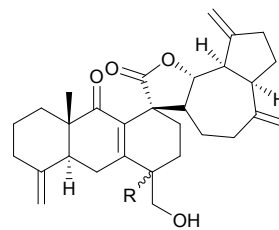
243



244

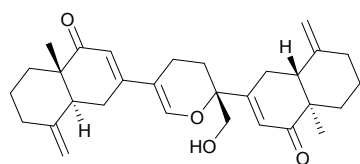


245

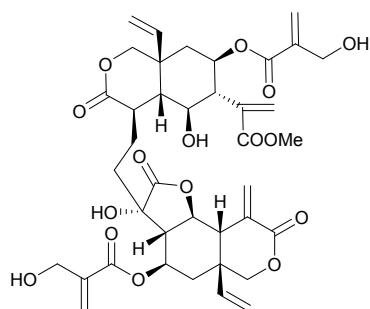


246 R = β H

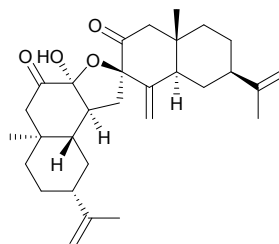
247 R = α H



248

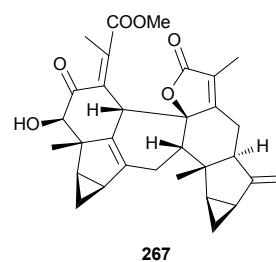
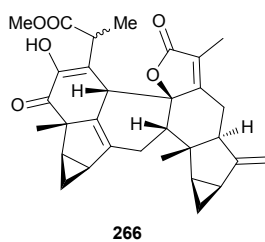
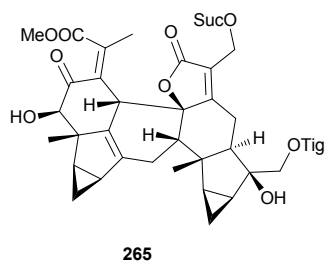
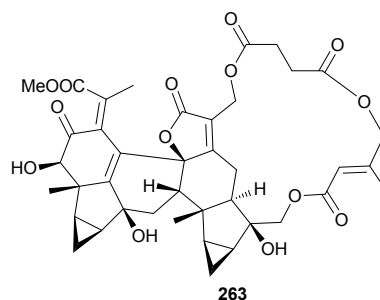
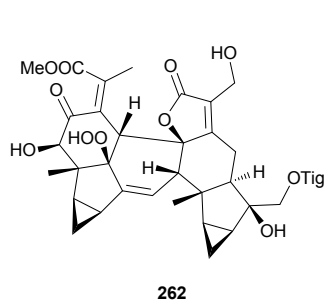
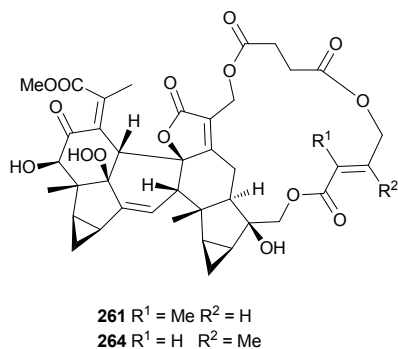
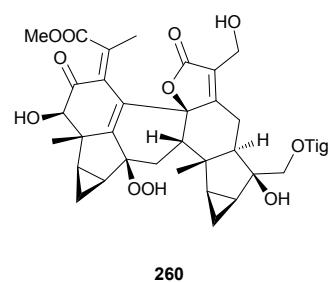
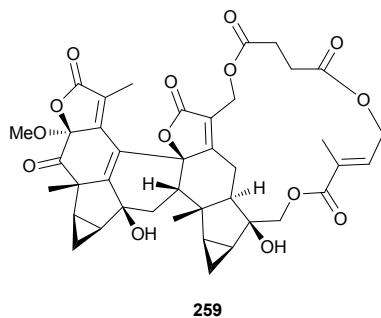
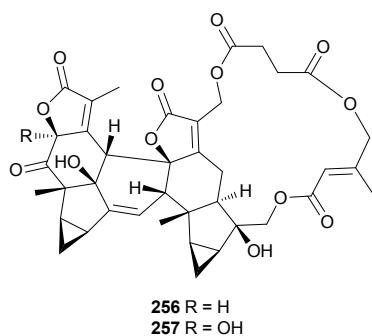
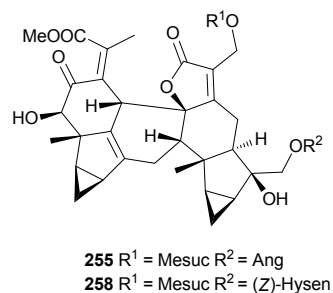
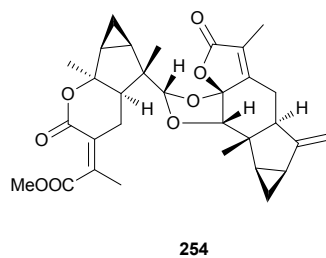
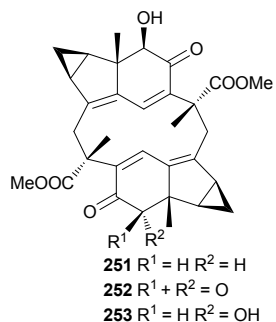


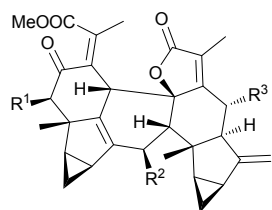
249



250

2.8 Lindenane sesquiterpenoid dimers (compounds 251–341)

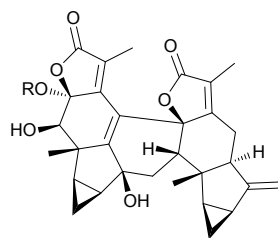




268 R¹ = OH R² = H R³ = OAc

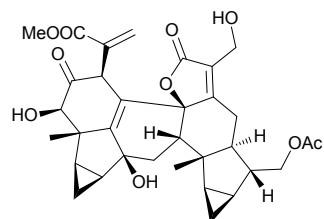
269 R¹ = OH R² = OH R³ = H

270 R¹ = R² = R³ = H

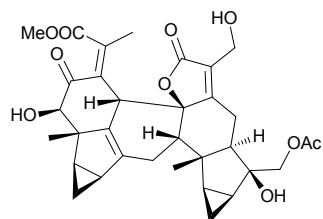


271 R = H

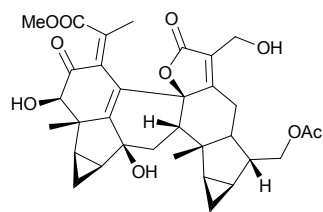
272 R = Bu



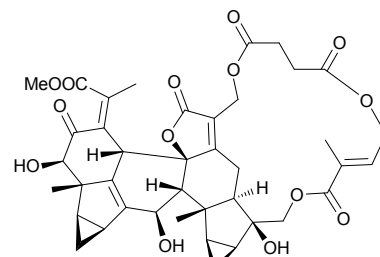
273



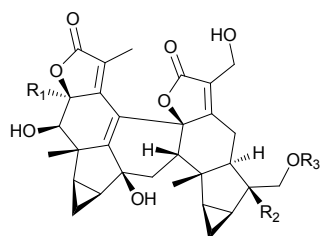
274



275



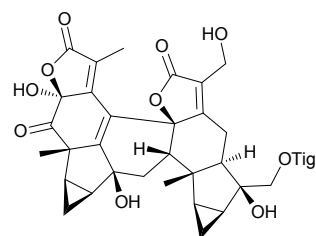
276



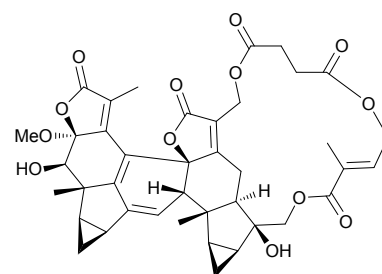
277 R₁ = OH R₂ = OH R₃ = H

278 R₁ = OMe R₂ = OH R₃ = Tig

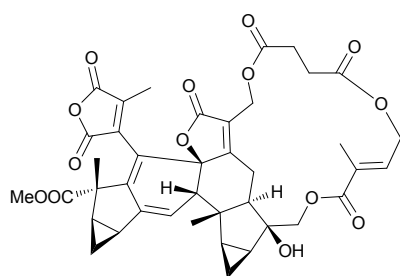
280 R₁ = OH R₂ = H R₃ = Ac



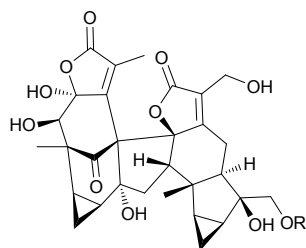
279



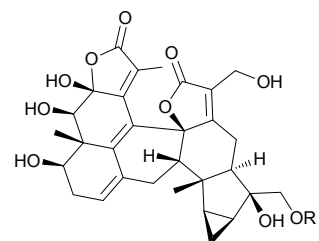
281



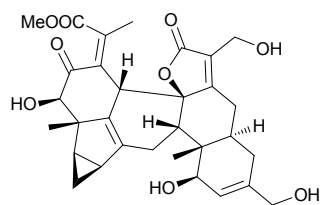
282



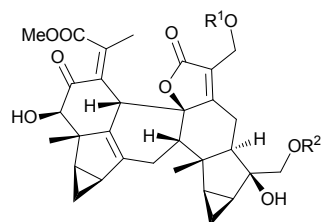
283 R = (*E*)-Hysen



284 R = (*E*)-Hysen

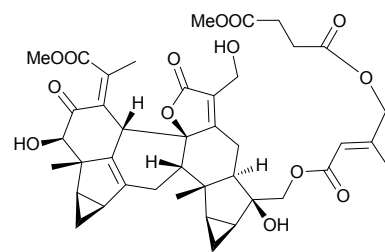


285

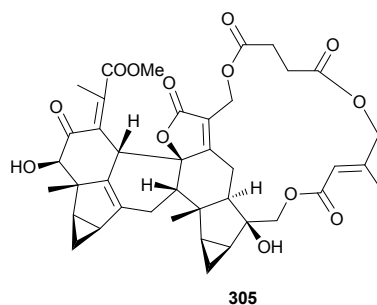
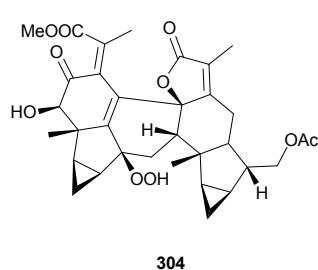
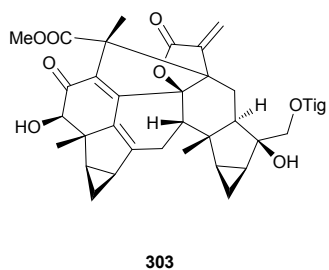
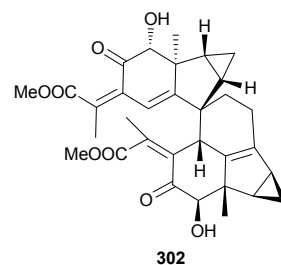
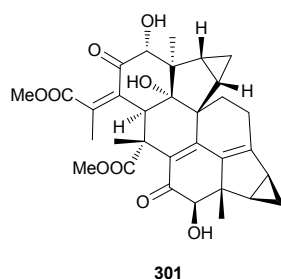
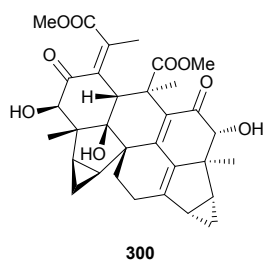
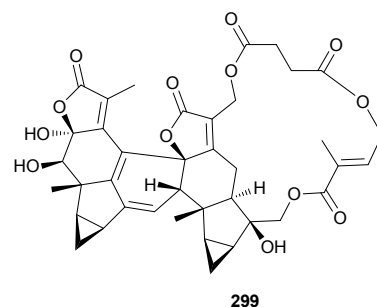
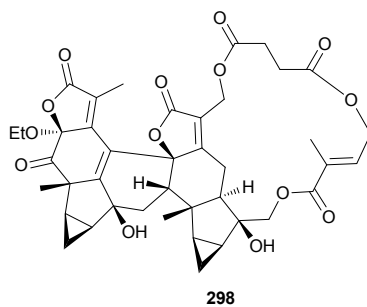
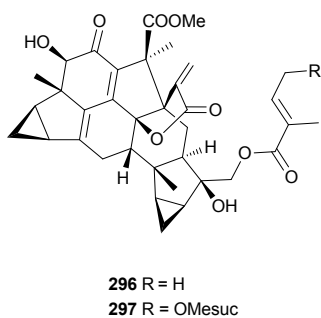
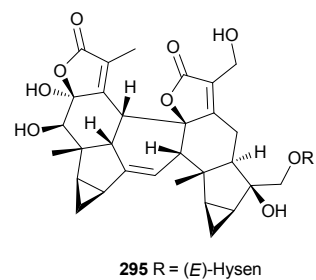
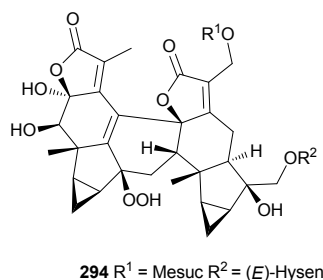
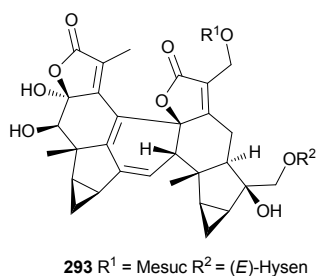
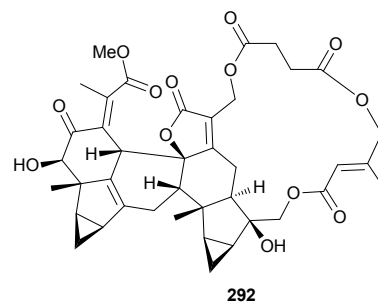
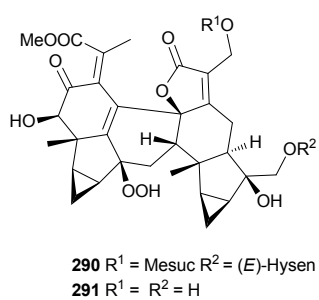
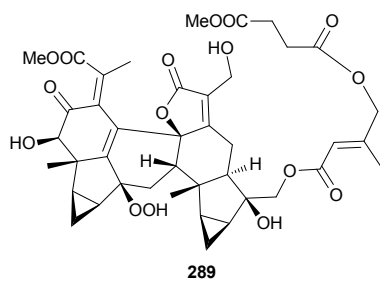


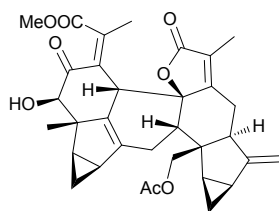
286 R¹ = Mesuc R² = Oxsen

288 R¹ = H R² = Sen

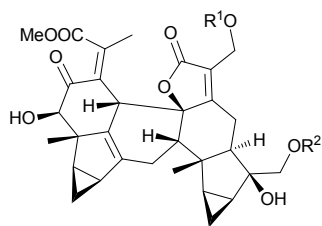


287



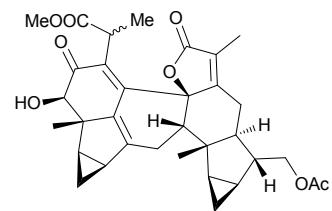


306

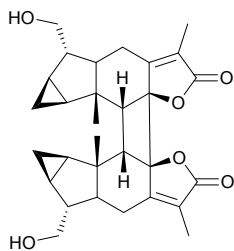


307 R¹ = Suc R² = (*E*)-Hysen

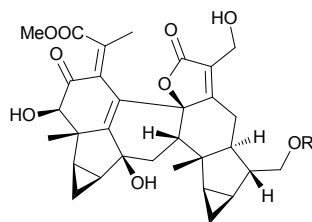
308 R¹ = Mesuc R² = (*E*)-Hysen



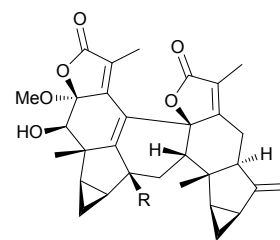
309



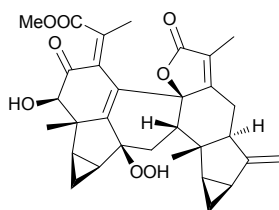
310



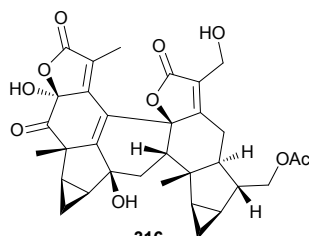
311 R = Ac
315 R = Tig



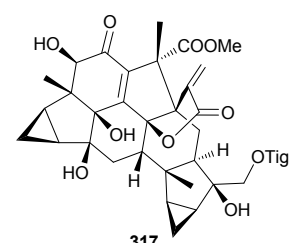
312 R = OH
313 R = OOH



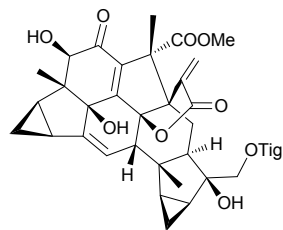
314



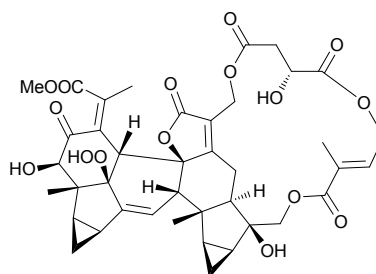
316



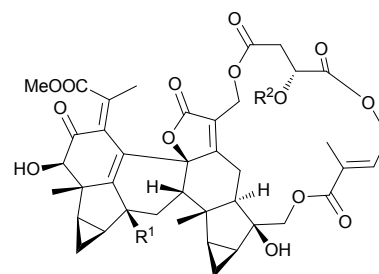
317



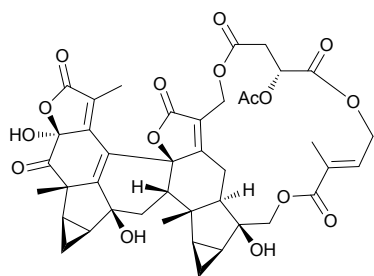
318



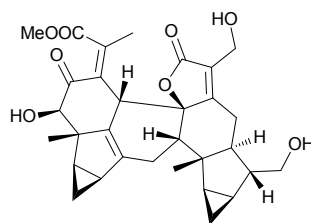
319



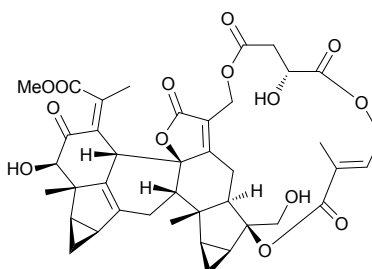
320 R¹ = OOH R² = H
321 R¹ = OH R² = Ac



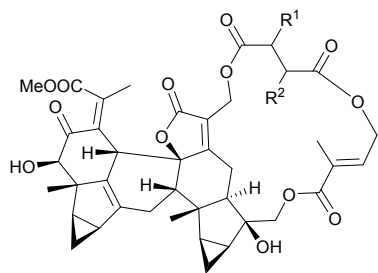
322



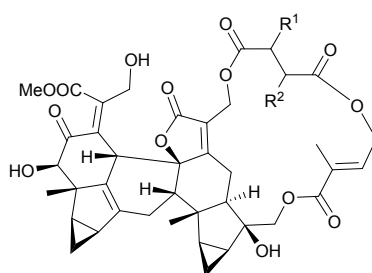
323



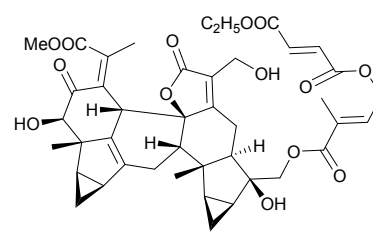
324



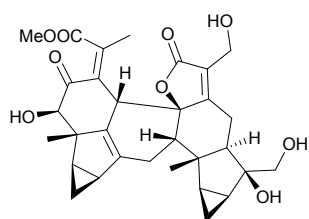
325 $R^1 = H$ $R^2 = \alpha OH$
 326 $R^1 = \alpha OH$ $R^2 = H$
 328 $R^1 = \beta OH$ $R^2 = \beta OH$



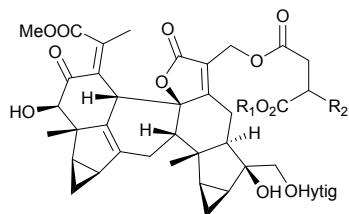
327 $R^1 = H$ $R^2 = \beta OH$
 329 $R^1 = \beta OH$ $R^2 = \beta OH$
 330 $R^1 = H$ $R^2 = H$



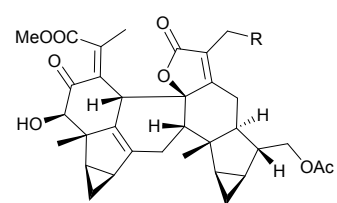
331



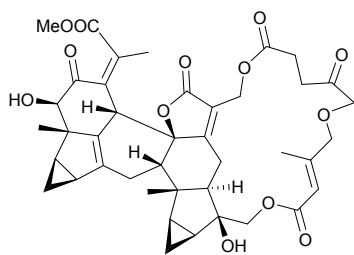
332



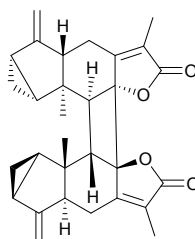
333 $R^1 = Me$ $R^2 = \alpha OH$
 334 $R^1 = Et$ $R^2 = \beta OH$



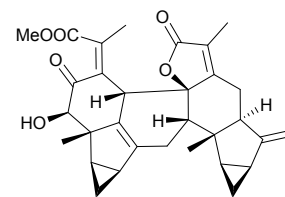
#335 $R = OH$
 #339 $R = H$



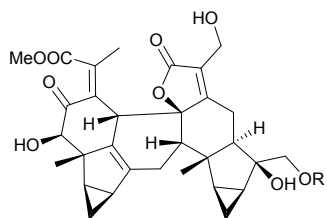
#336



#337

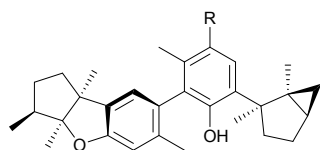


#338

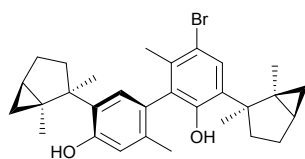


#340 $R = Tig$
 #341 $R = Hysen$

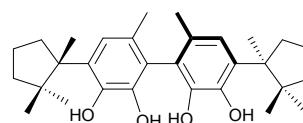
2.9 Cuparane, laurane and cyclolaurane sesquiterpenoid dimers (compounds 342–345)



342 R = Br
343 R = H

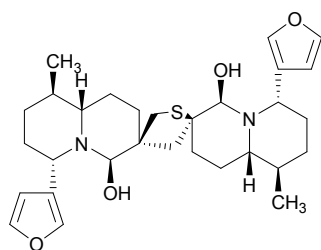


344

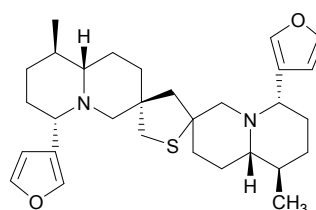


#345

2.10 Sesquiterpenoid alkaloid dimers (compounds 346–347)

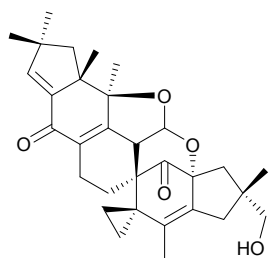


#346

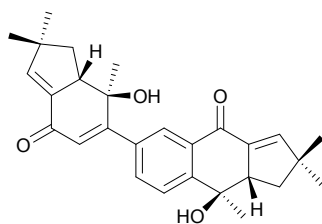


#347

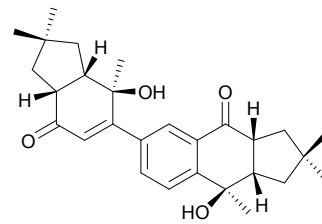
2.11 Miscellaneous sesquiterpenoid dimers (compounds 348–366)



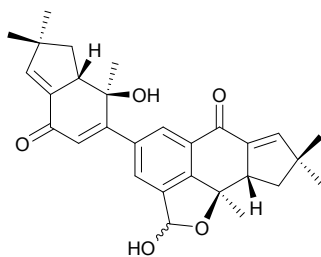
348



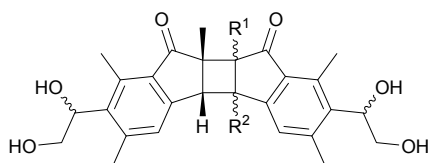
349



350

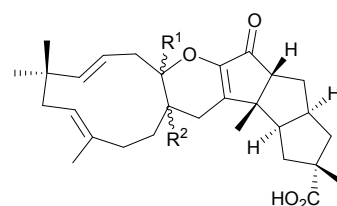


351



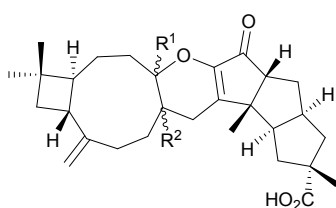
352 $R^1 = \alpha\text{Me}$ $R^2 = \alpha\text{H}$

353 $R^1 = \beta\text{Me}$ $R^2 = \beta\text{H}$



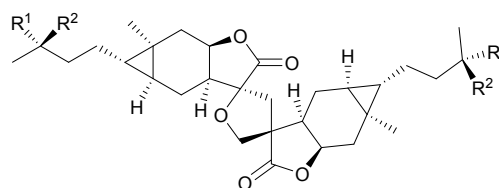
354 $R^1 = \alpha\text{Me}$ $R^2 = \beta\text{H}$

355 $R^1 = \beta\text{Me}$ $R^2 = \alpha\text{H}$



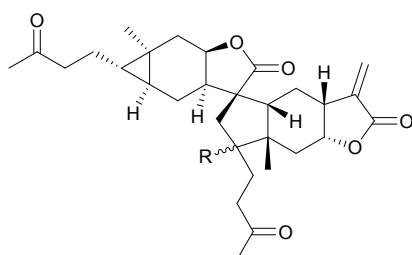
356 $R^1 = \alpha\text{Me}$ $R^2 = \beta\text{H}$

357 $R^1 = \beta\text{Me}$ $R^2 = \alpha\text{H}$



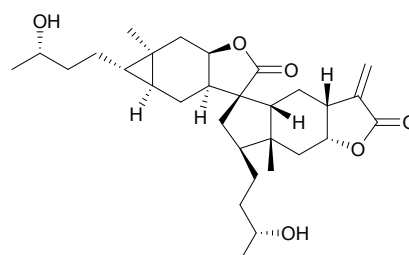
358 $R^1 = \text{OH}$ $R^2 = \text{H}$

359 $R^1 + R^2 = \text{O}$

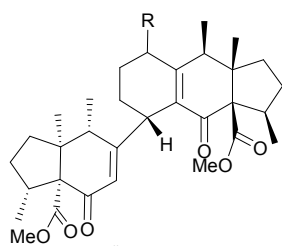


360 $R = \alpha\text{H}$

361 $R = \beta\text{H}$

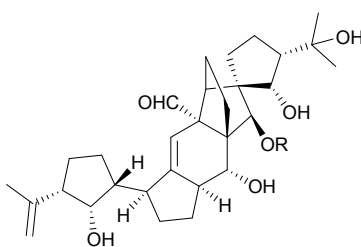


362



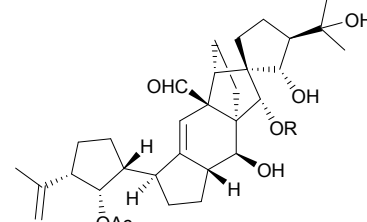
#363 $R = \beta\text{-OH}$

#364 $R = \alpha\text{-OH}$



#365a $R = \text{Ac}$

#366a $R = \text{H}$

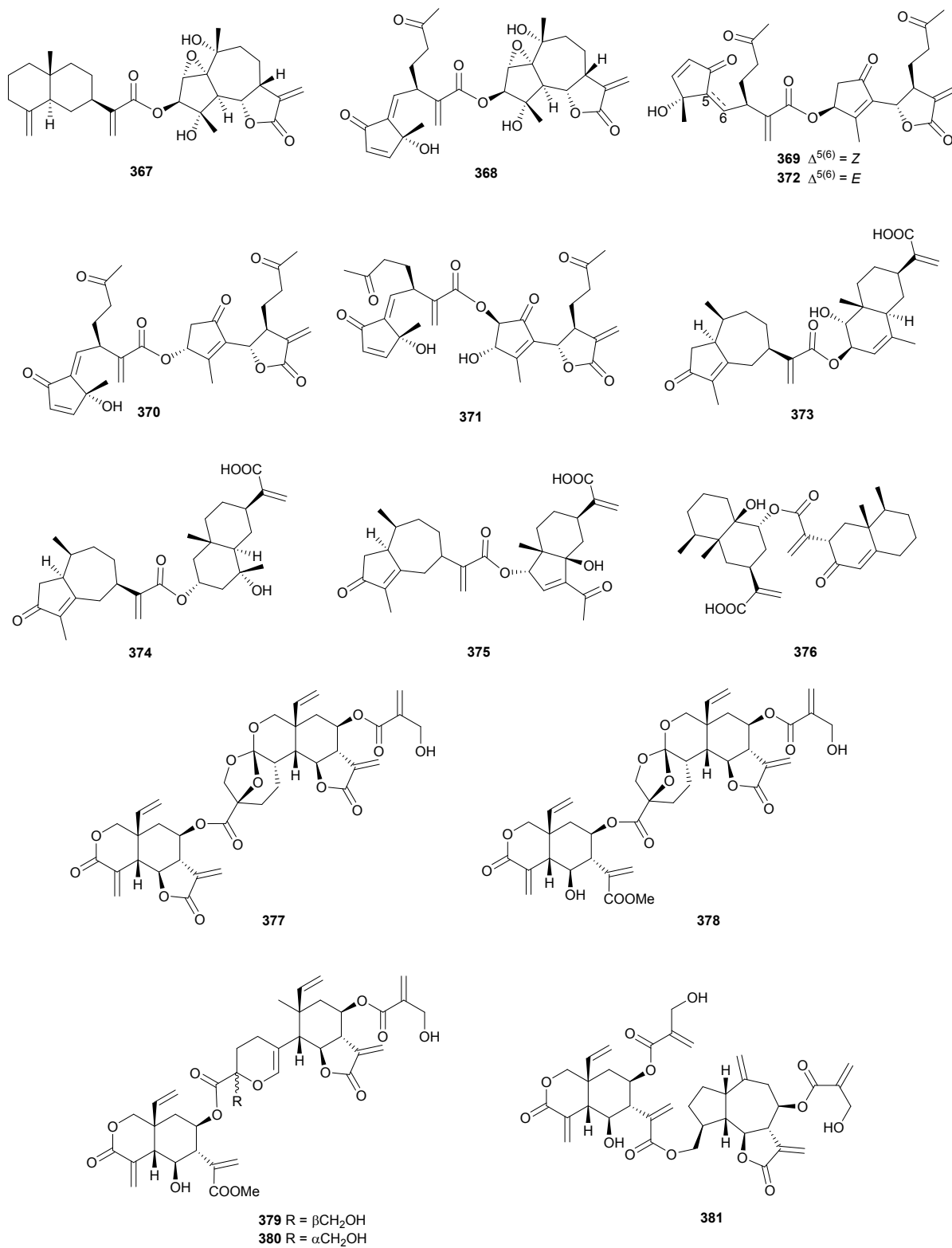


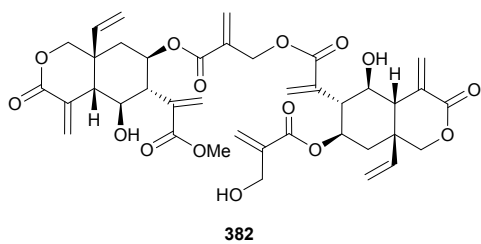
#365 $R = \text{Ac}$

#366 $R = \text{H}$

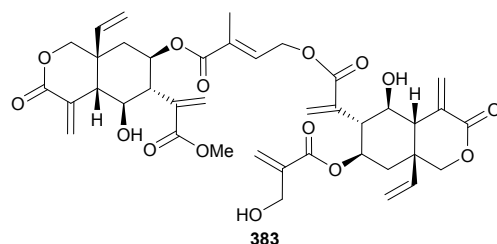
3 Pseudo-disesquiterpenoids

3.1 Ester linkage (compounds 367–401)

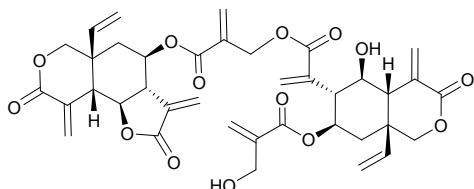




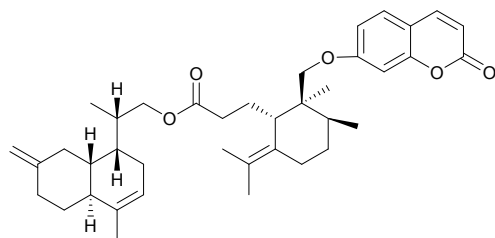
382



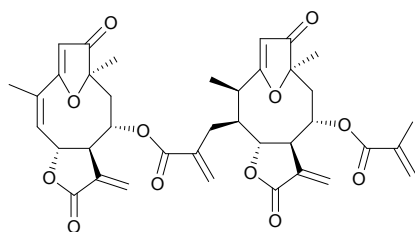
383



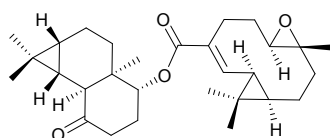
384



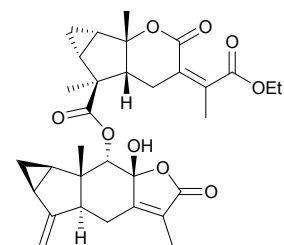
385



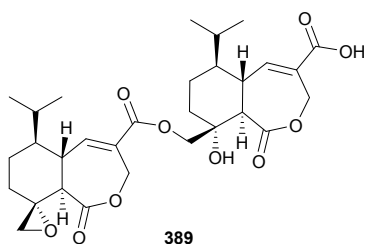
386



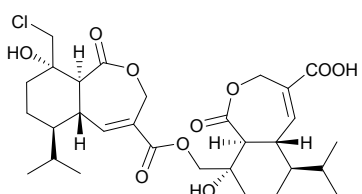
387



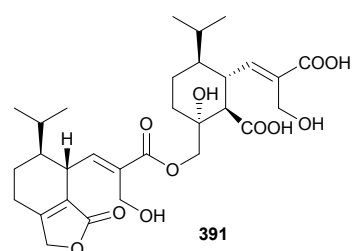
388



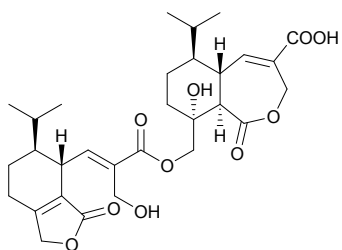
389



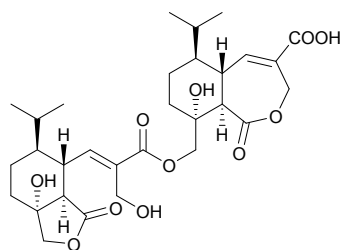
390



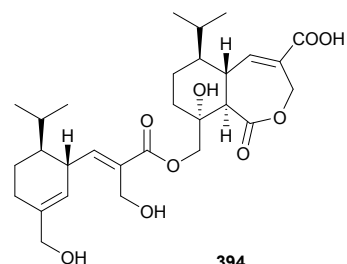
391



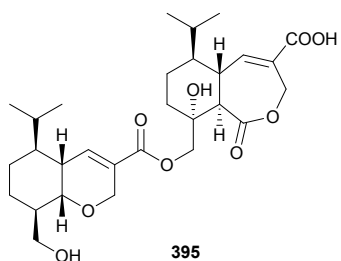
392



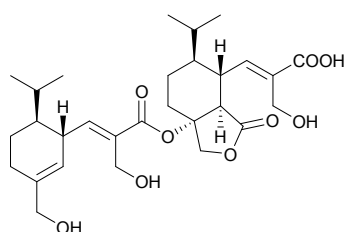
393



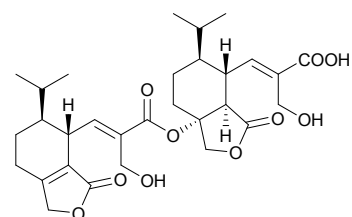
394



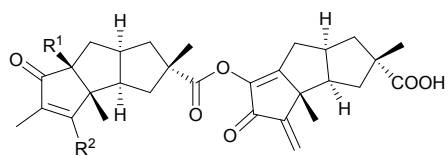
395



396

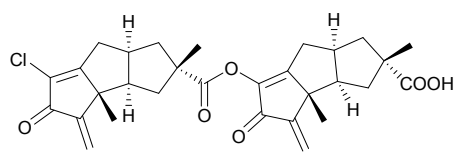


397

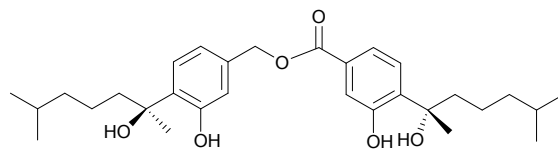


398 $R^1 = OH$ $R^2 = CH_3$

400 $R^1 = H$ $R^2 = CH_2OCH_3$

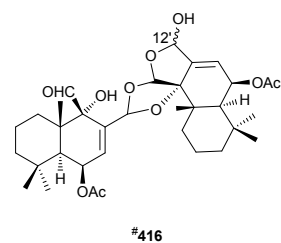
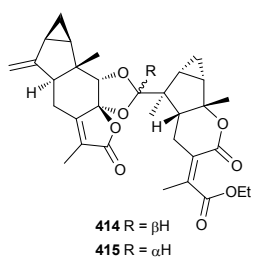
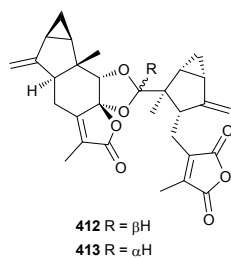
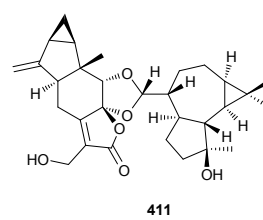
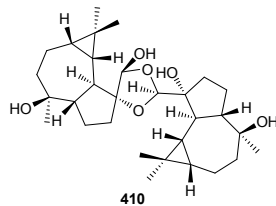
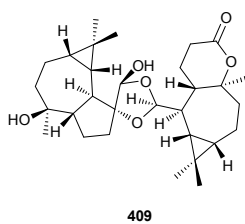
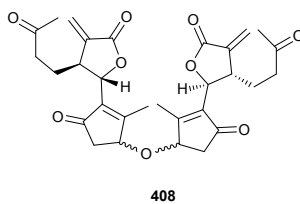
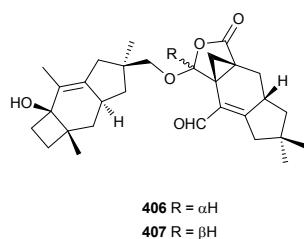
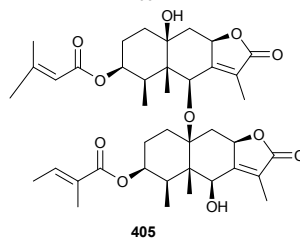
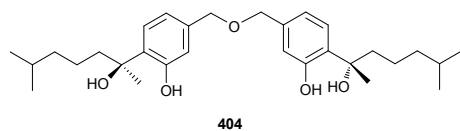
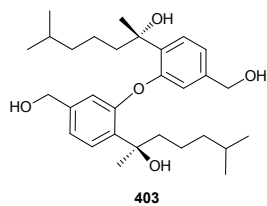
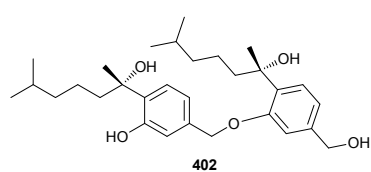


399

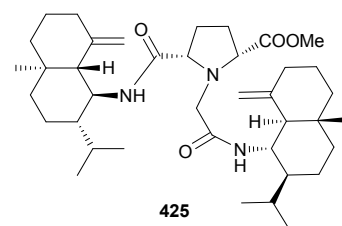
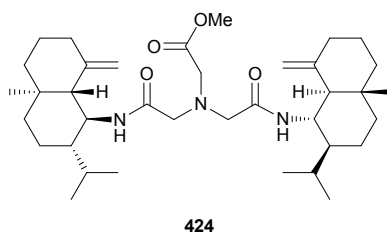
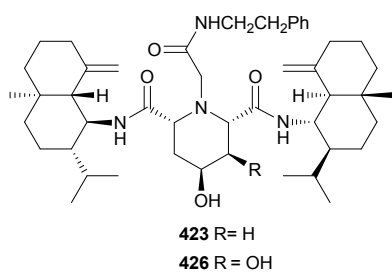
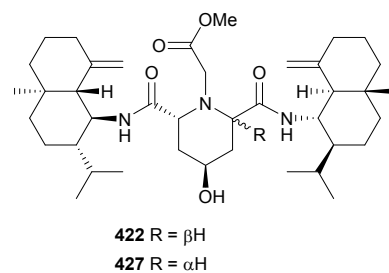
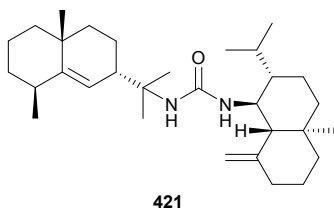
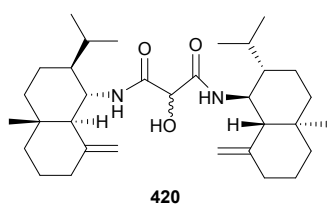
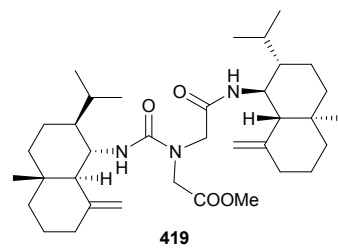
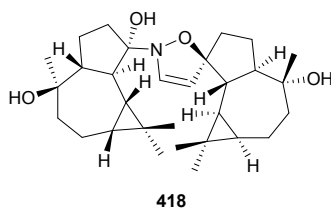
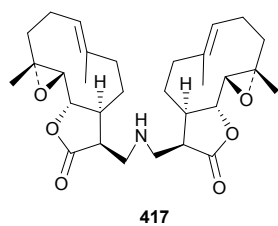


401

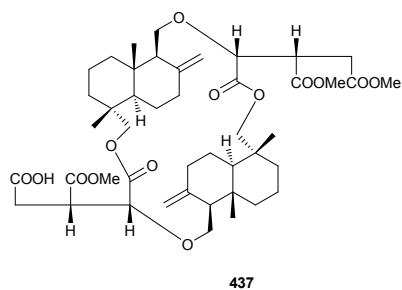
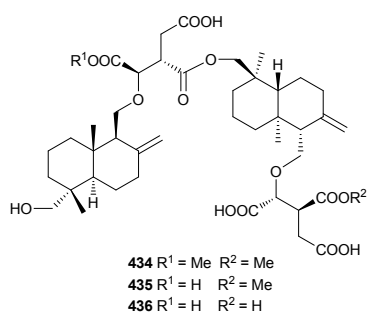
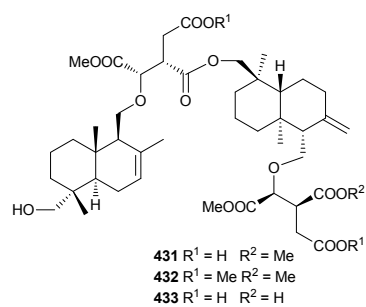
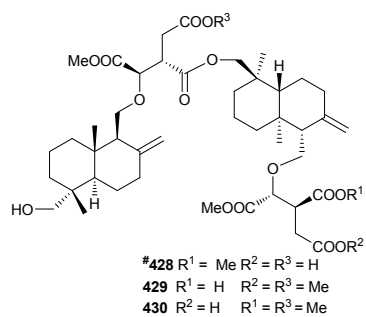
3.2 *O*-ether linkage (compounds 402–416)



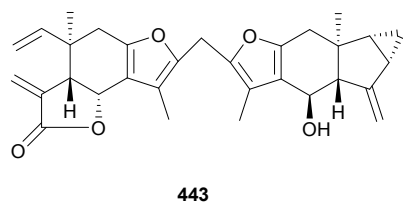
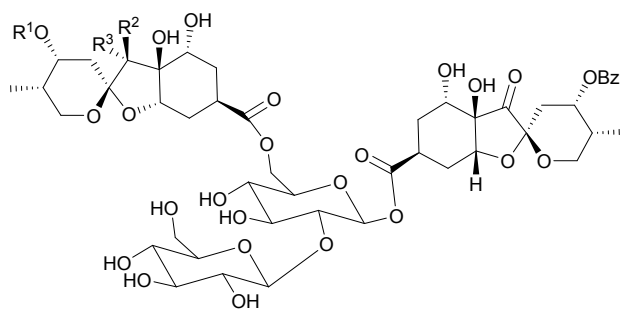
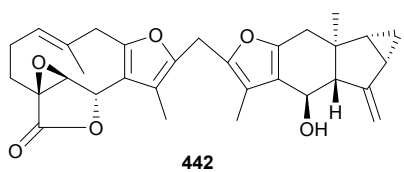
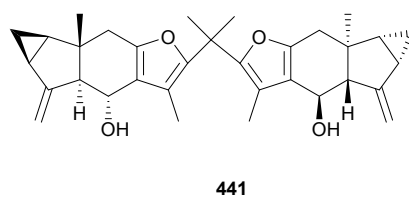
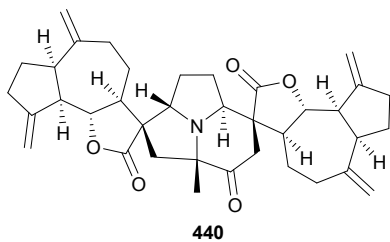
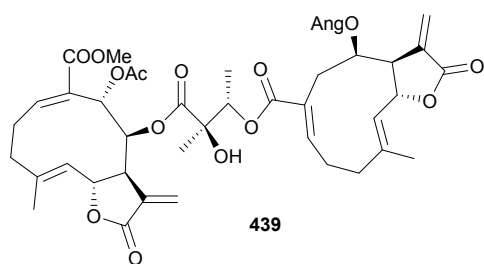
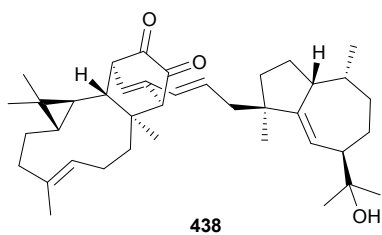
3.3 Nitrogen and urea linkage (compounds 417–427)



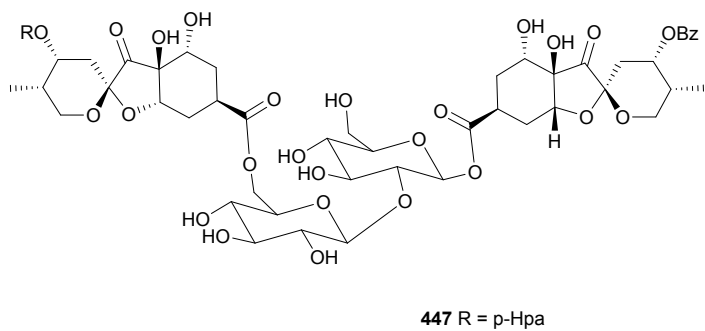
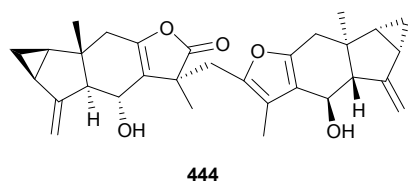
3.4 Isocitric acid linkage (compounds 428–437)



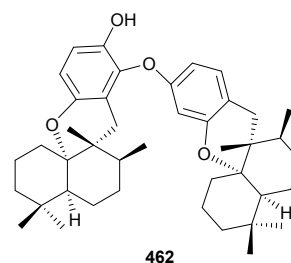
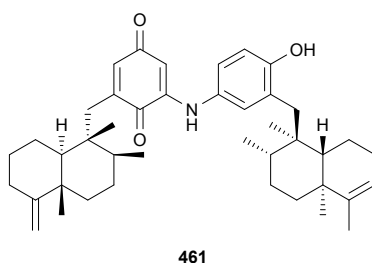
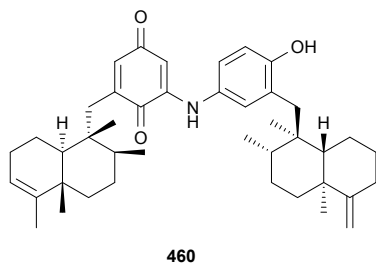
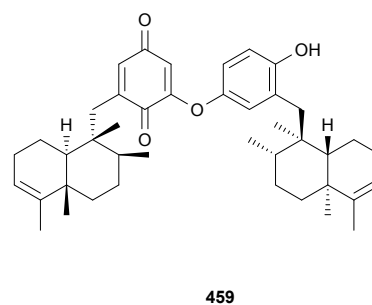
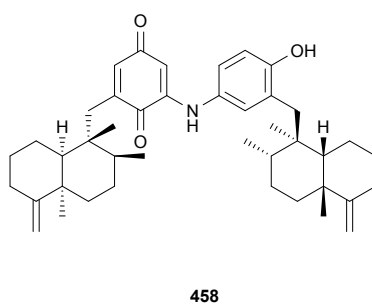
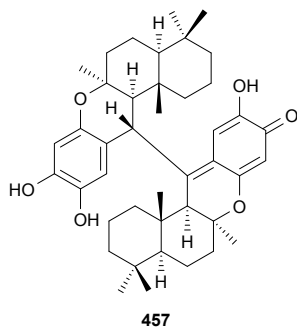
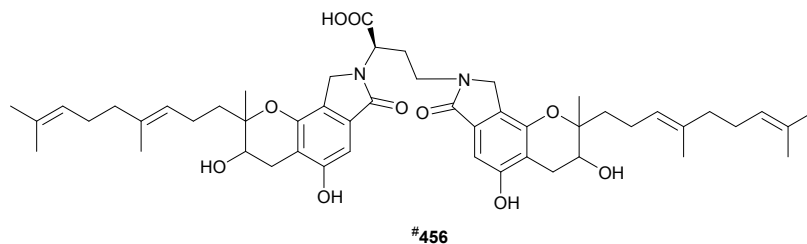
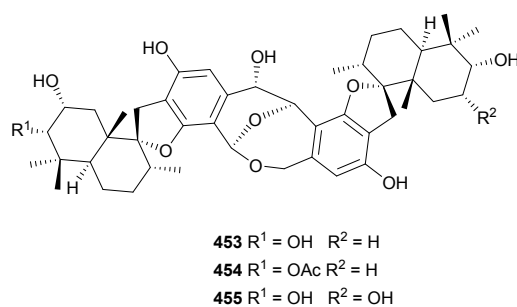
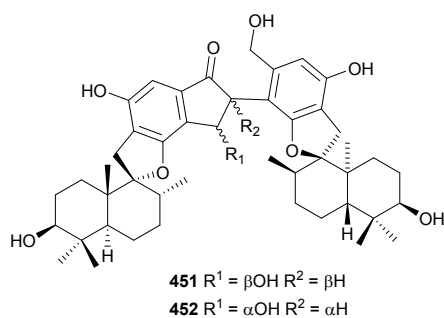
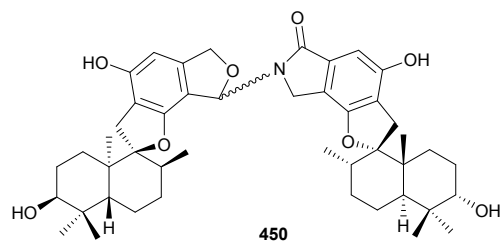
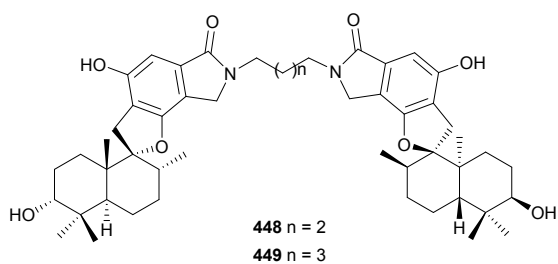
3.5 Others (compounds 438–447)

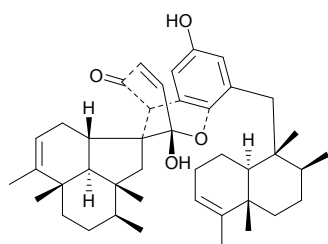


446 $R^1 = \text{p-Hpa}$ $R^2 + R^3 = \text{O}$

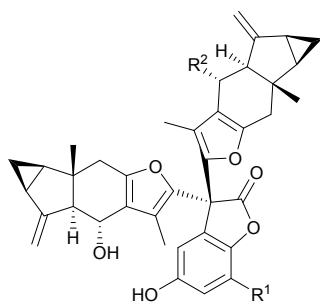


4 Merosesquiterpenoid dimers

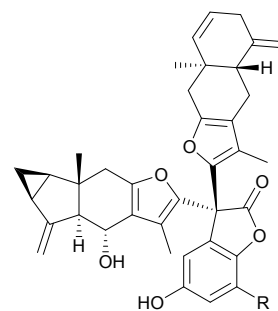




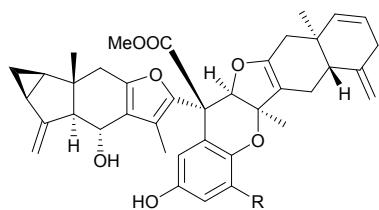
463



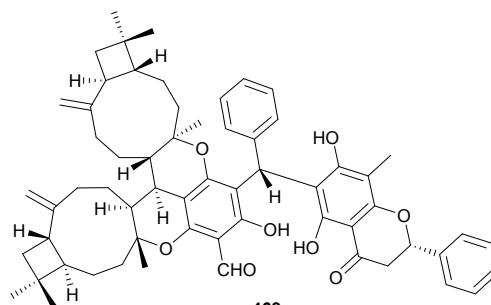
464 $R^1 = A$ $R^2 = OH$
465 $R^1 = A$ $R^2 = H$



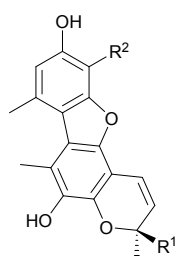
466 $R = A$



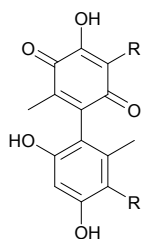
467 $R = A$



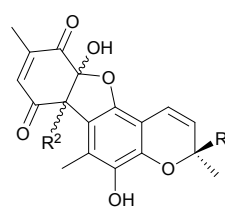
468



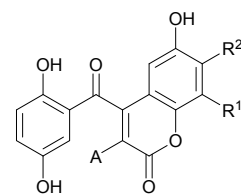
469 $R^1 = A$ $R^2 = B$



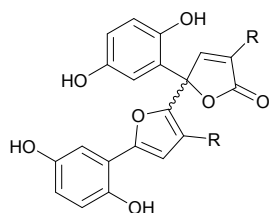
470 $R = B$



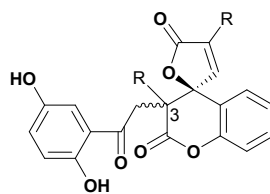
471 $R^1 = A$ $R^2 = C$



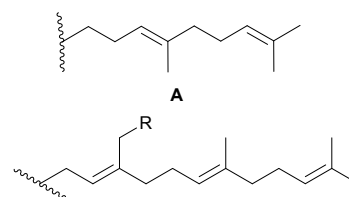
472 $R^1 = C$ $R^2 = H$
473 $R^1 = H$ $R^2 = C$



474 $R = A$



475 $R = A$ 3R
476 $R = A$ 3S



A
 B $R = H$
 C $R = OH$

