Structural Revisions of Natural Products by Total Synthesis

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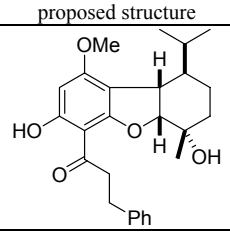
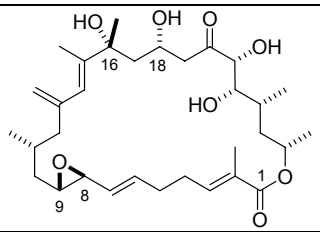
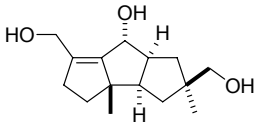
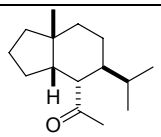
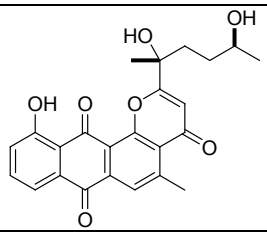
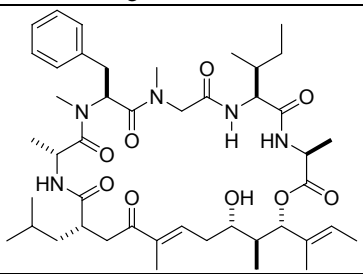
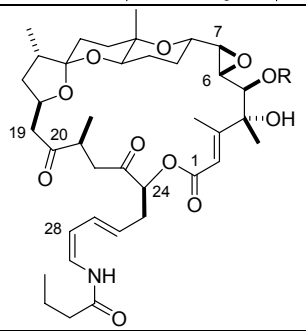
Tables

Table S1 Application of the Kishi database method to the determination of the C14-C19 region of cruentaren B.

cpd. **7** numbers	C14	C15	C16	C17	C18	C19	C31	C32	
Kishi ref. cpd. predicted	35.6	69.6	43.4	80.6	38.9	24.9	8.9	14.8	
crue b predicted	39.9	70.1	43.6	81.1	39.3	29.2	9	15.2	
crue b pred.-ref. cpd.	4.3	0.5	0.2	0.5	0.4	4.3	0.1	0.4	
crue b measured	33.4	77	37.2	80.2	36.5	30.7	4.4	15.8	
crue b adjusted	29.1	76.5	37	79.7	36.1	26.4	4.3	15.4	
									sum $\|\Delta\delta\|$
7a	33.01	73.55	39.03	77.63	37.01	26.62	11.87	12.79	
δ(**7a**-crue b adjd)	3.91	-2.95	2.03	-2.07	0.91	0.22	7.57	-2.61	22.27
7b	35.08	77	37.88	81.53	37.63	25.32	4.69	15.12	
δ(**7b**-crue b adjd)	5.98	0.5	0.88	1.83	1.53	-1.08	0.39	-0.28	**12.47**
7c	33.85	72.28	37.81	80.36	37.48	23.95	11.63	15.78	
δ(**7c**-crue b adjd)	4.75	-4.22	0.81	0.66	1.38	-2.45	7.33	0.38	21.98
7d	35.08	77.42	37.8	81.41	37.72	25.2	4.17	14.87	
δ(**7d**-crue b adjd)	5.98	0.92	0.8	1.71	1.62	-1.2	-0.13	-0.53	**12.89**
7e	34.18	76.68	40.88	79.3	36.82	27.03	12.97	11.56	
δ(**7e**-crue b adjd)	5.08	0.18	3.88	-0.4	0.72	0.63	8.67	-3.84	23.40
7f	35.07	76.48	38.22	75.28	37.35	25.21	10.82	15.32	
δ(**7f**-crue b adjd)	5.97	-0.02	1.22	-4.42	1.25	-1.19	6.52	-0.08	20.67
7g	34.25	76.54	40.79	82.03	37.01	21.18	13.36	16.68	
δ(**7g**-crue b adjd)	5.15	0.04	3.79	2.33	0.91	-5.22	9.06	1.28	27.78
7h	35.16	76.6	38.14	74.87	37.6	25.35	10.48	14.83	
δ(**7h**-crue b adjd)	6.06	0.1	1.14	-4.83	1.5	-1.05	6.18	-0.57	21.43

Table S2. Structures of natural products whose original assigned structures require revision

proposed structure	name of compound	remarks
	adunctin E	Ohta et al. (2007)[1]
	amphidinolide B_2	Carter et al. (2008)[2]
	dichomitol	Mehta et al. (2006)[3]
	faurinone	Procter et al. (2008)[4]
	δ-indomycinone	Tietze et al. (2007)[5]
	kulokekahilide-2	Kimura et al. (2007)[6]
	lituarines B (R = Ac) and C (R = H)	Smith, III et al. (2008)[7]

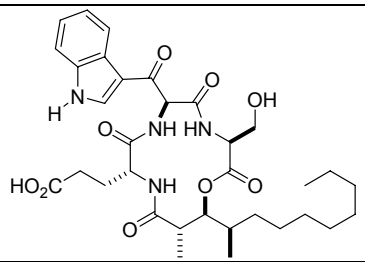
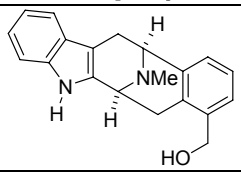
	LL15G256γ	Ye et al. (2008)[8]
	macrocaffrine	Ohba et al. (2007)[9]

Table S3. Structures of natural products where the correct structure had a different formula compared to the proposed one

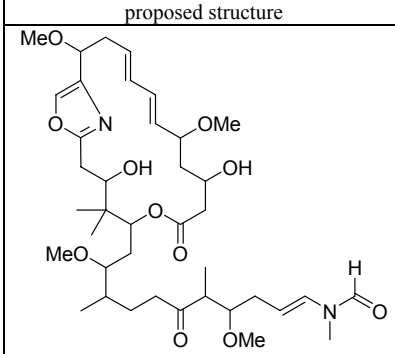
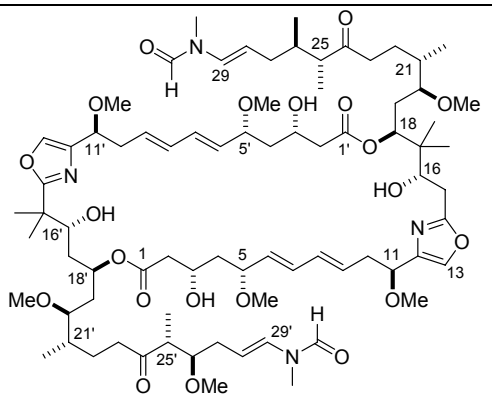
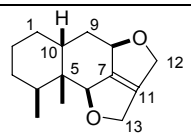
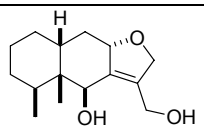
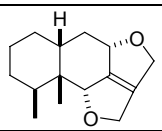
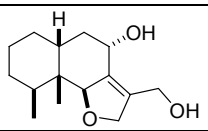
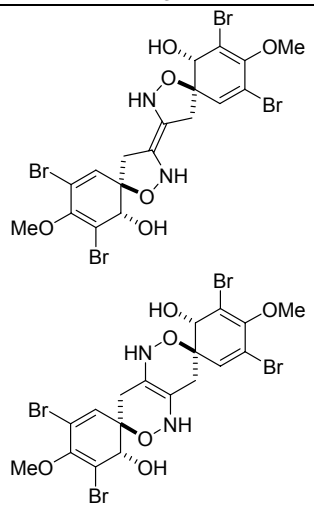
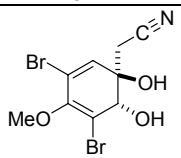
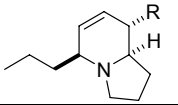
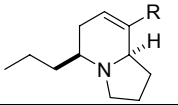
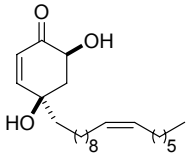
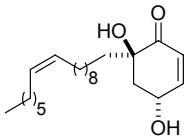
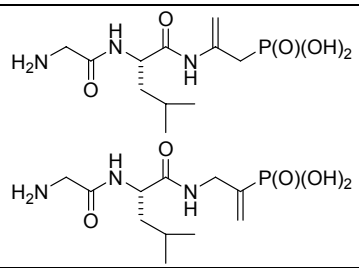
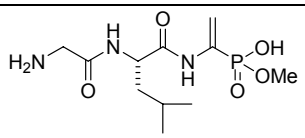
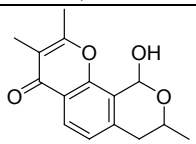
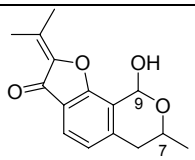
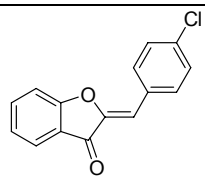
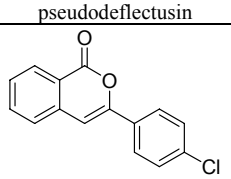
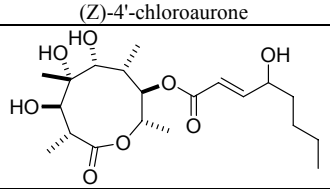
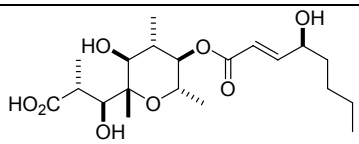
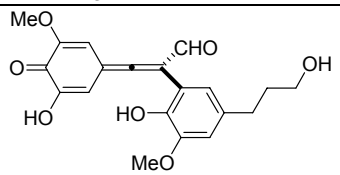
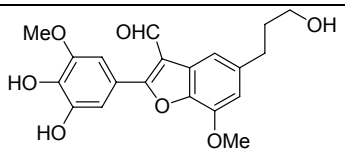
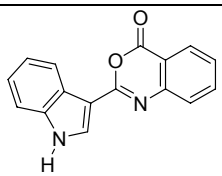
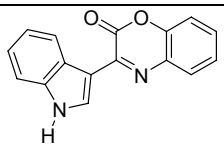
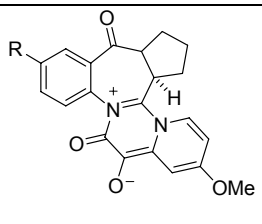
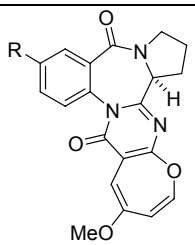
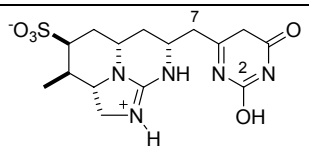
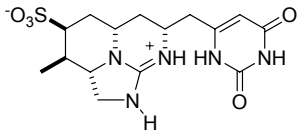
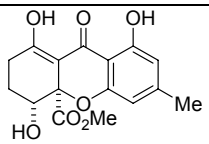
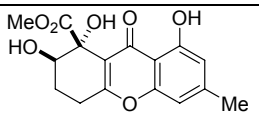
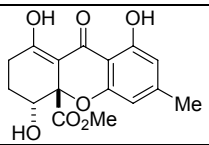
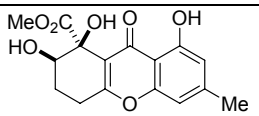
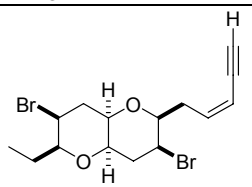
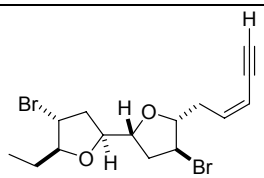
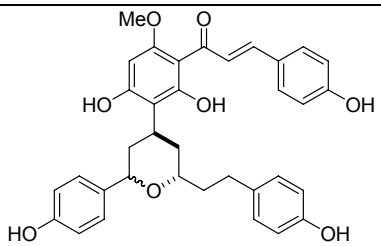
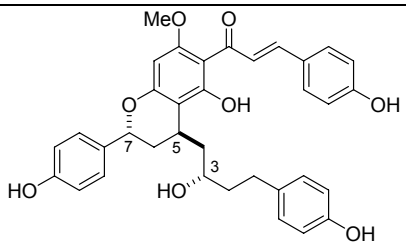
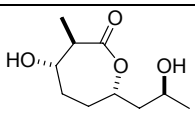
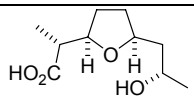
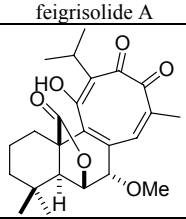
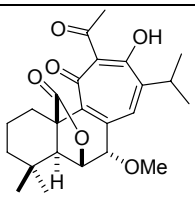
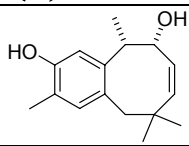
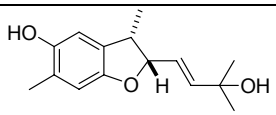
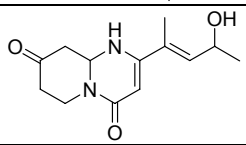
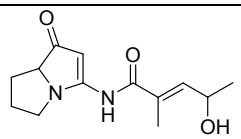
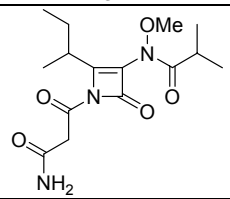
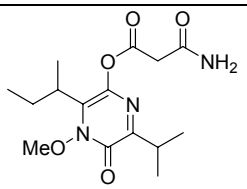
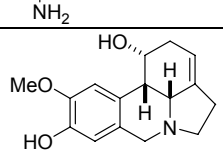
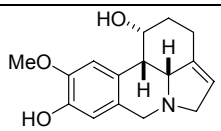
proposed structure	revised structure	name of compound	remarks
		rhizopodin	Höfle et al. (1993)[10] Jansen et al. (2008)[11] Menche et al. (2008)[12] Schubert et al. (2009)[13]
		peribysin C	Koshino et al. (2006)[14]
		peribysin D	Koshino et al. (2006)[14]
		zamamistatin	Uemura et al. (2001)[15] Kigoshi et al. (2005)[16] Kigoshi et al. (2008)[17]

Table S4. Structures of natural products where the correct structure turned out to be a constitutional isomer of the proposed one

proposed structure	revised structure	name of compound	remarks
		alkaloid 179 (R = Me) alkaloid 207E (R = *n*Pr)	Toyooka et al. (2008)
		4-alkyl-4-hydroxycyclohexenones	Pettus et al. (2008)[18]
		antibiotic A53868	Van der Donk et al. (2007)[19]
 aspergione B	 pseudodeflectusin		Kobayashi et al. (2006)[20]
 (Z)-4'-chloroaurone	 3-(4'-chloroisocoumarin)		Pale et al. (2008)[21]
		botcinolide	Nakajima et al. (2006)[22] Shiina et al. (2008)[23]
		brosimum allene	Williams et al. (2008)[24]
		cephalandole A	Bergman/Janosik et al. (2008)[25]
		R = OMe circumdatin A R = H circumdatin B	Kusumi et al. (2008)[26]

		7-deoxycylindrospermopsin	Williams et al. (2005)[27]
		α-diversonolic ester	Nicolaou et al. (2008)
		β-diversonolic ester	Nicolaou et al. (2008)
		elatenyne	Burton et al. (2006,[28] 2008,[29] 2009[30]); revision based on NMR data and GIAO ^{13}C NMR calculations
		epicalyxin F	Rychnovsky et al. (2007)[31]
 feigrisolide A	 (-)-nonactic acid		Marco et al. (2006)[32]
		hassanane	Huang/Zhao et al. (2008);[33] revision based on quantum mechanical ^{13}C NMR shifts
		heliannuol G	Shishido et al. (2006)[34]
		jenamide A	Snider et al. (2006)
		kasarin	Uemura et al. (2007)[35]
		kirkine (= fortucine)	Zard et al. (2008)[36]

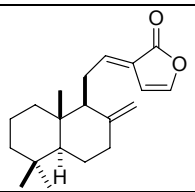
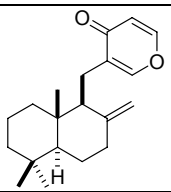
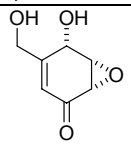
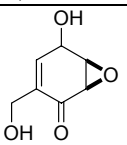
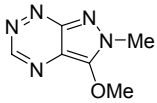
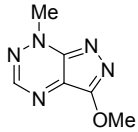
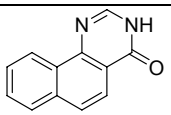
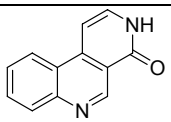
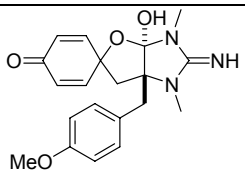
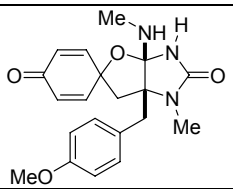
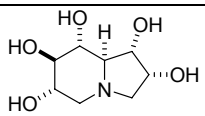
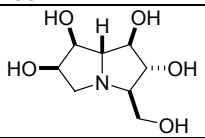
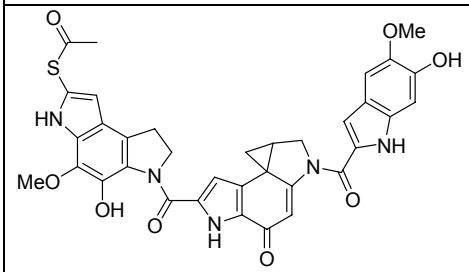
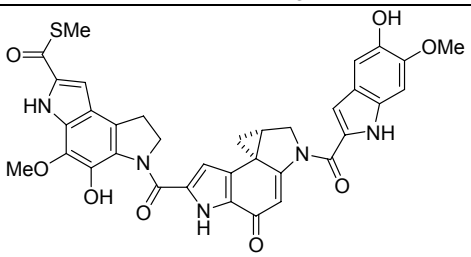
		ottensinin	Boukouvalas et al. (2008)[37]
 parasitenone	 (+)-epoxydon		Mehta et al. (2005)[38]
		pseudoiodinine	Kelly et al. (2006)[39]
		samoquasine	Timmons et al. (2008);[40] based on DFT calculation of ^{13}C NMR shifts
		spiroleucettadine	Watson et al. (2007)[41] Crews et al. (2008)[42]
		uniflorine A	Pyne et al. (2008)[43] Dhavale et al. (2006)[44]
 yatakemycin	 (+)-yatakemycin		Boger et al. (2004,[45] 2008[46]) Fukuyama et al. (2006)[47]

Table S5. Structures of natural products where the correct structure turned out to be a double bond isomer of the proposed one

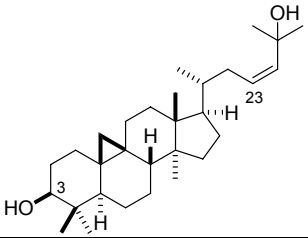
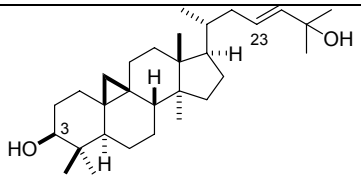
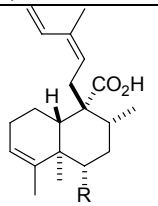
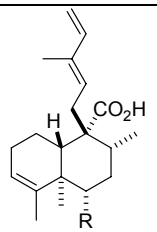
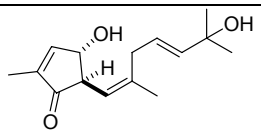
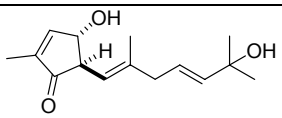
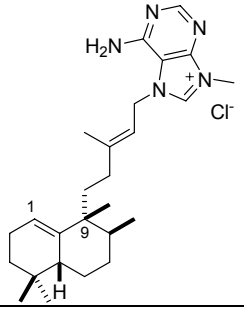
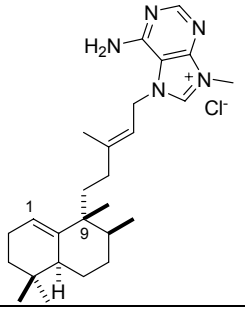
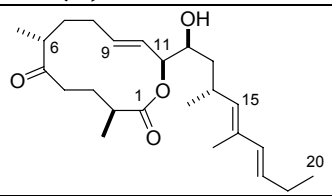
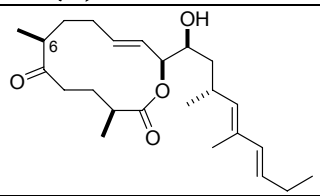
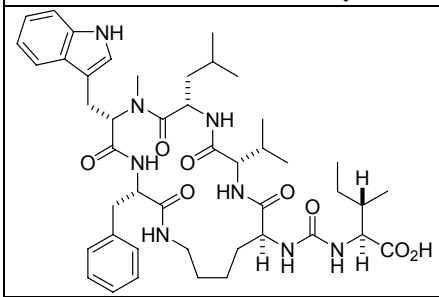
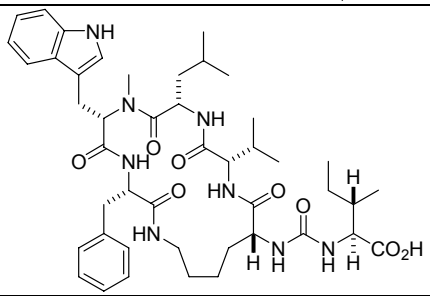
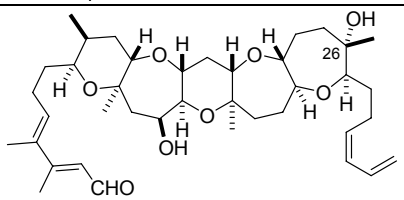
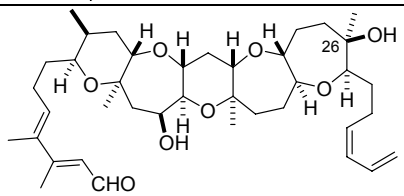
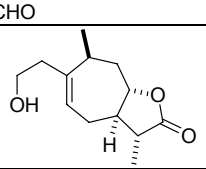
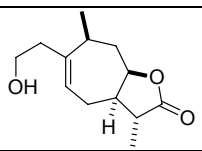
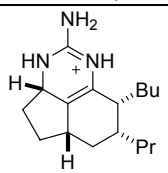
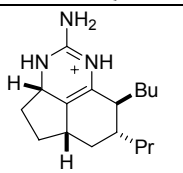
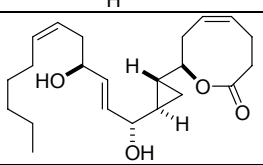
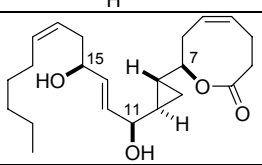
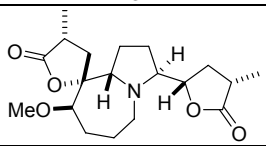
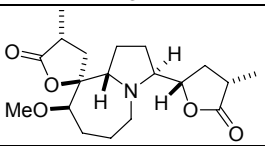
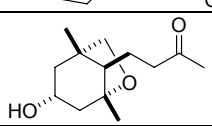
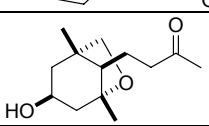
proposed structure	revised structure	name of compound	remarks
		cycloart-23-ene-3,25-diol	Takahashi et al. (2007)[48]
		heteroscyphic acid A (R = H) heteroscyphic acid B (R = OAc)	Donaldson et al. (2006)[49]
		litseaverticillol E	Vassilikogiannakis et al. (2005)[50]

Table S6. Structures of natural products where the correct structure turned out to be an epimer of the proposed one

proposed structure	revised structure	name of compound	remarks
		agelasine C	Marcos et al. (2005)[51]
		amphidinolide W	Ghosh et al. (2004,[52] 2006[53])
		brunsvicamide A	Waldmann et al. (2008)[54]
		brevenal	Sasaki et al. (2006)[55]
		diversifolide = 11-*epi*-sundiversifolide	Shishido et al. (2008)[56]
		netamine E	Snider et al. (2008)[57]
		solandelactone E	Martin et al. (2008)[58] Pietruszka et al. (2008)[59]
		stemonidine = stemospironine	Figueredo et al. (2007)[60]
		tanarifuranonol	Hsieh/Liao et al. (2008)[61]

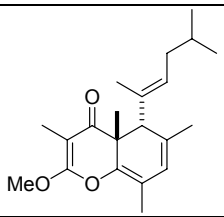
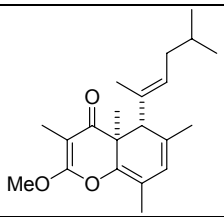
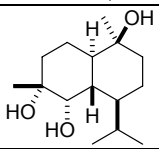
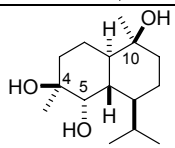
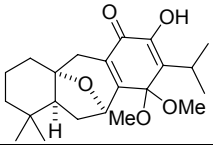
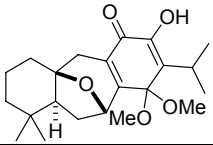
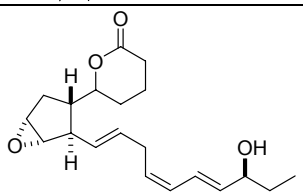
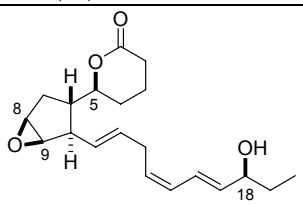
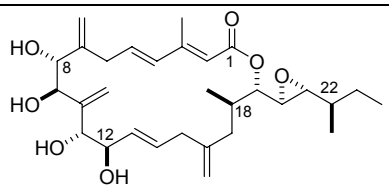
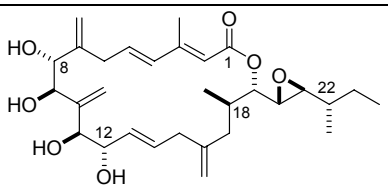
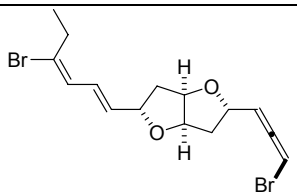
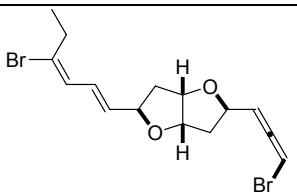
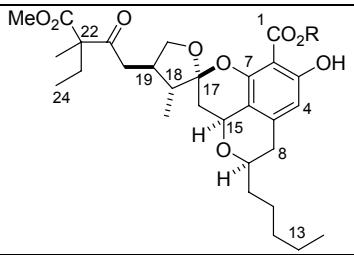
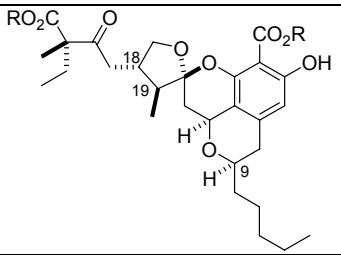
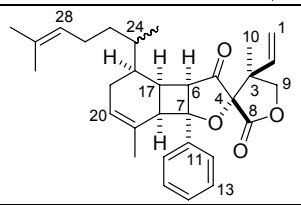
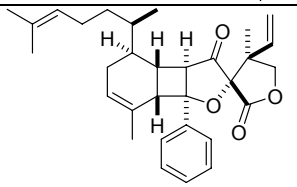
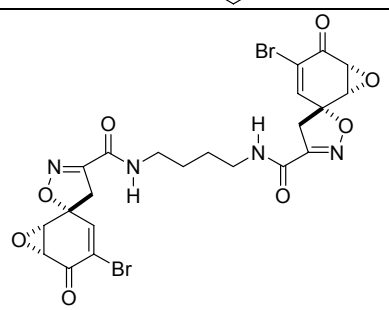
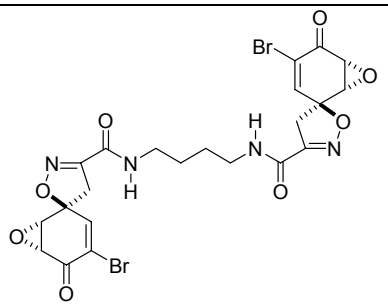
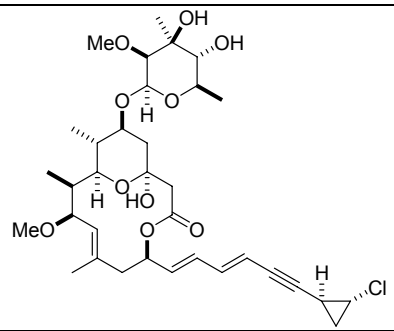
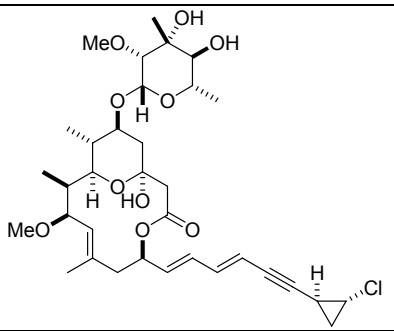
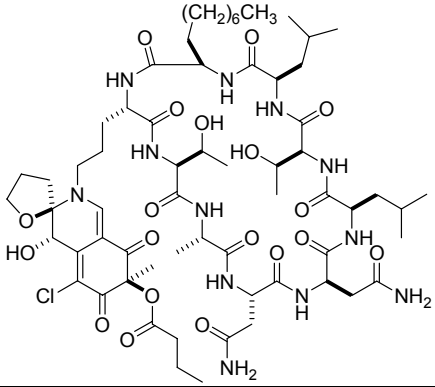
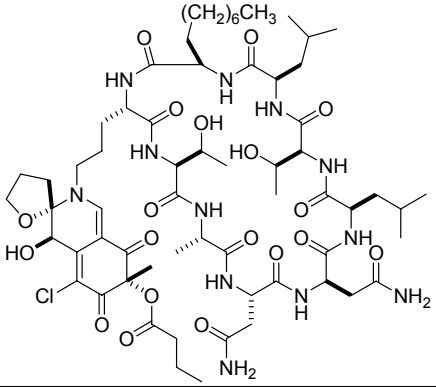
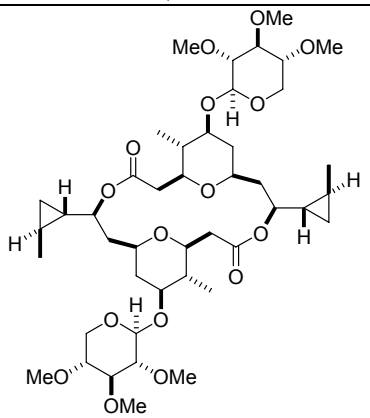
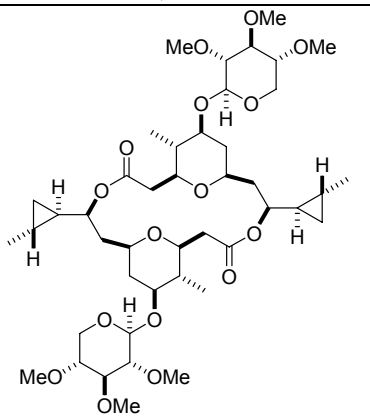
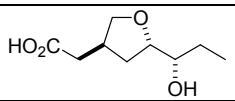
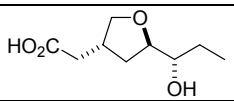
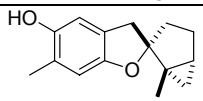
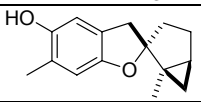
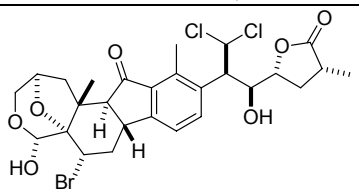
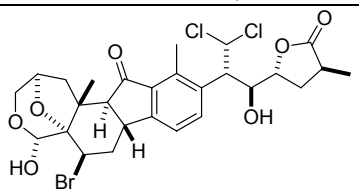
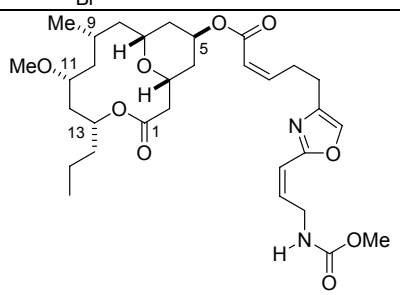
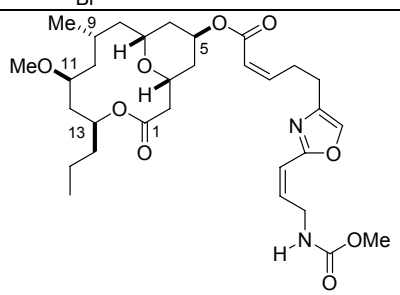
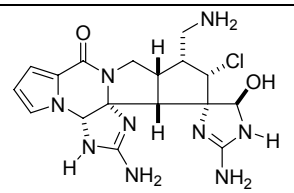
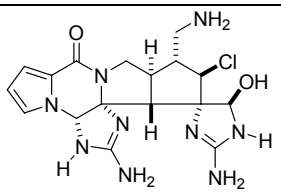
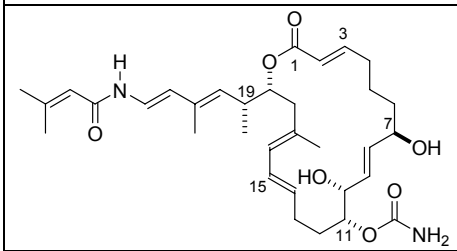
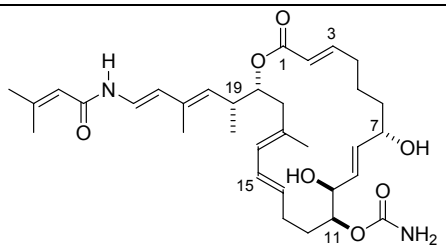
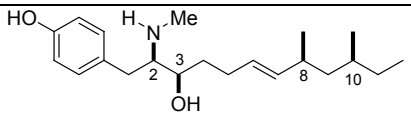
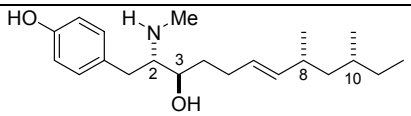
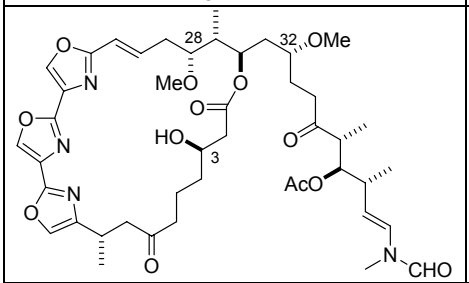
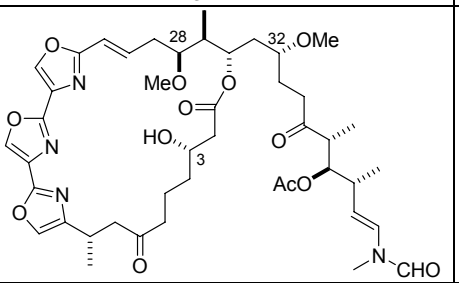
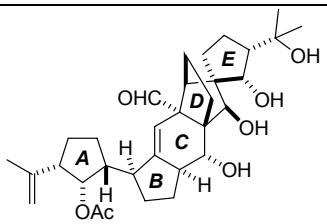
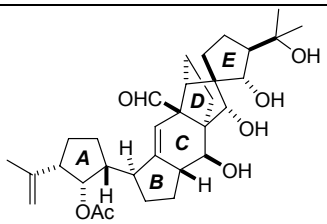
		tridachiahydropyrone	Perkins et al. (2005)[62] Moses et al. (2008)[63]
		trihydroxycadinane	Li et al. (2006)[64]

Table S7. Structures of natural products where several stereocenters had to be revised

proposed structure	revised structure	name of compound	remarks
		abrotanone	Sarpong et al. (2007)[65]
		agardhilactone	Miyaoka et al. (2005)[66]
		amphidinolide A	Trost et al. (2005)[67]
		aplysiallene	Pagenkopf et al. (2007)[68]
		berkelic acid	Fürstner et al. (2008)[69] Snider et al. (2009)[70]
		biyouyanagin	Nicolaou et al. (2008)[71]
		calafianin	Nishiyama et al. (2006)[72]

		callipeltoside C	MacMillan et al. (2008)[73]
		chlorofusin	Yao et al. (2007)[74] Boger et al. (2007)[75]
		(–)-clavosolide A	Chakraborty et al. (2008)[76] Willis et al. (2006)[77] Smith, III et al. (2006)[78] Lee et al. (2006)[79]
		communiol C	Kuwahara et al. (2008)[80]
		laurentristich-4-ol	Wang/Li et al. (2008)[81]
		nakiterpiosin	Chen et al. (2009)[82]
		neopeltolide	Panek et al. (2007)[83] Scheidt et al. (2008)[84] Maier et al. (2008)[85]

		palau'amine	Köck/Baran et al (2007).[86] Romo et al. (2006, 2008)[87] Overman et al. (2007)[88] Quinn et al. (2007)[89]
		palmerolide A	De Brabander et al. (2007)[90] Nicolaour et al. (2008)[91]
		tyroscherin	Watanabe et al. (2008)[92]
		(–)-ulapualide A	Pattenden et al. (2007)[93]
		vannusal B	Nicolaou et al. (2008)[94,95]

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