Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

SUPPORTING INFORMATION
Marine natural products from the deep Pacific as potential non-linear optical chromophores

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The nonlinear optical response relating to second harmonic generation in hyper-Rayleigh scattering experiments was calculated using the following expression

$$\beta_{\mathrm{HRS}}\left(-2\omega;\omega,\omega\right)=\sqrt{\{\langle\beta^2_{\mathrm{ZZZ}}\rangle+\langle\beta^2_{\mathrm{XZZ}}\rangle\}} \tag{S1}$$

where the β tensor orientational averages are given by

$$\begin{aligned}\langle\beta^2_{\mathrm{ZZZ}}\rangle =&\frac{1}{7}\sum_{\zeta}^{x,y,z}\beta^2_{\zeta\zeta\zeta}+\frac{4}{35}\sum_{\zeta\neq\eta}^{x,y,z}\beta^2_{\zeta\zeta\eta}+\frac{2}{35}\sum_{\zeta\neq\eta}^{x,y,z}\beta_{\zeta\zeta\zeta}\beta_{\zeta\eta\eta}+\frac{4}{35}\sum_{\zeta\neq\eta}^{x,y,z}\beta_{\eta\zeta\zeta}\beta_{\zeta\zeta\eta}\\&+\frac{4}{35}\sum_{\zeta\neq\eta}^{x,y,z}\beta_{\zeta\zeta\zeta}\beta_{\eta\eta\zeta}+\frac{1}{35}\sum_{\zeta\neq\eta}^{x,y,z}\beta^2_{\eta\zeta\zeta}+\frac{4}{105}\sum_{\zeta\neq\eta\neq\xi}^{x,y,z}\beta_{\zeta\zeta\eta}\beta_{\eta\xi\xi}\\&+\frac{1}{105}\sum_{\zeta\neq\eta\neq\xi}^{x,y,z}\beta_{\eta\zeta\zeta}\beta_{\eta\xi\xi}+\frac{4}{105}\sum_{\zeta\neq\eta\neq\xi}^{x,y,z}\beta_{\zeta\zeta\eta}\beta_{\xi\xi\eta}+\frac{2}{105}\sum_{\zeta\neq\eta\neq\xi}^{x,y,z}\beta^2_{\zeta\eta\xi}\\&+\frac{4}{105}\sum_{\zeta\neq\eta\neq\xi}^{x,y,z}\beta_{\zeta\eta\xi}\beta_{\eta\zeta\xi}\end{aligned} \tag{S2}$$

$$\begin{aligned}\langle\beta^2_{\mathrm{XZZ}}\rangle =&\frac{1}{35}\sum_{\zeta}^{x,y,z}\beta^2_{\zeta\zeta\zeta}+\frac{4}{105}\sum_{\zeta\neq\eta}^{x,y,z}\beta_{\zeta\zeta\zeta}\beta_{\zeta\eta\eta}-\frac{2}{35}\sum_{\zeta\neq\eta}^{x,y,z}\beta_{\zeta\zeta\zeta}\beta_{\eta\eta\zeta}+\frac{8}{105}\sum_{\zeta\neq\eta}^{x,y,z}\beta^2_{\zeta\zeta\eta}\\&+\frac{3}{35}\sum_{\zeta\neq\eta}^{x,y,z}\beta^2_{\zeta\eta\eta}-\frac{2}{35}\sum_{\zeta\neq\eta}^{x,y,z}\beta_{\zeta\zeta\eta}\beta_{\eta\zeta\zeta}+\frac{1}{35}\sum_{\zeta\neq\eta\neq\xi}^{x,y,z}\beta_{\zeta\eta\eta}\beta_{\zeta\xi\xi}\\&-\frac{2}{105}\sum_{\zeta\neq\eta\neq\xi}^{x,y,z}\beta_{\zeta\zeta\xi}\beta_{\eta\eta\xi}-\frac{2}{105}\sum_{\zeta\neq\eta\neq\xi}^{x,y,z}\beta_{\zeta\zeta\eta}\beta_{\eta\xi\xi}+\frac{2}{35}\sum_{\zeta\neq\eta\neq\xi}^{x,y,z}\beta^2_{\zeta\eta\xi}\\&-\frac{2}{105}\sum_{\zeta\neq\eta\neq\xi}^{x,y,z}\beta_{\zeta\eta\xi}\beta_{\eta\zeta\xi}\end{aligned} \tag{S3}$$

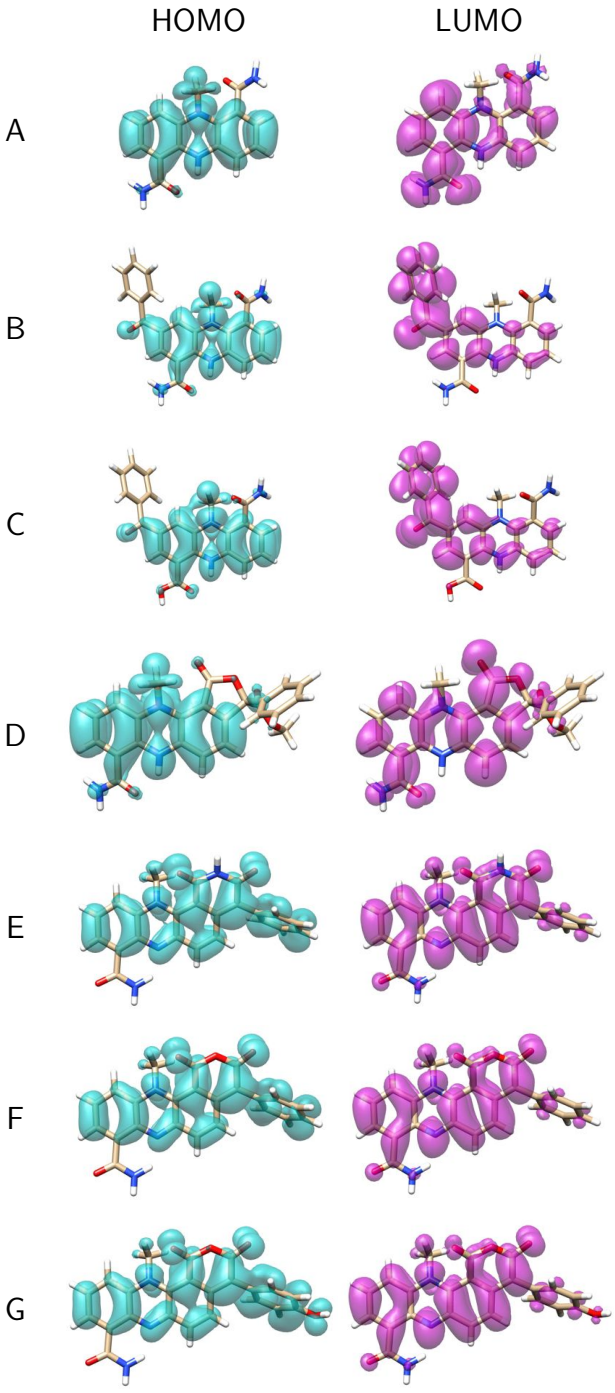

Figure S1: CAM-B3LYP/aug-cc-pVDZ frontier molecular orbitals of the dermacozines at their B3LYP/Def2-SVP optimised geometries

Table S1: TD-CAM-B3LYP/aug-cc-pVDZ first hyperpolarisability tensor components for dermacozines A–G in atomic units ($\lambda = 1907$ nm)

	Dermacozine						
Tensor component	A	B	C	D	E	F	G
xxx	450	3758	3893	-1611	13273	13556	24730
yyy	362	507	707	126	-181	-158	-240
zzz	55	-55	-25	-20	32	28	31
xxy	654	-2005	-1520	673	4704	4503	4106
xxz	423	-349	-450	13	2	212	-576
yyx	394	1379	1230	343	227	109	283
yyz	86	22	-87	-90	-212	-168	-172
zzx	15	-74	-110	110	-21	-12	8
zzy	-30	-12	-56	84	24	26	31
xyy	419	1330	1200	371	94	-22	162
xzz	16	-74	-112	132	-14	-4	18
yxx	618	-2058	-1615	647	3991	3809	3727
yzz	-30	-13	-58	87	25	27	32
zxx	416	-331	-451	-14	132	268	-312
zyy	86	24	-85	-86	-204	-163	-166
xyz	105	-168	167	-66	-87	-39	-31
xzy	105	-168	167	-66	-87	-39	-31
yxz	100	-166	167	-48	-89	-36	-50
yzx	100	-166	167	-48	-89	-36	-50
zxy	101	-168	169	-46	-28	0	18
zyx	101	-168	169	-46	-28	0	18

Table S2: TD-CAM-B3LYP/aug-cc-pVDZ first hyperpolarisability tensor components for dermacozines A–G in atomic units ($\lambda = 1064$ nm)

	Dermacozine						
Tensor component	A	B	C	D	E	F	G
xxx	1,401	9,695	9,758	-3,955	214,791	158,367	1,124,058
yyy	586	245	693	227	721	44	1,273
zzz	66	-62	-36	-10	46	39	67
xxy	1,542	-4,485	-2,904	1,471	89,827	60,481	233,665
xxz	733	-556	-659	-175	-2,062	1,054	-28,501
yyx	764	3,260	2,743	617	14,570	7,952	32,762
yyz	125	44	-100	-128	-228	-164	-77
zzx	14	-99	-144	128	-79	12	-553
zzy	-39	-11	-53	97	33	33	55
xyy	944	2,943	2,692	860	6,475	2,505	12,173
xzz	22	-105	-160	290	344	357	1,502
yxx	1,275	-4,620	-3,403	1,182	40,117	26,268	161,876
yzz	-36	-10	-63	123	88	79	245
zxx	666	-440	-624	-370	6,084	3,303	22,411
zyy	123	52	-81	-92	-27	-120	83
xyz	207	-321	346	-226	137	267	966
xzy	207	-321	346	-226	137	267	966
yxz	174	-300	316	-91	-456	97	-4,011
yzx	174	-300	316	-91	-456	97	-4,011
zxy	175	-298	338	-68	2642	1261	5,064
zyx	175	-298	338	-68	2642	1261	5,064

Table S3: TD-CAM-B3LYP/aug-cc-pVDZ first hyperpolarisability tensor components for dermacozines A–G in atomic units (λ = 800 nm)

	Dermacozine						
Tensor component	A	B	C	D	E	F	G
xxx	13943	-23044	-37988	97108	-17036	-23263	-28834
yyy	2274	3563	3394	551	-2033	-1561	-1721
zzz	87	-74	-67	-79	32	31	37
xxy	10175	20953	28531	-1462	-20332	-20475	-21190
xxz	2921	-3415	410	6119	460	86	851
yyx	3689	-116	8955	1819	-6943	-6182	-5832
yyz	379	-191	424	-283	-471	-352	-375
zzx	25	-166	-83	740	29	16	399
zzy	-47	-7	31	300	21	16	45
xyy	5839	-2132	-4118	-3088	-4171	-3394	-3395
xzz	116	-105	-289	715	-81	-133	-86
yxx	6492	8479	4227	11034	2696	2642	-3600
yzz	-15	-21	-60	372	6	-3	10
zxx	1782	-1095	-2144	6857	-3271	-1490	-10544
zyy	320	55	-50	-745	-205	-123	11
xyz	1024	-521	343	621	-421	-316	-334
xzy	1024	-521	343	621	-421	-316	-334
yxz	774	-546	1107	188	2	4	459
yzx	774	-546	1107	188	2	4	459
zxy	530	-554	2976	-979	-131	140	947
zyx	530	-554	2976	-979	-131	140	947

Table S4: TD-CAM-B3LYP/d-aug-cc-pVDZ first hyperpolarisability tensor components for dermacozines A–G in atomic units (λ = 1907 nm)

	Dermacozine						
Tensor component	A	B	C	D	E	F	G
xxx	448	3,776	3,914	-1,609	13,260	13,548	24,665
yyy	375	517	720	135	-180	-158	-235
zzz	48	-51	-22	-28	27	24	28
xxy	661	-2,006	-1,520	682	4,712	4,513	4,137
xxz	428	-354	-453	12	3	214	-567
yyx	400	1,383	1,234	348	229	110	276
yyz	85	23	-87	-93	-217	-172	-176
zzx	14	-73	-110	111	-16	-7	10
zzy	-30	-12	-55	87	24	24	31
xyy	426	1,334	1,204	377	96	-22	153
xzz	16	-74	-112	133	-9	1	20
yxx	626	-2,059	-1,615	656	3,997	3,816	3,753
yzz	-30	-12	-57	90	24	26	32
zxx	420	-336	-454	-15	132	270	-304
zyy	85	25	-85	-88	-208	-167	-170
xyz	107	-169	168	-68	-86	-38	-33
xzy	107	-169	168	-68	-86	-38	-33
yxz	102	-166	169	-50	-87	-35	-51
yzx	102	-166	169	-50	-87	-35	-51
zxy	103	-168	170	-48	-27	1	17
zyx	103	-168	170	-48	-27	1	17

Table S5: TD-CAM-B3LYP/d-aug-cc-pVDZ first hyperpolarisability tensor components for dermacozines A–G in atomic units ($\lambda = 1064$ nm)

	Dermacozine						
Tensor component	A	B	C	D	E	F	G
xxx	1,398	9,734	9,801	-3,950	216,510	159,146	1,144,010
yyy	606	260	710	239	732	44	1,288
zzz	58	-58	-34	-19	41	34	62
xxy	1,554	-4,492	-2,907	1,485	90,749	60,916	238,860
xxz	738	-562	-665	-179	-2,042	1,092	-28,843
yyx	775	3,268	2,751	626	14,747	8,020	33,506
yyz	124	45	-101	-132	-235	-169	-87
zzx	15	-98	-144	130	-73	18	-558
zzy	-39	-11	-53	101	32	31	54
xyy	961	2,956	2,706	875	6,531	2,514	12,233
xzz	25	-103	-160	297	352	364	1,497
yxx	1,288	-4,628	-3,407	1,194	40,464	26,410	164,860
yzz	-35	-10	-62	128	88	78	244
zxx	671	-448	-629	-371	6,150	3,325	22,862
zyy	122	53	-81	-94	-30	-125	79
xyz	210	-324	349	-233	132	268	931
xzy	210	-324	349	-233	132	268	931
yxz	177	-301	319	-95	-452	103	-4,065
yzx	177	-301	319	-95	-452	103	-4,065
zxy	178	-298	340	-72	2,676	1,271	5,174
zyx	178	-298	340	-72	2,676	1,271	5,174

Table S6: TD-CAM-B3LYP/d-aug-cc-pVDZ first hyperpolarisability tensor components for dermacozines A–G in atomic units (λ = 800 nm)

	Dermacozine						
Tensor component	A	B	C	D	E	F	G
xxx	14,162	-23,129	-38,132	97,057	-17,009	-23,248	-28,780
yyy	2,355	3,607	3,457	568	-2,039	-1,565	-1,719
zzz	78	-69	-64	-98	25	25	32
xxy	10,312	21,037	28,705	-1,495	-20,363	-20,502	-21,222
xxz	2,950	-3,440	423	6,106	454	80	850
yyx	3,761	-84	9,124	1,847	-6,963	-6,199	-5,867
yyz	381	-194	436	-289	-478	-358	-382
zzx	25	-165	-82	745	34	21	400
zzy	-46	-7	34	311	20	14	44
xyy	6.020	-2,091	-4,087	-3,168	-4,176	-3,396	-3,403
xzz	136	-100	-289	656	-72	-124	-79
yxx	6,599	8,514	4,199	11,161	2,716	2,664	-3,503
yzz	-8	-18	-55	380	5	-4	10
zxx	1,796	-1,102	-2,141	6,796	-3,270	-1,482	-10,520
zyy	321	56	-37	-756	-212	-129	5
xyz	1,040	-532	352	662	-418	-313	-333
xzy	1,040	-532	352	662	-418	-313	-333
yxz	784	-552	1,123	176	1	3	452
yzx	784	-552	1,123	176	1	3	452
zxy	537	-558	2,999	-986	-131	141	944
zyx	537	-558	2,999	-986	-131	141	944