SUPPLEMENTARY INFORMATION FOR:

VIBRATIONAL AND ELECTRONIC CIRCULAR DICHROISM OF DIMETHYL MESOBILIRUBINS-XIIIα

Sergio Abbate, France Lebon, Giovanna Longhi, Stefan E. Boiadjiev, David A. Lightner

Figure SI-1: (α*S*,α'*S*)-dimethylmesobirilubin XIIIα: *M* and *P* ridge-tile conformations obtained by DFT optimization.

Figure SI-2: (β*S*,β'*S*)-dimethylmesobirilubin XIIIα: *M* and *P* conformations obtained by DFT calculations and minimization of local minima.

TABLE SI-1 (α*S*, α′*S*)-dimethylmesobirilubin XIIIα: Normal Mode Number, calculated Frequencies (cm^{-1}), calculated Dipole Strengths (10^{-40} esu^2cm^2), calculated Rotational Strengths (10^{-45} esu^2cm^2) and Normal Mode assignments.

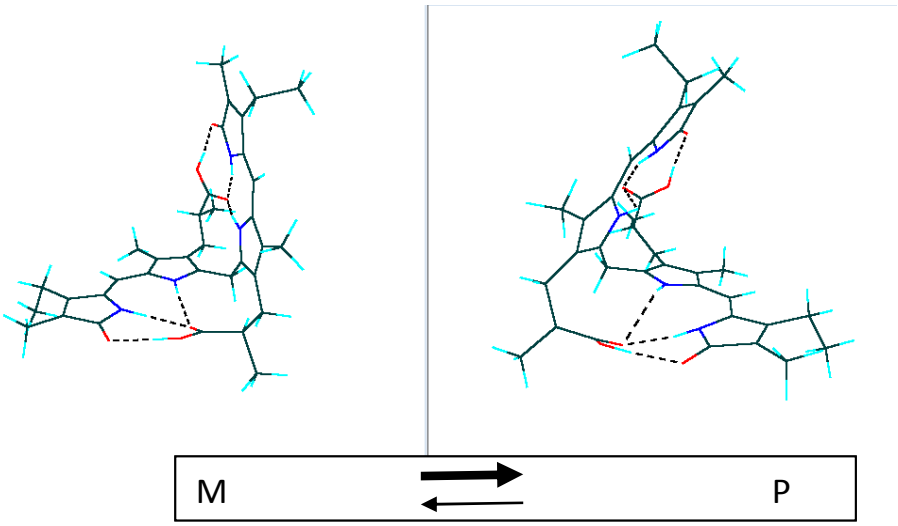
TABLE SI-2 (β*S*, β′*S*)-dimethylmesobirilubin XIIIα: Normal Mode Number, calculated Frequencies (cm^{-1}), calculated Dipole Strengths (10^{-40} esu^2cm^2), calculated Rotational Strengths (10^{-45} esu^2cm^2) and Normal Mode assignments.

TABLE SI-3: DFT calculated values for selected geometrical parameters of (α*S*,α′*S*)- and (β*S*,β′*S*)-dimethylmesobirilubin XIIIα for ridge-tile and pseudo-extended structures (for atomic numbering defining ϕ_1, ϕ_2 and θ angles, see Scheme 1)

Figure SI-3: View of the two highest occupied molecular orbitals and of the two lowest unoccupied molecular orbitals of the (α*S*,α′*S*)-dimethylmesobirilubin XIIIα a) (HOMO)-1 b) HOMO c) (LUMO) and d) (LUMO)+1 orbitals.

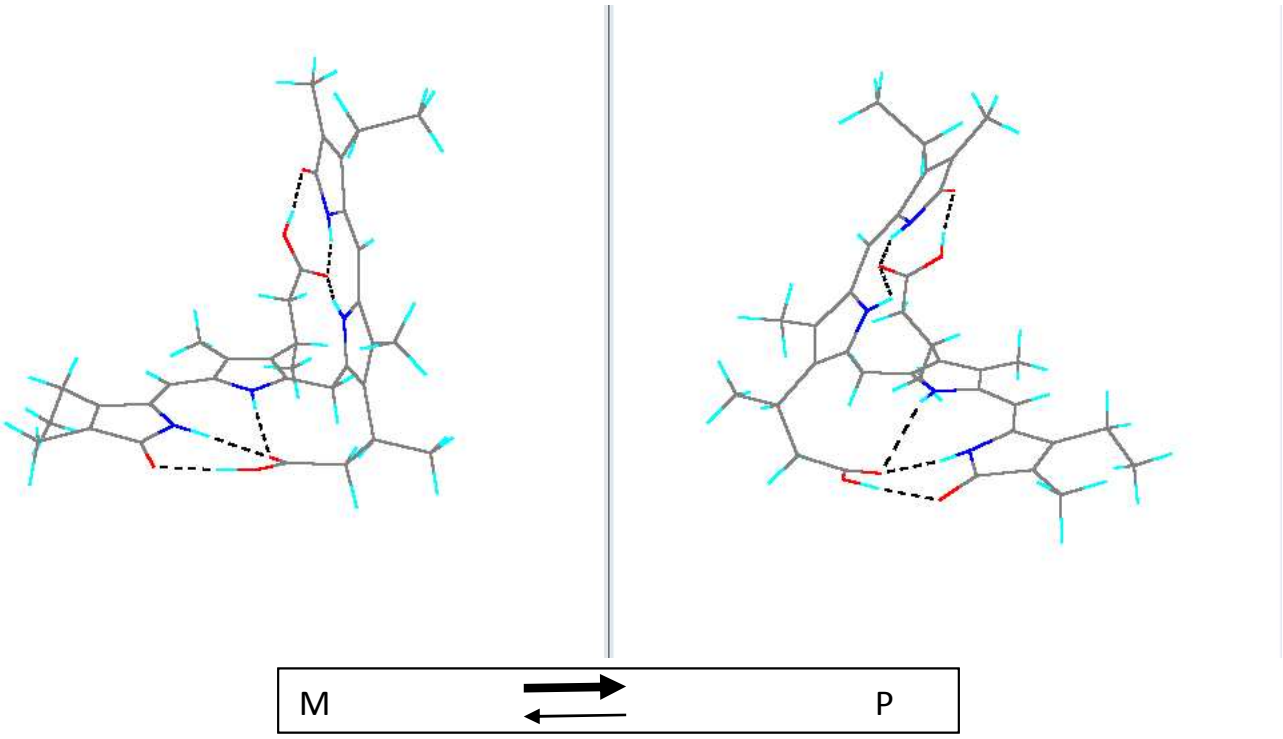
Figure SI-4A: TD-DFT calculated UV and ECD spectra of ridge-tile and pseudo-extended structure of (α*R*,α′*R*)-dimethylmesobilirubin-XIIIα *in vacuo*
Figure SI-4B: DFT calculated UV and ECD spectra of ridge-tile and pseudo-extended structure of (β*R*,β′*R*)-dimethylmesobilirubin-XIIIα *in vacuo*

Figure SI-1



13 Kcal/mol

Figure SI-2



11 Kcal/mol

TABLE SI-1: (αS, $\alpha' S$)-dimethylmesobirilubin XIIIα: Normal Mode Number, calculated Frequencies (cm^{-1}), calculated Dipole Strengths (10^{-40} esu^2cm^2), calculated Rotational Strengths (10^{-45} esu^2cm^2) and Normal Mode assignments.

#	Frequencies	Dip. Str.	Rot. Str.	Assignments
106	900.2	56.79	-143.80	In plane NH lactams + ethyl and CH3 lactams + rocking central CH2
107	909.3	4.26	-13.74	In plane NH lactams + CH3 ethyl and CH3 lactams + CH3 (α)+ CH2C*H
108	913.4	39.55	65.59	CH3 (α) + CH2C*H + CH3 pyrroles
109	915.1	19.92	15.30	CH3 (α) + CH2C*H + CH3 pyrroles + in plane NH pyrroles + =CH-
110	941.7	2.10	18.93	CH3 (α) + rocking central CH2 + CH2C*H
111	945.5	6.52	-68.59	CH3 (α) + CH2C*H
112	952.3	63.63	2.30	CH3 (α) + rocking central CH2 + in plane NH pyrroles
113	968.4	29.85	-23.09	ethyl lactams + in plane NH lactams
114	968.7	68.54	11.47	ethyl lactams + in plane NH lactams
115	993.1	145.60	501.22	CH3 pyrroles + CH3 lactams + ethyl lactams
116	994.8	582.56	-611.30	ethyl lactams + CH3 lactams + CH3 pyrroles
117	1003.6	5.13	-24.83	ethyl lactams + CH3 lactams + CH3 pyrroles + CH2C*H + CH3 (α)
118	1013.9	61.09	12.44	CH3 pyrroles + CH3 (α) + CH2C*H + wagging central CH2
119	1046.7	196.63	8.69	out of plane OH + CH3 pyrroles + CH2C*H + CH3 (α)
120	1047.4	181.63	-53.15	out of plane OH + CH3 pyrroles + CH2C*H + CH3 (α)
121	1053.8	13.01	-0.69	CH3 lactams
122	1053.8	14.41	-23.52	CH3 lactams
123	1055.6	10.75	-60.77	CH3 pyrroles + out of plane OH
124	1056.2	8.51	-66.54	CH3 pyrroles + out of plane OH
125	1066.4	480.79	-42.58	out of plane OH + CH2C*H
126	1067.0	155.33	-28.79	out of plane OH + CH2C*H
127	1078.5	56.22	109.65	CH3 ethyl lactams + CH3 lactams
128	1078.5	19.10	-77.95	CH3 ethyl lactams + CH3 lactams
129	1097.7	17.35	-48.34	CH2C*H + CH3 (α)
130	1102.1	51.83	-29.98	CH2C*H + CH3 (α) + CH3 pyrroles
131	1122.0	5.06	14.82	=CH- + ethyl lactams + in plane NH lactams and pyrroles
132	1123.6	9.09	-28.25	=CH- + ethyl lactams + in plane NH lactams and pyrroles
133	1131.0	33.15	83.63	Ethyl lactams + CH3 pyrroles
134	1132.5	35.08	-40.33	Ethyl lactams + CH3 pyrroles + CH2C*H
135	1144.5	0.28	11.29	Ethyl lactams + CH3 lactams
136	1144.9	23.26	48.93	Ethyl lactams + CH3 lactams
137	1147.6	0.00	-0.12	CH3 (α) + CH2C*H + twisting central CH2
138	1150.6	95.33	22.73	CH3 (α) + CH2C*H + wagging central CH2
139	1178.1	13.03	32.03	twisting central CH2 + CH2C*H + in plane NH pyrroles
140	1187.9	74.47	-31.80	wagging central CH2 + CH2C*H + CH3 pyrroles + =CH-
141	1197.9	196.27	468.56	twisting central CH2 + in plane NH lactams + CH3 lactams + ethyl lactams
142	1198.8	628.09	-491.49	in plane NH lactams + CH3 lactams + wagging central CH2
143	1210.6	2.33	23.45	twisting central CH2 + in plane NH pyrroles + CH2C*H
144	1235.7	79.95	87.82	CH2C*H
145	1236.6	187.56	-329.62	CH2C*H + twisting central CH2
146	1268.3	562.87	-1500.39	=CH- + ethyl lactams + in plane NH pyrroles + wagging central CH2
147	1280.1	49.40	195.88	ethyl lactams + =CH- + twisting central CH2
148	1289.7	154.82	-836.88	in plane OH + CH2C*H + in plane NH pyrroles
149	1292.1	493.34	891.37	CH2C*H + in plane OH + in plane NH pyrroles
150	1294.9	386.15	-813.34	ethyl lactams + in plane NH pyrroles
151	1304.5	195.23	514.66	CH2C*H + =CH- + CH2 ethyl lactams + twisting central CH2 + in plane NH pyrroles
152	1309.5	86.61	115.84	CH2C*H + wagging central CH2 + CH3 (α)
153	1312.7	19.92	240.77	CH2C*H + =CH- + CH2 ethyl lactams + twisting central CH2

154	13212.0	59.54	122.72	wagging central CH2 + in plane NH pyrroles + CH2 ethyl lactams + CH2C*H
155	1324.8	56.48	-211.62	In plane NH pyrroles + CH2 ethyl lactams + CH2C*H
156	1334.3	70.10	79.23	wagging central CH2 + =CH-
157	1346.9	39.69	24.77	CH2 ethyl lactams
158	1346.9	9.26	-50.72	CH2 ethyl lactams
159	1367.7	53.48	-26.93	CH2C*H + in plane OH + CH3 (α)
160	1368.4	65.77	107.62	CH2C*H + CH3 (α) + in plane OH
161	1371.2	83.33	-211.44	wagging central CH2 + =CH- + CH2C*H
162	1381.2	72.37	375.19	Twisting central CH2 + CH2C*H + in plane OH + =CH- + in plane NH lactams
163	1385.8	125.96	-17.46	In plane NH lactams + =CH- + ethyl lactams + CH3 lactams
164	1385.8	2.83	-65.69	=CH- + ethyl lactams + in plane NH lactams
165	1388.5	63.83	122.27	In plane NH lactams + CH2C*H + in plane OH
166	1388.8	19.79	-240.35	In plane NH lactams + CH2C*H + in plane OH
167	1398.1	51.80	38.67	CH3 (α) + CH2C*H+ =CH- + in plane NH lactams + in plane OH + CH3 lactams + ethyl lactams
168	1398.2	176.38	-146.66	CH3 (α) + CH2C*H + =CH- + in plane NH lactams + in plane OH + CH3 lactams + ethyl lactams
169	1410.5	4.52	-41.47	CH3 (α) umbrella motion + in plane OH
170	1411.0	46.80	-27.63	CH3 (α) umbrella motion + in plane OH
171	1418.3	41.47	23.64	CH3 lactams + CH3 ethyl lactams umbrella motion
172	1418.3	2.00	4.55	CH3 lactams + CH3 ethyl lactams umbrella motion
173	1423.4	4.05	-3.78	CH3 pyrroles umbrella motion
174	1423.6	22.60	-2.61	CH3 pyrroles umbrella motion
175	1431.6	2.36	-13.01	CH3 lactams + CH3 ethyl lactams umbrella motion
176	1431.6	38.82	39.11	CH3 lactams + CH3 ethyl lactams umbrella motion
177	1439.2	254.04	-501.77	In plane NH lactams + =CH-
178	1440.3	235.28	396.18	In plane NH lactams + =CH-
179	1463.4	2.99	3.02	scissoring central CH2 + CH2C*H
180	1468.8	226.76	-238.98	CH2C*H+in plane OH + CH3 pyrroles + in plane OH
181	1473.4	33.55	213.43	In plane OH + scissoring central CH2 + CH3 pyrroles + in plane NH lactams
182	1478.3	22.53	-9.79	CH2C*H + scissoring central CH2 + CH3 pyrroles + in plane NH lactams + in plane OH
183	1478.6	54.42	-28.06	CH3 lactams + CH3 pyrroles + CH2C*H
184	1479.8	13.31	4.72	CH3 lactams
185	1479.9	44.66	24.15	CH3 lactams
186	1482.3	4.48	64.29	in plane OH + in plane NH lactams + CH3 (α) + CH2C*H
187	1485.0	59.54	-92.82	in plane OH + CH3 lactams + in plane NH lactams + CH3 (α)
188	1487.0	31.38	4.61	CH3 lactams + CH3 pyrroles + CH2C*H + in plane NH pyrroles + CH3 (α)
189	1487.8	8.07	27.76	CH3 lactams + CH3 pyrroles + CH2 ethyl lactams
190	1489.5	1.31	0.05	CH3 lactams + CH3 pyrroles
191	1490.9	1.28	4.20	CH3 lactams + CH3 pyrroles + scissoring central CH2
192	1496.7	93.37	7.34	CH3 pyrroles
193	1497.4	0.31	7.05	CH3 pyrroles
194	1499.9	16.50	-24.80	CH3 ethyl lactams
195	1499.9	10.87	33.39	CH3 ethyl lactams
196	1501.4	43.87	0.35	CH3 (α)
197	1501.6	27.61	-4.39	CH3 (α)
198	1502.1	1.15	5.49	CH3 lactams + ethyl lactams
199	1502.1	0.01	-0.48	CH3 lactams + ethyl lactams
200	1510.9	59.45	115.89	CH3 (α)
201	1511.3	27.60	-149.19	CH3 (α)
202	1516.2	57.68	1.55	CH3 pyrroles + in plane NH pyrroles + ethyl lactams
203	1517.1	6.37	-24.53	ethyl lactams + CH3 pyrroles
204	1518.0	8.43	58.82	ethyl lactams + CH3 pyrroles
205	1518.8	26.91	-59.65	ethyl lactams + CH3 pyrroles + in plane NH pyrroles
206	1526.1	14.30	-4.66	in plane NH lactams + NH pyrroles + =CH- + wagging central CH2

207	1533.2	54.02	49.96	in plane NH lactams + NH pyrroles + twisting central CH2+ =CH-
208	1606.8	302.18	-1010.90	in plane NH pyrroles
209	1610.6	68.45	367.86	in plane NH pyrroles + twisting central CH2
210	1629.4	120.12	904.19	C=C lactams + CH3 lactams + in plane NH pyrroles + CH2 ethyl lactams
211	1629.6	642.37	-1145.24	C=C lactams + CH3 lactams + in plane NH pyrroles + CH2 ethyl lactams
212	1657.7	131.83	1441.34	in plane NH lactams + NH pyrroles + =CH-
213	1659.7	1318.12	-2199.69	in plane NH lactams + NH pyrroles + =CH-
214	1691.6	439.03	1241.47	in plane NH lactams +in plane OH + =CH-
215	1692.0	228.95	-1388.08	in plane NH lactams + in plane OH + =CH-
216	1721.7	56.55	1178.808	C=O carbonyl + C=O lactams + in plane OH + in plane NH lactams
217	1723.6	4685.16	-681.39	C=O carbonyl + C=O lactams + in plane OH + in plane NH lactams

TABLE SI-2: (β*S*, β′*S*)-dimethylmesobirilubin XIIIα: Normal Mode Number. calculated Frequencies (cm^{-1}). calculated Dipole Strengths (10^{-40} esu^2cm^2). calculated Rotational Strengths (10^{-45} esu^2cm^2) and Normal Mode assignments.

#	Frequencies	Dip. str.	Rot. str.	Assignments
106	901.9	11.93	-43.11	in plane NH lactams + CH3 ethyl and CH3 lactams + CH3 (β) + rocking central CH2
107	910.8	11.42	-24.36	in plane NH lactams + in plane NH pyrroles + CH3 ethyl and CH3 lactams + CH3 (β) + CH2C*H + =CH-
108	926.3	32.94	25.59	CH3 (β) + CH2C*H + rocking central CH2
109	927.7	22.68	-12.13	CH3 (β) + CH2C*H
110	941.4	7.34	-5.53	rocking central CH2 + CH2C*H
111	957.3	15.72	53.78	CH3 (β) + CH2C*H
112	961.4	3.73	-14.60	CH3 (β) + CH2C*H + rocking central CH2
113	968.7	29.61	-18.72	ethyl lactams + in plane NH lactams + CH3 lactams
114	969.1	52.94	1.90	ethyl lactams + in plane NH lactams + CH3 lactams
115	987.6	108.07	225.21	CH3 pyrroles + CH2 ethyl lactams + CH3 (β) + CH2C*H
116	993.9	471.86	-484.90	ethyl and CH3 lactams + CH3 pyrroles + CH3 (β) + CH2C*H
117	999.0	46.64	256.68	ethyl and CH3 lactams
118	1001.7	136.29	-68.85	ethyl and CH3 lactams + CH3 pyrroles + CH3 (β) + CH2C*H
119	1046.2	288.19	342.24	CH3 (β) + CH2C*H + CH3 pyrroles + out of plane OH
120	1049.3	357.91	-33.29	CH3 pyrroles + CH2C*H + CH3 (β) + out of plane OH
121	1054.1	1.81	-0.47	CH3 lactams + out of plane OH
122	1054.2	27.11	-45.80	CH3 lactams
123	1055.7	25.80	-45.72	CH3 pyrroles
124	1057.3	137.38	-223.94	CH3 pyrroles + out of plane OH
125	1061.1	133.90	-113.38	out of plane OH
126	1063.0	251.34	-54.37	out of plane OH
127	1079.4	49.81	102.28	CH3 ethyl lactams + CH3 lactams
128	1079.4	20.32	-75.92	CH3 ethyl lactams + CH3 lactams
129	1096.2	16.64	81.10	CH2C*H + twisting central CH2 + CH3 (β)
130	1102.3	232.35	-158.80	Wagging central CH2 + CH3 (β) + CH2C*H
131	1117.7	30.81	20.54	CH3 pyrroles + CH2C*H + CH3 (β) + =CH-
132	1118.0	6.99	46.58	CH3 pyrroles + CH2C*H + CH3 (β) + =CH-
133	1126.5	33.13	105.77	in plane NH lactams + in plane NH pyrroles + =CH- + ethyl lactams
134	1126.8	24.37	-46.28	in plane NH lactams + in plane NH pyrroles + =CH- + ethyl lactams
135	1138.0	0.02	1.93	CH3 pyrroles + CH3 (β) + CH2C*H + ethyl lactams
136	1138.6	0.48	-5.37	ethyl lactams + CH3 (β) + CH2C*H + CH3 pyrroles
137	1145.8	0.01	-0.76	CH3 lactams + ethyl lactams
138	1146.1	24.04	22.47	CH3 lactams + ethyl lactams
139	1188.9	0.25	-1.64	twisting central CH2 + CH2C*H + in plane NH pyrroles
140	1196.0	466.27	-391.01	CH2C*H + CH3 lactams + ethyl lactams + in plane NH lactams
141	1197.6	224.44	432.16	CH3 lactams + ethyl lactams + in plane NH lactams + twisting central CH2
142	1203.2	178.06	-117.51	CH3 lactams + CH3 pyrroles +CH2C*H + CH3 (β) + wagging central CH2
143	1214.8	0.52	4.99	twisting central CH2 + CH2C*H + CH3 pyrroles
144	1227.8	38.65	68.04	CH2C*H
145	1228.5	91.90	-145.18	CH2C*H
146	1268.6	220.13	-1030.79	=CH- + CH2 ethyl lactams + CH2C*H + in plane NH pyrroles + wagging central CH2
147	1273.2	183.52	-376.31	CH2C*H + in plane OH
148	1276.6	621.18	208.26	CH2C*H + =CH- + CH2 ethyl lactams + in plane OH
149	1281.8	1.38	51.48	ethyl lactams+ =CH- + twisting central CH2
150	1295.8	549.56	-928.70	ethyl lactams+ =CH- +in plane NH pyrroles
151	1307.2	198.05	885.94	twisting central CH2 + in plane NH pyrroles + =CH- + CH2 ethyl lactams

152	1317.1	22.58	64.18	wagging central CH2 + in plane NH pyrroles + CH2 ethyl lactams
153	1319.8	13.26	-135.00	in plane NH pyrroles + CH2 ethyl lactams + CH2C*H
154	1331.4	86.26	-420.55	in plane OH + CH2C*H + CH3 (β)
155	1332.0	80.97	264.92	in plane OH + CH2C*H + wagging central CH2 + CH3 (β)
156	1333.6	116.81	224.20	wagging central CH2 + =CH- + CH2 ethyl lactams
157	1347.3	45.55	54.15	CH2 ethyl lactams
158	1347.4	12.70	-71.28	CH2 ethyl lactams
159	1368.3	57.22	-177.89	wagging central CH2 + CH2C*H + =CH-
160	1377.2	113.57	-297.99	CH2C*H + in plane OH + in plane NH lactams
161	1378.7	127.23	317.45	CH2C*H + in plane OH+ in plane NH lactams
162	1379.4	198.60	245.76	CH2C*H + =CH- + twisting central CH2
163	1386.0	70.76	-51.83	=CH- + CH3 lactams + ethyl lactams + in plane NH lactams
164	1386.3	4.58	-86.94	=CH- + CH3 lactams + ethyl lactams + in plane NH lactams
165	1392.3	1.83	85.39	in plane NH lactams + in plane OH + CH2C*H
166	1394.6	43.42	137.46	in plane NH lactams + =CH- + CH2C*H + in plane OH
167	1401.1	285.84	-126.55	=CH- + in plane OH + in plane NH lactams + CH3 lactams + CH2C*H
168	1401.2	109.98	-51.47	in plane OH + in plane NH lactams + =CH- + CH3 lactams + CH3 ethyl lactams + CH2C*H
169	1414.1	1.71	-3.01	CH3 (β)umbrella motion + CH3 pyrroles umbrella motion
170	1414.3	7.32	19.69	CH3 (β) umbrella motion + CH3 pyrroles umbrella motion
171	1419.1	61.65	10.96	CH3 lactams + CH3 ethyl lactams umbrella motion
172	1419.2	1.42	1.51	CH3 lactams + CH3 ethyl lactams umbrella motion
173	1426.4	2.97	2.86	CH3 pyrroles + CH3 (β) umbrella motion
174	1426.6	26.83	10.41	CH3 pyrroles + CH3 (β) umbrella motion
175	1433.3	4.26	-19.73	CH3 lactams umbrella motion + CH3 ethyl lactams + in plane NH lactams
176	1433.3	42.45	33.22	CH3 lactams umbrella motion + in-plane NH lactams
177	1439.5	280.92	-556.66	in plane NH lactams + =CH-
178	1440.5	227.54	238.00	in plane NH lactams + =CH-
179	1463.3	4.69	14.03	scissoring CH2C*H
180	1463.6	110.86	55.38	scissoring CH2C*H
181	1471.5	140.37	-168.68	CH2C*H + in plane NH lactams + in plane OH
182	1474.5	13.23	-32.32	Scissoring central CH2
183	1476.5	58.55	235.04	CH3 lactams + CH3 pyrroles + in plane NH lactams + in plane OH + CH2C*H
184	1480.2	18.62	-17.41	CH3 lactams
185	1480.3	7.26	1.46	CH3 lactams
186	1486.5	28.92	-10.02	CH3 lactams + in plane NH pyrroles + CH3 pyrroles + CH2 ethyl lactams + in plane OH
187	1486.7	21.18	-74.91	CH3 pyrroles + in plane OH + CH3 lactames + CH3 (β)
188	1488.6	59.78	299.90	CH3 lactams + CH2C*H + in plane OH
189	1488.7	12.05	-100.82	CH3 lactams + in plane OH + CH2 ethyl lactams
190	1490.6	13.57	56.02	CH3 lactams + CH3 pyrroles + in plane OH
191	1492.8	0.68	-14.73	CH3 pyrroles + CH3 lactams + in plane OH + scissoring central CH2
192	1495.1	34.42	-33.20	CH2C*H + CH3 (β) + CH3 pyrroles
193	1497.0	1.37	-14.58	CH3 pyrroles + CH3 (β) + in plane OH
194	1499.6	15.10	-24.33	CH3 ethyl lactams
195	1499.7	10.97	34.26	CH3 ethyl lactams
196	1500.4	42.50	-9.13	CH3 (β) + CH3 pyrroles + CH3 ethyl lactams
197	1501.2	5.84	8.76	CH3 (β) + CH3 pyrroles
198	1502.3	12.78	15.14	CH3 lactams + ethyl lactams + CH3 (β)
199	1502.4	3.96	-4.89	CH3 lactams + ethyl lactams + CH3 (β)
200	1507.0	28.97	-62.40	CH3 (β) + CH3 pyrroles
201	1507.1	5.80	0.50	CH3 (β) + CH3 pyrroles
202	1515.9	51.54	11.13	ethyl lactams + CH3 pyrroles + =CH- + in plane NH pyrroles
203	1517.1	4.74	-17.89	ethyl lactams CH3 pyrroles
204	1518.3	3.52	39.48	CH3 pyrroles + CH2 ethyl lactams

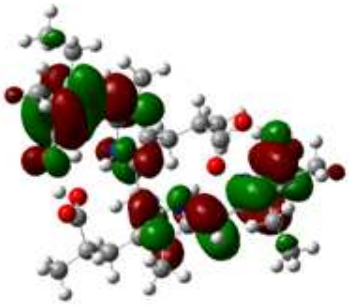
205	1519.1	34.07	-79.10	CH3 pyrroles + ethyl lactams + =CH- + in plane NH pyrroles
206	1524.0	6.00	16.08	in plane NH lactams + in plane NH pyrroles + CH3 pyrroles+CH3 (β)
207	1530.9	30.88	36.50	in plane NH lactams + in plane NH pyrroles + scissoring central CH2 + CH3 (β) + CH3 pyrroles
208	1605.0	248.93	-861.98	in plane NH pyrroles
209	1607.5	41.50	192.10	in plane NH pyrroles
210	1630.0	147.74	954.08	C=C lactams + CH3 lactams + CH2 ethyl lactams + in plane NH pyrroles
211	1630.0	661.45	-1266.35	C=C lactams + CH3 lactams + CH2 ethyl lactams + in plane NH pyrroles
212	1658.0	165.82	1474.65	in plane NH lactams + in plane NH pyrroles + =CH- + C=O stretching carbonyl
213	1659.6	1246.49	-2197.07	in plane NH lactams + in plane NH pyrroles + =CH- + C=C lactams
214	1692.8	496.00	1156.10	in plane NH lactams + in plane OH + =CH- + C=C lactams
215	1692.8	210.95	-1395.85	in plane NH lactams + C=O lactams + in plane OH + =CH-
216	1722.2	88.86	1451.94	in plane OH + C=O stretching carbonyl + C=O lactams + in plane NH lactams
217	1724.4	4500.11	-718.41	in plane OH + C=O stretching carbonyl + C=O lactams + in plane NH lactams

TABLE SI-3: Calculated values for selected geometrical parameters of (α*S*,α′*S*)- and (β*S*,β′*S*)-dimethylmesobirilubin XIIIα (for atomic numbering defining ϕ_1. ϕ_2 and θ angles. see Scheme 1) Comparison with calculated and experimental values from the literature on bilirubin is provided.

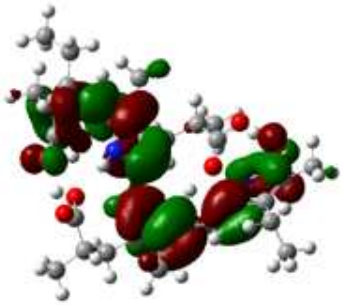
	(α*S*,α'*S*) *Ridge-tile structure*	(α*S*,α'*S*) *Pseudo-extended structure*	(β*S*,β'*S*) *Ridge-tile structure*	(β*S*,β'*S*) *Pseudo-extended structure*
ϕ_1(22-9-10-11) (°)	-61.1	-129.4	-59.4	-126
ϕ_2(23-11-10-9) (°)	-61.1	-129.4	-59.4	-126
θ(2-8-12-18) (°)	-102.3	146.4	-95.8	146.2
O-**H**··**O**= (Å)	1.625	5.27	1.631	5.26
N_{lactam}-**H**··**O**= (Å)	1.841	2.13	1.812	2.15
N_{pyrrol}-**H**··**O**= (Å)	1.978	2.52	1.983	2.28

Figure SI-3

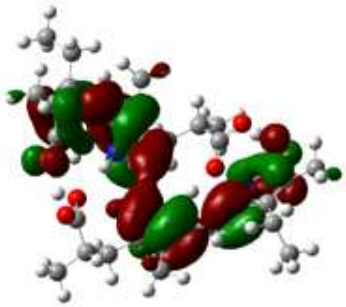
d) (LUMO)+1



c) (LUMO)



b) (HOMO)



a) (HOMO)-1

Figure SI-4A

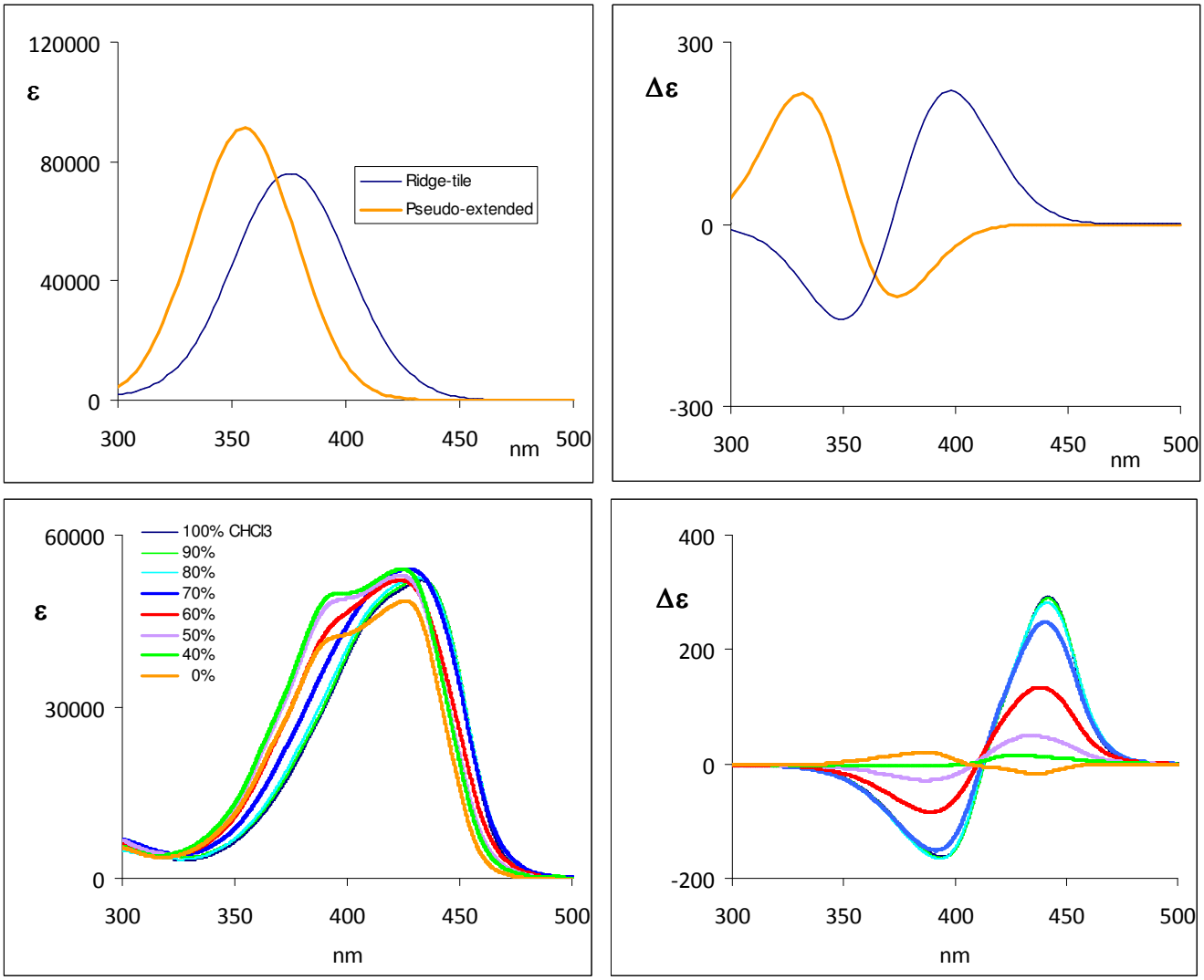
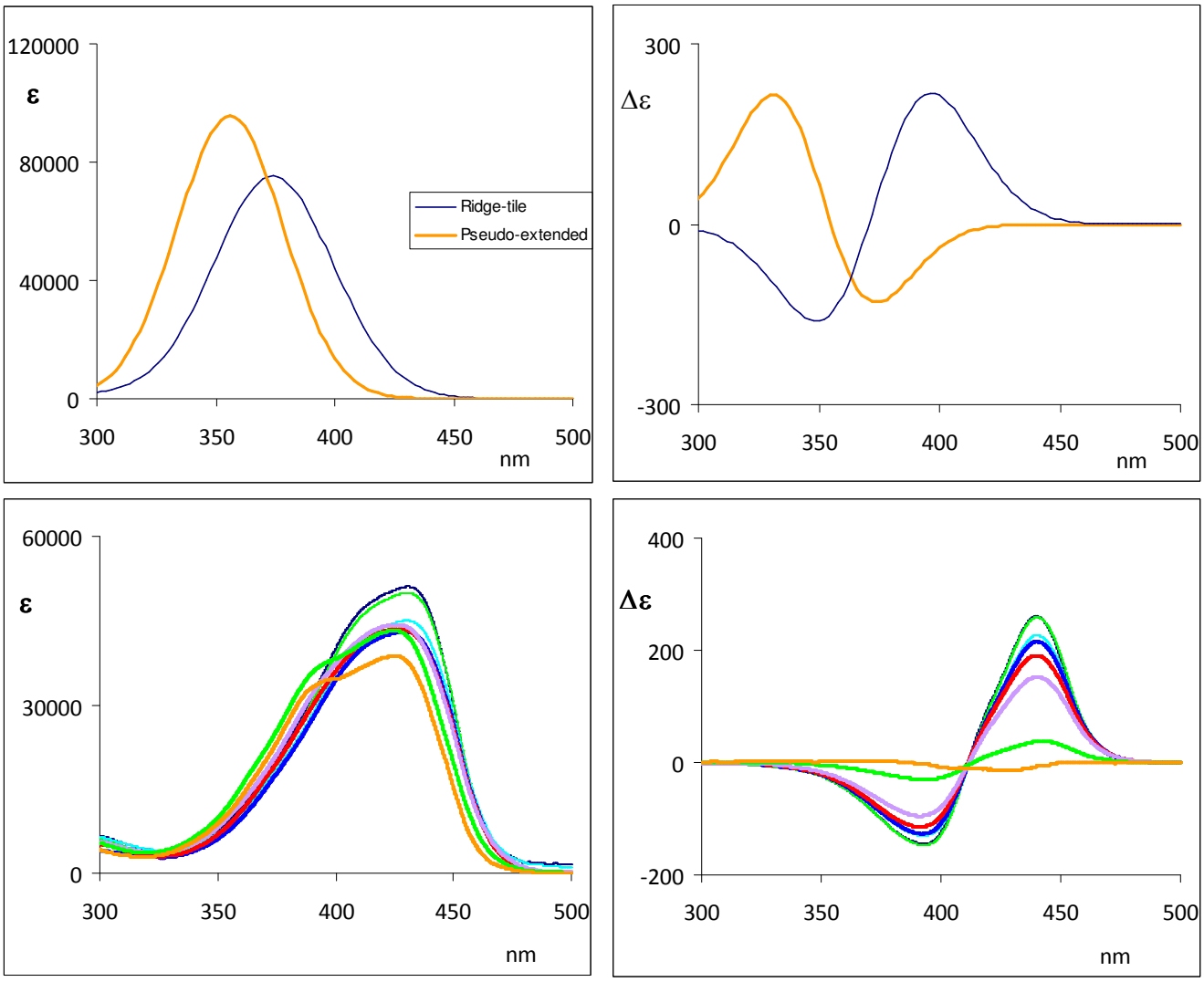

120000
ε
80000
40000
0
300
350
400
450
500
nm
Ridge-tile
Pseudo-extended
300
Δε
0
-300
300
350
400
450
500
nm
60000
ε
30000
0
100% CHCl3
90%
80%
70%
60%
50%
40%
0%
300
350
400
450
500
nm
400
Δε
200
0
-200
300
350
400
450
500
nm

Figure SI-4B


120000
ε
80000
40000
0
300
350
400
450
500
nm
Ridge-tile
Pseudo-extended
300
Δε
0
-300
300
350
400
450
500
nm
60000
ε
30000
0
300
350
400
450
500
nm
400
Δε
200
0
-200
300
350
400
450
500
nm