Electronic Supplementary Information (ESI)

Re-examining the stereochemistry of suffruticosine via TDDFT calculations, ECD spectroscopy, and chemical synthesis

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1. General Information

Calculations

All DFT and time-dependent DFT (TDDFT) calculations were conducted by Gaussian 09 package[1]. Geometry optimization, single point energies, analytical vibrational frequencies within the harmonic approximation, and excitation energies were conducted with using B3LYP functional[2, 3] and 6-311G(d) basis set[4-6]. The conductor-like polarizable continuum solvation model (CPCM)[7] was used with the dielectric constant of ε = 32.613 for methanol and ε = 35.68 for acetonitrile. Gauge-invariant atomic orbital (GIAO) calculations for NMR prediction were conducted with using B3LYP functional, 6-311G(d) basis set and polarizable continuum model (PCM) with the dielectric constant of ε = 4.7113 for chloroform. All optimized structures were checked whether they have imaginary frequencies or not. DP4+ analyses were performed with following Sarotti's protocol except Boltzmann average of conformers.[8] Calculating orbital contributions of electronic transitions were performed with the QMForge 2.4 software.[9]

All conformers were firstly manually found by systematical search with MM2 calculation embedded in Chem3D and subsequent DFT calculation. The conformations were found starting with the nitrogen lone pair, as allosecurinine, securinine and suffruticosine have rigid fused ring structures except for the piperidine ring. For allosecurinine and securinine, each was firstly differentiated whether the nitrogen lone pair and C2 methine lies *syn* or *anti*. For each case, a boat or chair conformation was found and optimized. Same systematic searching was done to find conformers of suffruticosine, starting with the position of nitrogen lone pair and oxygen.

Experiments

All reactions were performed in oven-dried or flame-dried flasks or vials. Unless otherwise noted, the flasks were fitted with rubber septa and reactions were conducted under a positive pressure of argon, and vials were tightly sealed with plastic septa and parafilm. Stainless steel syringes or cannula were used to transfer air- and moisture-sensitive liquids. Flash column chromatography was performed as described by Still et al. using silica gel (60-Å pore size, 40–63 μm, 4-6% H_2O content, Merck) or aluminum oxide (activated, basic, Brockmann I, 58 Å pore size, Merck).[10] Analytical thin–layer chromatography (TLC) was performed using glass plates pre-coated with 0.25 mm silica gel or basic aluminum oxide impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light, and/or an aqueous potassium permanganate ($KMnO_4$) solution.

Unless otherwise stated, all commercial reagents and solvents were used without additional purification with the following exceptions as indicated below. Dichloromethane and tetrahydrofuran were purchased from Merck and Daejung Inc., respectively and were purified by the method of Grubbs et al. under positive argon pressure.[11] Securinine (**1**) is supplied by Santa Cruz Biotechnology Inc. under catalog number SC-220097A.

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded with Agilent Technologies DD2 (600 MHz), Bruker AVANCE NEO (500 MHz) and calibrated by using the residual undeuterated chloroform (δ_H = 7.24 ppm) and $CDCl_3$ (δ_C = 77.23 ppm). Data are reported in the following manners: chemical shift in ppm [multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = quintet, m = multiplet, app = apparent, br = broad), coupling constant(s) in Hertz, integration]. Electronic circular dichroism spectra (ECD) and absorption spectra were measured with JASCO J-1500 circular dichroism spectrophotometer. Absorbance were converted to molar extinction coefficient (ε, $M^{-1}cm^{-1}$) by using Beer-Lambert law (A = εlC). Elipticity (mdeg) was converted to molar extinction coefficient (Δε, $M^{-1}cm^{-1}$) by using a factor of 32.98 (θ = 32.98ΔAbs). High resolution mass spectra were obtained from KAIST Analysis Center for Research Advancement (Daejeon) by using ESI ionization method. Specific rotations ($[\alpha]_D^T$) were obtained by JASCO P-2000 polarimeter.

2. Reconstructing ECD spectrum from the Isolation Paper

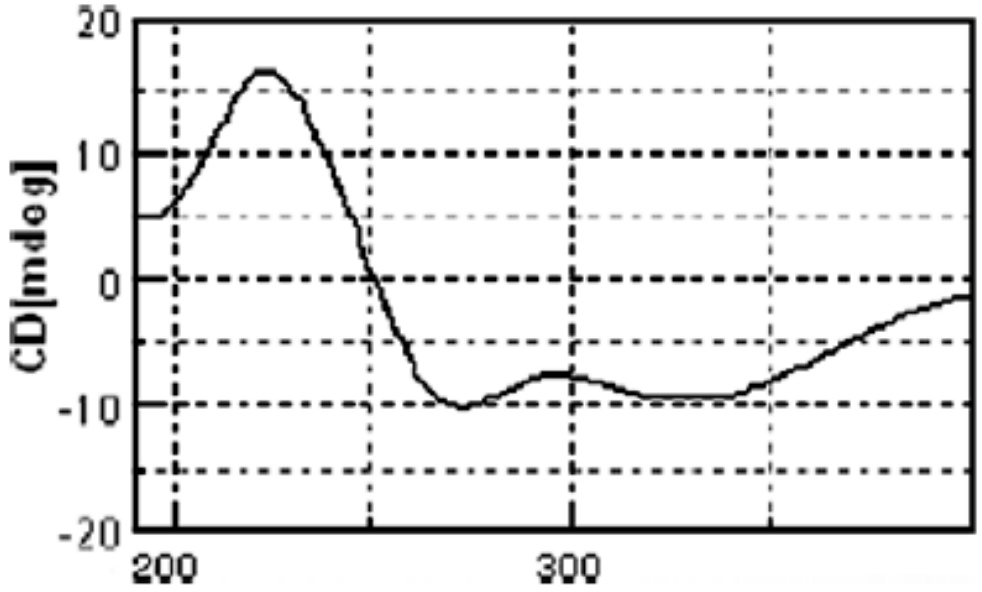


Figure S1. ECD spectrum of suffruticosine cropped from the original paper.[12] λ_{max} 223 nm (Δε +12.87, MeOH)

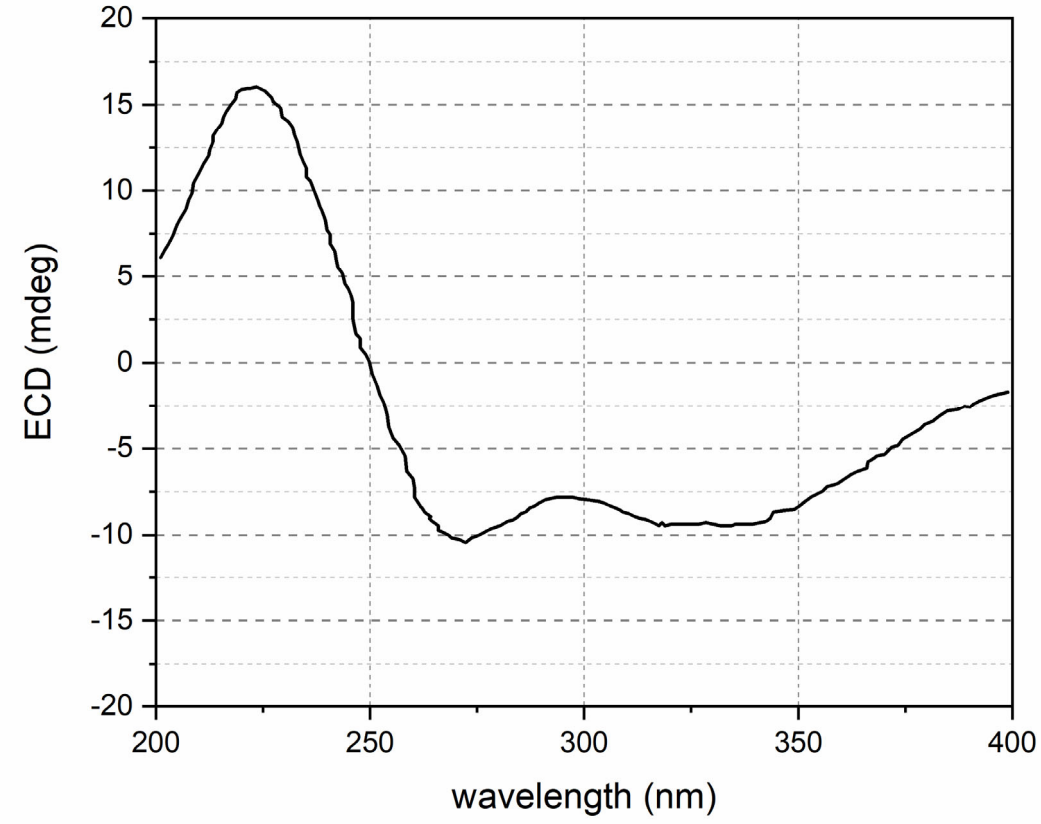


Figure S2. Reconstructed ECD spectrum by Graph Data Extractor (freeware) with 177 points.

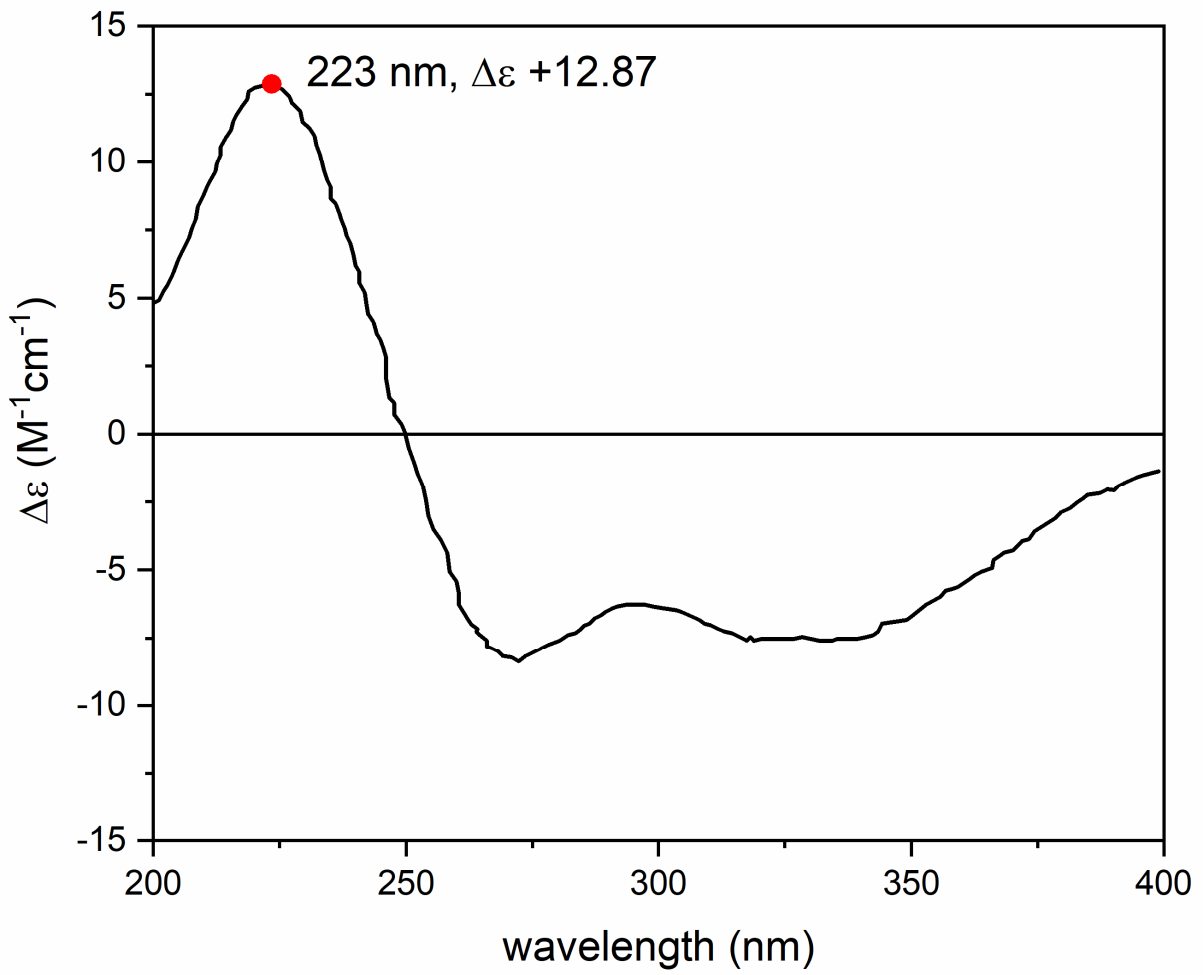


Figure S3. Reconstructed ECD spectrum in Δε ($M^{-1}cm^{-1}$)

Note

The UV/Vis spectrum of suffruticosine was not shown. Instead, only data were given.[12]

UV(MeOH) λ_{max} (log ε) 258 nm (4.06), ε = 11481 $M^{-1}cm^{-1}$

3. DFT functional validation

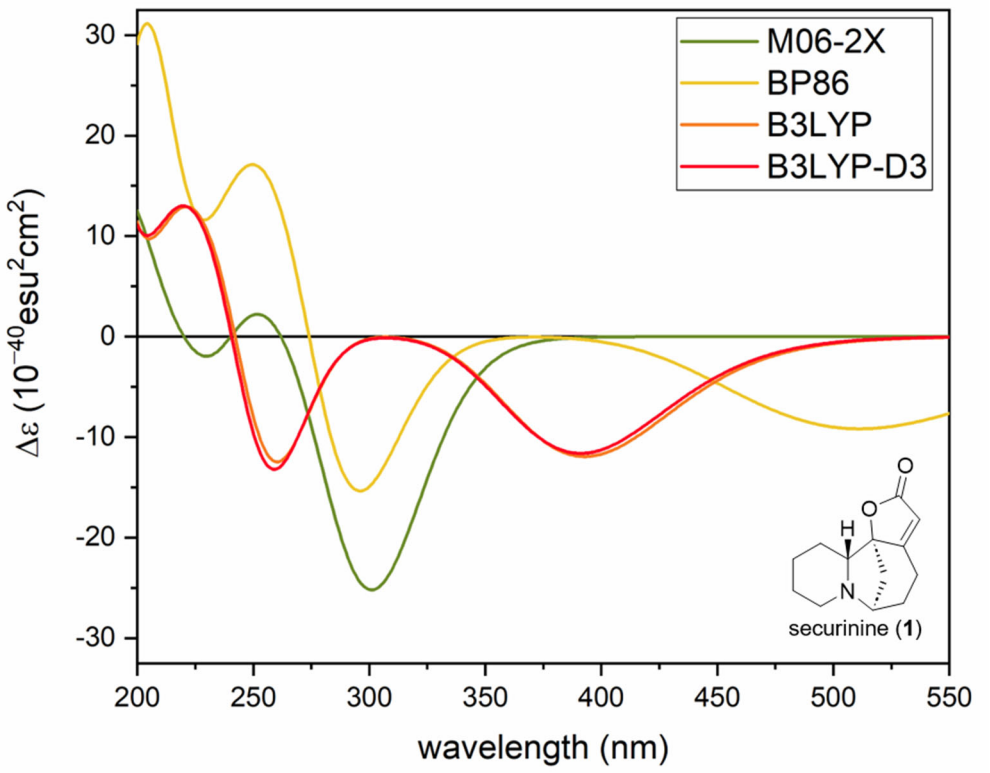


Figure S4. Simulated ECD spectra of **1** with various functionals.

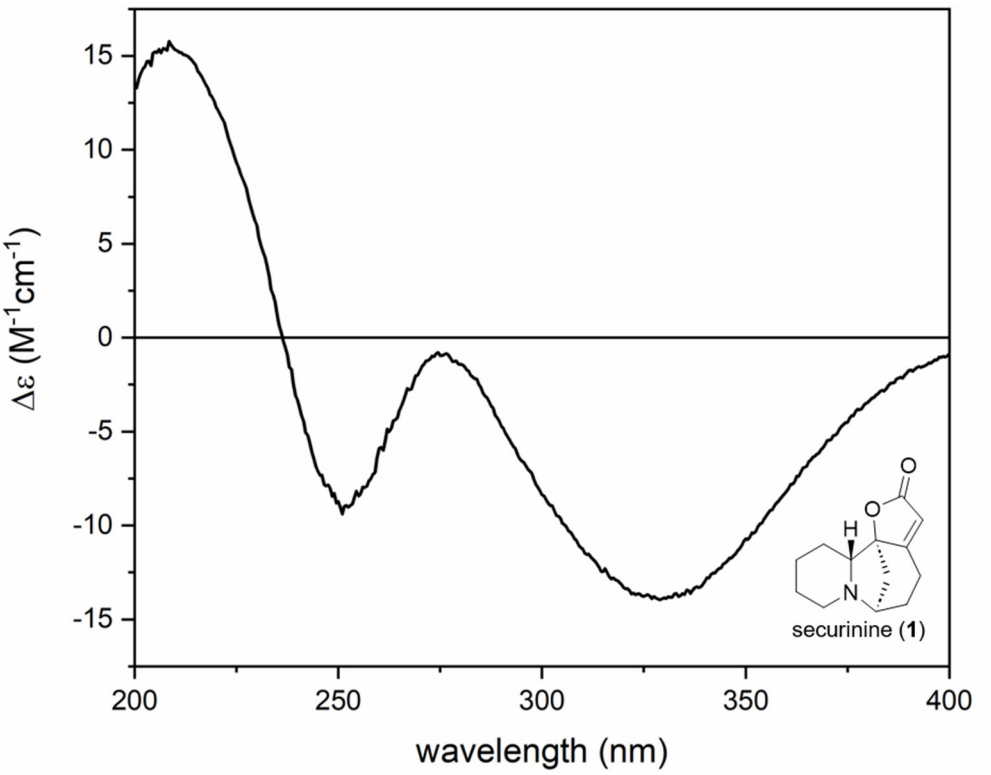


Figure S5. The experimental ECD spectrum of **1**.

Note

Since excitation energies are significantly underestimated, BP86 functional was excluded.
Employing the M06-2X functional for simulating the UV/Vis spectrum yields a major band at 242 nm (ε = ~20,000 $M^{-1}cm^{-1}$) and a minor band at 301 nm (ε = ~3,500 $M^{-1}cm^{-1}$), which closely resembles the actual system (Figure S8). However, the ECD spectrum exhibits zero intensity at 242 nm (Figure S4), a marked contrast to the negative ECD band at 250 nm. (Figure S5). Given the prioritization of ECD analyses over excitation energies within the context of our manuscript, we opted for B3LYP functional, which effectively simulates ECD patterns despite possibilities of energy underestimation.
Lastly, dispersion correction does not seem to have significant effects.

4. Computational Studies of the Originally Proposed Suffruticosine (10)

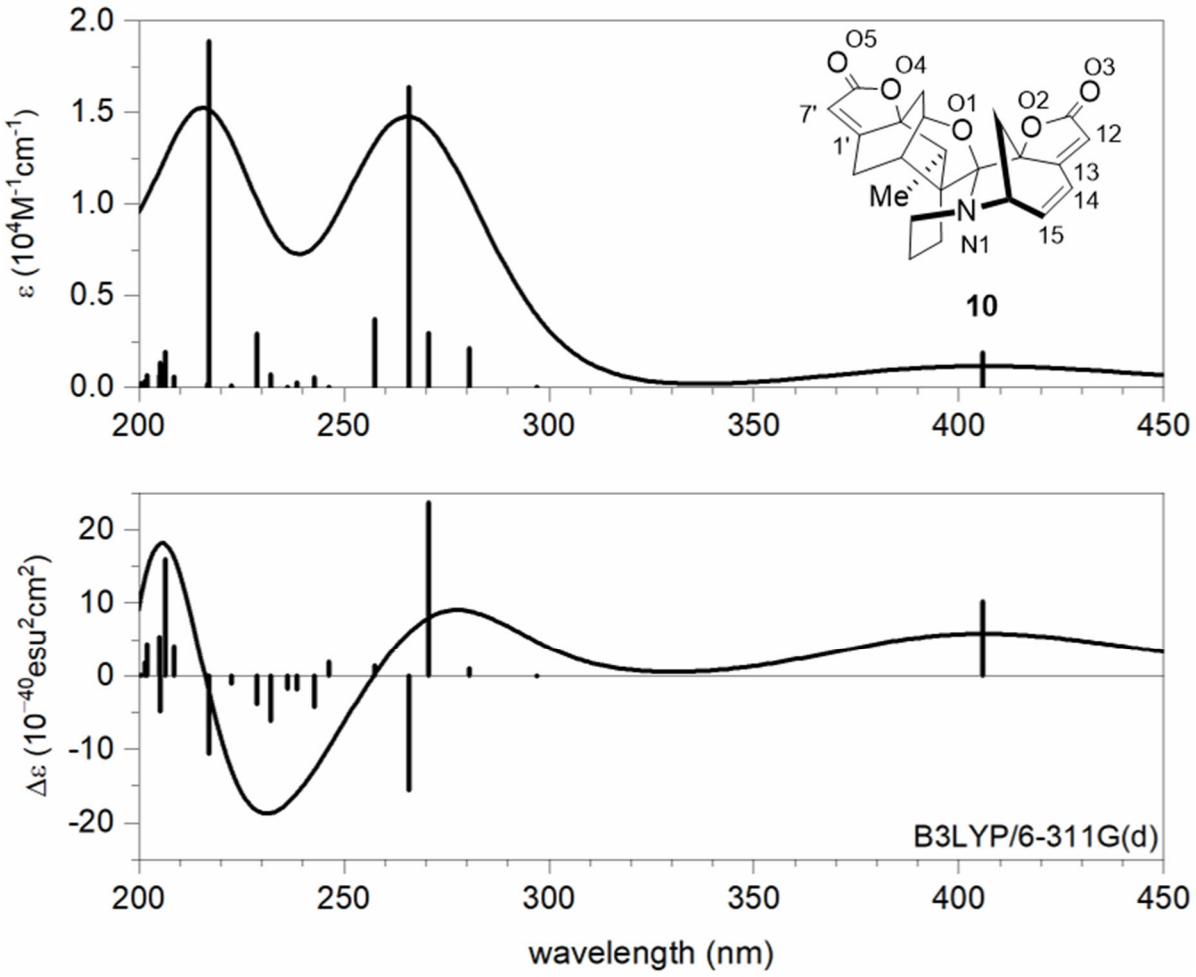


Figure S6. Calculated absorption and ECD spectrum of the originally proposed suffruticosine (**10**).

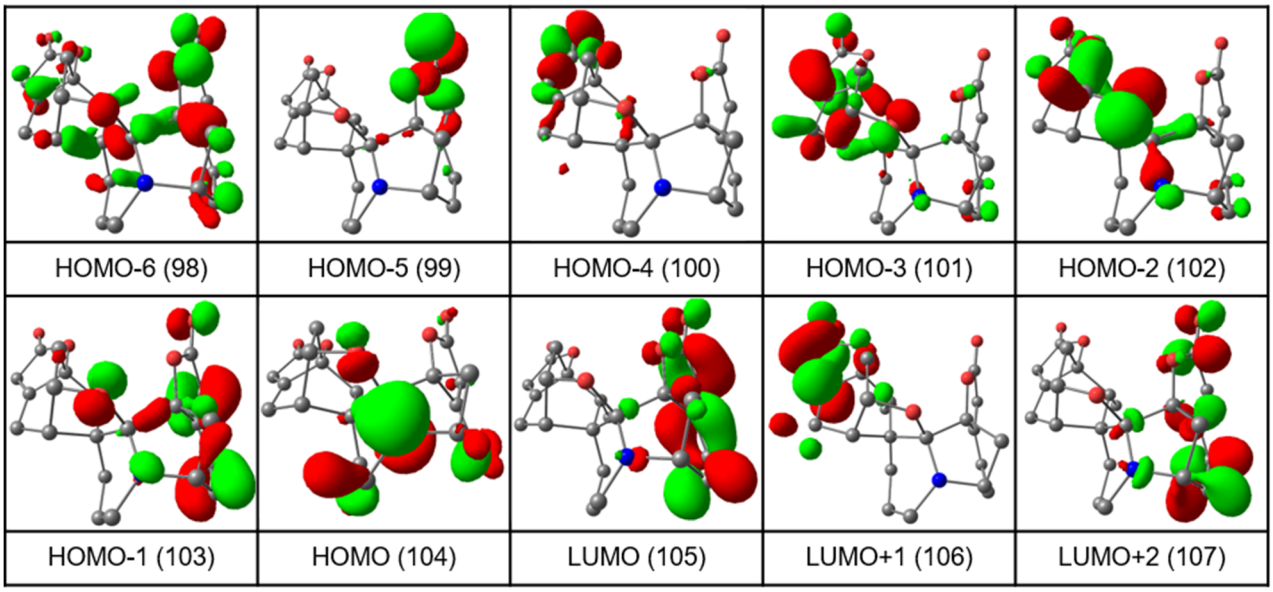


Figure S7. Molecular orbitals of the originally proposed suffruticosine (**10**) (contour value = 0.05).

Wavelength (nm)	Oscillator Strength	Rotatory Strength	Contributions	Assignments & notes
405.84	**0.0283**	**30.7645**	**98.3% H → L**	**N1 → π*(O2,O3–C15)**
297.15	0.0002	–0.2275	99.7% H → L+1	
280.54	0.0320	2.9409	64.5% H-2 → L, 26.2% H-1 → L, 6.86% H-3 → L	O1 → π*(O2,O3–C15) (major) π(O2,O3–C15) → π*(O2,O3–C15) (minor)
270.68	**0.0446**	**71.0856**	**78.4% H-5 → L, 13.9% H-1 → L, 2.70% H-6 → L**	**O3 → π*(O2,O3–C15) (carbonyl n→π*)**
265.77	**0.2457**	**–46.7742**	**51.1% H-1 → L, 30.7% H-2 → L, 12.2% H-5 → L, 2.04% H-6 → L**	**π(O2,O3–C15) → π*(O2,O3–C15) (major)** **O1 → π*(O2,O3–C15) (minor)**
257.51	0.0557	4.1056	87.4% H-3 → L, 5.44% H-1 → L, 2.40% H-6 → L, 2.24% H-2 → L	π(O4,O5–C1') → π*(O2,O3–C15) (western to eastern)
246.29	0.0005	5.6278	77.3% H-4 → L+1, 6.46% H-2 → L+1, 5.27% H-4 → L, 5.23% H-1 → L+1	O5 → π*(O4,O5–C1') (carbonyl n→π*)
242.73	**0.0083**	**–12.8213**	**48.9% H-6 → L, 38.8% H-4 → L, 2.87% H-3 → L,** **2.60% H-4 → L+1**	**O2, O3 σ bonding→ π*(O2,O3–C15)** **O5 → π*(O2,O3–C15) (western C=O n → eastern π*)**
238.55	0.0043	–5.5610	53.2% H-4 → L, 36.5% H-6 → L, 2.36% H-5 → L	
236.22	0.0005	–5.1600	79.8% H-1 → L+1, 10.9% H-4 → L+1, 6.81% H-2 → L+1	π(O2,O3–C15) → π*(O4,O5–C1')
232.18	**0.0107**	**–18.2685**	**93.8% H → L+2, 2.70% H-6 → L**	**N1 → π*(O2,O3–C15)**
228.82	**0.0438**	**–11.5967**	**77.4% H-2 → L+1, 11.9% H-1 → L+1, 4.17% H-3 → L+1,** **2.87% H-4 → L+1, 2.47% H-6 → L+1**	**O1 → π*(O4,O5–C1')**
222.53	0.0016	–3.2096	95.8% H-7 → LUMO	
216.99	0.2832	–31.7565	85.7% H-3 → L+1, 4.39% H-2 → L+1, 3.60% H-7 → L+1	π(O4,O5–C1') → π*(O4,O5–C1') (western π → π*)
216.65	0.0028	–1.3779	82.9% H-8 → L, 8.64% H-12 → L	
208.55	0.0085	12.2926	93.7% H-9 → L	
206.51	0.0291	47.8898	42.8% H-5 → L+1, 37.5% H-6 → L+1, 5.09% H-8 → L+1, 3.31% H-7 → L+1, 2.05% H-9 → L+1	
205.26	0.0203	–14.388	30.0% H-10 → L, 28.0% H-12 → L, 17.7% H-11 → L, 7.23% H → L+3, 7.06% H-8 → L, 3.82% H-1 → L+2	

Table S1. Excitation energies (wavelength in nm), oscillator strength, rotatory strength (velocity) and orbital contributions of each excited state of the originally reported suffruticosine (**10**). Excitation energies over 205 nm were only included. Bold transitions were mentioned in the text. H: HOMO, L: LUMO

5. Absorption and Electronic Circular Dichroism (ECD) Spectra of securinine (1) and allosecurinine (14)

5.1 Securinine (1)

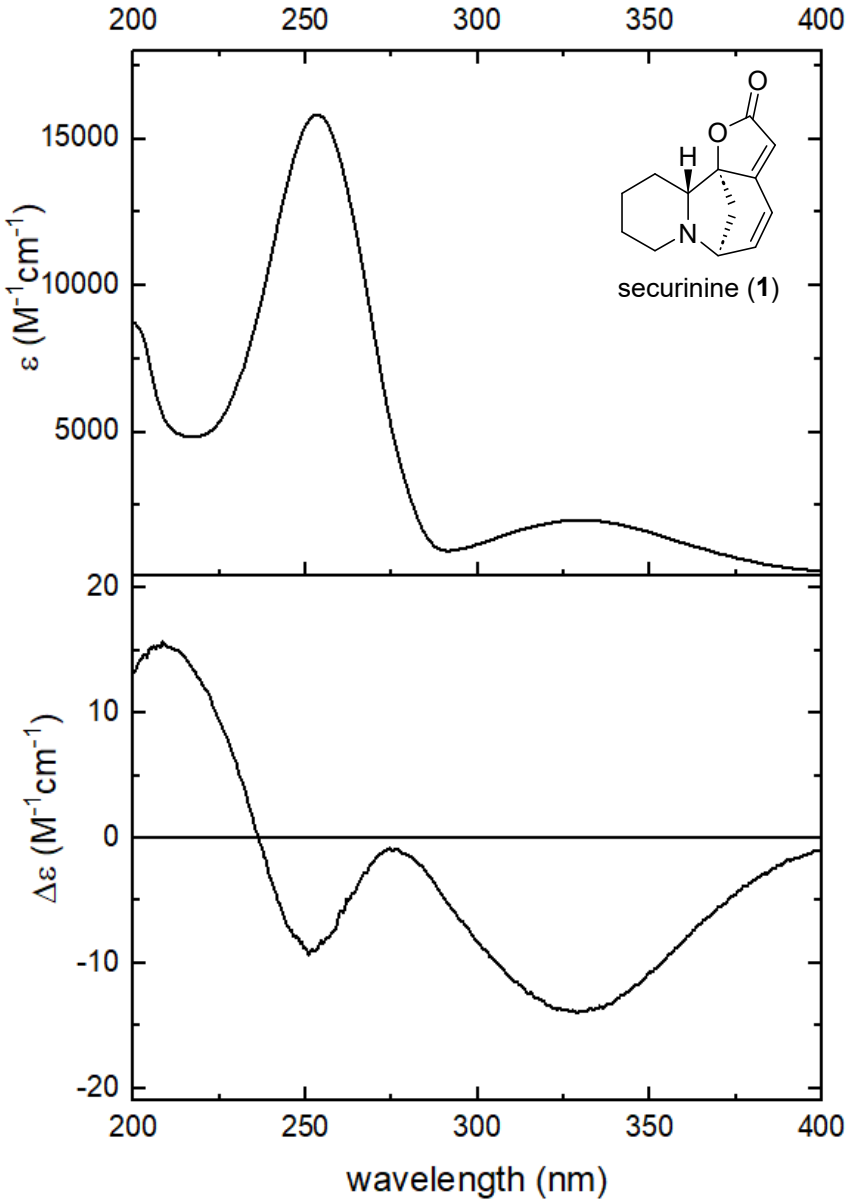


Figure S8. UV/Vis and ECD spectra of securinine (**1**) in acetonitrile.

UV λ_{max} (log ε, MeCN) 253.5 (4.20), 331 (3.30) (λ_{max}: nm, ε: $M^{-1}cm^{-1}$)

ECD λ_{max} (Δε, MeCN) 208.5 (+15.8) 251 (–9.38) 275.5 (–0.95) 329 (–13.9) (λ_{max}: nm, Δε: $M^{-1}cm^{-1}$)

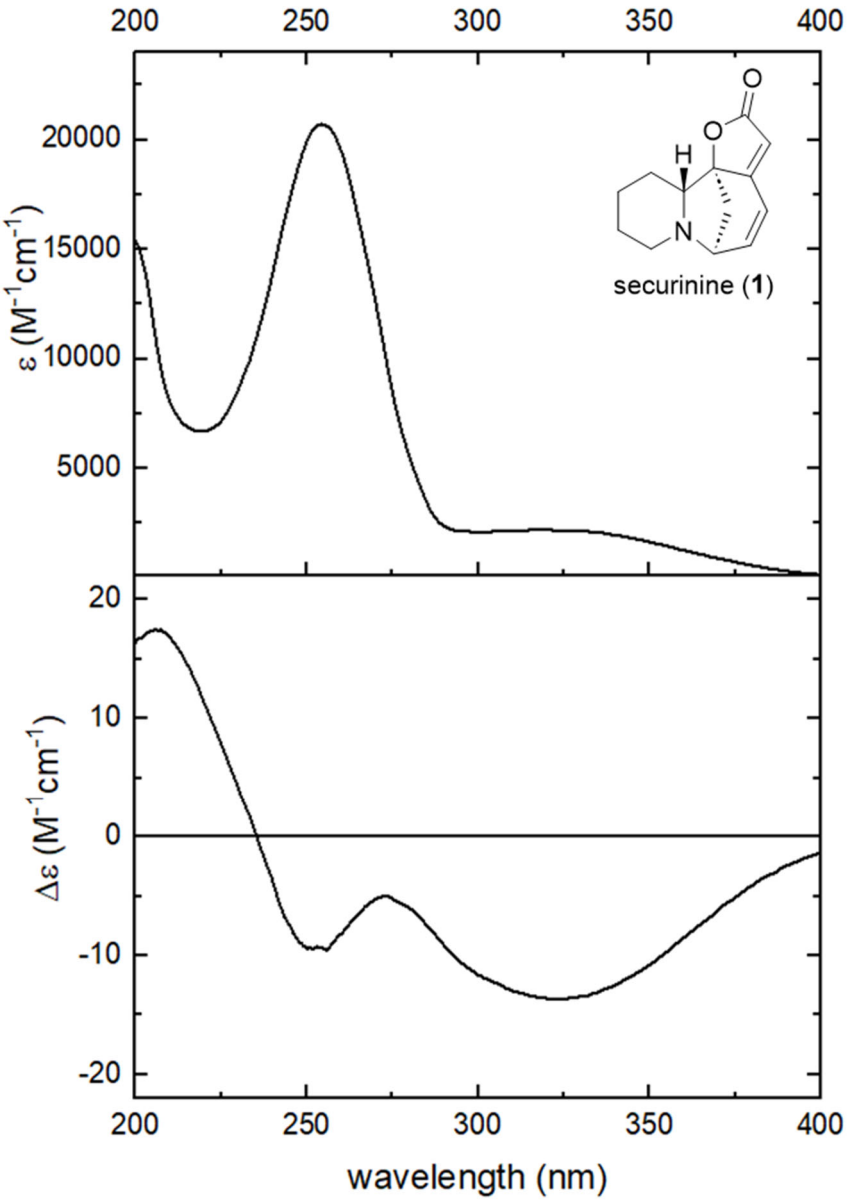


Figure S9. UV/Vis and ECD spectra of securinine (**1**) in methanol.

UV λ_{max} (log ε, MeOH) 254.5 (4.32), 324 (3.34) (λ_{max}: nm, ε: $M^{-1}cm^{-1}$)

ECD λ_{max} (Δε, MeOH) 206 (+17.5) 251.5 (–9.41) 272.5 (–4.97) 323 (–13.7) (λ_{max}: nm, Δε: $M^{-1}cm^{-1}$)

5.2 Allosecurinine (14)

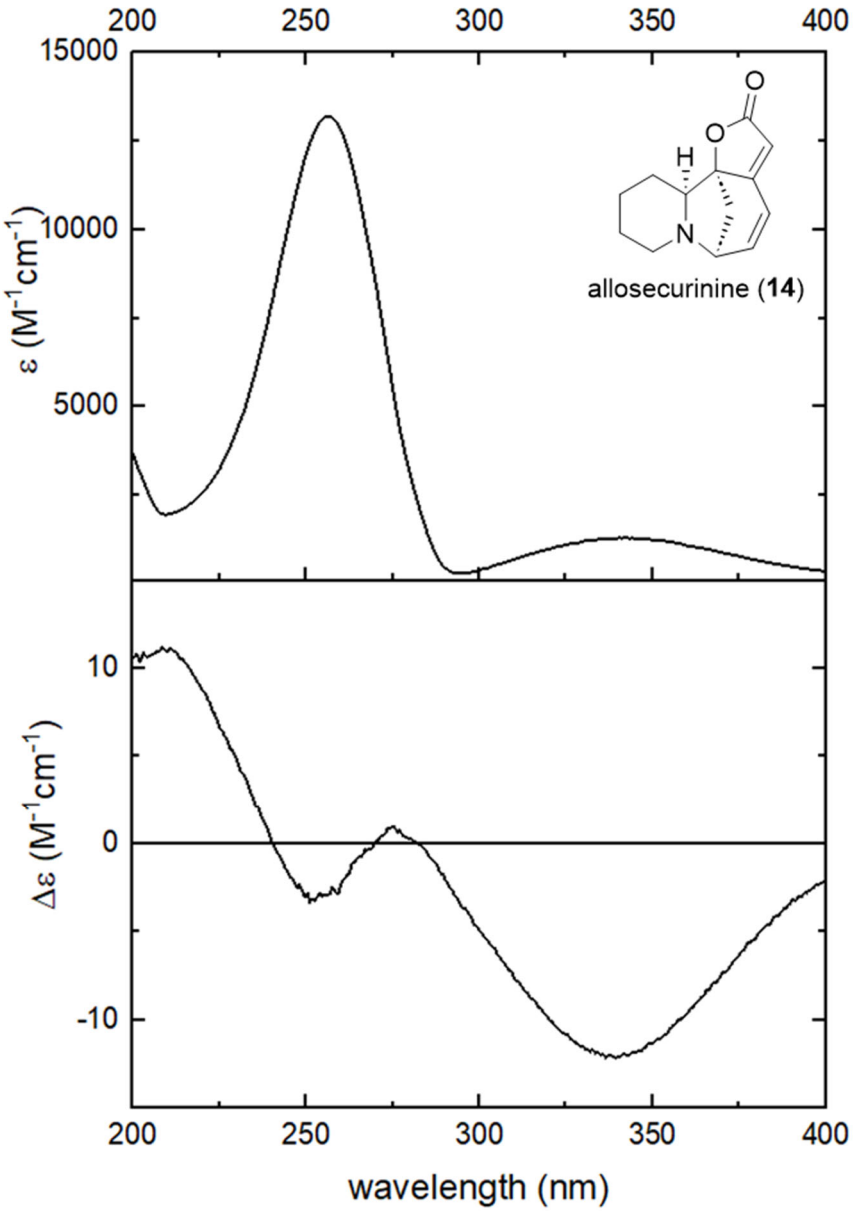


Figure S10. Absorption and ECD spectra of allosecurinine (**14**) in acetonitrile.

UV λ_{max} (log ε, MeCN) 256.5 (4.12), 342 (3.11) (λ_{max}: nm, ε: $M^{-1}cm^{-1}$)

ECD λ_{max} (Δε, MeCN) 208 (11.03) 251 (–3.33), 275 (+0.95), 339.5 (–12.15) (λ_{max}: nm, Δε: $M^{-1}cm^{-1}$)

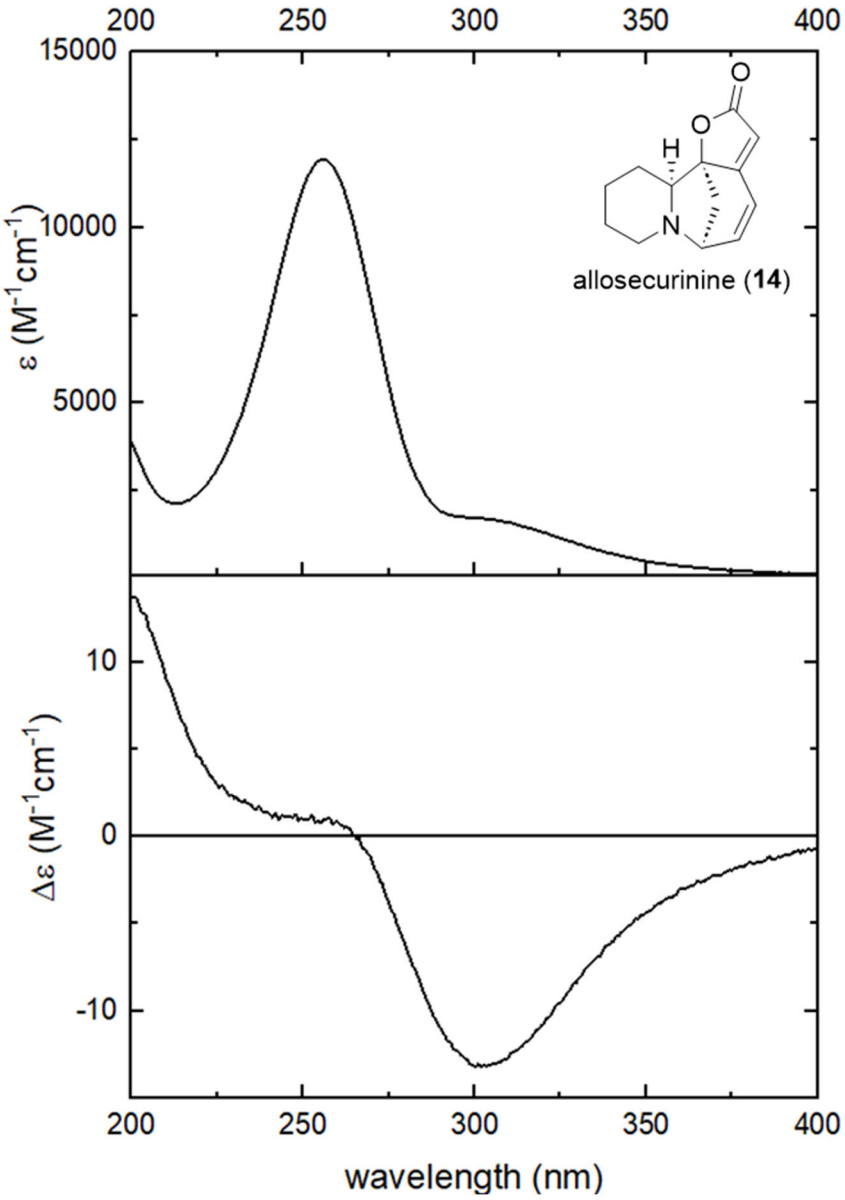


Figure S11. Absorption and ECD spectra of allosecurinine (**14**) in methanol.

UV λ_{max} (log ε, MeOH) 256 (4.08), 302 (3.24) (λ_{max}: nm, ε: $M^{-1}cm^{-1}$)

ECD λ_{max} (Δε, MeOH) 302 (–13.2) (λ_{max}: nm, Δε: $M^{-1}cm^{-1}$)

Note:

The disappearance of the negative ECD band around 250 nm is presumed to be a result of the hydrogen bonding effect involving the nitrogen atom. This effect is consistent with the findings reported in the previous literature[13], which stated that protonated allosecurinine exhibited a single negative band.

6. Computational Studies of Securinine (1)

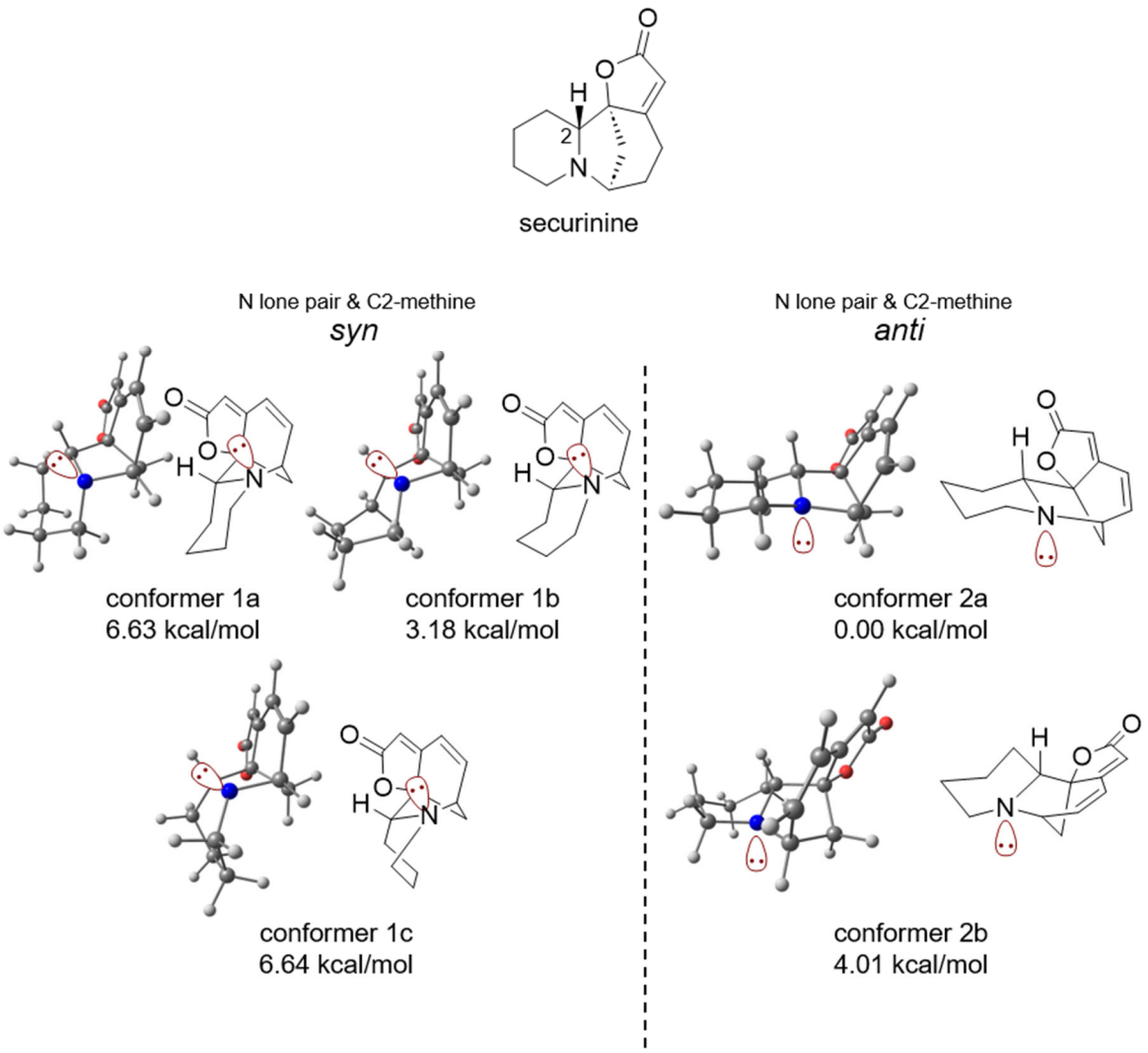


Figure S12. Conformers of securinine (**1**) with relative free energies.

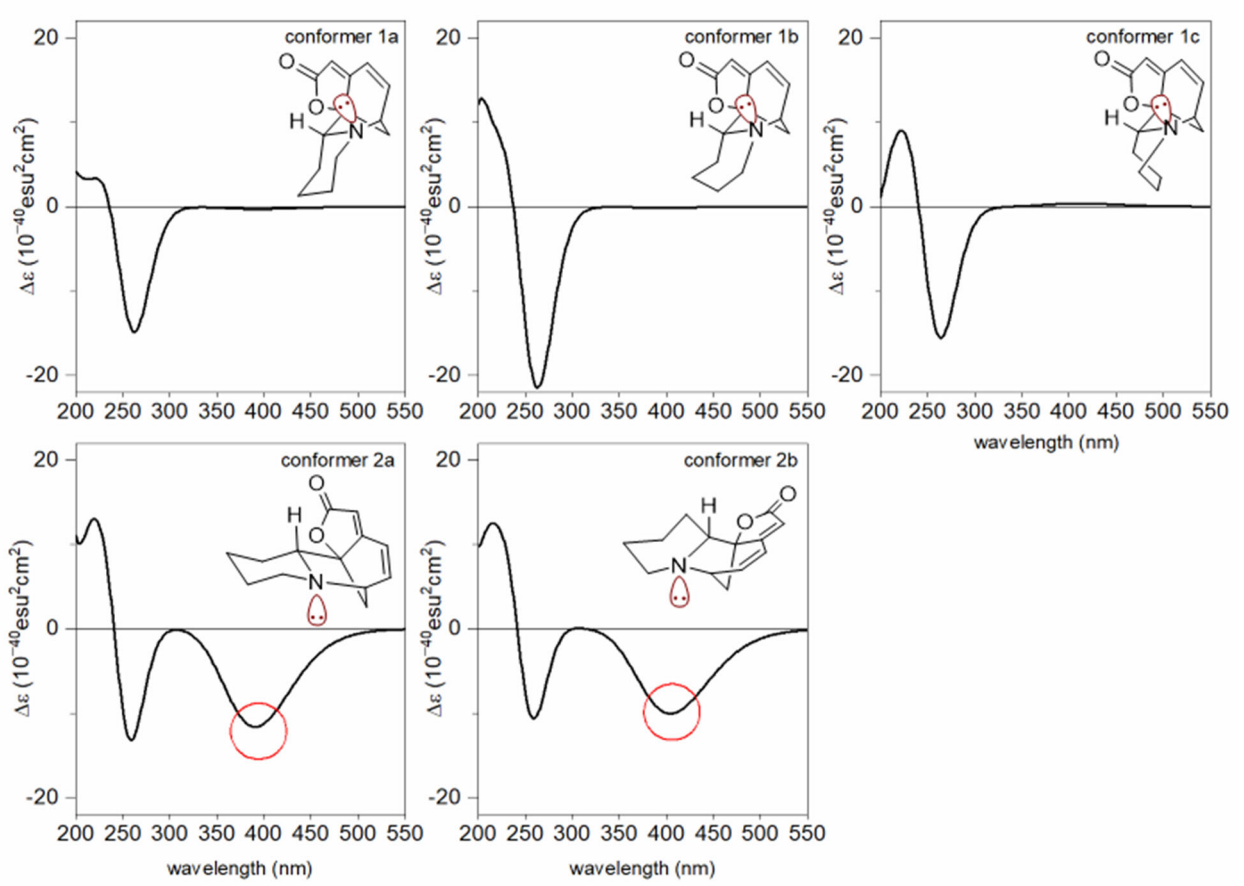


Figure S13. Computed ECD spectra of all conformers of securinine (**1**).

6.1 Conformer 1a, securinine

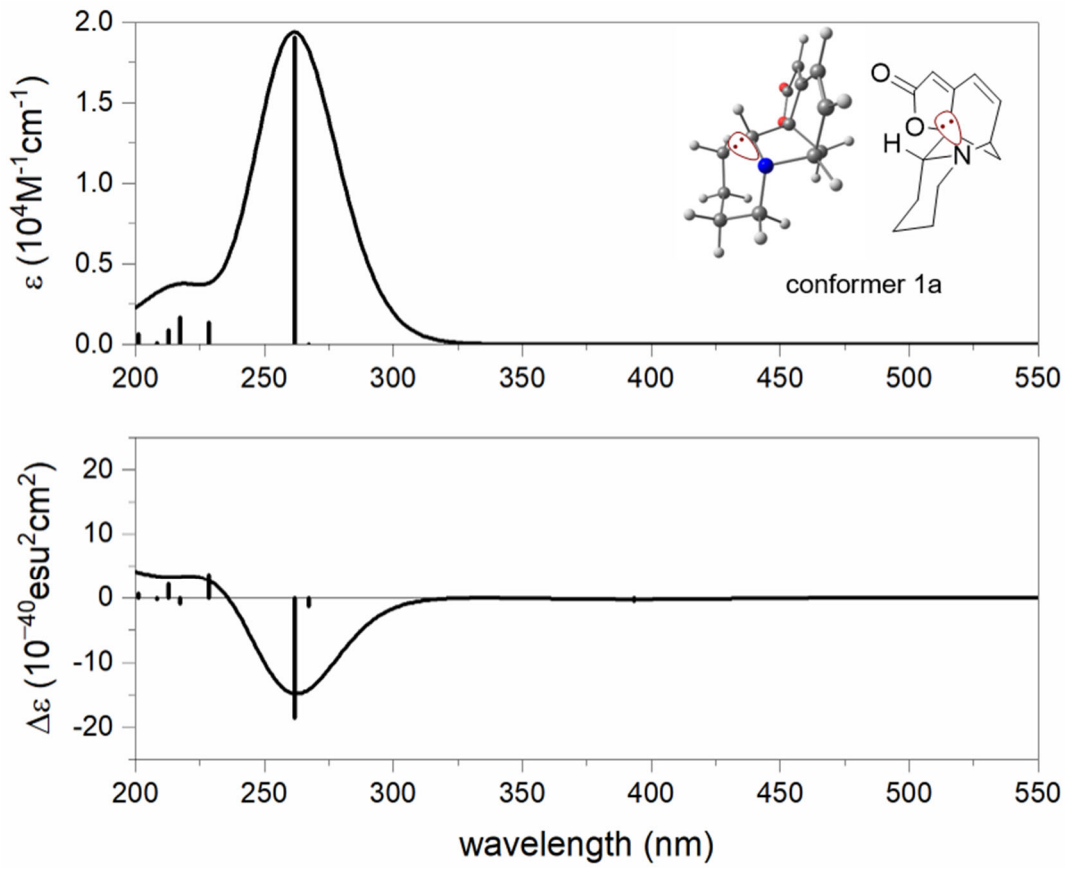


Figure S14. Calculated absorption and ECD spectra of conformer 1a, securinine.

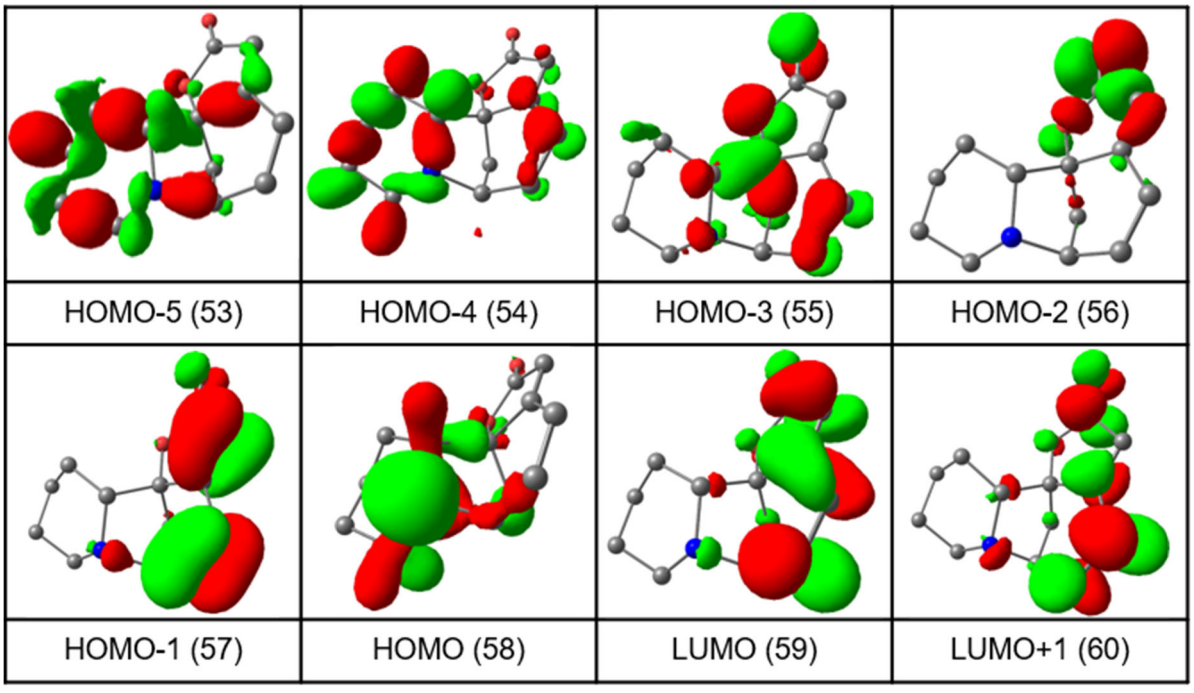


Figure S15. Molecular orbitals of conformer 1a, securinine (contour value = 0.05).

Wavelength (nm)	Oscillator Strength	Rotatory Strength	Contributions	Assignments & notes
393.46	**0.0006**	**–1.4365**	**99.6% H → L**	**Nitrogen lone pair → π*, diminished band intensity in Abs & ECD**
267.27	0.0001	–3.5225	96.5% H-2 → L, 2.48% H-2 → L+1	
261.76	**0.4765**	**–48.274**	**97.0% H-1 → L**	**π → π*, major absorption**
228.52	0.0344	9.5302	92.7% H-3 → L	
217.29	0.0419	–2.2955	96.8% H → L+1	
212.97	0.0217	5.7159	54.6% H-5 → L, 20.0% H-7 → L, 10.3% H-6 → L, 6.58% H-8 → L, 3.74% H-4 → L, 2.97% H-3 → L	
208.35	0.0023	–0.6217	91.9% H-4 → L, 2.11% H-1 → L+1	
201.22	0.0165	1.7296	40.4% H-6 → L, 36.4% H-5 → L, 16.8% H-7 → L, 2.53% H-8 → L	

Table S2. Excitation energies (wavelength in nm), oscillator strength, rotatory strength (velocity) and orbital contributions of each excited state of conformer 1a, securinine. Excitation energies over 200 nm were only included. H: HOMO, L: LUMO.

6.2 Conformer 1b, securinine

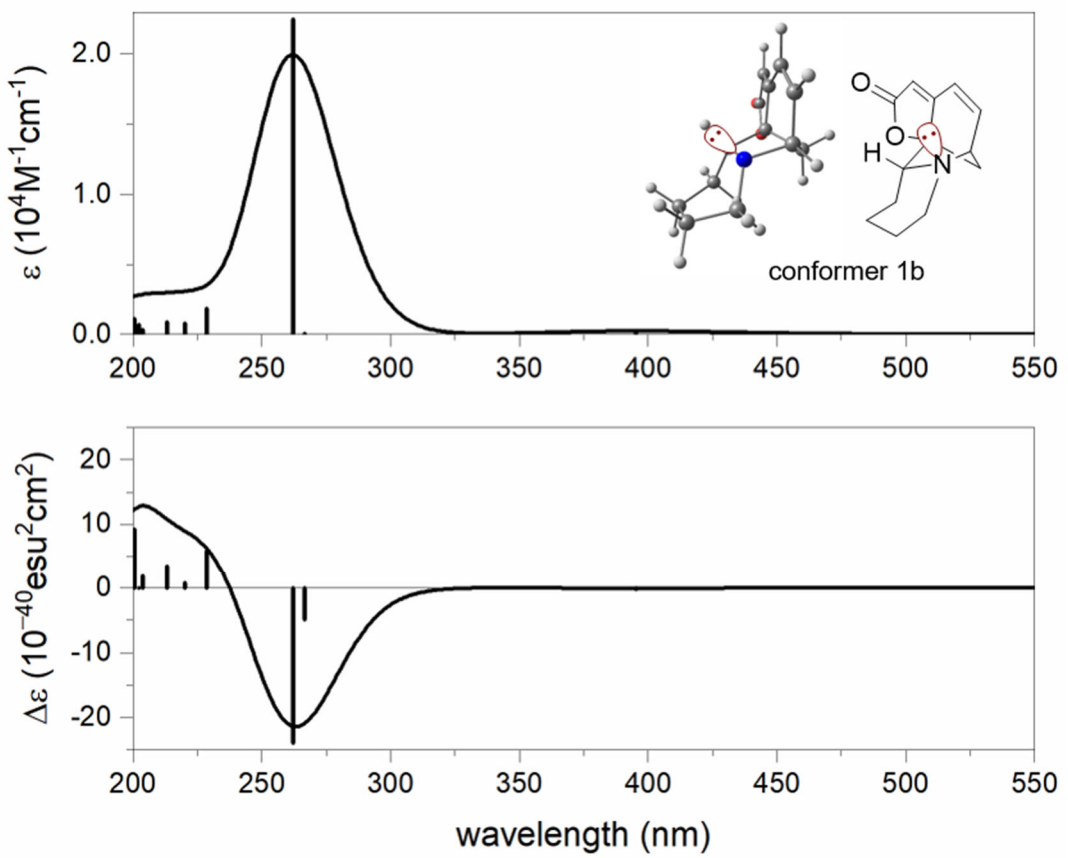


Figure S16. Calculated absorption and ECD spectra of conformer 1b, securinine.

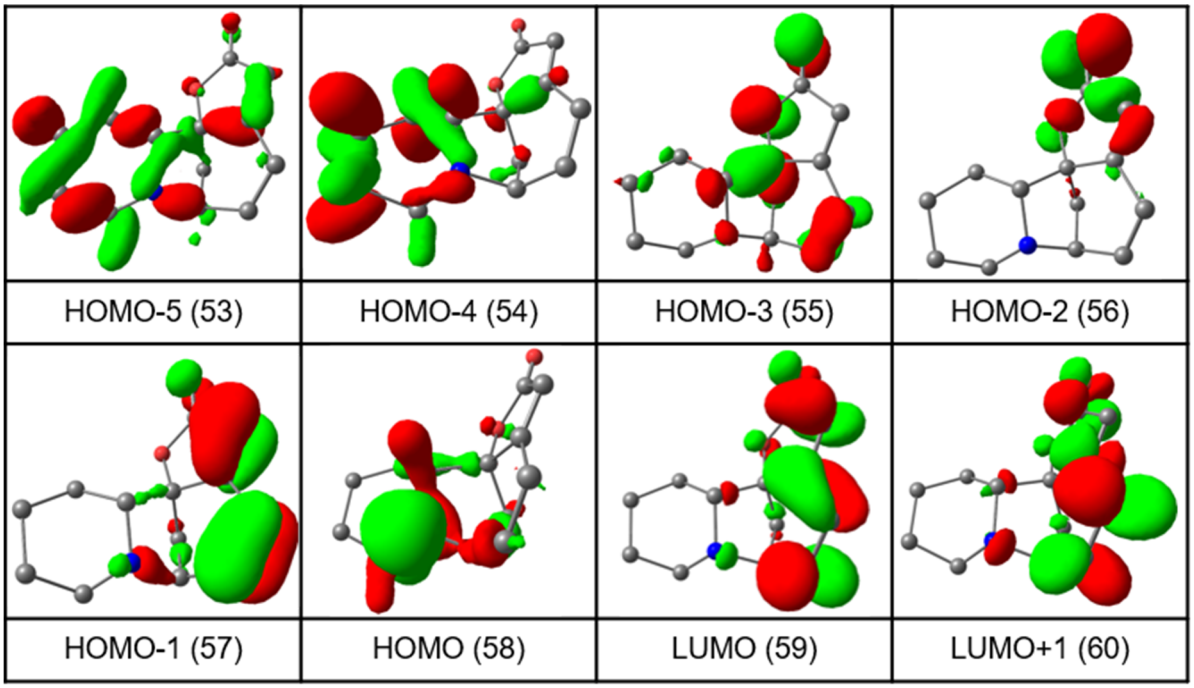


Figure S17. Molecular orbitals of conformer 1b, securinine (contour value = 0.05).

Wavelength (nm)	Oscillator Strength	Rotatory Strength	Contributions	Assignments & notes
395.17	**0.0057**	**–0.5603**	**99.4% H → L**	**Nitrogen lone pair → π*, diminished band intensity in Abs & ECD**
266.51	0.0013	–12.8118	96.2% H-2 → L, 2.43% H-2 → L+1	
262.14	**0.4892**	**–62.2657**	**96.7% H-1 → L**	**π → π*, major absorption**
228.61	0.0404	15.2227	91.9% H-3 → L, 3.03% H → L+1	
220.11	0.0172	2.0227	92.7% H → L+1, 3.66% H-3 → L	
213.24	0.0191	8.931	49.6% H-4 → L, 16.6% H-5 →L, 13.6% H-7 → L, 7.84% H-8 → L, 7.37% H-6 → L	
203.91	0.0071	4.8365	58.1% H-5 → L, 35.1% H-4 → L	
202.41	0.0151	–0.0390	95.9% H → L+2	
200.64	0.0245	23.9773	68.5% H-6 → L, 14.3% H-5 → L, 5.94% H-4 → L, 4.14% H-7 → L, 2.25% H → L+2	

Table S3. Excitation energies (wavelength in nm), oscillator strength, rotatory strength (velocity) and orbital contributions of each excited state of conformer 1b, securinine. Excitation energies over 200 nm were only included. H: HOMO, L: LUMO.

6.3 Conformer 1c, securinine

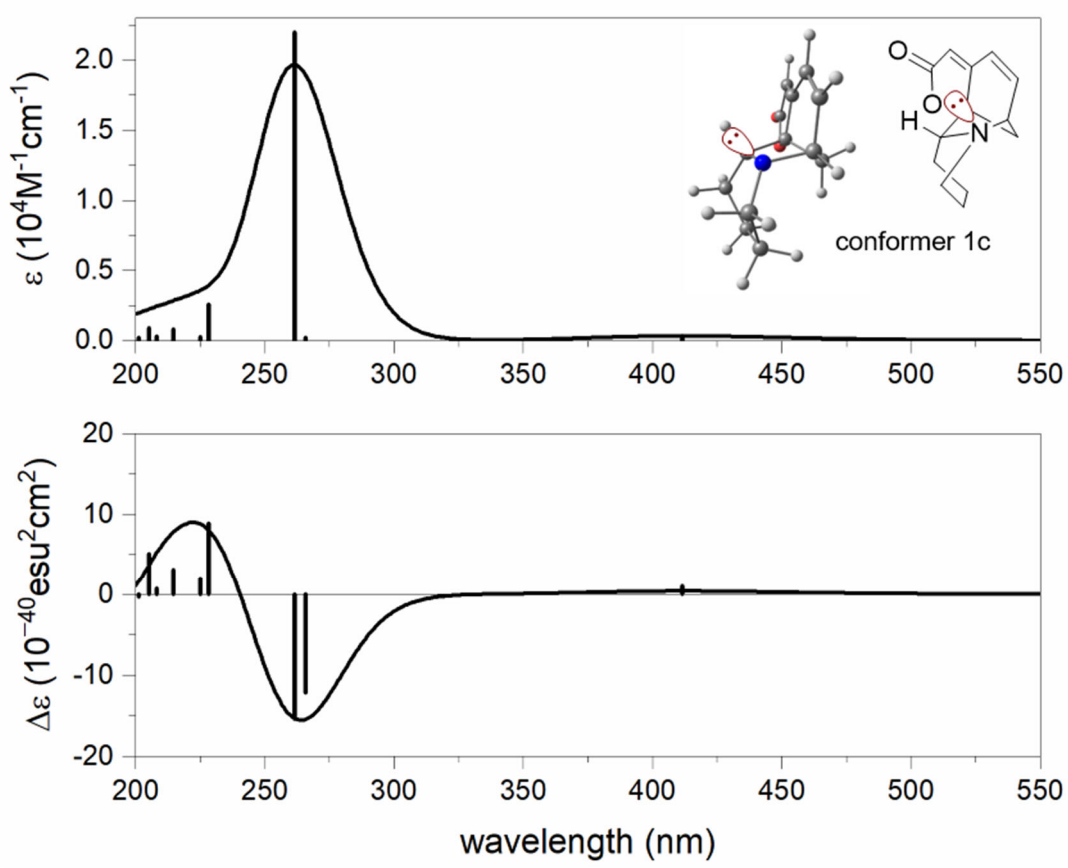


Figure S18. Calculated absorption and ECD spectra of conformer 1c, securinine.

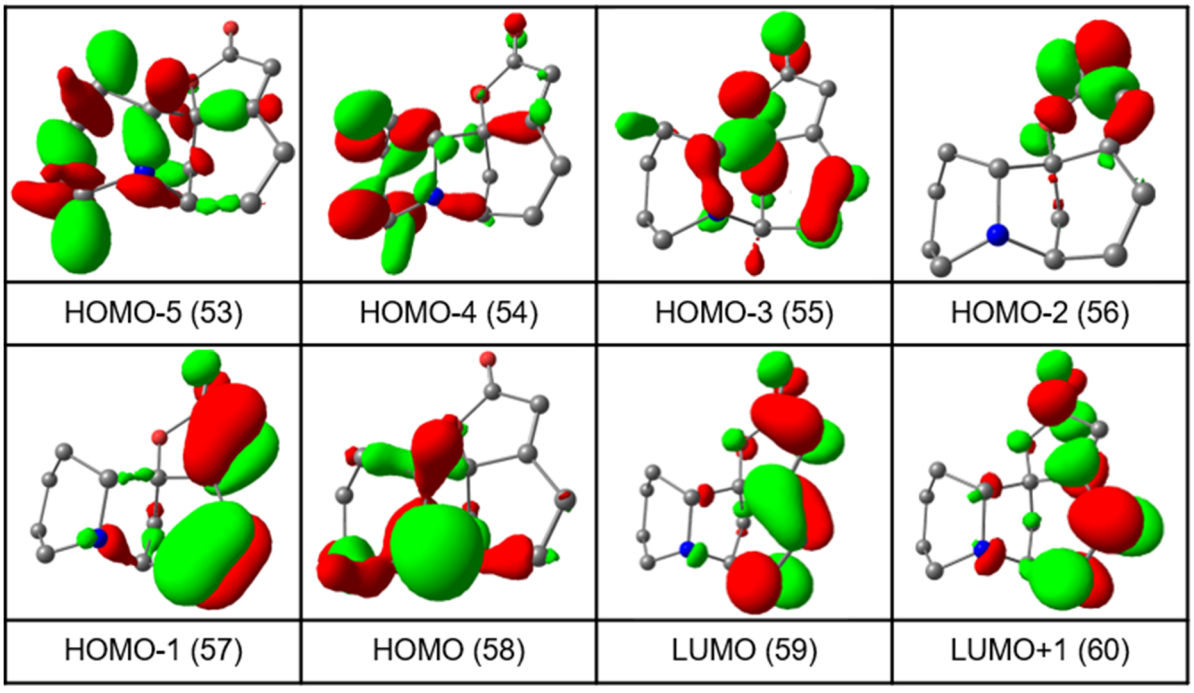


Figure S19. Molecular orbitals of conformer 1c, securinine (contour value = 0.05).

Wavelength (nm)	Oscillator Strength	Rotatory Strength	Contributions	Assignments & notes
411.51	**0.0079**	**2.0728**	**99.4% H → L**	**Nitrogen lone pair → π*, diminished band intensity in Abs & ECD**
265.85	0.0051	–24.2332	95.4% H-2 → L, 2.48% H-2 → L+1	
261.61	**0.4777**	**–30.7691**	**95.6% H-1 → L**	**π → π*, major absorption**
228.32	0.0563	17.7754	69.6% H-3 → L, 25.0% H → L+1	
224.93	0.0055	3.931	71.3% H → L+1, 26.0% H-3 → L	
214.68	0.0181	6.1847	35.8% H-5 → L, 30.6% H-6 → L, 23.6% H-4 → L, 2.82% H-7 → L, 2.27% H-8 → L	
208.04	0.0066	1.5358	98.0% H → L+2	
205.18	0.0191	10.1536	66.9% H-4 → L, 28.8% H-5 → L, 2.06% H-6 → L	
201.09	0.0052	–0.6472	59.9% H-6 → L, 30.2% H-5 → L, 5.21% H-4 → L, 2.71% H-1 → L+1	

Table S4. Excitation energies (wavelength in nm), oscillator strength, rotatory strength (velocity) and orbital contributions of each excited state of conformer 1c, securinine. Excitation energies over 200 nm were only included. H: HOMO, L: LUMO.

6.4 Conformer 2a, securinine

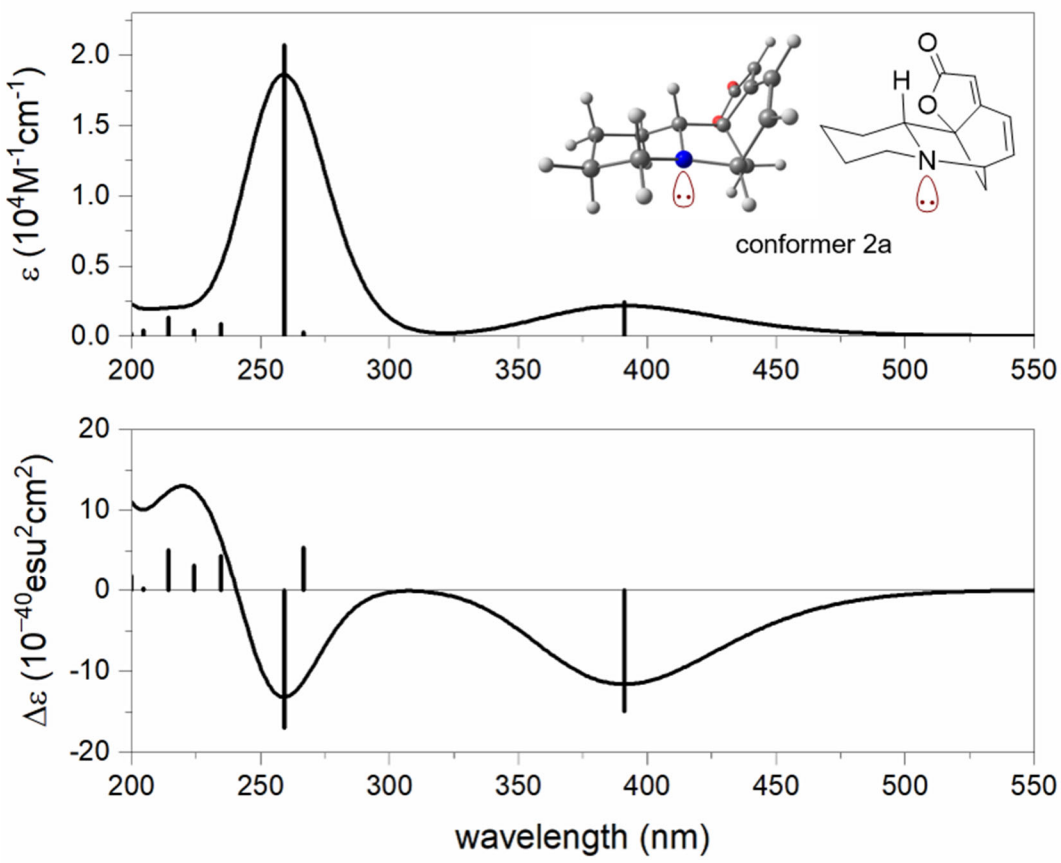


Figure S20. Calculated absorption and ECD spectra of conformer 2a, securinine.

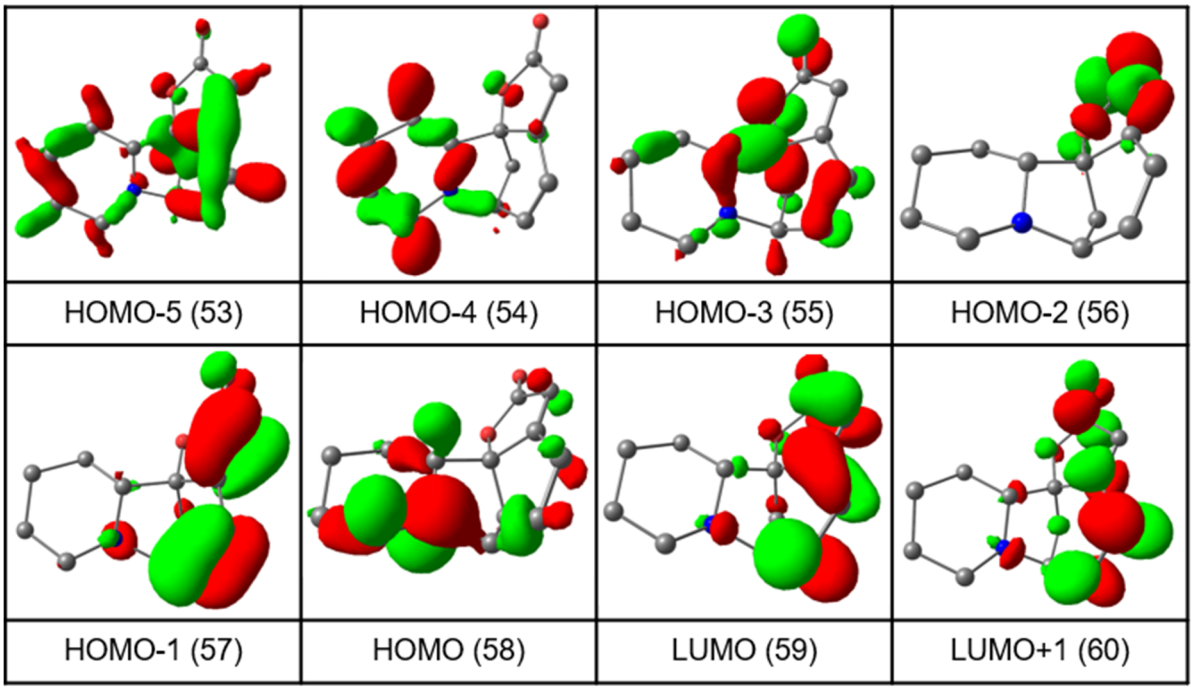


Figure S21. Molecular orbitals of conformer 2a, securinine (contour value = 0.05).

Wavelength (nm)	Oscillator Strength	Rotatory Strength	Contributions	Assignments & notes
391.14	**0.0532**	**–59.6583**	**98.3% H → L**	**Nitrogen lone pair → π*, minor absorption**
266.62	0.0061	21.4521	94.7% H-2 → L, 2.48% H-2 → L+1	
259.15	**0.4505**	**–68.0437**	**94.3% H-1 → L**	**π → π*, major absorption**
234.65	0.0188	17.2977	96.2% H-3 → L	
224.08	0.0096	12.4925	91.2% H → L+1, 4.88% H-5 → L	
214.22	0.0289	20.1484	75.6% H-5 → L, 8.20% H-8 → L, 5.59% H → L+1, 4.73% H-4 → L	
204.42	0.0093	0.8319	92.3% H-4 → L, 5.95% H-5 → L	

Table S5. Excitation energies (wavelength in nm), oscillator strength, rotatory strength (velocity) and orbital contributions of each excited state of conformer 2a, securinine. Excitation energies over 200 nm were only included. H: HOMO, L: LUMO.

6.5 Conformer 2b, securinine

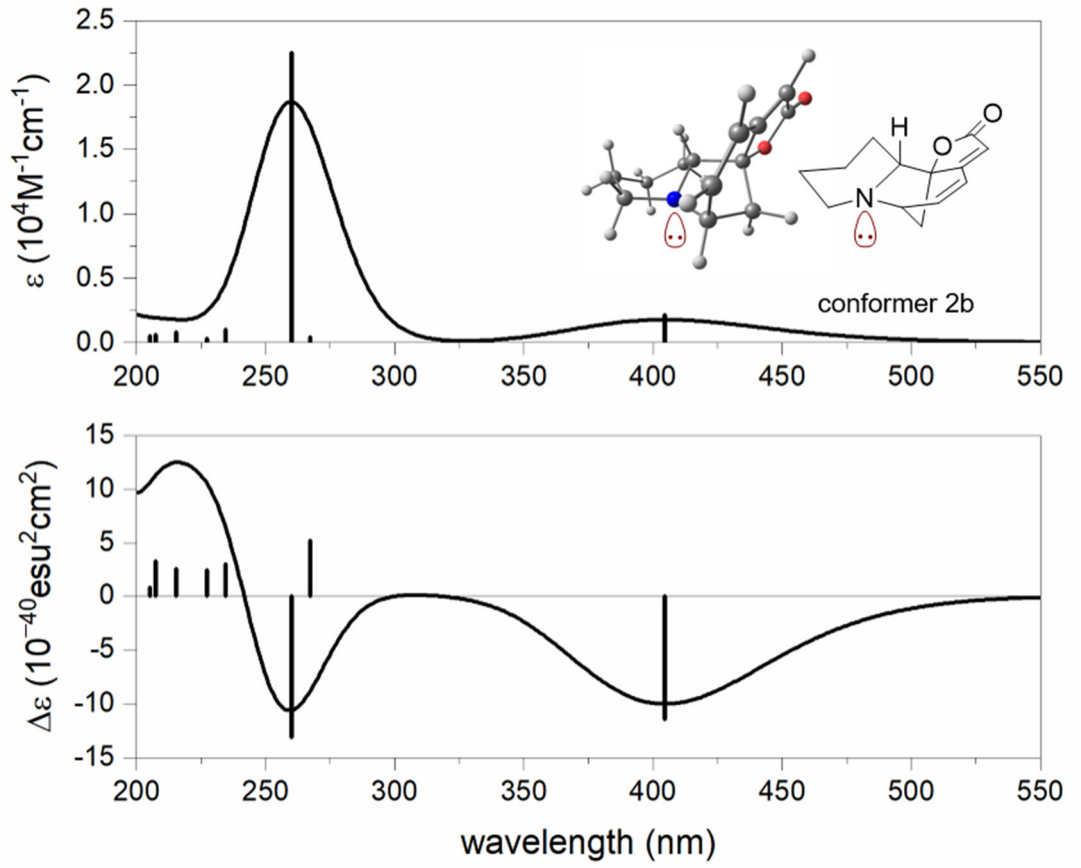


Figure S22. Calculated absorption and ECD spectra of conformer 2b, securinine.

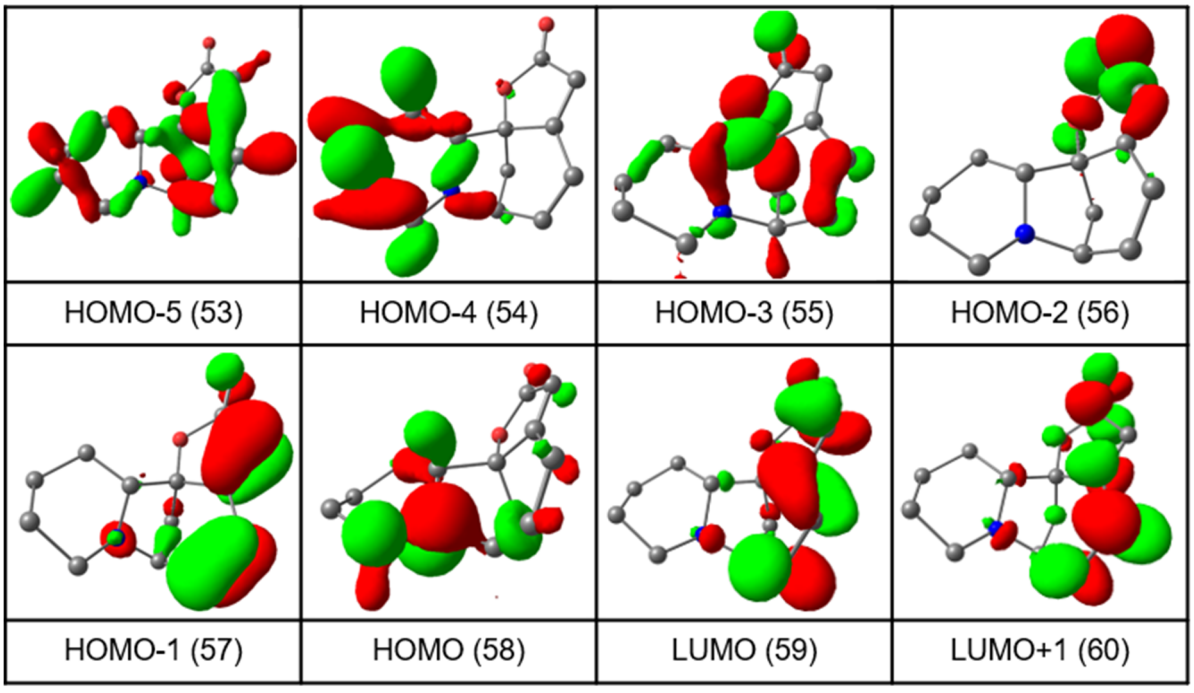


Figure S23. Molecular orbitals of conformer 2b, securinine (contour value = 0.05).

Wavelength (nm)	Oscillator Strength	Rotatory Strength	Contributions	Assignments & notes
404.54	**0.0433**	**–53.3006**	**98.6% H → L**	**Nitrogen lone pair → π*, minor absorption**
267.18	0.0080	24.2926	94.1% H-2 → L, 2.42% H-2 → L+1, 2.23% H-1 → LUMO	
259.98	**0.4498**	**–61.2288**	**94.3% H-1 → L, 2.15% H-2 → L**	**π → π*, major absorption**
234.47	0.0205	14.1433	94.2% H-3 → L, 2.77% H → L+1	
227.27	0.0061	11.6466	92.3% H → L+1, 3.00% H-3 → L, 2.66% H-5 → L	
215.41	0.0166	12.2239	84.2% H-5 → L, 4.78% H-8 → L, 3.11% H-7 → L, 3.06% H → L+1	
207.34	0.0122	15.4416	95.9% H-4 → L	
205.27	0.0103	3.6572	95.1% H → L+2	

Table S6. Excitation energies (wavelength in nm), oscillator strength, rotatory strength (velocity) and orbital contributions of each excited state of conformer 2b, securinine. Excitation energies over 200 nm were only included. H: HOMO, L: LUMO.

7. Computational Studies of Allosecurinine (14)

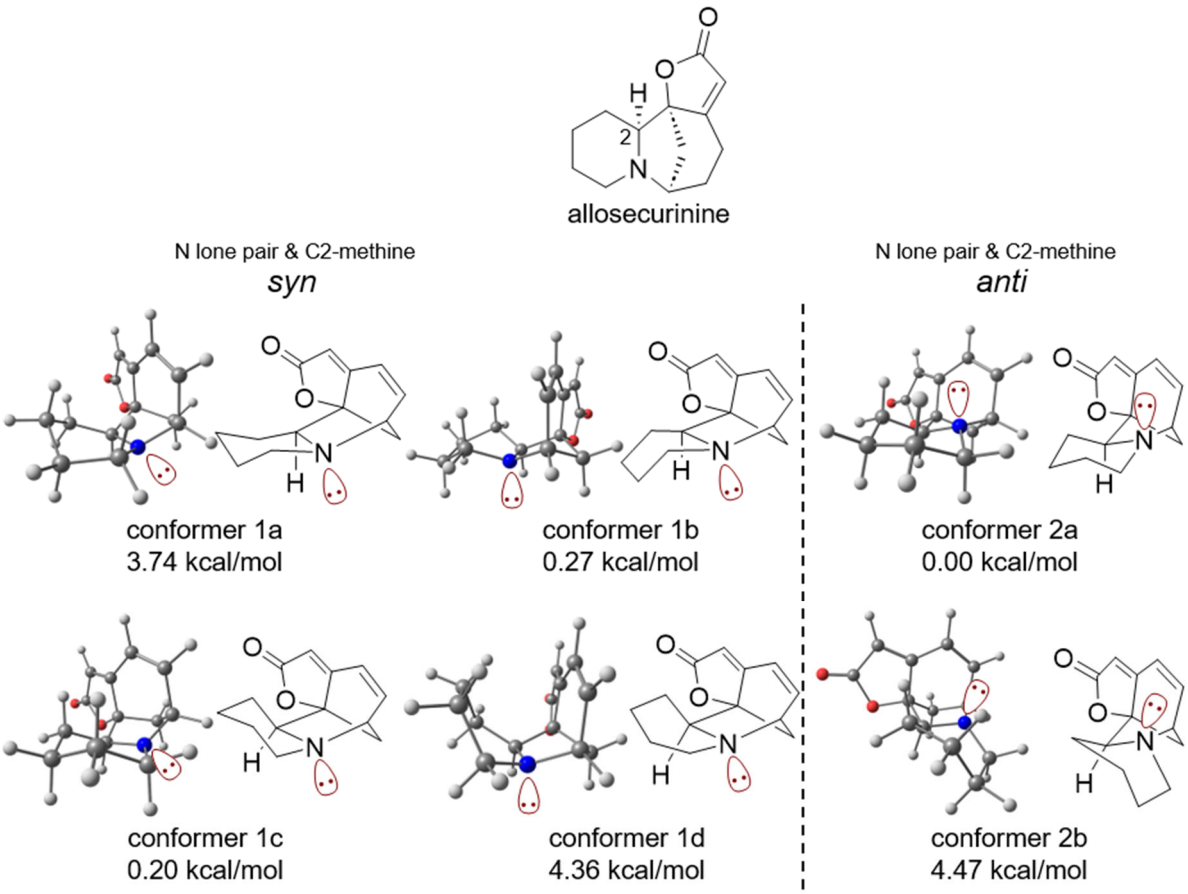


Figure S24. Conformers of allosecurinine (**14**) with relative free energies.

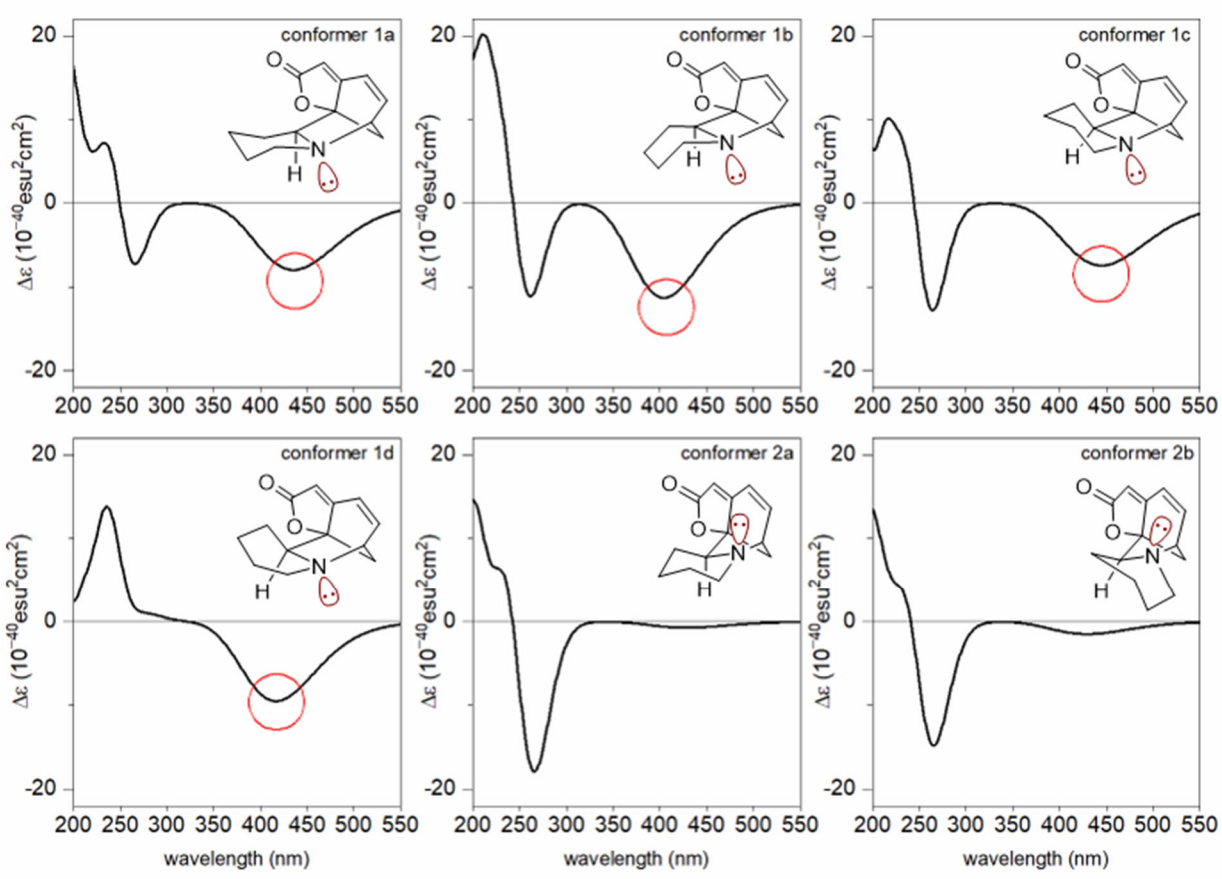


Figure S25. Computed ECD spectra of all conformers of allosecurinine (**14**).

7.1 Conformer 1a, allosecurinine

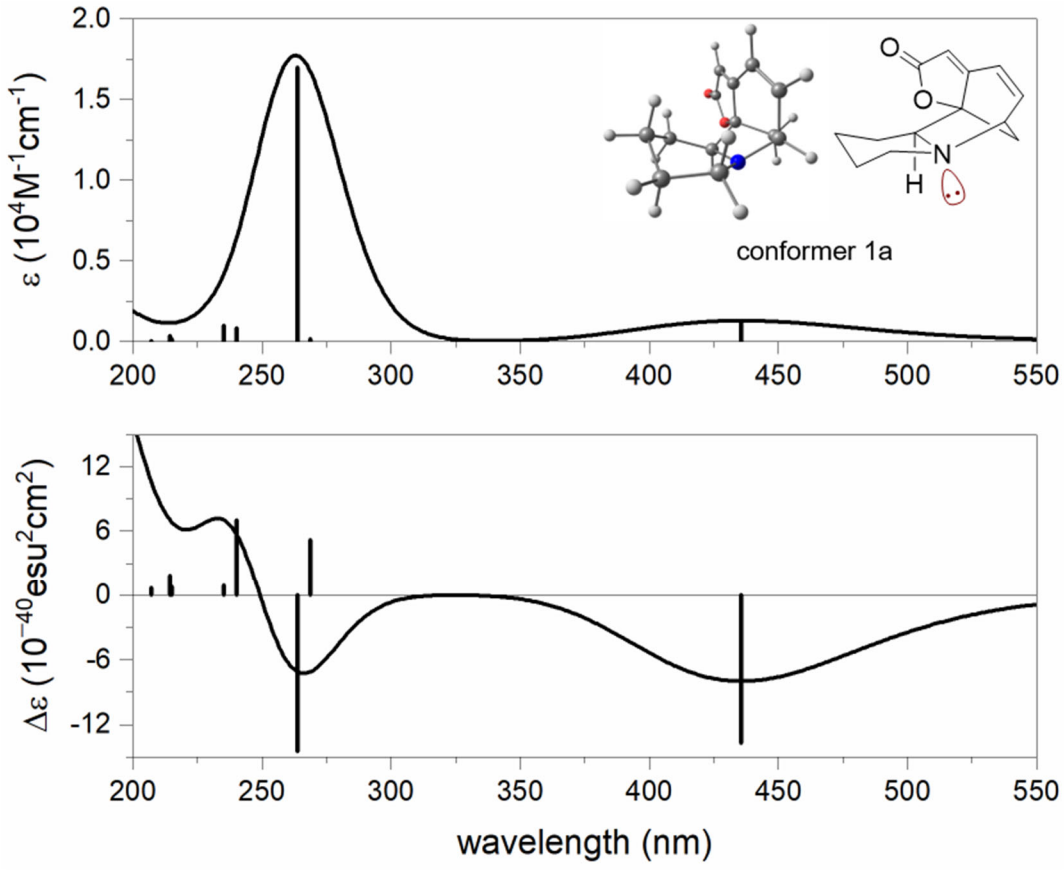


Figure S26. Calculated absorption and ECD spectra of conformer 1a, allosecurinine.

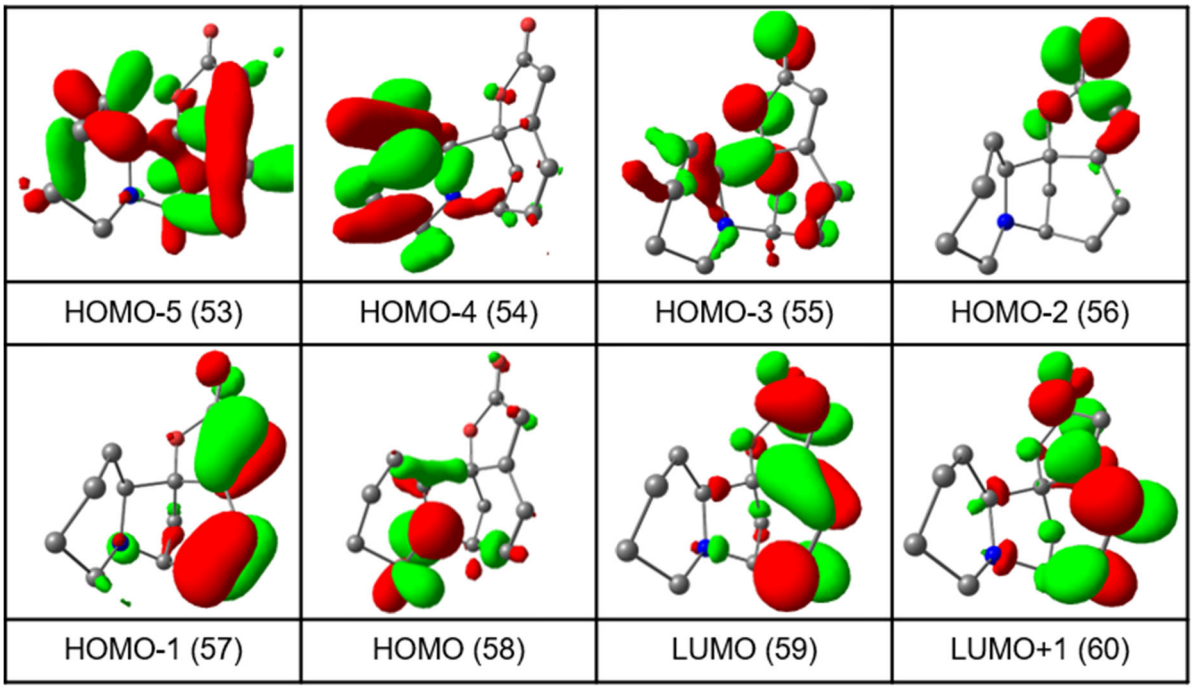


Figure S27. Molecular orbitals of conformer 1a, allosecurinine (contour value = 0.05).

Wavelength (nm)	Oscillator Strength	Rotatory Strength	Contributions	Assignments & notes
435.61	**0.0319**	**–45.6687**	**98.7% H → L**	**Nitrogen lone pair → π*, minor absorption**
268.64	0.0042	17.3839	95.5% H-2 → L, 2.31% H-2 → L+1	
263.64	**0.425**	**–48.1454**	**95.4% H-1 → L**	**π → π*, major absorption**
240.21	0.0207	23.4212	96.2% H → L+1	
235.21	0.0248	3.0714	96.7% H-3 → L	
214.99	0.0046	2.6094	71.0% H → L+2, 22.8% H-5 → L	
214.31	0.0093	6.2619	61.0% H-5 → L, 26.1% H → L+2, 3.18% H-9 → L, 2.84% H-4 → L, 2.72% H-6 → L	
207.20	0.0017	2.1457	93.9% H-4 → L, 4.43% H-5 → L	

Table S7. Excitation energies (wavelength in nm), oscillator strength, rotatory strength (velocity) and orbital contributions of each excited state of conformer 1a, allosecurinine. Excitation energies over 200 nm were only included. H: HOMO, L: LUMO.

7.2 Conformer 1b, allosecurinine

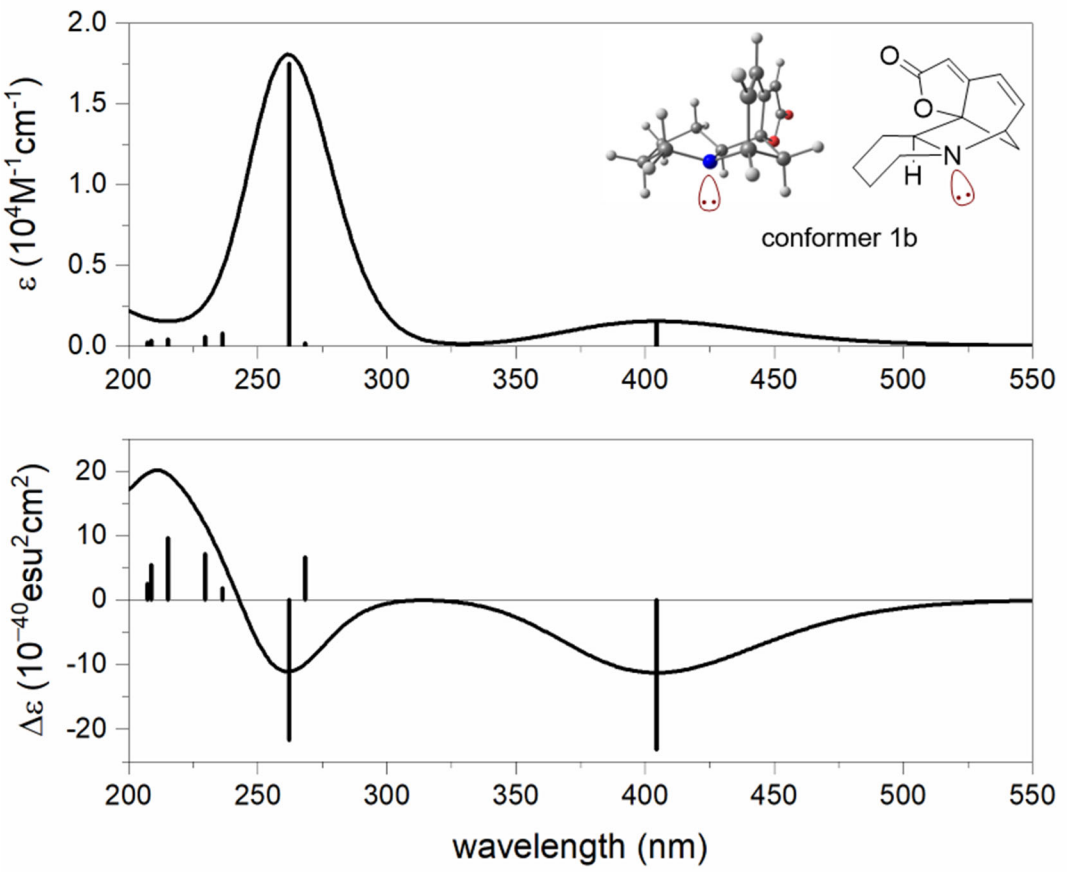


Figure S28. Calculated absorption and ECD spectra of conformer 1b, allosecurinine.

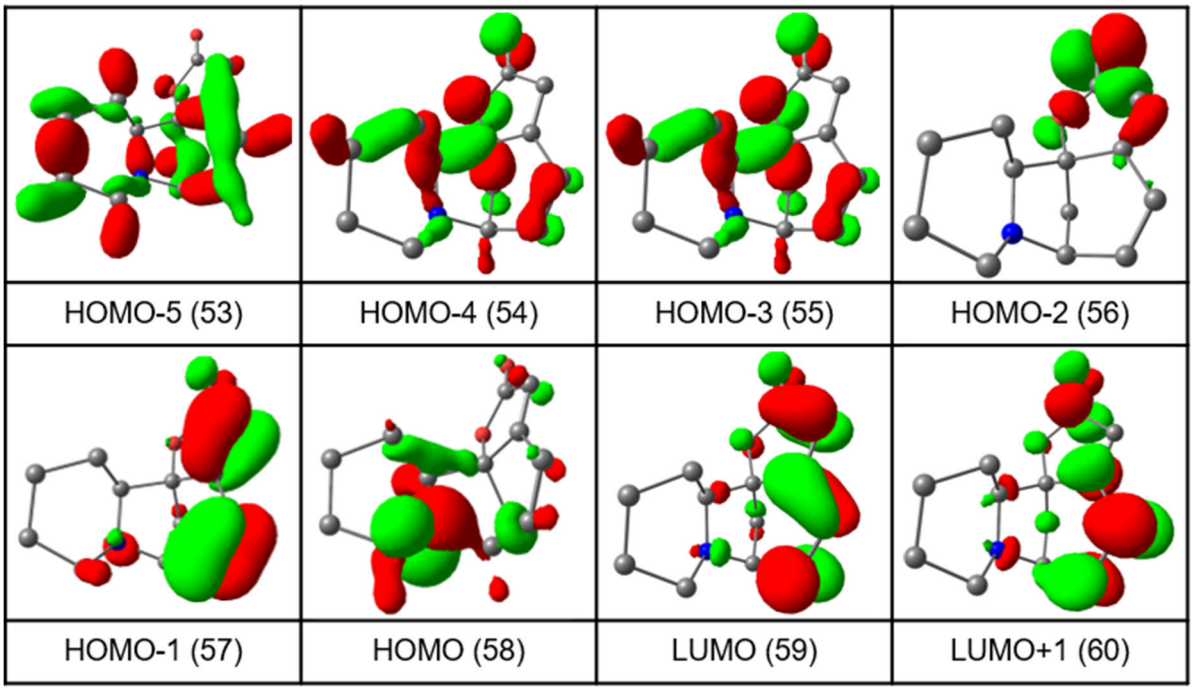


Figure S29. Molecular orbitals of conformer 1b, allosecurinine (contour value = 0.05).

Wavelength (nm)	Oscillator Strength	Rotatory Strength	Contributions	Assignments & notes
404.39	**0.0377**	**–60.0514**	**98.3% H → L**	**Nitrogen lone pair → π*, minor absorption**
268.41	0.0044	17.477	95.5% H-2 → L, 2.34% H-2 → L+1	
262.09	**0.4371**	**–56.2999**	**95.2% H-1 → L**	**π → π*, major absorption**
236.23	0.0192	4.6248	97.0% H-3 → L	
229.53	0.0147	18.7075	94.6% H → L+1	
215.17	0.0108	25.3121	50.1% H-4 → L, 36.0% H-5 → L, 5.73% H-8 → L, 2.66% H → L+1	
208.76	0.0087	14.3649	97.5% H → L+2	
207.14	0.0055	6.315	49.8% H-5 → L, 44.9% H-4 → L, 2.47% H-6 → L	

Table S8. Excitation energies (wavelength in nm), oscillator strength, rotatory strength (velocity) and orbital contributions of each excited state of conformer 1b, allosecurinine. Excitation energies over 200 nm were only included. H: HOMO, L: LUMO.

7.3 Conformer 1c, allosecurinine

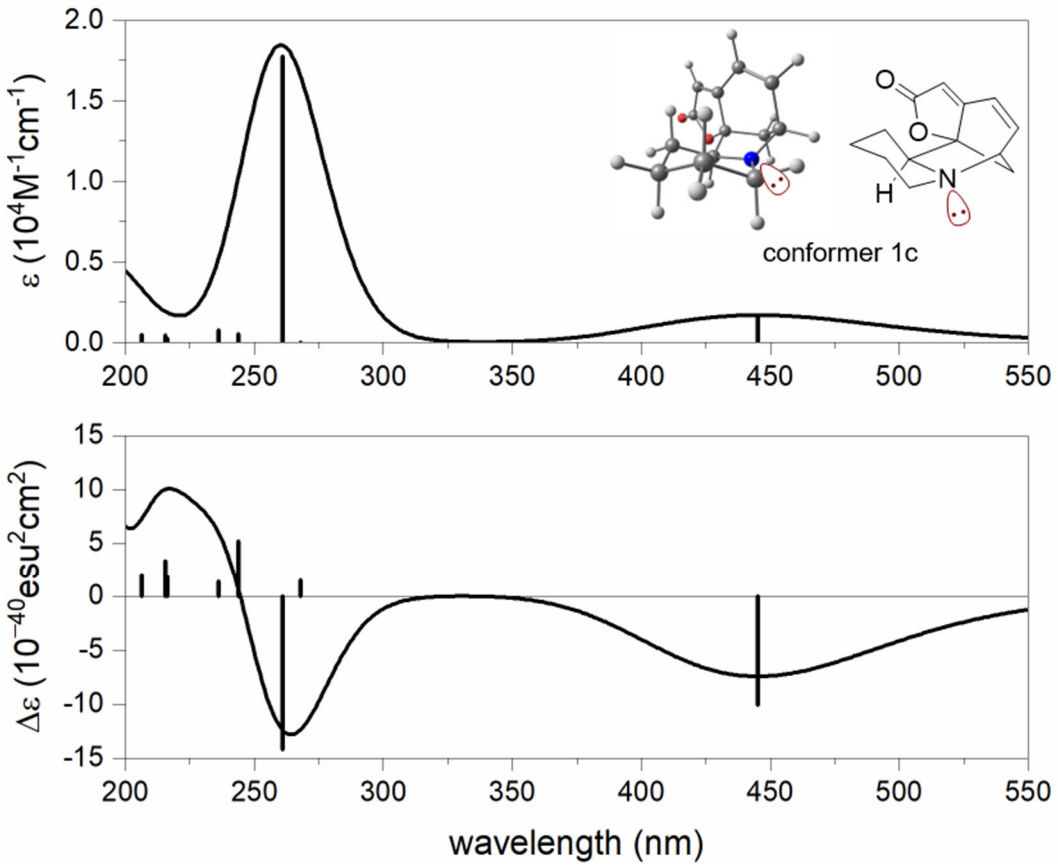


Figure S30. Calculated absorption and ECD spectra of conformer 1c, allosecurinine.

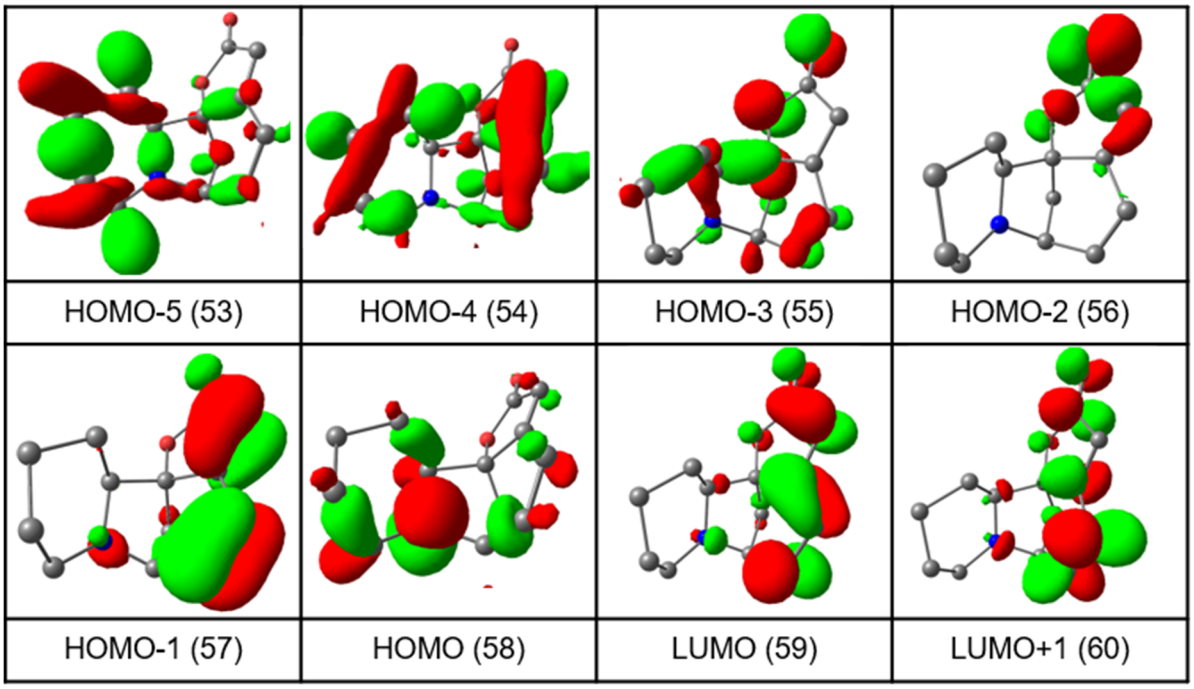


Figure S31. Molecular orbitals of conformer 1c, allosecurinine (contour value = 0.05).

Wavelength (nm)	Oscillator Strength	Rotatory Strength	Contributions	Assignments & notes
445.12	**0.0417**	**–43.5627**	**98.9% H → L**	**Nitrogen lone pair → π*, minor absorption**
267.77	0.0007	6.4939	96.5% H-2 → L, 2.46% H-2 → L+1	
260.79	**0.4441**	**–61.4092**	**96.4% H-1 → L**	**π → π*, major absorption**
243.65	0.0135	22.4874	95.8% H → L+1	
235.96	0.0187	5.8151	96.0% H-3 → L	
216.29	0.0059	8.0098	44.7% H → L+2, 32.2% H-4 → L, 14.2% H-5 → L, 3.19% H-6 → L	
215.4	0.0111	14.3147	51.5% H → L+2, 27.1% H-4 → L, 12.3% H-5 → L, 2.82% H-6 → L	
206.16	0.0123	8.7169	67.5% H-5 → L, 30.2% H-4 → L	

Table S9. Excitation energies (wavelength in nm), oscillator strength, rotatory strength (velocity) and orbital contributions of each excited state of conformer 1c, allosecurinine. Excitation energies over 200 nm were only included. H: HOMO, L: LUMO.

7.4 Conformer 1d, allosecurinine

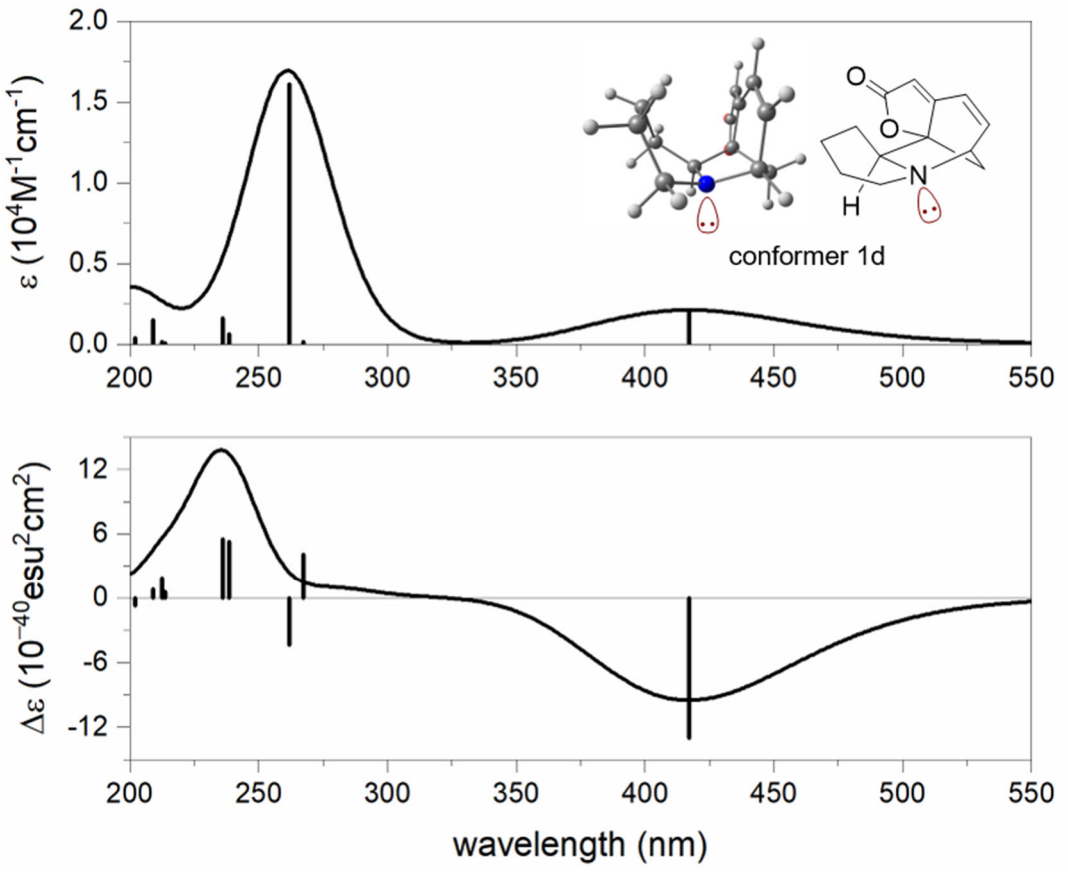


Figure S32. Calculated absorption and ECD spectra of conformer 1d, allosecurinine.

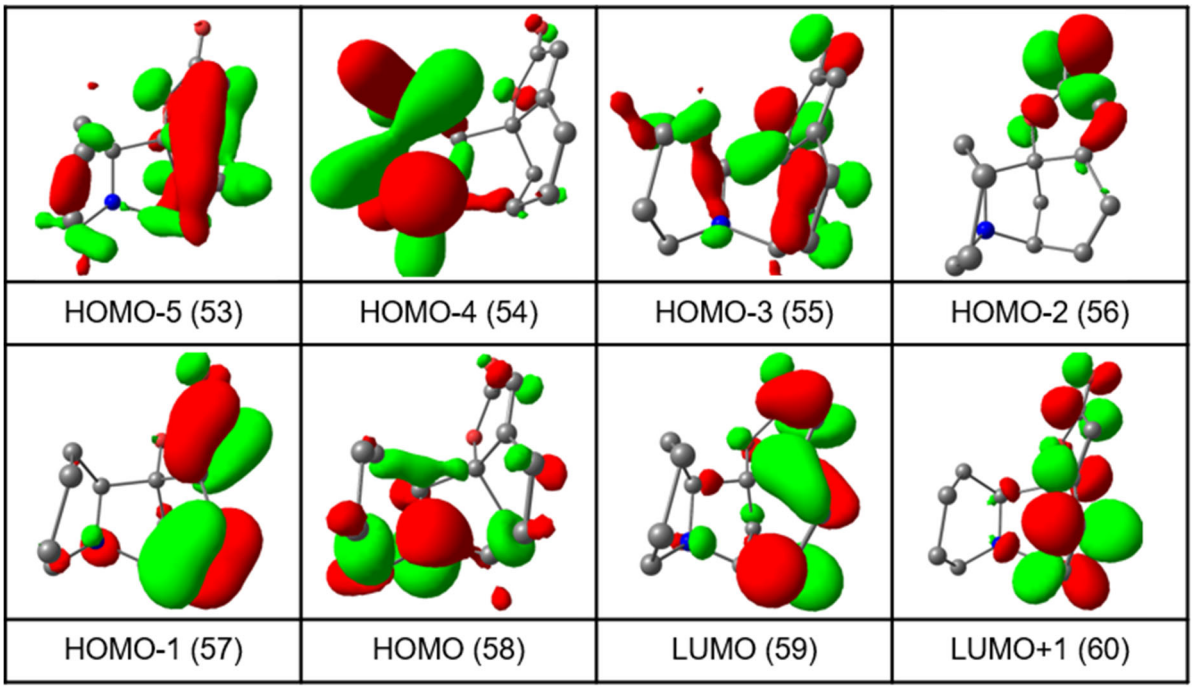


Figure S33. Molecular orbitals of conformer 1d, allosecurinine (contour value = 0.05)

Wavelength (nm)	Oscillator Strength	Rotatory Strength	Contributions	Assignments & notes
416.99	**0.0520**	**–52.0201**	**98.4% H → L**	**Nitrogen lone pair → π*, minor absorption**
267.31	0.0036	16.4208	95.6% H-2 → L, 2.36% H-2 → L+1	
261.94	**0.4029**	**–17.4734**	**94.7% H-1 → L**	**π → π*, major absorption**
238.52	0.0154	21.2031	83.2% H → L+1, 14.2% H-3 → L	
236.00	0.0409	22.1381	83.1% H-3 → L, 13.7% H → L+1	
213.74	0.0017	2.2752	78.6% H → L+2, 7.10% H-5 → L, 6.70% H-6 → L, 3.81% H-4 → L	
212.60	0.0037	7.6093	27.2% H-6 → L, 26.7% H-5 → L, 20.2% H-4 → L, 18.4% H → L+2, 2.75% H-7 → L	
208.90	0.0370	3.3846	74.0% H-4 → L, 10.4% H-5 → L, 9.77% H-6 → L, 3.70% H-7 → L	
202.11	0.0100	–2.8976	50.9% H-6 → L, 45.0% H-5 → L, 2.65% H-1 → L+1	

Table S10. Excitation energies (wavelength in nm), oscillator strength, rotatory strength (velocity) and orbital contributions of each excited state of conformer 1d, allosecurinine. Excitation energies over 200 nm were only included. H: HOMO, L: LUMO

7.5 Conformer 2a, allosecurinine

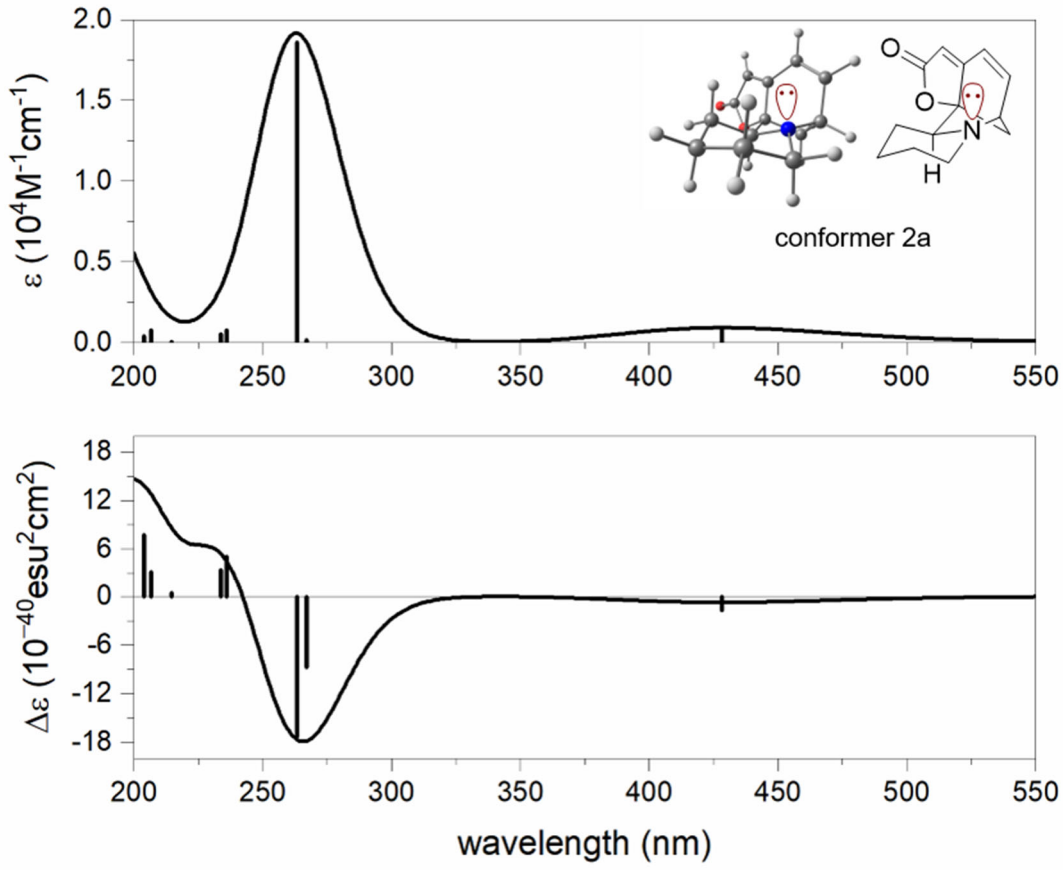


Figure S34. Calculated absorption and ECD spectra of conformer 2a, allosecurinine.

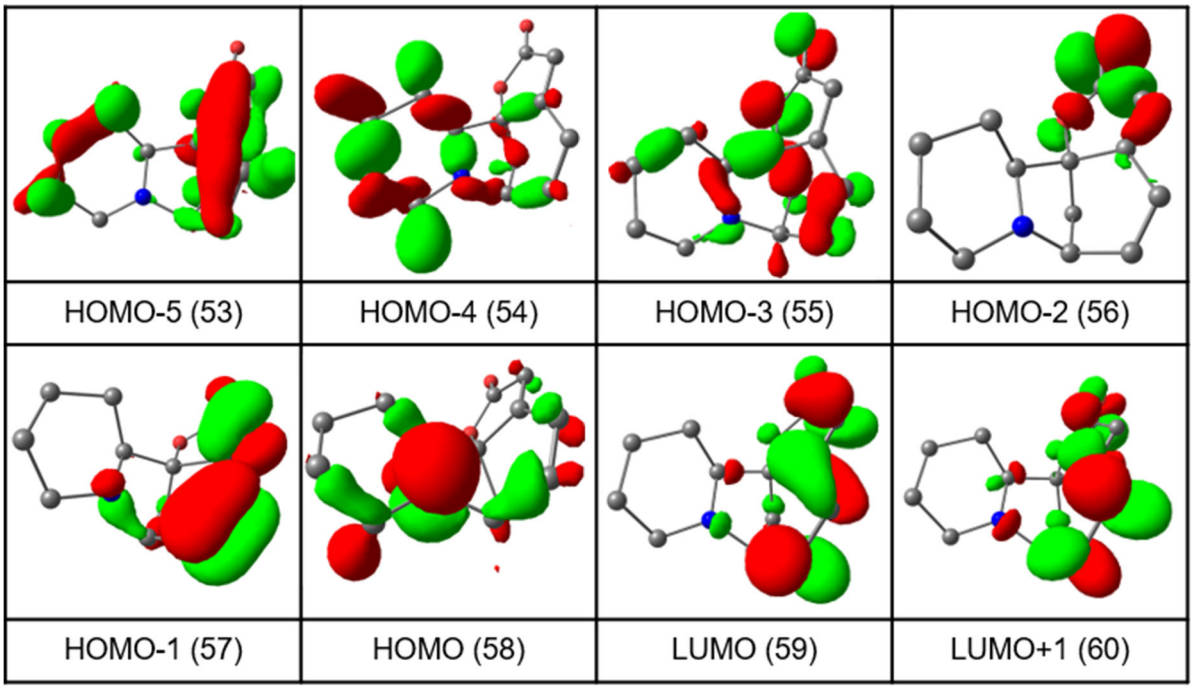


Figure S35. Molecular orbitals of conformer 2a, allosecurinine (contour value = 0.05).

Wavelength (nm)	Oscillator Strength	Rotatory Strength	Contributions	Assignments & notes
428.25	**0.0224**	**–4.2073**	**98.6% H → L**	**Nitrogen lone pair → π*, diminished intensity**
266.94	0.0038	–21.8909	95.8% H-2 → L, 2.38% H-2 → L+1	
263.19	**0.4649**	**–43.2254**	**95.7% H-1 → L**	**π → π*, major absorption**
235.93	0.0189	12.6932	67.9% H → L+1, 29.6% H-3 → L	
233.59	0.0133	8.4537	68.3% H-3 → L, 29.3% H → L+1	
214.47	0.0009	1.1283	53.8% H-4 → L, 35.4% H-5 → L, 4.07% H-8 → L, 2.49% H-9 → L	
206.65	0.0195	7.9207	95.5% H → L+2, 2.66% H → L+3	
203.94	0.0105	19.3951	51.2% H-5 → L, 42.6% H-4 → L, 2.02% H-1 → L+1	

Table S11. Excitation energies (wavelength in nm), oscillator strength, rotatory strength (velocity) and orbital contributions of each excited state of conformer 2a, allosecurinine. Excitation energies over 200 nm were only included. H: HOMO, L: LUMO

7.6 Conformer 2b, allosecurinine

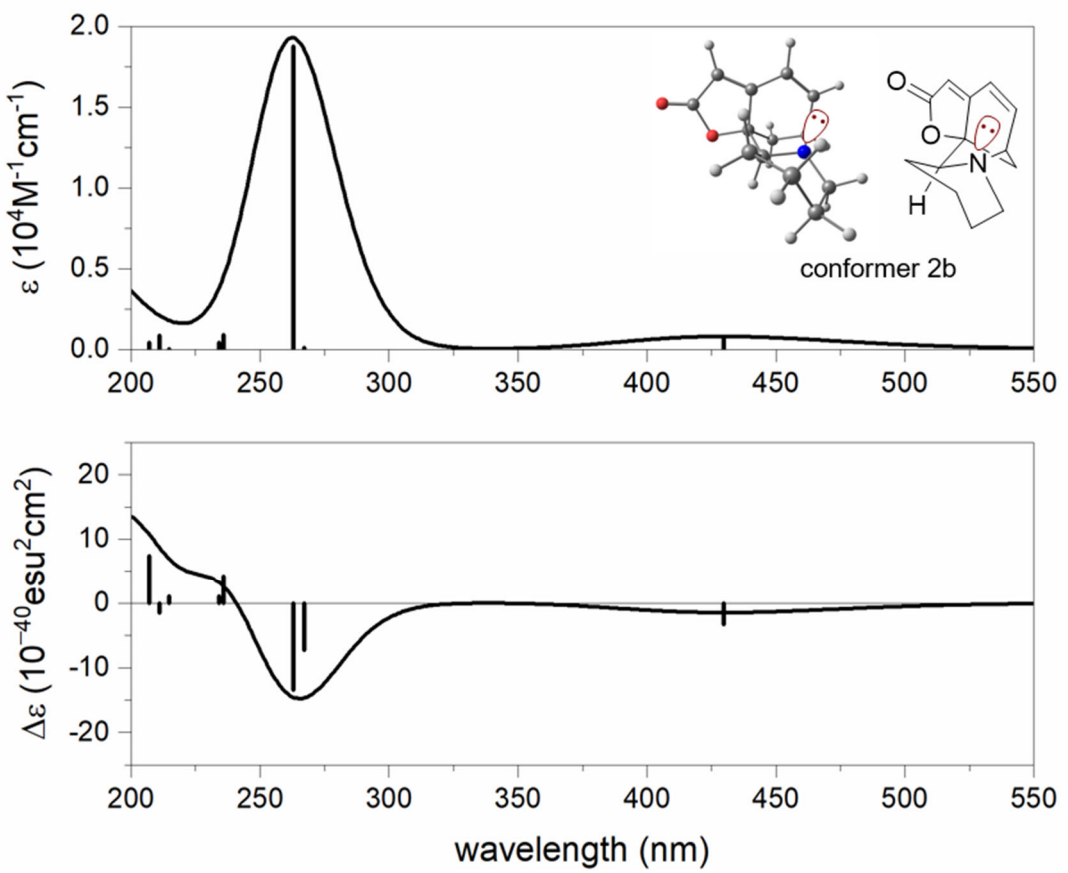


Figure S36. Calculated absorption and ECD spectra of conformer 2b, allosecurinine.

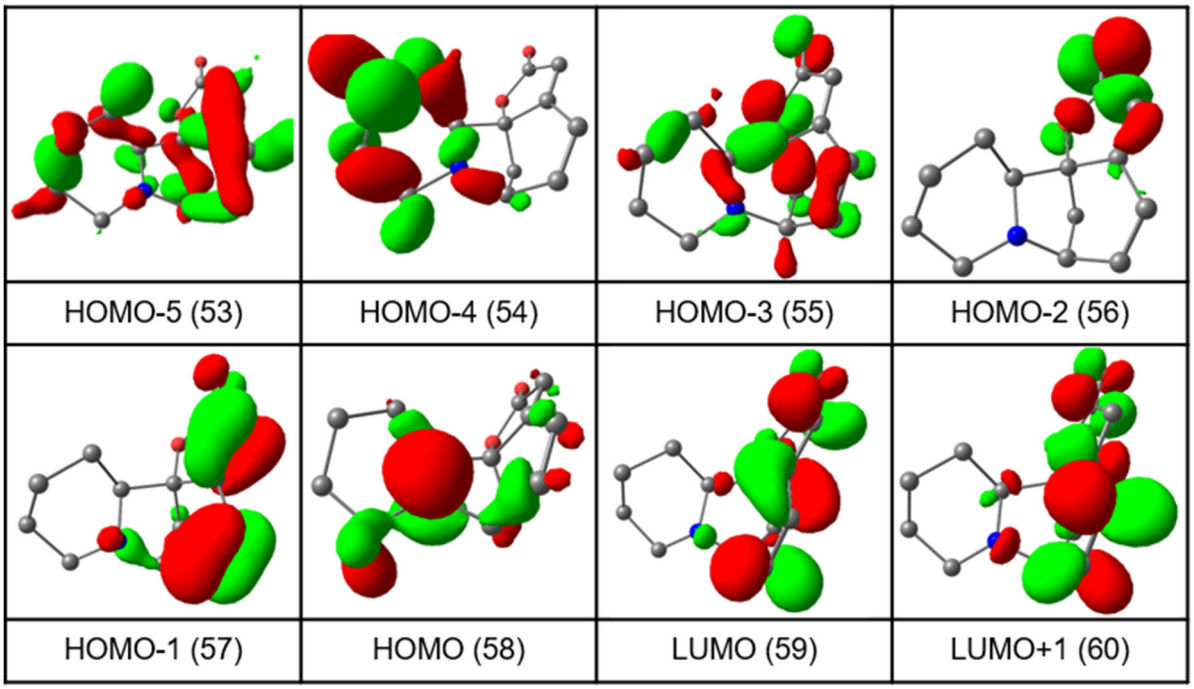


Figure S37. Molecular orbitals of conformer 2b, allosecurinine (contour value = 0.05).

Wavelength (nm)	Oscillator Strength	Rotatory Strength	Contributions	Assignments & notes
429.79	**0.0195**	**–8.5088**	**98.8% H → L**	**Nitrogen lone pair → π*, diminished intensity**
267.11	0.0028	–18.7652	96.0% H-2 → L, 2.33% H-2 → L+1	
262.84	**0.4689**	**–34.7718**	**96.0% H-1 → L**	**π → π*, major absorption**
235.88	0.0222	11.0064	61.2% H → L+1, 36.1% H-3 → L	
234.04	0.0107	2.7471	61.8% H-3 → L, 35.9% H → L+1	
214.7	0.0011	2.7362	81.2% H-5 → L, 5.73% H-4 → L, 5.22% H-8 → L, 2.50% H-6 → L	
210.9	0.0216	–4.0168	96.9% H → L+2	
207.1	0.0102	19.2212	92.3% H-4 → L, 5.52% H-5 → L	

Table S12. Excitation energies (wavelength in nm), oscillator strength, rotatory strength (velocity) and orbital contributions of each excited state of conformer 2b, allosecurinine. Excitation energies over 200 nm were only included. H: HOMO, L: LUMO.

7.7 Results of TDDFT calculation: relation between conformation and ECD spectra

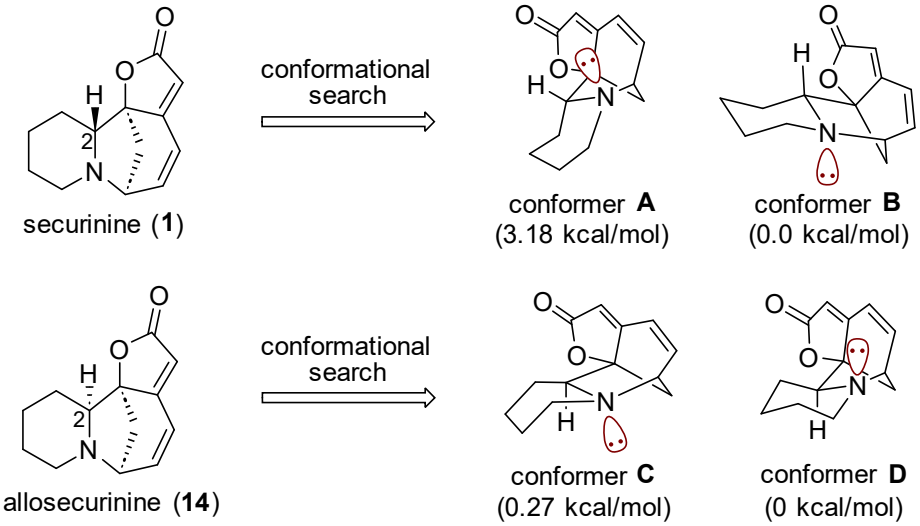


Figure S38. Conformational search of securinine (**1**) and allosecurinine (**14**).

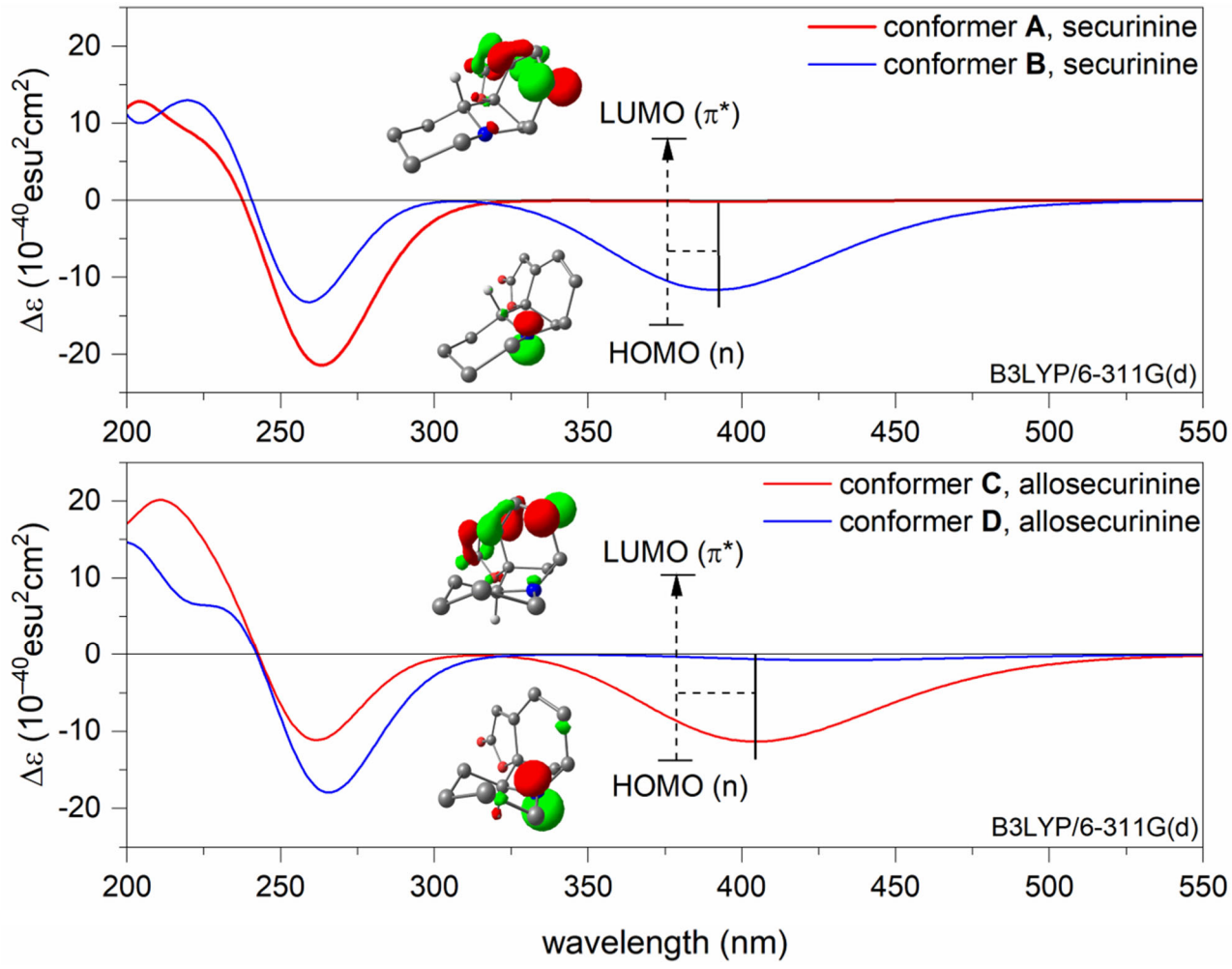
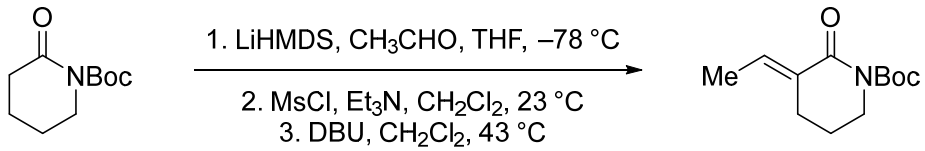


Figure S39. Calculated ECD spectra of securinine (**1**) and allosecurinine (**14**).

During calculations, five different conformers of **1** and six different conformers of **14** were obtained (Figure S12 and S24). Notably, only a subset of these conformers reproduced the observed ECD spectra (Figure S13 and S25). The conformers were categorized into two groups based on the orientation of the nitrogen lone pair in relation to the conjugated π system. The representative lowest-energy conformers from each group are displayed in Figure S38. As depicted in Figure S39, their TDDFT-simulated ECD spectra displayed distinct patterns. Only conformer **B** of **1** and conformer **C** of **14** reproduced the spectroscopically observed two strong negative ECD features at 340 nm and 250 nm, respectively, although TDDFT-calculated transition energies were underestimated to 405 nm and 270 nm (Figure S39).

TDDFT computations showed that the lowest-energy ECD features of securinine (**1**), allosecurinine (**14**) and suffruticosine are all associated with the same electronic transition, from N lone pair to the π* CT transition. Regardless of conformations, the experimentally observed negative feature at 250 nm and the positive feature at 210 nm, could be reproduced. Bands 2 and 3 are associated with π to π* and N lone pair to higher π*, respectively, which are not affected by the configuration of C2. These assignments and similarity of structures prove the chirality of only C7 and C9. Our findings also suggest that the band 3 in suffruticosine is attributed to the positioning of its N1 lone pair in the opposite orientation of the conjugated π-system (O2, O3–C15).

8. Experimental Procedures and Physical Data for Newly Synthesized Compounds



15 67% (3 steps) **16**

8.1 Unsaturated δ-lactam 16

15 was prepared in one step.[14] Solution of **15** (7.15 g, 29.6 mmol, 1.0 eq) in 30 mL THF was slowly added into prepared LiHMDS solution (1.0 M in THF, 32.6 mL, 32.6 mmol, 1.1 eq) via cannula at –78 °C, and the mixture was stirred at –78 °C for 0.5 h. Acetaldehyde solution (3 M in THF, 19.7 mL, 59.3 mmol, 2.0 eq) was added dropwise via syringe, and the reaction mixture was stirred for additional 1 h at –78 °C. The reaction mixture was quenched by slowly adding saturated aqueous ammonium chloride solution (100 mL). The aqueous layer was extracted with ethyl acetate (3 × 100 mL), and the combined organic layers were dried over anhydrous magnesium sulfate. The resulting filtrate was concentrated under reduced pressure.

The resulting crude was dissolved in dichloromethane (150 mL) and cooled to 0 °C. Methanesulfonyl chloride (4.6 mL, 59.3 mmol, 2.0 eq) was added, followed by triethylamine (12.5 mL, 88.8 mmol, 3.0 eq) at 0 °C. The reaction mixture was warmed to 23 °C and stirred for 20 h. The reaction mixture was quenched by adding water (100 mL). The aqueous layer was extracted with dichloromethane (3 × 100 mL), and the combined organic layers were dried over anhydrous magnesium sulfate. The resulting filtrate was concentrated under reduced pressure.

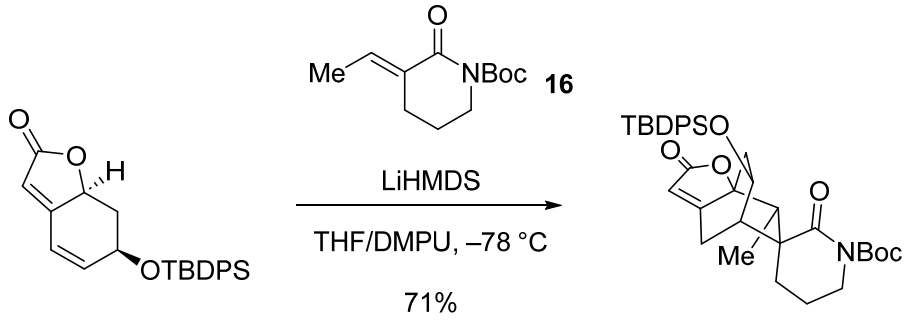
The resulting crude was dissolved in dichloromethane (150 mL). 1,8-Diazabicyclo-[5.4.0]undec-7-ene (5.3 mL, 35.6 mmol, 1.2 eq) was added dropwise and the solution was refluxed for 16 h. The reaction mixture was quenched by adding saturated aqueous ammonium chloride solution (100 mL). The aqueous layer was extracted with dichloromethane (3 × 100 mL), and the combined organic layers were dried over anhydrous magnesium sulfate. The resulting filtrate was concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 6 cm, ht. 14 cm; eluent: ethyl acetate/hexane = 1/4) to afford **16** (4.5 g, 67%) as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (qt, J = 7.2, 2.2 Hz, 1H), 3.68 – 3.63 (m, 2H), 2.46 – 2.39 (m, 2H), 1.87 – 1.79 (m, 2H), 1.73 (dt, J = 7.3, 1.4 Hz, 3H), 1.50 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 165.62, 153.38, 137.62, 131.06, 82.90, 46.01, 28.25, 24.31, 22.40, 14.26.

HRMS (ESI): Calculated for $C_{12}H_{19}NO_3$ $[M+Na]^+$: 248.1258, found: 248.1259.

TLC (ethyl acetate/hexane = 1/4) R*f*: 0.23 (UV, $KMnO_4$).



17 **20**

8.2 Boc-protected spiro-δ-lactam 20

17 (118 mg, 0.302 mmol, 1.0 eq) in THF (1.0 mL) was slowly added to solution of LiHMDS (0.5 M in THF, 0.66 mL, 0.332 mmol, 1.1 eq) via syringe at –78 °C. The yellow solution was stirred for 15 min. Solution of **16** (75 mg, 0.332 mmol, 1.1 eq) in THF/DMPU (1.1 mL/0.66 mL) was then added dropwise into the reaction mixture. The mixture instantly turned into red, and was stirred for additional 4 h at –78 °C. The reaction mixture was quenched by adding with precooled aqueous ammonium chloride solution (1.0 mL) at 0 °C, and the mixture was vigorously stirred until reaching room temperature. The aqueous layer was extracted with ethyl acetate (3 × 10 mL), and the combined organic layers were washed with water (3 × 10 mL). The combined layers were dried over anhydrous sodium sulfate. The resulting filtrate was concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 2 cm, ht. 12 cm; eluent: ethyl acetate/hexane = 1/10 to 1/5 to 1/2) to afford **20** (132 mg, 71%) as a white foam.

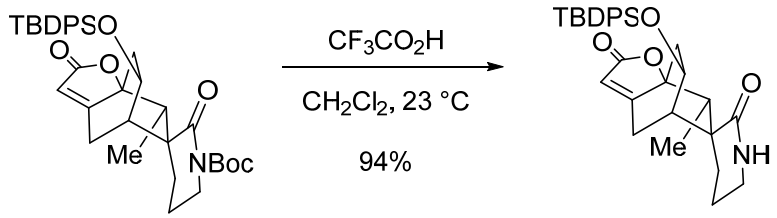
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 7.3 Hz, 2H), 7.48 (d, J = 7.3 Hz, 2H), 7.39 (dd, J = 9.6, 7.3 Hz, 2H), 7.33 (t, J = 8.1 Hz, 4H), 5.75 (s, 1H), 4.21 (d, J = 9.0 Hz, 1H), 3.28 (q, J = 7.3, 5.2 Hz, 3H), 3.15 (d, J = 19.7 Hz, 1H), 2.76 (dd, J = 13.1, 9.1 Hz, 1H), 2.41 (d, J = 19.7 Hz, 1H), 1.75 (d, J = 3.6 Hz, 1H), 1.67 – 1.60 (m, 1H), 1.59 – 1.50 (m, 3H), 1.31 – 1.26 (m, 1H), 1.23 (s, 9H), 1.02 (s, 9H), 0.56 (d, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.70, 173.84, 171.53, 154.88, 135.89, 135.70, 134.47, 132.97, 130.16, 130.14, 128.10, 127.99, 112.36, 86.55, 83.04, 65.75, 47.55, 46.82, 41.84, 37.91, 35.65, 27.82, 27.14, 26.95, 20.88, 19.09, 18.32, 9.18.

HRMS (ESI): Calculated for $C_{36}H_{45}NO_6Si$ $[M+Na]^+$: 638.2909, found: 638.2905.

TLC (ethyl acetate/hexane = 1/3) R*f*: 0.29 (UV, $KMnO_4$).

$[\alpha]_D^{25}$: –0.84 (c = 2.0, $CHCl_3$).



20 **21**

83 Spiro-δ-lactam 21

Trifluoroacetic acid (0.15 mL, 1.96 mmol, 30 eq) was added to the solution of **20** (40 mg, 0.065 mmol, 1.0 eq) in dichloromethane (1.5 mL) at 23 °C. The reaction mixture was stirred for 16 h. The resulting mixture was evaporated to remove residual acid, and neutralized with saturated aqueous sodium bicarbonate (1.5 mL). The aqueous layer was extracted with dichloromethane (3 × 3.0 mL) and the combined organic layers were dried over anhydrous sodium sulfate. The resulting filtrate was concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 2 cm, ht. 7 cm; eluent: ethyl acetate/hexane = 2/1) to afford **21** (31.5 mg, 94%) as white crystalline solid.

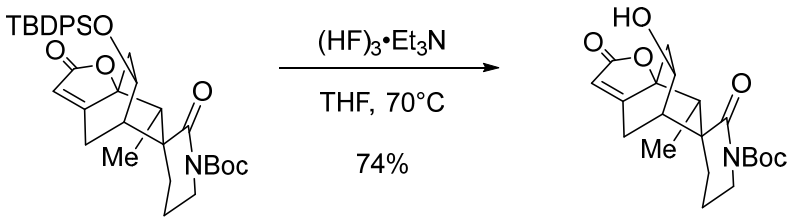
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.63 – 7.56 (m, 2H), 7.55 – 7.50 (m, 2H), 7.43 – 7.30 (m, 6H), 5.75 (s, 1H), 5.17 (s, 1H), 4.46 – 4.39 (m, 1H), 3.22 – 3.14 (m, 2H), 3.14 – 3.04 (m, 1H), 2.91 (dd, J = 12.0, 6.6 Hz, 1H), 2.74 (dd, J = 12.7, 9.5 Hz, 1H), 2.57 – 2.48 (m, 1H), 1.74 (q, J = 2.9 Hz, 1H), 1.64 – 1.38 (m, 5H), 1.03 (s, 9H), 0.56 (d, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 174.39, 173.84, 172.00, 135.93, 135.80, 134.22, 133.40, 129.98, 129.86, 127.93, 127.89, 112.20, 86.40, 66.01, 44.42, 41.76, 41.44, 38.88, 36.59, 27.20, 25.11, 21.25, 19.21, 17.28, 9.02.

HRMS (ESI): Calculated for $C_{31}H_{37}NO_4Si$ $[M+Na]^+$: 538.2385, found: 538.2382.

TLC (ethyl acetate/hexanes = 2/1) R*f*: 0.30 ($KMnO_4$).

$[\alpha]_D^{25}$: 34.9 (c = 1.0, $CHCl_3$).



20 **22**

8.4 Alcohol 22

Triethylamine trihydrofluoride (549 mg, 3.41 mmol, 15.0 eq) was added to **20** (140 mg, 0.227 mmol, 1.0 equiv.) in THF (4.5 mL) at 23 °C. The reaction mixture was stirred at 70 °C for 18 h. The reaction mixture was quenched by slowly adding aqueous sodium bicarbonate solution (8.0 mL). The aqueous layer was extracted with ethyl acetate (3 × 8.0 mL), and the combined organic layers were washed with brine (1 × 8.0 mL). The combined layers were dried over anhydrous sodium sulfate. The resulting filtrate was concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 2 cm, ht. 8 cm; eluent: ethyl acetate/hexane = 1/2 to 2/1) afford **22** (64 mg, 75%) as a white foam.

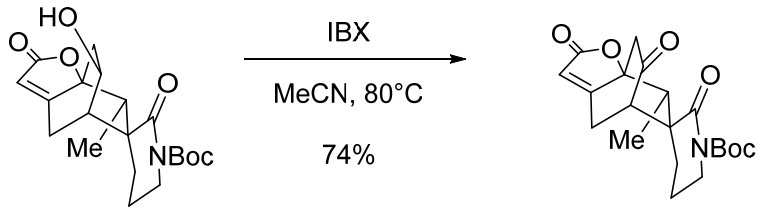
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 (t, J = 2.0 Hz, 1H), 4.25 (dtd, J = 9.4, 3.2, 1.3 Hz, 1H), 3.75 – 3.69 (m, 1H), 3.54 – 3.45 (m, 1H), 3.37 (q, J = 7.3 Hz, 1H), 3.16 (dt, J = 19.9, 2.5 Hz, 1H), 2.79 (dd, J = 13.0, 9.5 Hz, 1H), 2.64 (ddt, J = 20.0, 3.2, 1.7 Hz, 1H), 2.37 (q, J = 3.0 Hz, 1H), 1.97 – 1.87 (m, 2H), 1.81 – 1.72 (m, 3H), 1.48 (s, 9H), 1.41 – 1.35 (m, 1H), 0.64 (d, J = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 176.02, 173.65, 171.27, 154.10, 112.51, 86.17, 83.29, 64.30, 48.18, 47.31, 41.09, 39.37, 36.22, 28.16, 26.95, 20.93, 18.94, 9.20.

HRMS (ESI): Calculated for $C_{20}H_{27}NO_6$ $[M+Na]^+$: 400.1731, found: 400.1738.

TLC (ethyl acetate/hexane = 2/1) R*f*: 0.17 ($KMnO_4$).

$[\boldsymbol{\alpha}]_D^{25}$: –27.7 (c = 0.5, $CHCl_3$).



22 **23**

8.5 Ketone 23

2-iodobenzoic acid (222 mg, 0.794 mmol, 2.0 eq) was added to **22** (150 mg, 0.397 mmol, 1.0 eq) in acetonitrile (8.0 mL) at 23 °C. The reaction mixture was stirred at 80 °C for 8 h. The resulting mixture was cooled to 23 °C, and was filtrated through Celite pad. The filtrate was concentrated under reduced pressure and diluted by ethyl acetate (16.0 mL). The organic layer was washed with 10% aqueous sodium thiosulfate (1 × 8.0 mL), followed by washing with saturated aqueous sodium bicarbonate solution (1 × 8.0 mL). The organic layer was dried over anhydrous sodium sulfate. The resulting filtrate was concentrated under reduced pressure. The resulting crude residue was purified by flash column chromatography (silica gel: diam. 2 cm, ht. 10 cm; eluent: ethyl acetate/hexane = 2/1) to afford **23** (111 mg, 74%) as a white foam.

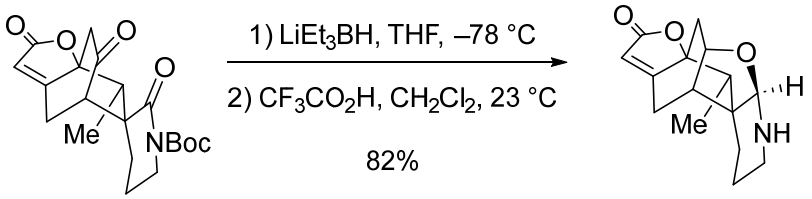
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.89 (t, J = 2.1 Hz, 1H), 3.67 – 3.54 (m, 2H), 3.36 (d, J = 18.0 Hz, 1H), 3.30 (d, J = 7.3 Hz, 1H), 3.00 (dt, J = 20.5, 2.6 Hz, 1H), 2.73 (dt, J = 20.4, 2.5 Hz, 1H), 2.68 (d, J = 3.0 Hz, 1H), 2.29 (d, J = 18.0 Hz, 1H), 1.97 (ddd, J = 13.7, 9.2, 4.0 Hz, 1H), 1.82 (dtt, J = 13.9, 10.1, 4.0 Hz, 2H), 1.66 (ddd, J = 14.1, 7.1, 3.6 Hz, 1H), 1.48 (s, 9H), 0.86 (d, J = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.49, 175.25, 172.60, 167.06, 152.93, 114.55, 85.60, 83.89, 51.30, 48.36, 46.85, 46.70, 39.99, 28.08, 26.84, 23.77, 19.96, 9.74.

HRMS (ESI): Calculated for $C_{20}H_{25}NO_6$ $[M+Na]^+$: 398.1575, found: 398.1577

TLC (ethyl acetate/hexane = 2/1) R*f*: 0.17 ($KMnO_4$).

$[\alpha]_D^{25}$: 7.9 (c = 0.5, $CHCl_3$).



23 **25**

8.6 Hemiaminal ether 25

Lithium triethylborohydride (1 M in THF, 0.12 mmol, 2.2 eq) was added to the stirred solution of **23** (21 mg, 0.056 mmol, 1.0 eq) in THF (1.1 mL) at –78 °C. The reaction mixture was stirred for 0.5 h and quenched with saturated ammonium chloride. The aqueous layer was extracted with ethyl acetate (3 × 5 mL). The combined layers were dried over anhydrous sodium sulfate. The resulting filtrate was concentrated and was used without further purification.

The resulting crude was dissolved in dichloromethane (1.4 mL) and trifluoroacetic acid (0.14 mL) was added at 23 °C. The reaction mixture was stirred for 20 h and evaporated. The crude mixture was neutralized with saturated sodium bicarbonate solution, and aqueous layer was extracted with ethyl acetate (3 × 5 mL). The combined layers were dried over anhydrous sodium sulfate and concentrated in vacuo. The resulting crude residue was purified by flash column chromatography (aluminum oxide, basic: diam. 1 cm, ht. 5 cm; eluent: dichloromethane/methanol = 50/1) to afford **25** (12 mg, 82%) as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$): δ 5.68 (t, J = 2.1 Hz, 1H), 4.49 (t, J = 6.1 Hz, 1H), 4.36 (s, 1H), 3.03 – 2.97 (m, 2H), 2.74 (t, J = 2.6 Hz, 2H), 2.63 (ddd, J = 12.2, 9.7, 5.0 Hz, 1H), 2.19 (q, J = 7.4, 6.9 Hz, 2H), 1.71 – 1.63 (m, 3H), 1.52 (ddt, J = 12.2, 8.1, 4.1 Hz, 2H), 0.74 (d, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 173.75, 171.42, 111.51, 94.32, 85.41, 75.17, 44.65, 43.07, 42.23, 40.33, 34.19, 24.54, 20.97, 20.43, 9.27.

HRMS (ESI): Calculated for $C_{15}H_{19}NO_3$ $[M+H]^+$: 262.1438, found: 262.1430.

TLC (dichloromethane/methanol = 10/1) R*f*: 0.25 ($KMnO_4$).

$[\boldsymbol{\alpha}]_D^{25}$: –55.9 (c = 1.0, $CHCl_3$).

9. Single Crystal X-Ray Diffraction Analysis of Spiro-δ-lactam 21

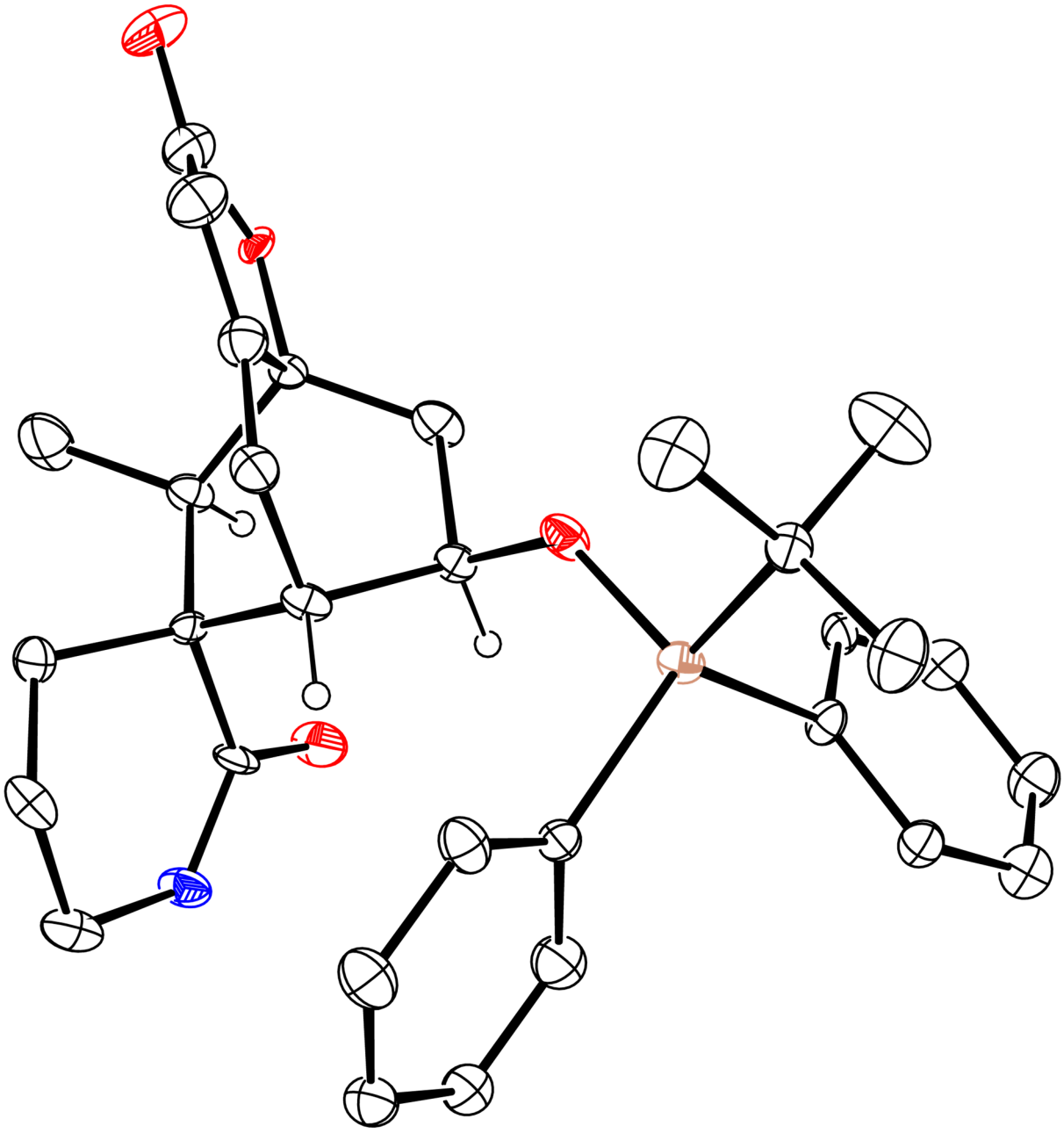


Figure S40. Thermal ellipsoid representation of compound **21.**

Table S13. Crystal data and structure refinement for spiro-δ-lactam **21**.

Empirical formula	$C_{31}H_{37}NO_4Si$	
Formula weight	515.70	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 16.1777(13) Å	α = 90°
	b = 11.4407(11) Å	β = 116.100(2)°
	c = 17.1218(15) Å	γ = 90°
Volume	2845.8(4) $Å^3$	
Z	4	
Density (calculated)	1.204 Mg/m^3	
Absorption coefficient	0.118 mm^{-1}	
F(000)	1104	
Crystal size	0.312 x 0.086 x 0.072 mm^3	
Theta range for data collection	2.520 to 27.216°.	
Index ranges	–20<=h<=20, –14<=k<=14, –22<=l<=21	
Reflections collected	33521	
Independent reflections	12303 [R(int) = 0.1482]	
Completeness to theta = 25.242°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.1871	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12303 / 2143 / 993	
Goodness-of-fit on F^2	1.055	
Final R indices [I>2sigma(I)]	R1 = 0.1336, wR2 = 0.3058	
R indices (all data)	R1 = 0.1834, wR2 = 0.3350	
Absolute structure parameter	0.45(15)	
Largest diff. peak and hole	0.655 and –0.787 $e \cdot Å^{-3}$	

Table S14. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for spiro-δ-lactam **21**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	8416(5)	5439(8)	3930(5)	41(2)
C(2)	7684(7)	5886(10)	3839(6)	26(2)
N(3)	7056(6)	6218(9)	3060(5)	33(2)
C(4)	6198(7)	6837(13)	2829(7)	40(3)
C(5)	5937(7)	6893(12)	3585(7)	34(3)
C(6)	6800(7)	7086(10)	4424(7)	32(3)
C(7)	7471(6)	6054(9)	4625(5)	22(2)
C(8)	8407(7)	6265(10)	5466(6)	27(2)
C(9)	8586(10)	7516(12)	5801(9)	52(4)
C(16)	6731(8)	5057(11)	5489(7)	31(3)
C(17)	7027(6)	4886(10)	4752(6)	25(2)
C(18)	7695(6)	3866(10)	4996(6)	23(2)
C(19)	8543(7)	4155(11)	5857(7)	32(3)
O(20)	7272(5)	2838(7)	5114(5)	31(2)
Si(21)	6667(2)	1859(3)	4379(2)	24(1)
C(22)	6222(7)	864(10)	4987(7)	28(2)
C(23)	5546(10)	-10(13)	4381(10)	49(3)
C(24)	5747(10)	1547(14)	5464(10)	52(4)
C(25)	7025(9)	205(16)	5672(10)	59(4)
C(56)	9143(7)	6409(10)	38(7)	27(2)
C(57)	8661(6)	6099(10)	615(6)	22(2)
C(58)	7618(6)	6148(9)	55(6)	22(2)
C(59)	7355(8)	7325(11)	-444(8)	35(3)
O(60)	7357(5)	5241(7)	-574(5)	33(2)
Si(61)	6900(2)	3986(3)	-506(2)	30(1)
C(62)	6910(9)	3115(12)	-1433(8)	42(3)
C(63)	7865(10)	3132(15)	-1415(11)	61(4)
C(64)	6226(10)	3771(15)	-2291(9)	58(4)
C(65)	6566(10)	1887(15)	-1481(10)	58(4)
C(10)	8430(17)	5310(20)	6174(15)	19(4)
O(11)	9129(11)	5705(15)	6982(11)	24(3)
O(12)	9234(17)	6370(20)	8240(14)	66(6)

C(13)	8778(17)	6040(30)	7500(16)	42(5)
C(14)	7763(18)	5630(30)	7078(17)	44(5)
C(15)	7570(30)	5330(30)	6270(30)	34(5)
C(26)	7484(10)	946(16)	4047(13)	24(4)
C(27)	7134(9)	199(17)	3335(13)	30(4)
C(28)	7724(12)	-522(17)	3159(10)	40(5)
C(29)	8665(11)	-494(18)	3697(11)	41(4)
C(30)	9015(9)	254(18)	4409(10)	36(4)
C(31)	8425(11)	974(15)	4584(10)	24(4)
C(32)	5782(10)	2690(15)	3374(10)	26(4)
C(33)	5980(10)	2851(18)	2669(12)	41(4)
C(34)	5382(12)	3491(18)	1952(10)	37(4)
C(35)	4587(11)	3969(15)	1941(9)	37(4)
C(36)	4389(10)	3808(16)	2646(10)	41(4)
C(37)	4987(10)	3168(16)	3363(8)	34(4)
O(41)	7739(15)	6930(30)	1860(20)	37(7)
C(42)	8531(14)	6710(30)	1988(16)	29(5)
N(43)	9101(11)	6160(20)	2690(12)	31(4)
C(44)	10088(13)	5960(30)	3030(12)	35(5)
C(45)	10403(14)	6280(20)	2329(13)	36(5)
C(46)	9927(13)	7370(20)	1857(13)	31(5)
C(47)	8882(13)	7131(19)	1330(14)	27(4)
C(48)	8341(16)	8278(17)	876(14)	29(4)
C(49)	8820(20)	9420(20)	1300(20)	63(8)
C(50)	8130(30)	8130(50)	-110(20)	28(5)
O(51)	8048(14)	9310(20)	-312(13)	38(4)
O(52)	8649(15)	10510(20)	-978(16)	53(6)
C(53)	8657(18)	9600(30)	-642(17)	35(5)
C(54)	9223(19)	8570(20)	-538(17)	34(5)
C(55)	8910(30)	7740(30)	-180(20)	34(6)
C(66)	5650(11)	4340(18)	-634(17)	23(4)
C(67)	5275(14)	5455(16)	-843(15)	36(5)
C(68)	4389(13)	5665(14)	-940(14)	36(5)
C(69)	3877(11)	4761(17)	-827(15)	40(5)
C(70)	4252(13)	3646(15)	-618(16)	36(5)
C(71)	5139(13)	3436(14)	-521(17)	34(5)
C(72)	7598(13)	3390(20)	596(10)	29(4)
C(73)	7377(14)	3760(20)	1255(13)	37(5)

C(74)	7922(14)	3420(20)	2110(11)	43(5)
C(75)	8688(13)	2718(19)	2306(9)	46(5)
C(76)	8909(12)	2350(17)	1647(12)	51(5)
C(77)	8364(13)	2686(19)	793(11)	42(5)
C(10B)	8480(40)	5510(50)	6060(30)	25(7)
O(11B)	9280(30)	5420(30)	6990(20)	29(6)
O(12B)	9320(20)	5840(40)	8330(20)	39(8)
C(13B)	8780(30)	5600(40)	7580(20)	30(6)
C(14B)	7880(30)	6040(40)	7100(30)	36(6)
C(15B)	7610(50)	5560(50)	6260(50)	33(7)
C(26B)	7490(20)	1160(30)	4060(30)	28(6)
C(27B)	7198(17)	390(30)	3360(30)	34(7)
C(28B)	7840(20)	-250(30)	3210(20)	36(6)
C(29B)	8770(20)	-120(30)	3750(20)	41(6)
C(30B)	9065(17)	650(30)	4450(20)	33(6)
C(31B)	8420(20)	1290(30)	4610(20)	33(6)
C(32B)	5680(20)	2470(30)	3410(20)	31(6)
C(33B)	5851(19)	2840(30)	2720(20)	34(6)
C(34B)	5220(20)	3550(30)	2070(20)	41(6)
C(35B)	4414(19)	3890(30)	2116(19)	33(6)
C(36B)	4241(17)	3520(30)	2803(19)	35(6)
C(37B)	4870(20)	2810(30)	3447(16)	39(6)
O(41B)	7778(17)	6620(30)	1830(30)	39(8)
C(42B)	8606(16)	6470(30)	2050(20)	25(5)
N(43B)	9123(15)	5760(20)	2676(15)	30(5)
C(44B)	10064(16)	5390(30)	2953(16)	37(5)
C(45B)	10425(15)	5670(30)	2289(15)	28(5)
C(46B)	10065(15)	6870(20)	1921(16)	31(5)
C(47B)	9008(15)	6880(20)	1428(16)	23(5)
C(48B)	8620(20)	8110(20)	1030(20)	37(6)
C(49B)	9290(30)	9130(30)	1360(30)	78(11)
C(50B)	8210(40)	8120(60)	20(30)	25(5)
O(51B)	7886(18)	9200(20)	-590(17)	36(5)
O(52B)	8450(20)	10210(30)	-1340(20)	68(9)
C(53B)	8520(20)	9360(30)	-910(20)	37(6)
C(54B)	9070(30)	8270(30)	-740(20)	38(6)
C(55B)	8930(30)	7510(40)	-270(30)	30(6)
C(66B)	5727(15)	4140(20)	-660(20)	26(5)

C(67B)	5276(17)	3217(19)	-490(20)	38(6)
C(68B)	4379(17)	3357(19)	-600(20)	40(6)
C(69B)	3934(14)	4420(20)	-873(19)	41(6)
C(70B)	4384(16)	5350(18)	-1045(18)	40(6)
C(71B)	5281(17)	5210(20)	-940(19)	31(5)
C(72B)	7515(19)	3360(30)	704(13)	40(6)
C(73B)	7257(19)	3850(30)	1306(17)	43(6)
C(74B)	7711(18)	3530(30)	2177(15)	43(6)
C(75B)	8422(16)	2720(20)	2445(11)	40(6)
C(76B)	8679(15)	2230(20)	1842(14)	44(6)
C(77B)	8226(17)	2550(20)	971(13)	40(6)

Table S15. Bond lengths [Å] and angles [°] for spiro-δ-lactam **21**.

O(1)-C(2)	1.235(12)
C(2)-N(3)	1.329(11)
C(2)-C(7)	1.540(12)
N(3)-C(4)	1.450(14)
N(3)-H(3)	0.8800
C(4)-C(5)	1.530(14)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.515(14)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-C(7)	1.537(13)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(17)	1.577(15)
C(7)-C(8)	1.583(12)
C(8)-C(10B)	1.30(5)
C(8)-C(9)	1.521(16)
C(8)-C(10)	1.62(2)
C(8)-H(8)	1.0000
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(16)-C(15)	1.46(4)
C(16)-C(17)	1.547(15)
C(16)-C(15B)	1.57(7)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.519(15)
C(17)-H(17)	1.0000
C(18)-O(20)	1.420(13)
C(18)-C(19)	1.545(13)
C(18)-H(18)	1.0000
C(19)-C(10)	1.47(3)
C(19)-C(10B)	1.61(6)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
O(20)-Si(21)	1.647(8)
Si(21)-C(26B)	1.83(3)
Si(21)-C(32B)	1.86(2)
Si(21)-C(22)	1.887(11)
Si(21)-C(32)	1.935(11)
Si(21)-C(26)	1.955(14)
C(22)-C(23)	1.509(17)
C(22)-C(25)	1.514(18)
C(22)-C(24)	1.555(17)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(56)-C(55B)	1.36(4)
C(56)-C(57)	1.546(14)
C(56)-C(55)	1.57(4)
C(56)-H(56A)	0.9900
C(56)-H(56B)	0.9900
C(57)-C(58)	1.532(13)
C(57)-C(47B)	1.54(3)
C(57)-C(47)	1.62(3)
C(57)-H(57)	1.04(13)
C(58)-O(60)	1.419(13)
C(58)-C(59)	1.551(16)

C(58)-H(58)	0.99(12)	C(28)-H(28)	0.9500
C(59)-C(50)	1.45(5)	C(29)-C(30)	1.3900
C(59)-C(50B)	1.55(6)	C(29)-H(29)	0.9500
C(59)-H(59A)	0.9900	C(30)-C(31)	1.3900
C(59)-H(59B)	0.9900	C(30)-H(30)	0.9500
O(60)-Si(61)	1.643(9)	C(31)-H(31)	0.9500
Si(61)-C(66B)	1.81(2)	C(32)-C(33)	1.3900
Si(61)-C(72)	1.850(13)	C(32)-C(37)	1.3900
Si(61)-C(62)	1.881(12)	C(33)-C(34)	1.3900
Si(61)-C(66)	1.978(16)	C(33)-H(33)	0.9500
Si(61)-C(72B)	1.993(17)	C(34)-C(35)	1.3900
C(62)-C(65)	1.50(2)	C(34)-H(34)	0.9500
C(62)-C(63)	1.53(2)	C(35)-C(36)	1.3900
C(62)-C(64)	1.59(2)	C(35)-H(35)	0.9500
C(63)-H(63A)	0.9800	C(36)-C(37)	1.3900
C(63)-H(63B)	0.9800	C(36)-H(36)	0.9500
C(63)-H(63C)	0.9800	C(37)-H(37)	0.9500
C(64)-H(64A)	0.9800	O(41)-C(42)	1.226(18)
C(64)-H(64B)	0.9800	C(42)-N(43)	1.307(19)
C(64)-H(64C)	0.9800	C(42)-C(47)	1.547(19)
C(65)-H(65A)	0.9800	N(43)-C(44)	1.457(19)
C(65)-H(65B)	0.9800	N(43)-H(43)	0.8800
C(65)-H(65C)	0.9800	C(44)-C(45)	1.54(2)
C(10)-O(11)	1.42(3)	C(44)-H(44A)	0.9900
C(10)-C(15)	1.47(5)	C(44)-H(44B)	0.9900
O(11)-C(13)	1.30(3)	C(45)-C(46)	1.50(2)
O(12)-C(13)	1.21(3)	C(45)-H(45A)	0.9900
C(13)-C(14)	1.55(4)	C(45)-H(45B)	0.9900
C(14)-C(15)	1.33(5)	C(46)-C(47)	1.551(19)
C(14)-H(14)	0.9500	C(46)-H(46A)	0.9900
C(26)-C(27)	1.3900	C(46)-H(46B)	0.9900
C(26)-C(31)	1.3900	C(47)-C(48)	1.58(2)
C(27)-C(28)	1.3900	C(48)-C(49)	1.53(2)
C(27)-H(27)	0.9500	C(48)-C(50)	1.57(5)
C(28)-C(29)	1.3900	C(48)-H(48)	1.0000

C(49)-H(49A)	0.9800	O(12B)-C(13B)	1.22(5)
C(49)-H(49B)	0.9800	C(13B)-C(14B)	1.41(6)
C(49)-H(49C)	0.9800	C(14B)-C(15B)	1.41(9)
C(50)-C(55)	1.39(7)	C(14B)-H(14G)	0.9500
C(50)-O(51)	1.39(6)	C(26B)-C(27B)	1.3900
O(51)-C(53)	1.37(4)	C(26B)-C(31B)	1.3900
O(52)-C(53)	1.19(3)	C(27B)-C(28B)	1.3900
C(53)-C(54)	1.45(4)	C(27B)-H(27G)	0.9500
C(54)-C(55)	1.35(5)	C(28B)-C(29B)	1.3900
C(54)-H(54)	0.9500	C(28B)-H(28G)	0.9500
C(66)-C(67)	1.3900	C(29B)-C(30B)	1.3900
C(66)-C(71)	1.3900	C(29B)-H(29G)	0.9500
C(67)-C(68)	1.3900	C(30B)-C(31B)	1.3900
C(67)-H(67)	0.9500	C(30B)-H(30G)	0.9500
C(68)-C(69)	1.3900	C(31B)-H(31G)	0.9500
C(68)-H(68)	0.9500	C(32B)-C(33B)	1.3900
C(69)-C(70)	1.3900	C(32B)-C(37B)	1.3900
C(69)-H(69)	0.9500	C(33B)-C(34B)	1.3900
C(70)-C(71)	1.3900	C(33B)-H(33G)	0.9500
C(70)-H(70)	0.9500	C(34B)-C(35B)	1.3900
C(71)-H(71)	0.9500	C(34B)-H(34G)	0.9500
C(72)-C(73)	1.3900	C(35B)-C(36B)	1.3900
C(72)-C(77)	1.3900	C(35B)-H(35G)	0.9500
C(73)-C(74)	1.3900	C(36B)-C(37B)	1.3900
C(73)-H(73)	0.9500	C(36B)-H(36G)	0.9500
C(74)-C(75)	1.3900	C(37B)-H(37G)	0.9500
C(74)-H(74)	0.9500	O(41B)-C(42B)	1.24(2)
C(75)-C(76)	1.3900	C(42B)-N(43B)	1.31(2)
C(75)-H(75)	0.9500	C(42B)-C(47B)	1.54(2)
C(76)-C(77)	1.3900	N(43B)-C(44B)	1.45(2)
C(76)-H(76)	0.9500	N(43B)-H(43G)	0.8800
C(77)-H(77)	0.9500	C(44B)-C(45B)	1.52(2)
C(10B)-O(11B)	1.56(6)	C(44B)-H(44G)	0.9900
C(10B)-C(15B)	1.58(10)	C(44B)-H(44H)	0.9900
O(11B)-C(13B)	1.57(6)	C(45B)-C(46B)	1.52(2)

C(45B)-H(45G)	0.9900	C(74B)-H(74G)	0.9500
C(45B)-H(45H)	0.9900	C(75B)-C(76B)	1.3900
C(46B)-C(47B)	1.54(2)	C(75B)-H(75G)	0.9500
C(46B)-H(46G)	0.9900	C(76B)-C(77B)	1.3900
C(46B)-H(46H)	0.9900	C(76B)-H(76G)	0.9500
C(47B)-C(48B)	1.57(2)	C(77B)-H(77G)	0.9500
C(48B)-C(49B)	1.52(3)		
C(48B)-C(50B)	1.54(5)	O(1)-C(2)-N(3)	120.8(9)
C(48B)-H(48G)	1.0000	O(1)-C(2)-C(7)	120.8(8)
C(49B)-H(49G)	0.9800	N(3)-C(2)-C(7)	118.4(9)
C(49B)-H(49H)	0.9800	C(2)-N(3)-C(4)	129.1(9)
C(49B)-H(49I)	0.9800	C(2)-N(3)-H(3)	115.4
C(50B)-O(51B)	1.56(6)	C(4)-N(3)-H(3)	115.4
C(50B)-C(55B)	1.62(8)	N(3)-C(4)-C(5)	112.2(8)
O(51B)-C(53B)	1.38(4)	N(3)-C(4)-H(4A)	109.2
O(52B)-C(53B)	1.19(4)	C(5)-C(4)-H(4A)	109.2
C(53B)-C(54B)	1.49(5)	N(3)-C(4)-H(4B)	109.2
C(54B)-C(55B)	1.27(6)	C(5)-C(4)-H(4B)	109.2
C(54B)-H(54G)	0.9500	H(4A)-C(4)-H(4B)	107.9
C(66B)-C(67B)	1.3900	C(6)-C(5)-C(4)	109.0(9)
C(66B)-C(71B)	1.3900	C(6)-C(5)-H(5A)	109.9
C(67B)-C(68B)	1.3900	C(4)-C(5)-H(5A)	109.9
C(67B)-H(67G)	0.9500	C(6)-C(5)-H(5B)	109.9
C(68B)-C(69B)	1.3900	C(4)-C(5)-H(5B)	109.9
C(68B)-H(68G)	0.9500	H(5A)-C(5)-H(5B)	108.3
C(69B)-C(70B)	1.3900	C(5)-C(6)-C(7)	111.5(9)
C(69B)-H(69G)	0.9500	C(5)-C(6)-H(6A)	109.3
C(70B)-C(71B)	1.3900	C(7)-C(6)-H(6A)	109.3
C(70B)-H(70G)	0.9500	C(5)-C(6)-H(6B)	109.3
C(71B)-H(71G)	0.9500	C(7)-C(6)-H(6B)	109.3
C(72B)-C(73B)	1.3900	H(6A)-C(6)-H(6B)	108.0
C(72B)-C(77B)	1.3900	C(6)-C(7)-C(2)	107.9(8)
C(73B)-C(74B)	1.3900	C(6)-C(7)-C(17)	111.2(8)
C(73B)-H(73G)	0.9500	C(2)-C(7)-C(17)	107.8(8)
C(74B)-C(75B)	1.3900	C(6)-C(7)-C(8)	112.7(8)

C(2)-C(7)-C(8)	108.8(8)	C(10)-C(19)-C(18)	110.0(12)
C(17)-C(7)-C(8)	108.4(8)	C(18)-C(19)-C(10B)	107(2)
C(10B)-C(8)-C(9)	113(2)	C(10)-C(19)-H(19A)	109.7
C(10B)-C(8)-C(7)	109(2)	C(18)-C(19)-H(19A)	109.7
C(9)-C(8)-C(7)	115.7(9)	C(10)-C(19)-H(19B)	109.7
C(9)-C(8)-C(10)	114.4(13)	C(18)-C(19)-H(19B)	109.7
C(7)-C(8)-C(10)	106.0(11)	H(19A)-C(19)-H(19B)	108.2
C(9)-C(8)-H(8)	106.7	C(18)-O(20)-Si(21)	128.0(7)
C(7)-C(8)-H(8)	106.7	O(20)-Si(21)-C(26B)	105.0(12)
C(10)-C(8)-H(8)	106.7	O(20)-Si(21)-C(32B)	114.7(13)
C(8)-C(9)-H(9A)	109.5	C(26B)-Si(21)-C(32B)	110.4(17)
C(8)-C(9)-H(9B)	109.5	O(20)-Si(21)-C(22)	103.3(5)
H(9A)-C(9)-H(9B)	109.5	C(26B)-Si(21)-C(22)	113.8(15)
C(8)-C(9)-H(9C)	109.5	C(32B)-Si(21)-C(22)	109.5(12)
H(9A)-C(9)-H(9C)	109.5	O(20)-Si(21)-C(32)	107.7(6)
H(9B)-C(9)-H(9C)	109.5	C(22)-Si(21)-C(32)	118.4(7)
C(15)-C(16)-C(17)	105.9(19)	O(20)-Si(21)-C(26)	109.6(6)
C(17)-C(16)-C(15B)	104(3)	C(22)-Si(21)-C(26)	108.0(7)
C(15)-C(16)-H(16A)	110.5	C(32)-Si(21)-C(26)	109.6(8)
C(17)-C(16)-H(16A)	110.5	C(23)-C(22)-C(25)	108.5(12)
C(15)-C(16)-H(16B)	110.5	C(23)-C(22)-C(24)	108.6(10)
C(17)-C(16)-H(16B)	110.5	C(25)-C(22)-C(24)	107.3(11)
H(16A)-C(16)-H(16B)	108.7	C(23)-C(22)-Si(21)	110.9(8)
C(18)-C(17)-C(16)	108.1(8)	C(25)-C(22)-Si(21)	108.8(8)
C(18)-C(17)-C(7)	112.1(8)	C(24)-C(22)-Si(21)	112.6(9)
C(16)-C(17)-C(7)	109.2(9)	C(22)-C(23)-H(23A)	109.5
C(18)-C(17)-H(17)	109.1	C(22)-C(23)-H(23B)	109.5
C(16)-C(17)-H(17)	109.1	H(23A)-C(23)-H(23B)	109.5
C(7)-C(17)-H(17)	109.1	C(22)-C(23)-H(23C)	109.5
O(20)-C(18)-C(17)	110.3(8)	H(23A)-C(23)-H(23C)	109.5
O(20)-C(18)-C(19)	108.8(8)	H(23B)-C(23)-H(23C)	109.5
C(17)-C(18)-C(19)	108.9(9)	C(22)-C(24)-H(24A)	109.5
O(20)-C(18)-H(18)	109.6	C(22)-C(24)-H(24B)	109.5
C(17)-C(18)-H(18)	109.6	H(24A)-C(24)-H(24B)	109.5
C(19)-C(18)-H(18)	109.6	C(22)-C(24)-H(24C)	109.5

H(24A)-C(24)-H(24C)	109.5	C(58)-C(59)-H(59B)	109.6
H(24B)-C(24)-H(24C)	109.5	H(59A)-C(59)-H(59B)	108.1
C(22)-C(25)-H(25A)	109.5	C(58)-O(60)-Si(61)	125.3(7)
C(22)-C(25)-H(25B)	109.5	O(60)-Si(61)-C(66B)	112.3(9)
H(25A)-C(25)-H(25B)	109.5	O(60)-Si(61)-C(72)	107.6(9)
C(22)-C(25)-H(25C)	109.5	O(60)-Si(61)-C(62)	103.3(5)
H(25A)-C(25)-H(25C)	109.5	C(66B)-Si(61)-C(62)	109.1(11)
H(25B)-C(25)-H(25C)	109.5	C(72)-Si(61)-C(62)	116.0(9)
C(55B)-C(56)-C(57)	111(2)	O(60)-Si(61)-C(66)	106.5(7)
C(57)-C(56)-C(55)	103.6(17)	C(72)-Si(61)-C(66)	108.9(10)
C(57)-C(56)-H(56A)	111.0	C(62)-Si(61)-C(66)	113.8(8)
C(55)-C(56)-H(56A)	111.0	O(60)-Si(61)-C(72B)	110.6(11)
C(57)-C(56)-H(56B)	111.0	C(66B)-Si(61)-C(72B)	101.7(13)
C(55)-C(56)-H(56B)	111.0	C(62)-Si(61)-C(72B)	120.1(10)
H(56A)-C(56)-H(56B)	109.0	C(65)-C(62)-C(63)	111.1(12)
C(58)-C(57)-C(47B)	114.2(11)	C(65)-C(62)-C(64)	107.5(11)
C(58)-C(57)-C(56)	108.6(8)	C(63)-C(62)-C(64)	107.4(13)
C(47B)-C(57)-C(56)	111.1(11)	C(65)-C(62)-Si(61)	113.6(10)
C(58)-C(57)-C(47)	105.2(10)	C(63)-C(62)-Si(61)	111.1(9)
C(56)-C(57)-C(47)	108.0(11)	C(64)-C(62)-Si(61)	105.6(9)
C(58)-C(57)-H(57)	113(7)	C(62)-C(63)-H(63A)	109.5
C(47B)-C(57)-H(57)	106(7)	C(62)-C(63)-H(63B)	109.5
C(56)-C(57)-H(57)	103(7)	H(63A)-C(63)-H(63B)	109.5
C(47)-C(57)-H(57)	118(7)	C(62)-C(63)-H(63C)	109.5
O(60)-C(58)-C(57)	109.0(8)	H(63A)-C(63)-H(63C)	109.5
O(60)-C(58)-C(59)	107.4(8)	H(63B)-C(63)-H(63C)	109.5
C(57)-C(58)-C(59)	109.6(8)	C(62)-C(64)-H(64A)	109.5
O(60)-C(58)-H(58)	97(7)	C(62)-C(64)-H(64B)	109.5
C(57)-C(58)-H(58)	115(7)	H(64A)-C(64)-H(64B)	109.5
C(59)-C(58)-H(58)	118(7)	C(62)-C(64)-H(64C)	109.5
C(50)-C(59)-C(58)	110(2)	H(64A)-C(64)-H(64C)	109.5
C(50B)-C(59)-C(58)	105(2)	H(64B)-C(64)-H(64C)	109.5
C(50)-C(59)-H(59A)	109.6	C(62)-C(65)-H(65A)	109.5
C(58)-C(59)-H(59A)	109.6	C(62)-C(65)-H(65B)	109.5
C(50)-C(59)-H(59B)	109.6	H(65A)-C(65)-H(65B)	109.5

C(62)-C(65)-H(65C)	109.5	C(30)-C(31)-H(31)	120.0
H(65A)-C(65)-H(65C)	109.5	C(26)-C(31)-H(31)	120.0
H(65B)-C(65)-H(65C)	109.5	C(33)-C(32)-C(37)	120.0
O(11)-C(10)-C(15)	106(2)	C(33)-C(32)-Si(21)	118.3(9)
O(11)-C(10)-C(19)	117.8(19)	C(37)-C(32)-Si(21)	121.6(9)
C(15)-C(10)-C(19)	109.4(19)	C(32)-C(33)-C(34)	120.0
O(11)-C(10)-C(8)	105.3(17)	C(32)-C(33)-H(33)	120.0
C(15)-C(10)-C(8)	111(2)	C(34)-C(33)-H(33)	120.0
C(19)-C(10)-C(8)	107.2(15)	C(35)-C(34)-C(33)	120.0
C(13)-O(11)-C(10)	110.9(19)	C(35)-C(34)-H(34)	120.0
O(12)-C(13)-O(11)	124(3)	C(33)-C(34)-H(34)	120.0
O(12)-C(13)-C(14)	128(3)	C(36)-C(35)-C(34)	120.0
O(11)-C(13)-C(14)	107(2)	C(36)-C(35)-H(35)	120.0
C(15)-C(14)-C(13)	106(3)	C(34)-C(35)-H(35)	120.0
C(15)-C(14)-H(14)	126.9	C(35)-C(36)-C(37)	120.0
C(13)-C(14)-H(14)	126.9	C(35)-C(36)-H(36)	120.0
C(14)-C(15)-C(16)	135(4)	C(37)-C(36)-H(36)	120.0
C(14)-C(15)-C(10)	109(3)	C(36)-C(37)-C(32)	120.0
C(16)-C(15)-C(10)	116(3)	C(36)-C(37)-H(37)	120.0
C(27)-C(26)-C(31)	120.0	C(32)-C(37)-H(37)	120.0
C(27)-C(26)-Si(21)	121.1(9)	O(41)-C(42)-N(43)	122(2)
C(31)-C(26)-Si(21)	118.7(9)	O(41)-C(42)-C(47)	119.4(18)
C(26)-C(27)-C(28)	120.0	N(43)-C(42)-C(47)	118.9(16)
C(26)-C(27)-H(27)	120.0	C(42)-N(43)-C(44)	130.4(17)
C(28)-C(27)-H(27)	120.0	C(42)-N(43)-H(43)	114.8
C(29)-C(28)-C(27)	120.0	C(44)-N(43)-H(43)	114.8
C(29)-C(28)-H(28)	120.0	N(43)-C(44)-C(45)	109.4(15)
C(27)-C(28)-H(28)	120.0	N(43)-C(44)-H(44A)	109.8
C(30)-C(29)-C(28)	120.0	C(45)-C(44)-H(44A)	109.8
C(30)-C(29)-H(29)	120.0	N(43)-C(44)-H(44B)	109.8
C(28)-C(29)-H(29)	120.0	C(45)-C(44)-H(44B)	109.8
C(29)-C(30)-C(31)	120.0	H(44A)-C(44)-H(44B)	108.2
C(29)-C(30)-H(30)	120.0	C(46)-C(45)-C(44)	110.4(17)
C(31)-C(30)-H(30)	120.0	C(46)-C(45)-H(45A)	109.6
C(30)-C(31)-C(26)	120.0	C(44)-C(45)-H(45A)	109.6

C(46)-C(45)-H(45B)	109.6	O(52)-C(53)-C(54)	130(3)
C(44)-C(45)-H(45B)	109.6	O(51)-C(53)-C(54)	107(2)
H(45A)-C(45)-H(45B)	108.1	C(55)-C(54)-C(53)	106(3)
C(45)-C(46)-C(47)	109.4(16)	C(55)-C(54)-H(54)	126.8
C(45)-C(46)-H(46A)	109.8	C(53)-C(54)-H(54)	126.8
C(47)-C(46)-H(46A)	109.8	C(54)-C(55)-C(50)	110(3)
C(45)-C(46)-H(46B)	109.8	C(54)-C(55)-C(56)	134(3)
C(47)-C(46)-H(46B)	109.8	C(50)-C(55)-C(56)	115(4)
H(46A)-C(46)-H(46B)	108.2	C(67)-C(66)-C(71)	120.0
C(42)-C(47)-C(46)	106.7(15)	C(67)-C(66)-Si(61)	121.7(11)
C(42)-C(47)-C(48)	108.5(16)	C(71)-C(66)-Si(61)	118.3(11)
C(46)-C(47)-C(48)	111.3(15)	C(68)-C(67)-C(66)	120.0
C(42)-C(47)-C(57)	107.0(17)	C(68)-C(67)-H(67)	120.0
C(46)-C(47)-C(57)	113.1(16)	C(66)-C(67)-H(67)	120.0
C(48)-C(47)-C(57)	110.1(14)	C(67)-C(68)-C(69)	120.0
C(49)-C(48)-C(50)	116(3)	C(67)-C(68)-H(68)	120.0
C(49)-C(48)-C(47)	114.8(18)	C(69)-C(68)-H(68)	120.0
C(50)-C(48)-C(47)	104(2)	C(70)-C(69)-C(68)	120.0
C(49)-C(48)-H(48)	107.2	C(70)-C(69)-H(69)	120.0
C(50)-C(48)-H(48)	107.2	C(68)-C(69)-H(69)	120.0
C(47)-C(48)-H(48)	107.2	C(69)-C(70)-C(71)	120.0
C(48)-C(49)-H(49A)	109.5	C(69)-C(70)-H(70)	120.0
C(48)-C(49)-H(49B)	109.5	C(71)-C(70)-H(70)	120.0
H(49A)-C(49)-H(49B)	109.5	C(70)-C(71)-C(66)	120.0
C(48)-C(49)-H(49C)	109.5	C(70)-C(71)-H(71)	120.0
H(49A)-C(49)-H(49C)	109.5	C(66)-C(71)-H(71)	120.0
H(49B)-C(49)-H(49C)	109.5	C(73)-C(72)-C(77)	120.0
C(55)-C(50)-O(51)	106(4)	C(73)-C(72)-Si(61)	117.1(11)
C(55)-C(50)-C(59)	115(4)	C(77)-C(72)-Si(61)	122.6(11)
O(51)-C(50)-C(59)	123(3)	C(72)-C(73)-C(74)	120.0
C(55)-C(50)-C(48)	111(3)	C(72)-C(73)-H(73)	120.0
O(51)-C(50)-C(48)	97(3)	C(74)-C(73)-H(73)	120.0
C(59)-C(50)-C(48)	104(3)	C(75)-C(74)-C(73)	120.0
C(53)-O(51)-C(50)	109(3)	C(75)-C(74)-H(74)	120.0
O(52)-C(53)-O(51)	123(3)	C(73)-C(74)-H(74)	120.0

C(76)-C(75)-C(74)	120.0	C(28B)-C(29B)-H(29G)	120.0
C(76)-C(75)-H(75)	120.0	C(30B)-C(29B)-H(29G)	120.0
C(74)-C(75)-H(75)	120.0	C(31B)-C(30B)-C(29B)	120.0
C(77)-C(76)-C(75)	120.0	C(31B)-C(30B)-H(30G)	120.0
C(77)-C(76)-H(76)	120.0	C(29B)-C(30B)-H(30G)	120.0
C(75)-C(76)-H(76)	120.0	C(30B)-C(31B)-C(26B)	120.0
C(76)-C(77)-C(72)	120.0	C(30B)-C(31B)-H(31G)	120.0
C(76)-C(77)-H(77)	120.0	C(26B)-C(31B)-H(31G)	120.0
C(72)-C(77)-H(77)	120.0	C(33B)-C(32B)-C(37B)	120.0
C(8)-C(10B)-O(11B)	126(4)	C(33B)-C(32B)-Si(21)	117.3(17)
C(8)-C(10B)-C(15B)	112(4)	C(37B)-C(32B)-Si(21)	120.8(18)
O(11B)-C(10B)-C(15B)	102(4)	C(32B)-C(33B)-C(34B)	120.0
C(8)-C(10B)-C(19)	118(4)	C(32B)-C(33B)-H(33G)	120.0
O(11B)-C(10B)-C(19)	93(3)	C(34B)-C(33B)-H(33G)	120.0
C(15B)-C(10B)-C(19)	103(4)	C(35B)-C(34B)-C(33B)	120.0
C(10B)-O(11B)-C(13B)	102(3)	C(35B)-C(34B)-H(34G)	120.0
O(12B)-C(13B)-C(14B)	128(4)	C(33B)-C(34B)-H(34G)	120.0
O(12B)-C(13B)-O(11B)	111(4)	C(34B)-C(35B)-C(36B)	120.0
C(14B)-C(13B)-O(11B)	111(3)	C(34B)-C(35B)-H(35G)	120.0
C(15B)-C(14B)-C(13B)	104(5)	C(36B)-C(35B)-H(35G)	120.0
C(15B)-C(14B)-H(14G)	128.2	C(37B)-C(36B)-C(35B)	120.0
C(13B)-C(14B)-H(14G)	128.2	C(37B)-C(36B)-H(36G)	120.0
C(14B)-C(15B)-C(16)	139(6)	C(35B)-C(36B)-H(36G)	120.0
C(14B)-C(15B)-C(10B)	109(5)	C(36B)-C(37B)-C(32B)	120.0
C(16)-C(15B)-C(10B)	111(5)	C(36B)-C(37B)-H(37G)	120.0
C(27B)-C(26B)-C(31B)	120.0	C(32B)-C(37B)-H(37G)	120.0
C(27B)-C(26B)-Si(21)	121(2)	O(41B)-C(42B)-N(43B)	123(2)
C(31B)-C(26B)-Si(21)	118(2)	O(41B)-C(42B)-C(47B)	119(2)
C(26B)-C(27B)-C(28B)	120.0	N(43B)-C(42B)-C(47B)	116.1(18)
C(26B)-C(27B)-H(27G)	120.0	C(42B)-N(43B)-C(44B)	131(2)
C(28B)-C(27B)-H(27G)	120.0	C(42B)-N(43B)-H(43G)	114.7
C(29B)-C(28B)-C(27B)	120.0	C(44B)-N(43B)-H(43G)	114.7
C(29B)-C(28B)-H(28G)	120.0	N(43B)-C(44B)-C(45B)	112.7(18)
C(27B)-C(28B)-H(28G)	120.0	N(43B)-C(44B)-H(44G)	109.0
C(28B)-C(29B)-C(30B)	120.0	C(45B)-C(44B)-H(44G)	109.0

N(43B)-C(44B)-H(44H)	109.0	C(59)-C(50B)-O(51B)	99(3)
C(45B)-C(44B)-H(44H)	109.0	C(48B)-C(50B)-C(55B)	109(4)
H(44G)-C(44B)-H(44H)	107.8	C(59)-C(50B)-C(55B)	101(4)
C(46B)-C(45B)-C(44B)	107.3(19)	O(51B)-C(50B)-C(55B)	102(4)
C(46B)-C(45B)-H(45G)	110.2	(53B)-O(51B)-C(50B)	107(3)
C(44B)-C(45B)-H(45G)	110.2	O(52B)-C(53B)-O(51B)	118(3)
C(46B)-C(45B)-H(45H)	110.2	O(52B)-C(53B)-C(54B)	133(3)
C(44B)-C(45B)-H(45H)	110.2	O(51B)-C(53B)-C(54B)	107(3)
H(45G)-C(45B)-H(45H)	108.5	C(55B)-C(54B)-C(53B)	115(4)
C(45B)-C(46B)-C(47B)	111.5(18)	C(55B)-C(54B)-H(54G)	122.3
C(45B)-C(46B)-H(46G)	109.3	C(53B)-C(54B)-H(54G)	122.3
C(47B)-C(46B)-H(46G)	109.3	C(54B)-C(55B)-C(56)	143(4)
C(45B)-C(46B)-H(46H)	109.3	C(54B)-C(55B)-C(50B)	106(4)
C(47B)-C(46B)-H(46H)	109.3	C(56)-C(55B)-C(50B)	112(4)
H(46G)-C(46B)-H(46H)	108.0	C(67B)-C(66B)-C(71B)	120.0
C(57)-C(47B)-C(46B)	111.6(18)	C(67B)-C(66B)-Si(61)	120.5(14)
C(57)-C(47B)-C(42B)	111(2)	C(71B)-C(66B)-Si(61)	119.5(14)
C(46B)-C(47B)-C(42B)	108.9(17)	C(68B)-C(67B)-C(66B)	120.0
C(57)-C(47B)-C(48B)	101.8(17)	C(68B)-C(67B)-H(67G)	120.0
C(46B)-C(47B)-C(48B)	112.2(18)	C(66B)-C(67B)-H(67G)	120.0
C(42B)-C(47B)-C(48B)	111.5(19)	C(67B)-C(68B)-C(69B)	120.0
C(49B)-C(48B)-C(50B)	107(3)	C(67B)-C(68B)-H(68G)	120.0
C(49B)-C(48B)-C(47B)	117(2)	C(69B)-C(68B)-H(68G)	120.0
C(50B)-C(48B)-C(47B)	113(3)	C(70B)-C(69B)-C(68B)	120.0
C(49B)-C(48B)-H(48G)	106.3	C(70B)-C(69B)-H(69G)	120.0
C(50B)-C(48B)-H(48G)	106.3	C(68B)-C(69B)-H(69G)	120.0
C(47B)-C(48B)-H(48G)	106.3	C(71B)-C(70B)-C(69B)	120.0
C(48B)-C(49B)-H(49G)	109.5	C(71B)-C(70B)-H(70G)	120.0
C(48B)-C(49B)-H(49H)	109.5	C(69B)-C(70B)-H(70G)	120.0
H(49G)-C(49B)-H(49H)	109.5	C(70B)-C(71B)-C(66B)	120.0
C(48B)-C(49B)-H(49I)	109.5	C(70B)-C(71B)-H(71G)	120.0
H(49G)-C(49B)-H(49I)	109.5	C(66B)-C(71B)-H(71G)	120.0
H(49H)-C(49B)-H(49I)	109.5	C(73B)-C(72B)-C(77B)	120.0
C(48B)-C(50B)-C(59)	115(4)	C(73B)-C(72B)-Si(61)	116.8(14)
C(48B)-C(50B)-O(51B)	128(4)	C(77B)-C(72B)-Si(61)	123.0(14)

C(74B)-C(73B)-C(72B)	120.0
C(74B)-C(73B)-H(73G)	120.0
C(72B)-C(73B)-H(73G)	120.0
C(73B)-C(74B)-C(75B)	120.0
C(73B)-C(74B)-H(74G)	120.0
C(75B)-C(74B)-H(74G)	120.0
C(76B)-C(75B)-C(74B)	120.0
C(76B)-C(75B)-H(75G)	120.0
C(74B)-C(75B)-H(75G)	120.0
C(75B)-C(76B)-C(77B)	120.0
C(75B)-C(76B)-H(76G)	120.0
C(77B)-C(76B)-H(76G)	120.0
C(76B)-C(77B)-C(72B)	120.0
C(76B)-C(77B)-H(77G)	120.0
C(72B)-C(77B)-H(77G)	120.0

Symmetry transformations used to generate equivalent atoms:

Table S16. Anisotropic displacement parameters ($Å^2$ x 10^3) for spiro-δ-lactam **21**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	35(4)	58(6)	32(4)	6(4)	17(3)	15(4)
C(2)	32(5)	30(6)	13(4)	9(4)	7(4)	1(5)
N(3)	22(4)	46(6)	23(4)	5(4)	5(3)	8(4)
C(4)	35(5)	50(7)	26(5)	7(5)	6(4)	-6(6)
C(5)	25(5)	36(6)	40(5)	16(5)	14(4)	5(5)
C(6)	34(5)	32(6)	31(5)	2(4)	15(4)	10(5)
C(7)	18(4)	24(5)	15(4)	-4(4)	0(3)	1(4)
C(8)	23(5)	30(6)	22(5)	2(4)	5(4)	-6(4)
C(9)	41(7)	42(8)	47(7)	3(6)	-5(6)	-4(6)
C(16)	33(5)	34(6)	32(5)	6(5)	20(4)	6(5)
C(17)	13(4)	34(6)	20(4)	4(4)	2(4)	-2(4)
C(18)	15(4)	27(5)	21(4)	0(4)	3(3)	2(4)
C(19)	18(5)	38(7)	30(5)	6(5)	2(4)	-3(5)
O(20)	23(4)	31(4)	28(4)	8(3)	4(3)	2(3)
Si(21)	11(1)	30(2)	23(1)	0(1)	-1(1)	1(1)
C(22)	31(5)	27(6)	31(5)	0(4)	19(4)	-2(5)
C(23)	45(7)	42(8)	65(9)	-10(7)	29(7)	-6(6)
C(24)	52(8)	57(9)	67(9)	-6(7)	45(7)	-9(7)
C(25)	38(7)	79(11)	67(9)	32(8)	31(7)	-1(7)
C(56)	13(4)	38(6)	34(5)	2(4)	15(4)	8(4)
C(57)	19(4)	31(6)	16(4)	-7(4)	7(3)	3(4)
C(58)	18(4)	23(5)	24(4)	-1(4)	9(4)	-11(4)
C(59)	27(5)	38(6)	36(6)	9(5)	10(4)	3(5)
O(60)	37(4)	31(4)	23(3)	-3(3)	4(3)	-12(4)
Si(61)	24(2)	28(2)	28(1)	-4(1)	3(1)	-7(1)
C(62)	41(6)	46(7)	36(6)	-29(5)	13(5)	-13(6)
C(63)	54(9)	62(10)	65(9)	-24(8)	22(7)	-22(8)
C(64)	60(9)	63(10)	40(7)	-16(7)	11(6)	-22(8)
C(65)	54(8)	57(9)	56(8)	-18(8)	19(7)	-5(8)
C(10)	19(6)	22(7)	18(6)	2(5)	12(4)	0(5)
O(11)	24(5)	26(6)	19(4)	-6(4)	8(4)	10(4)
O(12)	88(10)	65(11)	34(8)	-22(8)	17(7)	1(9)
C(13)	46(6)	42(7)	36(6)	-6(6)	15(5)	1(6)

C(14)	46(7)	51(8)	44(6)	-5(6)	27(5)	-2(6)
C(15)	35(7)	34(8)	36(6)	0(6)	17(5)	1(6)
C(26)	20(5)	25(7)	29(6)	-6(5)	11(4)	3(5)
C(27)	28(6)	29(7)	31(6)	-3(5)	12(4)	0(5)
C(28)	38(6)	40(7)	43(6)	-2(5)	19(5)	-1(5)
C(29)	38(6)	42(7)	48(6)	-5(5)	24(5)	5(5)
C(30)	29(6)	40(7)	39(6)	-2(6)	16(5)	0(5)
C(31)	23(5)	19(6)	25(5)	1(5)	6(4)	3(5)
C(32)	27(6)	22(6)	23(5)	-2(5)	4(4)	-5(5)
C(33)	42(6)	42(7)	39(6)	1(5)	18(5)	3(5)
C(34)	40(6)	37(6)	34(6)	-1(5)	15(5)	4(5)
C(35)	37(6)	36(6)	32(6)	1(5)	9(5)	0(5)
C(36)	32(6)	42(7)	45(7)	8(5)	15(5)	5(5)
C(37)	28(6)	33(7)	39(6)	5(5)	12(5)	2(5)
O(41)	51(10)	37(12)	33(8)	2(8)	26(7)	14(8)
C(42)	29(7)	29(7)	26(6)	1(5)	10(5)	-2(5)
N(43)	27(6)	32(7)	30(6)	0(5)	10(5)	-1(5)
C(44)	35(6)	36(7)	30(6)	3(5)	9(5)	1(6)
C(45)	32(6)	39(7)	35(6)	2(6)	13(5)	-1(6)
C(46)	29(6)	30(7)	29(6)	2(6)	8(5)	-4(6)
C(47)	24(6)	27(7)	27(6)	-3(5)	10(5)	-1(5)
C(48)	27(7)	29(7)	29(6)	-1(5)	11(5)	1(5)
C(49)	58(12)	62(13)	65(12)	-11(10)	22(10)	7(10)
C(50)	29(7)	28(7)	30(7)	-2(6)	16(5)	2(5)
O(51)	37(6)	39(6)	36(7)	-3(5)	15(5)	-3(5)
O(52)	48(9)	49(10)	57(10)	16(8)	20(8)	-17(8)
C(53)	34(7)	37(7)	34(7)	3(6)	16(5)	-4(5)
C(54)	34(7)	38(7)	34(7)	3(5)	20(5)	-8(6)
C(55)	32(7)	34(8)	35(7)	1(6)	13(5)	-1(6)
C(66)	20(6)	22(7)	26(6)	-5(5)	9(5)	1(5)
C(67)	33(7)	36(7)	36(7)	-1(6)	12(5)	-3(6)
C(68)	38(7)	35(7)	33(7)	-3(6)	13(5)	1(6)
C(69)	37(7)	41(7)	39(7)	0(6)	15(5)	0(6)
C(70)	33(7)	37(7)	41(7)	6(6)	20(5)	-2(6)
C(71)	33(7)	36(7)	34(6)	1(5)	16(5)	5(5)
C(72)	32(7)	30(7)	27(6)	4(5)	15(5)	-4(5)
C(73)	36(7)	39(7)	37(7)	3(5)	16(5)	3(6)
C(74)	46(7)	44(7)	37(7)	3(6)	18(5)	3(6)

C(75)	45(7)	47(7)	44(7)	3(6)	18(5)	0(6)
C(76)	48(7)	50(7)	50(7)	3(6)	17(5)	2(6)
C(77)	43(7)	40(7)	40(7)	3(6)	16(5)	-5(6)
C(10B)	25(8)	24(8)	25(8)	-4(6)	10(6)	1(6)
O(11B)	32(8)	31(8)	23(7)	-1(6)	12(5)	2(6)
O(12B)	49(12)	49(14)	25(10)	-4(10)	21(8)	5(10)
C(13B)	33(7)	32(8)	26(7)	0(6)	15(5)	-1(6)
C(14B)	41(8)	38(8)	36(8)	-3(6)	22(6)	1(6)
C(15B)	33(8)	34(9)	33(8)	-1(6)	15(6)	0(6)
C(26B)	25(8)	26(8)	30(8)	-2(6)	10(5)	1(6)
C(27B)	32(8)	34(8)	34(8)	-3(6)	12(5)	0(6)
C(28B)	35(8)	34(8)	37(8)	-1(6)	15(5)	-1(6)
C(29B)	37(8)	41(8)	46(8)	-1(6)	20(6)	1(6)
C(30B)	33(8)	32(8)	34(7)	0(6)	15(5)	-2(6)
C(31B)	30(8)	33(8)	35(8)	3(6)	13(5)	3(6)
C(32B)	32(8)	32(8)	27(8)	2(6)	12(5)	-2(6)
C(33B)	34(8)	36(8)	34(8)	0(6)	17(5)	2(6)
C(34B)	40(8)	43(8)	40(8)	0(6)	16(6)	1(6)
C(35B)	31(8)	34(8)	32(8)	-2(6)	13(5)	2(6)
C(36B)	32(8)	36(8)	38(8)	6(6)	16(5)	1(6)
C(37B)	34(8)	39(8)	41(8)	1(6)	15(6)	1(6)
O(41B)	42(11)	44(14)	36(11)	4(10)	22(8)	17(9)
C(42B)	26(7)	28(8)	25(7)	-2(6)	13(5)	1(6)
N(43B)	33(7)	27(7)	29(6)	1(6)	13(5)	0(6)
C(44B)	36(7)	35(7)	36(7)	2(6)	13(5)	-1(6)
C(45B)	24(7)	29(7)	29(7)	-1(6)	10(5)	1(6)
C(46B)	28(7)	27(7)	33(7)	-5(6)	9(5)	2(6)
C(47B)	23(6)	23(7)	26(6)	-3(5)	14(5)	0(5)
C(48B)	39(8)	36(7)	36(7)	-6(6)	15(5)	1(6)
C(49B)	81(15)	70(15)	72(15)	-1(12)	21(11)	-7(12)
C(50B)	24(7)	25(7)	27(8)	-2(6)	14(5)	3(5)
O(51B)	35(7)	38(7)	38(7)	4(6)	19(5)	-1(5)
O(52B)	71(13)	68(14)	75(13)	10(11)	40(10)	-8(10)
C(53B)	38(7)	42(8)	38(7)	2(6)	24(5)	-4(6)
C(54B)	39(8)	40(8)	38(8)	2(6)	21(6)	-4(6)
C(55B)	28(7)	33(8)	34(8)	-4(6)	16(5)	1(6)
C(66B)	22(7)	25(7)	29(7)	0(6)	10(5)	1(6)
C(67B)	38(7)	39(8)	37(7)	0(6)	16(5)	3(6)

C(68B)	38(8)	42(8)	43(7)	1(6)	23(5)	-3(6)
C(69B)	38(7)	41(8)	42(7)	1(6)	14(5)	1(6)
C(70B)	41(7)	36(8)	39(7)	1(6)	13(5)	-3(6)
C(71B)	27(7)	28(7)	32(7)	0(6)	8(5)	-4(6)
C(72B)	38(8)	38(8)	41(8)	3(6)	15(5)	-2(6)
C(73B)	45(7)	41(8)	39(7)	1(6)	15(5)	1(6)
C(74B)	44(8)	45(8)	39(7)	2(6)	18(5)	1(6)
C(75B)	40(7)	43(7)	40(7)	2(6)	19(5)	3(6)
C(76B)	40(7)	46(8)	44(7)	1(6)	18(5)	4(6)
C(77B)	42(7)	45(8)	37(7)	-4(6)	22(5)	1(6)

Table S17. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for spiro-δ-lactam **21**.

	x	y	z	U(eq)
H(3)	7177	6035	2622	39
H(4A)	5700	6441	2329	48
H(4B)	6256	7642	2646	48
H(5A)	5498	7542	3492	40
H(5B)	5636	6154	3619	40
H(6A)	6629	7186	4909	38
H(6B)	7108	7812	4376	38
H(8)	8914	6053	5308	32
H(9A)	9169	7550	6331	79
H(9B)	8084	7776	5933	79
H(9C)	8621	8026	5357	79
H(16A)	6281	5703	5347	37
H(16B)	6446	4334	5578	37
H(17)	6472	4697	4200	30
H(18)	7893	3735	4526	28
H(19A)	8615	3554	6299	38
H(19B)	9105	4150	5763	38
H(23A)	5546	-713	4708	73
H(23B)	5725	-219	3921	73
H(23C)	4928	333	4120	73
H(24A)	5527	994	5767	77
H(24B)	5226	1992	5039	77
H(24C)	6191	2085	5887	77
H(25A)	6810	-261	6027	88
H(25B)	7492	763	6045	88
H(25C)	7293	-313	5389	88
H(56A)	8899	5932	-499	32
H(56B)	9817	6288	356	32
H(57)	8900(80)	5260(110)	840(80)	33
H(58)	7240(80)	5880(110)	350(80)	33
H(59A)	7166	7185	-1070	42
H(59B)	6828	7677	-382	42

H(63A)	7832	2770	-1947	92
H(63B)	8299	2696	-908	92
H(63C)	8076	3942	-1380	92
H(64A)	6270	3426	-2795	88
H(64B)	6391	4601	-2248	88
H(64C)	5595	3693	-2359	88
H(65A)	6511	1517	-2018	86
H(65B)	5962	1899	-1477	86
H(65C)	7000	1441	-979	86
H(14)	7359	5602	7346	53
H(27)	6491	180	2968	36
H(28)	7484	-1032	2673	48
H(29)	9068	-986	3577	49
H(30)	9659	272	4776	43
H(31)	8665	1485	5071	29
H(33)	6523	2524	2677	49
H(34)	5517	3601	1471	45
H(35)	4178	4406	1451	44
H(36)	3846	4135	2638	49
H(37)	4852	3058	3844	41
H(43)	8849	5870	3009	37
H(44A)	10229	5131	3195	42
H(44B)	10423	6447	3554	42
H(45A)	11078	6404	2605	43
H(45B)	10260	5629	1909	43
H(46A)	10189	7628	1460	37
H(46B)	10023	8010	2281	37
H(48)	7738	8257	906	35
H(49A)	8410	10078	1022	95
H(49B)	9388	9503	1236	95
H(49C)	8966	9403	1922	95
H(54)	9718	8502	-692	40
H(67)	5624	6073	-920	44
H(68)	4132	6427	-1082	44
H(69)	3272	4905	-893	47
H(70)	3903	3028	-541	43
H(71)	5395	2674	-379	41
H(73)	6854	4242	1121	45

H(74)	7771	3675	2560	51
H(75)	9060	2488	2890	55
H(76)	9432	1868	1782	61
H(77)	8515	2434	342	50
H(14G)	7532	6533	7288	44
H(27G)	6560	306	2990	41
H(28G)	7642	-770	2728	43
H(29G)	9214	-556	3644	49
H(30G)	9703	735	4823	39
H(31G)	8621	1811	5086	40
H(33G)	6401	2612	2690	41
H(34G)	5337	3809	1605	49
H(35G)	3982	4376	1676	39
H(36G)	3691	3747	2832	42
H(37G)	4755	2550	3917	47
H(43G)	8852	5464	2977	36
H(44G)	10103	4532	3056	44
H(44H)	10461	5773	3510	44
H(45G)	11107	5664	2571	34
H(45H)	10206	5075	1819	34
H(46G)	10328	7102	1521	37
H(46H)	10267	7442	2401	37
H(48G)	8108	8281	1178	45
H(49G)	9018	9817	993	118
H(49H)	9869	8929	1339	118
H(49I)	9410	9308	1960	118
H(54G)	9507	8149	-972	45
H(67G)	5580	2488	-300	45
H(68G)	4071	2724	-477	47
H(69G)	3321	4519	-944	50
H(70G)	4080	6078	-1235	49
H(71G)	5589	5843	-1058	37
H(73G)	6771	4409	1123	51
H(74G)	7535	3869	2589	52
H(75G)	8732	2502	3039	48
H(76G)	9165	1675	2025	52
H(77G)	8401	2215	560	48

Table S18. Hydrogen bonds for spiro-δ-lactam **21** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3)...O(41)	0.88	2.15	2.85(3)	135.9
N(3)-H(3)...O(41B)	0.88	2.09	2.85(4)	144.7
N(43)-H(43)...O(1)	0.88	2.05	2.91(2)	168.4
N(43B)-H(43G)...O(1)	0.88	2.04	2.87(3)	155.6

Symmetry transformations used to generate equivalent atoms:

10. Absorption and ECD Spectra of hemiaminal ether 25

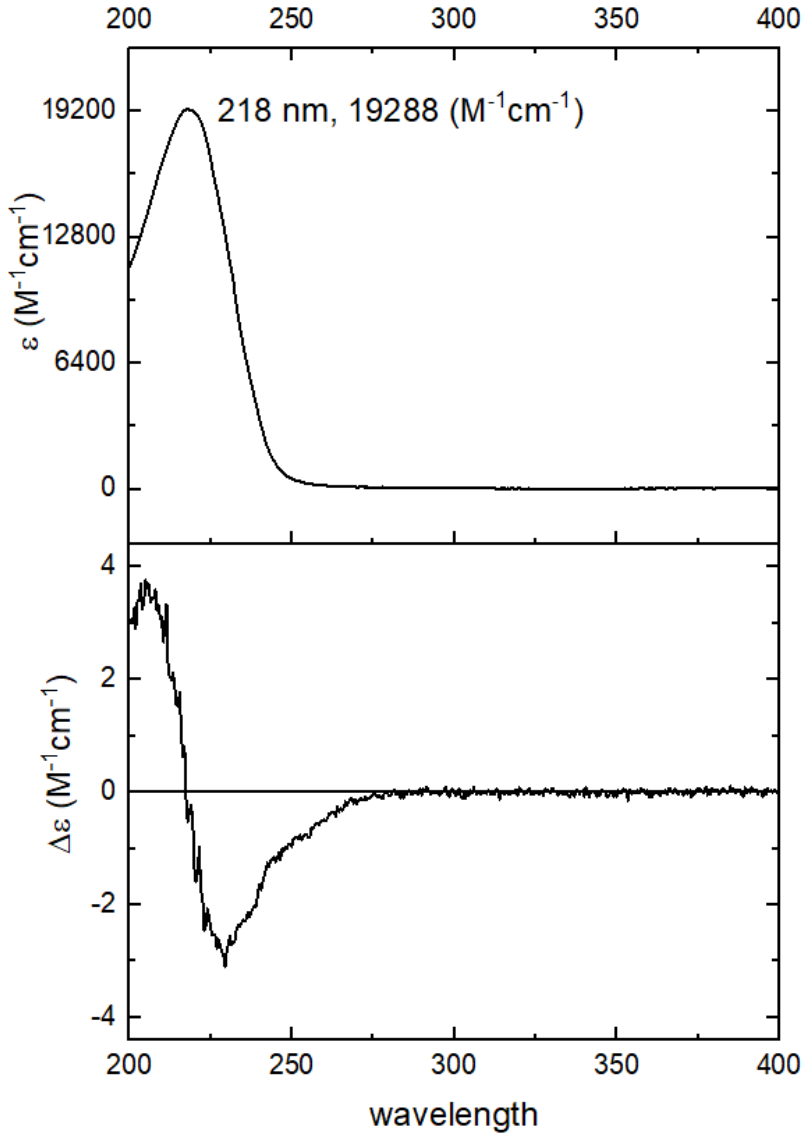


Figure S41. UV/Vis and ECD spectra of hemiaminal ether **25** in acetonitrile

UV λ_{max} (log ε, MeCN) 218 (4.28) (λ_{max}: nm, ε: $M^{-1}cm^{-1}$)

ECD λ_{max} (Δε, MeCN) 206 (+3.69) 229.5 (–2.90) (λ_{max}: nm, Δε: $M^{-1}cm^{-1}$)

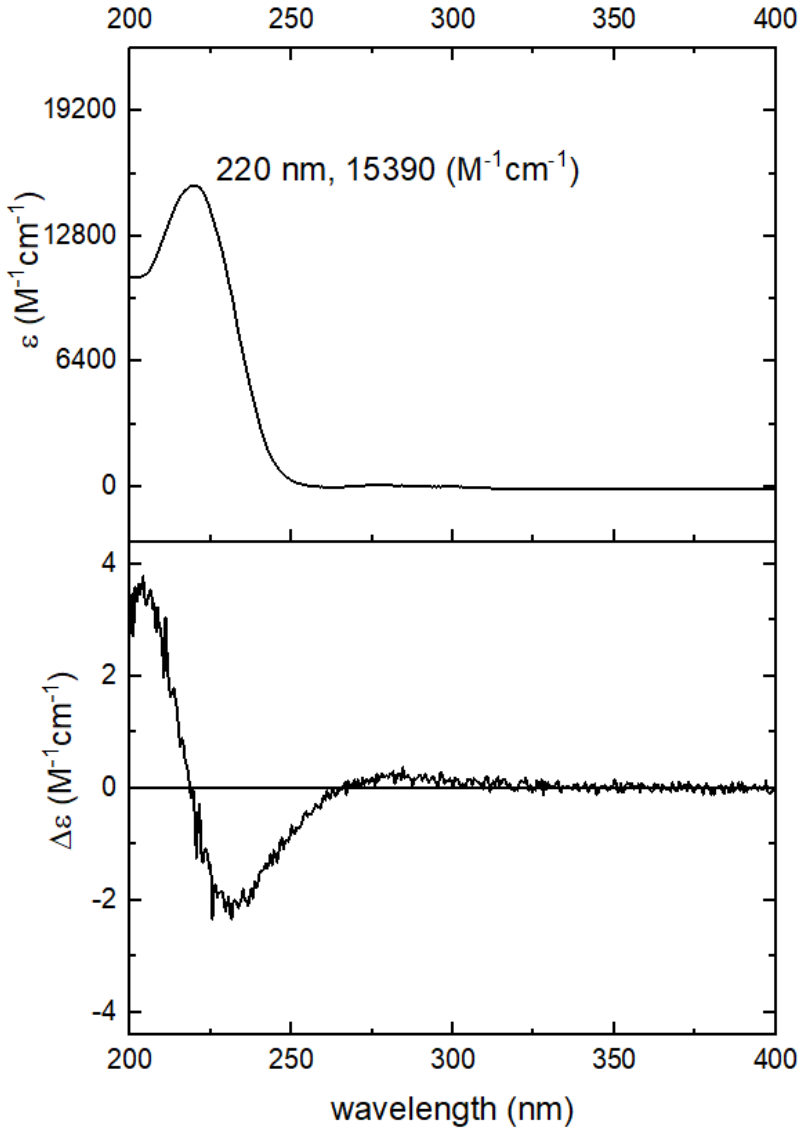


Figure S42. UV/Vis and ECD spectra of hemiaminal ether **25** in methanol

UV λ_{max} (log ε, MeOH) 220 (4.19) (λ_{max}: nm, ε: $M^{-1}cm^{-1}$)

ECD λ_{max} (Δε, MeCN) 206 (+3.69) 229 (–2.90) (λ_{max}: nm, Δε: $M^{-1}cm^{-1}$)

11. Computational Studies of hemiaminal ether 25

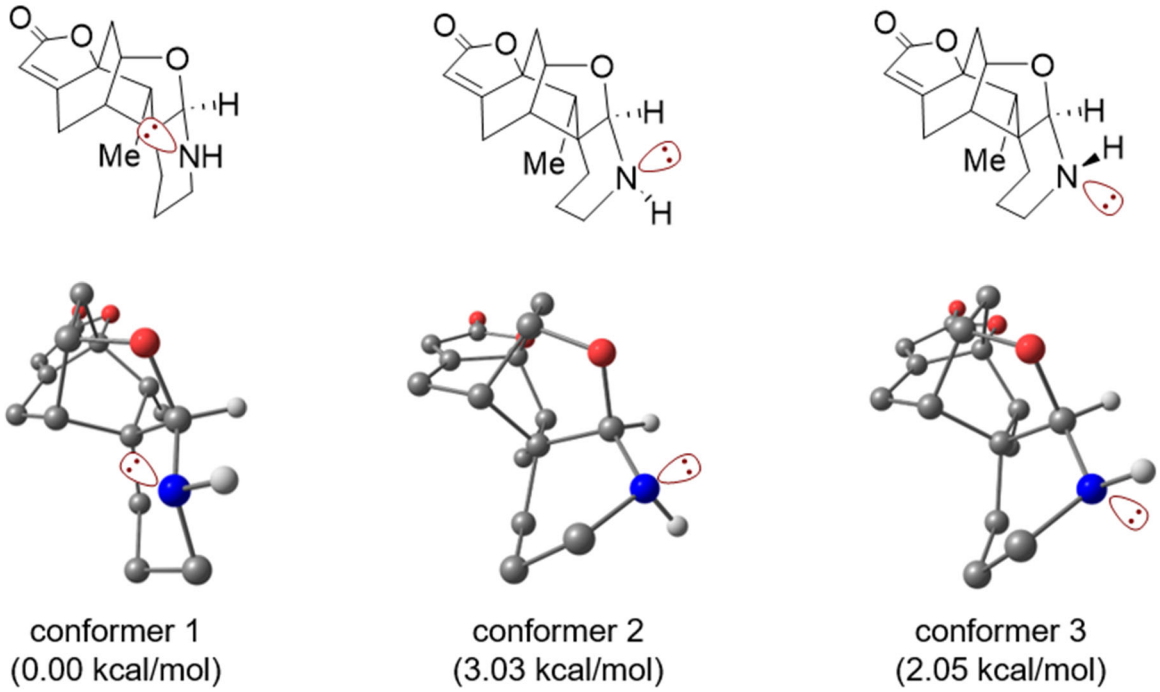


Figure S43. Conformers of hemiaminal ether **25** with relative free energies.

Note:

Unlike securinine or allosecurinine, there was no significant difference in absorption or ECD by changing the conformation. (vide infra)

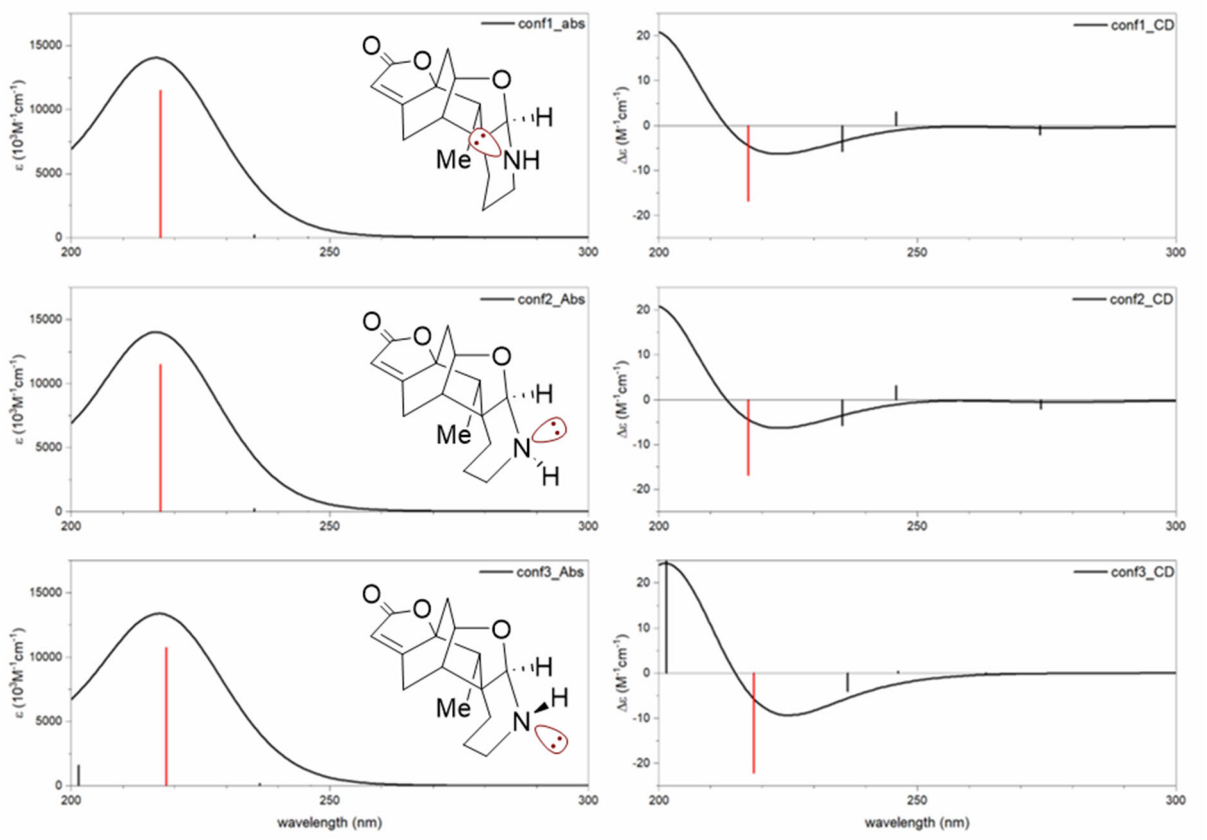


Figure S44. Computed absorption and ECD spectra of all conformers of hemiaminal ether **25**.

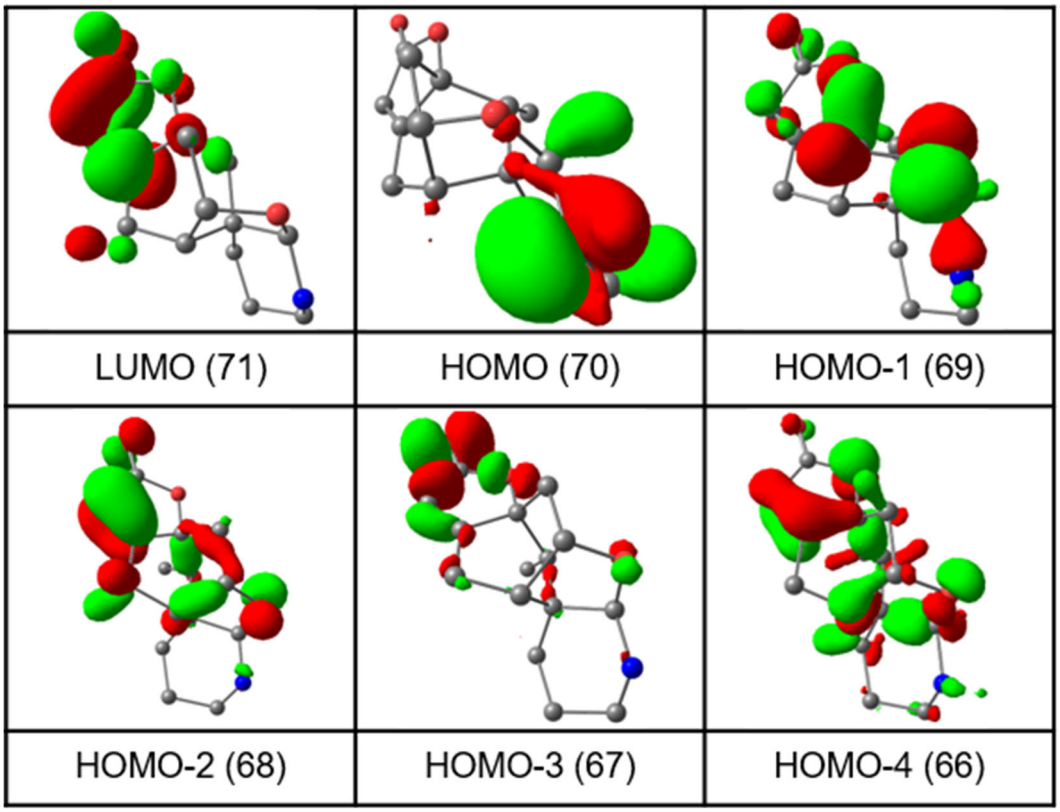


Figure S45. Molecular orbitals of conformer 1, hemiaminal ether **25** (contour value = 0.05).

Wavelength (nm)	Oscillator Strength	Rotatory Strength	Contributions	Assignments & notes
273.75	0.0008	–2.4476	99.2% H → L	Nitrogen lone pair → π*
245.86	0.0004	3.6037	82.6% H-3 → L, 13.5% H-1 → L	
235.48	0.0063	–6.8439	85.1% H-1 → L, 13.4% H-3 → L	Hemiaminal oxygen lone pair → π*
217.3	**0.3286**	**–20.143**	**89.4% H-2 → L, 6.94% H-4 → L**	**π → π*, major absorption**

Table S19. Excitation energies (wavelength), oscillator strength, rotatory strength (velocity) and orbital contributions of each excited state of conformer 1, hemiaminal ether **25**. Excited states over 200 nm were only included. H: HOMO, L: LUMO.

12. Computational Studies of Possible Suffruticosine Candidates (26–33)

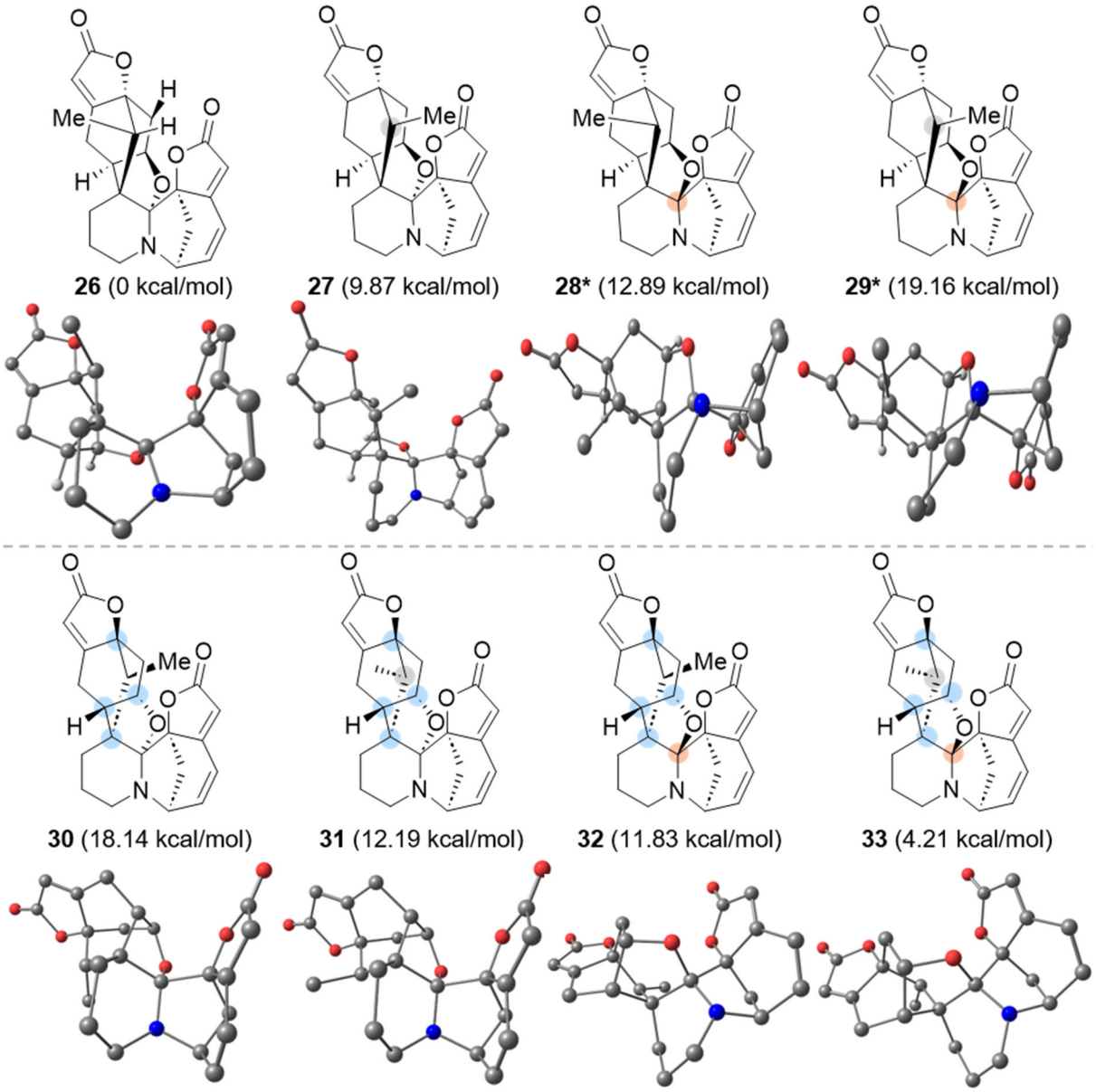


Figure S46. Possible candidates of suffruticosine (**26**–**33**) and their ground state conformations with relative free energies. (*: see below *Note*)

Note: Attempts to search the geometry of structure **28** *and* **29** *having a negative ECD intensity around 400 nm*

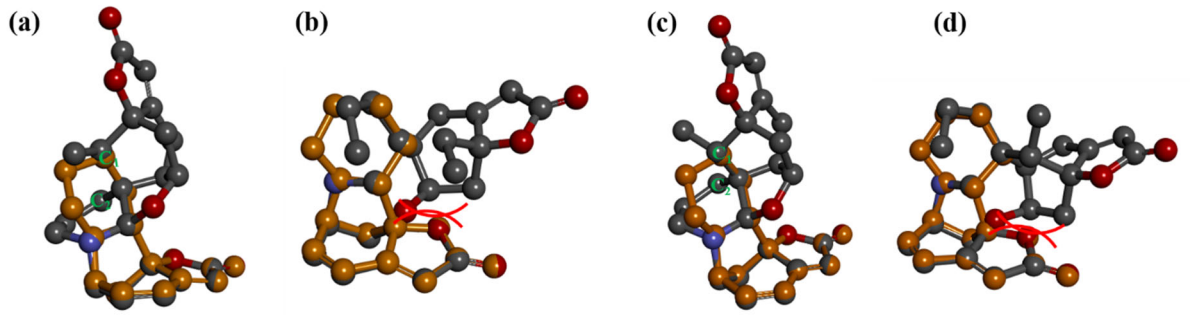


Figure (a) represents an overlay of optimized geometry structures of a securinine, conformer 2a (orange) and **28** (black, red, and blue) with zero ECD signal near 400 nm (i.e., nitrogen lone pair to π* transition). To reproduce the ECD intensity from 400 nm, the geometry of suffruticosine has to be changed into the geometry of the conformer 2a (or either 2b). It means that the carbon, C_2 from **28** needs be shifted to the position of carbon, C_1 from securinine. Figure (b) represents an overlay of an optimized geometry structure of a securinine, conformer 2a (orange) and modified geometry of **28** (black, red, and blue) to overlap the two carbons, C_1 and C_2 from figure (a). From figure (b), two conjugated systems from the modified **28** are crashed in geometric manner. This result states that there is no possible geometry for **28** with non-zero ECD signal.

Figure (c) represents an overlay of optimized geometry structures of a securinine, conformer 2a (orange) and **29** (black, red, and blue) with zero ECD signal near 400 nm. While figure (d) shows an overlay of an optimized geometry structure of a securinine, conformer 2a (orange) of **29** (black, red, and blue) to overlap the two carbons, C_1 and C_2 from figure (c). As a similar fashion that described above, there is no plausible geometry that reproduces **29** with non-zero ECD signal.

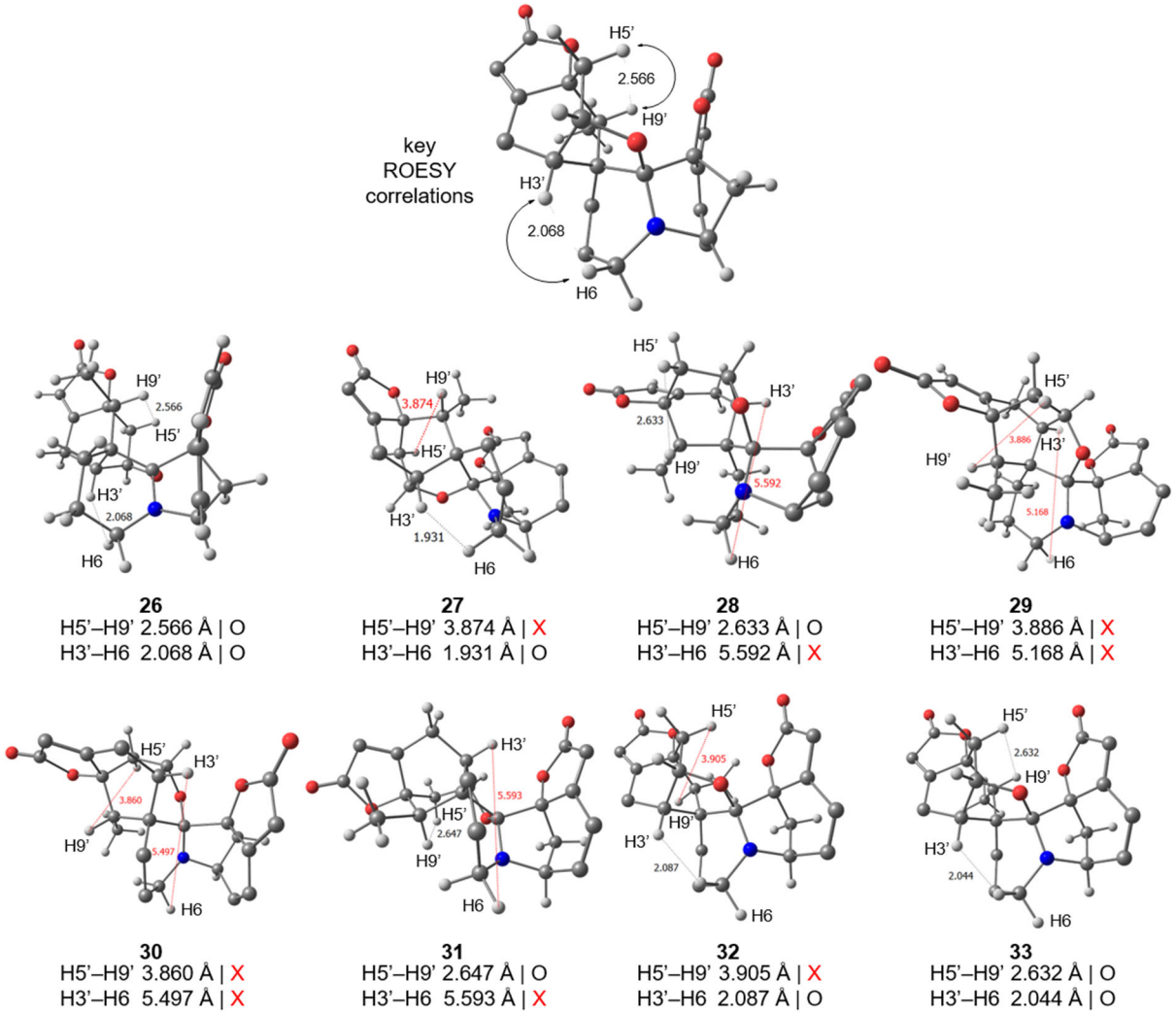


Figure S47. Examinations of the key ROESY correlations[12] to all possible stereoisomeric candidates of suffruticosine.

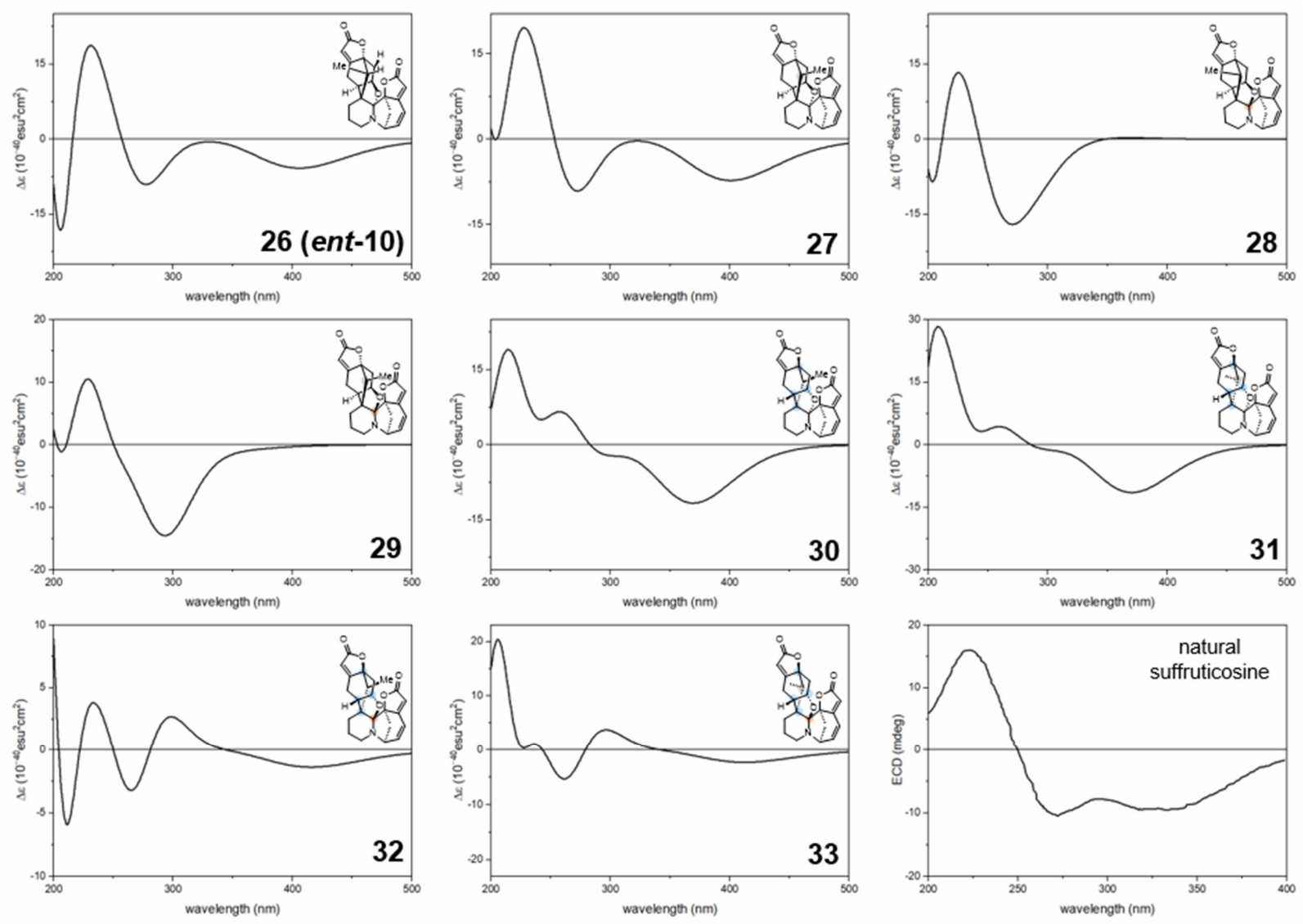


Figure S48. Calculated ECD spectra of all possible structures of suffruticosine and experimental ECD spectrum of suffruticosine[12].

12.1 Analysis of shifts of band 3 by TDDFT calculation

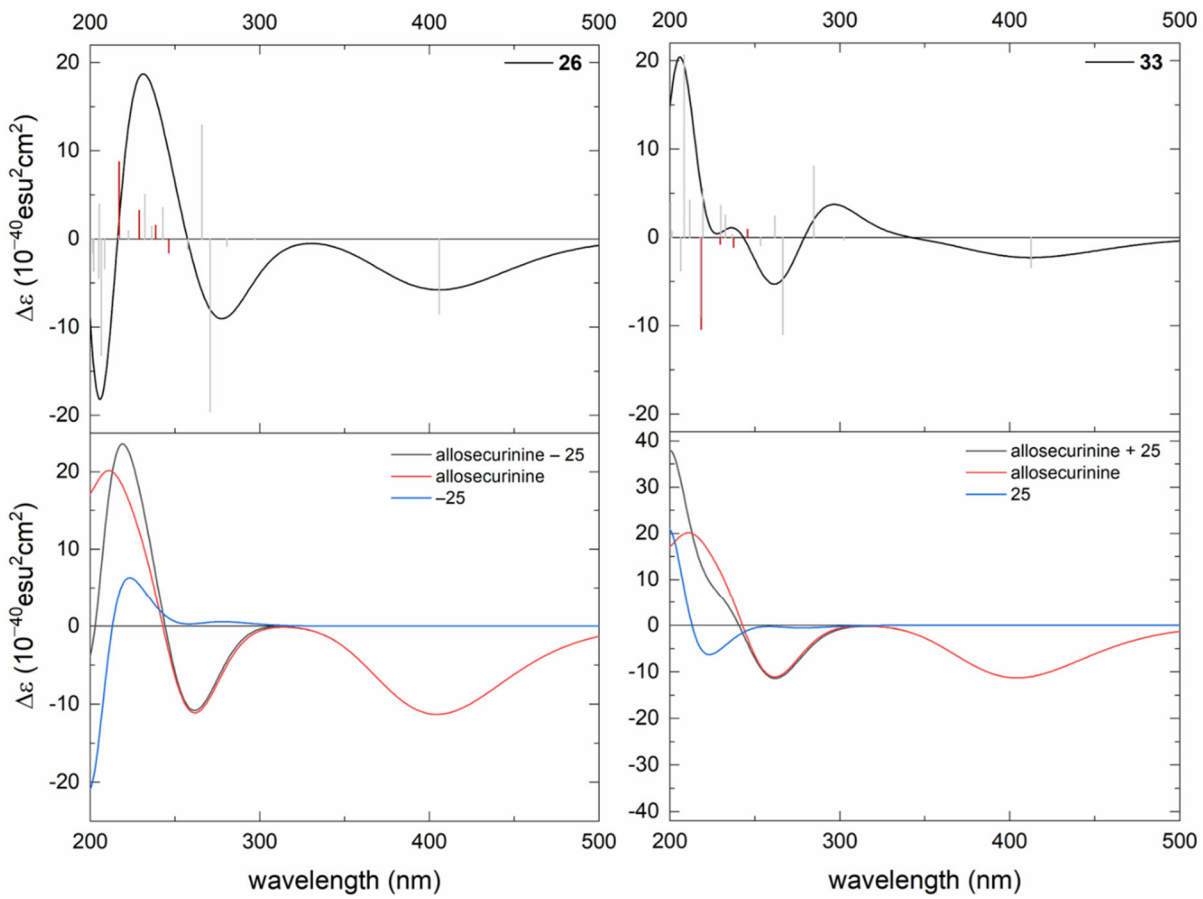


Figure S49. Fragment analysis of ECD spectrum by using TDDFT calculations.

Among the DFT models, structures **26** and **33** play a crucial role in the comparison, considering factors such as relative energies and ROESY correlations. Structure **26** was compared by overlaying the simulated ECD spectra of *ent*-**25** (–**25**) and allosecurinine (**14**), while structure **33** was compared using the overlay of simulated ECD spectra of **25** and allosecurinine (**14**). Consistent with the experimental results, the DFT model exhibits a redshift in band 3 for ent-**25** (Figure S48, bottom left) and a blueshift in band 3 for **25** (Figure S48, bottom right).

To identify which specific transition contributes to the energy shift, we analyzed each transition individually. In the band 3 region (250 nm), the red sticks corresponding to the same transition but exhibits an opposite sign (Table S20, S21). All transitions involve the western π*, and it is evident that the major discrepancy in band 3 arises from the opposite sign and intensity of the O1 to the western π*.

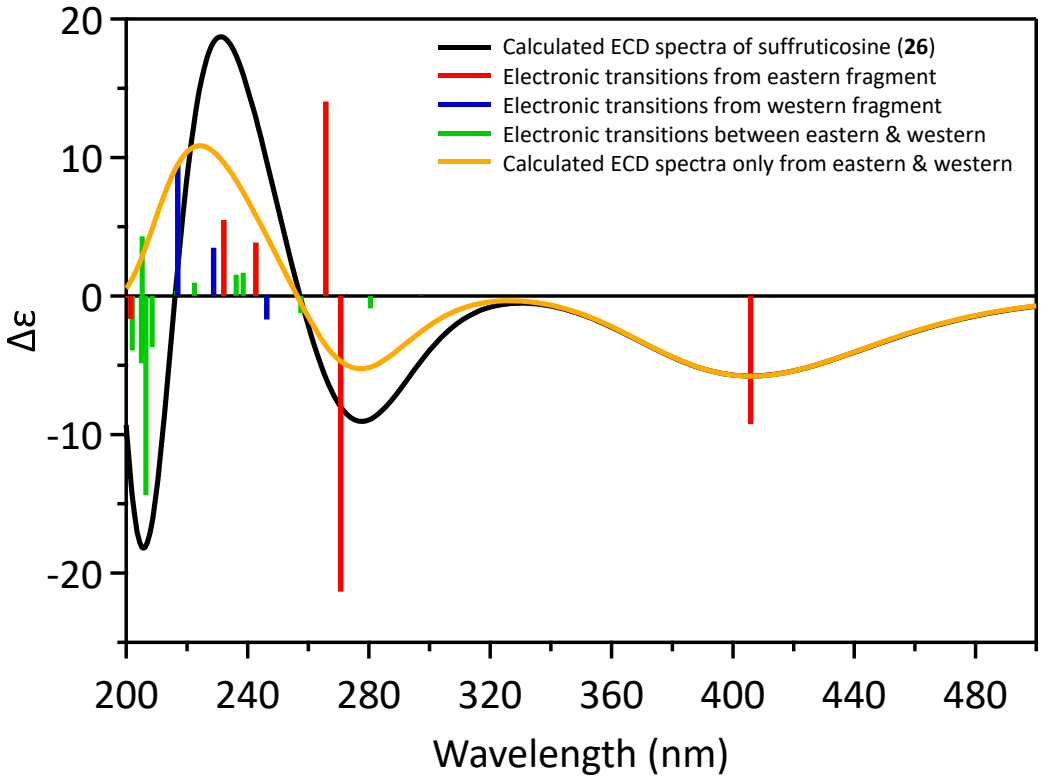


Figure S50. Calculated ECD spectra of suffruticosine and the categorization of its electronic transitions.

The calculated CD spectrum of suffruticosine (black) and the sum of those of the eastern and western parts (orange) are overlaid, displaying that the energy positions of band 3 are predicted to be different while those of band 1 and band 2 are identical. This discrepancy in band 3 is well reproduced with experimental data comparisons as seen in Figure 5 in the main text. Details of the transition characters can explain this discrepancy. The calculated excited states of suffruticosine are noted with sticks in Figure S50 and can be classified into three groups, transitions within the eastern part (red), those within the western part (blue), and CT transitions between the two fragments (green). This plot reveals that the band 3 of suffruticosine indeed contains significant contributions from CT transitions between the two fragments. Thus, the limit in reconstructing the CD spectrum of suffruticosine by adding those of the two fragments can be attributed to the CT transitions between the fragments.

Wavelength (nm)	Oscillator Strength	Rotatory Strength	Contributions	Assignments & notes
246.29	0.0005	–5.6275	77.3% H-4 → L+1, 6.46% H-2 → L+1, 5.27% H-4 → L, 5.23% H-1 → L+1	O4, O5 → π*(O4,O5–C1')
242.73	0.0083	12.821	48.9% H-6 → L, 38.8% H-4 → L, 2.87% H-3 → L, 2.60% H-4 → L+1	
238.55	0.0043	5.561	53.2% H-4 → L, 36.5% H-6 → L, 2.36% H-5 → L	
236.22	0.0005	5.1597	79.8% H-1 → L+1, 10.9% H-4 → L+1, 6.81% H-2 → L+1	π(O2,O3–C15) → π*(O4,O5–C1')
232.18	0.0107	18.2686	93.8% H → L+2, 2.70% H-6 → L	
228.82	0.0438	11.5965	77.4% H-2 → L+1, 11.9% H-1 → L+1, 4.17% H-3 → L+1, 2.87% H-4 → L+1, 2.47% H-6 → L+1	O1 → π*(O4,O5–C1')
222.53	0.0016	3.2096	95.8% H-7 → LUMO	
216.99	0.2832	31.7582	85.7% H-3 → L+1, 4.39% H-2 → L+1, 3.60% H-7 → L+1	π(O4,O5–C1') → π*(O4,O5–C1')
216.65	0.0028	1.3765	82.9% H-8 → L, 8.64% H-12 → L	
208.55	0.0085	–12.2926	93.7% H-9 → L	
206.51	0.0291	–47.8907	42.8% H-5 → L+1, 37.5% H-6 → L+1, 5.09% H-8 → L+1, 3.31% H-7 → L+1, 2.05% H-9 → L+1	
205.26	0.0203	14.3872	30.0% H-10 → L, 28.0% H-12 → L, 17.7% H-11 → L, 7.23% H → L+3, 7.06% H-8 → L, 3.82% H-1 → L+2	

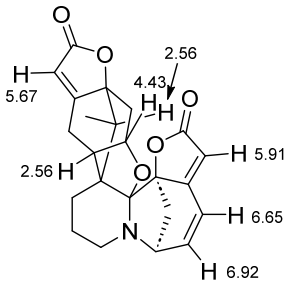
Table S20. Excitation energies (wavelength), oscillator strength, rotatory strength (velocity) and orbital contributions of each excited state of **26**. Excited states between 200 nm and 250 nm were only included. H: HOMO, L: LUMO.

Wavelength (nm)	Oscillator Strength	Rotatory Strength	Contributions	Assignments & notes
245.62	0.0003	3.1569	85.6% H-4 → L+1, 5.38% H-2 → L+1, 2.42% H-1 → L+1	O4, O5 → π*(O4,O5–C1')
237.48	0.0011	–4.071	80.4% H-1 → L+1, 9.88% H-2 → L+1, 3.84% H-4 → L, 3.69% H-4 → L+1	π(O2,O3–C15) → π*(O4,O5–C1')
236.66	0.0051	0.9631	80.9% H-4 → L, 10.3% H-6 → L, 3.11% H-1 → L+1, 2.26% H-4 → L+1	
232.61	0.0093	9.0795	76.5% H → L+2, 10.1% H-6 → L, 4.91% H-8 → L, 2.91% H-4 → L	
229.96	0.0464	13.0661	40.8% H-6 → L, 27.6% H-2 → L+1, 12.2% H → L+2, 5.85% H-4 → L, 4.49% H-1 → L+1, 3.08% H-5 → L, 2.14% H-7 → L	
229.60	0.0009	–2.7627	53.3% H-2 → L+1, 20.2% H-6 → L, 9.19% H-1 → L+1, 5.43% H → L+2, 2.84% H-4 → L, 2.25% H-4 → L+1	O1 → π*(O4,O5–C1')
219.46	0.0156	19.9403	56.3% H-8 → L, 29.5% H-7 → L, 2.93% H-3 → L+1, 2.70% H-10 → L, 2.31% H → L+2	
218.49	0.1832	–37.7836	60.2% H-3 → L+1, 25.6% H-7 → L, 4.47% H-6 → L+1	π(O4,O5–C1') → π*(O4,O5–C1')
217.86	0.1029	–32.9253	38.5% H-7 → L, 22.1% H-8 → L, 21.7% H-3 → L+1, 8.70% H-6 → L, 2.24% H-10 → L	
211.67	0.0143	15.1546	91.6% H → L+3, 4.19% H → L+4, 2.91% H → L+5	
208.39	0.0503	75.0425	45.0% H-5 → L+1, 28.0% H-6 → L+1, 11.8% H-7 → L+1, 4.04% H-3 → L+1, 3.32% H-11 → L+1, 2.61% H-4 → L+1, 2.24% H-9 → L+1	
206.47	0.0057	–13.696	89.4% H-9 → L, 4.86% H-10 → L, 2.11% H-11 → L	

Table S21. Excitation energies (wavelength), oscillator strength, rotatory strength (velocity) and orbital contributions of each excited state of **33**. Excited states between 200 nm and 250 nm were only included. H: HOMO, L: LUMO.

12.2 DP4+ Probability analysis of possible eight candidates of suffruticosine (26–33)

All carbons were used for DP4+ analysis.[8] Protons used for DP4+ analysis were indicated in following chemical structures.



Settings	Type of data (shifts)
Default	Shielding tensors

Functional	Solvent?	Basis Set
B3LYP	PCM	6-311G(d)

TMS 1H	32.198	TMS 13C	184.105
Default	μ	σ	ν
13Cu,sp2	7.279	2.647	14.742
13Cu,sp3	5.165	2.355	20.697
1Hu,sp2	0.063	0.148	8.854
1Hu,sp3	0.019	0.112	3.466
13Cs	-	1.841	7.315
1Hs	-	0.103	3.228

Isomer №			1	2	3	4	5	6	7	8
DP4+ (%)		H data	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
		C data	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
		All data	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
Type	sp2?	Exp	1	2	3	4	5	6	7	8
C		99.5	74.783	69.536	67.211	68.578	69.564	68.018	70.324	71.513
C		44.5	131.43	125.86	125.964	125.865	126.252	128.523	123.823	127.908
C		20.5	159.169	151.999	160.98	154.991	154.487	159.832	149.958	157.151
C		18.9	160.289	159.732	158.927	161.543	164.635	161.108	161.176	161.684
C		39.8	141.875	140.158	129.172	127.473	135.283	134.226	141.512	130.181
C		56.5	122.072	121.948	112.413	114.327	120.364	120.71	119.925	119.534
C		46.3	131.602	129.99	133.782	136.306	133.311	132.629	135.492	135.279
C		91.5	84.912	84.718	76.169	73.188	81.168	81.045	82.854	80.967
C	x	171	6.869	6.202	5.797	5.69	7.487	7.519	6.319	7.37
C	x	111.9	68.112	66.92	74.283	74.461	70.47	69.898	70.252	70.537
C	x	164.3	8.145	6.602	1.071	1.561	7.87	7.216	1.841	2.423
C	x	122.6	55.276	55.075	53.417	51.729	53.241	51.687	55.259	56.187
C	x	146.5	25.479	25.116	31.265	33.111	21.773	22.471	24.665	25.811
C	x	169	-0.573	-4.999	-1.579	-4.524	-3.551	-2.012	-6.199	-1.115
C		21.1	158.76	158.681	159.135	159.268	158.916	158.754	158.442	158.522
C		38.9	139.583	136.556	142.545	143.068	138.663	139.437	138.217	140.662
C		71.5	106.447	107.571	104.927	104.31	105.019	105.197	106.246	106.496
C		38.7	140.836	144.504	140.552	146.159	146.576	140.557	143.064	139.822
C		85.1	91.88	92.636	91.655	91.62	90.198	91.063	92.721	91.724
C	x	111.5	67.876	71.806	68.535	71.23	70.475	68.635	73.112	68.376
C	x	173.3	5.707	6.195	5.521	6.554	6.901	5.427	5.595	5.539
C		33.7	143.915	129.414	135.614	128.719	129.066	134.909	131.568	147.399
C		9.1	173.368	170.029	171.554	167.832	168.75	171.796	169.902	172.527
H		3.79	28.585	28.598	28.648	28.76	28.218	28.28	28.584	28.654
H	x	5.91	26.652	26.687	26.955	26.978	26.762	26.712	26.73	26.717
H	x	6.65	25.571	25.551	25.548	25.49	25.461	25.446	25.6	25.609
H	x	6.92	25.126	25.107	25.339	25.382	24.957	24.979	24.952	25.01
H		2.56	29.818	29.537	29.383	29.303	30.485	30.099	29.852	29.857
H		4.43	28.033	28.053	28.522	28.555	27.744	27.787	28.275	28.26
H	x	5.67	26.901	27.067	26.897	27.01	26.998	26.888	27.129	26.93
H		2.3	30.244	30.708	29.543	30.842	30.78	29.491	30.368	27.875

Table S22. Insertion of shielding tensor values of 8 candidates for DP4+ analysis (1: **26**, 2: **27**, 3: **28**, 4: **29**, 5: **30**, 6: **31**, 7: **32**, 8: **33**).

Type	Exp	1	2	3	4	5	6	7	8
C	99.5	9.82	15.07	17.39	16.03	15.04	16.59	14.28	13.09
C	44.5	8.18	13.75	13.64	13.74	13.35	11.08	15.78	11.70
C	20.5	4.44	11.61	2.63	8.61	9.12	3.77	13.65	6.45
C	18.9	4.92	5.47	6.28	3.66	0.57	4.10	4.03	3.52
C	39.8	2.43	4.15	15.13	16.83	9.02	10.08	2.79	14.12
C	56.5	5.53	5.66	15.19	13.28	7.24	6.90	7.68	8.07
C	46.3	6.20	7.82	4.02	1.50	4.49	5.18	2.31	2.53
C	91.5	7.69	7.89	16.44	19.42	11.44	11.56	9.75	11.64
C	171	6.24	6.90	7.31	7.42	5.62	5.59	6.79	5.74
C	111.9	4.09	5.29	-2.08	-2.26	1.74	2.31	1.95	1.67
C	164.3	11.66	13.20	18.73	18.24	11.94	12.59	17.96	17.38
C	122.6	6.23	6.43	8.09	9.78	8.26	9.82	6.25	5.32
C	146.5	12.13	12.49	6.34	4.49	15.83	15.13	12.94	11.79
C	169	15.68	20.10	16.68	19.63	18.66	17.12	21.30	16.22
C	21.1	4.25	4.32	3.87	3.74	4.09	4.25	4.56	4.48
C	38.9	5.62	8.65	2.66	2.14	6.54	5.77	6.99	4.54
C	71.5	6.16	5.03	7.68	8.30	7.59	7.41	6.36	6.11
C	38.7	4.57	0.90	4.85	-0.75	-1.17	4.85	2.34	5.58
C	85.1	7.13	6.37	7.35	7.39	8.81	7.94	6.28	7.28
C	111.5	4.73	0.80	4.07	1.38	2.13	3.97	-0.51	4.23
C	173.3	5.10	4.61	5.28	4.25	3.90	5.38	5.21	5.27
C	33.7	6.49	20.99	14.79	21.69	21.34	15.50	18.84	3.01
C	9.1	1.64	4.98	3.45	7.17	6.26	3.21	5.10	2.48
-	-	-	-	-	-	-	-	-	-
H	3.79	-0.18	-0.19	-0.24	-0.35	0.19	0.13	-0.18	-0.25
H	5.91	-0.36	-0.40	-0.67	-0.69	-0.47	-0.42	-0.44	-0.43
H	6.65	-0.02	0.00	0.00	0.06	0.09	0.10	-0.05	-0.06
H	6.92	0.15	0.17	-0.06	-0.10	0.32	0.30	0.33	0.27
H	2.56	-0.18	0.10	0.26	0.34	-0.85	-0.46	-0.21	-0.22
H	4.43	-0.26	-0.28	-0.75	-0.79	0.02	-0.02	-0.51	-0.49
H	5.67	-0.37	-0.54	-0.37	-0.48	-0.47	-0.36	-0.60	-0.40
H	2.3	-0.35	-0.81	0.36	-0.94	-0.88	0.41	-0.47	2.02

Table S23. Unscaled errors for 8 candidates (1: **26**, 2: **27**, 3: **28**, 4: **29**, 5: **30**, 6: **31**, 7: **32**, 8: **33**).

Type	Exp	1	2	3	4	5	6	7	8
C	99.5	2.55	6.27	8.11	6.69	6.18	7.56	5.29	4.83
C	44.5	2.84	5.95	5.70	5.32	5.71	3.84	8.20	5.32
C	20.5	0.05	4.27	-4.52	0.66	2.08	-2.54	6.75	1.05
C	18.9	0.57	-1.73	-0.91	-4.18	-6.25	-2.18	-2.58	-1.73
C	39.8	-2.55	-3.40	7.26	8.44	1.58	3.01	-4.33	7.82
C	56.5	-0.12	-2.21	6.94	4.68	-0.53	-0.57	-0.01	1.41
C	46.3	0.87	0.09	-3.74	-6.75	-2.99	-1.94	-4.97	-3.61
C	91.5	0.77	-0.64	7.35	10.16	2.83	2.92	1.09	3.69
C	171	-3.36	-3.02	-3.39	-2.93	-4.58	-5.23	-3.89	-4.66
C	111.9	-3.41	-3.56	-11.20	-11.50	-7.11	-6.67	-7.04	-6.62
C	164.3	2.11	3.29	7.93	7.84	1.75	1.76	7.18	6.82
C	122.6	-1.71	-2.62	-1.52	0.17	-0.95	0.31	-3.14	-3.45
C	146.5	3.17	2.90	-3.77	-5.41	5.94	4.76	2.75	2.01
C	169	5.83	9.99	5.82	9.12	8.22	6.02	10.30	5.54
C	21.1	-0.16	-2.89	-3.31	-4.15	-2.85	-2.09	-2.11	-0.88
C	38.9	0.57	1.04	-4.90	-6.01	-0.83	-1.15	-0.22	-1.41
C	71.5	-0.03	-3.09	-0.75	-0.47	-0.51	-0.52	-1.69	-0.98
C	38.7	-0.44	-6.57	-2.76	-8.85	-8.37	-2.03	-4.74	-0.40
C	85.1	0.44	-2.02	-1.38	-1.58	0.39	-0.40	-2.12	-0.30
C	111.5	-2.78	-7.96	-5.19	-7.92	-6.71	-5.04	-9.42	-4.13
C	173.3	-4.53	-5.31	-5.42	-6.08	-6.30	-5.50	-5.48	-5.19
C	33.7	1.58	13.25	7.07	13.31	13.76	8.45	11.45	-2.72
C	9.1	-2.26	-2.04	-3.45	-0.57	-0.47	-2.75	-1.27	-2.41
-	-	-	-	-	-	-	-	-	-
H	3.79	0.06	0.11	-0.17	0.06	0.52	0.17	0.15	-0.63
H	5.91	-0.21	-0.22	-0.41	-0.35	-0.35	-0.38	-0.24	-0.32
H	6.65	0.08	0.11	0.41	0.34	0.02	0.15	0.08	0.33
H	6.92	0.24	0.25	0.37	0.17	0.19	0.35	0.41	0.81
H	2.56	0.12	0.46	0.25	0.76	-0.19	-0.43	0.19	-0.90
H	4.43	-0.05	-0.02	-0.67	-0.39	0.29	0.02	-0.20	-0.77
H	5.67	-0.21	-0.33	-0.11	-0.14	-0.31	-0.32	-0.37	-0.35
H	2.3	-0.03	-0.37	0.33	-0.46	-0.18	0.44	-0.03	1.84

Table S24. Scaled errors for 8 candidates (1: **26**, 2: **27**, 3: **28**, 4: **29**, 5: **30**, 6: **31**, 7: **32**, 8: **33**).

Default parameters	1	2	3	4	5	6	7	8
sDP4+ (H data)	99.70%	0.05%	0.00%	0.00%	0.01%	0.00%	0.24%	0.00%
sDP4+ (C data)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
sDP4+ (all data)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
uDP4+ (H data)	64.91%	2.10%	0.12%	0.00%	0.08%	32.74%	0.04%	0.00%
uDP4+ (C data)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
uDP4+ (all data)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
DP4+ (H data)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
DP4+ (C data)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
DP4+ (all data)	100.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%

Table S25. Detalied results for 8 candidates (1: **26**, 2: **27**, 3: **28**, 4: **29**, 5: **30**, 6: **31**, 7: **32**, 8: **33**).

13. Cartesian Coordinates of the Optimized Geometries

All optimized structures have no imaginary frequencies.

Allosecurinine, conformer 1a

C	-0.98241	1.033132	2.105534	H	0.10805	1.071134	2.212702
C	-1.43772	-0.42502	2.15116	H	-1.39865	1.604726	2.940244
C	-0.67536	-1.21874	1.094751	H	-1.24661	-0.87185	3.131037
N	-0.80171	-0.63439	-0.24331	H	-2.51905	-0.48789	1.977434
C	-1.254	0.761345	-0.45653	H	-1.02717	-2.25791	1.060763
C	-1.42183	1.675206	0.784312	H	0.377608	-1.25441	1.412484
C	0.296513	-0.92529	-1.19115	H	-2.22793	0.729799	-0.96128
C	1.657662	-0.50345	-0.63901	H	-0.89848	2.623005	0.628744
C	1.98309	0.801201	-0.563	H	-2.48226	1.930232	0.865509
C	1.04981	1.769332	-1.09456	H	0.299752	-1.98637	-1.45007
C	-0.28882	1.270074	-1.57355	H	2.35155	-1.26308	-0.29289
C	1.156032	3.078927	-1.39205	H	2.941558	1.134314	-0.17879
C	-0.03639	3.484915	-2.14088	H	1.982779	3.748506	-1.20208
O	-0.86356	2.382812	-2.26394	H	-0.99127	-0.34876	-2.86177
O	-0.33613	4.547312	-2.62999	H	0.723051	0.069174	-3.12492
C	-0.06912	-0.017	-2.38091				

Allosecurinine, conformer 1b

C	-1.34996	0.383821	2.425413	H	-0.90646	0.740156	3.359412
C	-1.37125	-1.16871	2.391241	H	-2.37578	0.764231	2.408476
C	-0.34445	-1.73225	1.406897	H	-1.18193	-1.58064	3.386116
N	-0.64703	-1.23745	0.063126	H	-2.36115	-1.52373	2.087929
C	-0.89553	0.224753	-0.04424	H	-0.39718	-2.82567	1.385414
C	-0.56261	0.979531	1.241935	H	0.672724	-1.47175	1.741751
C	0.273745	-1.62394	-1.03166	H	-1.95685	0.392647	-0.27377
C	1.737233	-1.34073	-0.70333	H	0.510232	0.920299	1.444445
C	2.216684	-0.08231	-0.72463	H	-0.80144	2.040431	1.122581
C	1.322605	0.981274	-1.12541	H	0.134455	-2.67851	-1.2771
C	-0.12811	0.628933	-1.3386	H	2.384687	-2.16929	-0.43321
C	1.512752	2.267841	-1.47254	H	3.254725	0.141702	-0.50214
C	0.251376	2.799618	-1.99721	H	2.425739	2.845615	-1.45086
O	-0.6993	1.796226	-1.93621	H	-1.21625	-0.90317	-2.45723
O	-0.01774	3.887016	-2.44693	H	0.458805	-0.66762	-3.02504
C	-0.19376	-0.67333	-2.15163				

Allosecurinine, conformer 1c

C	0.000674	-0.00698	2.702561	H	1.654806	-1.29289	2.169384
C	0.605132	-1.39605	2.468941	H	0.58833	-1.98881	3.389666
C	-0.18339	-2.13602	1.380321	H	-1.03862	-0.10858	3.04281
N	-0.41738	-1.35413	0.174515	H	0.538369	0.520729	3.495974
C	-0.67976	0.087739	0.262759	H	0.320331	-3.06361	1.096699
C	0.057582	0.809559	1.405061	H	-1.15578	-2.42808	1.807816
C	0.197956	-1.6695	-1.11924	H	-1.75839	0.258706	0.400185
C	1.688364	-1.33686	-1.16148	H	1.108872	0.9651	1.146989
C	2.103401	-0.05933	-1.27351	H	-0.38577	1.800396	1.547001
C	1.100038	0.975745	-1.38662	H	0.02672	-2.71659	-1.37426
C	-0.3415	0.571795	-1.18602	H	2.409228	-2.1448	-1.07829
C	1.141736	2.275296	-1.73551	H	3.155528	0.203202	-1.30954
C	-0.23228	2.772465	-1.84686	H	2.00369	2.885817	-1.9641
O	-1.0949	1.735347	-1.53887	H	-1.63685	-0.96375	-2.06161
O	-0.65283	3.859539	-2.16195	H	-0.18409	-0.60886	-3.03866
C	-0.58023	-0.69359	-2.02615				

Allosecurinine, conformer 1d

C	0.738675	0.197039	2.151086	H	1.693644	-1.74823	1.959943
C	0.7347	-1.34645	2.298671	H	0.638961	-1.63265	3.35138
C	-0.41605	-2.01338	1.514468	H	0.886583	0.671192	3.125405
N	-0.74071	-1.41374	0.224871	H	1.591328	0.501099	1.540952
C	-0.98436	0.042749	0.227766	H	-0.20456	-3.07381	1.35174
C	-0.55361	0.74526	1.527637	H	-1.32801	-1.97757	2.122283
C	0.034415	-1.76527	-0.98731	H	-2.0579	0.234215	0.09034
C	1.53554	-1.53233	-0.85023	H	-0.46591	1.821387	1.346041
C	2.042892	-0.28458	-0.8848	H	-1.37259	0.635279	2.24656
C	1.13013	0.817728	-1.08929	H	-0.16793	-2.80125	-1.26505
C	-0.34556	0.508507	-1.12149	H	2.18831	-2.3887	-0.71057
C	1.30755	2.119262	-1.38954	H	3.107321	-0.093	-0.7993
C	0.00496	2.704579	-1.71242	H	2.232228	2.673429	-1.46471
O	-0.95648	1.718175	-1.57713	H	-1.60337	-0.94065	-2.17625
O	-0.29285	3.819423	-2.06845	H	-0.00563	-0.7026	-2.93536
C	-0.54572	-0.74613	-1.98927				

Allosecurinine, conformer 2a

C	-1.54023	0.61408	1.113366	H	-1.47276	1.528519	1.710485
C	-0.8987	-0.55827	1.88013	H	-2.61059	0.412666	0.977853
C	-0.82031	-1.83907	1.031323	H	0.11983	-0.28425	2.176548
N	-0.20441	-1.49408	-0.23336	H	-1.46111	-0.75562	2.798799
C	-0.93218	-0.5	-1.006	H	-1.83271	-2.26728	0.897762
C	-0.90403	0.836433	-0.27466	H	-0.21243	-2.59197	1.539545
C	0.415698	-2.46812	-1.15788	H	-1.99595	-0.78645	-1.12605
C	1.873327	-2.04526	-1.31292	H	0.129427	1.182874	-0.17217
C	2.165314	-0.91415	-1.98364	H	-1.4621	1.598597	-0.82799
C	1.085186	-0.19431	-2.62625	H	0.324097	-3.49241	-0.79562
C	-0.33143	-0.68186	-2.42379	H	2.654806	-2.63636	-0.84557
C	1.069538	0.784953	-3.55165	H	3.184544	-0.56187	-2.1018
C	-0.29725	0.932598	-4.05747	H	1.902687	1.342919	-3.95479
O	-1.10283	0.019029	-3.40023	H	-1.33568	-2.62294	-2.47655
O	-0.7477	1.658885	-4.91023	H	0.2079	-2.61119	-3.36811
C	-0.31998	-2.22211	-2.49711				

Allosecurinine, conformer 2b

C	-0.80041	0.6417	1.064752	H	0.211179	0.581123	1.476111
C	-1.54715	-0.66646	1.379765	H	-1.29104	1.480306	1.567114
C	-0.8391	-1.89633	0.754863	H	-1.6345	-0.80515	2.460632
N	-0.08323	-1.44679	-0.40443	H	-2.57083	-0.59644	0.9973
C	-0.77061	-0.43398	-1.2005	H	-1.58738	-2.66852	0.500143
C	-0.72154	0.909481	-0.46324	H	-0.1454	-2.34392	1.474148
C	0.582749	-2.40042	-1.32175	H	-1.82978	-0.70417	-1.35936
C	2.03879	-1.96175	-1.41972	H	0.198618	1.45325	-0.69638
C	2.347961	-0.83156	-2.08368	H	-1.55665	1.536673	-0.78991
C	1.286372	-0.12214	-2.76635	H	0.491519	-3.42796	-0.96874
C	-0.13298	-0.61545	-2.60233	H	2.805813	-2.54291	-0.91743
C	1.293316	0.858034	-3.69021	H	3.368037	-0.47109	-2.16361
C	-0.06052	1.003045	-4.23194	H	2.135069	1.420407	-4.06861
O	-0.88074	0.087648	-3.59715	H	-1.12826	-2.5593	-2.68965
O	-0.48963	1.729983	-5.09497	H	0.438051	-2.53974	-3.53945
C	-0.11375	-2.15456	-2.68142				

Securinine, conformer 1a

C	0.120888	-0.09653	0.784806	H	0.992199	-0.42855	1.354673
N	-0.47098	-1.32316	0.172874	H	-0.47413	-2.04387	-1.82021
C	0.101999	-1.35541	-1.2022	H	1.782951	-2.83491	-1.35432
C	1.557849	-1.7923	-1.15438	H	3.586965	-1.22077	-0.8495
C	2.544281	-0.9216	-0.86706	H	3.92465	1.770411	-0.47251
C	2.178389	0.451327	-0.58471	H	-1.0315	0.444912	-1.74405
C	0.702347	0.731885	-0.44616	H	0.520675	0.330076	-2.59909
C	2.857775	1.601594	-0.44071	H	-0.58507	0.250488	2.775168
C	1.888516	2.692197	-0.27287	H	-0.42209	1.708871	1.821294
O	0.614697	2.150267	-0.30621	H	-2.8148	1.048644	2.332336
O	2.057512	3.879263	-0.14017	H	-2.53142	1.15425	0.600863
C	0.006013	0.117806	-1.66078	H	-3.73421	-0.99148	1.190375
C	-0.76518	0.673216	1.781086	H	-2.38339	-1.44338	2.227009
C	-2.26577	0.591039	1.503891	H	-2.17467	-2.50968	-0.01036
C	-2.65501	-0.87614	1.328489	H	-2.35603	-0.93768	-0.78013
C	-1.94548	-1.44579	0.107547				

Securinine, conformer 1b

C	-0.14904	0.803552	0.880863	H	0.581193	0.518164	1.646887
N	-0.65856	-0.42906	0.204924	H	-0.87425	-0.91091	-1.85088
C	-0.19926	-0.34789	-1.20706	H	1.334409	-1.93803	-1.62428
C	1.207605	-0.91863	-1.27415	H	3.277894	-0.58156	-0.90009
C	2.265568	-0.19292	-0.8676	H	3.907647	2.248677	-0.14968
C	2.026328	1.158697	-0.41127	H	-1.1886	1.580309	-1.5346
C	0.587657	1.594419	-0.25863	H	0.334955	1.430277	-2.43928
C	2.827945	2.204322	-0.14175	H	-0.8219	2.440763	2.105982
C	1.989101	3.378692	0.117927	H	-1.91798	2.052708	0.798011
O	0.664002	2.997603	0.00741	H	-1.49607	0.514524	3.40119
O	2.290096	4.52026	0.368242	H	-2.96963	1.263925	2.827719
C	-0.17853	1.165465	-1.51386	H	-3.56127	-0.80325	1.921338
C	-1.26435	1.608364	1.555058	H	-1.98578	-1.46166	2.327475
C	-2.08316	0.714239	2.499454	H	-2.32609	-1.64343	-0.07149
C	-2.48622	-0.62653	1.828284	H	-2.70996	0.069182	-0.21458
C	-2.10278	-0.65942	0.349358				

Securinine, conformer 1c

C	-0.0164	0.711402	0.865621	H	0.780991	0.416927	1.557986
N	-0.52945	-0.4903	0.153055	H	-0.82863	-0.89262	-1.91222
C	-0.14177	-0.33899	-1.27296	H	1.41398	-1.87745	-1.80367
C	1.276209	-0.87426	-1.41301	H	3.350271	-0.50145	-1.09686
C	2.331286	-0.13805	-1.0157	H	3.940233	2.321755	-0.27175
C	2.078857	1.190181	-0.49986	H	-1.16005	1.586592	-1.53418
C	0.635665	1.582026	-0.27639	H	0.355369	1.479548	-2.45297
C	2.863324	2.246815	-0.22258	H	-1.28519	0.824677	2.580625
C	2.005853	3.387296	0.115356	H	-0.70032	2.380131	2.041885
O	0.686653	2.973795	0.04395	H	-3.16929	2.016604	1.643703
O	2.286445	4.526635	0.396759	H	-2.29656	2.443225	0.19862
C	-0.14824	1.183364	-1.53136	H	-3.10155	0.527806	-0.82011
C	-1.10087	1.428515	1.686045	H	-3.89649	0.04181	0.656994
C	-2.42341	1.645643	0.935711	H	-1.99525	-1.19096	1.447394
C	-2.92927	0.348647	0.245537	H	-2.21285	-1.65462	-0.22148
C	-1.93679	-0.81483	0.420843				

Securinine, conformer 2a

C	-1.44582	-1.37133	2.307048	H	-0.6422	-1.64189	3.003697
C	-1.50429	-2.4182	1.17671	H	-2.37487	-1.39912	2.884766
C	-0.30423	-2.31564	0.219579	H	-2.41834	-2.27038	0.591366
N	-0.21307	-0.93068	-0.20282	H	-1.55461	-3.42498	1.604447
C	0.049961	-0.00274	0.895089	H	-0.4595	-2.95115	-0.6568
C	-1.18272	0.060188	1.793009	H	0.617182	-2.66299	0.721251
C	0.539311	-0.46719	-1.37932	H	0.882848	-0.36709	1.523646
C	2.04955	-0.61635	-1.22844	H	-2.04038	0.433387	1.224259
C	2.761275	0.237757	-0.46448	H	-1.01767	0.740375	2.633779
C	2.059382	1.322671	0.189614	H	0.181943	-0.97664	-2.27519
C	0.551066	1.275032	0.141605	H	2.54441	-1.44259	-1.72997
C	0.148912	1.027217	-1.32178	H	3.836495	0.144977	-0.35221
C	2.437315	2.446722	0.823588	H	0.697592	1.662304	-2.01854
C	1.233375	3.213668	1.165163	H	-0.92393	1.144398	-1.47785
O	0.126331	2.506087	0.726014	H	3.434443	2.800784	1.042824
O	1.112236	4.28339	1.709942				

Securinine, conformer 2b

C	-1.94615	-1.09117	1.479296	H	-2.42773	-1.07621	2.461279
C	-1.10052	-2.36854	1.331352	H	-2.75098	-1.11167	0.73909
C	-0.45103	-2.46656	-0.07429	H	-1.71364	-3.25477	1.515425
N	-0.34441	-1.12016	-0.61429	H	-0.3189	-2.37347	2.098374
C	0.08905	-0.12394	0.366382	H	-1.077	-3.05793	-0.75119
C	-1.09928	0.196113	1.286008	H	0.52297	-2.97895	0.001613
C	0.295703	-0.82018	-1.90227	H	0.914192	-0.50951	0.987229
C	1.789967	-1.12809	-1.91458	H	-1.71742	0.98803	0.854694
C	2.669292	-0.31854	-1.29045	H	-0.72801	0.567598	2.246061
C	2.164948	0.876189	-0.64694	H	-0.2184	-1.34729	-2.70785
C	0.665112	1.011795	-0.54022	H	2.135293	-2.02794	-2.41436
C	0.073402	0.708811	-1.92726	H	3.735146	-0.52177	-1.2907
C	2.737544	1.985609	-0.14656	H	0.601391	1.225799	-2.72942
C	1.676113	2.918769	0.246555	H	-0.99183	0.937649	-1.97771
O	0.454077	2.326756	-0.02343	H	3.787264	2.226425	-0.05831
O	1.739836	4.030142	0.712464				

Hemiaminal ether 25, conformer 1

C	1.720871	-0.97194	0.931222	C	-0.43464	-1.88511	0.742249
C	0.763134	0.106063	0.378845	C	-0.00933	2.289163	1.685355
C	1.491461	1.132209	-0.50821	H	0.768501	1.748252	-1.05123
C	2.492372	0.501023	-1.48501	H	2.048017	1.81953	0.135513
C	3.424254	-0.45225	-0.74271	H	3.071491	1.293781	-1.96866
N	2.612477	-1.49162	-0.09981	H	1.977334	-0.04769	-2.27946
H	3.208752	-2.19593	0.324111	H	4.115449	-0.94001	-1.43487
H	2.270485	-0.61675	1.815931	H	4.03713	0.117925	-0.02126
O	0.86463	-2.02879	1.367759	H	0.282134	-1.30186	-1.21715
C	-0.2253	-0.83633	-0.37463	H	0.461302	0.395744	2.529572
C	-0.0158	0.757573	1.612772	H	-2.19198	-0.86355	-1.3162
C	-1.46674	0.182283	1.63575	H	-1.29261	0.602947	-1.61437
C	-1.51302	-0.14398	-0.84551	H	-2.43198	-1.75474	1.648117
C	-2.16393	0.481152	0.343833	H	-1.08691	-1.62471	2.790573
C	-1.42818	-1.34543	1.791699	H	-3.99426	1.588354	-0.11187
O	-2.28502	0.802602	2.641365	H	-0.73358	-2.86657	0.371911
C	-3.35475	1.430486	2.035727	H	-0.58028	2.619016	2.55457
C	-3.2558	1.213365	0.582868	H	1.004752	2.671884	1.806654
O	-4.183	2.0225	2.683719	H	-0.44234	2.762252	0.801305

Hemiaminal ether 25, conformer 2

C	1.644451	-1.08228	0.60694	C	-0.51938	-1.96509	0.595433
C	0.642148	-0.01376	0.029244	C	-0.08888	2.340994	0.996943
C	1.379159	0.831148	-1.02068	H	0.7193	1.58949	-1.44845
C	1.995459	-0.01098	-2.15646	H	2.177857	1.383058	-0.51315
C	2.571812	-1.35662	-1.64421	H	2.782339	0.57987	-2.63429
N	2.800556	-1.39525	-0.19643	H	1.248642	-0.20429	-2.93299
H	3.571331	-0.7908	0.064379	H	1.894214	-2.17895	-1.88764
H	2.022974	-0.75696	1.580914	H	3.517302	-1.58819	-2.13878
O	0.861089	-2.28147	0.794378	H	-0.16783	-1.4159	-1.45778
C	-0.49051	-0.92531	-0.53972	H	0.709902	0.70725	2.09631
C	0.046027	0.831759	1.234265	H	-2.57793	-0.9359	-1.16721
C	-1.31037	0.183545	1.628229	H	-1.74198	0.549804	-1.54998
C	-1.838	-0.22611	-0.7828	H	-2.12693	-1.76146	2.085413
C	-2.29094	0.36613	0.510348	H	-0.50143	-1.51442	2.725995
C	-1.14799	-1.32885	1.865011	H	-4.26113	1.312471	0.429742
O	-1.92245	0.828579	2.757974	H	-1.0187	-2.89713	0.328895
C	-3.15475	1.327028	2.384859	H	-0.50781	2.820182	1.884042
C	-3.36389	1.023597	0.959045	H	0.885956	2.795128	0.814867
O	-3.865	1.899501	3.17476	H	-0.73465	2.585334	0.151095

Hemiamianl ether 25, conformer 3

C	1.450638	-1.38509	0.297464	C	-2.93417	1.740914	0.998719
C	0.696448	-0.10373	-0.20146	O	-3.11519	2.593604	3.272131
C	1.538988	0.591279	-1.28232	C	-0.85429	-1.77774	0.34922
C	1.896554	-0.34189	-2.45904	C	0.536882	2.319279	0.854
C	2.184588	-1.78837	-1.9967	H	1.024005	1.475732	-1.66531
N	2.520622	-1.77808	-0.57113	H	2.462867	0.950676	-0.82114
H	2.913968	-2.66207	-0.26791	H	2.771789	0.071167	-2.96783
H	1.884236	-1.2319	1.289335	H	1.090529	-0.34901	-3.1981
O	0.422859	-2.41177	0.441455	H	1.327777	-2.44204	-2.21256
C	-0.64083	-0.71264	-0.73922	H	3.036014	-2.20212	-2.54048
C	0.360519	0.808777	1.052177	H	-0.4788	-1.21448	-1.69271
C	-1.0811	0.445951	1.508327	H	1.026638	0.519652	1.870796
C	-1.80534	0.281495	-0.87892	H	-2.70128	-0.22641	-1.25058
C	-2.05499	0.891062	0.460552	H	-1.57334	1.055772	-1.61824
C	-1.24554	-1.0768	1.681257	H	-2.28204	-1.28945	1.954127
O	-1.47645	1.152363	2.696226	H	-0.60911	-1.44237	2.490524
C	-2.58919	1.921536	2.419039	H	-3.77305	2.242469	0.536821

H	-1.57538	-2.54993	0.078361	H	1.578536	2.563778	0.642221
H	0.260995	2.84677	1.769313	H	-0.07238	2.722606	0.042571

Suffruticosine, originally proposed (10)

C	0.508315	-1.23541	-0.10853	O	-4.3007	2.849532	2.634253
C	-0.30855	0.046659	-0.54025	C	-1.82687	-1.64025	0.065752
C	0.467641	0.823649	-1.6184	C	-0.51263	2.458449	0.550249
C	0.794191	0.00054	-2.87789	H	-0.08995	1.714144	-1.91376
C	1.057782	-1.49327	-2.57061	H	1.399423	1.18922	-1.18123
N	1.323147	-1.77574	-1.16928	H	1.66701	0.446347	-3.36229
C	1.555185	-1.22423	1.090037	H	-0.02475	0.074738	-3.59967
C	2.674315	-2.13097	-0.71297	H	0.205758	-2.09773	-2.90251
C	2.387447	-2.4763	0.755427	H	1.912531	-1.85633	-3.14361
C	2.534729	-0.06933	1.145934	H	3.053582	-2.97931	-1.28446
C	3.627008	-0.94275	-0.79613	H	3.279212	-2.55891	1.376736
C	3.510022	0.067656	0.08514	H	1.787067	-3.38204	0.836891
O	0.947149	-1.23944	2.379629	H	4.37835	-0.91557	-1.57904
C	2.439573	0.519596	2.353492	H	4.16603	0.931437	0.06891
C	1.463014	-0.21486	3.158049	H	3.024337	1.338293	2.747709
O	1.103102	-0.06204	4.299291	H	-1.4126	-1.18503	-1.99424
O	-0.52048	-2.18917	0.285013	H	-0.13355	0.648109	1.569243
C	-1.6119	-0.63472	-1.07654	H	-3.66495	-0.24338	-1.67672
C	-0.72235	0.946872	0.709527	H	-2.56232	1.042779	-2.09986
C	-2.1933	0.606674	1.089045	H	-3.40586	-1.13035	1.506622
C	-2.79599	0.316211	-1.31485	H	-1.77894	-1.21864	2.195726
C	-3.10658	1.003329	-0.02773	H	-4.8116	2.371168	-0.11364
C	-2.35247	-0.90407	1.322815	H	-2.47502	-2.47436	-0.20599
O	-2.65085	1.366246	2.220196	H	-0.80352	2.962863	1.473303
C	-3.73595	2.133032	1.844655	H	0.537263	2.693006	0.372797
C	-4.00384	1.887322	0.417357	H	-1.09673	2.893998	-0.26256

Suffruticosine, structure 26

C	0.508315	-1.23541	0.108528	C	2.674315	-2.13097	0.712965
C	-0.30855	0.046659	0.540247	C	2.387447	-2.4763	-0.75543
C	0.467641	0.823649	1.618404	C	2.534729	-0.06933	-1.14593
C	0.794191	0.00054	2.877889	C	3.627008	-0.94275	0.796128
C	1.057782	-1.49327	2.570605	C	3.510022	0.067656	-0.08514
N	1.323147	-1.77574	1.169282	O	0.947149	-1.23944	-2.37963
C	1.555185	-1.22423	-1.09004	C	2.439573	0.519596	-2.35349

C	1.463014	-0.21486	-3.15805	H	0.205758	-2.09773	2.902507
O	1.103102	-0.06204	-4.29929	H	1.912531	-1.85633	3.143605
O	-0.52048	-2.18917	-0.28501	H	3.053582	-2.97931	1.284464
C	-1.6119	-0.63472	1.076537	H	3.279212	-2.55891	-1.37674
C	-0.72235	0.946872	-0.70953	H	1.787067	-3.38204	-0.83689
C	-2.1933	0.606674	-1.08905	H	4.37835	-0.91557	1.579043
C	-2.79599	0.316211	1.314848	H	4.16603	0.931437	-0.06891
C	-3.10658	1.003329	0.02773	H	3.024337	1.338293	-2.74771
C	-2.35247	-0.90407	-1.32282	H	-1.4126	-1.18503	1.994238
O	-2.65085	1.366246	-2.2202	H	-0.13355	0.648109	-1.56924
C	-3.73595	2.133032	-1.84466	H	-3.66495	-0.24338	1.676719
C	-4.00384	1.887322	-0.41736	H	-2.56232	1.042779	2.099862
O	-4.3007	2.849532	-2.63425	H	-3.40586	-1.13035	-1.50662
C	-1.82687	-1.64025	-0.06575	H	-1.77894	-1.21864	-2.19573
C	-0.51263	2.458449	-0.55025	H	-4.8116	2.371168	0.113638
H	-0.08995	1.714144	1.91376	H	-2.47502	-2.47436	0.205989
H	1.399423	1.18922	1.18123	H	-0.80352	2.962863	-1.4733
H	1.66701	0.446347	3.362289	H	0.537263	2.693006	-0.3728
H	-0.02475	0.074738	3.599671	H	-1.09673	2.893998	0.262562

Suffruticosine, structure 27

C	-3.6747	1.761859	-1.81979	C	2.04832	-0.66729	0.546312
C	-2.84571	0.767512	-1.49129	C	2.90991	-1.93699	0.355059
C	-1.46448	1.305995	-1.28082	C	2.827256	0.948733	2.028199
O	-1.59312	2.719899	-1.50776	C	3.01852	1.414772	0.65688
C	-2.90025	3.013569	-1.84099	O	2.513095	0.453046	-0.20014
O	-3.24533	4.143353	-2.08622	O	3.52638	2.422878	0.228216
C	-2.9447	-0.69919	-1.24329	O	0.753111	-1.23851	-1.38063
C	-1.53779	-1.22894	-0.92577	C	-1.06649	0.96832	0.190282
C	-0.48663	-0.87168	-1.99041	C	-0.814	-0.5995	0.323244
C	-0.52339	0.647731	-2.29688	H	-4.735	1.730352	-2.02739
C	-0.07773	1.982582	0.759385	H	-3.64008	-0.90831	-0.42387
C	-1.34733	-1.05421	1.696446	H	-3.34976	-1.2191	-2.11766
C	-1.46052	-2.57621	1.89118	H	-1.58946	-2.31081	-0.84328
C	-0.4402	-3.36469	1.043286	H	-0.58366	-1.46328	-2.90198
N	0.70392	-2.57995	0.60372	H	0.486068	1.053646	-2.21602
C	0.630472	-1.22853	0.074224	H	-0.88745	0.848622	-3.30753
C	2.027427	-2.89922	1.155075	H	-0.58132	2.944838	0.86198
C	2.087248	-2.56841	2.64198	H	0.780914	2.140472	0.112613
C	2.142253	-1.28178	3.028592	H	0.267658	1.689231	1.749461
C	2.264929	-0.27376	1.995755	H	-2.32675	-0.60198	1.871456

H	-0.68978	-0.63181	2.463505	H	2.068805	-3.37176	3.371625
H	-1.32474	-2.805	2.951379	H	2.197706	-0.98917	4.071696
H	-2.46853	-2.91357	1.631941	H	2.959637	-2.22189	-0.69472
H	-0.04798	-4.20625	1.61628	H	3.914497	-1.81336	0.759578
H	-0.93941	-3.81557	0.17813	H	3.179868	1.499011	2.888778
H	2.270752	-3.94785	0.974875	H	-1.98347	1.118137	0.768307

Suffruticosine, structure 28

C	-0.00309	1.685599	-0.72187	O	0.541779	-1.78878	2.396064
C	0.25187	0.694142	0.53749	O	-0.90182	-2.99826	3.641465
C	-2.95924	3.346623	-0.16454	O	-0.2978	-1.1458	-0.77044
C	-2.28753	2.237676	0.157167	H	0.466135	1.246236	-1.60314
C	-1.53709	1.737416	-1.03686	H	-3.61306	3.953614	0.445843
O	-1.84271	2.67939	-2.07804	H	-3.10292	0.94558	1.649393
C	-2.6926	3.64851	-1.58099	H	-1.77472	1.926642	2.217888
O	-3.09631	4.545213	-2.27981	H	-1.06278	-0.42011	1.867338
C	-2.13373	1.360919	1.352322	H	-2.21889	-1.41385	-0.04923
C	-1.15136	0.230822	1.004616	H	-3.17583	0.364593	-1.3736
C	-1.53842	-0.5884	-0.26502	H	-1.73414	-0.00234	-2.33186
C	-2.08274	0.342196	-1.35667	H	0.029496	3.656381	0.257341
C	0.521647	3.120128	-0.55675	H	1.591741	3.155439	-0.37092
C	1.227902	1.268328	1.566114	H	0.339531	3.679955	-1.47493
C	2.678219	1.2938	0.993654	H	0.923922	2.264859	1.888609
C	2.813717	0.686219	-0.42577	H	1.193465	0.638649	2.45765
N	2.04982	-0.56204	-0.71306	H	3.351569	0.782136	1.683332
C	0.799432	-0.67844	0.035857	H	3.051124	2.320079	0.943118
C	2.848958	-1.78958	-0.42232	H	3.864858	0.470508	-0.62174
C	2.286194	-2.98833	-1.16819	H	3.882165	-1.62015	-0.71972
C	1.225499	-3.66012	-0.69054	H	2.768391	-3.28937	-2.0922
C	0.632427	-3.19609	0.546861	H	0.822453	-4.53562	-1.18815
C	1.137453	-1.88052	1.101718	H	3.140268	-1.197	1.672097
C	2.661861	-1.98507	1.094663	H	3.010708	-2.95011	1.465575
C	-0.21876	-3.74581	1.429284	H	-0.7413	-4.68955	1.366409
C	-0.28924	-2.88224	2.609794	H	2.528467	1.429927	-1.1693

Suffruticosine, structure 29, conformer 1

C	0.054725	1.68375	-0.73832	C	-1.48329	1.735073	-1.01795
C	0.342006	0.658654	0.489278	O	-1.80197	2.723241	-2.01441
C	-2.82033	3.36134	-0.04124	C	-2.58921	3.70729	-1.45187
C	-2.18942	2.211327	0.211596	O	-2.97469	4.648061	-2.10183

C	-2.03204	1.290405	1.368926	H	-3.41844	3.973518	0.618922
C	-1.05024	0.180782	0.972042	H	-2.99981	0.85848	1.647721
C	-1.43904	-0.6121	-0.31288	H	-1.67519	1.819007	2.258059
C	-2.02221	0.342193	-1.36728	H	-0.9438	-0.48583	1.818341
C	0.799598	1.536294	-2.07586	H	-2.10334	-1.45467	-0.11347
C	1.32226	1.282125	1.472363	H	-3.11553	0.346588	-1.34977
C	2.616573	1.595183	0.703525	H	-1.70517	0.027438	-2.36245
C	3.130892	0.4594	-0.22004	H	0.379658	2.251127	-2.78533
N	2.183266	-0.63299	-0.6617	H	1.858419	1.764712	-1.98257
C	0.89795	-0.71048	0.021622	H	0.708735	0.535546	-2.49021
C	2.86454	-1.94594	-0.42988	H	0.925611	2.202967	1.910219
C	2.211414	-3.08455	-1.19361	H	1.505593	0.593401	2.30193
C	1.119575	-3.70381	-0.71497	H	3.415083	1.842036	1.407698
C	0.564251	-3.22531	0.534389	H	2.457347	2.497796	0.110849
C	1.149733	-1.94902	1.095911	H	3.970581	-0.01857	0.287444
C	2.663323	-2.14465	1.085199	H	3.906927	-1.85819	-0.73123
C	-0.30565	-3.73635	1.422058	H	2.666094	-3.39879	-2.12709
C	-0.30734	-2.88607	2.615102	H	0.662943	-4.54603	-1.22355
O	0.578428	-1.83614	2.399774	H	3.181545	-1.38552	1.67214
O	-0.90756	-2.98288	3.655936	H	2.957299	-3.12903	1.452146
O	-0.18732	-1.14272	-0.83611	H	-0.88181	-4.64819	1.356814
H	0.298922	2.67498	-0.34377	H	3.552094	0.902091	-1.12564

Suffruticosine, structure 29, conformer 2

C	0.088154	1.663862	-0.80808	C	0.872732	-0.74486	0.005713
C	0.351324	0.649885	0.447792	C	2.878646	-1.97261	-0.34779
C	-2.73788	3.431635	-0.06473	C	2.275359	-3.14351	-1.10566
C	-2.13953	2.263048	0.182691	C	1.164042	-3.75377	-0.6618
C	-1.45564	1.765285	-1.0494	C	0.557155	-3.25028	0.552778
O	-1.76037	2.759547	-2.0454	C	1.109966	-1.95715	1.111153
C	-2.51087	3.76823	-1.47761	C	2.62546	-2.13459	1.160814
O	-2.87445	4.71866	-2.1263	C	-0.34196	-3.75234	1.416177
C	-2.00646	1.336586	1.336702	C	-0.39499	-2.882	2.592543
C	-1.0542	0.205986	0.932731	O	0.491985	-1.82986	2.3918
C	-1.46304	-0.58729	-0.3394	O	-1.0321	-2.96453	3.612372
C	-2.01931	0.380163	-1.39838	O	-0.22317	-1.16859	-0.84284
C	0.756601	1.455581	-2.19231	H	0.39022	2.64839	-0.44186
C	1.285798	1.260059	1.490858	H	-3.31191	4.06083	0.600805
C	2.770957	1.194276	1.03474	H	-2.98494	0.928271	1.614062
C	2.998811	0.497984	-0.32896	H	-1.63509	1.851422	2.227871
N	2.167887	-0.69992	-0.66597	H	-0.95363	-0.45723	1.781682

H	-2.15439	-1.40651	-0.13557	H	3.183056	2.202755	0.941623
H	-3.11237	0.40383	-1.38572	H	4.042517	0.188216	-0.39499
H	-1.70301	0.061187	-2.39249	H	3.929473	-1.86674	-0.60994
H	0.074364	1.780152	-2.97728	H	2.773315	-3.47899	-2.00923
H	1.647363	2.073865	-2.29945	H	0.732838	-4.61111	-1.16736
H	1.026321	0.420646	-2.38017	H	3.118534	-1.35624	1.74114
H	0.994232	2.290356	1.707727	H	2.912483	-3.1076	1.562665
H	1.166818	0.70655	2.425816	H	-0.90731	-4.67049	1.345419
H	3.363736	0.707046	1.811662	H	2.863166	1.230014	-1.11814

Suffruticosine, structure 30

C	0.067785	1.75695	0.694129	C	2.777175	-2.47951	-1.57332
C	0.228487	0.515001	-0.35763	C	1.332894	-2.49677	-1.64768
C	-2.50278	3.677199	-0.47107	C	0.53715	-2.28437	-0.38299
C	-2.05076	2.41997	-0.47799	C	1.216792	-3.08689	0.739345
C	-1.45502	2.081766	0.850023	C	0.500566	-2.92072	-2.62111
O	-1.65031	3.271879	1.636349	C	-0.83073	-3.10155	-2.04858
C	-2.25887	4.240276	0.865095	O	-0.77122	-2.74758	-0.71003
O	-2.51252	5.330988	1.314974	O	-1.85856	-3.50352	-2.53847
C	-2.01755	1.284014	-1.43581	O	-0.55164	-0.92221	1.258676
C	-1.20578	0.148635	-0.80082	H	0.495605	2.620289	0.178512
C	-1.71845	-0.34515	0.589809	H	-2.98401	4.235779	-1.26149
C	-2.19197	0.860296	1.417941	H	-3.03512	0.944659	-1.66075
H	0.609867	-3.07889	1.643699	H	-1.58147	1.576582	-2.39569
C	0.678135	1.712698	2.120649	H	-1.18041	-0.66956	-1.5118
H	1.430538	-4.11401	0.444955	H	-2.47932	-1.1207	0.513542
C	1.252836	0.84282	-1.43889	H	-3.27348	1.001835	1.342059
H	3.840289	-0.16702	0.670333	H	-1.94815	0.702419	2.469303
C	2.696691	0.84587	-0.86716	H	1.602198	2.288134	2.172557
H	2.761455	1.032286	1.289414	H	-0.00447	2.18395	2.827159
C	2.834325	0.238763	0.553982	H	0.870488	0.702181	2.468921
H	3.076871	1.869702	-0.81441	H	1.024992	1.805696	-1.90306
N	1.891537	-0.84481	0.927083	H	1.173531	0.099327	-2.23633
H	3.350413	0.313733	-1.55968	H	3.036432	-2.41713	1.789204
C	0.575894	-0.82806	0.337831	H	4.422058	-2.48319	-0.24098
C	2.471647	-2.21974	0.877209	H	3.361275	-2.62069	-2.47633
C	3.345499	-2.41249	-0.35599	H	0.745164	-3.19715	-3.63671

Suffruticosine, structure 31

C	0.015632	1.73898	0.790632	C	0.838341	-2.86906	-2.55241
C	0.197347	0.554782	-0.30793	C	-0.56429	-3.02253	-2.17449
C	-2.60628	3.708701	-0.23957	O	-0.68616	-2.67948	-0.83811
C	-2.09509	2.479376	-0.34887	O	-1.52092	-3.39799	-2.80855
C	-1.51211	2.055864	0.962398	O	-0.68508	-0.9393	1.227598
O	-1.73961	3.17219	1.837423	H	0.350253	1.363481	1.758339
C	-2.39218	4.171605	1.141756	H	-3.1166	4.30773	-0.98067
O	-2.69794	5.209154	1.676078	H	-3.00407	1.109821	-1.71217
C	-2.00308	1.42263	-1.39554	H	-1.50829	1.796936	-2.29735
C	-1.22567	0.229109	-0.81569	H	-1.19534	-0.55201	-1.56919
C	-1.8058	-0.33308	0.525932	H	-2.56765	-1.09615	0.368505
C	-2.28983	0.816393	1.415755	H	-3.36429	0.994173	1.317376
H	0.37764	-3.04304	1.688634	H	-2.07818	0.579332	2.459854
C	0.760484	3.050593	0.496445	H	0.444479	3.511579	-0.44135
H	1.361182	-4.06618	0.60782	H	1.838836	2.923078	0.454717
C	1.308375	0.852893	-1.31489	H	0.559871	3.764804	1.295825
C	2.70863	0.782366	-0.63236	H	1.161035	1.823481	-1.79036
C	2.675645	0.309443	0.844245	H	1.25399	0.117511	-2.12085
N	1.734264	-0.7907	1.15122	H	3.352746	0.118736	-1.20721
C	0.497876	-0.79749	0.408492	H	3.19447	1.760885	-0.65621
C	2.321953	-2.16548	1.180559	H	3.672092	-0.02766	1.1356
C	3.354011	-2.37447	0.080752	H	2.755858	-2.36039	2.162077
C	2.953792	-2.46088	-1.20018	H	4.404734	-2.44766	0.341535
C	1.532646	-2.45583	-1.47231	H	3.652679	-2.61956	-2.0145
C	0.570142	-2.23634	-0.32871	H	1.218302	-3.15075	-3.52397
C	1.098523	-3.04268	0.873306	H	2.453649	1.151071	1.501553

Suffruticosine, structure 32

C	0.730089	0.402164	-1.06741	C	3.628866	1.922438	-1.45933
C	-0.81366	-0.10787	-0.93468	O	1.130469	1.432207	1.193124
C	-1.68196	0.619794	-1.98581	C	3.413941	1.290645	0.978672
C	-1.23159	0.432273	-3.44467	C	2.296643	1.228063	1.910885
C	0.310974	0.40791	-3.55468	O	2.261613	1.064705	3.106303
N	0.959526	0.952551	-2.37874	O	1.513607	-0.78932	-0.81365
C	1.401998	1.550562	-0.19422	C	-0.59455	-1.63546	-1.25816
C	1.380932	2.364578	-2.34001	C	-1.58849	-0.09915	0.443601
C	0.961561	2.822293	-0.92203	C	-1.21155	-1.40528	1.216901
C	2.934161	1.517372	-0.2569	C	-1.74672	-2.5937	-0.90598
C	2.895508	2.412018	-2.47193	C	-2.00616	-2.49443	0.561506

C	0.277404	-1.78187	1.101436	H	-0.11375	2.988477	-0.85599
O	-1.65235	-1.41058	2.583571	H	3.352222	2.79687	-3.37793
C	-2.58724	-2.41207	2.758389	H	4.71312	1.897477	-1.47835
C	-2.79697	-3.08168	1.463381	H	4.445656	1.242779	1.29615
O	-3.09237	-2.6158	3.83496	H	-0.32957	-1.77851	-2.30389
C	0.655713	-1.85813	-0.40552	H	-2.62082	-0.26912	0.120058
C	-1.69613	1.163776	1.309779	H	-1.47976	-3.61579	-1.19269
H	-2.71779	0.282755	-1.88929	H	-2.65174	-2.35189	-1.47303
H	-1.70043	1.686721	-1.74492	H	0.430562	-2.74621	1.592324
H	-1.64785	1.244255	-4.04734	H	0.900985	-1.05226	1.614794
H	-1.64456	-0.49443	-3.855	H	-3.50533	-3.88782	1.334164
H	0.653256	0.978902	-4.41942	H	1.185952	-2.78268	-0.63588
H	0.669046	-0.61322	-3.71868	H	-0.85645	1.306794	1.977593
H	0.889191	2.938733	-3.12541	H	-1.7893	2.055977	0.685309
H	1.485343	3.7153	-0.58036	H	-2.60525	1.097858	1.910973

Suffruticosine, structure 33

C	0.31486	0.29288	-1.10477	C	-3.15067	-3.09823	2.037214
C	-1.2187	-0.20228	-1.0881	C	-3.4036	-3.43276	0.62524
C	-2.06678	0.729919	-1.97585	O	-3.68376	-3.49877	3.043125
C	-1.60115	0.798685	-3.44244	C	0.192509	-2.07135	-0.91758
C	-0.05922	0.742775	-3.56297	C	-3.27383	0.081627	0.561885
N	0.61011	1.031103	-2.30852	H	-3.11132	0.416014	-1.95634
C	0.941092	1.2955	-0.02078	H	-2.057	1.7347	-1.54452
C	1.155874	2.370535	-2.03718	H	-1.9846	1.722711	-3.88385
C	0.642079	2.672112	-0.61373	H	-2.04272	-0.01942	-4.01986
C	2.46137	1.168383	0.065474	H	0.263158	-0.23691	-3.93079
C	2.675427	2.28223	-2.03768	H	0.299603	1.461214	-4.30148
C	3.283019	1.634708	-1.02923	H	0.797256	3.087578	-2.77511
O	0.513217	1.069685	1.318546	H	1.18184	3.474415	-0.10929
C	2.795723	0.78326	1.309767	H	-0.4247	2.898838	-0.61386
C	1.586083	0.705773	2.120168	H	3.23795	2.702855	-2.86499
O	1.419193	0.427423	3.281606	H	4.359856	1.515619	-0.97552
O	1.071211	-0.94266	-1.00405	H	3.783855	0.6294	1.718971
C	-1.03856	-1.62874	-1.71473	H	-0.76686	-1.56313	-2.76572
C	-1.82879	-0.4005	0.368773	H	-1.22792	0.153624	1.079137
C	-1.66992	-1.90022	0.751344	H	-2.03088	-3.53525	-2.04499
C	-2.24847	-2.56918	-1.57776	H	-3.11706	-2.16888	-2.11128
C	-2.54914	-2.73281	-0.12621	H	-0.16236	-3.4448	0.758533
C	-0.21904	-2.37419	0.546261	H	0.453889	-1.86498	1.23774
O	-2.12481	-2.17574	2.087402	H	-4.16777	-4.13497	0.322585

H	0.723951	-2.91297	-1.3631	H	-3.35351	1.155094	0.384352
H	-3.57705	-0.09518	1.595837	H	-3.99793	-0.41976	-0.08369

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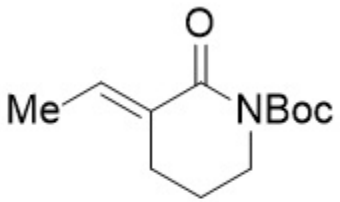
15. Copies of NMR spectra of newly synthesized compounds

Parameter	Value
Origin	Bruker BioSpin GmbH
Instrument	Avance
Solvent	CDCl3
Temperature	298.0
Experiment	1D
Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
Number of Scans	16
Spectrometer Frequency	500.23
Nucleus	1H



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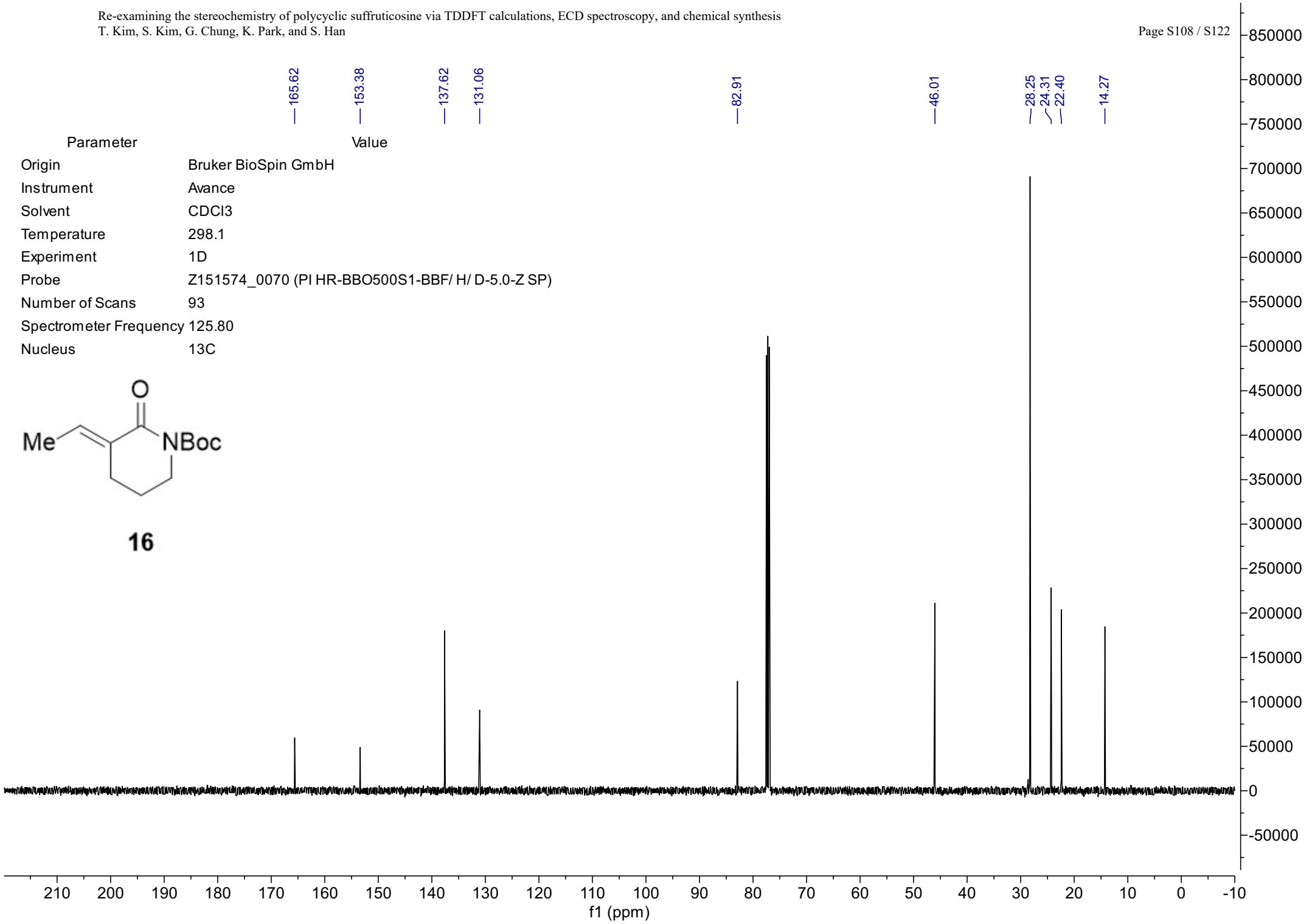
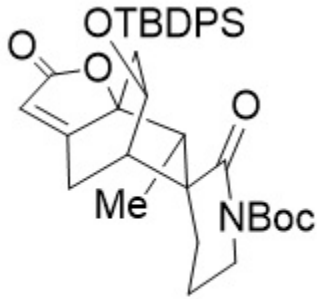

165.62
153.38
137.62
131.06
82.91
46.01
28.25
24.31
22.40
14.27
Parameter Value
Origin Bruker BioSpin GmbH
Instrument Avance
Solvent CDCl3
Temperature 298.1
Experiment 1D
Probe Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
Number of Scans 93
Spectrometer Frequency 125.80
Nucleus 13C
O
Me
NBoc
16
850000
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

Parameter	Value
Origin	Bruker BioSpin GmbH
Instrument	Avance
Solvent	CDCl3
Temperature	298.0
Experiment	1D
Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
Number of Scans	7
Spectrometer Frequency	500.23
Nucleus	1H



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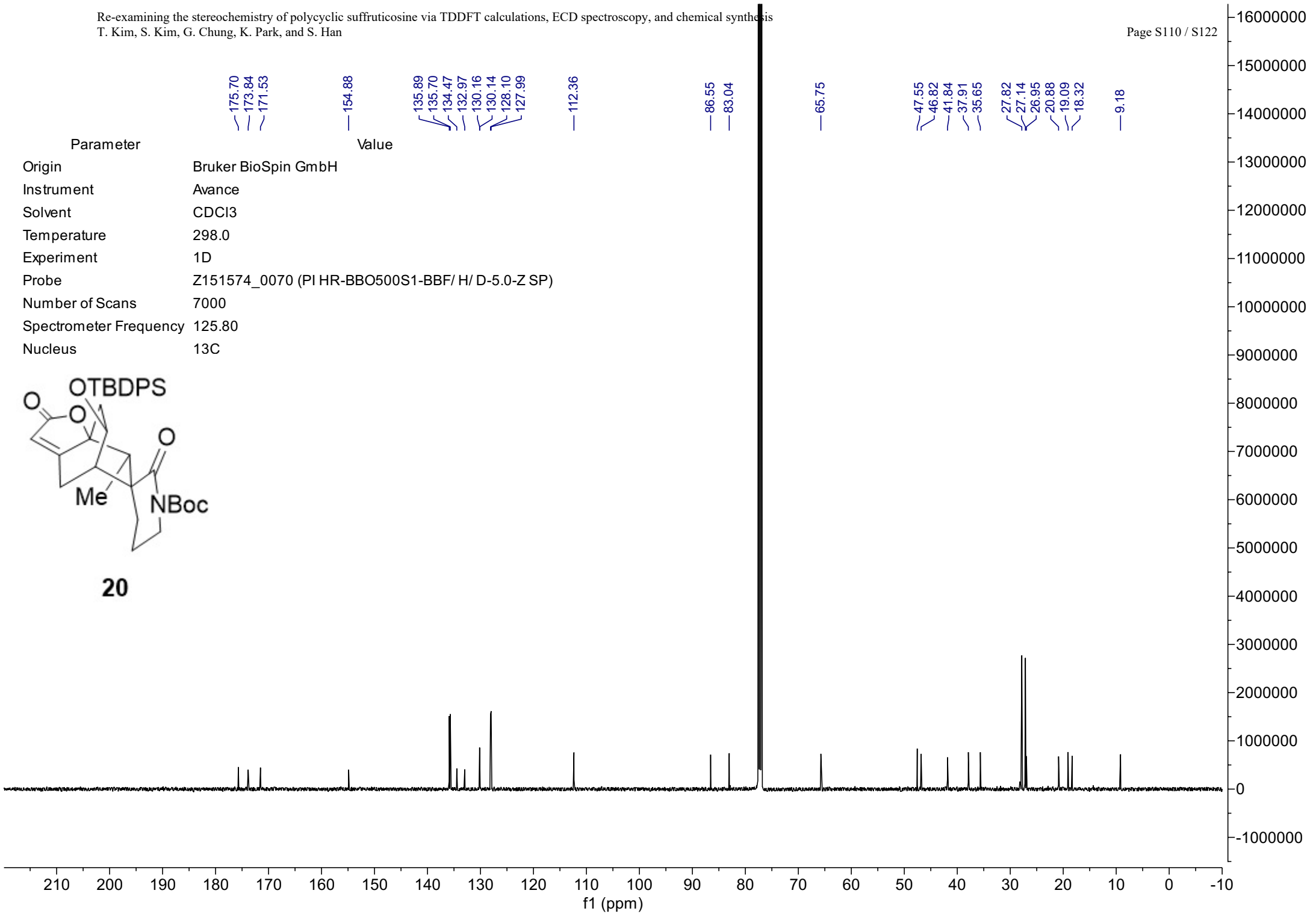
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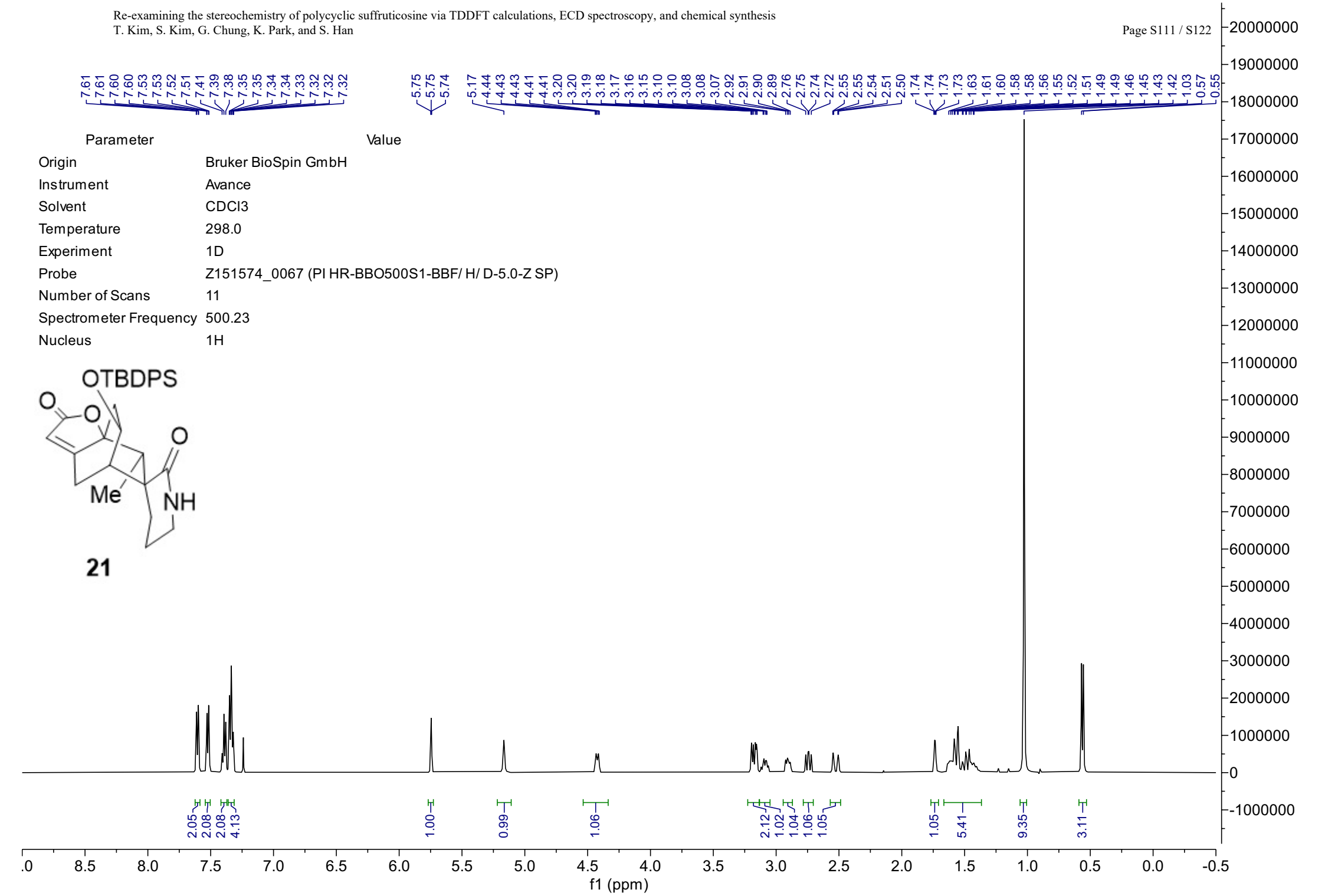
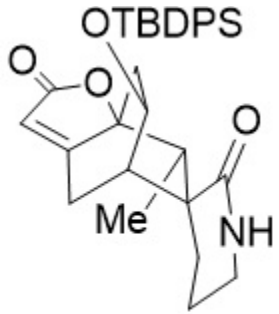
173.84
171.53
154.88
135.89
135.70
134.47
132.97
130.16
130.14
128.10
127.99
112.36
86.55
83.04
65.75
47.55
46.82
41.84
37.91
35.65
27.82
27.14
26.95
20.88
19.09
18.32
9.18
Parameter
Value
Origin
Bruker BioSpin GmbH
Instrument
Avance
Solvent
CDCl3
Temperature
298.0
Experiment
1D
Probe
Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
Number of Scans
7000
Spectrometer Frequency
125.80
Nucleus
13C
OTBDPS
O
O
O
Me
NBoc
20
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.61 7.61 7.60 7.60 7.53 7.53 7.52 7.51 7.41 7.39 7.38 7.35 7.35 7.34 7.34 7.33 7.32 7.32 7.32
5.75 5.75 5.74
5.17 4.44 4.43 4.43 4.41 4.41 3.20 3.20 3.19 3.18 3.17 3.16 3.15 3.10 3.10 3.08 3.08 3.07 2.92 2.91 2.90 2.89 2.76 2.75 2.74 2.72 2.55 2.55 2.54 2.51 2.50
1.74 1.74 1.73 1.73 1.63 1.61 1.60 1.58 1.58 1.56 1.55 1.52 1.51 1.49 1.49 1.46 1.45 1.43 1.42 1.03 0.57 0.55
Parameter Value
Origin Bruker BioSpin GmbH
Instrument Avance
Solvent CDCl3
Temperature 298.0
Experiment 1D
Probe Z151574_0067 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
Number of Scans 11
Spectrometer Frequency 500.23
Nucleus 1H
OTBDPS
O
O
O
Me
NH
21
20000000
19000000
18000000
17000000
16000000
15000000
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
2.05 2.08 2.08 4.13 1.00 0.99 1.06 2.12 1.02 1.04 1.06 1.05 1.05 5.41 9.35 3.11
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

Parameter	Value
Origin	Bruker BioSpin GmbH
Instrument	Avance
Solvent	CDCl3
Temperature	298.0
Experiment	1D
Probe	Z151574_0067 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
Number of Scans	4352
Spectrometer Frequency	125.80
Nucleus	13C



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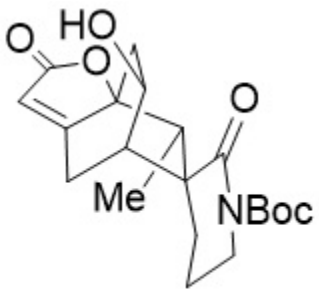
Parameter	Value
Origin	Bruker BioSpin GmbH
Instrument	Avance
Solvent	CDCl3
Temperature	298.0
Experiment	1D
Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
Number of Scans	15
Spectrometer Frequency	500.23
Nucleus	1H



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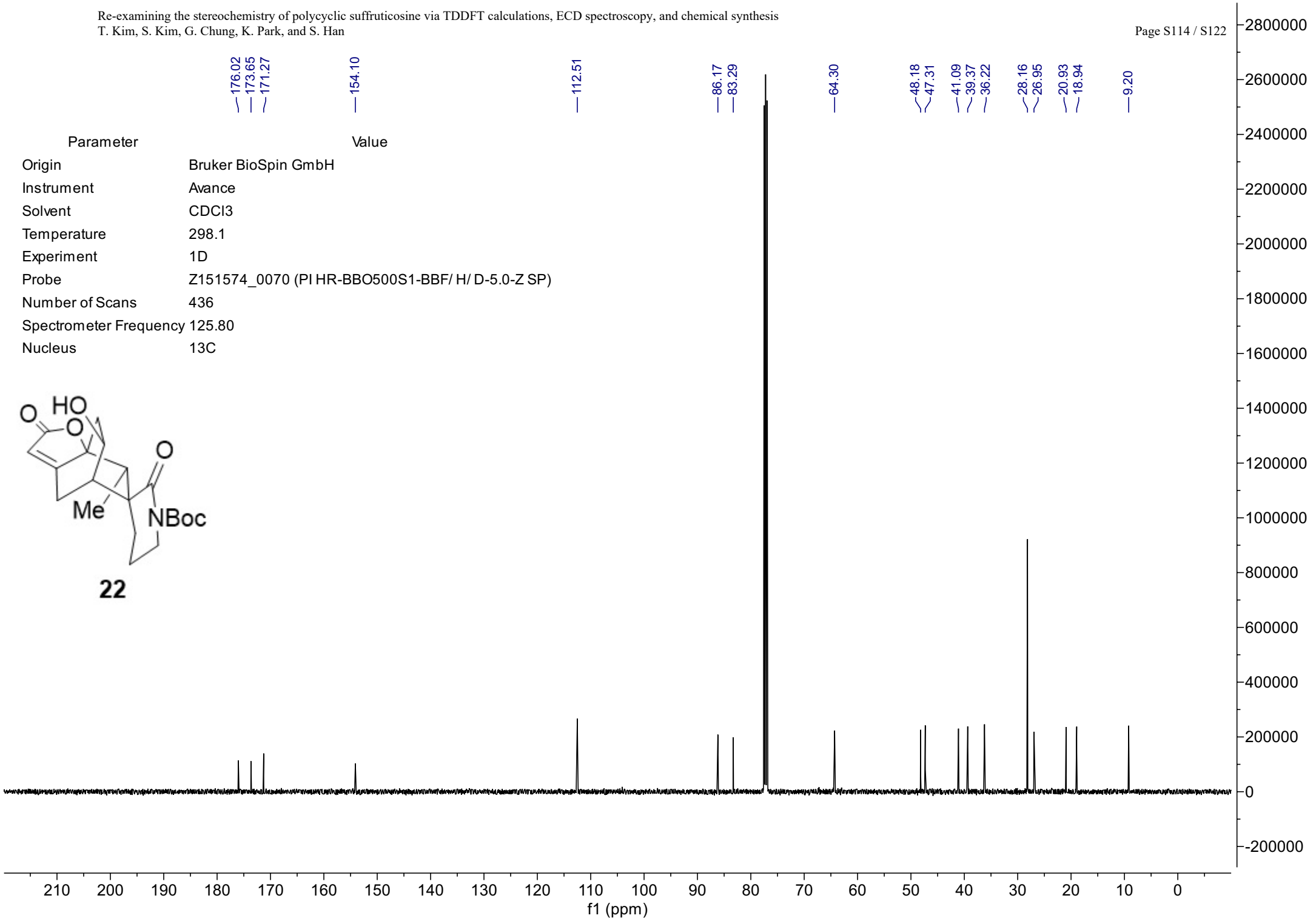
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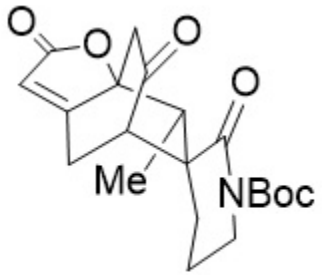
112.51
86.17
83.29
64.30
48.18
47.31
41.09
39.37
36.22
28.16
26.95
20.93
18.94
9.20
Parameter Value
Origin Bruker BioSpin GmbH
Instrument Avance
Solvent CDCl3
Temperature 298.1
Experiment 1D
Probe Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
Number of Scans 436
Spectrometer Frequency 125.80
Nucleus 13C
HO
O
O
O
Me
NBoc
22
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

Parameter	Value
Origin	Bruker BioSpin GmbH
Instrument	Avance
Solvent	CDCl3
Temperature	298.0
Experiment	1D
Probe	Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
Number of Scans	16
Spectrometer Frequency	500.23
Nucleus	1H



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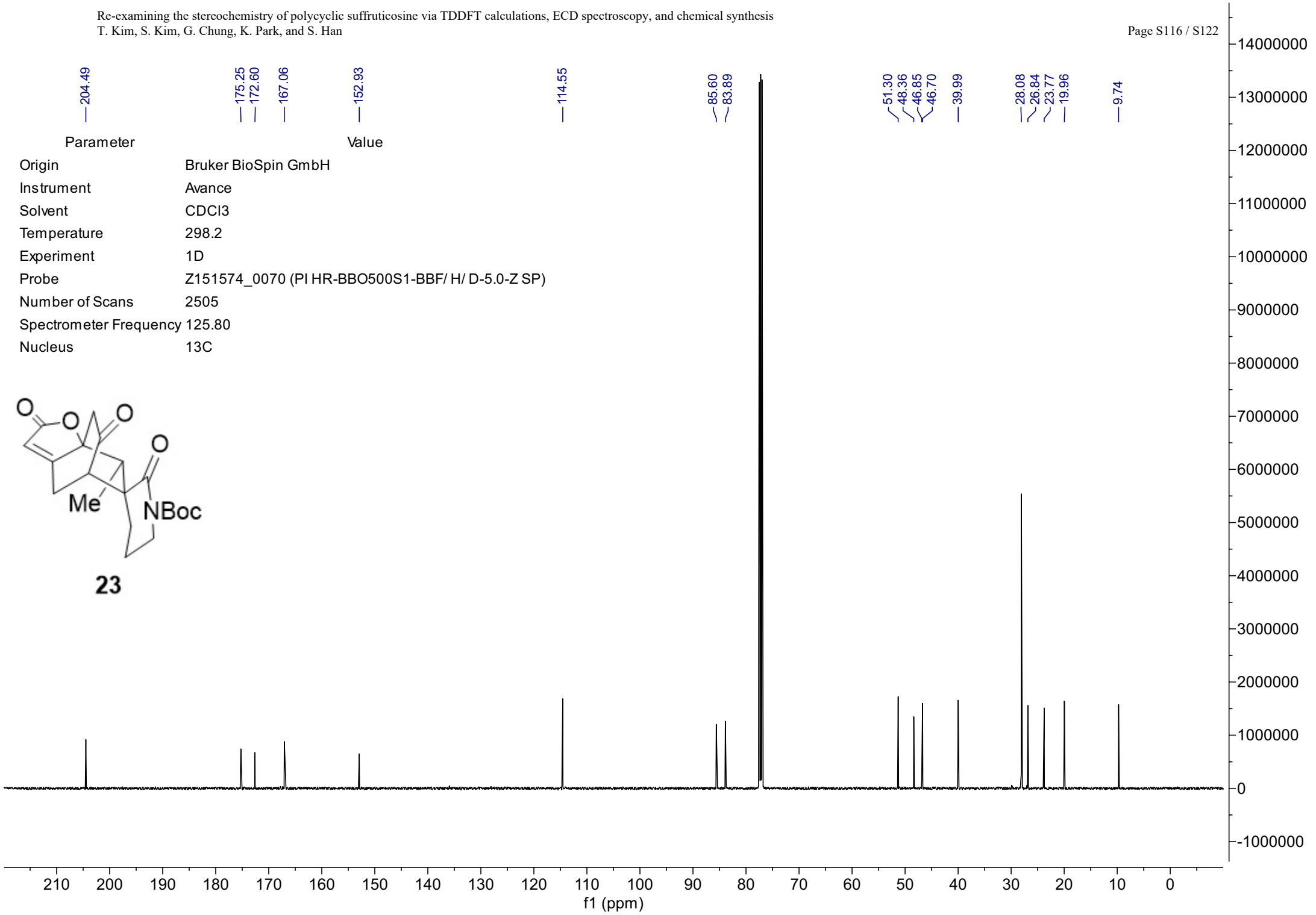
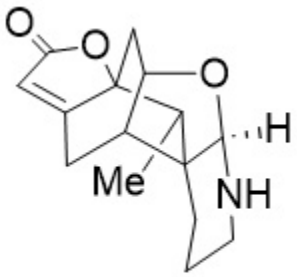

204.49
175.25
172.60
167.06
152.93
114.55
85.60
83.89
51.30
48.36
46.85
46.70
39.99
28.08
26.84
23.77
19.96
9.74
Parameter
Value
Origin
Bruker BioSpin GmbH
Instrument
Avance
Solvent
CDCl3
Temperature
298.2
Experiment
1D
Probe
Z151574_0070 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
Number of Scans
2505
Spectrometer Frequency
125.80
Nucleus
13C
O
O
O
O
Me
NBoc
23
14000000
13000000
12000000
11000000
10000000
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
-1000000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Parameter	Value
Origin	Varian
Instrument	vnmrs
Solvent	cdcl3
Temperature	25.0
Experiment	1D
Probe	5mm_One_probe
Number of Scans	20
Spectrometer Frequency	599.78
Nucleus	1H



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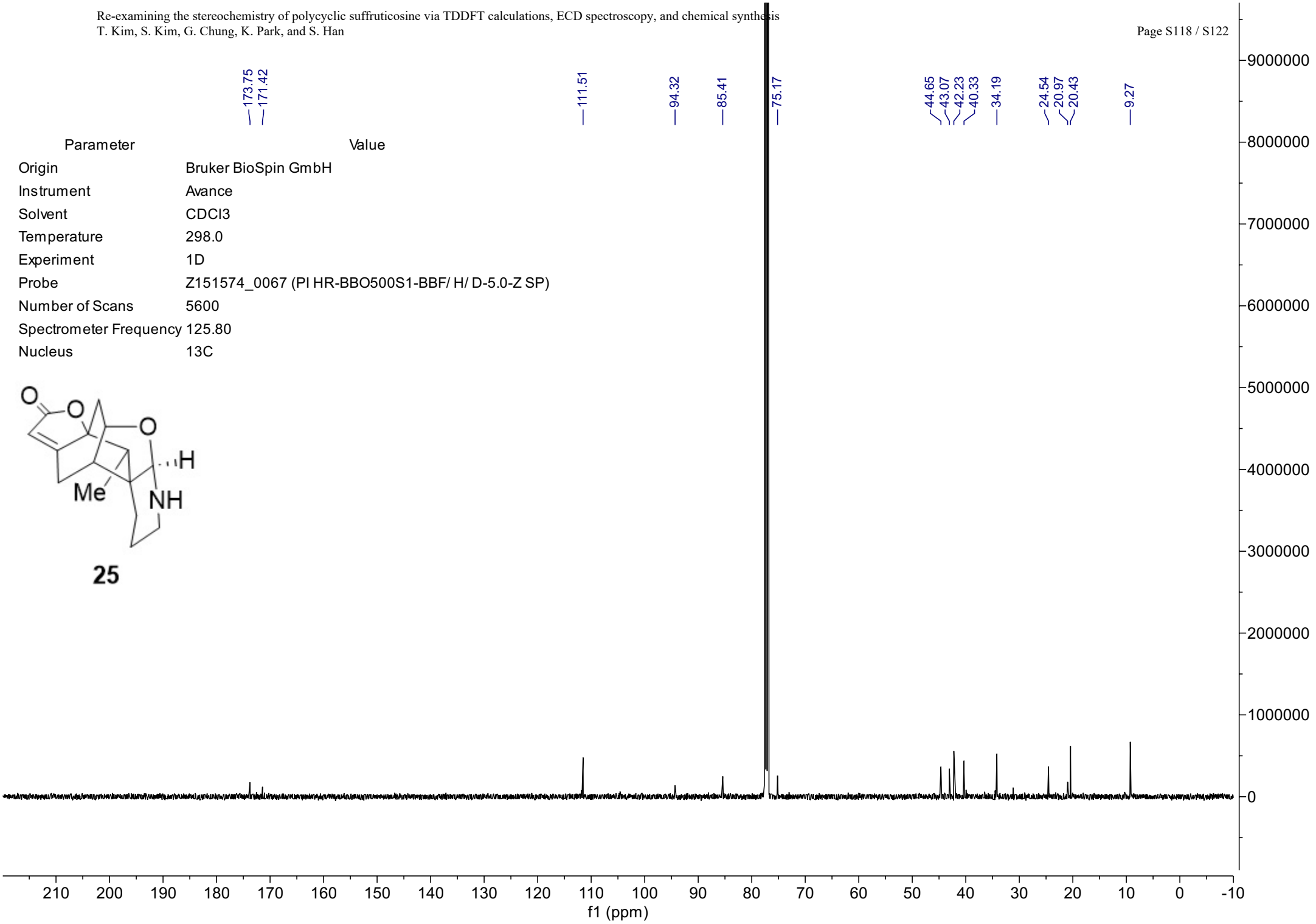
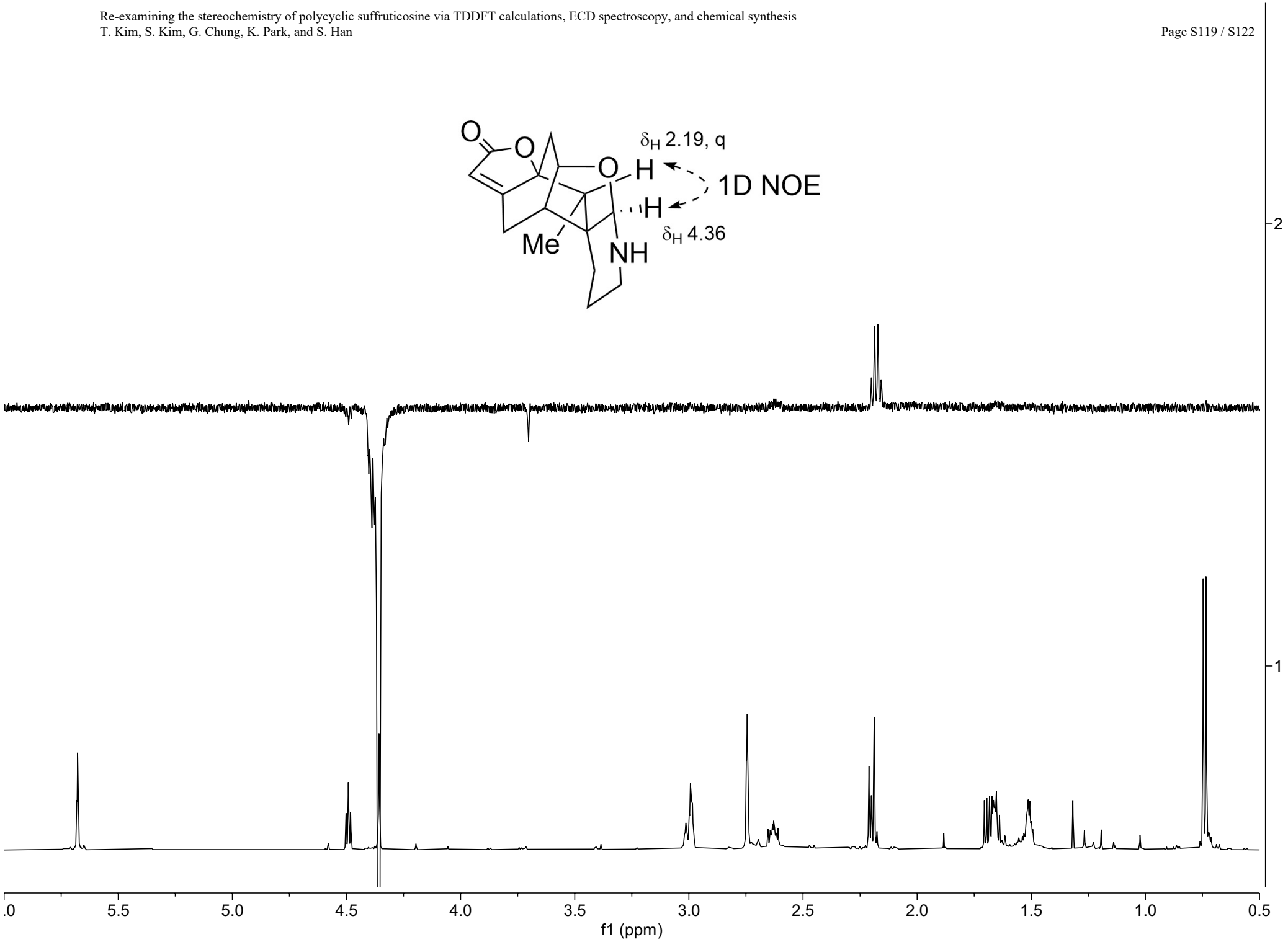
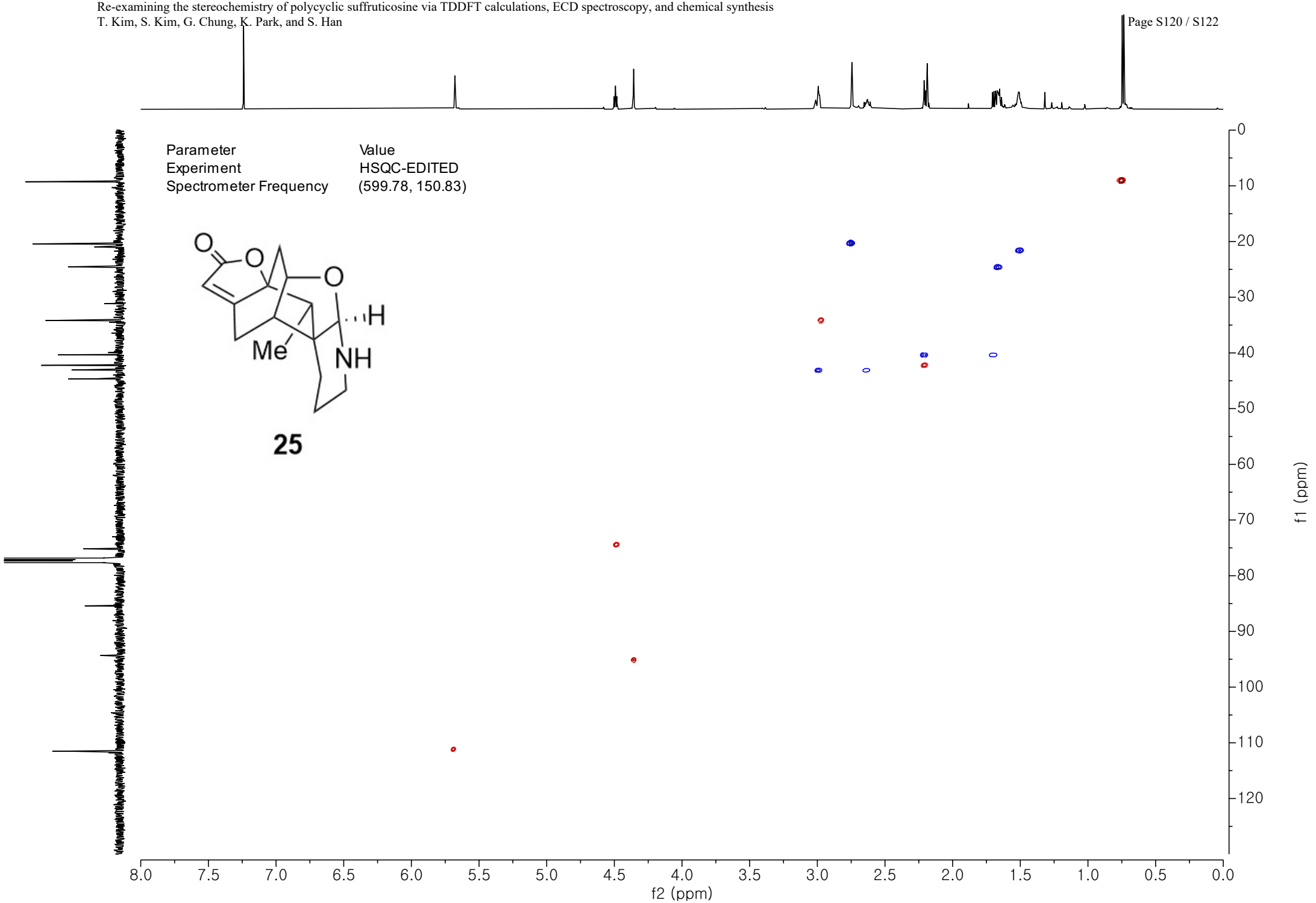


Parameter	Value
Origin	Bruker BioSpin GmbH
Instrument	Avance
Solvent	CDCl3
Temperature	298.0
Experiment	1D
Probe	Z151574_0067 (PI HR-BBO500S1-BBF/ H/ D-5.0-Z SP)
Number of Scans	5600
Spectrometer Frequency	125.80
Nucleus	13C

25


O
O
O
H
H
Me
NH
δH 2.19, q
1D NOE
δH 4.36
2
1
.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


Parameter Value
Experiment HSQC-EDITED
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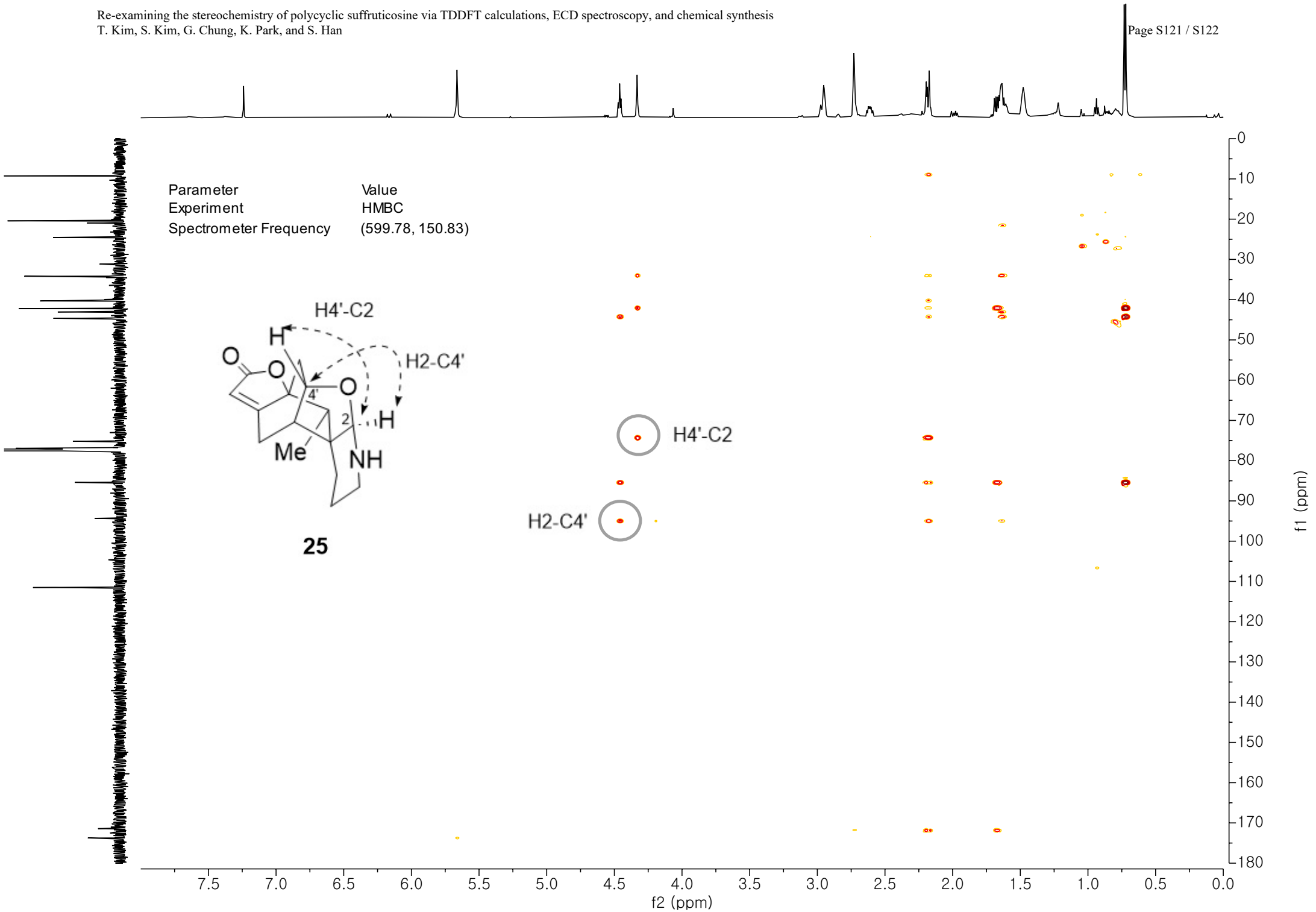
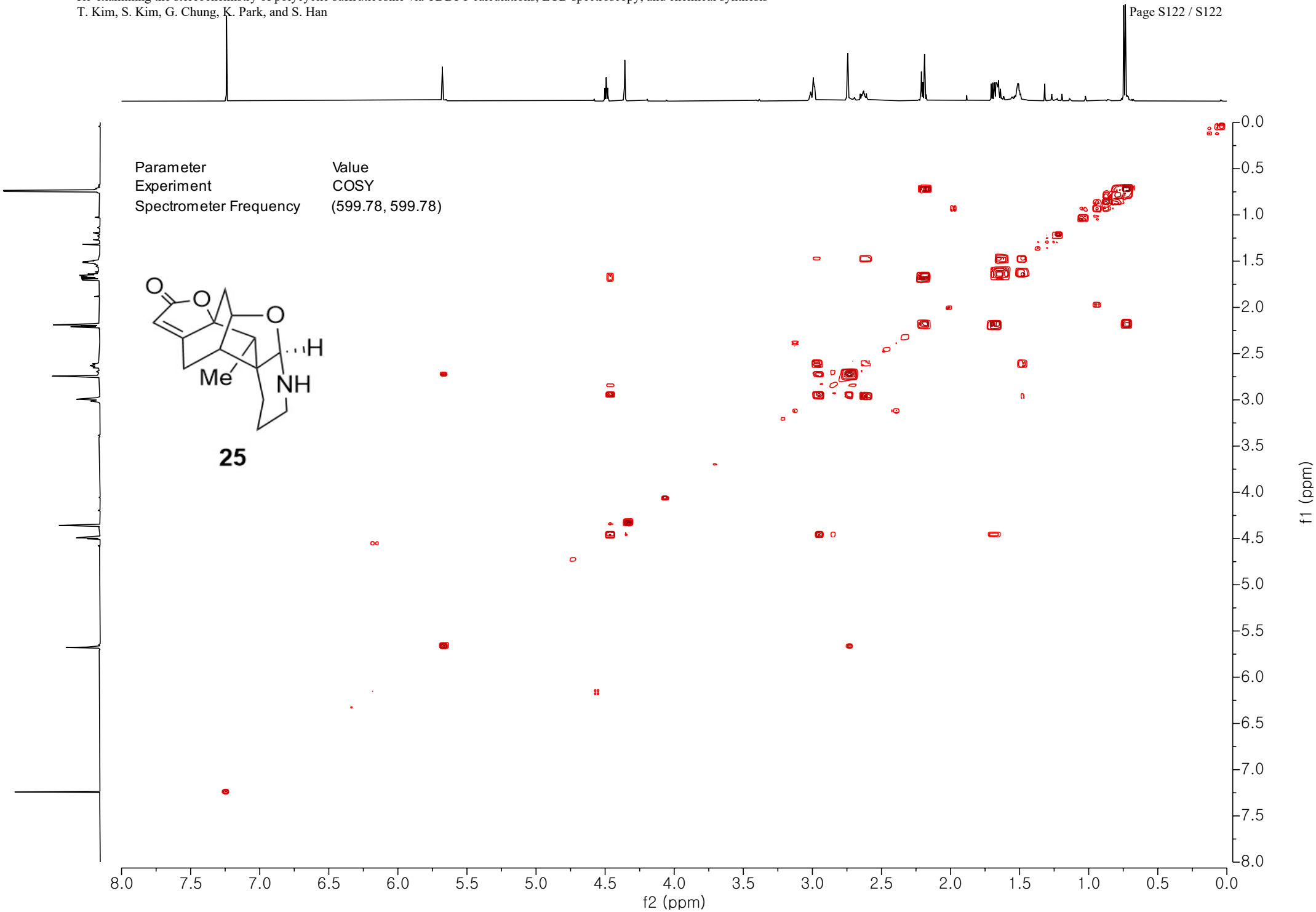
O
H
Me
NH
25
f2 (ppm)
f1 (ppm)


Parameter Value
Experiment HMBC
Spectrometer Frequency (599.78, 150.83)
H4'-C2
H2-C4'
H
O
O
O
4'
2
H
Me
NH
25
H4'-C2
H2-C4'
f2 (ppm)
f1 (ppm)


Parameter Value
Experiment COSY
Spectrometer Frequency (599.78, 599.78)
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O
O
H
Me
NH
25
f2 (ppm)
f1 (ppm)