Supporting Information

Wavelength-Dependent Photochemistry and Biological Relevance of a Bilirubin Dipyrrinone Subunit

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Contents

Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$): **2**.

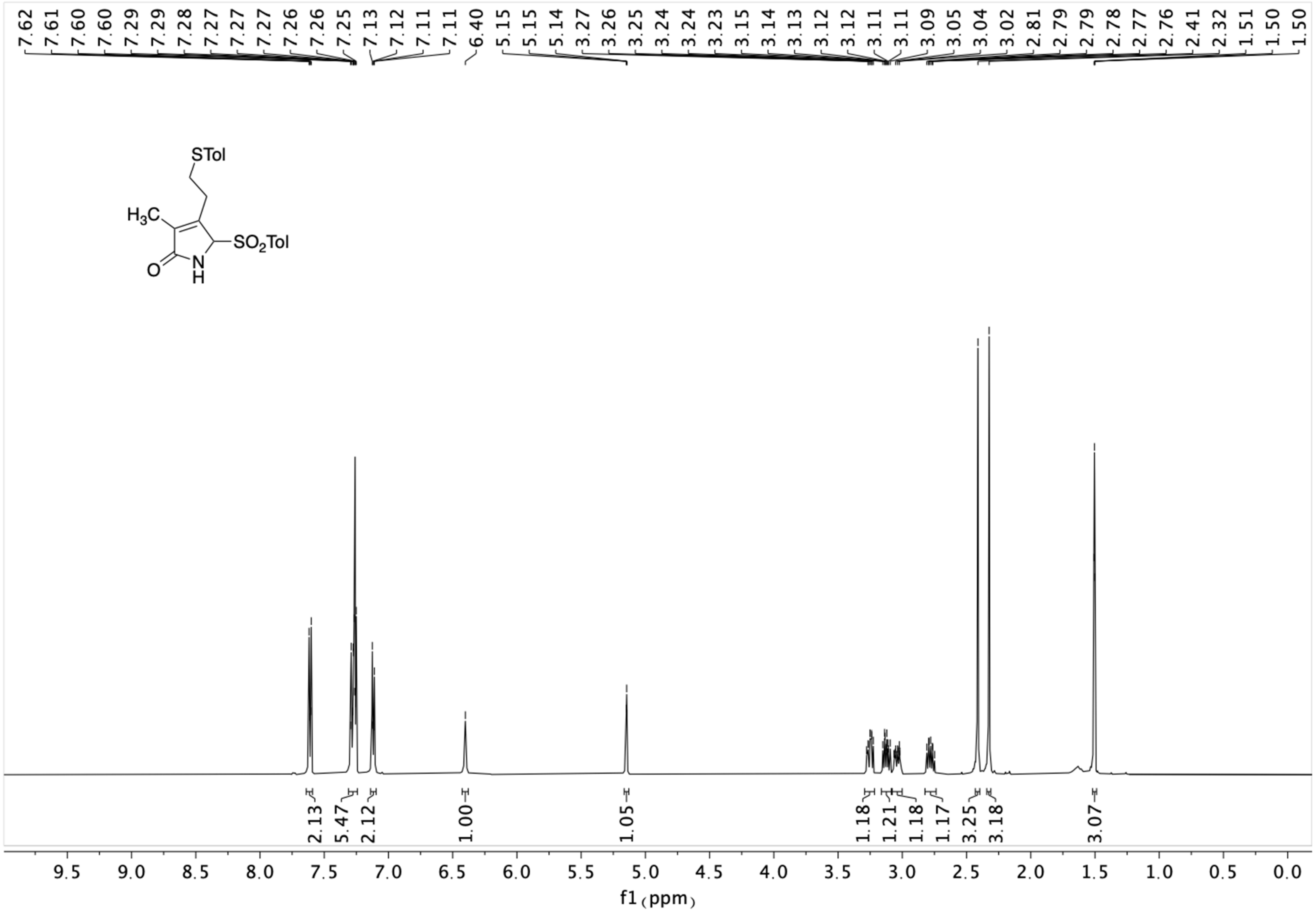


Figure S2. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): **2**.

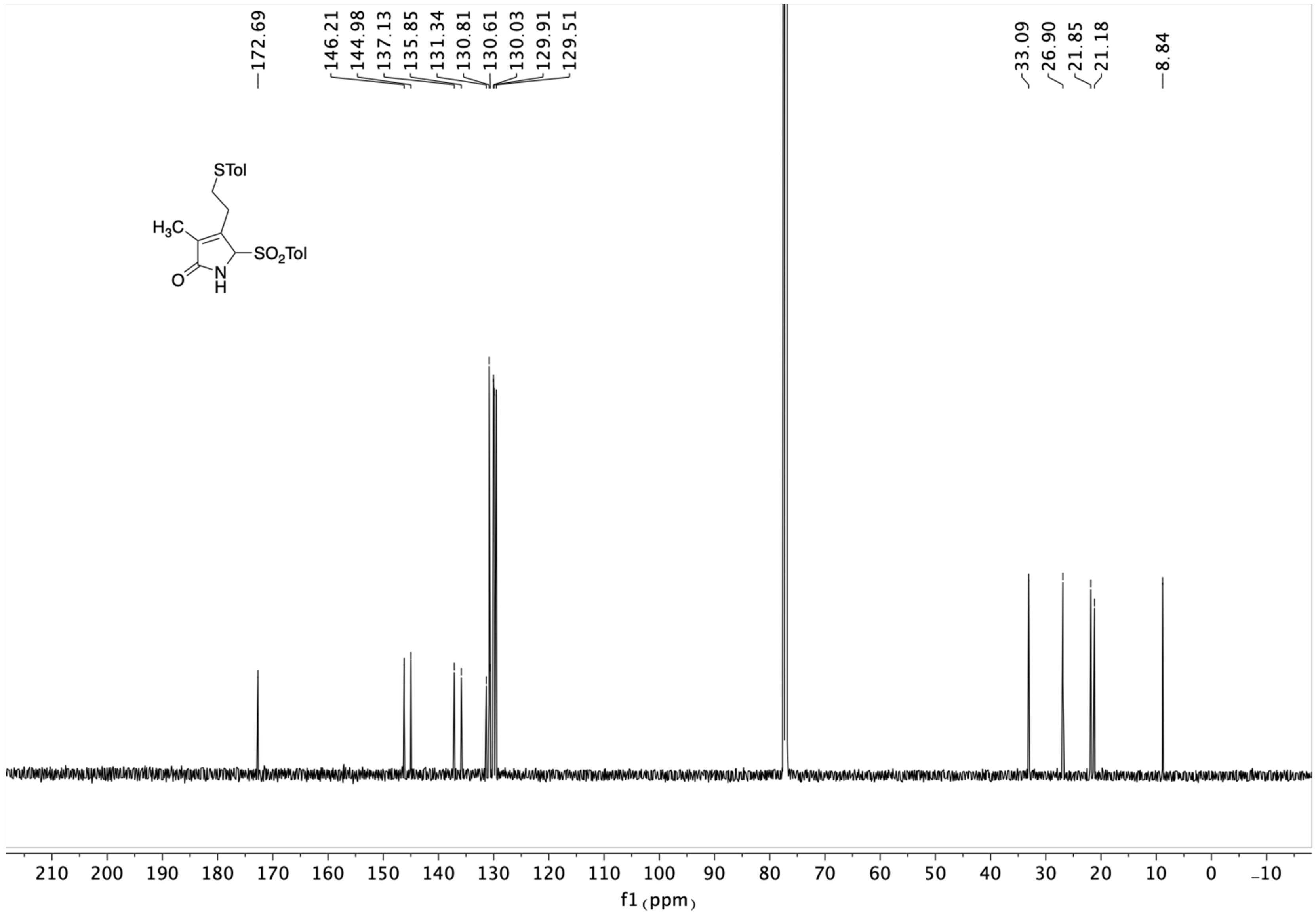


Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$): **3**.

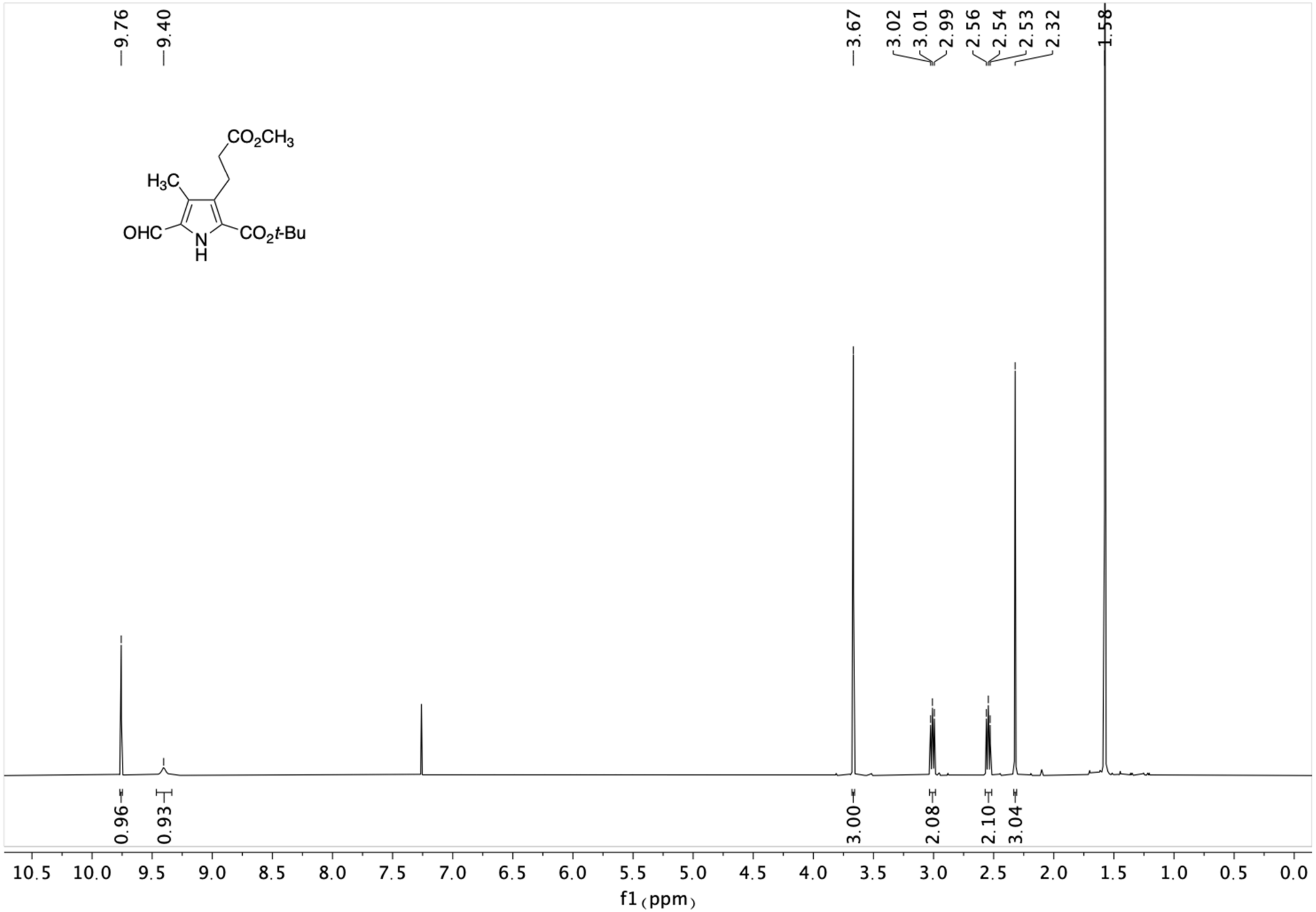


Figure S4. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): **3**.

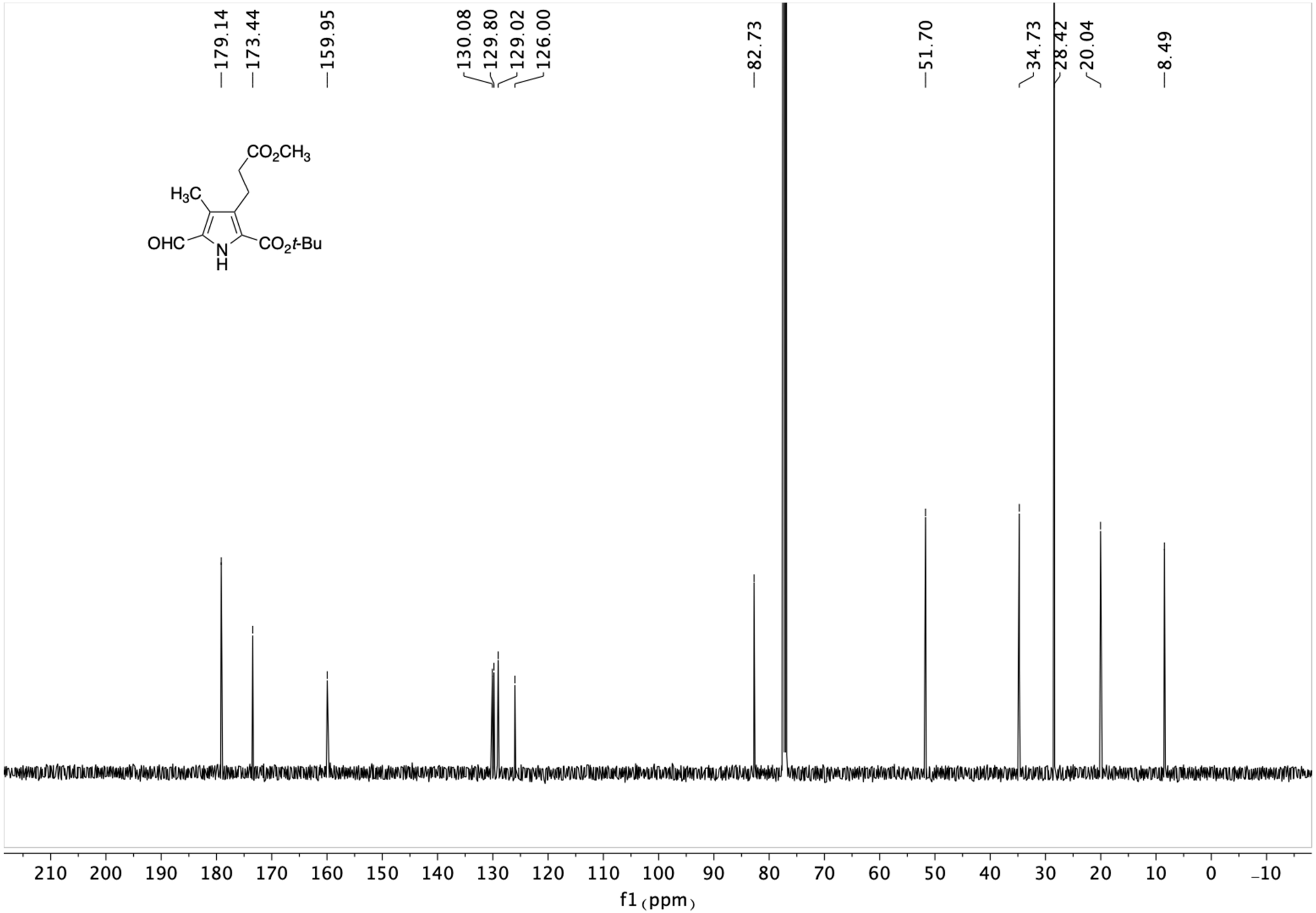


Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$): *E*-**4.**

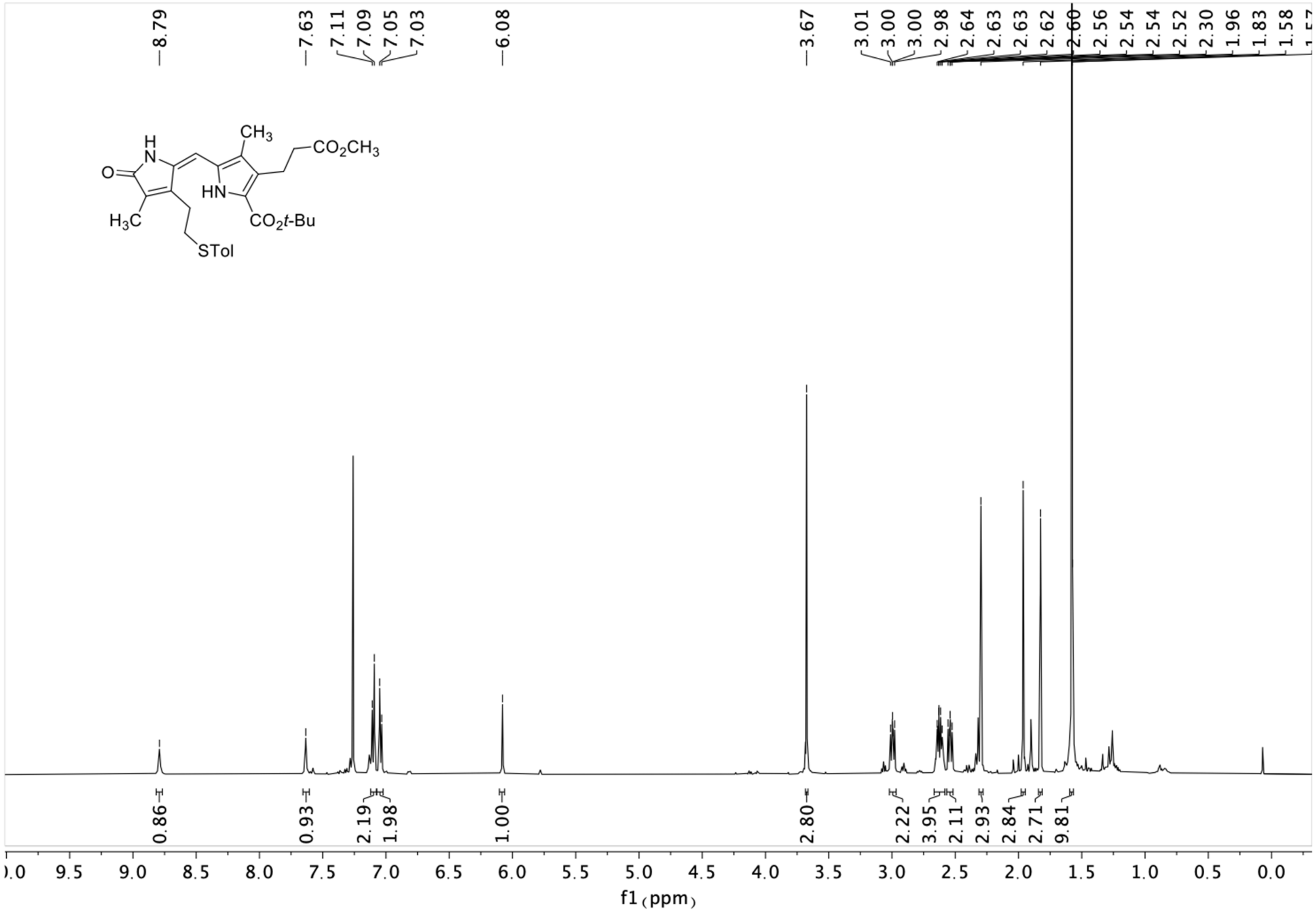


Figure S6. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): *E*-**4.**

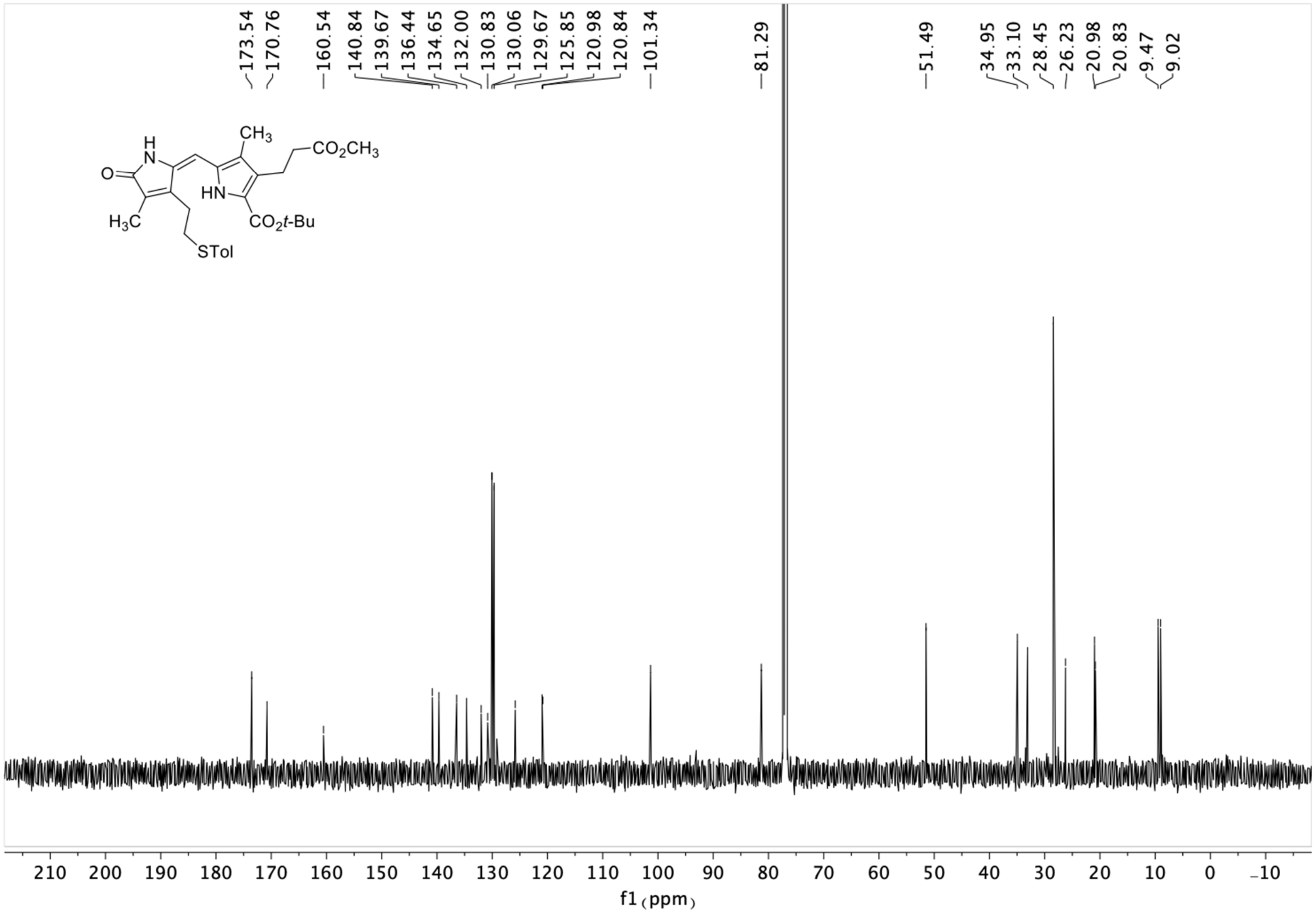
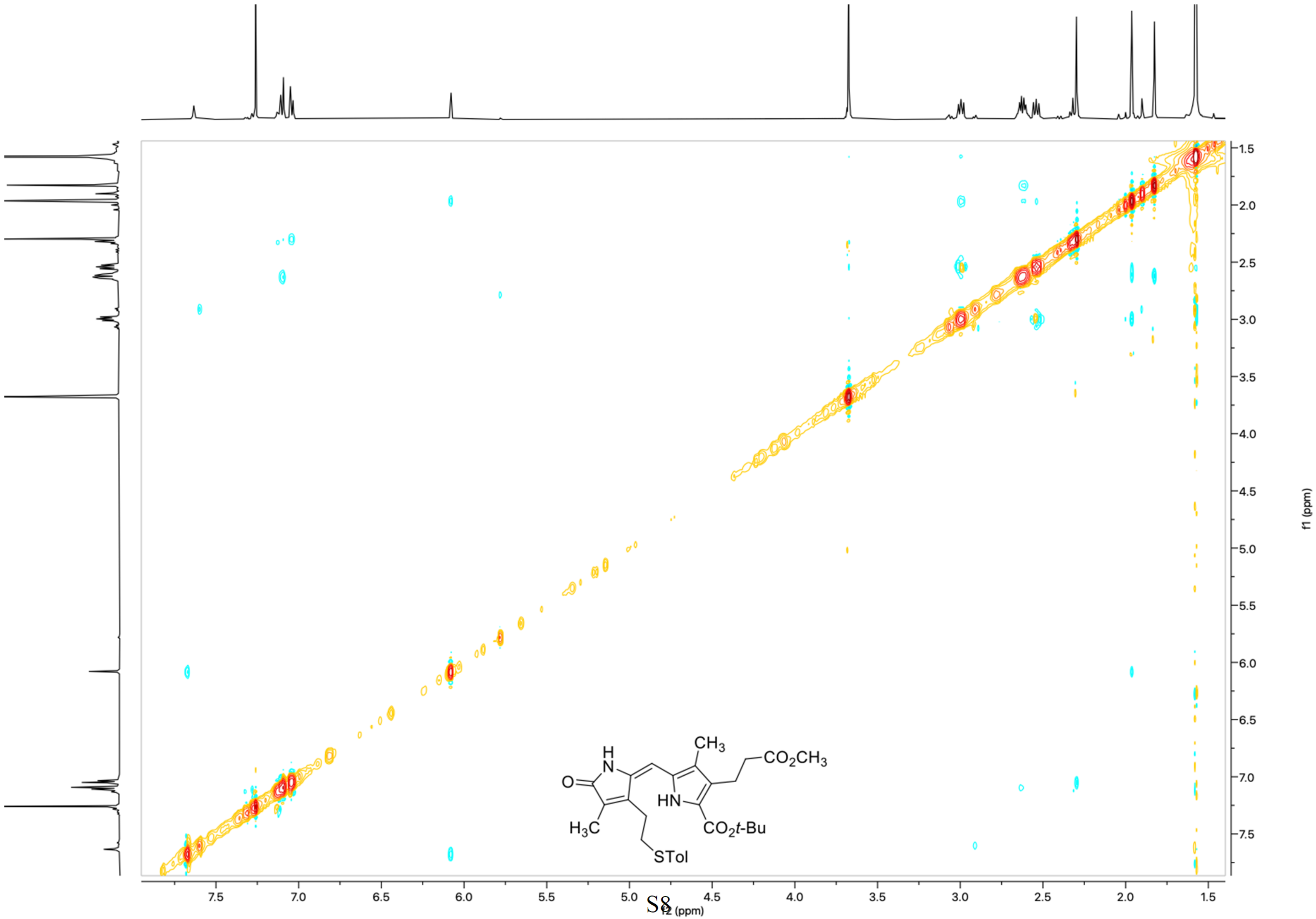


Figure S7. ^1H-^1H NOESY (500 MHz, $CDCl_3$): *E*-**4**: (**A**) The full spectrum; (**B**) a detail of the range of 5.80–6.35 ppm, a circled cross-peaks depict the NOE effect between the bridge hydrogen and the hydrogen of lactam NH and a methyl group.

A



B

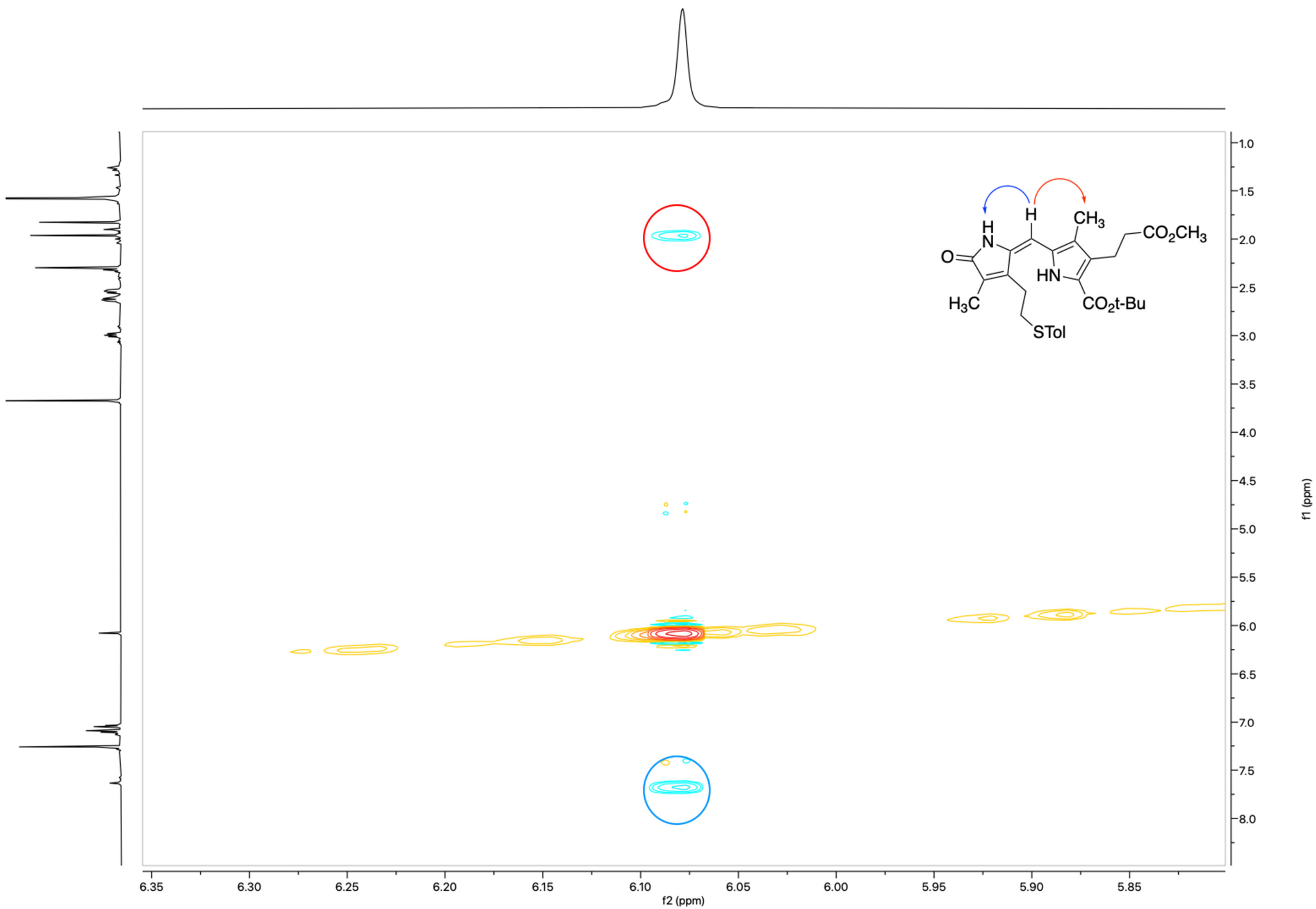


Figure S8. ^{1}H NMR (500 MHz, $CDCl_3$): *Z*-**4.**

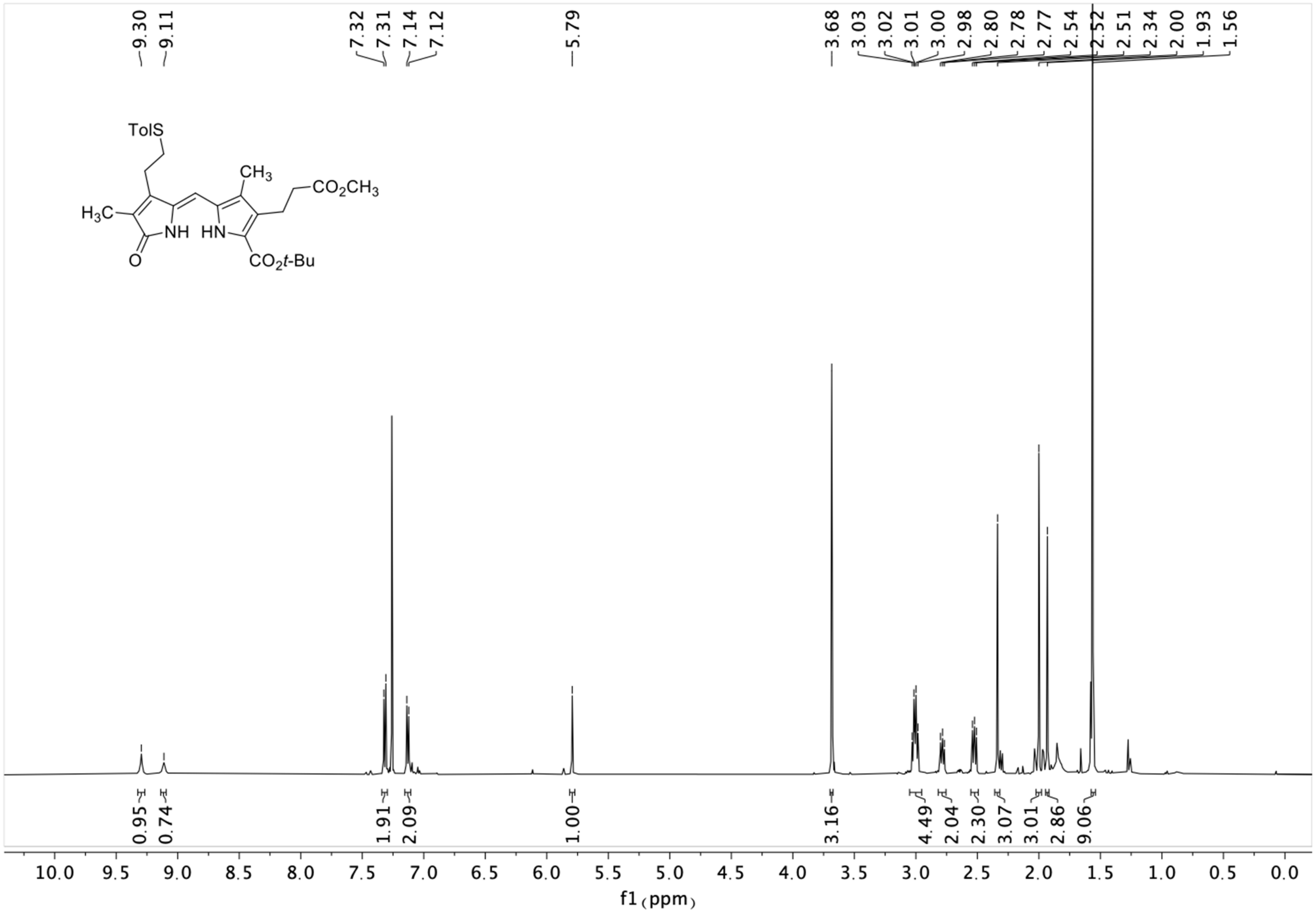


Figure S9. $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): *Z*-**4.**

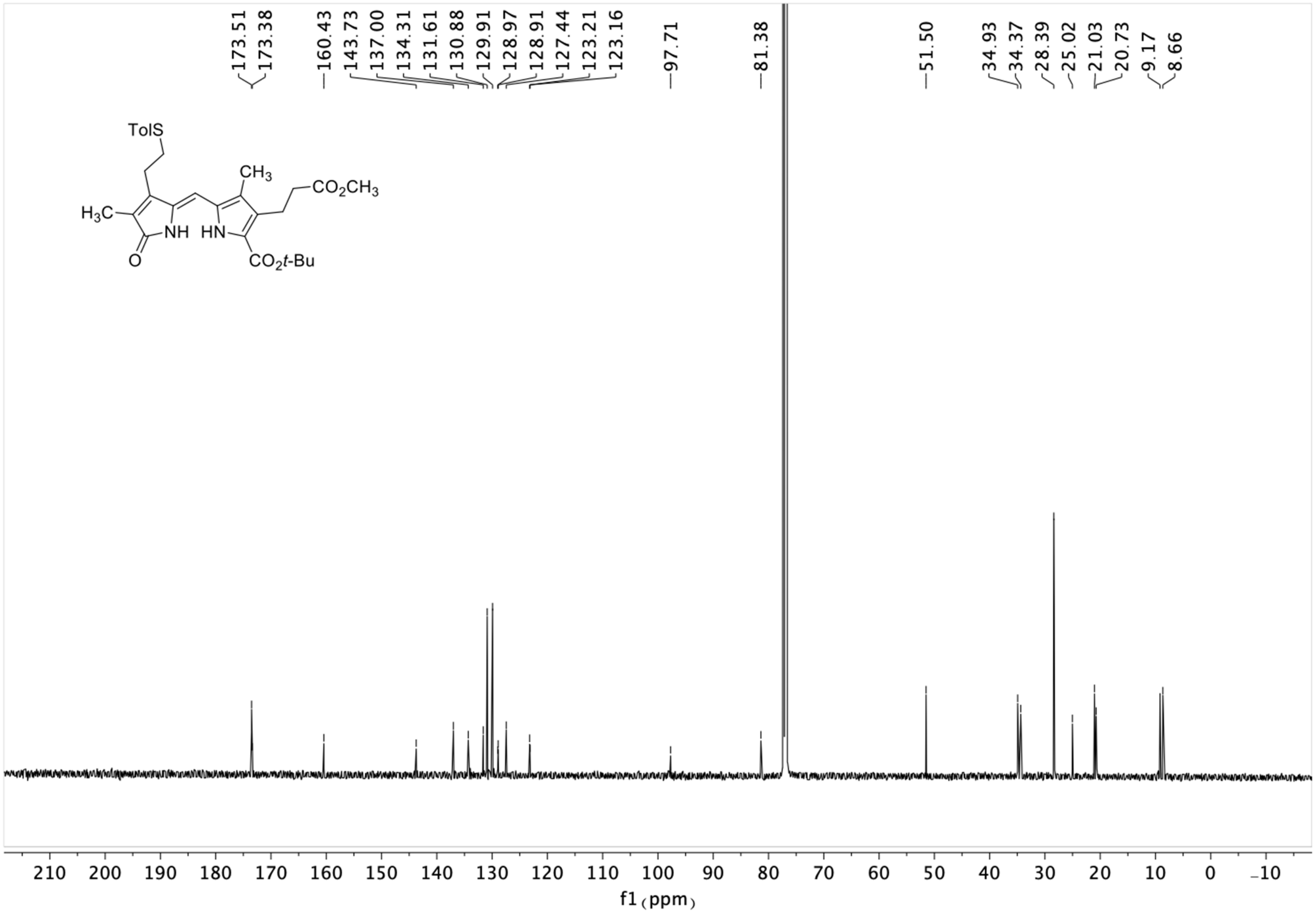
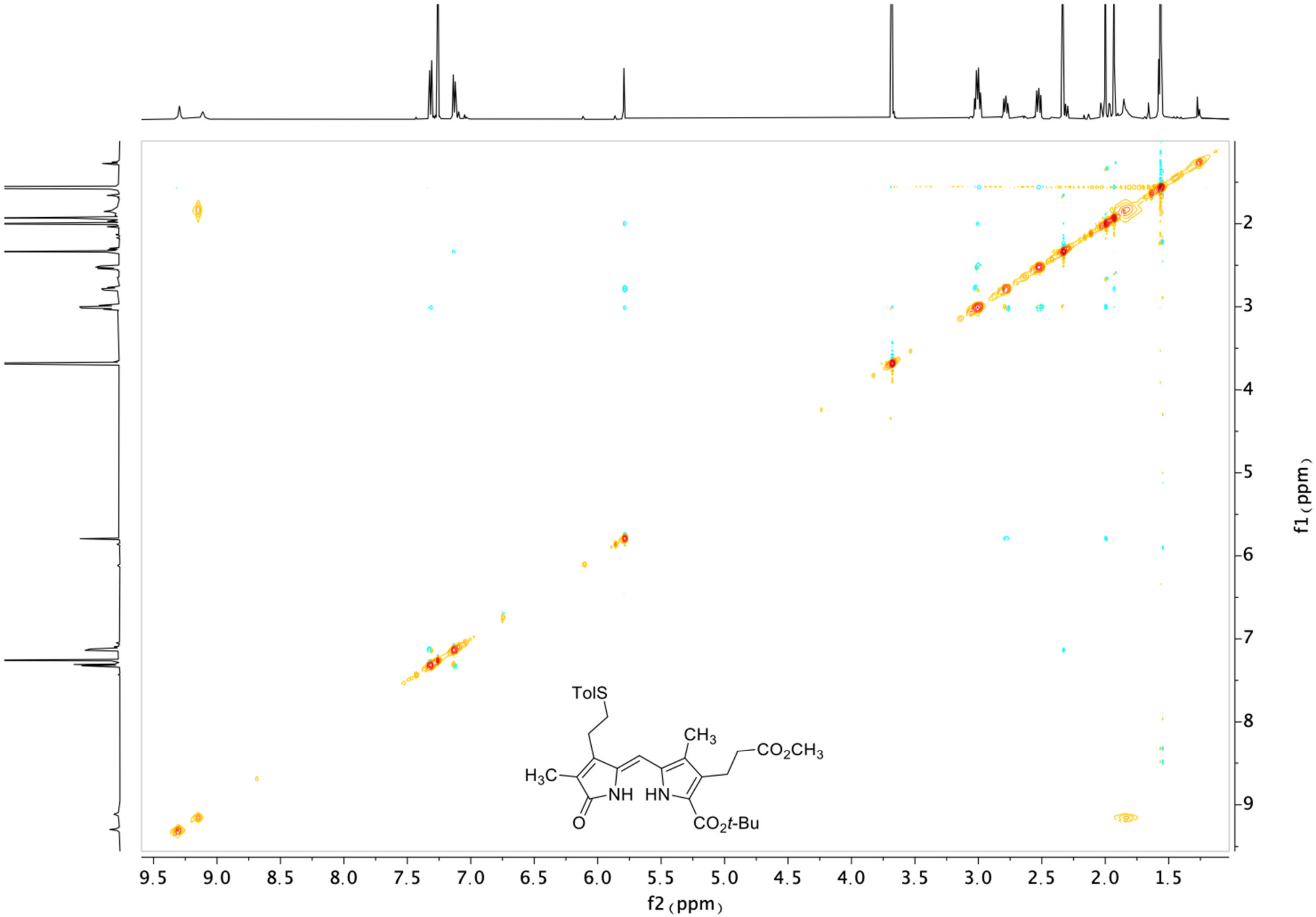


Figure S10. [1]H-[1]H NOESY (500 MHz, CDCl3): *Z*-**4.** (**A**) The full spectrum; (**B**) a detail of the range of 5.20–6.30 ppm, a circled cross-peaks depict the NOE effect between the bridge hydrogen and methyl as well as methylene group.

A



B

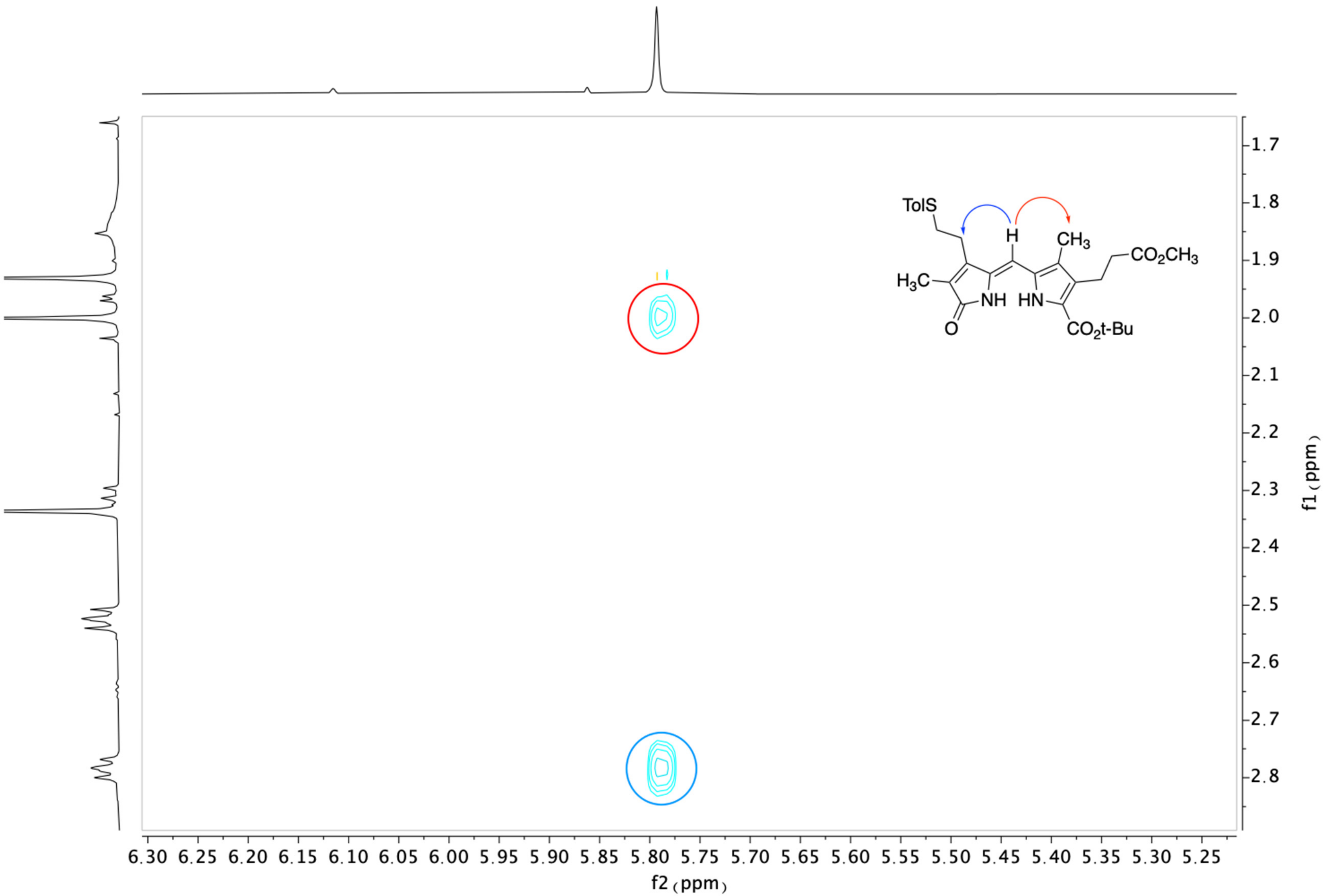


Figure S11. ^{1}H NMR (500 MHz, CD_2Cl_2): *Z*-**1a**.

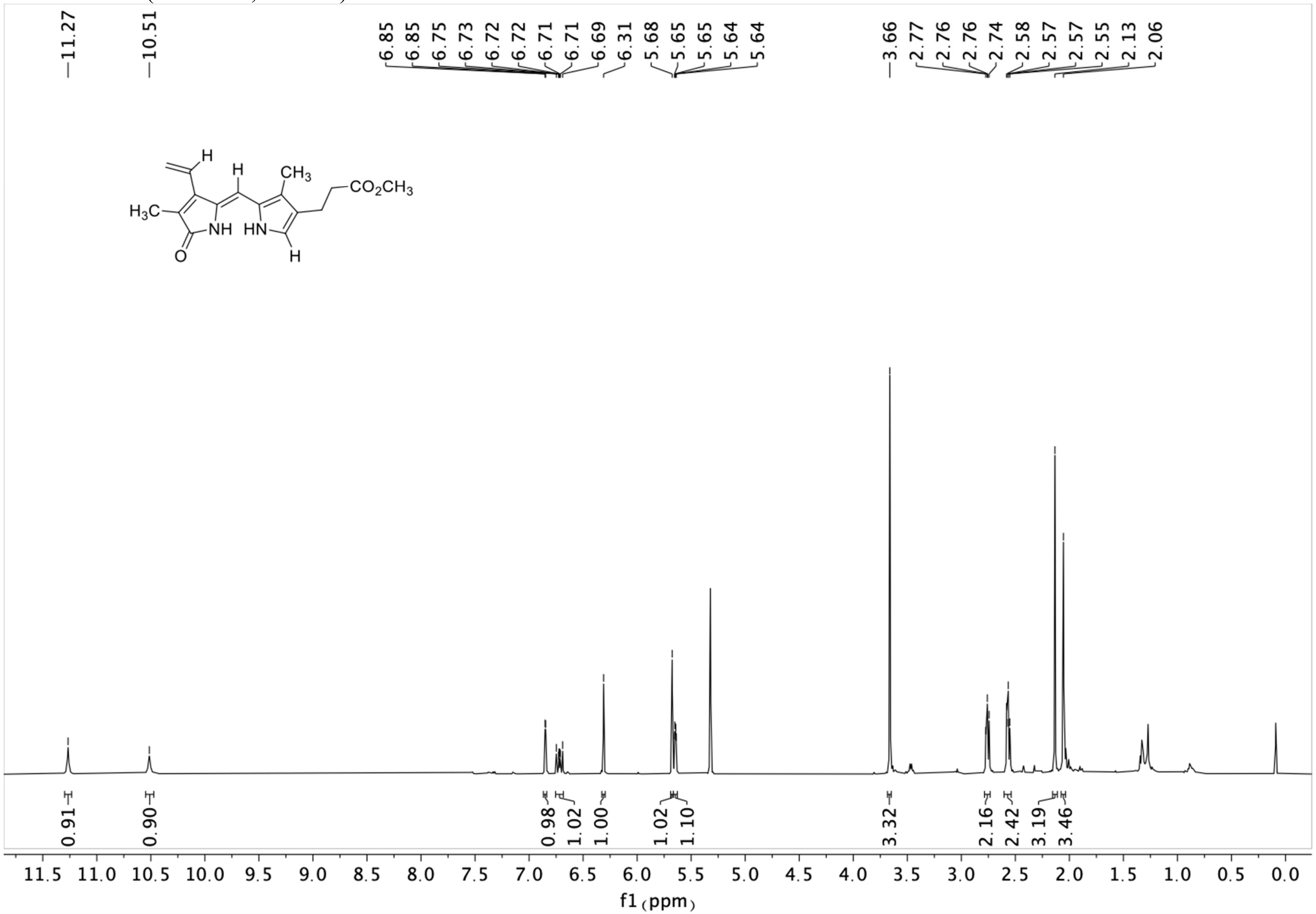


Figure S12. $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2): *Z*-**1a**.

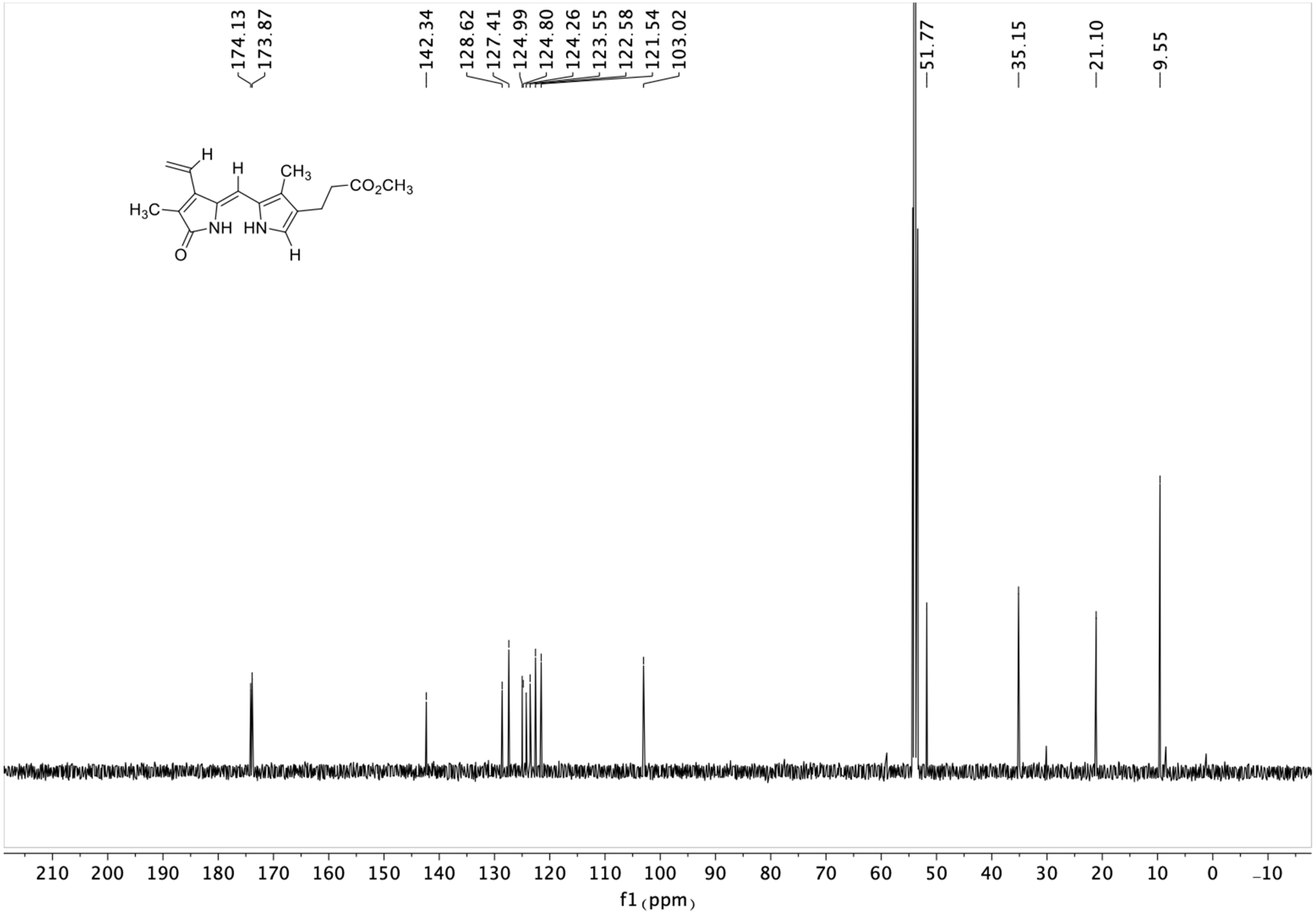


Figure S13. 1D NOESY (500 MHz, CD_2Cl_2): *Z*-**1a**.

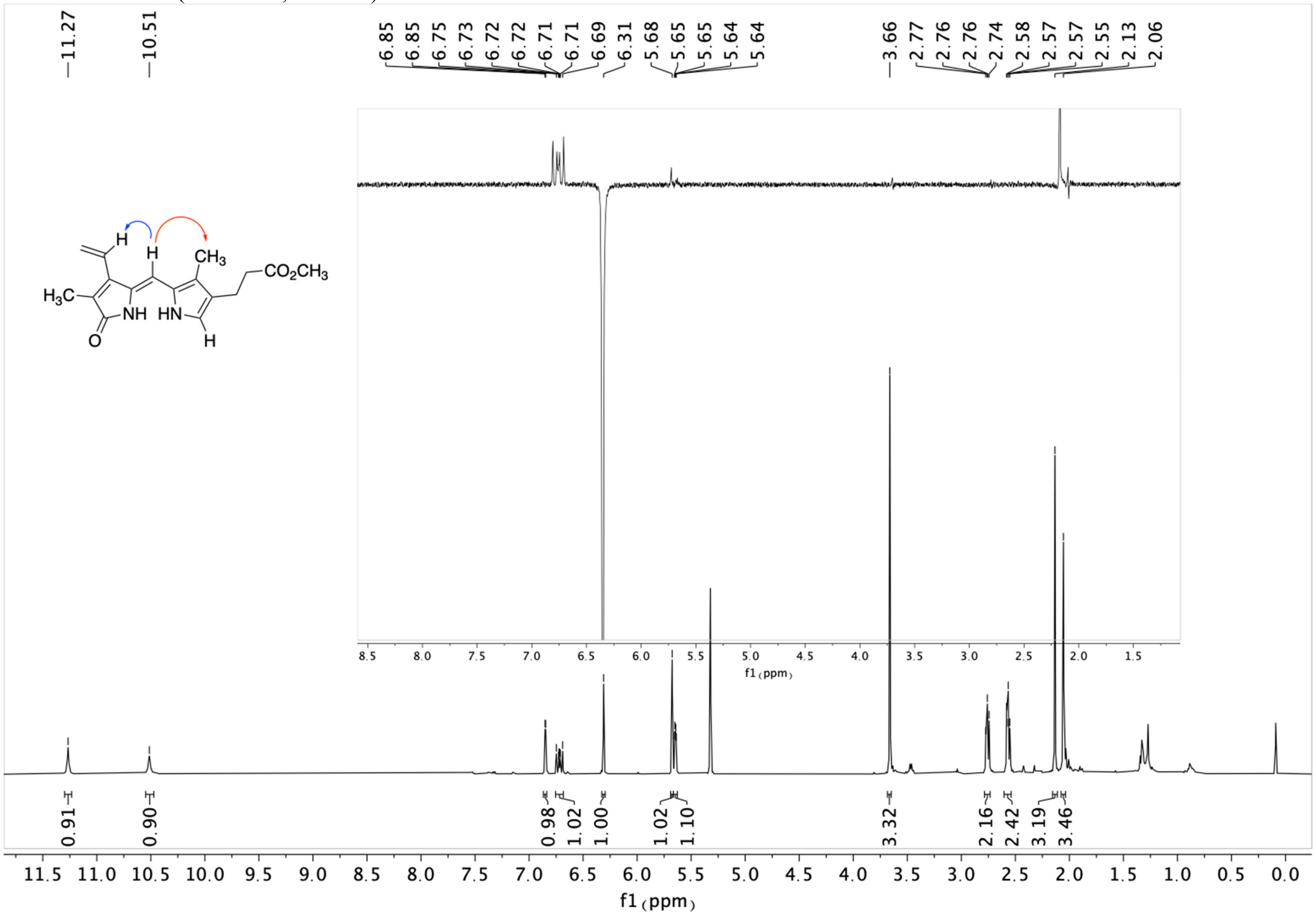


Figure S14. ^{1}H NMR (300 MHz, CD_2Cl_2): *E*-**1a**.

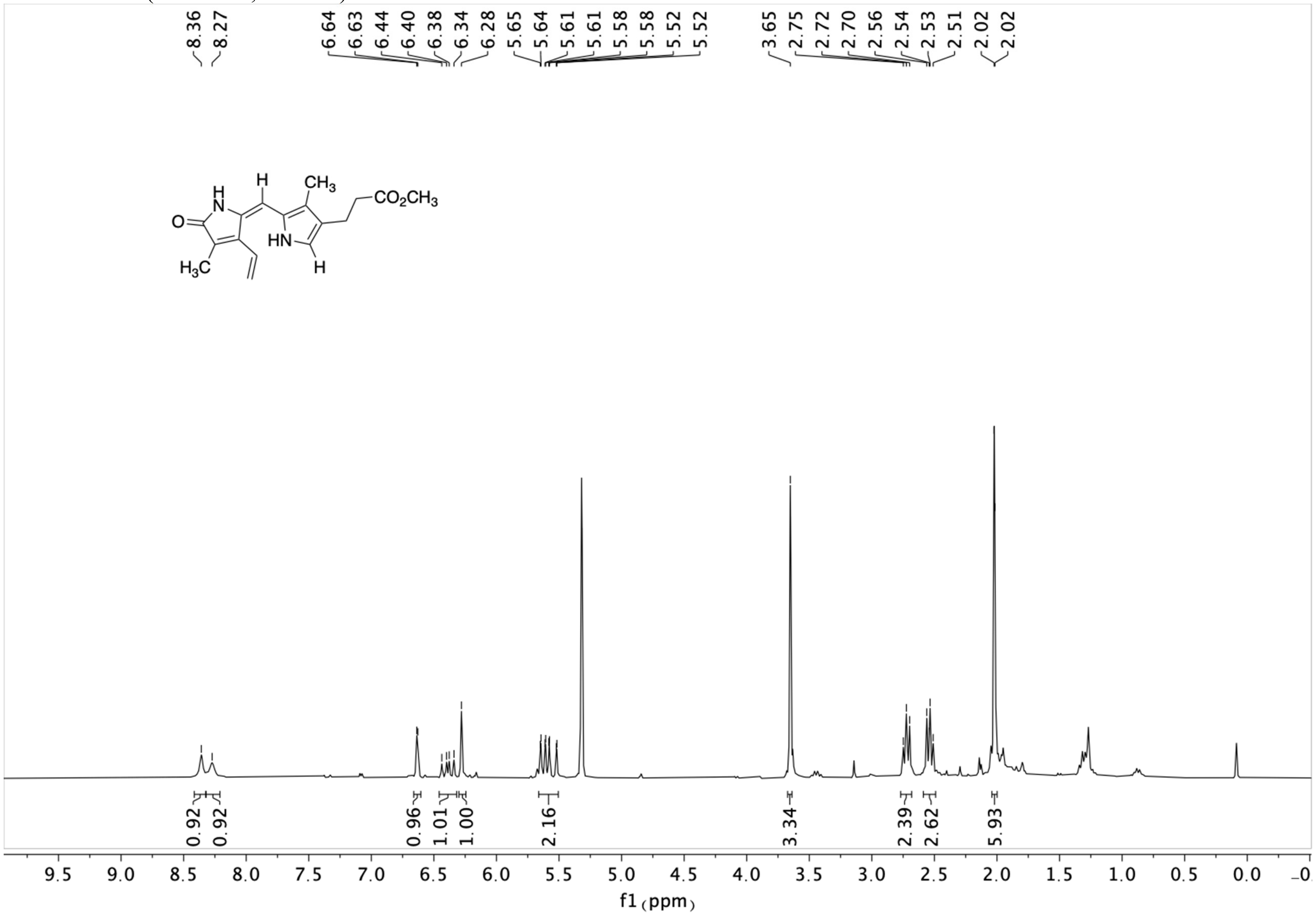


Figure S15. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2): *E*-**1a**.

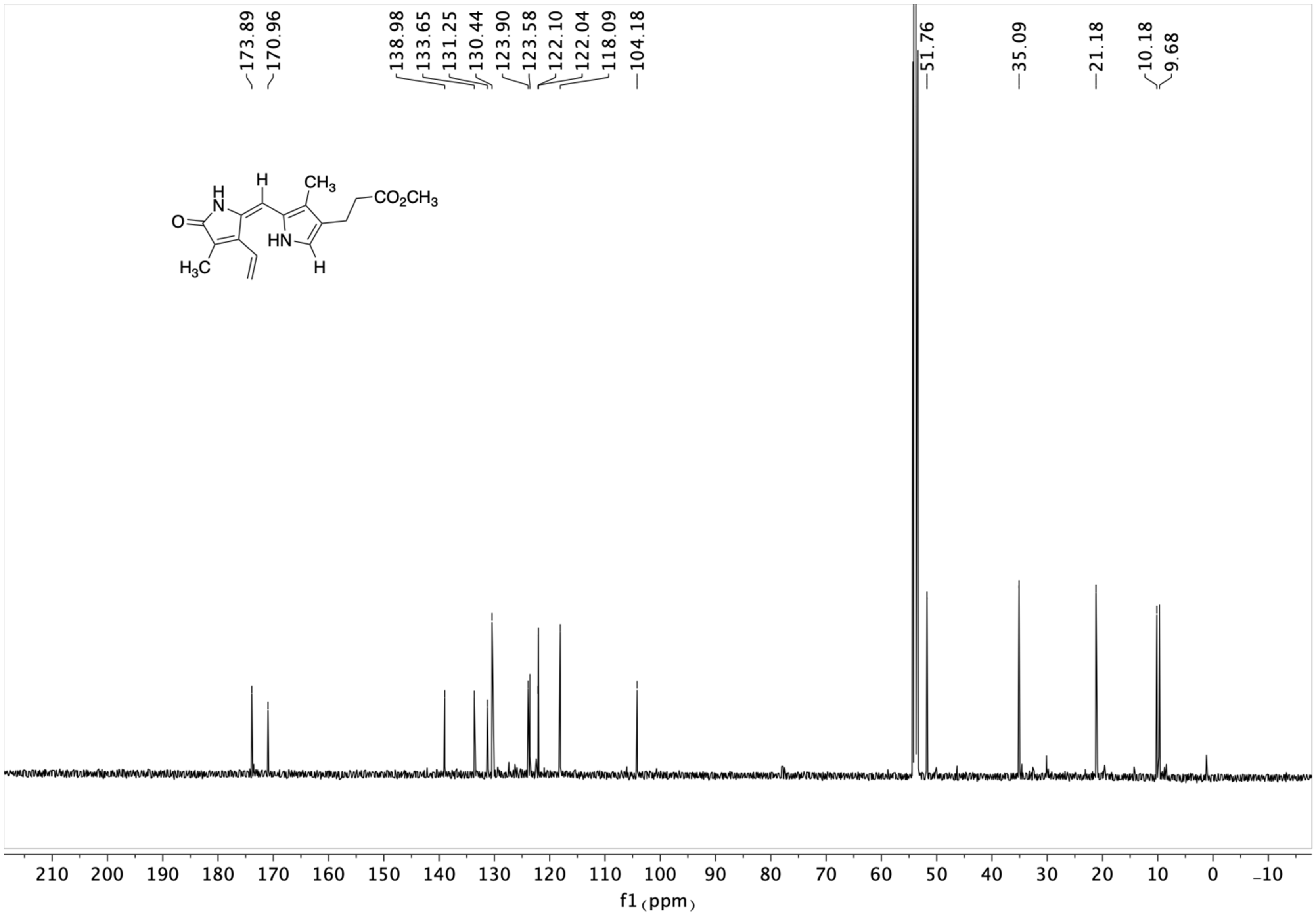


Figure S16. 1D NOESY (300 MHz, CD_2Cl_2): *E*-**1a**.

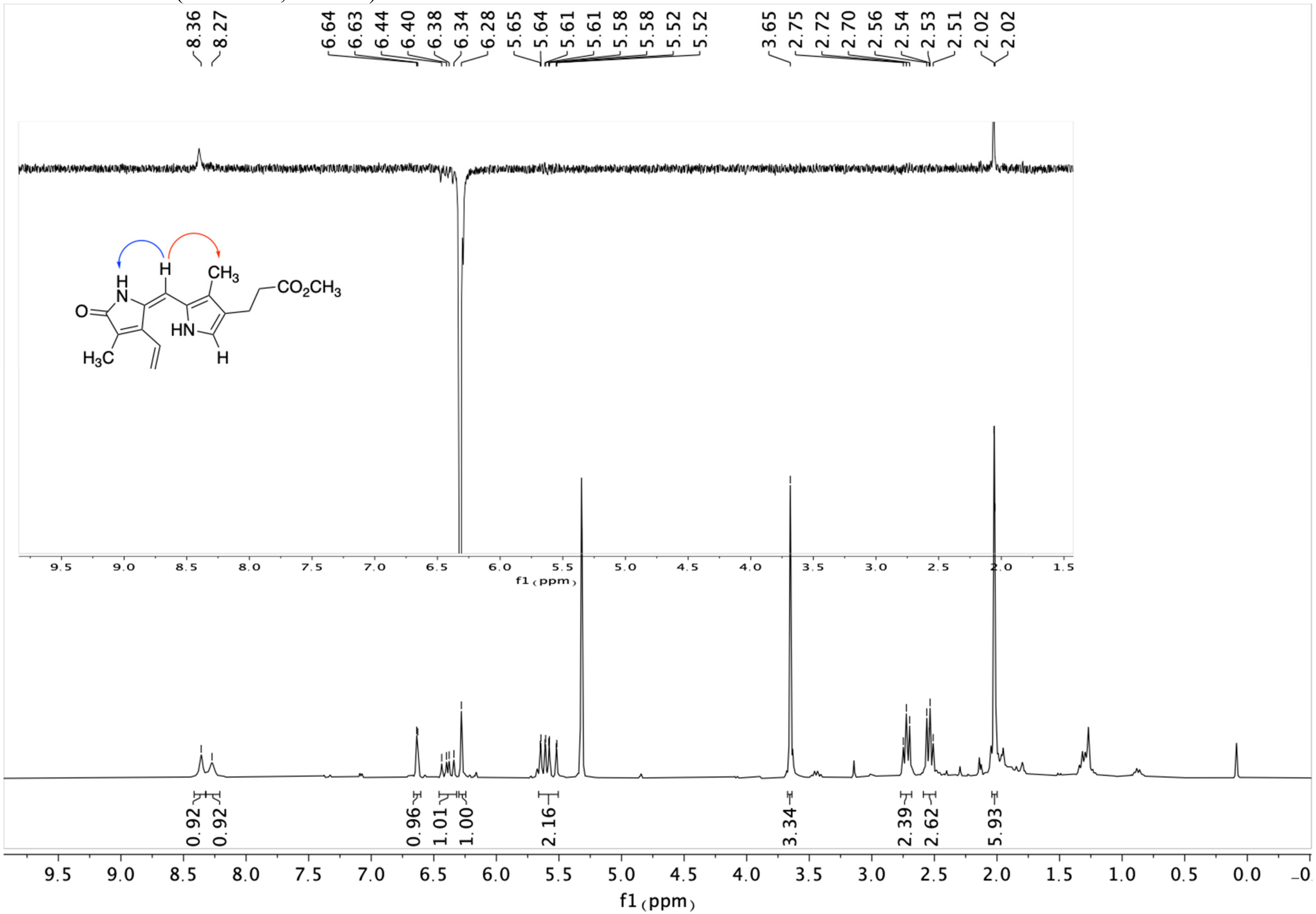
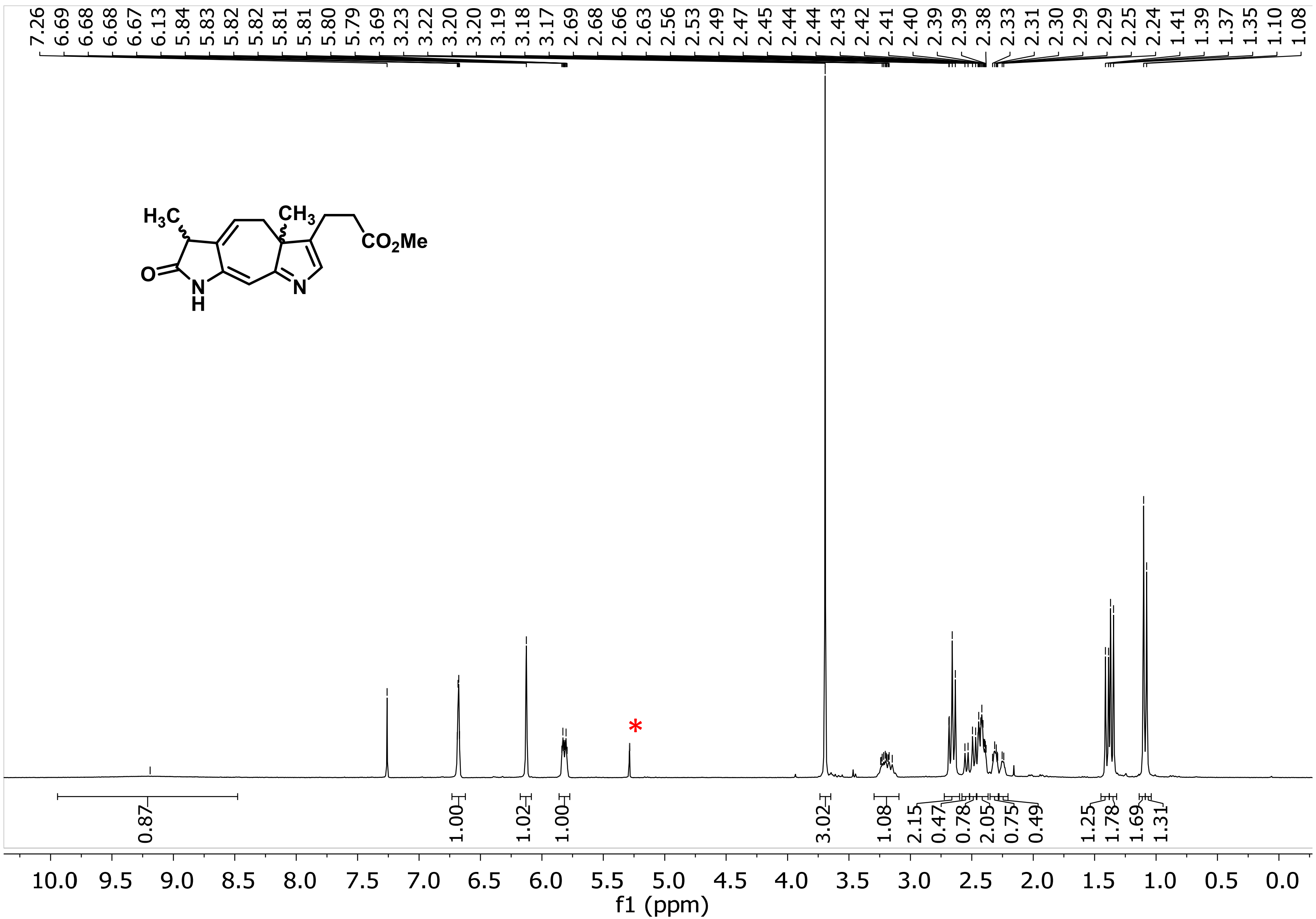
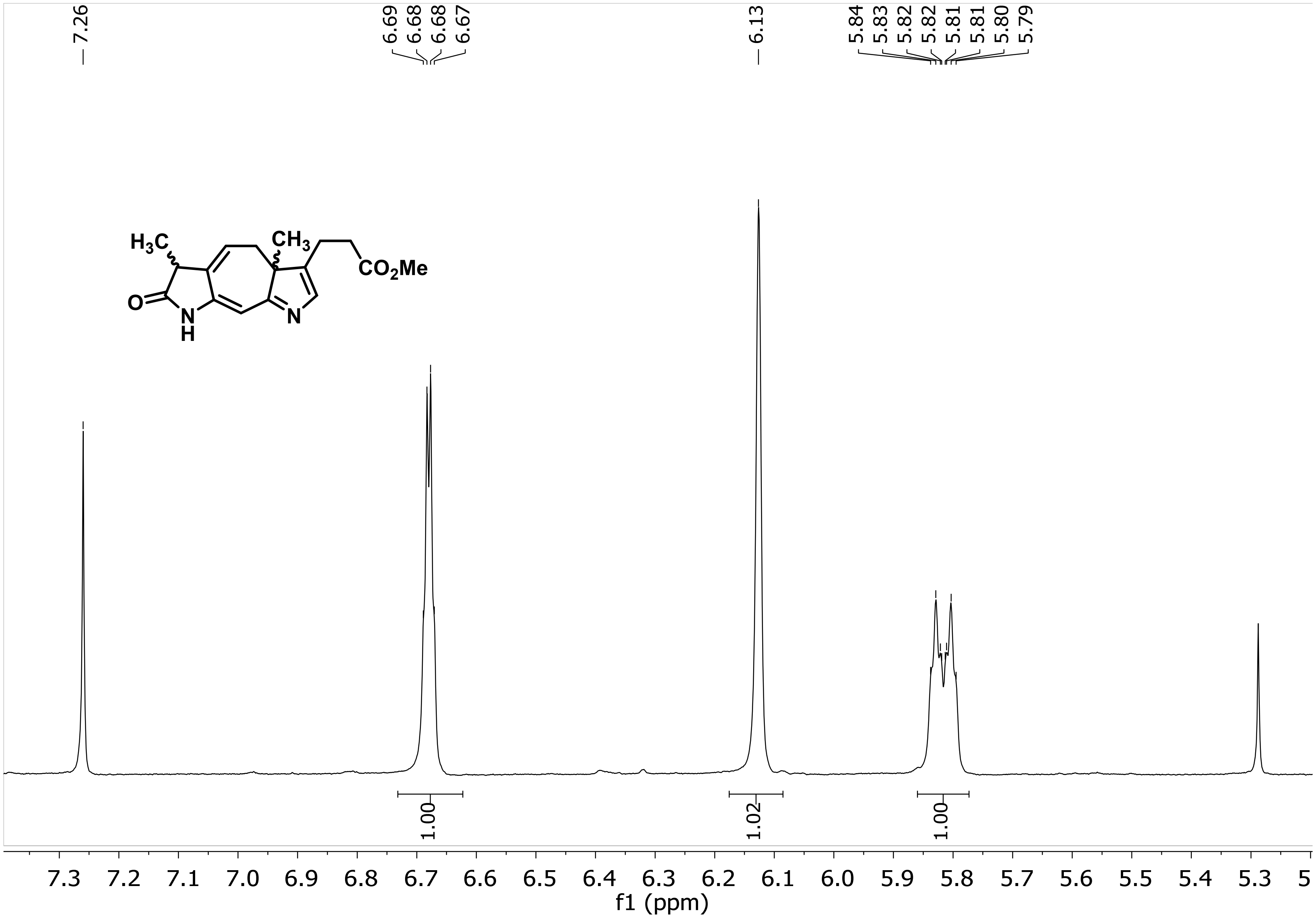


Figure S17. ^{1}H NMR (300 MHz, $CDCl_3$): **1b**. (**A**) The full spectrum. Red asterisk denotes the signal of residual CH_2Cl_2; (**B**, **C**: the spectra details).

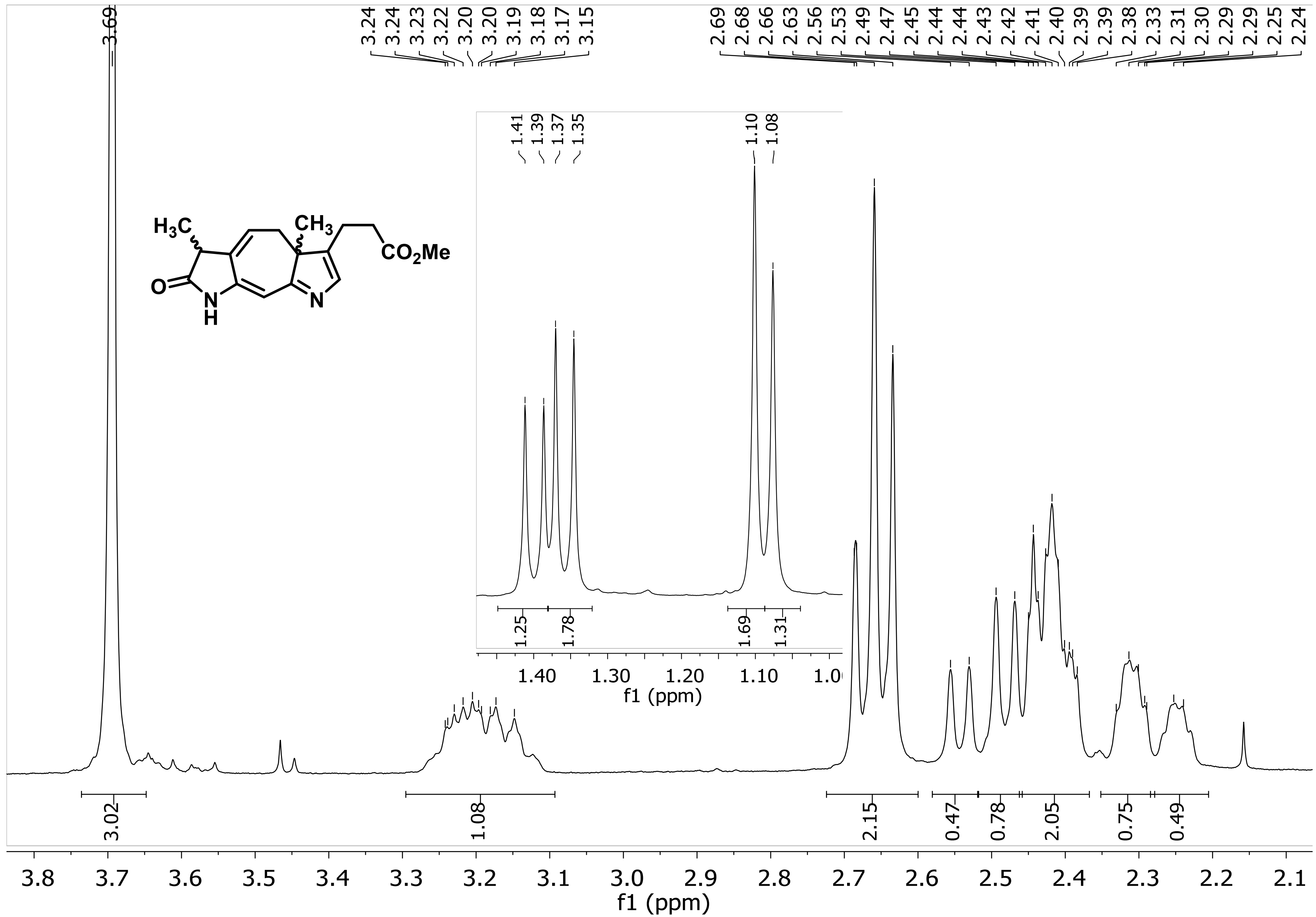
A



B


7.26
6.69 6.68 6.68 6.67
6.13
5.84 5.83 5.82 5.82 5.81 5.81 5.80 5.79
H3C
CH3
CO2Me
O
N
H
N
1.00
1.02
1.00
7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4 6.3 6.2 6.1 6.0 5.9 5.8 5.7 5.6 5.5 5.4 5.3 5
f1 (ppm)

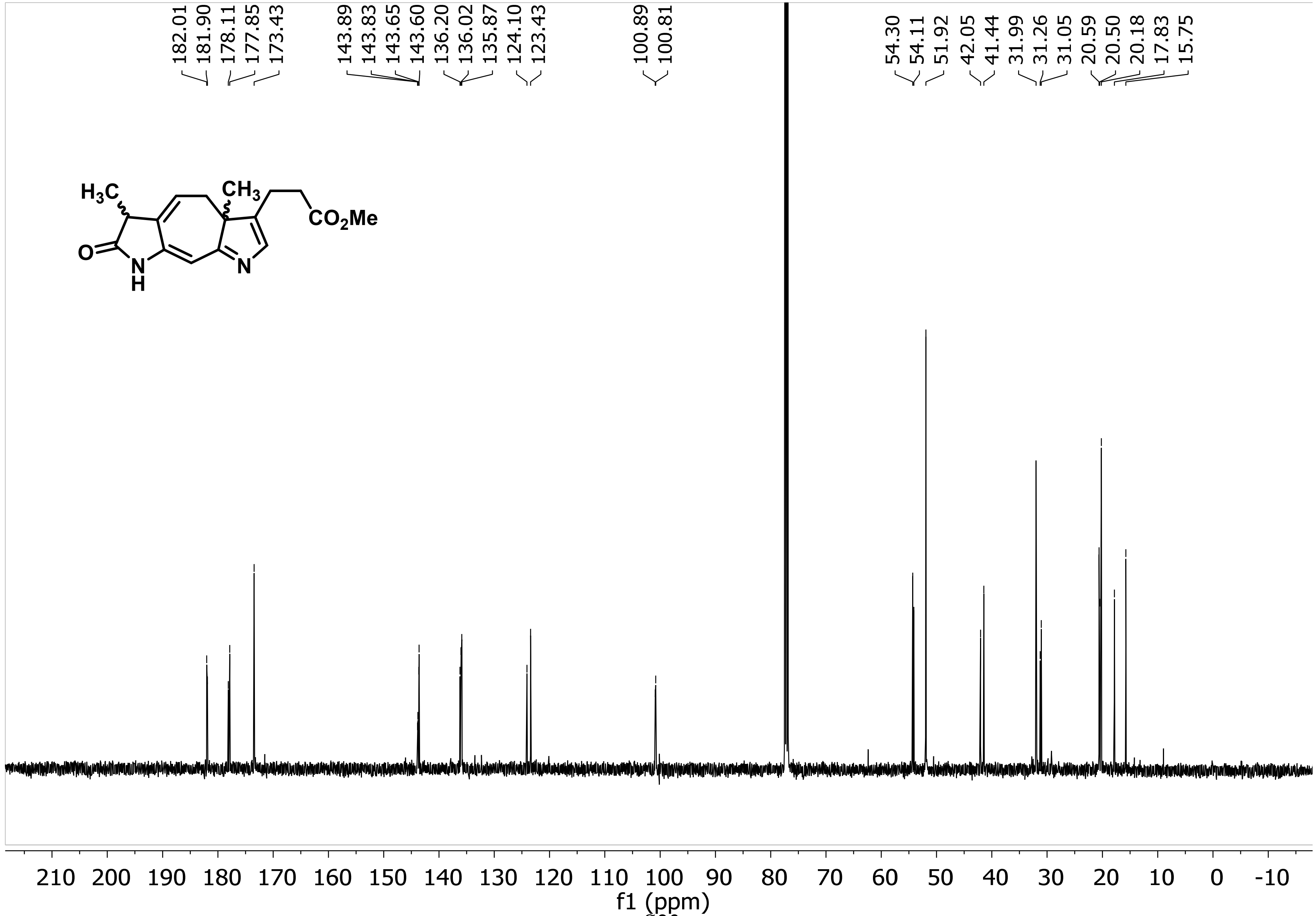
C



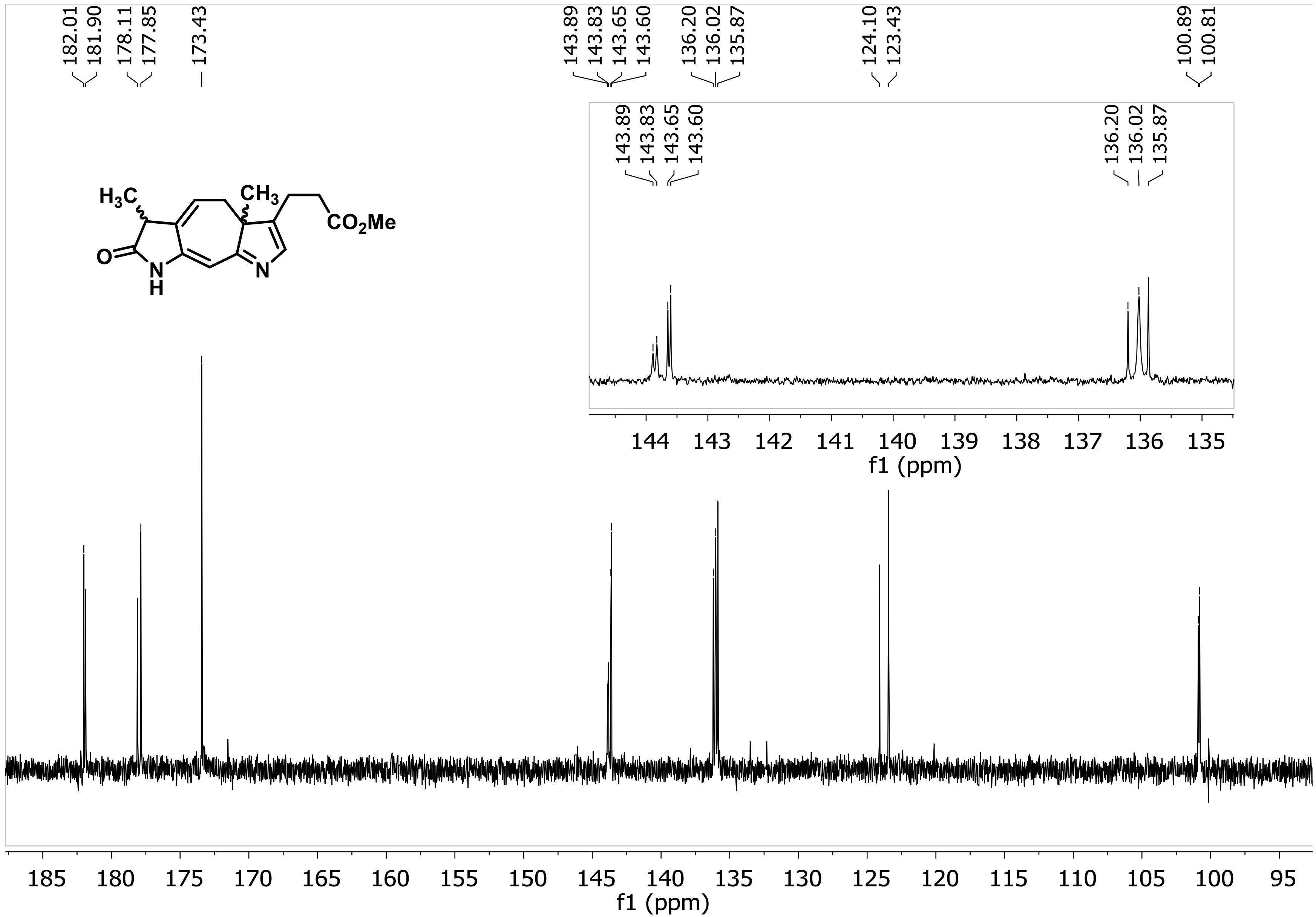
3.69
3.24 3.24 3.23 3.22 3.20 3.20 3.19 3.18 3.17 3.15
2.69 2.68 2.66 2.63 2.56 2.53 2.49 2.47 2.45 2.44 2.44 2.43 2.42 2.41 2.40 2.39 2.39 2.38 2.33 2.31 2.30 2.29 2.29 2.25 2.24
H3C
CH3
CO2Me
O
NH
N
1.41 1.39 1.37 1.35
1.10 1.08
1.25 1.78 1.69 1.31
1.40 1.30 1.20 1.10
f1 (ppm)
3.02 1.08 2.15 0.47 0.78 2.05 0.75 0.49
3.8 3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0 2.9 2.8 2.7 2.6 2.5 2.4 2.3 2.2 2.1
f1 (ppm)

Figure S18. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): **1b**. (**A**) The full spectrum. (**B**, **C**: the spectra details).

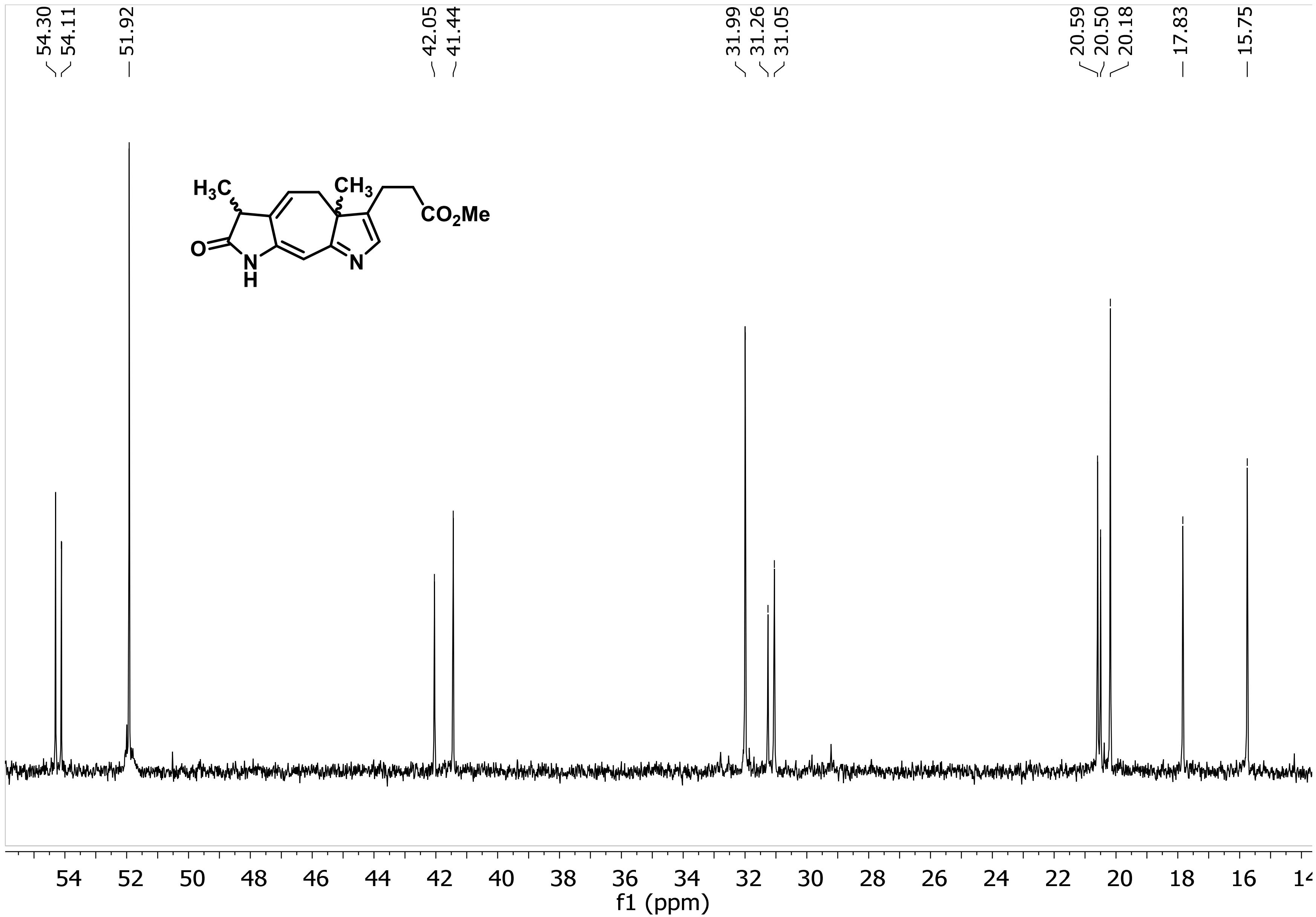
A



B


182.01
181.90
178.11
177.85
173.43
143.89
143.83
143.65
143.60
136.20
136.02
135.87
124.10
123.43
100.89
100.81
H3C
CH3
CO2Me
O
NH
H
N
144 143 142 141 140 139 138 137 136 135
f1 (ppm)
185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95
f1 (ppm)

C



54.30
54.11
51.92
42.05
41.44
31.99
31.26
31.05
20.59
20.50
20.18
17.83
15.75
H_3C
CH_3
CO_2Me
O
N
H
N
54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14
f1 (ppm)

Figure S19. ^{1}H-^{13}C HSQCEDETGP (500 MHz, $CDCl_3$): **1b**. Red cross-peaks belongs to the CH and CH_3 groups and blue cross-peaks to the CH_2 groups.

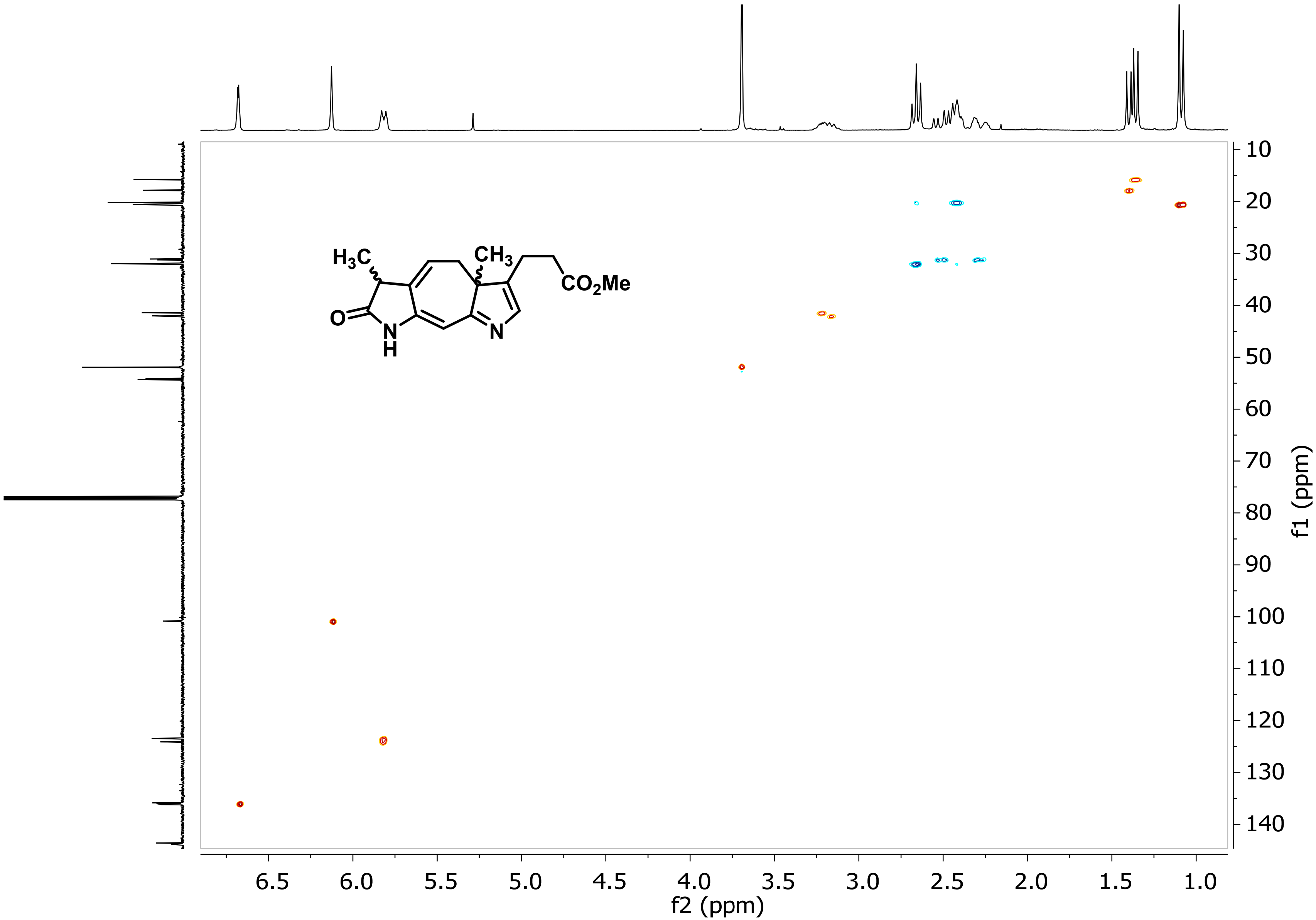
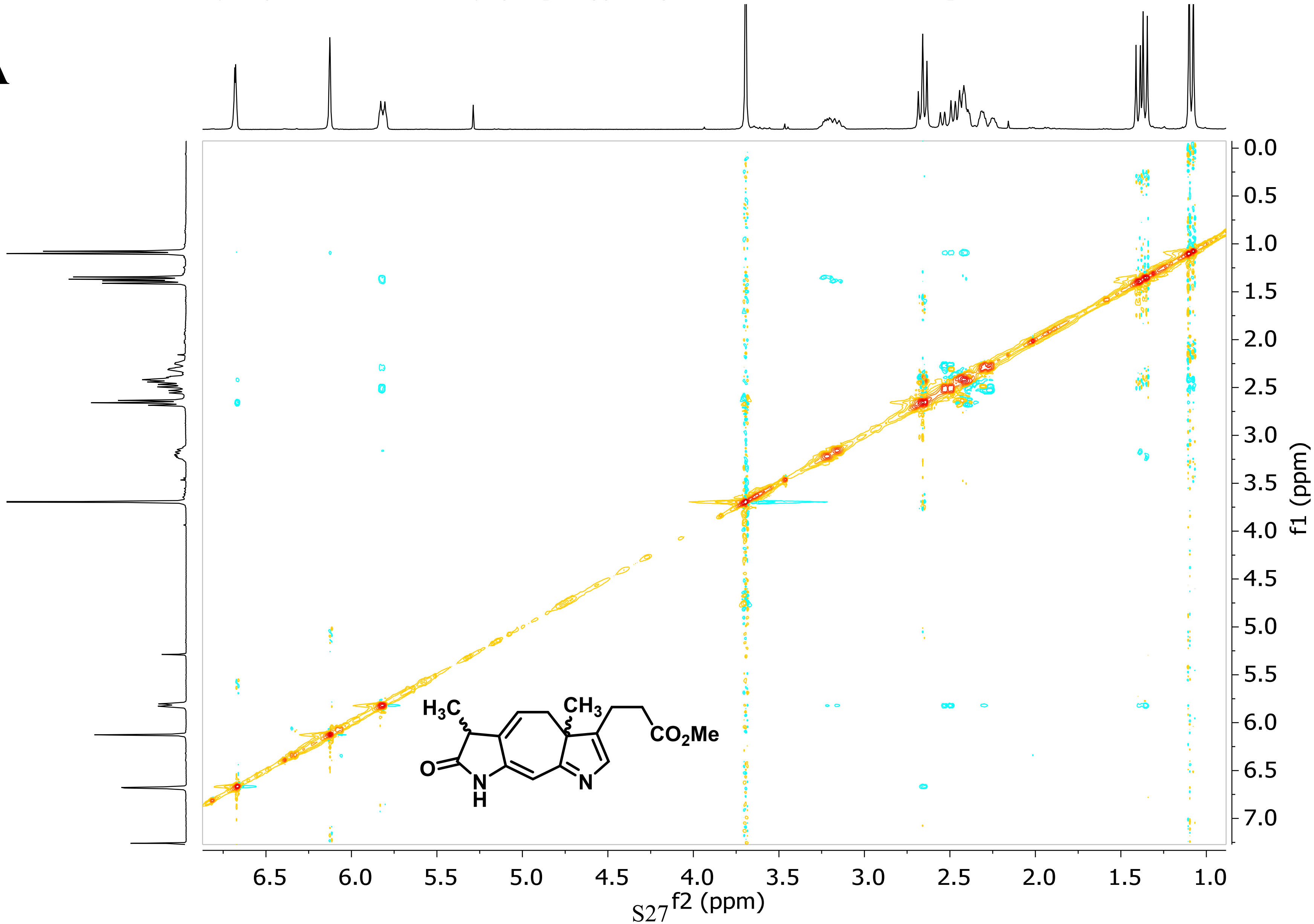


Figure S20. ^{1}H-^{1}H NOESY (500 MHz, $CDCl_3$): **1b**. (**A**) The full spectrum; (**B**) a detail of the range of 2.85–3.60 ppm, a circled cross-peak depict the NOE effect between the α hydrogen and denoted methyl group, suggesting that this diastereomer is the prevalent one in the mixture (~60 %).

A



B

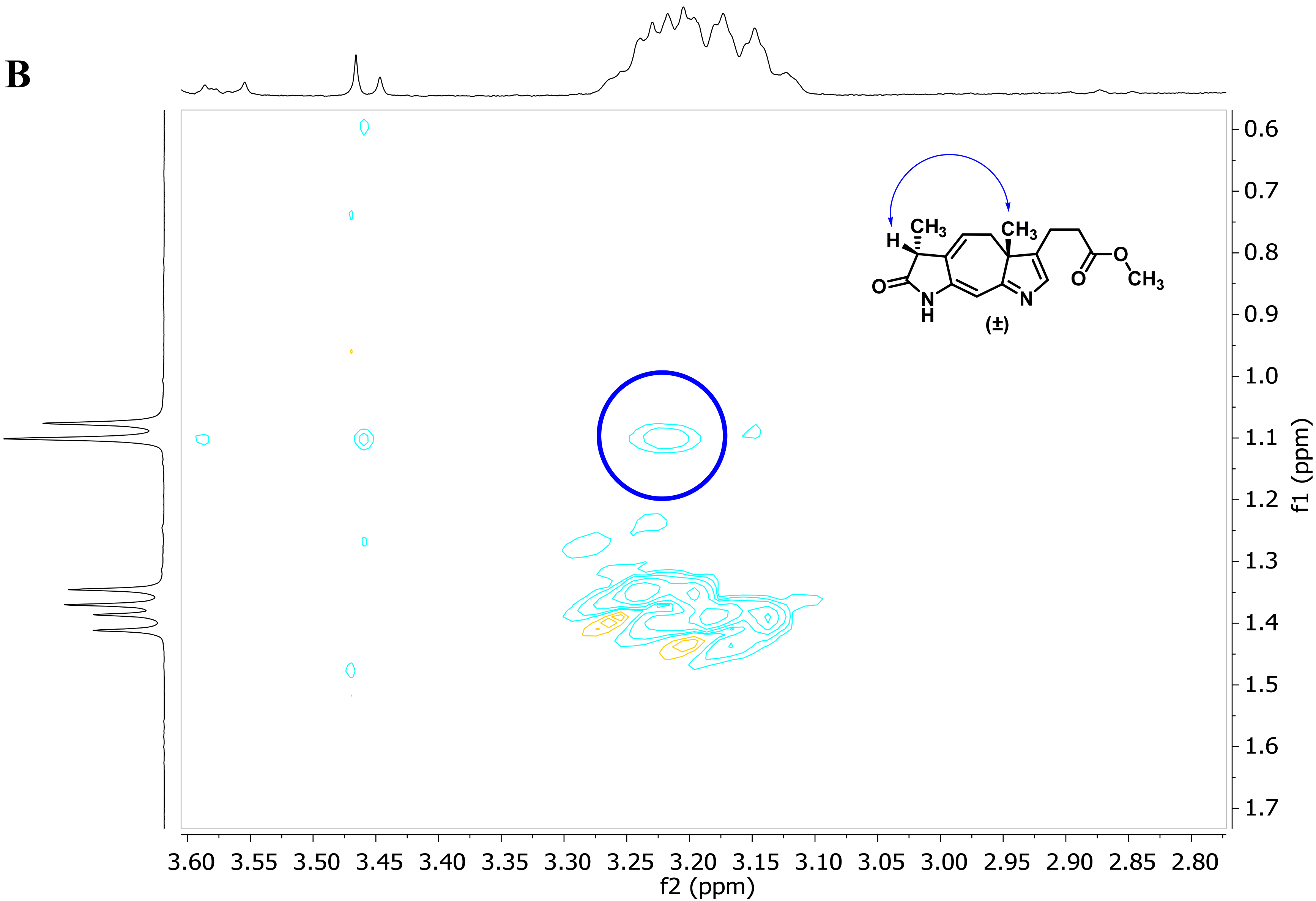
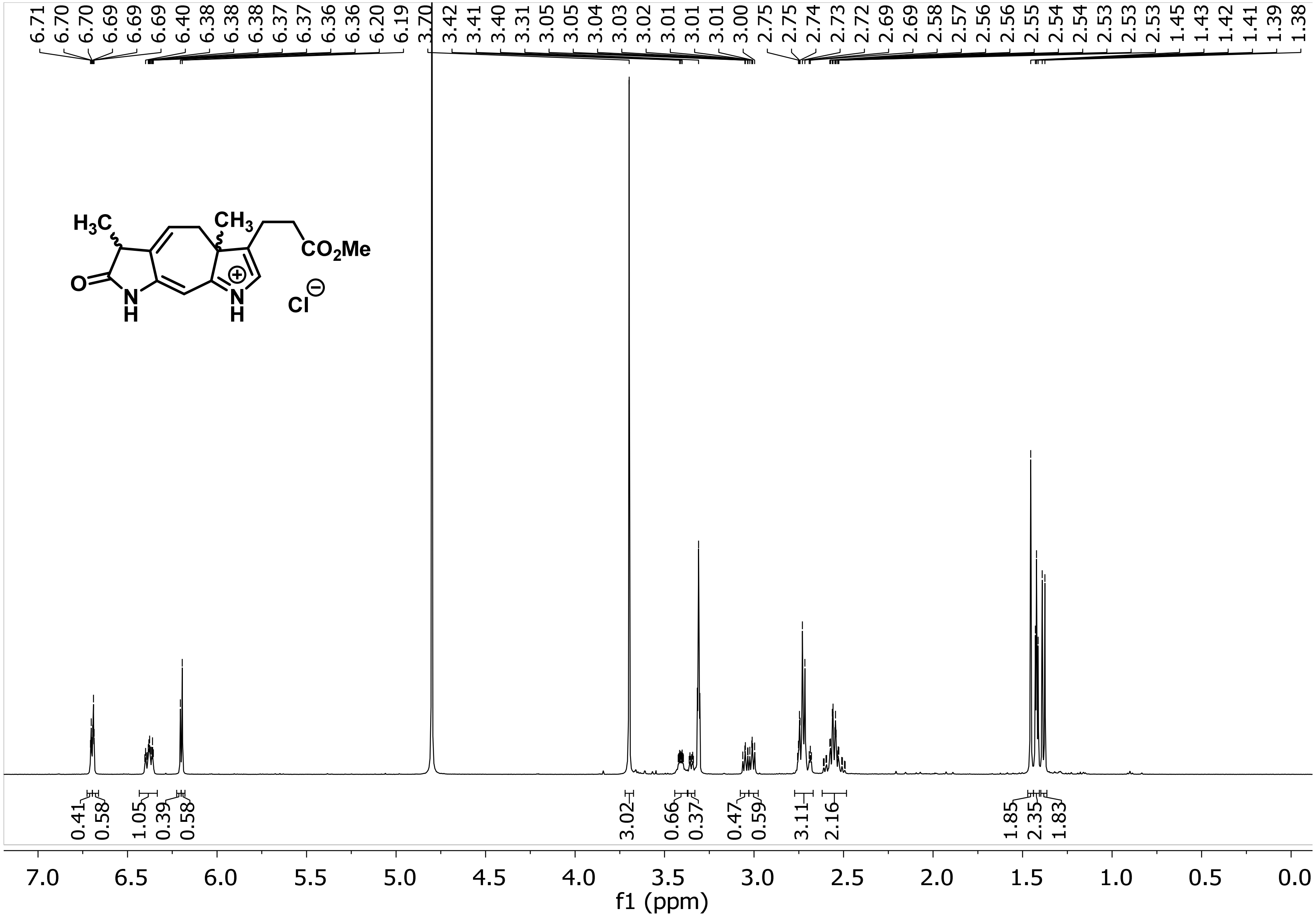
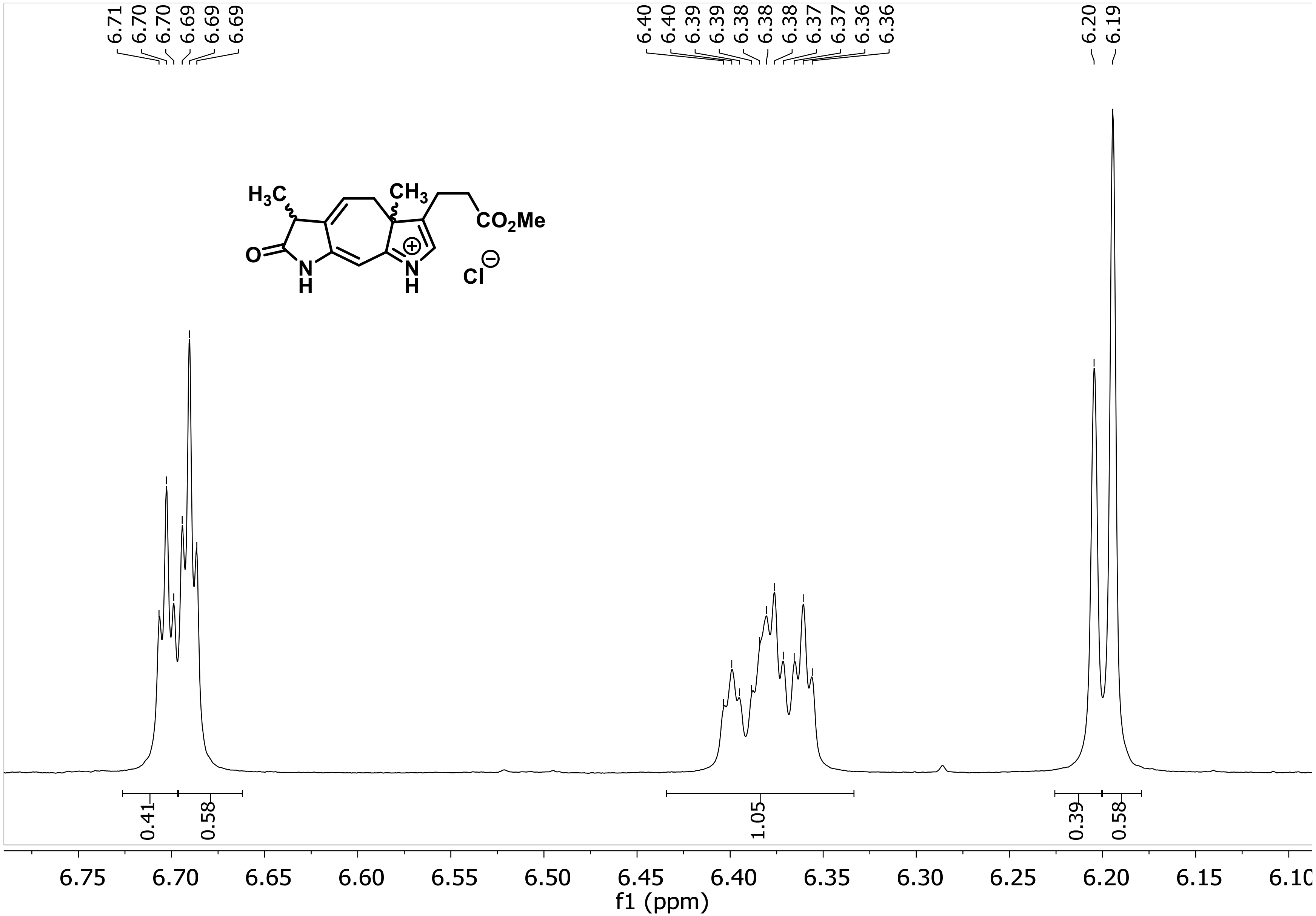


Figure S21. ^{1}H NMR (500 MHz, CD_3OD): **1b.HCl**. (**A**) The full spectrum. (**B**, **C**: the spectra details).

A



B



6.71
6.70
6.70
6.69
6.69
6.69
6.40
6.40
6.39
6.39
6.38
6.38
6.38
6.37
6.37
6.36
6.36
6.20
6.19
H3C
CH3
CO2Me
O
N
H
N
H
Cl
0.41
0.58
1.05
0.39
0.58
6.75
6.70
6.65
6.60
6.55
6.50
6.45
6.40
6.35
6.30
6.25
6.20
6.15
6.10
f1 (ppm)

C

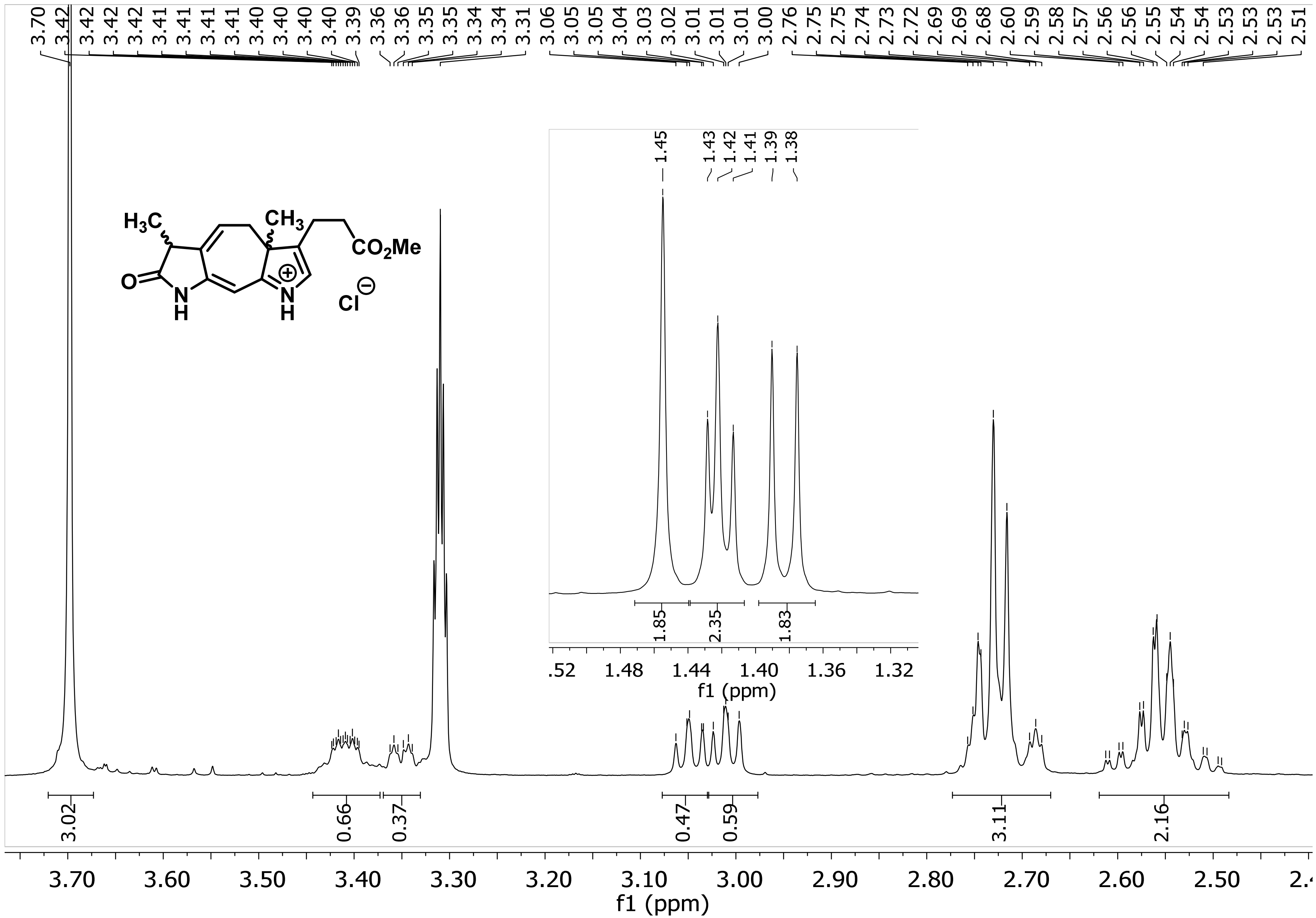
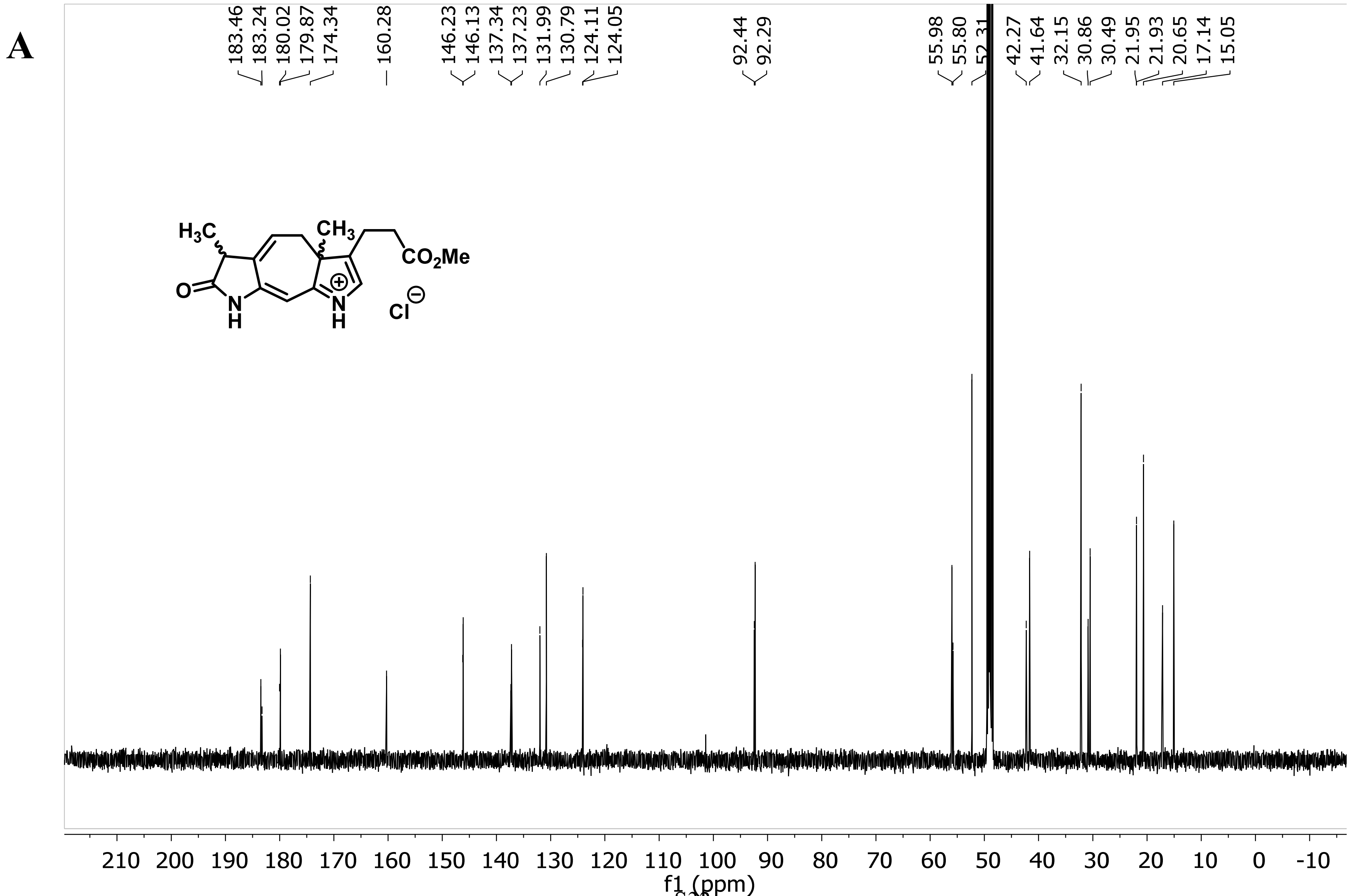
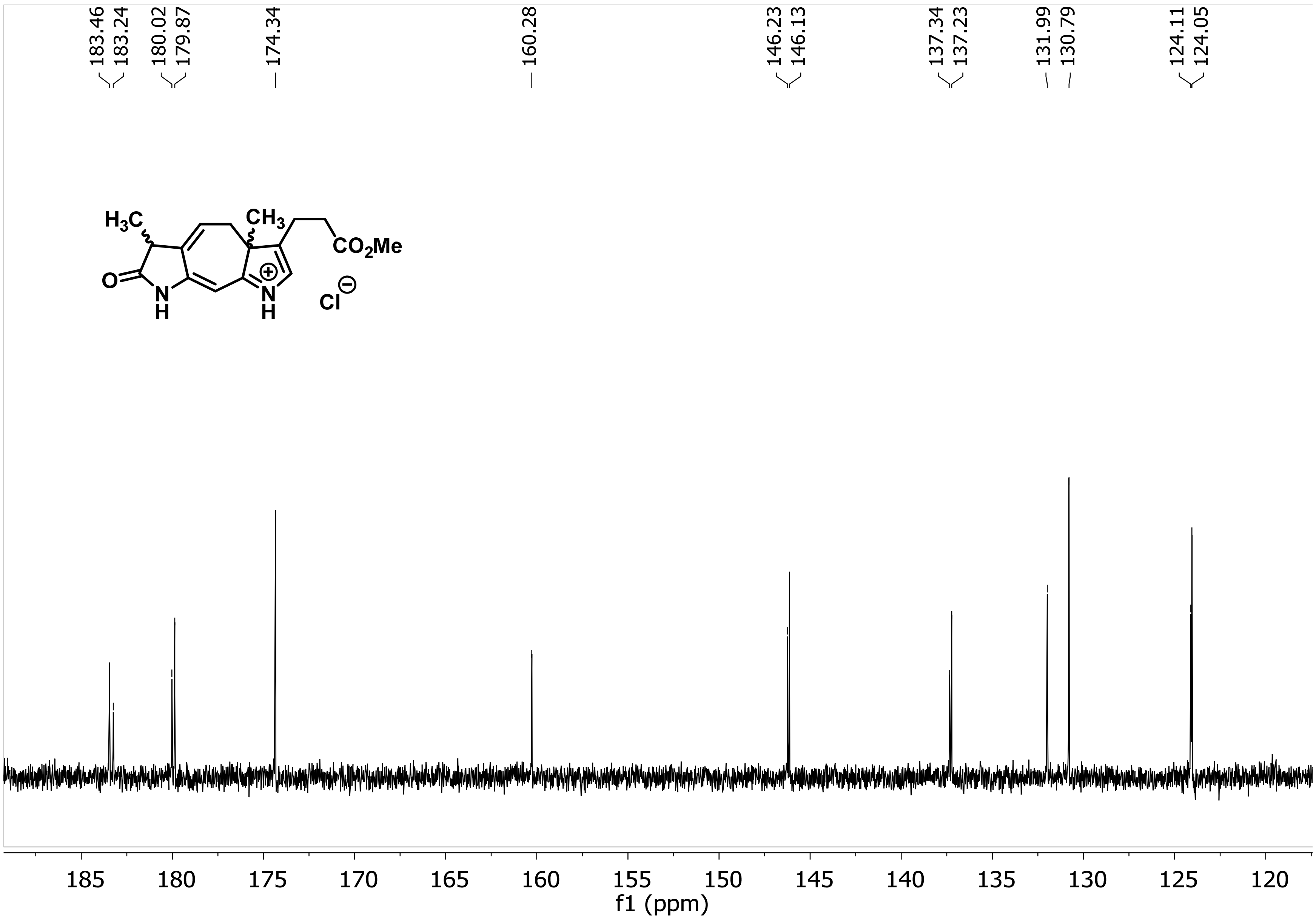


Figure S22. $^{13}C\{^1H\}$ NMR (126 MHz, CD_3OD): **1b.HCl**. (**A**) The full spectrum. (**B**, **C**: the spectra details).



B


183.46
183.24
180.02
179.87
174.34
160.28
146.23
146.13
137.34
137.23
131.99
130.79
124.11
124.05
H3C
CH3
CO2Me
O
N
H
N
H
Cl
185
180
175
170
165
160
155
150
145
140
135
130
125
120
f1 (ppm)

C

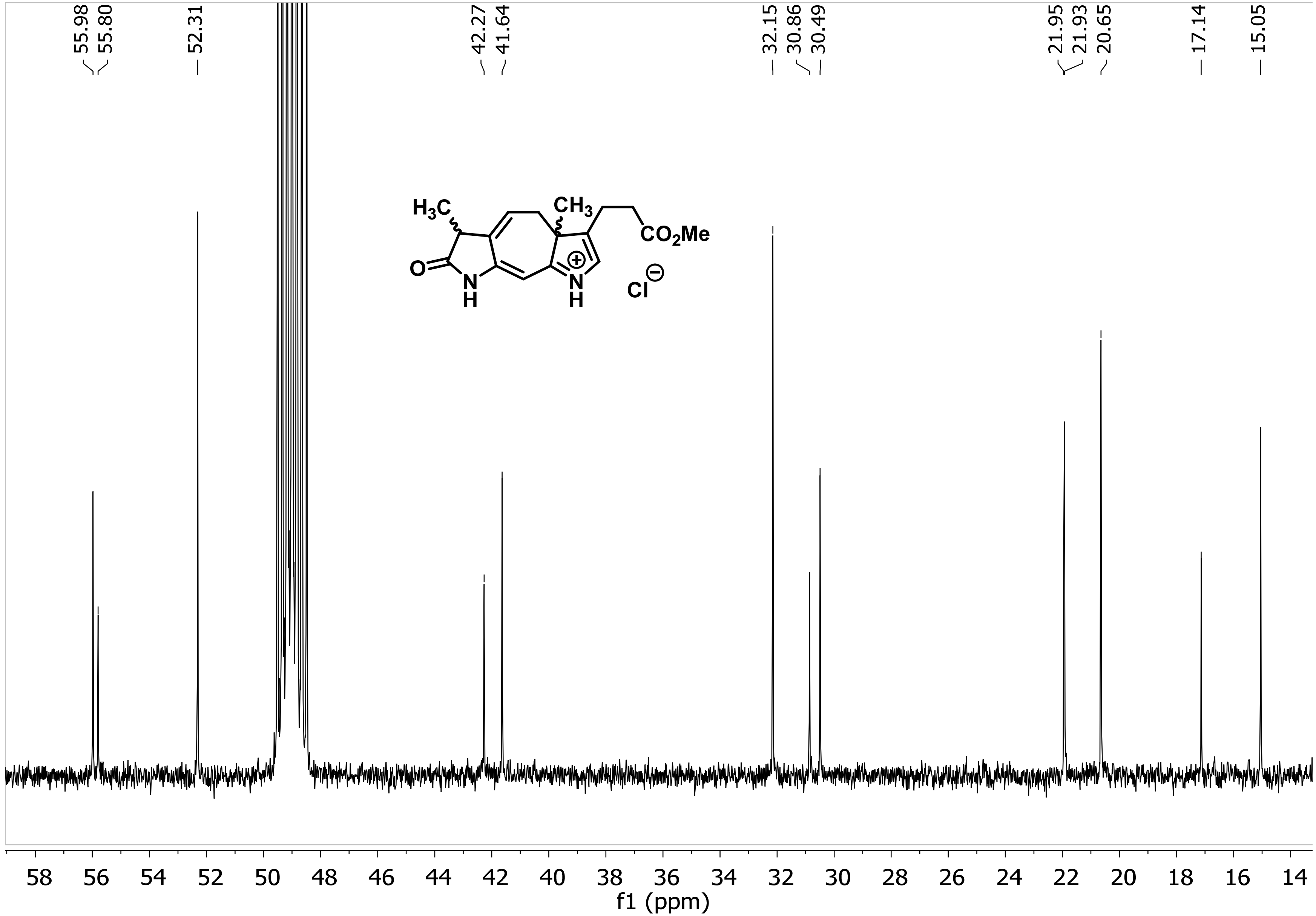

55.98
55.80
52.31
42.27
41.64
32.15
30.86
30.49
21.95
21.93
20.65
17.14
15.05
H3C
CH3
CO2Me
O
N
H
N
H
Cl
58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14
f1 (ppm)

Figure S23. ^{1}H NMR (500 MHz, $CDCl_3$): **1c**. Red asterisk denotes the signal from residual CH_2Cl_2 and red cross from TMS.

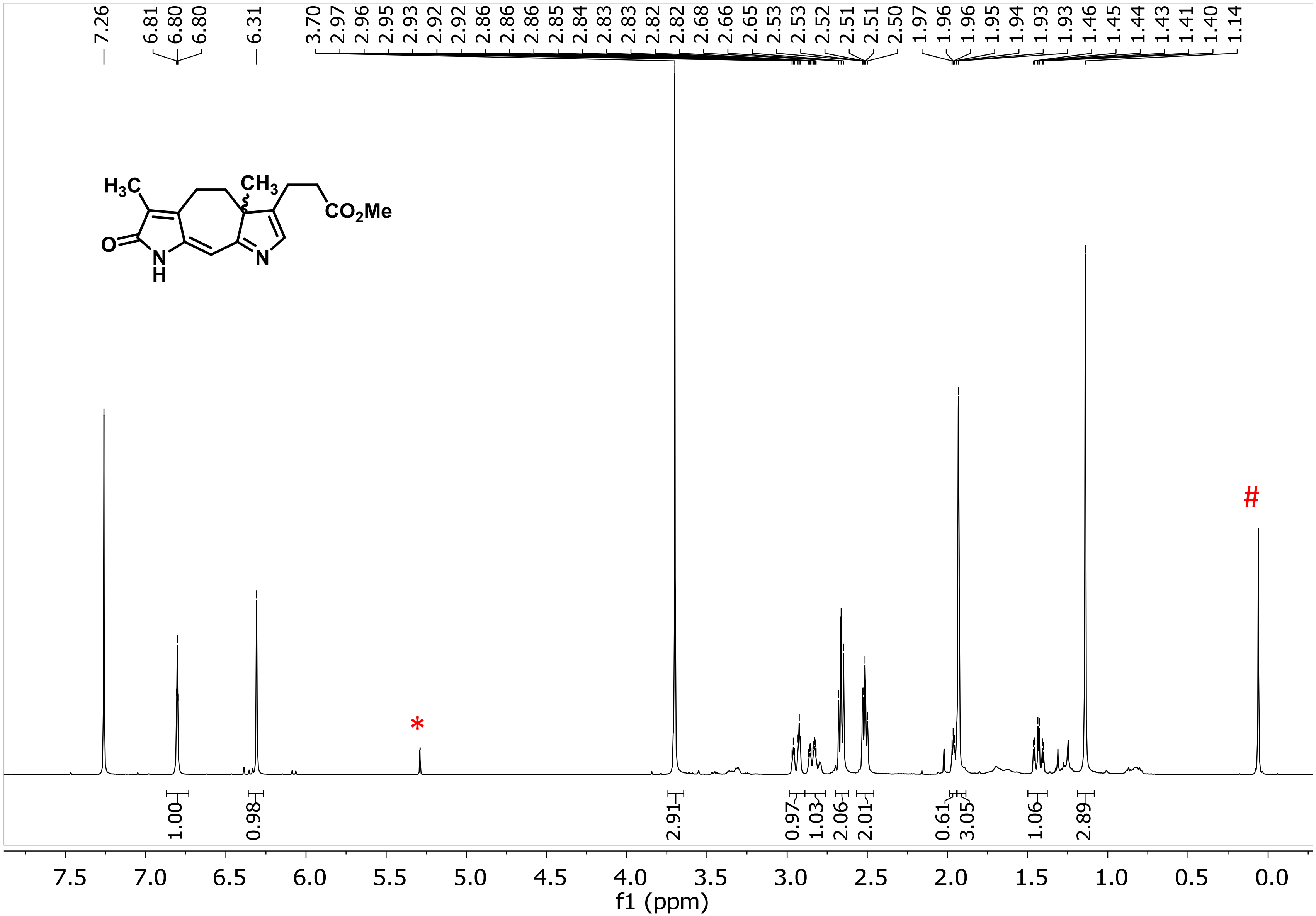


Figure S24. $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): **1c**. Red asterisk denotes the signal from TMS.

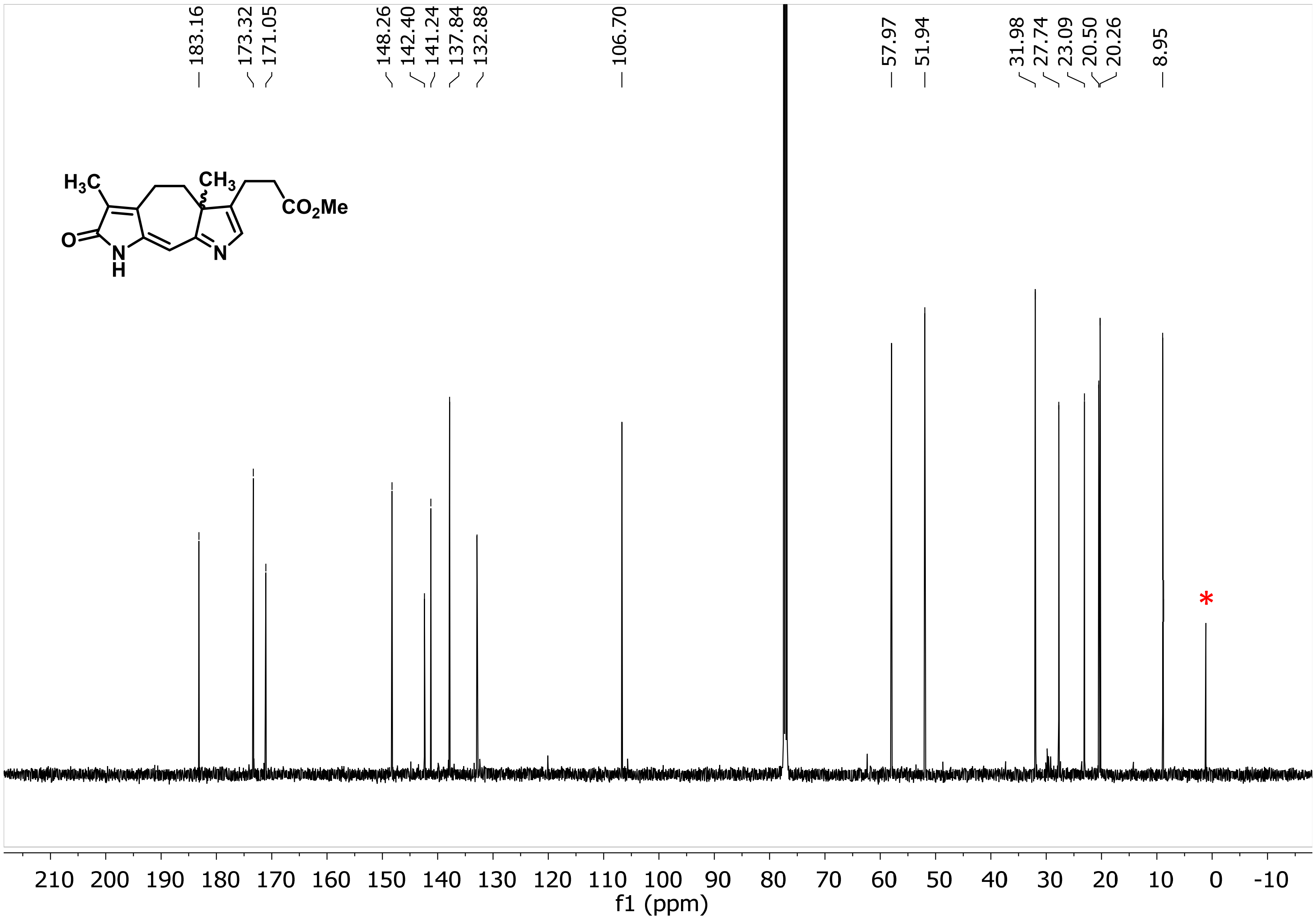


Figure S25. ^{1}H–^{1}H COSY (500 MHz, $CDCl_3$): **1c**. Only the aliphatic part is displayed.

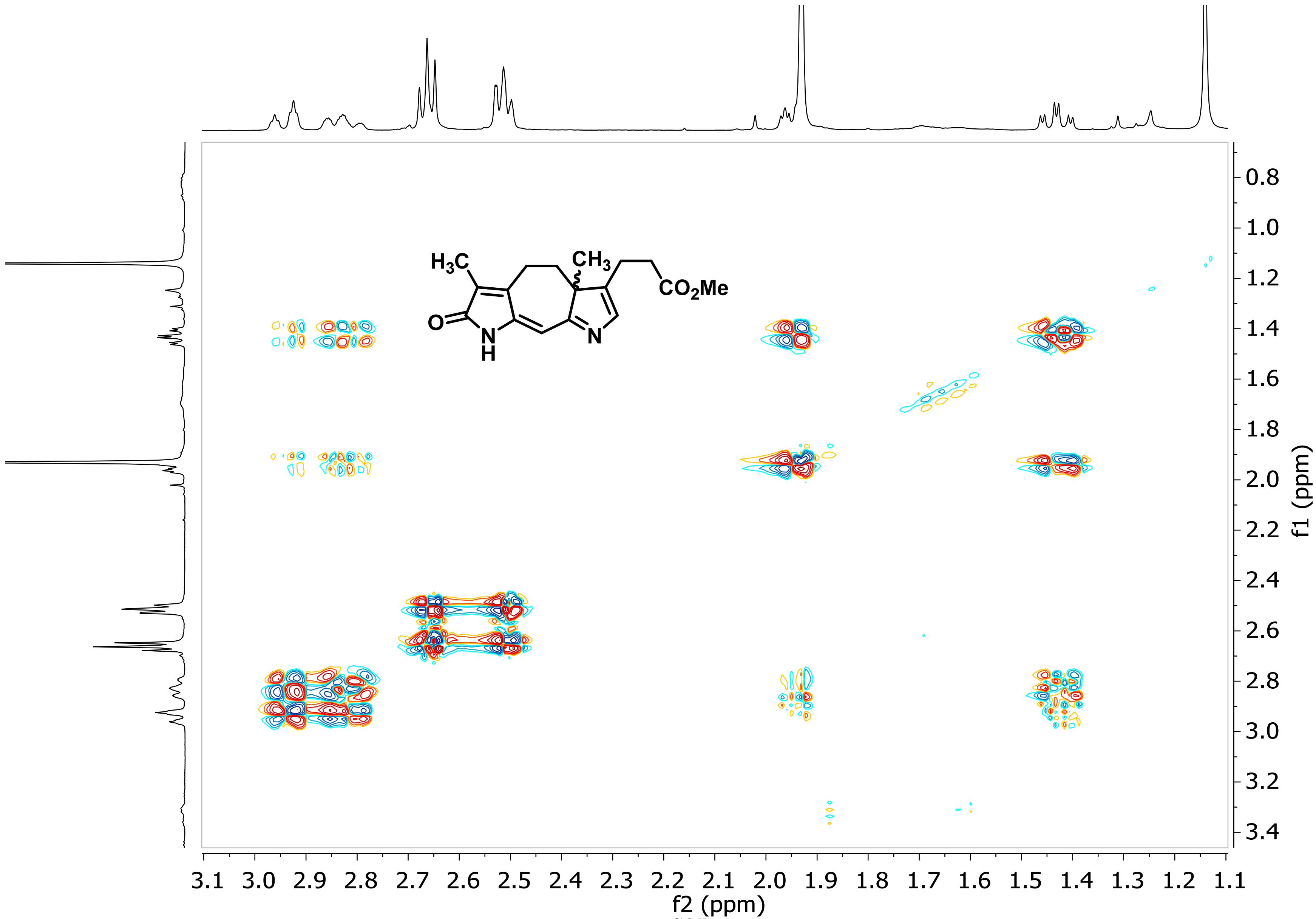


Figure S26. HPLC chromatogram of purified *Z*-**1a**. A basic mobile phase was used (gradient elution with 90:10 to 0:100 of solutions *A*:*B*, where *A* = 0.1% NH_3 in water and *B* = methanol).

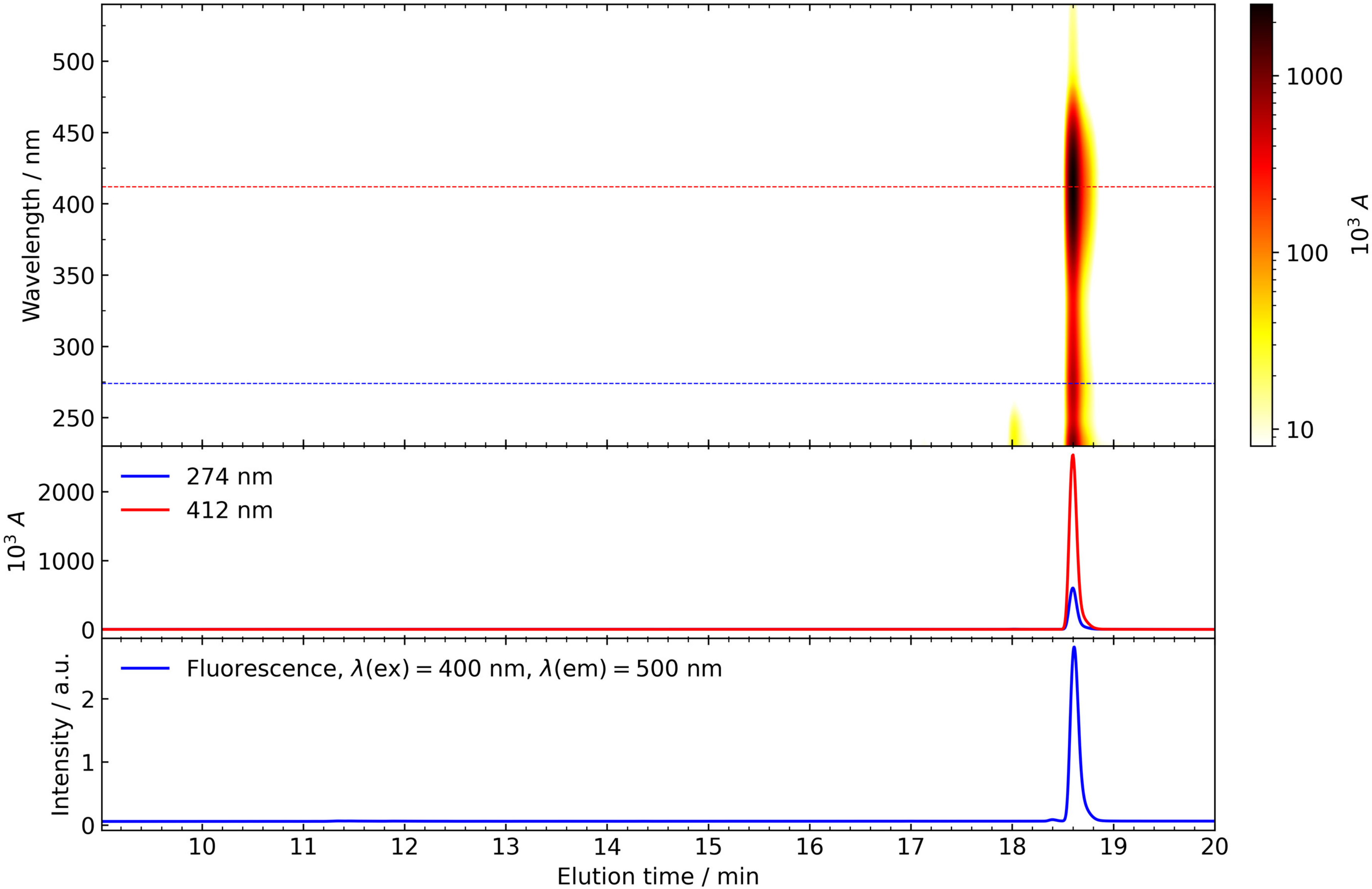


Figure S27. HPLC chromatogram of purified *E*-**1a**, containing 6.8% of *Z*-**1a**. The purity was determined by the integration of the signal at 445 nm where both isomers have the same values of molar absorption coefficients. A basic mobile phase was used (gradient elution with 90:10 to 0:100 of solutions *A*:*B*, where *A* = 0.1% NH_3 in water and *B* = methanol).

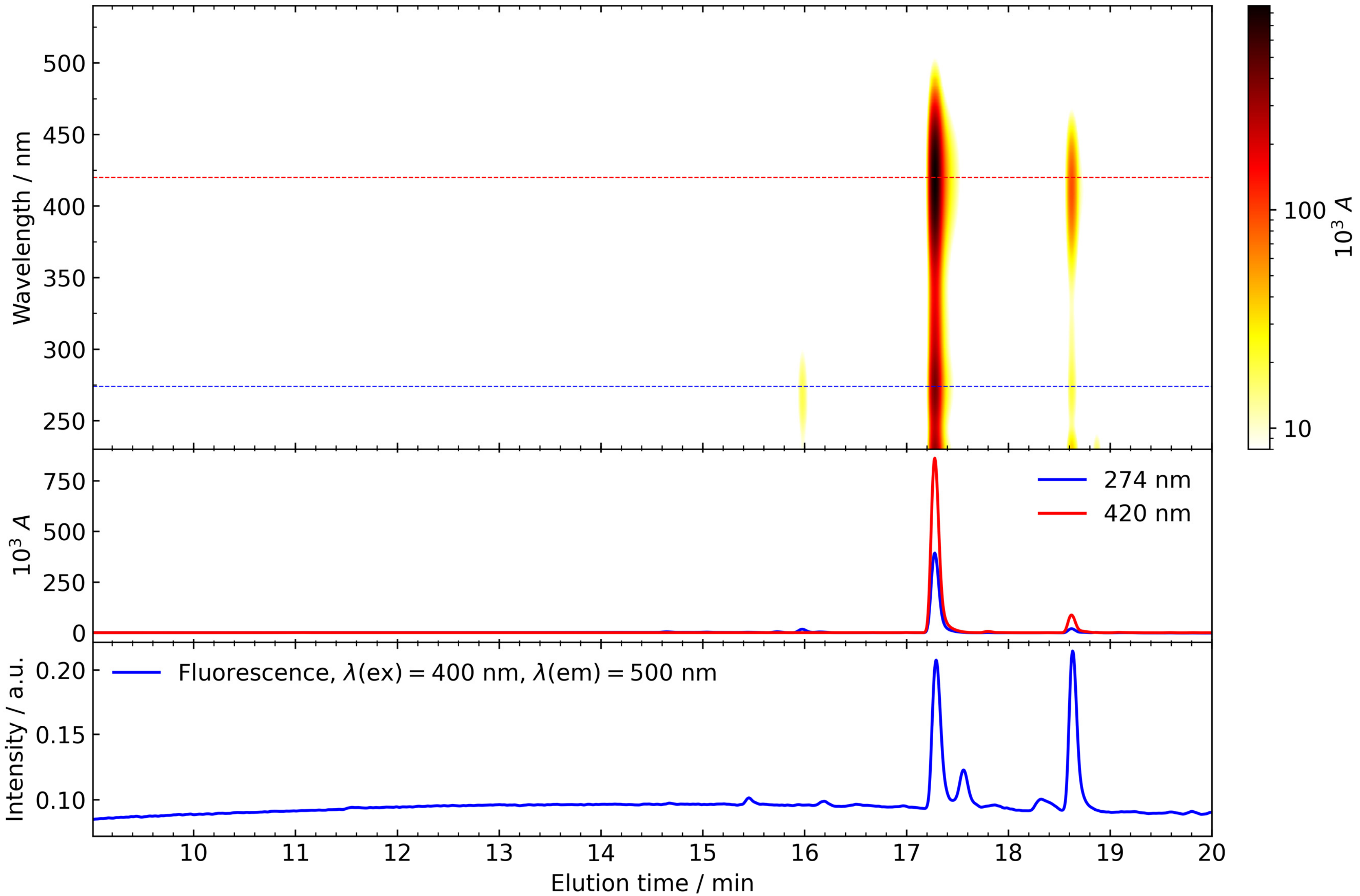


Figure S28. HPLC chromatogram of purified **1b**. A basic mobile phase was used (gradient elution with 90:10 to 0:100 of solutions *A*:*B*, where *A* = 0.1% NH_3 in water and *B* = methanol) and therefore **1b** exists in its less polar free-base form.

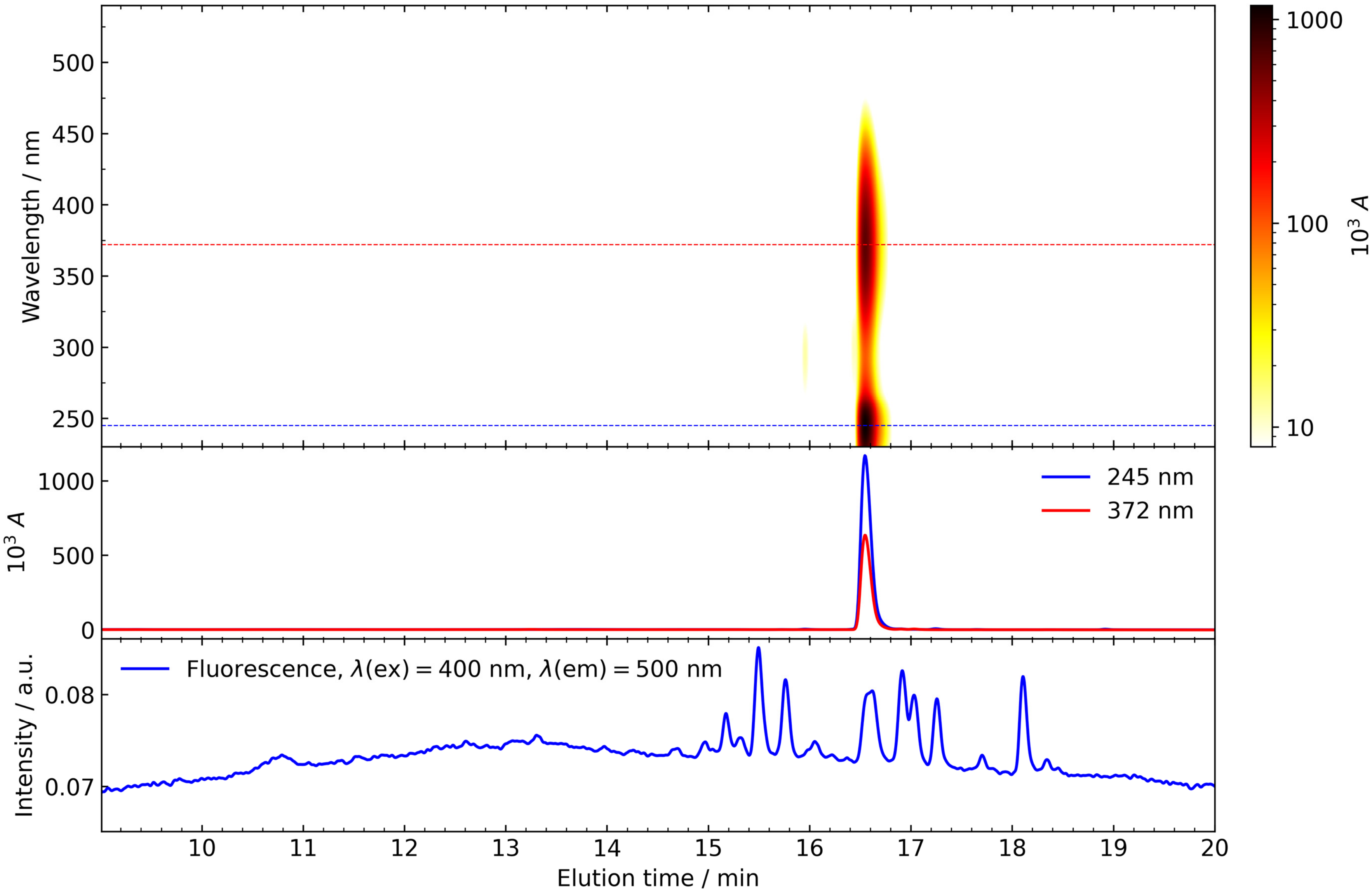


Figure S29. Irradiation of *Z*-**1a** (~220 μM) with 370 nm LED in methanol. HPLC traces at 245 nm (blue solid line) and 412 nm (red solid line) are shown. A basic mobile phase was used (gradient elution with 90:10 to 0:100 of solutions *A*:*B*, where *A* = 0.1% NH_3 in water and *B* = methanol).

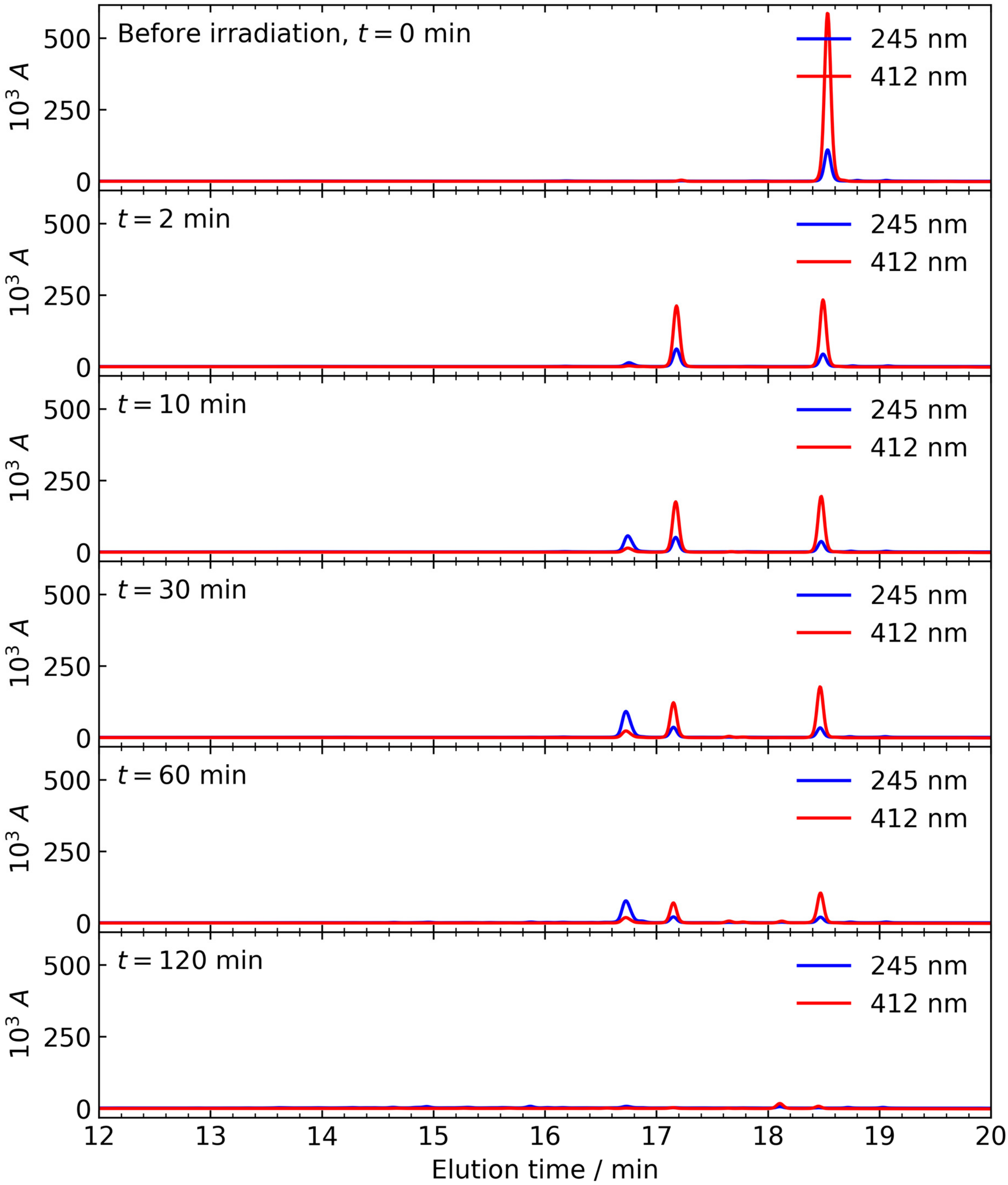


Figure S30. Irradiation of *E*-**1a** (~1.0 mM) with 445 nm LED in methanol. HPLC traces at 245 nm (blue solid line) and 412 nm (red solid line) are shown. A basic mobile phase was used (gradient elution with 90:10 to 0:100 of solutions *A*:*B*, where *A* = 0.1% NH_3 in water and *B* = methanol).

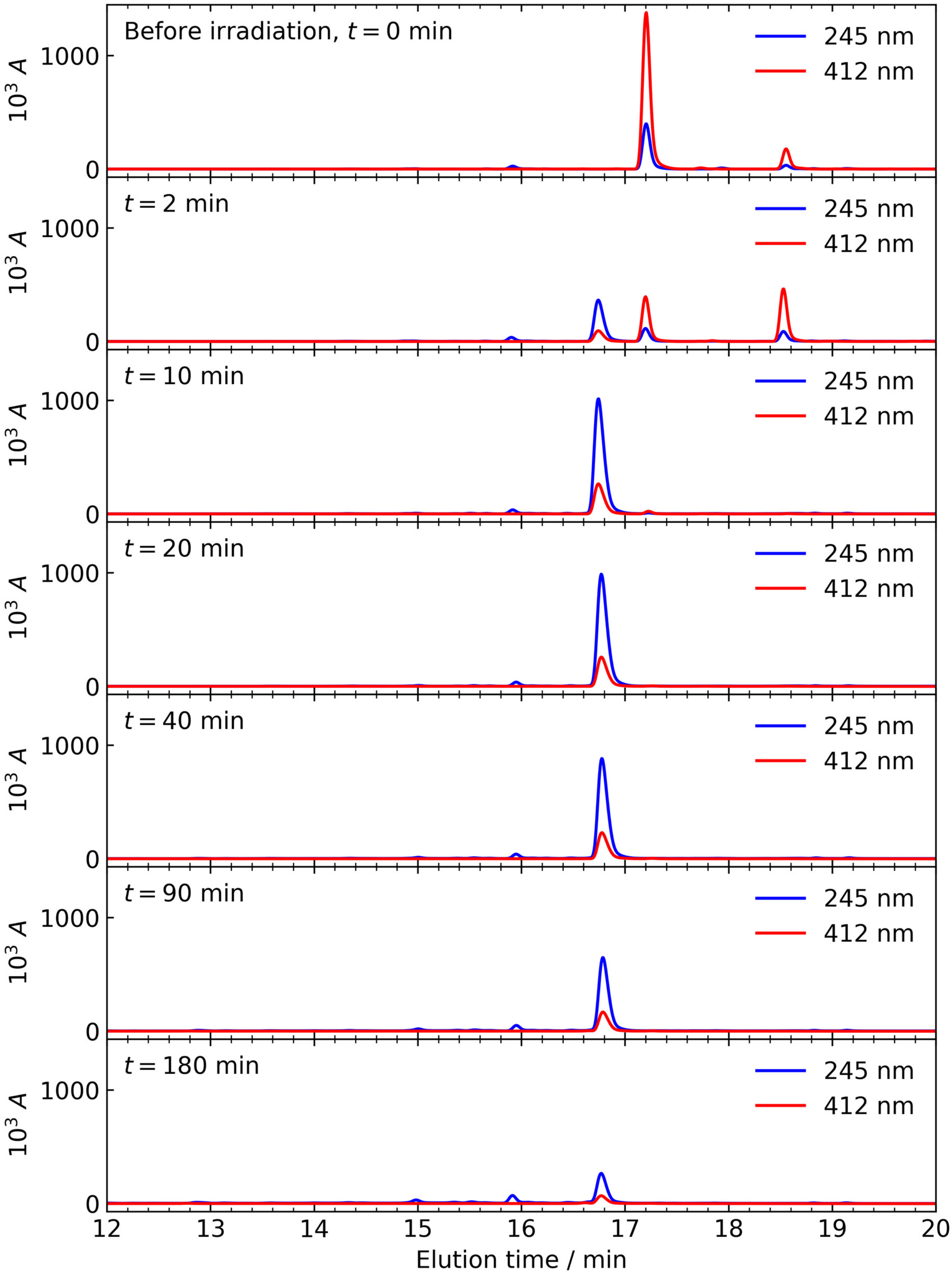


Figure S31. Irradiation of **1b** (~130 μM) with 375 nm LED in methanol. HPLC traces at 245 nm (blue solid line) and 412 nm (red solid line) are shown. A basic mobile phase was used (gradient elution with 90:10 to 0:100 of solutions *A*:*B*, where *A* = 0.1% NH_3 in water and *B* = methanol).

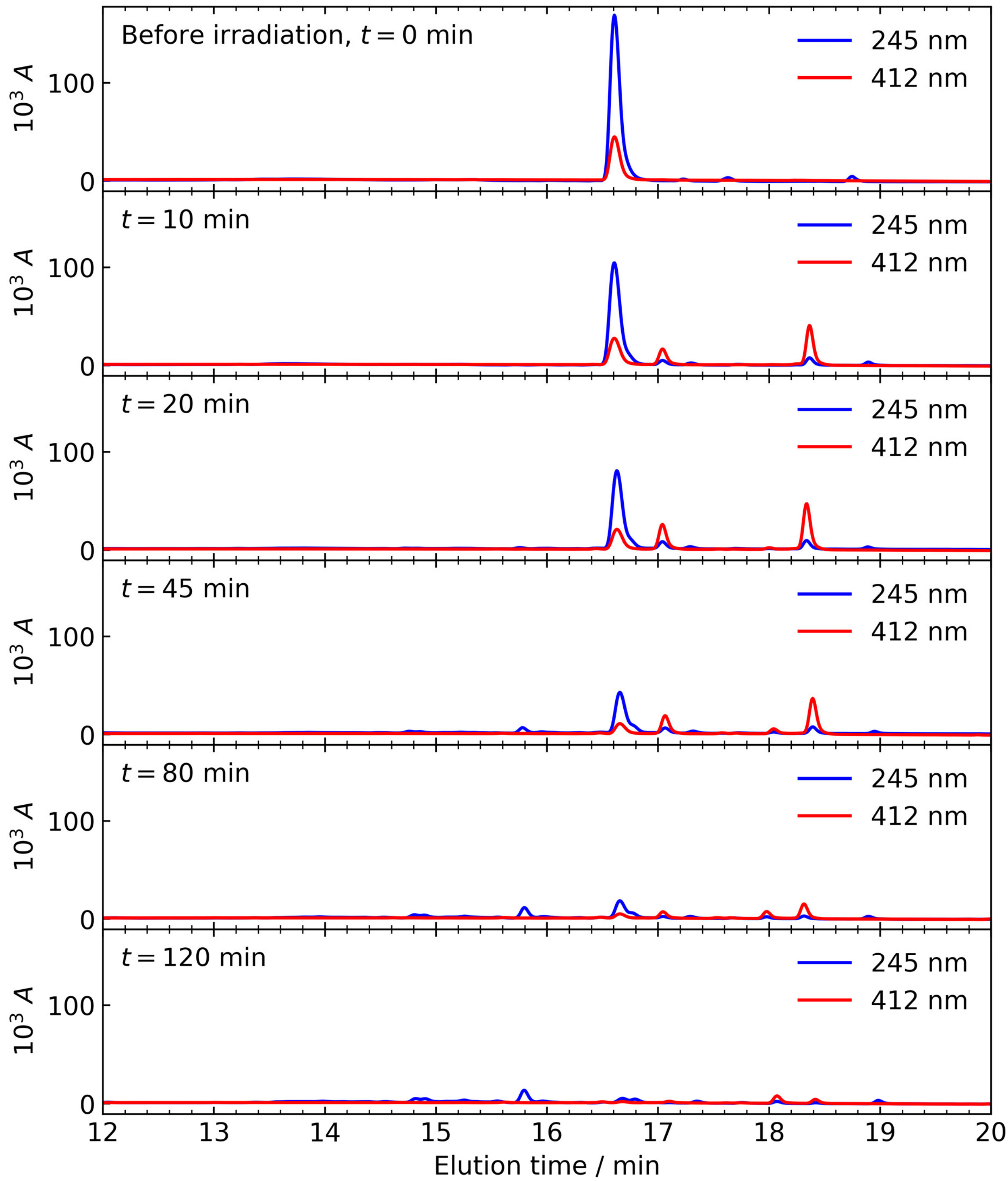
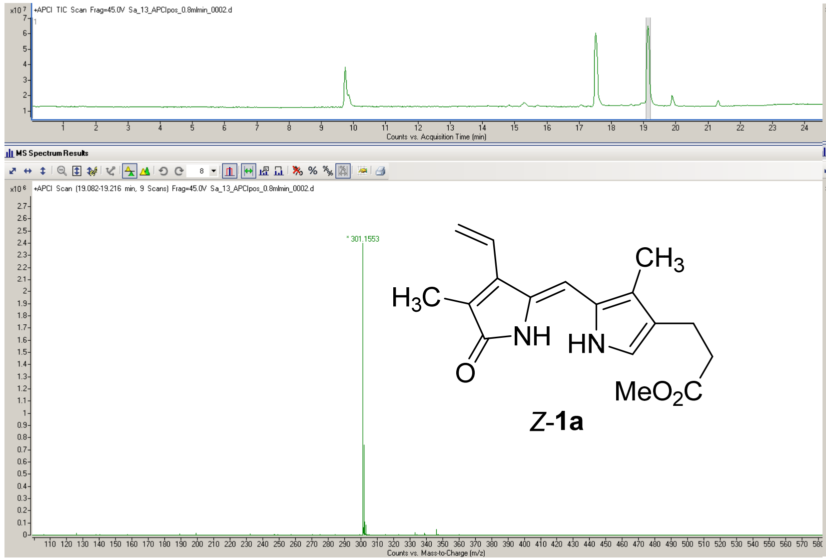
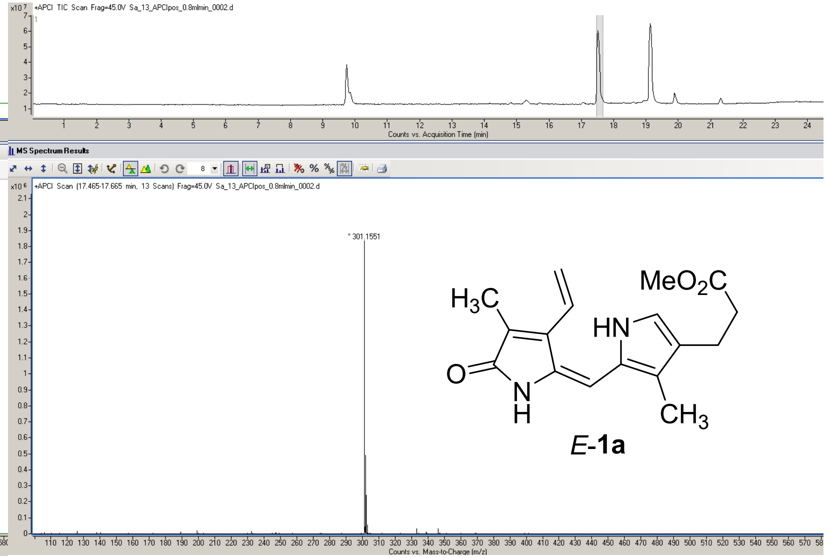


Figure S32. HPLC-MS spectra of prepared isomers. Acidic mobile phase was used here (gradient elution with 90:10 to 0:100 of solutions *A*:*B*, where *A* = 0.1% TFA in water and *B* = methanol), therefore, **1b** exists in its more polar protonated form **1b**H$^+$.





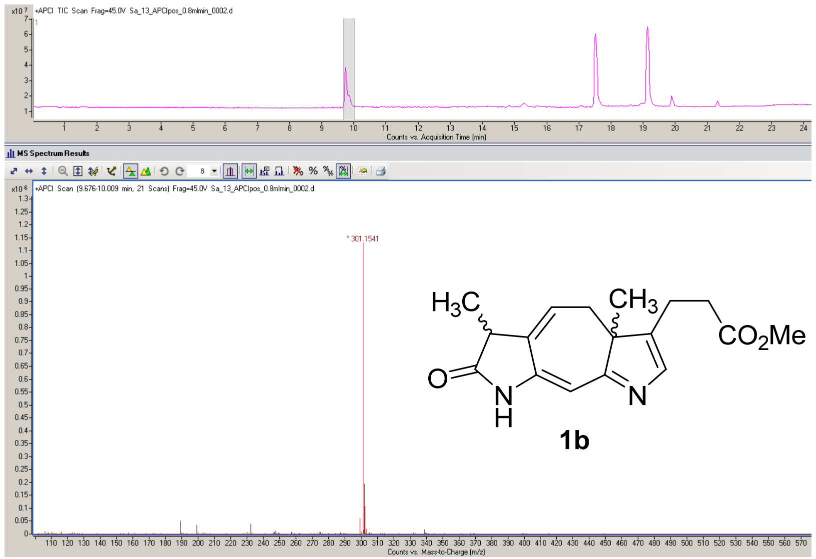
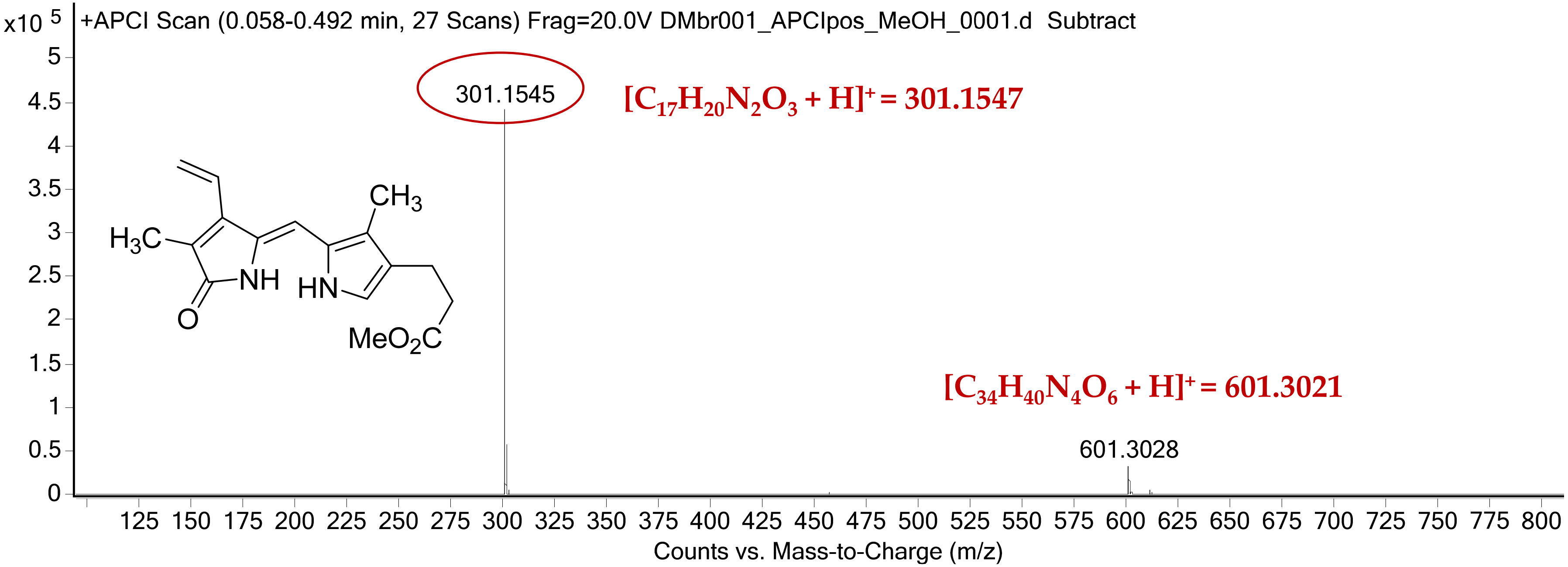


Figure S33. HRMS (APCI$^+$) of *Z*-**1a**.

APCI + (MMI)

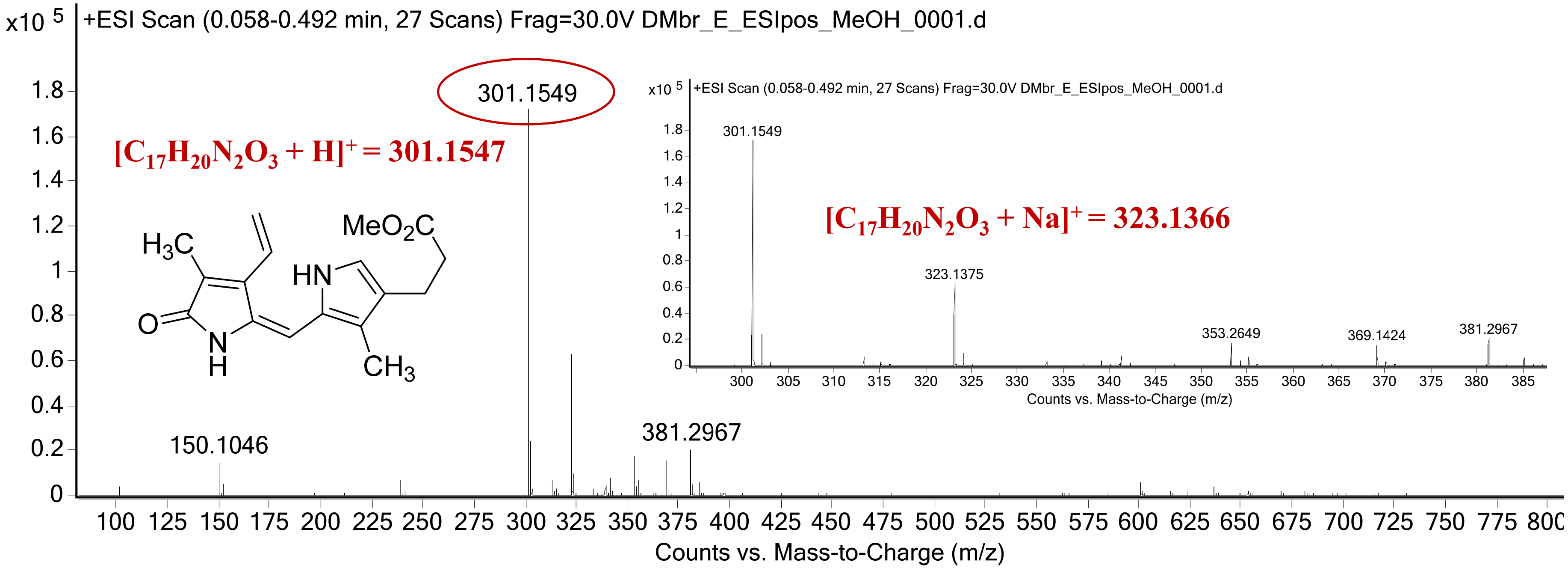
nitrogen flow 5 L/min, gas temperature 325°C, nebulizer 45 psig, skimmer 65 V, vaporizer 200°C, fragmentor 20 V, dissolved in methanol



expected mass: $[M+H]^+$ = 301.1547 observed mass: $[M+H]^+$ = 301.1545 mass accuracy = - 0.7 ppm

Figure S34. HRMS (ESI$^+$) of *E*-**1a**.

ESI + (MMI)
nitrogen flow 5 L/min, gas temperature 325°C, nebulizer 45 psig, skimmer 65 V, Vcap -2200 V, fragmentor 30 V, dissolved in methanol

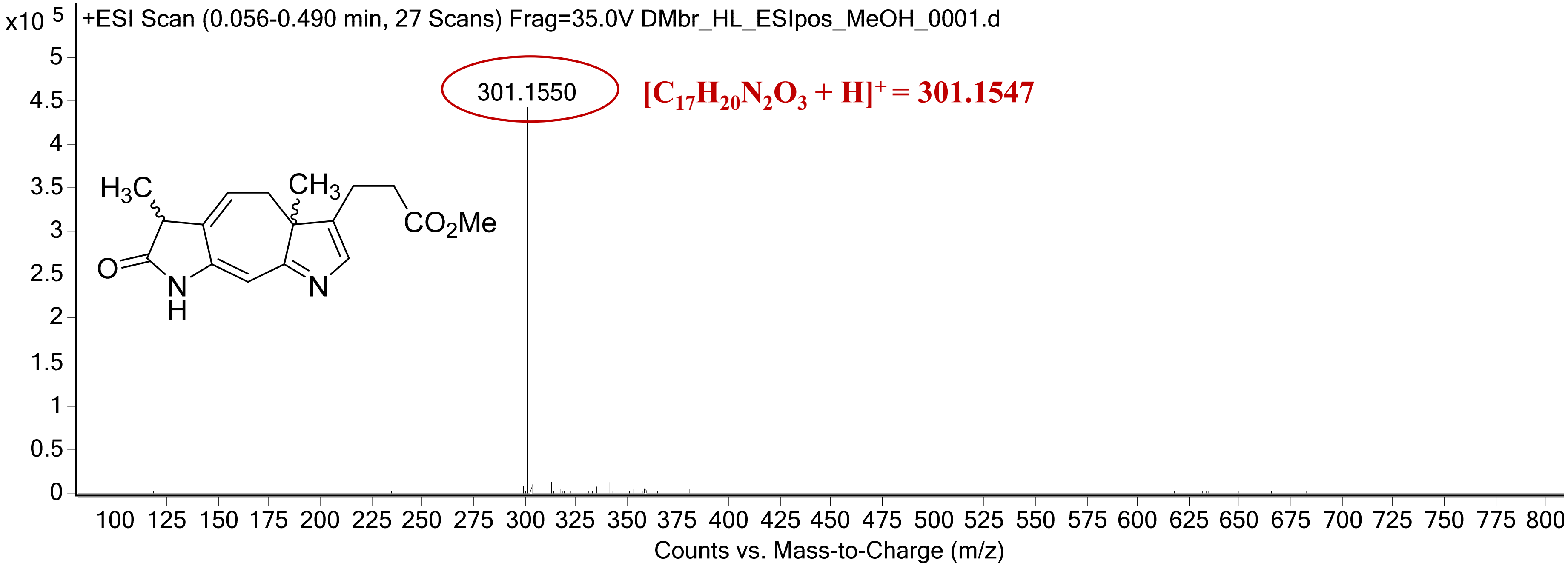


expected mass: [M+H]$^+$ = 301.1547 observed mass: [M+H]$^+$ = 301.1549 mass accuracy = 0.7 ppm

Figure S35. HRMS (ESI$^+$) of **1b**.

ESI + (MMI)

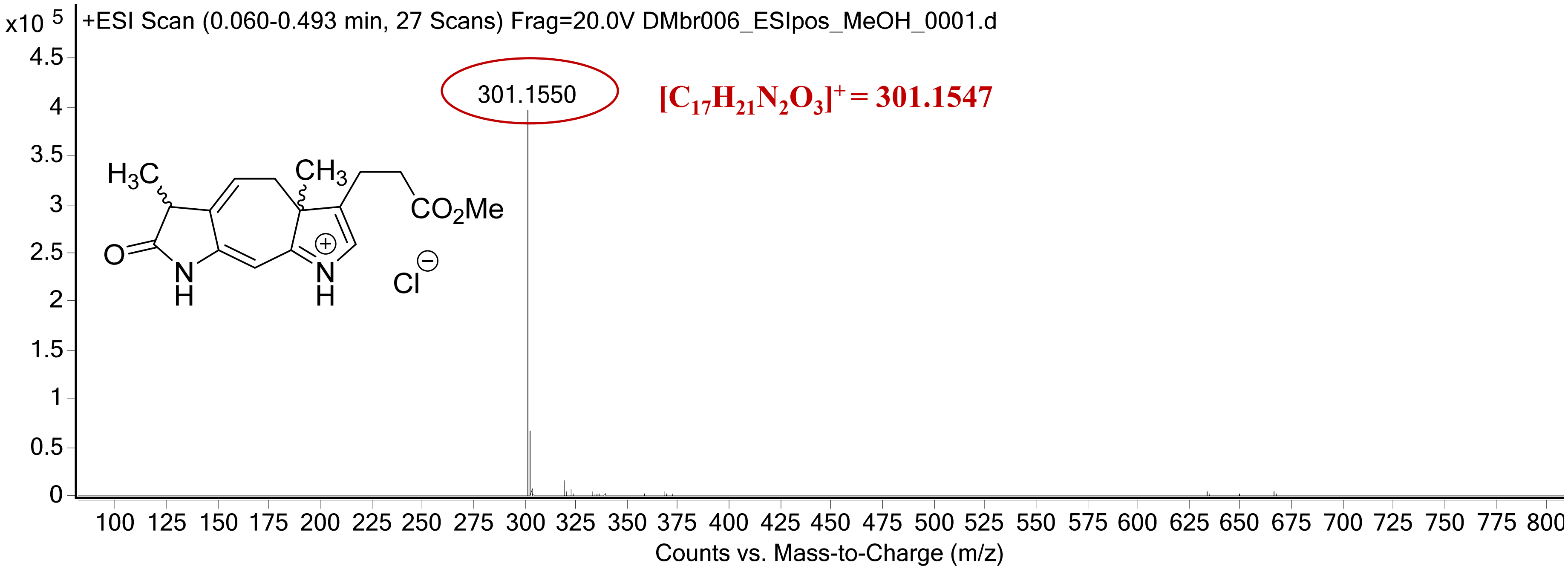
nitrogen flow 5 L/min, gas temperature 325°C, nebulizer 45 psig, skimmer 65 V, Vcap -2200 V, fragmentor 35 V, dissolved in methanol



expected mass: $[M+H]^+ = 301.1547$ observed mass: $[M+H]^+ = 301.1550$ mass accuracy = 1.0 ppm

Figure S36. HRMS (ESI+) of **1b.HCl**.

ESI + (MMI)
nitrogen flow 5 L/min, gas temperature 325°C, nebulizer 45 psig, skimmer 65 V, Vcap -2200 V, fragmentor 20 V, dissolved in methanol

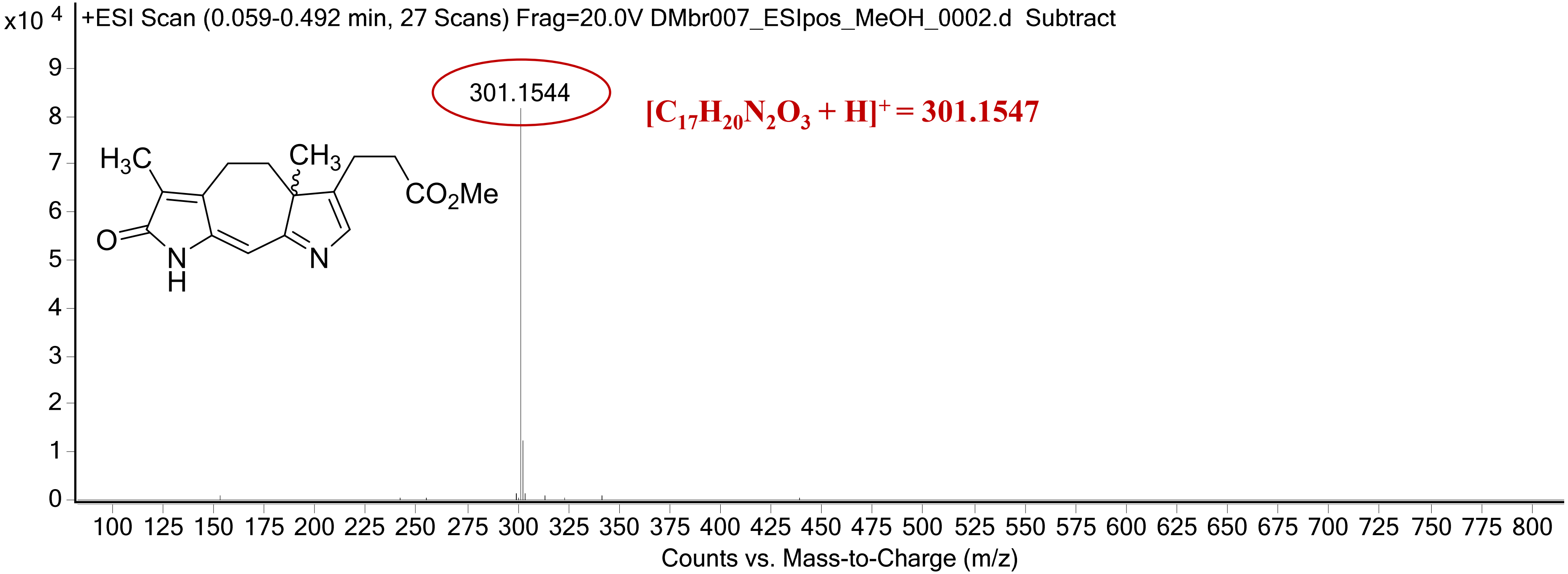


expected mass: $[M]^+ = 301.1547$ observed mass: $[M]^+ = 301.1550$ mass accuracy = 1.0 ppm

Figure S37. HRMS (ESI+) of **1c**.

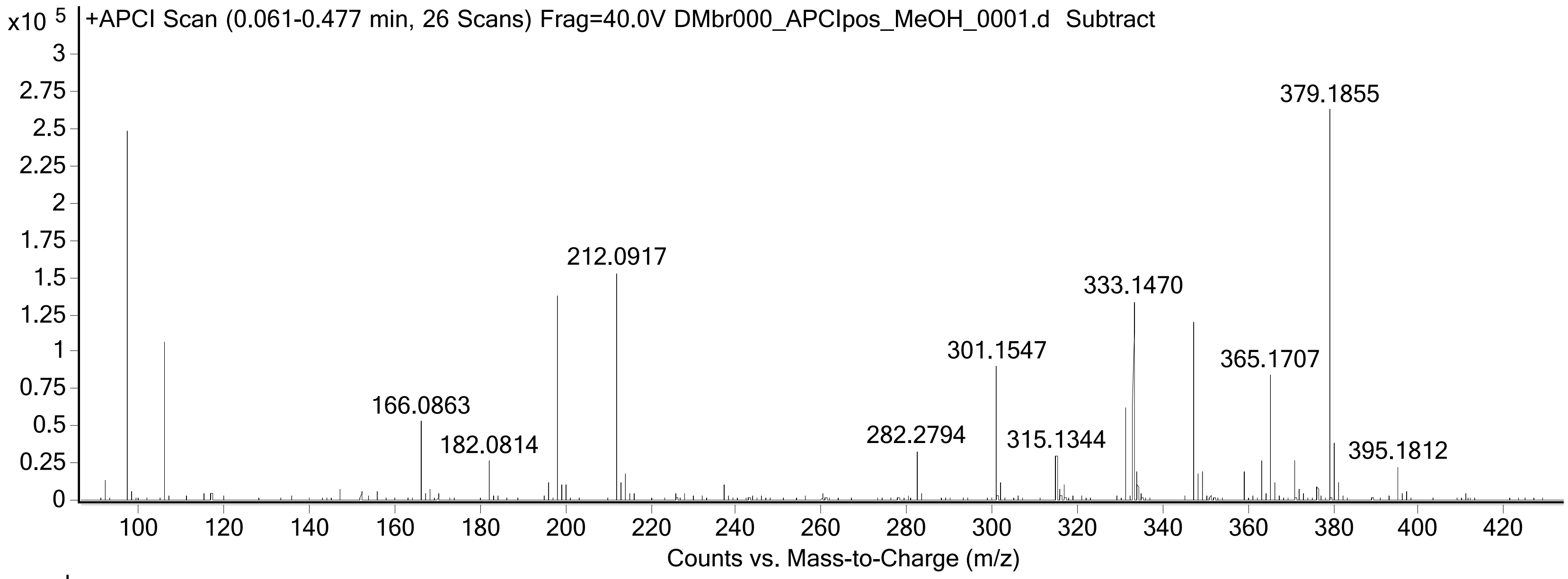
ESI + (MMI)

nitrogen flow 5 L/min, gas temperature 325°C, nebulizer 45 psig, skimmer 65 V, Vcap -2200 V, fragmentor 20 V, dissolved in methanol



expected mass: $[M+H]^+ = 301.1547$ observed mass: $[M+H]^+ = 301.1544$ mass accuracy = - 1.0 ppm

Figure S38. HRMS (APCI$^+$) of the mixture after exhaustive irradiation of *Z*-**1a** in methanol with 375 nm LED (under Ar atmosphere).



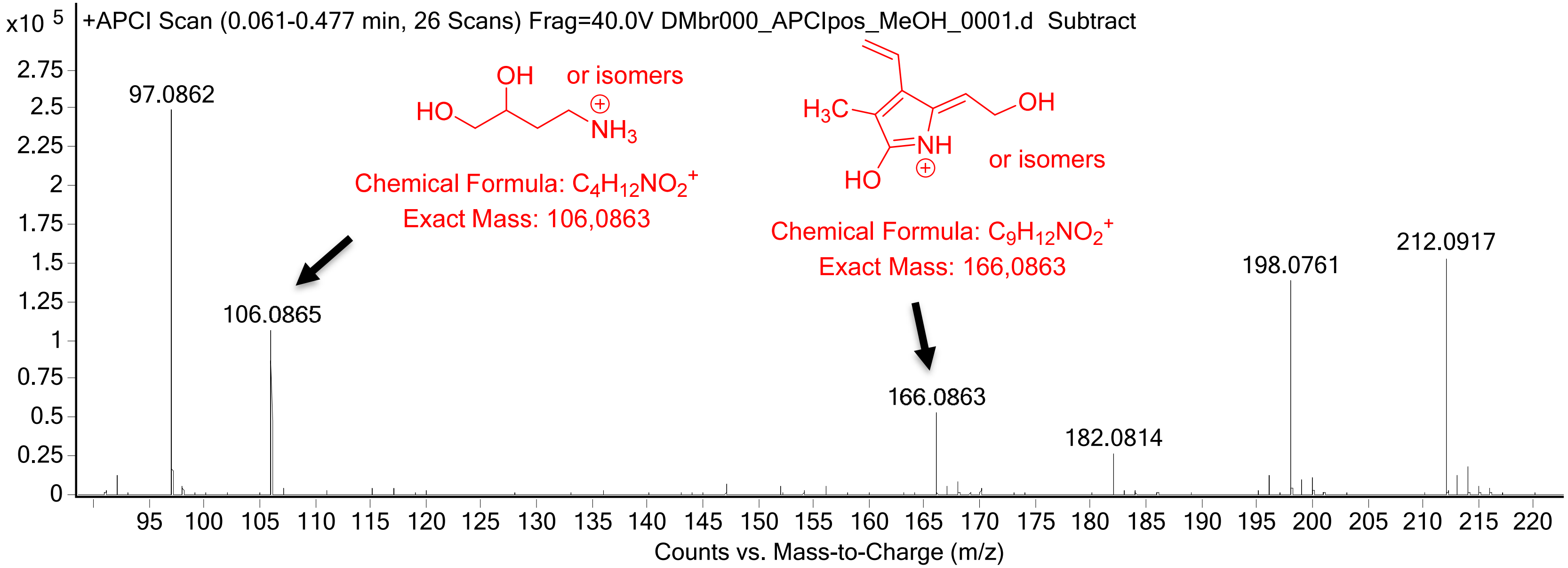


Figure S39. (**A**) Concentration dependence of absorption spectra of *Z*-**1a** in methanol (the values of *A* > 2.5 were removed). Dashed vertical lines at the local absorption maxima are visual guides. (**B**) Concentration-dependent absorbance at the local maxima and the corresponding molar absorption coefficients.

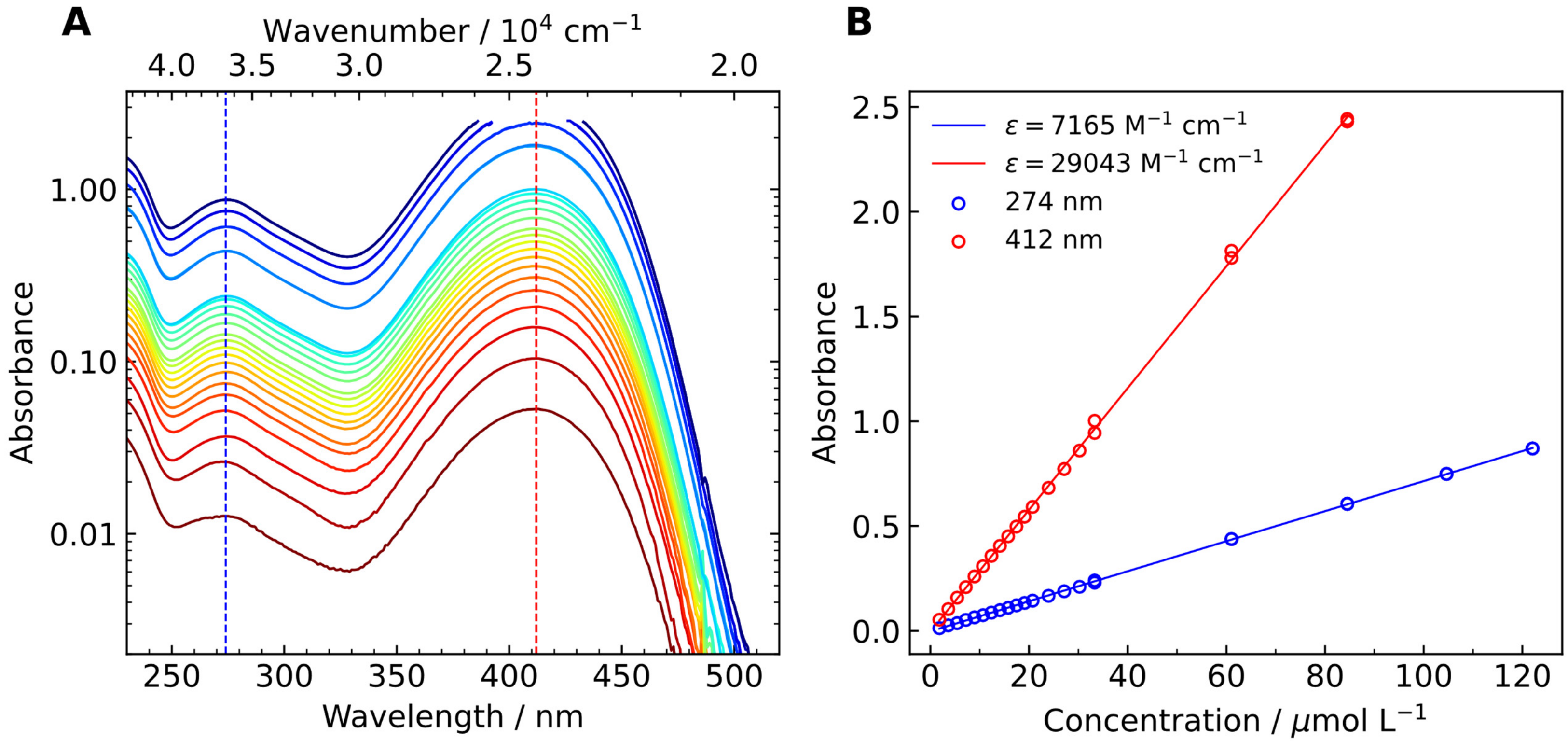


Figure S40. (**A**) Concentration dependence of absorption spectra of *Z*-**1a** in acetonitrile (the values of $A > 2.5$ were removed). Dashed vertical lines at the local absorption maxima are visual guides. (**B**) Concentration-dependent absorbance at the local maxima and corresponding molar absorption coefficients.

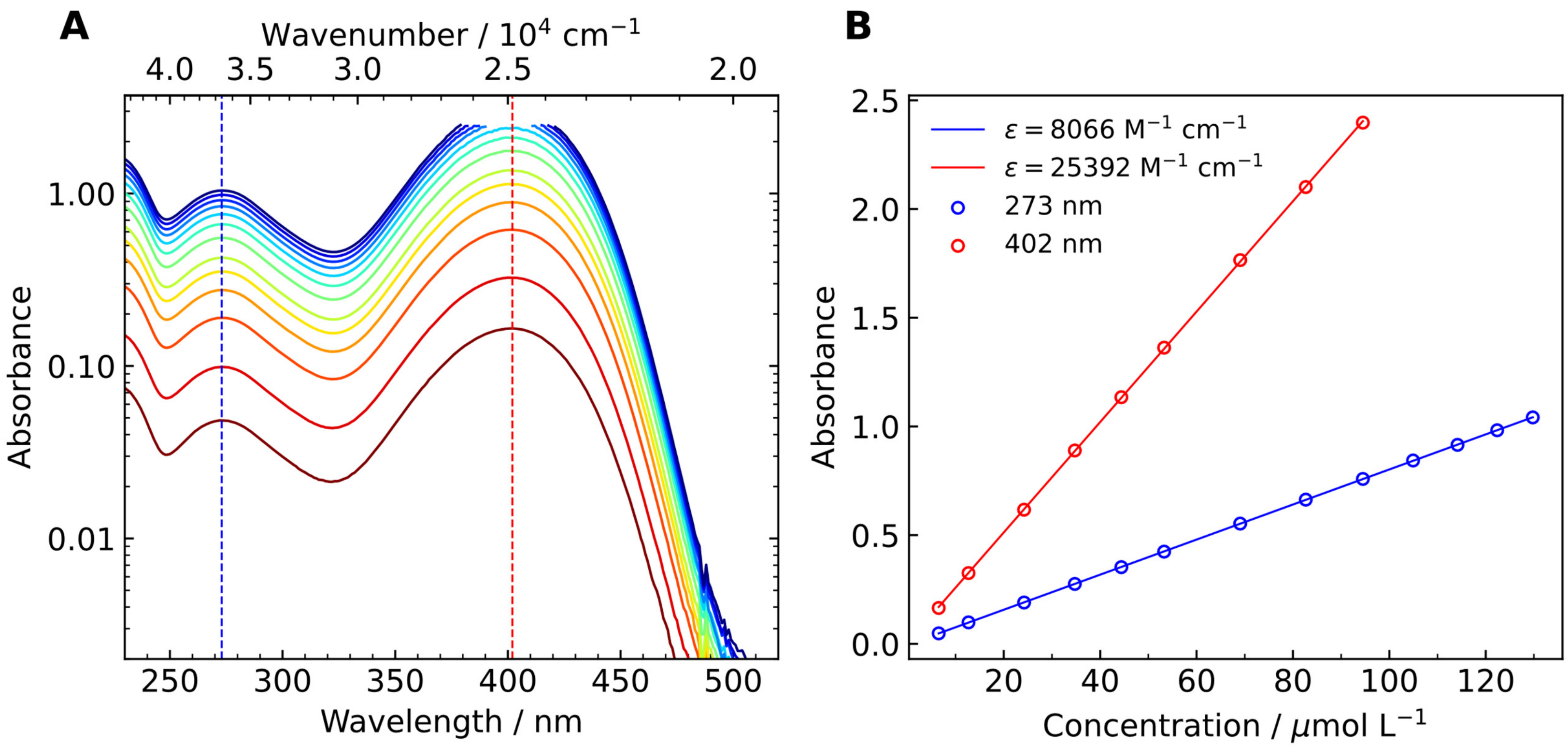


Figure S41. Molar absorption coefficients of *Z*-**1a** in methanol and acetonitrile.

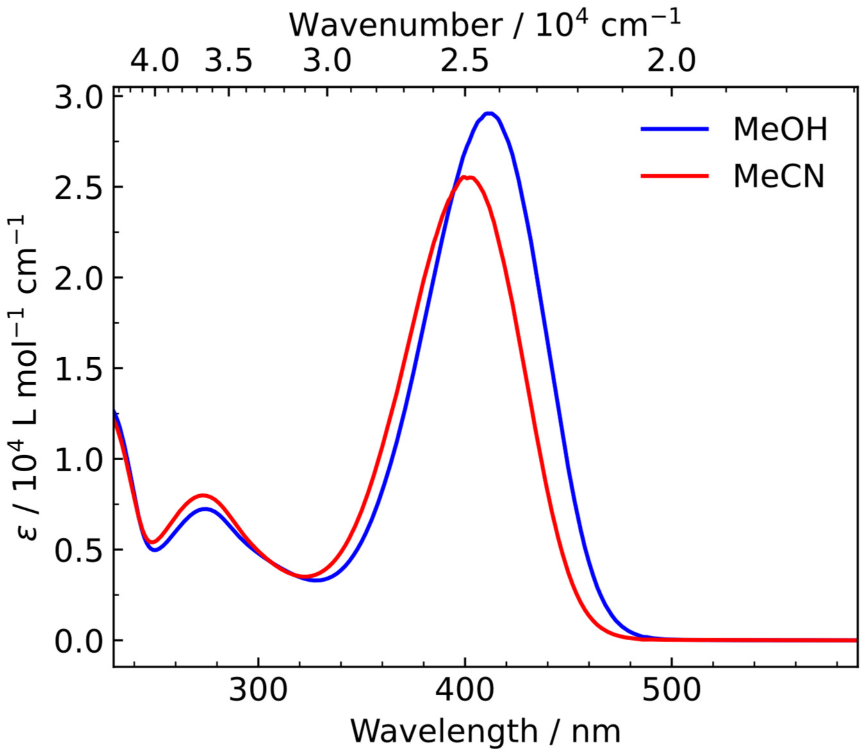


Figure S42. (**A**) Absorption, emission (λ(ex) = 390 nm) and excitation (λ(em) = 470, 500 and 530 nm) spectra of *Z*-**1a** in methanol. Raman scattering peaks were subtracted from emission and excitation spectra. (**B**) Emission map of *Z*-**1a** in methanol. The most intense line corresponds to Rayleigh scattering, the less intense to Raman scattering signals from methanol.

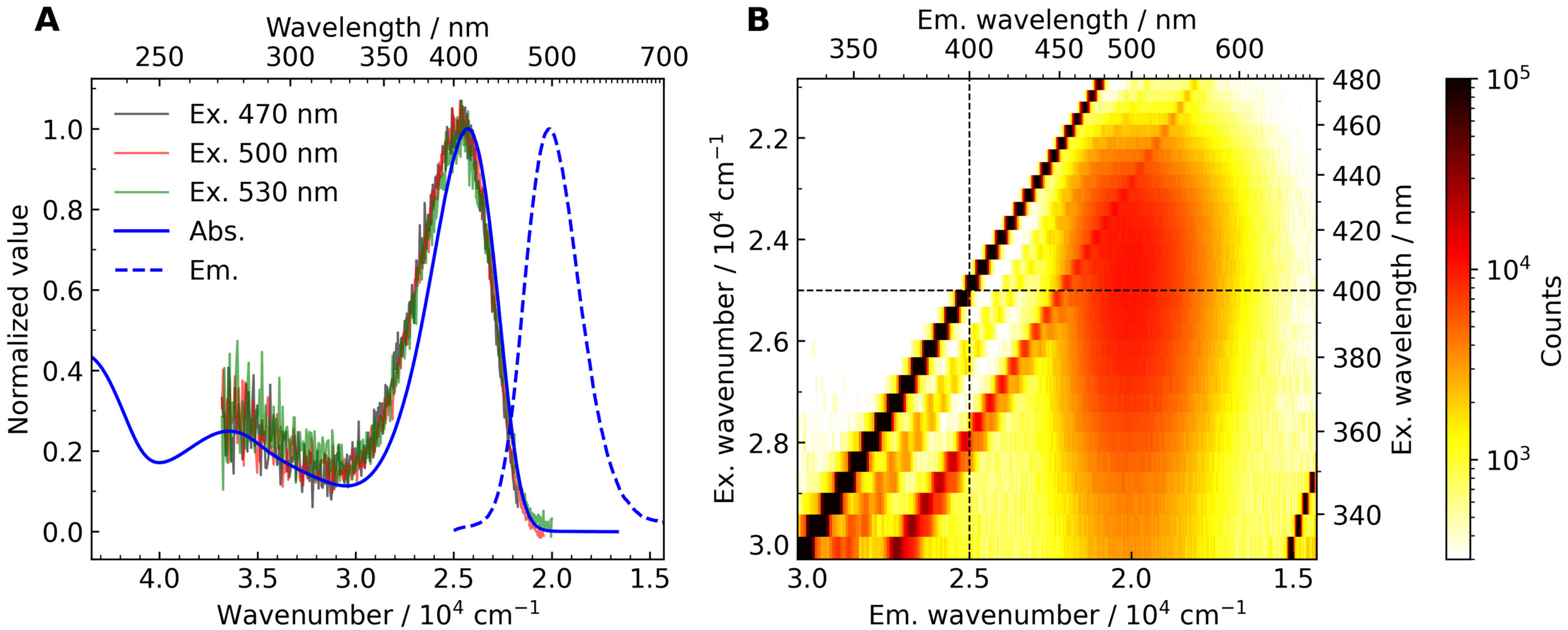


Figure S43. Irradiation of *Z*-**1a** (~60 µM) in methanol with 445 nm LED under argon (**left**) and oxygen (**right**) saturated conditions. LED light intensity and initial concentration of *Z*-**1a** were the same for both experiments. The gray-shaded area represents the spectrum of the irradiation source. Colorbar is plotted with a lin-log scale (linear until 20 s and then logarithmic).

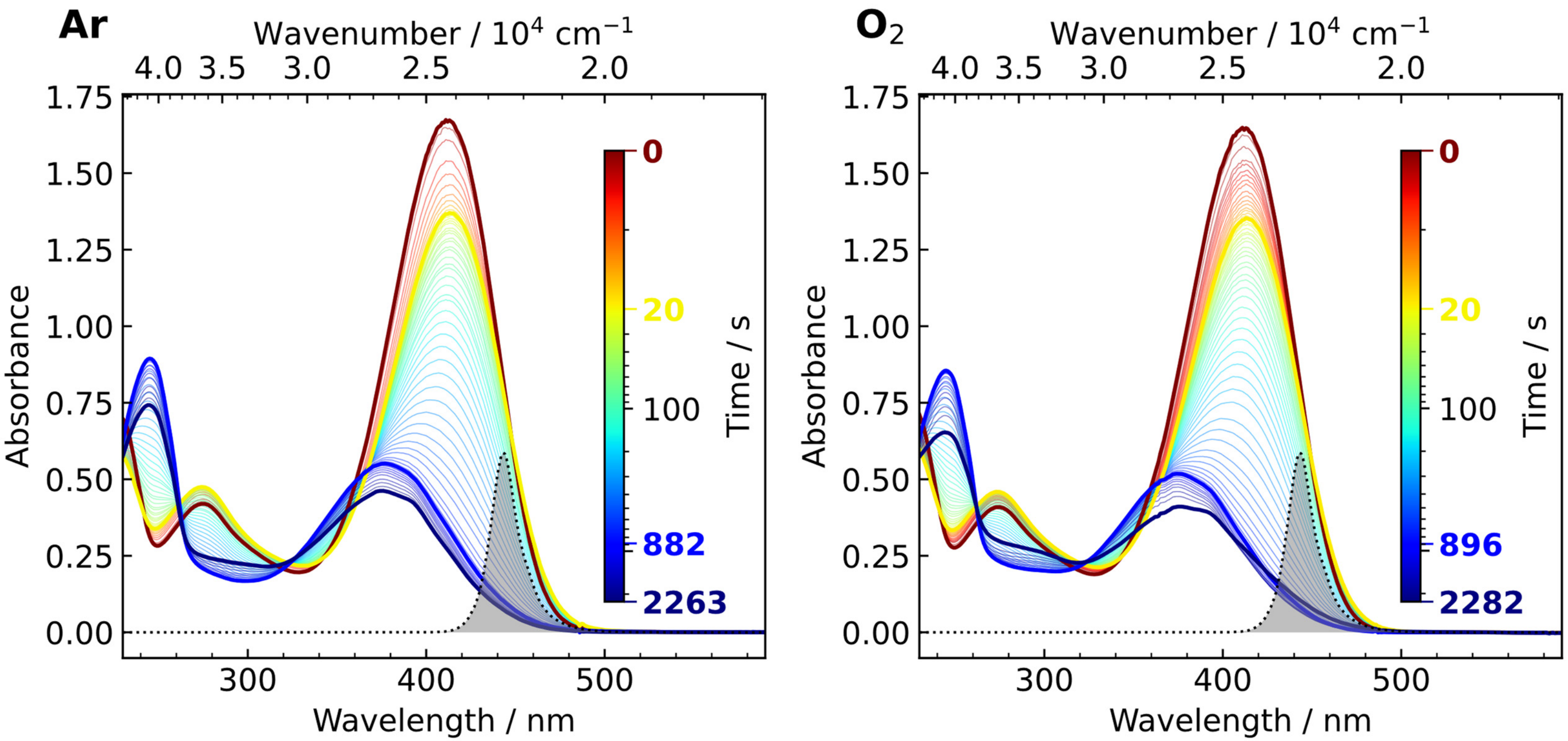


Figure S44. Irradiation of **1b** in methanol with 375 nm LED under argon (**left**) and oxygen (**right**) saturated conditions. LED light intensity and initial concentration of **1b** were the same for both experiments. The gray-shaded area represents the spectrum of the irradiation source. Colorbar is plotted with a lin-log scale (linear until 100 s and then logarithmic).

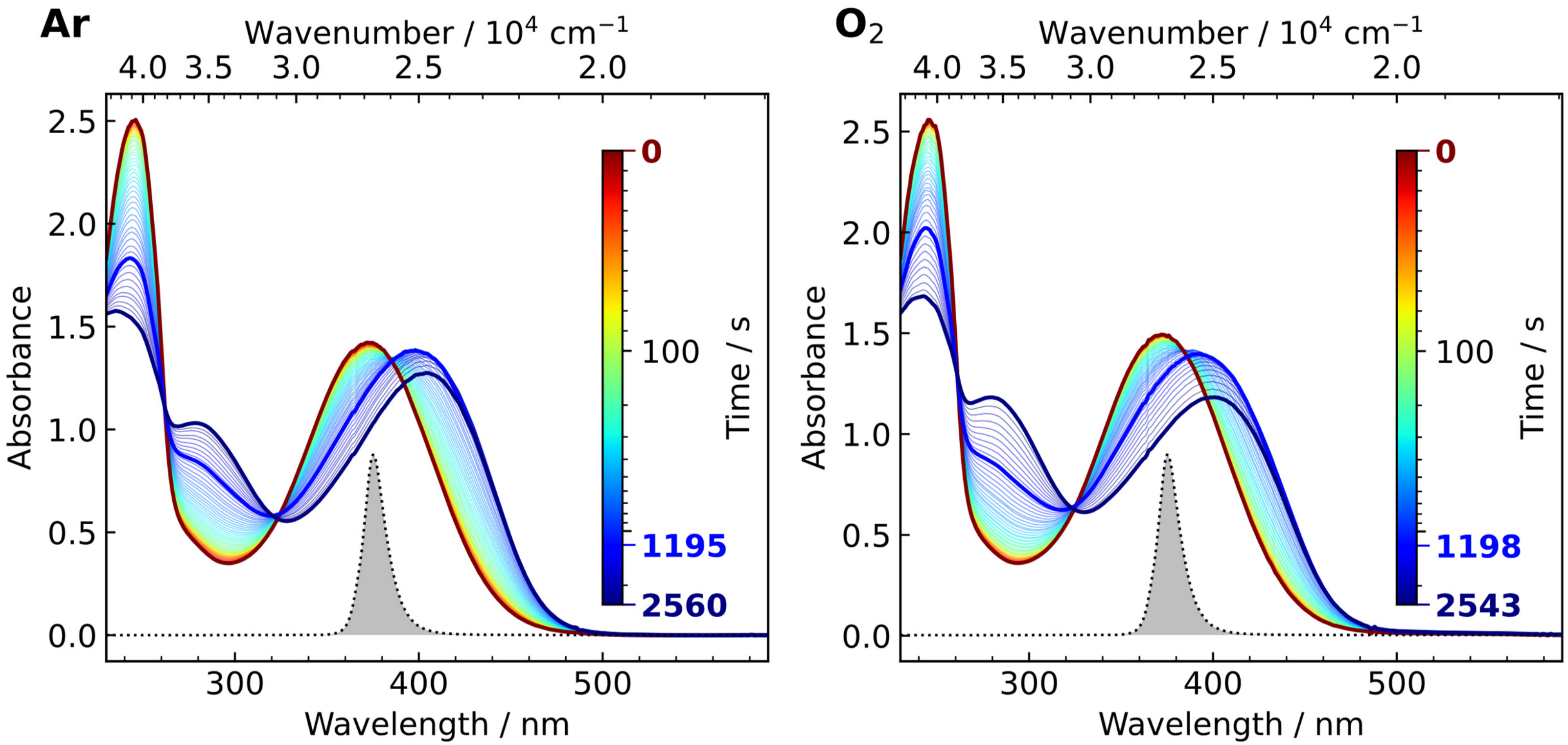


Figure S45. Irradiation of *Z*-**1a** (~60 μM) in dry (**A**) and wet (33 % water, v/v) (**B**) acetonitrile with 470 nm LED under argon atmosphere. LED light intensity of *Z*-**1a** was the same for both experiments. The gray-shaded area represents the spectrum of the irradiation source. Colorbar is plotted with a lin-log scale (linear until 5 s and then logarithmic).

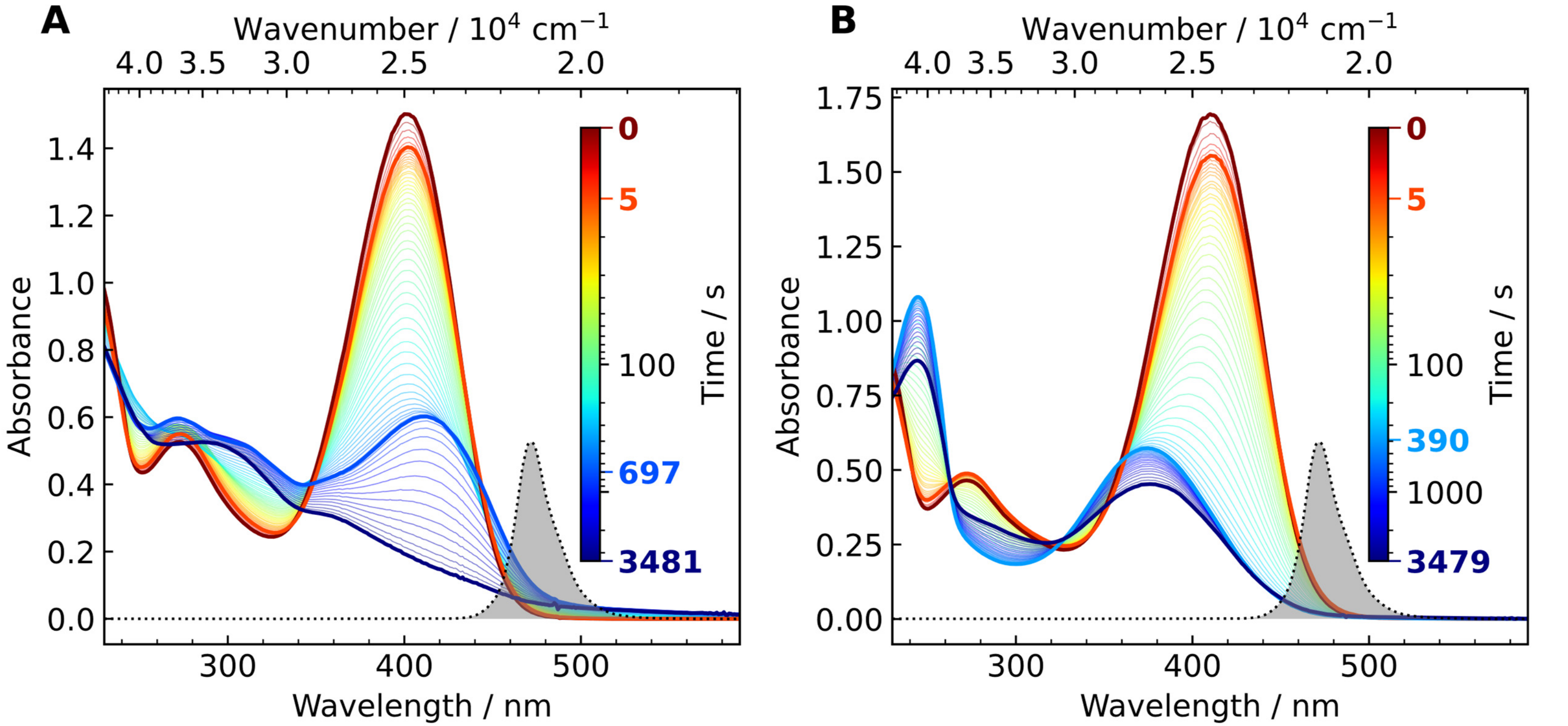


Figure S46. Addition of 10 µL (**A**) and 50 µL (**B**) of TfOH (0.45 mM solution in methanol) to solution of *E*-**1a** (2.0 mL, ~40 µM) in methanol. Recorded kinetics show the formation of *Z*-**1a** after the addition of acid.

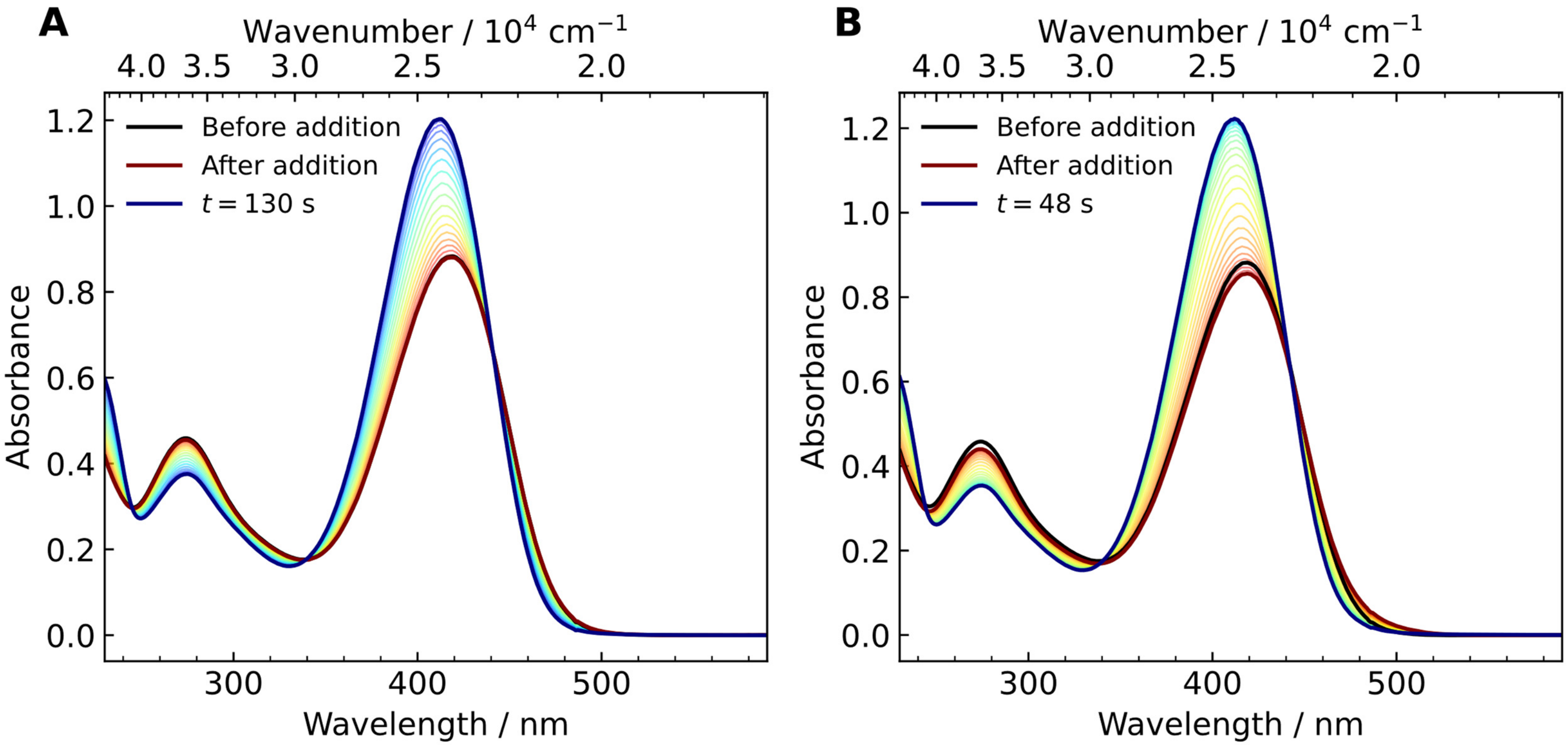


Figure S47. pK_a titration of *Z*-**1a** in MeOH by additions of triflic acid solution in MeOH. (**A**) Absorption spectra at different pH values. (**B**) Absorbances at 410 nm (blue circles) and 470 nm (red circles) with fitted curves (solid lines) as obtained from target fitting. The best value of pK_a is plotted as a black dashed vertical line. The value of pH = 5 for a neutral solution was chosen so that its population mainly contains *Z*-**1a**.

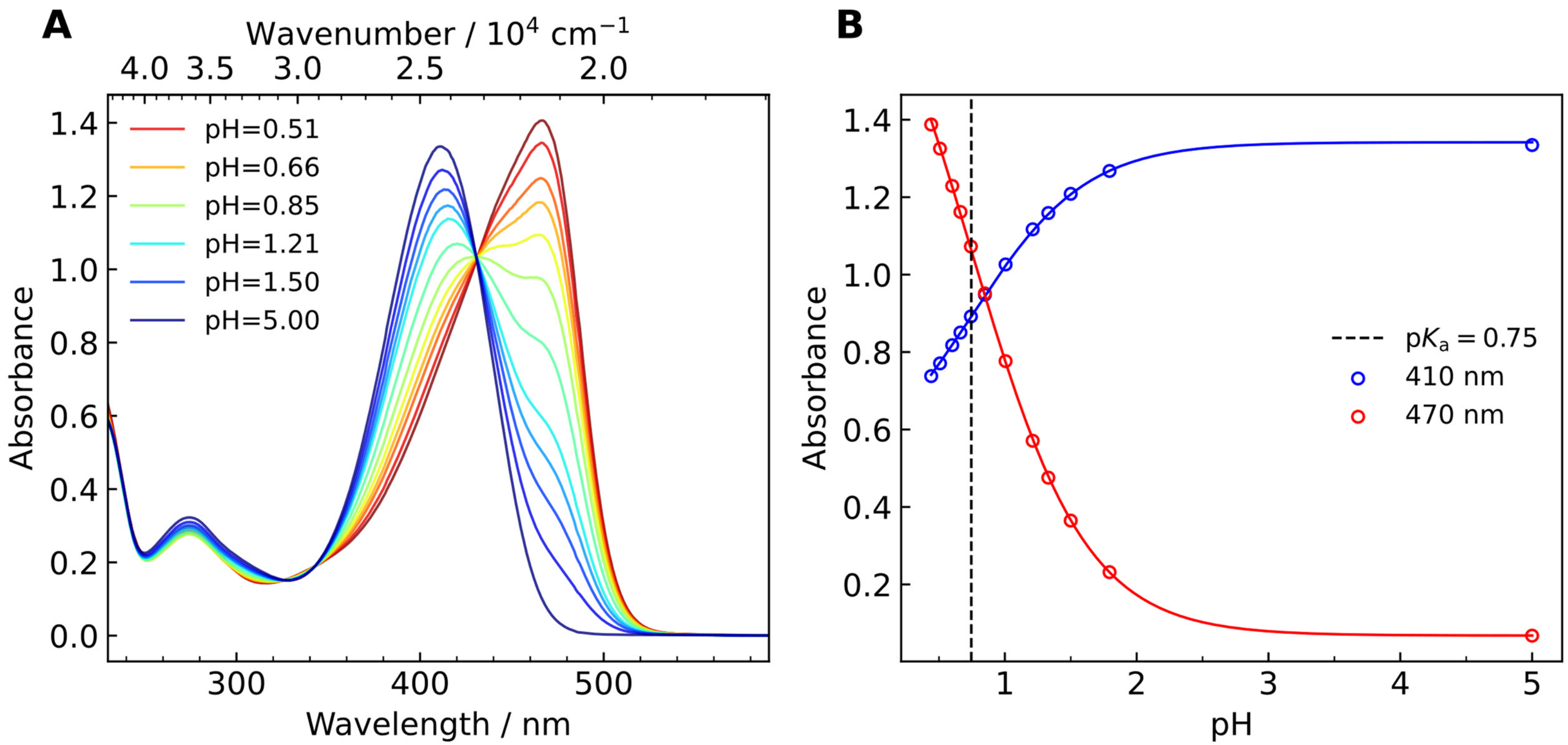


Figure S48. (**Left**) Molar absorption coefficients of *Z*-**1a** and its conjugate acid in methanol. The spectrum of *Z*-**1a**H$^+$ was obtained from target fit (pK_a titration). (**Right**) Molar absorption coefficients of *Z*-**1a** and its conjugate acid in acetonitrile. The spectrum of *Z*-**1a**H$^+$ was obtained by acidification of acetonitrile solution of *Z*-**1a** with triflic acid.

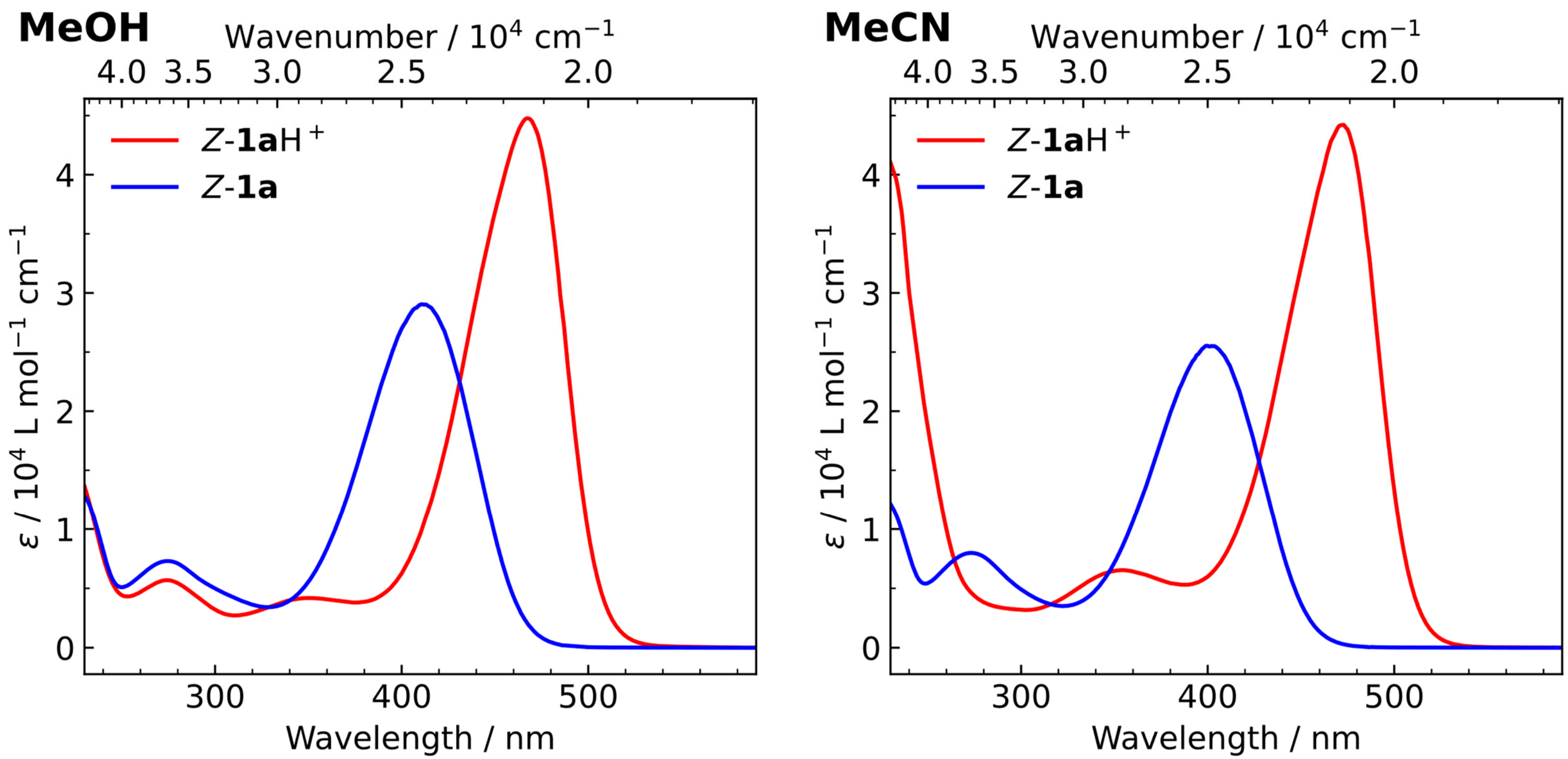


Figure S49. pK_a titration of **1b** in aqueous KCl (I = 0.1 M, 10% MeOH). (**A**) Absorption spectra at different pH values. (**B**) Absorbances at 350 nm (blue circles) and 430 nm (red circles) with fitted curves (solid lines) as obtained from global fitting. The best value of pK_a is plotted as a black dashed vertical line.

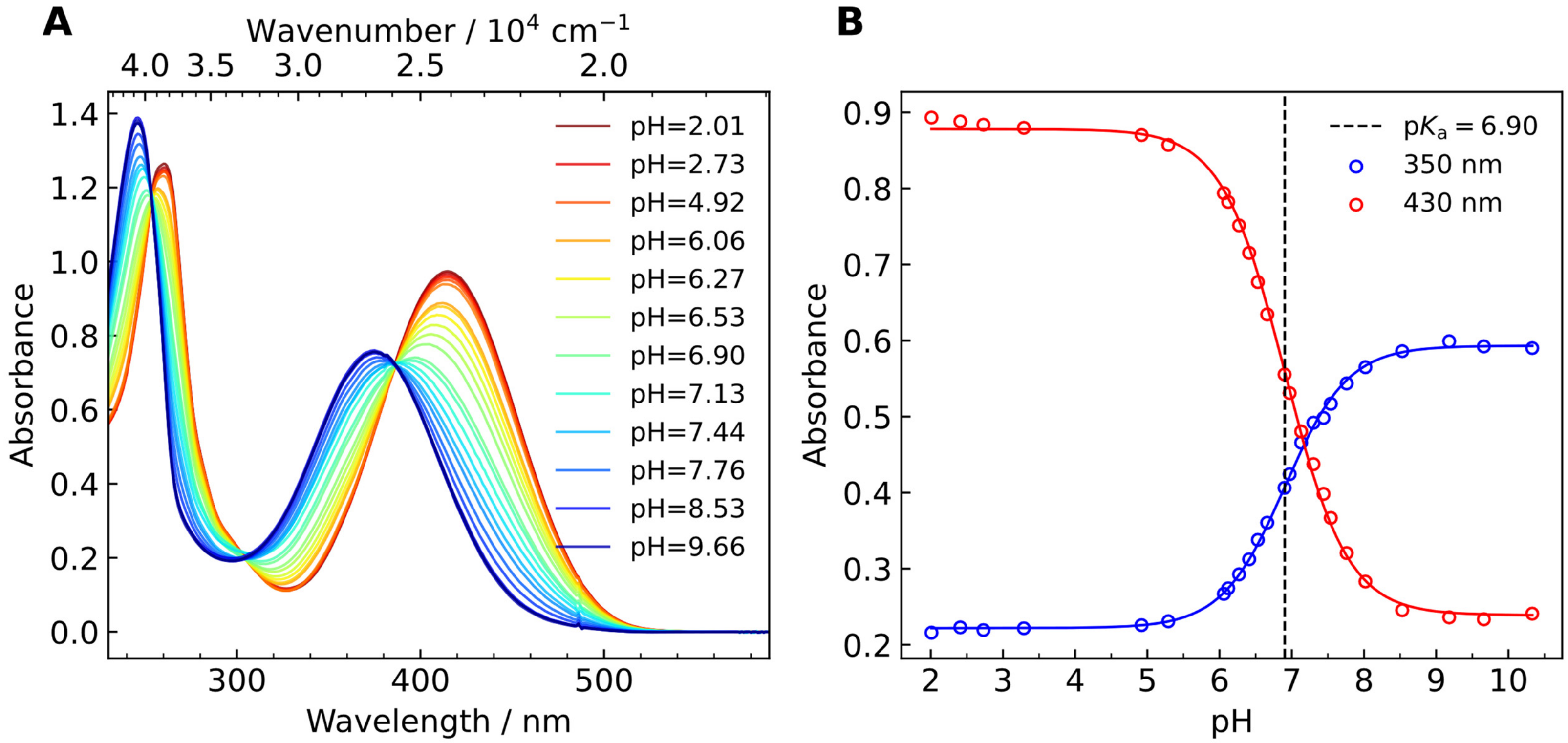


Figure S50. Molar absorption coefficients of **1b** and its conjugate acid in aqueous KCl (I = 0.1 M, 10% MeOH) (**A**) and in methanol (**B**).

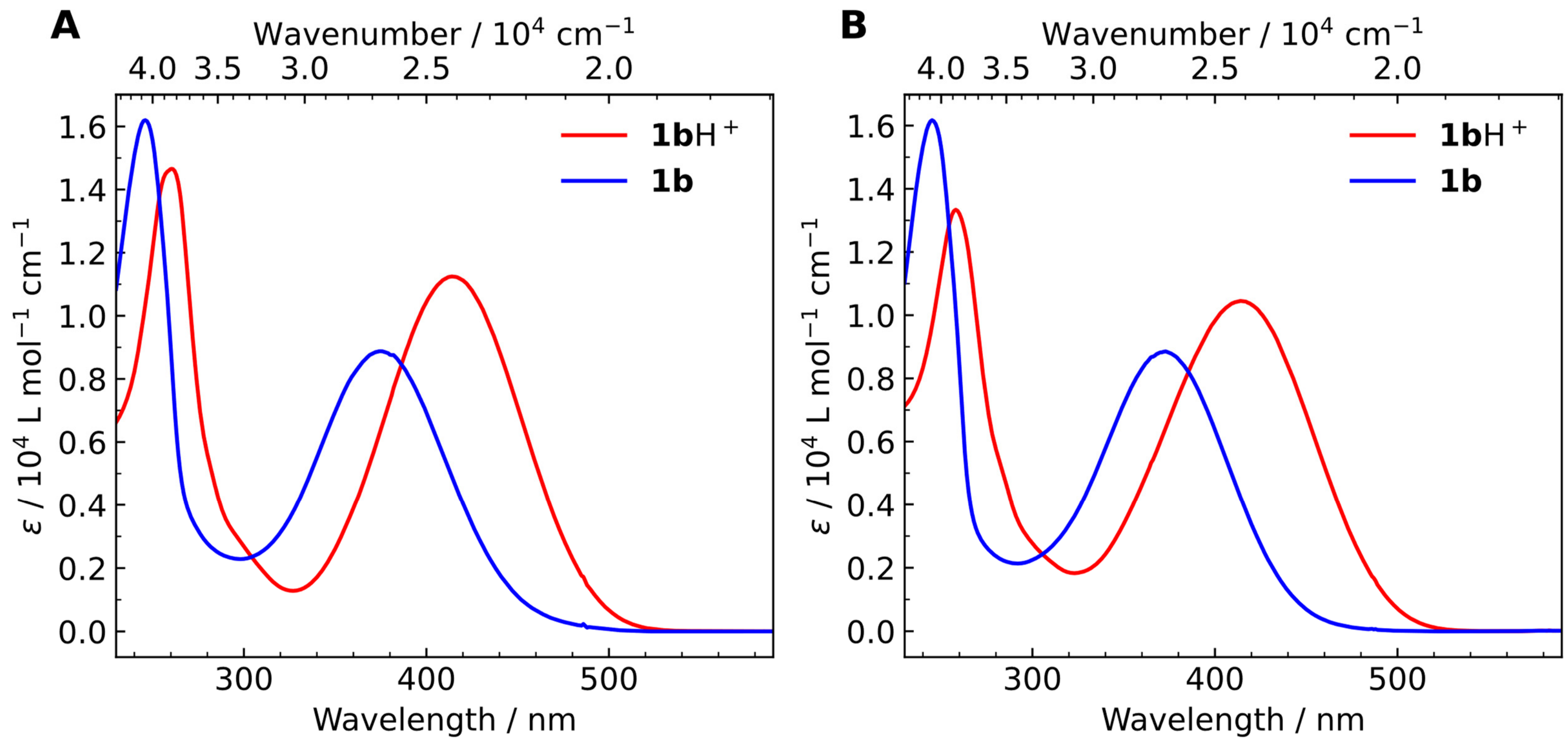


Figure S51. pK_a titration of **1c** in aqueous KCl (I = 0.1 M, 10% MeOH). (**A**) Absorption spectra at different pH values. (**B**) Absorbances at 335 nm (blue circles) and 425 nm (red circles) with fitted curves (solid lines) as obtained from global fitting. The best value of pK_a is plotted as a black dashed vertical line.

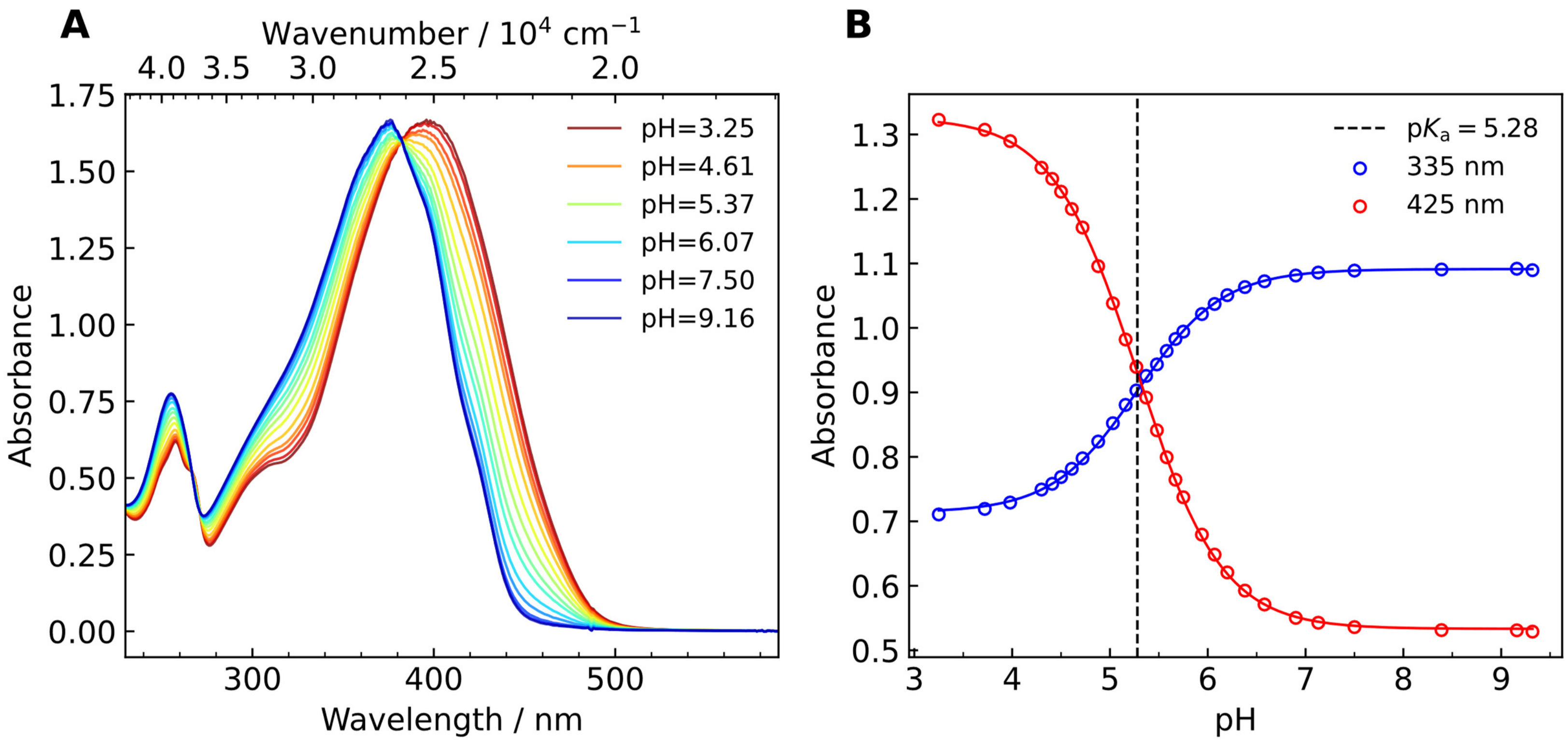


Figure S52. Molar absorption coefficients of **1c** and its conjugate acid in methanol.

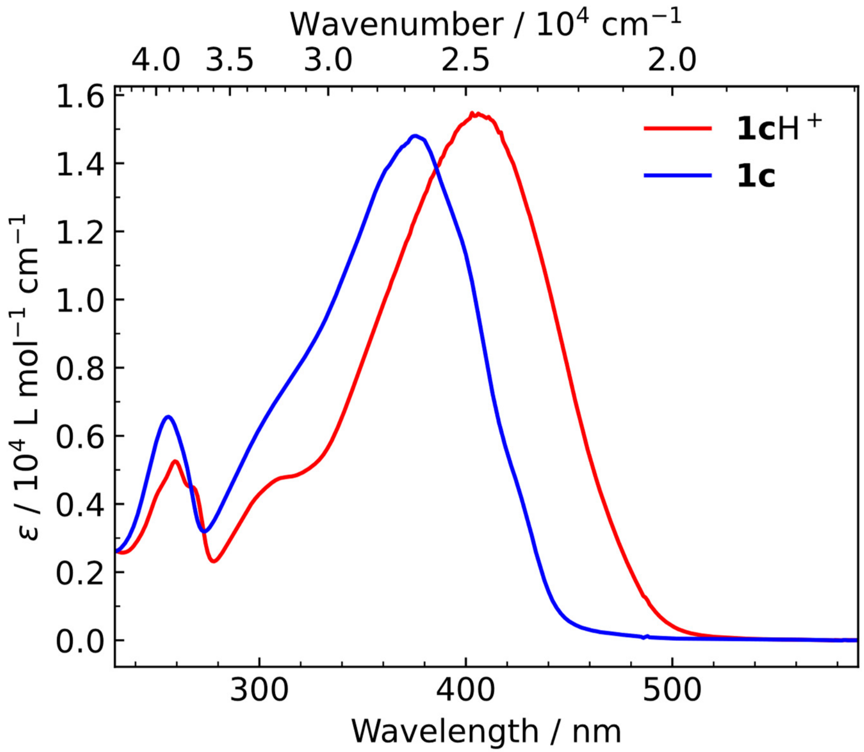


Figure S53. (**Left**) Irradiation of **1b**H$^+$ (~170 µM) in methanol with 375 nm LED under argon atmosphere. The gray-shaded area represents the spectrum of the irradiation source. Colorbar is plotted with a lin-log scale (linear until 100 s and then logarithmic). (**Right**) The complementary experiment with **1b**H$^+$ (~1.1 mM) in methanol followed by HPLC (determined in a basic mobile phase). The unusual shift at an elution time of *Z*-**1a** at *t* = 110 min is caused by instability in the HPLC system. The signal from *E*-**1a** is smaller because it is converted to *Z*-**1a** in acidic conditions.

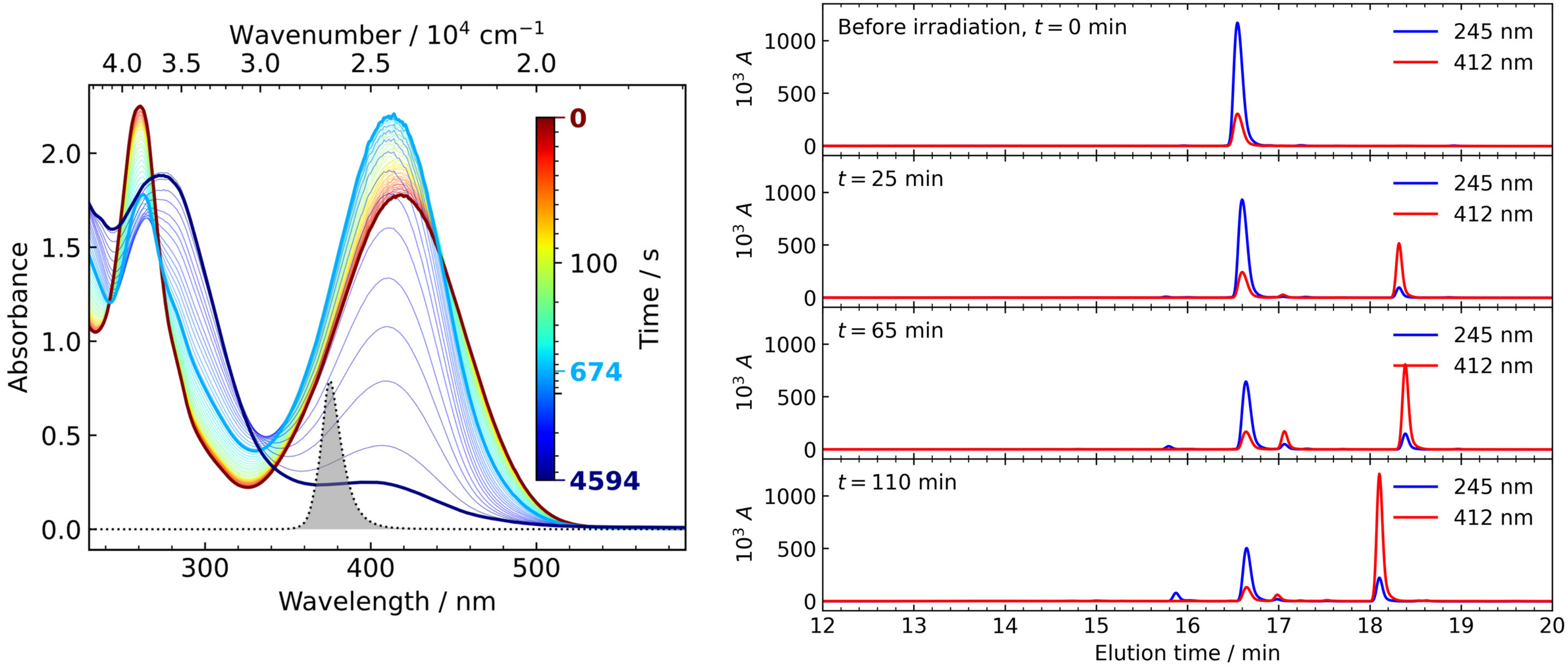
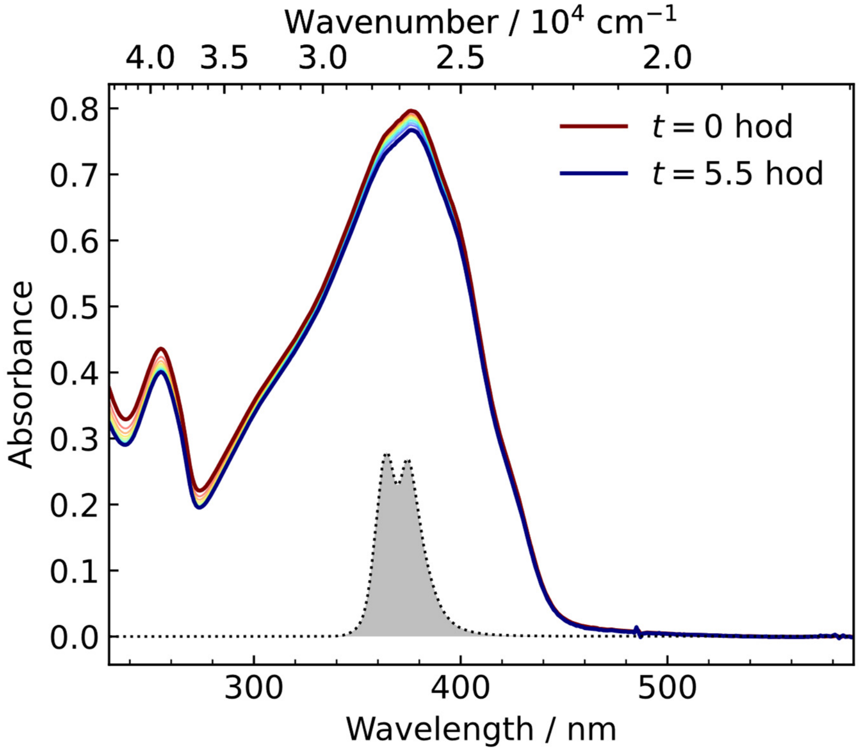


Figure S54. Irradiation of **1c** (~50 μM) in methanol with 370 nm LED under air. The gray-shaded area represents the spectrum of the irradiation source.



Photokinetic Model and Data Analysis

The general photokinetic model excluding thermal processes can be formulated as a compartmental model. Concentration changes of the individual compartments can be described by the following matrix differential equation:

$$\frac{\mathrm{d}\boldsymbol{c}(t)}{\mathrm{d}t} = \frac{1}{V}\boldsymbol{\Phi}\boldsymbol{q}_{\mathrm{m}}(t) \tag{S1}$$

where $\boldsymbol{c}(t) = [c_1(t) \ldots c_n(t)]^{\mathrm{T}}$ is a column vector that contains actual concentrations of individual compartments ($[c_i]$ = mol L^{-1}); V ($[V]$ = L) is the total sample volume in a cuvette; and molar photon flux $\boldsymbol{q}_{\mathrm{m}}(t) = \left[q_{1,\mathrm{m}}(t) \ldots q_{n,\mathrm{m}}(t)\right]^{\mathrm{T}}$ is a column vector that contains the total amount of absorbed photons per unit time ($\left[q_{i,\mathrm{m}}\right]$ = einstein s^{-1}) for each compartment; that is the driving force of all photoreactions. Finally, $\boldsymbol{\Phi}$ ($n \times n$) is the transfer matrix with n being the number of compartments that describes the model. The main diagonal of $\boldsymbol{\Phi}$ contains the total decay quantum yields of individual compartments, and the off-diagonal elements correspond to quantum yields of transformations between compartments.

In general, quantum yields depend on the irradiation wavelength. Also, if non-monochromatic light is used for irradiation, the amount of absorbed light depends on the wavelength, and the matrix product needs to be integrated over wavelengths:[1]

$$\frac{\mathrm{d}\boldsymbol{c}(t)}{\mathrm{d}t} = \frac{1}{V}\int \boldsymbol{\Phi}(\lambda)\boldsymbol{I}_{\mathrm{m}}(\lambda, t)\,\mathrm{d}\lambda \tag{S2}$$

$\boldsymbol{I}_{\mathrm{m}} = \left[I_{1,\mathrm{m}}(\lambda, t) \ldots I_{n,\mathrm{m}}(\lambda, t)\right]^{\mathrm{T}}$ is the molar spectral flux ($\left[I_{i,\mathrm{m}}\right]$ = einstein s^{-1} nm^{-1}) absorbed by each compartment. The determination of the amount of absorbed light is crucial for solving a differential equation (S2). $\boldsymbol{I}_{\mathrm{m}}$ can be calculated from molar absorption coefficients of individual compartments (time- and wavelength-dependences of $\boldsymbol{c}$ and $\boldsymbol{\varepsilon}$, respectively, were omitted for clarity):

$$\boldsymbol{I}_{\mathrm{m}}(\lambda, t) = I_{0,\mathrm{m}}(\lambda)\frac{\boldsymbol{c} \circ \boldsymbol{\varepsilon}}{\boldsymbol{c} \cdot \boldsymbol{\varepsilon}}\left(1 - 10^{-l\boldsymbol{c}\cdot\boldsymbol{\varepsilon}}\right) = I_{0,\mathrm{m}}(\lambda)lF(\lambda, t)\mathrm{diag}(\boldsymbol{\varepsilon})\boldsymbol{c} \tag{S3}$$

where $I_{0,\mathrm{m}}(\lambda)$ is incident spectral flux ($\left[I_{0,\mathrm{m}}\right]$= einstein s^{-1} nm^{-1}); $\boldsymbol{\varepsilon}(\lambda) = [\varepsilon_1(\lambda) \ldots \varepsilon_n(\lambda)]^{\mathrm{T}}$ are molar absorption coefficients of individual compartments; $\boldsymbol{c} \circ \boldsymbol{\varepsilon} = [c_1(t)\varepsilon_1(\lambda) \ldots c_n(t)\varepsilon_n(\lambda)]^{\mathrm{T}}$ denotes a Hadamard product (elementwise multiplication) of concentration and epsilon vectors; l is a length of a cuvette ([l] = cm). Dot product $l\boldsymbol{c}\cdot\boldsymbol{\varepsilon} = A(\lambda, t)$ is just another way how to express the additivity of Beer-Lambert law. Photokinetic factor[2,3] $F(\lambda, t) = \frac{1-10^{-A}}{A}$ can be estimated from experimental data by interpolation, or calculated explicitly from $\boldsymbol{\varepsilon}$ and actual species concentrations which was done in this work. The combination of equations (S2) and (S3) and simplification of the integral to a simple sum leads to equation (S4). The eq (1) of the main article was obtained by setting $l = 1$ cm of eq (S4), because only 1.0 cm quartz cuvettes were used in our measurements.

$$\frac{\mathrm{d}\boldsymbol{c}(t)}{\mathrm{d}t} = \frac{l}{V}\left(\sum_{i=1}^{n_w} I_{0,\mathrm{m}}(\lambda_i)F(\lambda_i,\, t)\boldsymbol{\Phi}(\lambda_i)\mathrm{diag}\big(\boldsymbol{\varepsilon}(\lambda_i)\big)\,\Delta\lambda\right)\boldsymbol{c}(t) \tag{S4}$$

The approximation of the integral is reasonable, because of the following approximations. First, the integral of function $f(\lambda) = I_{0,\mathrm{m}}(\lambda)F(\lambda,\, t)\boldsymbol{\Phi}(\lambda)\mathrm{diag}\big(\boldsymbol{\varepsilon}(\lambda)\big)$ is approximated using the trapezoidal rule:

$$\int f(\lambda)\,\mathrm{d}\lambda \approx \frac{1}{2}\sum_{i=1}^{n_w-1}\big(f(\lambda_i) + f(\lambda_{i+1})\big)\Delta\lambda_i \tag{S5}$$

Here, n_w is the total number of wavelength points acquired in the experiment and $\Delta\lambda_i = \lambda_{i+1} - \lambda_i$ is finite difference in wavelength. As data were acquired by uniform spacing ($\Delta\lambda_i = 1$ nm), $\Delta\lambda$ can be factored out from summation:

$$\frac{\Delta\lambda}{2}\sum_{i=1}^{n_w-1}\big(f(\lambda_i) + f(\lambda_{i+1})\big) = \frac{\Delta\lambda}{2}\left(f(\lambda_1) + 2\sum_{i=2}^{n_w-1}\big(f(\lambda_i)\big) + f\big(\lambda_{n_w}\big)\right) \tag{S6}$$

As spectral photon flux $I_{0,\mathrm{m}}(\lambda)$ is usually centered somewhere in the wavelength range (230 nm to 600 nm) and goes to zero at the beginning and the end of this range, therefore the terms $f(\lambda_1)$ and $f\big(\lambda_{n_w}\big)$ are small and can be neglected:

$$\int f(\lambda)\,\mathrm{d}\lambda \approx \Delta\lambda \sum_{i=1}^{n_w} f(\lambda_i)$$

(S7)

The initial value problem (IVP) of an eq (S4) does not have an analytical solution for an explicit photokinetic factor and needs to be integrated numerically. The analytical solution is possible for known (experimental) photokinetic factors but in this work, we used numerical integration with the use of explicit photokinetic factor. Numerical integration is more precise if experimental photokinetic factor cannot be determined frequently and, in this case, the use of measured experimental photokinetic factor would lead to higher error as it need to be integrated in analytical solution. However, for frequently determined photokinetic factor, the computational speed of the analytical solution would be an advantage.

Multivariate curve resolution (MCR) methods are based on bilinear Beer-Lambert law and tries to solve the mixture analysis problem:[4]

$$\boldsymbol{D} = \boldsymbol{C}\boldsymbol{S}^{\mathrm{T}} + \boldsymbol{E}$$

(S8)

The observed data matrix $\boldsymbol{D}$ $(n_t \times n_w)$ can be decomposed into concentration profiles $\boldsymbol{C}$ $(n_t \times n)$ and pure spectra $\boldsymbol{S}$ $(n_w \times n)$ with n_t being the number of time points, n_w the number of wavelength points acquired in the experiment and n is number of species (compartments). The residual matrix $\boldsymbol{E}$ $(n_t \times n_w)$ contains the error unexplained by the bilinear model (noise). Without any information about the system, the decomposition of the data $\boldsymbol{D}$ into concentration profiles and pure spectra is ambiguous as the infinite number of matrices $\boldsymbol{C}$ and $\boldsymbol{S}$ would satisfy eq (S8). This can be represented with the following equation:

$$\boldsymbol{D} \cong \boldsymbol{C}\boldsymbol{T}^{-1}\boldsymbol{T}\boldsymbol{S}^{\mathrm{T}} = (\boldsymbol{C}\boldsymbol{T}^{-1})(\boldsymbol{T}\boldsymbol{S}^{\mathrm{T}}) = \boldsymbol{C}'\boldsymbol{S}'^{\mathrm{T}}$$

(S9)

Where $\boldsymbol{T}$ is a non-singular matrix that rotates and stretches matrices $\boldsymbol{C}$ and $\boldsymbol{S}^{\mathrm{T}}$ to a new solution $\boldsymbol{C}' = \boldsymbol{C}\boldsymbol{T}^{-1}$ and $\boldsymbol{S}'^{\mathrm{T}} = \boldsymbol{T}\boldsymbol{S}^{\mathrm{T}}$. The inability to obtain unique solution is then paraphrased as *rotational ambiguity*.[4,5] The soft and hard constraints aim to reduce or eliminate the rotational ambiguity imposed by the bilinear model. The idea is to take all know information about the system and use it to solve the mixture analysis problem. The soft constraints include, for example, non-negativity of spectra and/or concentration profiles, closure (sum of individual concentrations is constant at each time point), known spectra, etc. Hard constraints involve the kinetic model applied to some or all of the concentration profiles in matrix $\boldsymbol{C}$. Another approach to reduce the rotation ambiguity is combining multiple experiments:

$$\underbrace{\begin{pmatrix} \boldsymbol{D}_1 \\ \vdots \\ \boldsymbol{D}_p \end{pmatrix}}_{\boldsymbol{D}} = \underbrace{\begin{pmatrix} \boldsymbol{C}_1 \\ \vdots \\ \boldsymbol{C}_p \end{pmatrix}}_{\boldsymbol{C}} \boldsymbol{S}^{\mathrm{T}} + \underbrace{\begin{pmatrix} \boldsymbol{E}_1 \\ \vdots \\ \boldsymbol{E}_p \end{pmatrix}}_{\boldsymbol{E}} \tag{S10}$$

Augmented data matrix $\boldsymbol{D}$ is formed by concatenation of individual datasets $\boldsymbol{D}_i$ with p being the number of datasets. The multiset analysis was perfectly suited for our system as the spectra are unique and independent on experimental conditions (the temperature and solvent were kept the same), stored in the spectra matrix $\boldsymbol{S}$. However, changing of the irradiation source or initial conditions (starting with different isomers or different concentrations) leads to different concentration profiles $\boldsymbol{C}_i$, and therefore different datasets $\boldsymbol{D}_i$. The photokinetic model was applied to each experiment. The solutions of ordinary differential equations (ODEs) (S4) for all experiments can be written as follow:

$$\boldsymbol{C}^{ode}(\boldsymbol{\theta}, \boldsymbol{S}) = \begin{pmatrix} \boldsymbol{C}_1^{ode}(\boldsymbol{\theta}, \boldsymbol{S}) \\ \vdots \\ \boldsymbol{C}_p^{ode}(\boldsymbol{\theta}, \boldsymbol{S}) \end{pmatrix} \tag{S11}$$

Unknown vector of parameters $\boldsymbol{\theta}$ is determined during the fitting process and contains the unknown quantum yields among other parameters (see main text, *vide infra*). The solution of ordinary differential equations (ODEs) depends on these parameters but also on spectra $\boldsymbol{S}$. Spectra matrix, in this case, equals to the discretized epsilon vector $\boldsymbol{\varepsilon}(\lambda)$, presented in eq (S4) ($(S)_{ij} = \varepsilon_j(\lambda_i)$).

The classical MCR-ALS[4] algorithm was not able to find the global minimum. Therefore, the used fitting method was adapted from Resolving Factor Analysis[6] and MCR-FMIN[7] methods, where the solution of spectra and concentration profiles is always located in the subspace spanned by an appropriate orthogonal basis, usually obtained by singular value decomposition (SVD) or principal component analysis (PCA). In other words, the spectra and concentration profiles are represented as linear combinations of appropriate basis vectors. The low rank representation of augmented data matrix $\boldsymbol{D}$ (eq (S10)) can be formulated by truncated SVD:

$$\boldsymbol{D} \approx \boldsymbol{U}_r \boldsymbol{\Sigma}_r \boldsymbol{V}_r^{\mathrm{T}} = (\boldsymbol{U}_r \boldsymbol{\Sigma}_r \boldsymbol{T}^{-1})(\boldsymbol{T} \boldsymbol{V}_r^{\mathrm{T}}) = \widehat{\boldsymbol{C}} \widehat{\boldsymbol{S}}^{\mathrm{T}} \tag{S12}$$

Similarly to eq (S9), the estimated concentration profiles $\hat{\boldsymbol{C}}$ and spectra $\hat{\boldsymbol{S}}$ are obtained by linear combination of left ($\boldsymbol{U_r}$) and right ($\boldsymbol{V_r^{\mathrm{T}}}$) singular vectors, respectively, of truncated SVD. Entries of $\boldsymbol{T}$ (4×4 matrix because of 4 species and rank 4 truncated SVD) are treated as fitting parameters and so $\boldsymbol{T} = \boldsymbol{T}(\boldsymbol{\theta})$. Matrix of residuals $\boldsymbol{R}$ ($4 + 1 + n_t \times n_w$) with non-negativity constraint of spectra and normalization constraint of *Z*-**1a** (first row of $\hat{\boldsymbol{S}}^{\mathrm{T}}$) is defined as:

$$\boldsymbol{R}(\boldsymbol{\theta}) = \begin{pmatrix} \textit{nonnegativity of spectra} \\ \textit{normalization} \\ \textit{simulated data} - \textit{real data} \end{pmatrix} = \begin{pmatrix} \alpha\, \hat{\boldsymbol{S}}^{\mathrm{T}} \circ \left(\hat{\boldsymbol{S}}^{\mathrm{T}} < \boldsymbol{0}\right) / \max \hat{\boldsymbol{S}}^{\mathrm{T}} \\ \vec{\boldsymbol{1}}\left[\max \hat{\boldsymbol{S}}^{\mathrm{T}}[0,:] - \varepsilon_{\mathrm{Z-\mathbf{Xa}}}(\lambda_{max})\right] \\ \boldsymbol{C}^{ode}\left(\boldsymbol{\theta}, \hat{\boldsymbol{S}}\right)\hat{\boldsymbol{S}}^{\mathrm{T}} - \boldsymbol{D} \end{pmatrix}$$

(S13)

where $\hat{\boldsymbol{S}}^{\mathrm{T}} = \boldsymbol{T}(\boldsymbol{\theta})\boldsymbol{V_r^{\mathrm{T}}}$ and $\circ$ denotes elementwise multiplication (Hadamard product). Parameter α controls the "strenght" of non-negativity constraint of spectra and was setup to $\alpha = 2$. Low values of α allows some spectra to be slightly negative, while higher values enforces strict non-negativity. In contrast to the method published before[8] where the constraints are included in the objective **scalar** function, here, we kept the vectorized form of the residuals so that the gradient-based minimization algorithms can be utilized. The minimization of the sum of squares of residuals with Trust Region Reflective Method gave the optimized parameters:

$$\hat{\boldsymbol{\theta}} = \arg\min_{\boldsymbol{\theta}} \|\boldsymbol{R}(\boldsymbol{\theta})\|_2^2$$

(S14)

Rotational ambiguity is still significant upon application of a hard photokinetic model[8] because the model depends on spectra that are allowed to vary during the fitting routine. However, because we isolated pure isomers, the spectra are known. Purified *E*-**1a** contained 6.8 mol% of *Z*-**1a** and this information was included in the initial conditions for ODEs for experiments that started with *E*-**1a** isomer. The initial absolute concentrations of isomers were calculated by a least-squares from estimated spectra $\hat{\boldsymbol{S}}$ at each iteration and absorption spectrum at time zero (before irradiation started). Spectrum (its ε values) of *Z*-**1a** isomer was not fixed but normalized to the known value determined before. Spectrum of *Z*-**1a** was not fixed as a common sense would suggest because the ε values were determined in different spectrometer. The slight variation in the shape of spectrum would cause erroneous results from fitting. Non-negativity constraint was applied to the spectra matrix as the spectra of individual components cannot be negative. The non-negativity constraint is not strict, so it means that some values can be slightly negative as it is defined in eq (S13). Non-negativity and closure constraints of concentration profiles are ensured by the photokinetic model (quantum yields can vary only from 0 to 1). The results are shown in the following pages.

Figure S55. Low-intensity light irradiation (monochromator) kinetics (**A1-6**) used for fitting with the calculated concentration profiles (**B1-6**). The gray-shaded area represents the molar spectral flux of the irradiation source. Colorbars are plotted with a lin-log scale (linear until 100 s and then logarithmic).

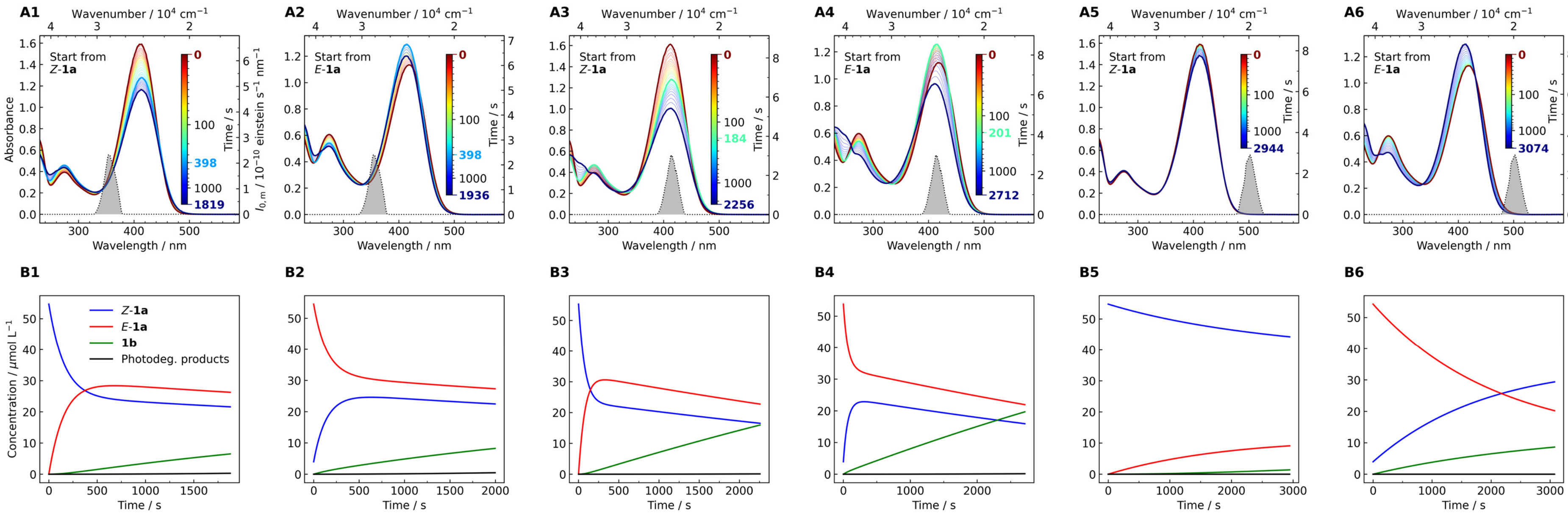


Figure S56. High-intensity light irradiation (LEDs) kinetics (**A1-4**) that were used for fitting with the calculated concentration profiles (**B1-4**). The gray-shaded area represents the molar spectral flux of the irradiation source. Colorbars are plotted with a lin-log scale (linear until 100 s and then logarithmic).

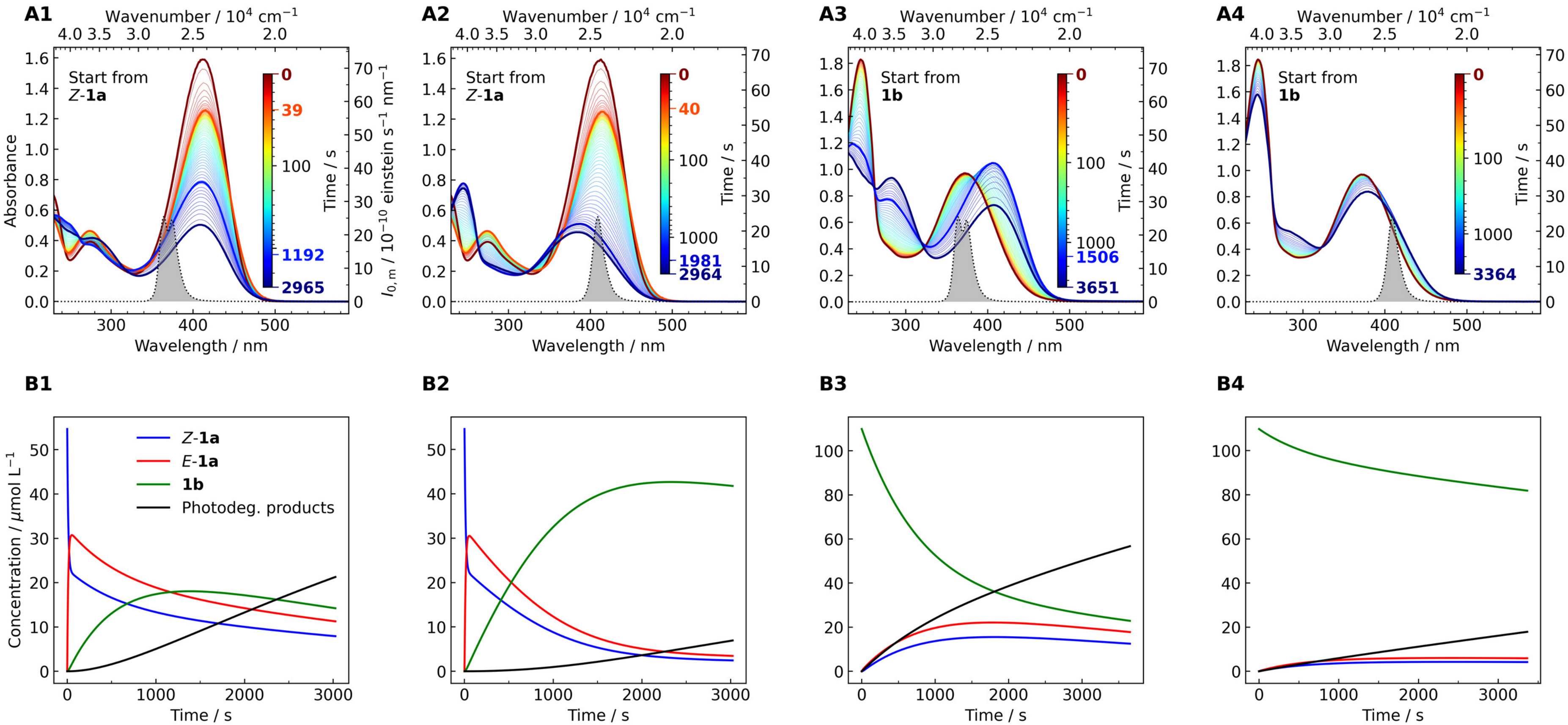


Figure S57. Experimental (solid lines) and fitted traces (dashed black lines) at selected wavelengths for experiments (**A**) Figure S55A1, (**B**) Figure S55A6, (**C**) Figure S56A1 and (**D**) Figure S56A3.

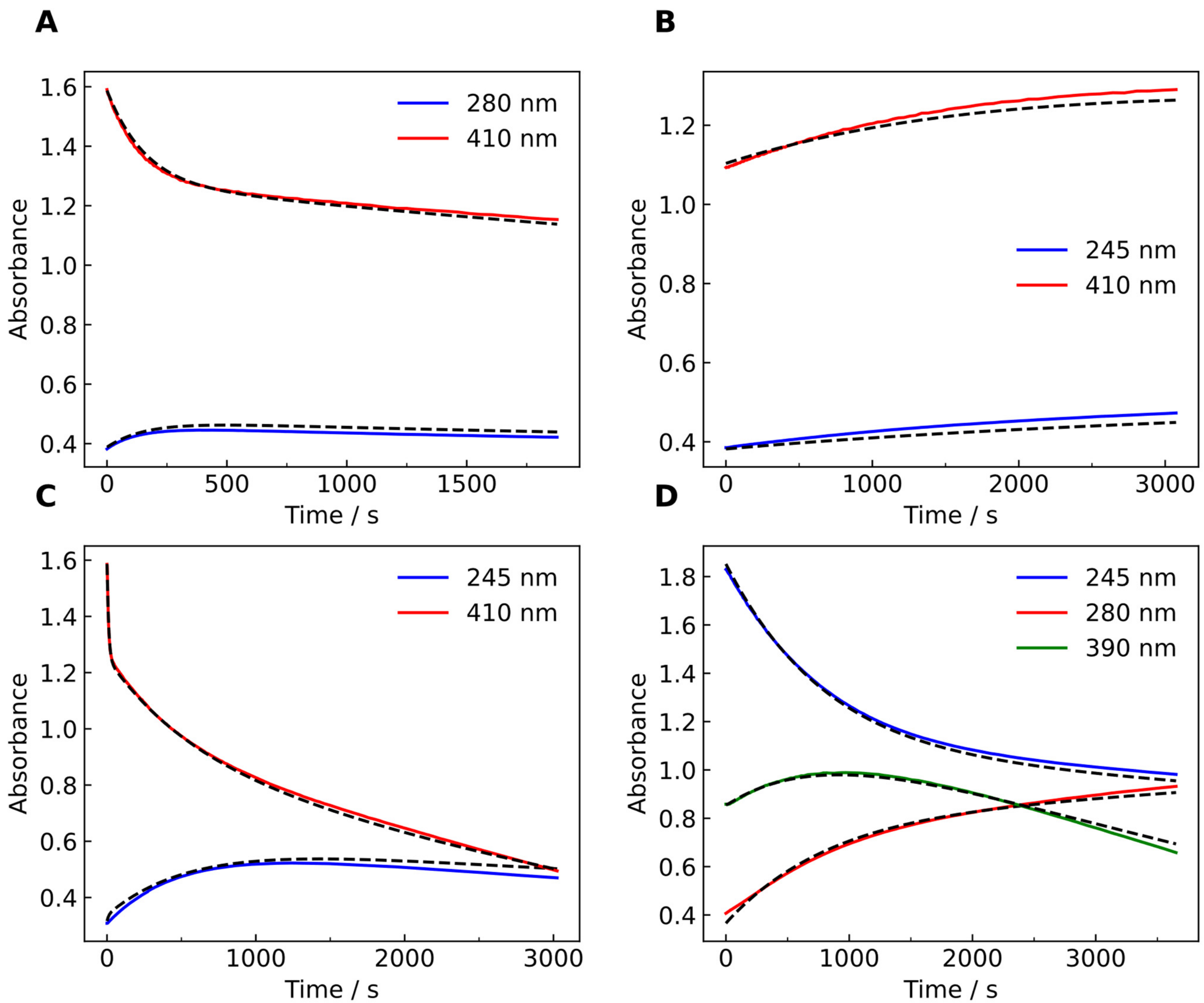
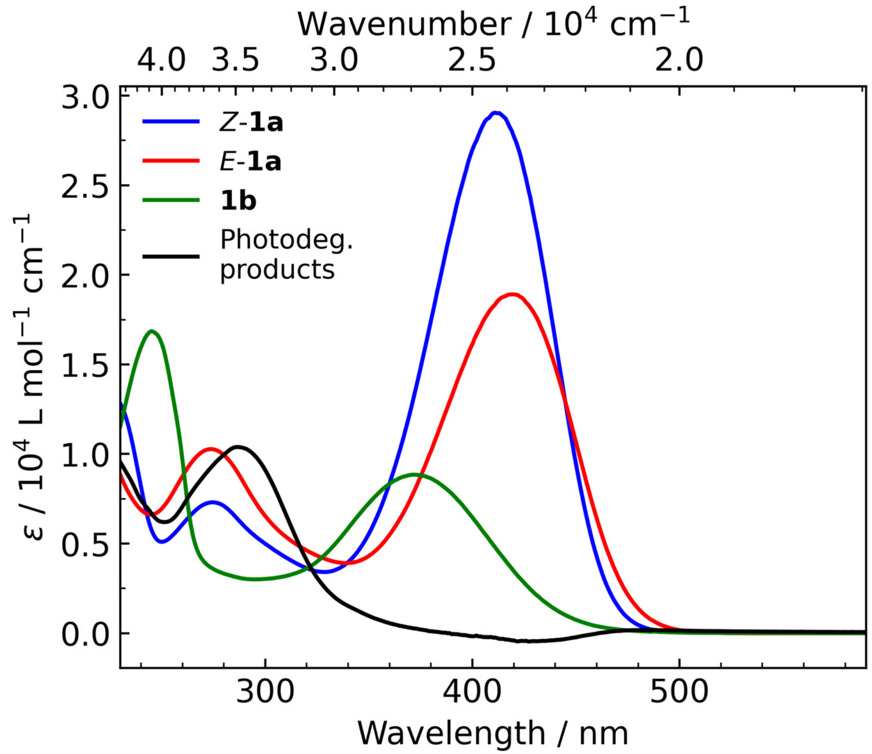


Figure S58. Molar absorption coefficients of all species including spectra of the products of photodegradation obtained form HS-MCR fitting routine.



Photostationary State (PSS)

If the photodegradation of **1b** ($\Phi_{\mathrm{deg}} = 0$) is neglected, the studied system represents a photoequilibrium among 3 species (Scheme 3 of the main article). The photostationary state (PSS) is reached when the concentrations of all components do not change over time:

$$\frac{\mathrm{d}\boldsymbol{c}(t)}{\mathrm{d}t} = \mathbf{0} \tag{S15}$$

The composition of the system thus depends only on wavelength-dependent quantum yields and $\boldsymbol{\varepsilon}$**.** The composition at the PSS can be calculated by the combination of eq (S15) and modified eq (S4) if monochromatic light is used for irradiation. The solution for $\boldsymbol{c}_{\mathrm{PSS}}$ can be expressed as a null space of a matrix (the wavelength dependence on $\boldsymbol{\varepsilon}$ and quantum yields was omitted for clarity):

$$\boldsymbol{c}_{\mathrm{PSS}}(\lambda) \propto \mathrm{Null}[\boldsymbol{\Phi}_{\mathbf{r}}\mathrm{diag}(\boldsymbol{\varepsilon}_{\mathbf{r}})] = \mathrm{Null}\begin{bmatrix} -\Phi_{ZE}\varepsilon_{Z-\mathbf{1a}} & \Phi_{EZ}\varepsilon_{E-\mathbf{1a}} & 0 \\ \Phi_{ZE}\varepsilon_{Z-\mathbf{1a}} & -\Phi_{EZ}\varepsilon_{E-\mathbf{1a}} - \Phi_{\mathrm{c}}\varepsilon_{E-\mathbf{Xa}} & \Phi_{-\mathrm{c}}\varepsilon_{\mathbf{1b}} \\ 0 & \Phi_{\mathrm{c}}\varepsilon_{E-\mathbf{1a}} & -\Phi_{-\mathrm{c}}\varepsilon_{\mathbf{1b}} \end{bmatrix} \tag{S16}$$

where $\boldsymbol{\Phi}_{\mathbf{r}}$ is the [0:3, 0:3] submatrix of $\boldsymbol{\Phi}$ for $\Phi_{\mathrm{deg}} = 0$ and similarly, $\boldsymbol{\varepsilon}_{\mathbf{r}}$ contains only molar absorption coefficients of *Z*-**1a**, *E*-**1a,** and **1b**. The solution of null space and normalization to 1 for each wavelength gives the composition of PSS that is reached by prolonged irradiation (in case that isomers would be infinitely photostable). Figure S59A quantitatively describes our observations (Figure S55 and S56). Irradiation at longer wavelengths (>450 nm) of any isomer results in an exclusive formation of **1b** because it does not absorb at these wavelengths. However, only a mixture of isomers is obtained by irradiation at shorter wavelengths (<400 nm) because of a significant absorbance of **1b**, resulting in cycloreversion. Figure S59B shows the calculated absorption spectra in the PSS for different irradiation wavelengths.

Figure S59. (**A**) The calculated dependence of the population of individual species in the PSS on irradiation wavelength if photobleaching is neglected. (**B**) The calculated absorption spectra in the PSS for irradiation at 360, 400, and 450 nm (total concentration of species is set to 10^{-4} mol L^{-1}).

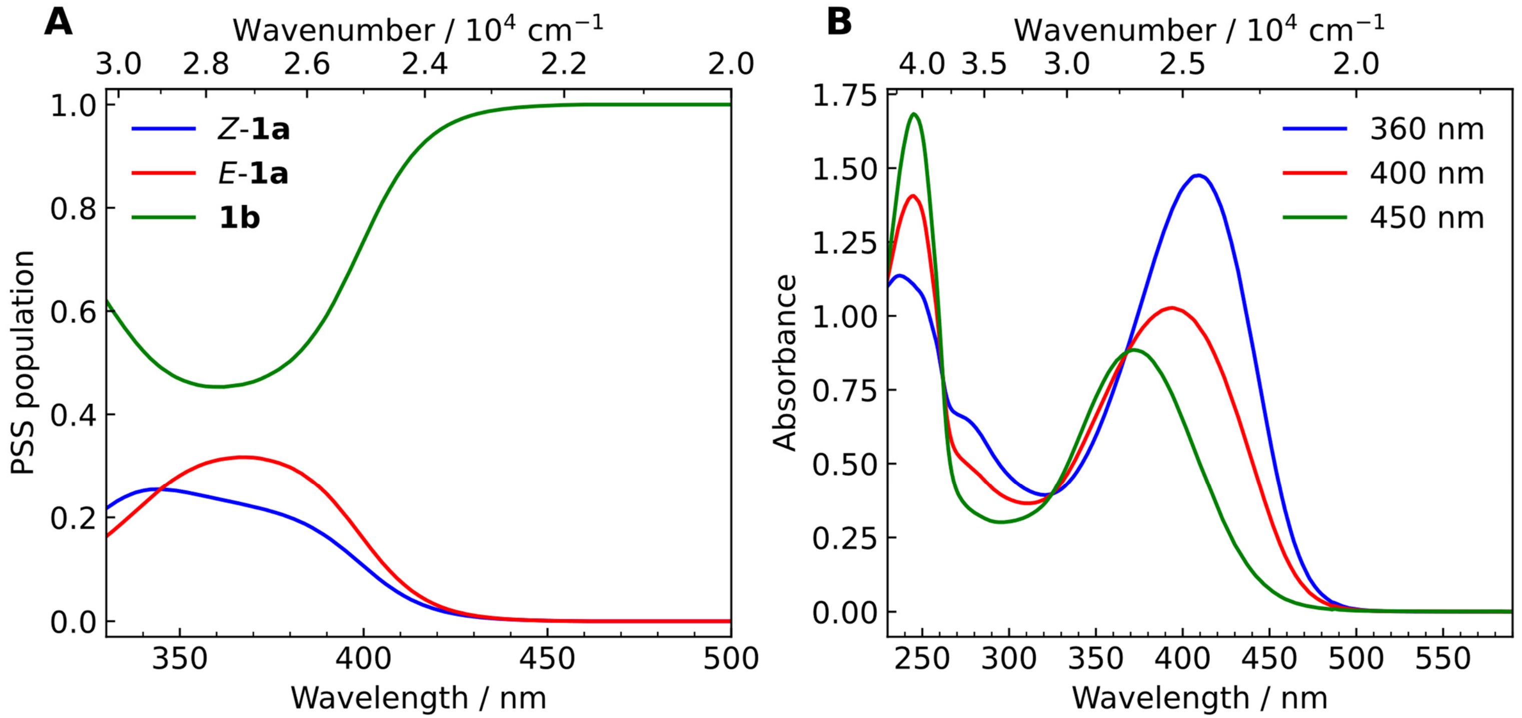


Figure S60. Emission spectra of used LEDs. The area under the curve is normalized to 1 $\left(\int PDF(\lambda)\mathrm{d}\lambda = 1\right)$. *PDF* = Probability density function.

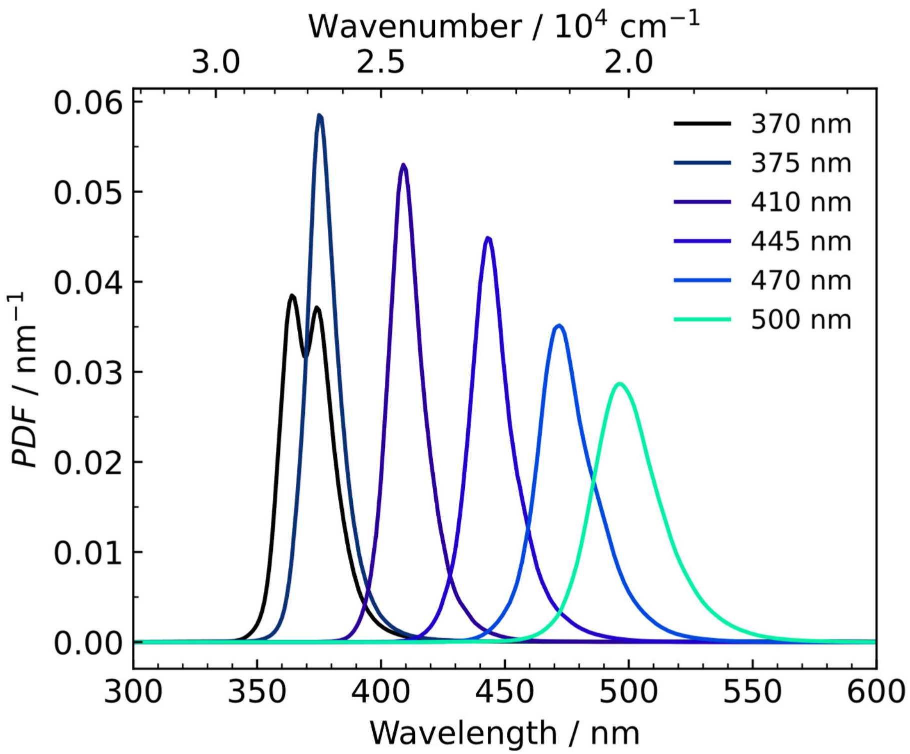


Figure S61. The transmittance of a filter used in the preparation of *E*-**1a**.

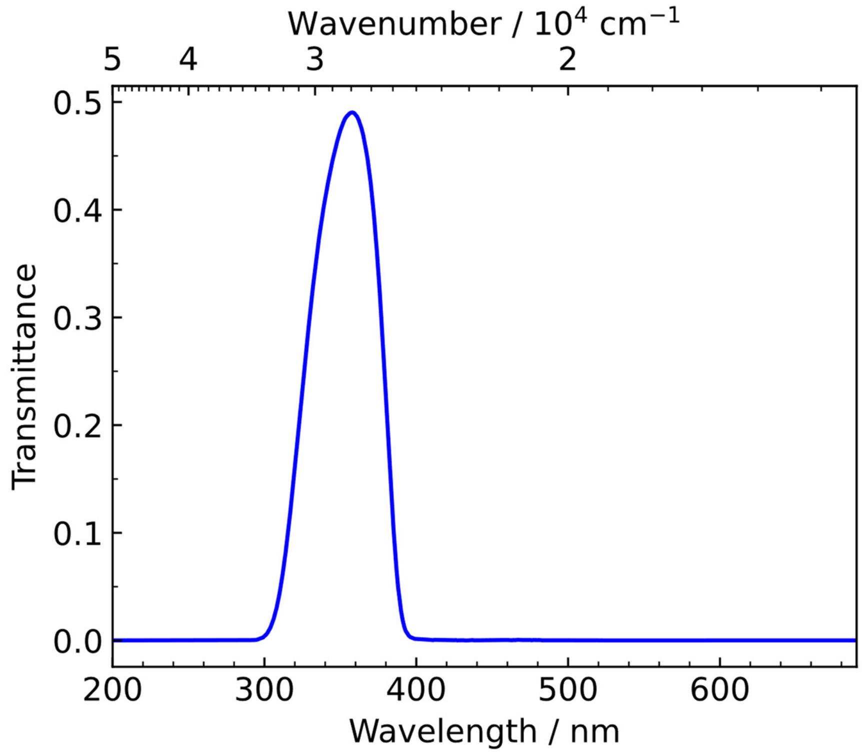


Figure S62. A custom-made 3D-printed LED reactor (two plug-in LED modules, 14 low-power LEDs per module, an integrated cooling fan and a stirring pad with adjustable speed) used for simultaneous irradiation and UV-vis spectroscopy measurements of the samples in 1.0 cm cuvettes.

Figure S63. Experimental setup for determination of quantum yields using the 450 W Xe(Hg) lamp equipped with a monochromator.

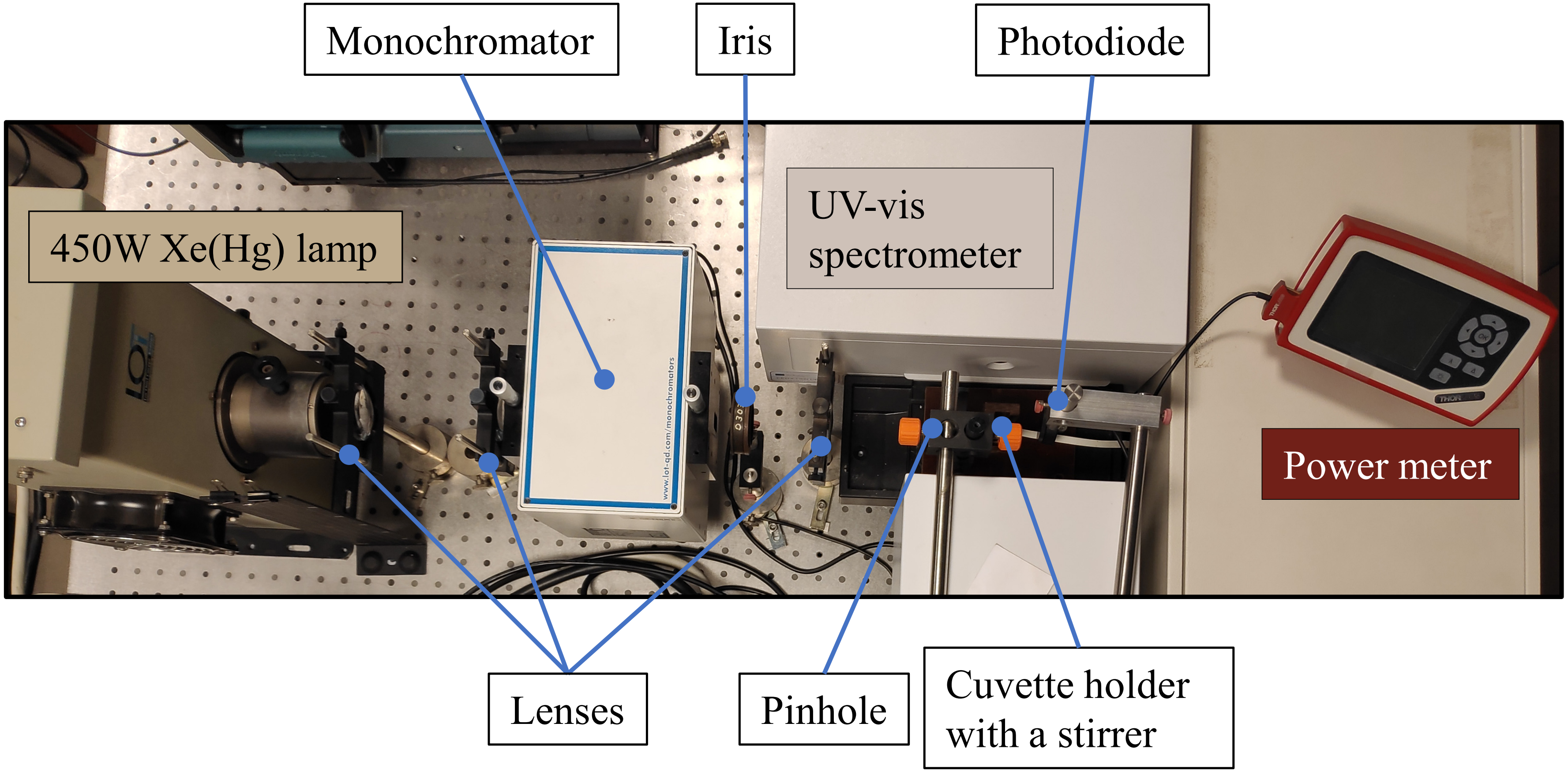


Figure S64. Viability of U2OS (**A**), HepaRG (**B**), and HepG2 (**C**) cell lines exposed to Bilirubin, *Z*-**1a**, *E*-**1a**, and **1b** (*p<0.05, #p<0.001).

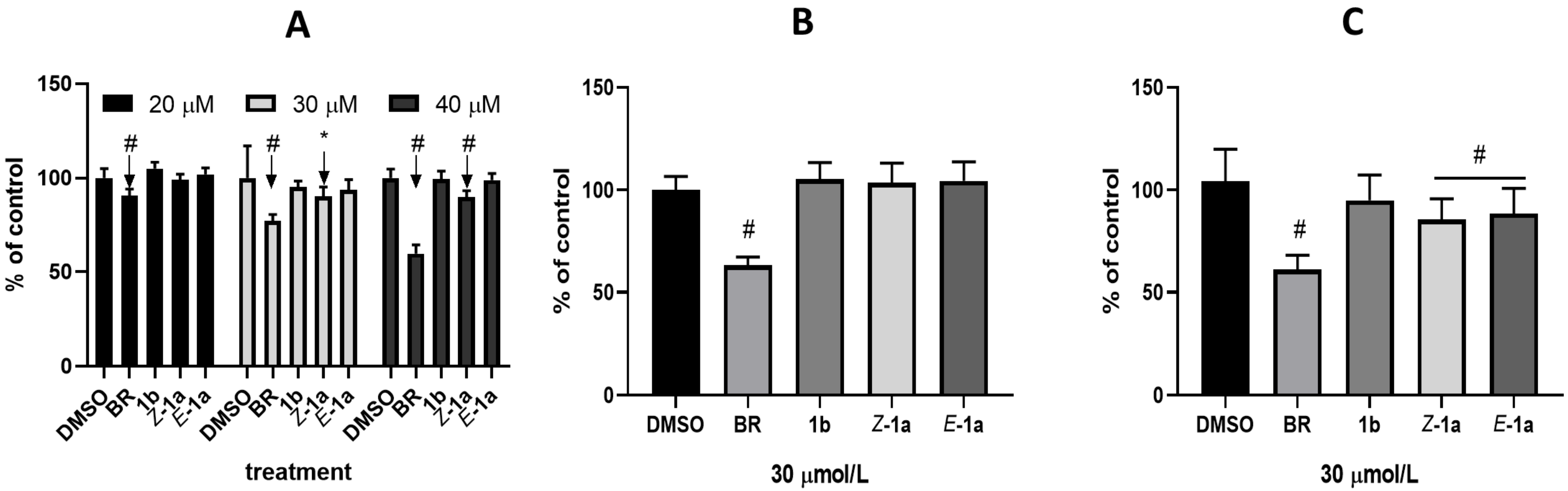


Figure S65. The effects of Bilirubin, *Z*-**1a**, *E*-**1a**, and **1b** on (**A**) superoxide production in U2OS cells and (**B**) peroxyl radical scavenging capacity (#p<0.001; *p<0.05; **p<0.01; AOX = peroxyl radical scavenging capacity).

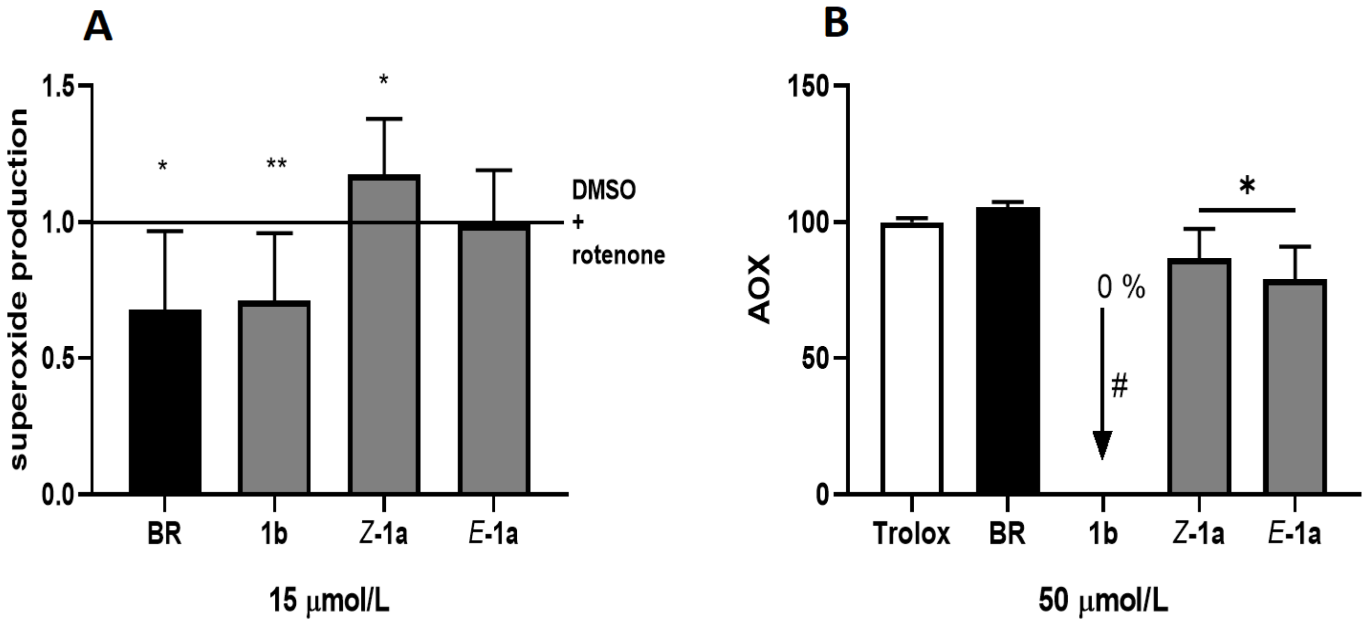
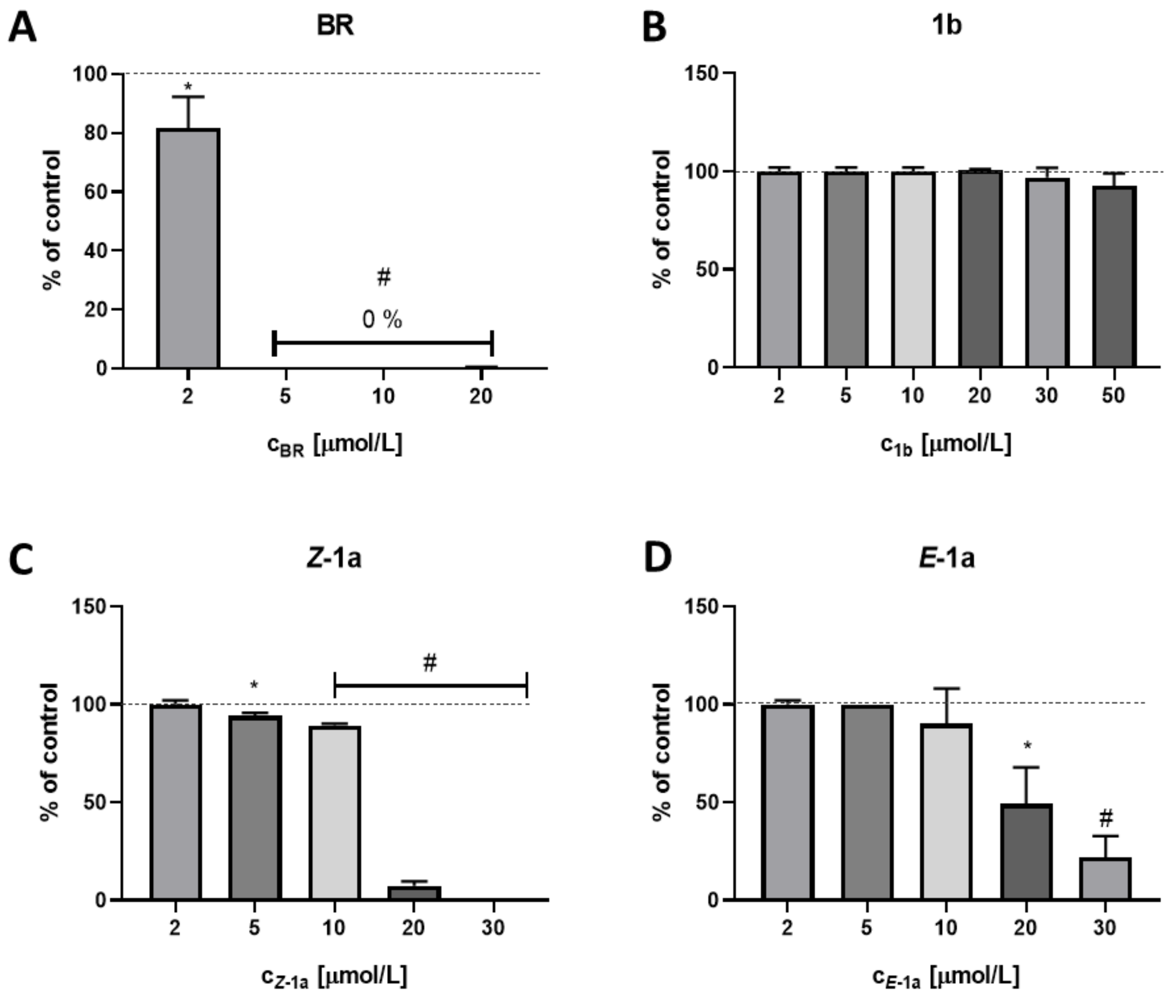


Figure S66. The effects of (**A**) Bilirubin, (**B**) **1b**, (**C**) *Z*-**1a**, and (**D**) *E*-**1a** on lipoperoxidation (#p<0.001; *p<0.05).



Simulated UV absorption spectra of 1a conformers

Absorption spectra of **1a** isomers were calculated within the reflection principle approach at the B3LYP/6-31g* level (Figure S67). We used 300 representative geometries, sampled from adiabatic molecular dynamics at the semi-empirical OM3 level[9] with Generalized Langevin equation-based thermostat,[10] keeping the temperature at 300 K. In this way, both the thermal broadening and nuclear quantum effects are taken into account. As we can see for both isomers, *Z* and *E*, the absorption of the *s-trans* conformer tends to exceed the absorptions of the *s-cis* form at higher wavelengths, which implies a larger fraction of the excited *s-trans* conformer. This allows us to explain the wavelength dependence of *E/Z* and *Z/E* isomerization quantum yield from different photoisomerization mechanisms of *s-trans* and *s-cis* conformers. The calculations were performed with Gaussian09 code, version D.01.[11]

Mapping the potential energy surface of 1a

We observe two kinds of conical intersections (points of true degeneracies) connected to photoisomerization, denoted as CI1 and CI2, see Figures S68−S71. The conical intersection CI1 corresponds to rotation around double bond and the *E/Z* and *Z/E* photoisomerization proceeds via this intersection. The CI1 intersection is also connected to the initial structure. On the contrary, the CI2 intersection leads exclusively to a reformation of the initial structure and no photoisomerization is possible. For the *s-cis* structures, both of these CIs are energetically accessible. However, for the *s-trans* form, the photochemistry is dominated only by the CI1 as it follows from our preliminary MD simulations. This leads to the higher photoisomerization quantum yield. All calculations were performed at the CASSCF(2,2)/6-31g* averaged over 2 states, using MOLPRO 2012.1 code.[12,13]

Mechanism of the cyclization for the *s-trans E*-1a#

We mapped the potential energy surface of *s-trans E*-**1a#**, leading to the photocyclization (Figure S72). The structures were again calculated at the CASSCF(2,2)/6-31g* level, averaged over 2 states. The *s-trans E*-**1a#** isomer is the only structure for which we were able to localize the conical intersection leading to cyclization.

Wavelength dependence of 1a cyclization

We calculated the excitation characteristics of the structures in Scheme 7 of the main text to explain the wavelength dependence of the cyclization quantum yield of *E*-**1a** to **1b**. The excitation characteristics were calculated for their minimal structures. The excitation properties were calculated at the B3LYP/aug-cc-pVDZ level, with GD3 dispersion correction.

Table S1. Excitation properties of different *E*-**1a** conformers.

Structure	Wavelength / nm	Oscillator strength
s-cis E-**1a**	425	0.4908
s-trans E-**1a**	409	0.3989
s-cis E-**1a**$^{\#}$	449	0.3424
s-trans E-**1a**$^{\#}$	452	0.1943

Figure S67. Simulated UV absorption spectra of the *s-cis* (blue) and *s-trans* (orange) conformers of *Z*- (**left**) and *E*- (**right**) isomers of **1a**.

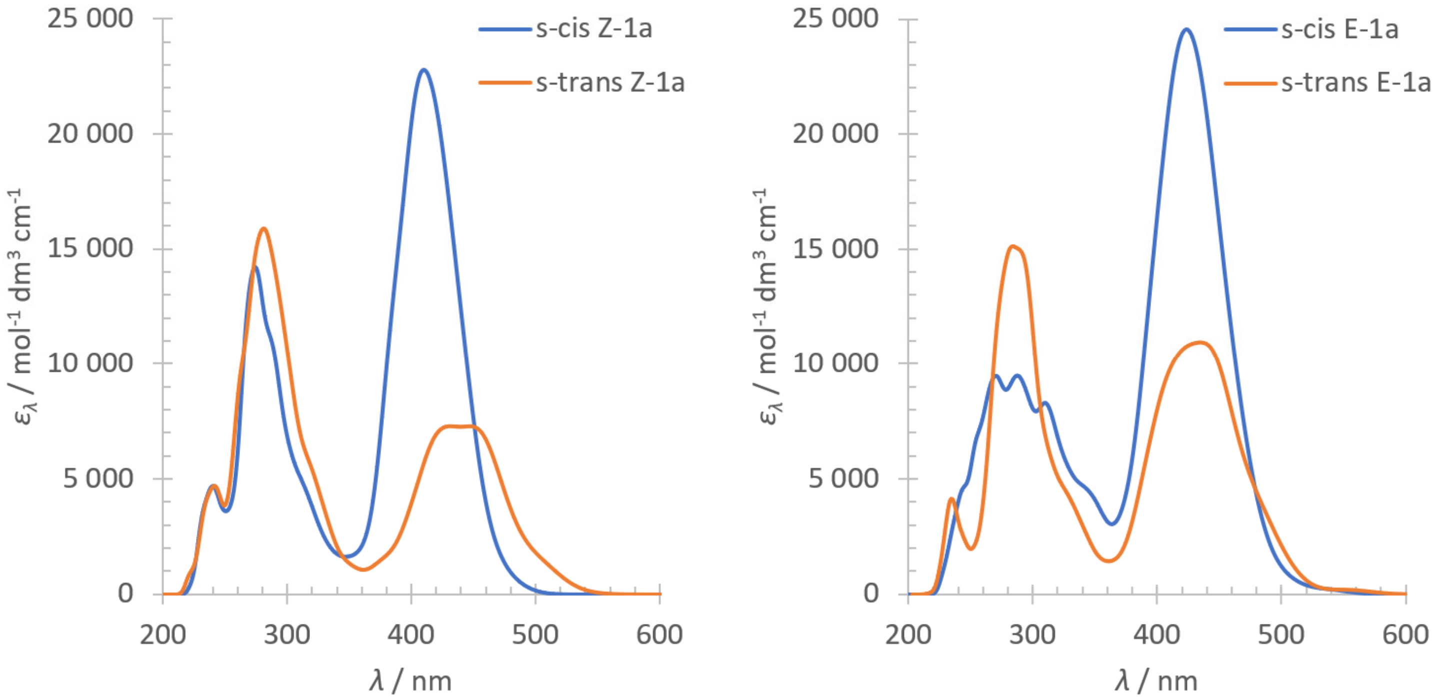


Figure S68. The reaction pathways following the excitation of *s-cis Z*-**1a** and photoisomerization to *s-cis E*-**1a**.

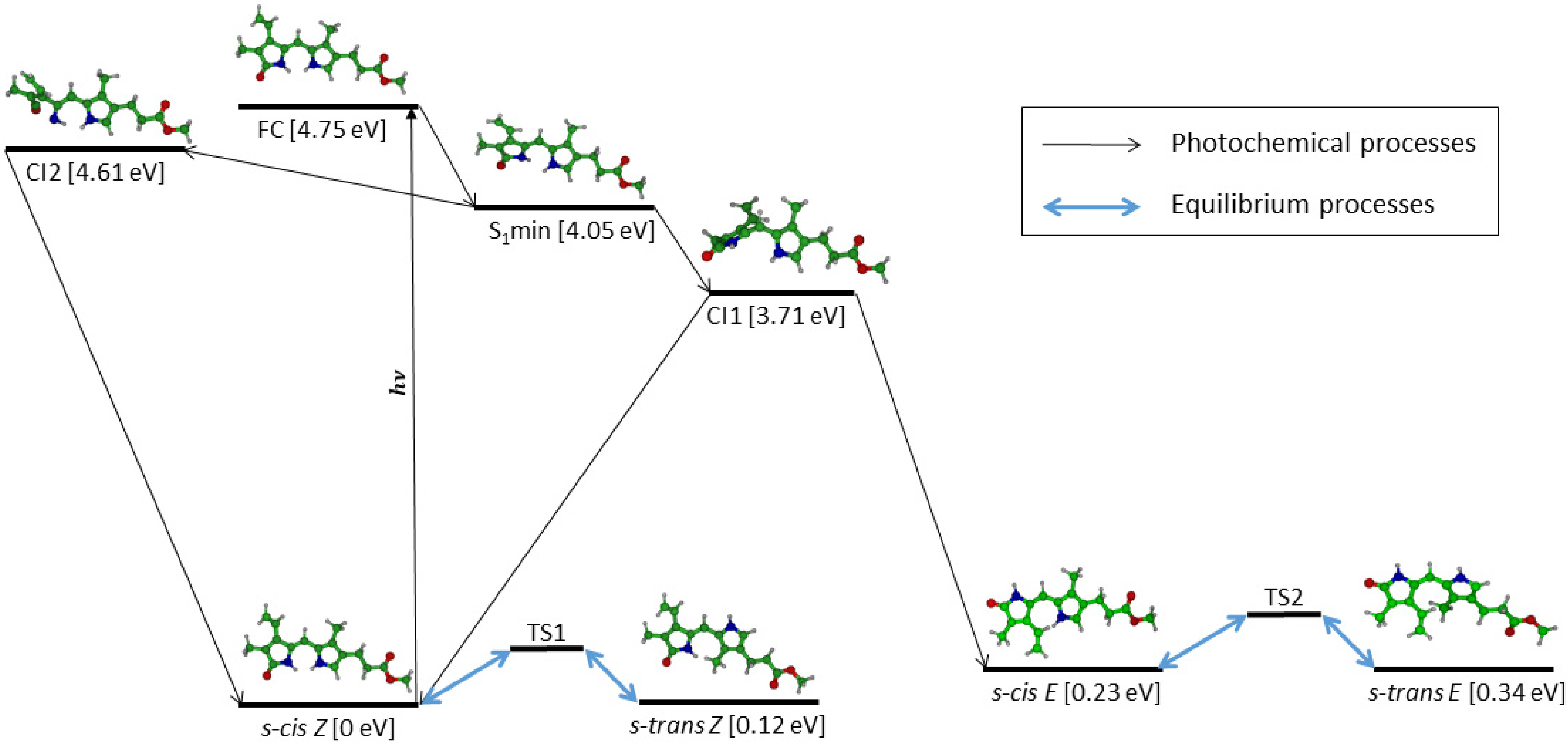


Figure S69. The reaction pathways following the excitation of *s-cis E*-**1a** and photoisomerization to *s-cis Z*-**1a**.

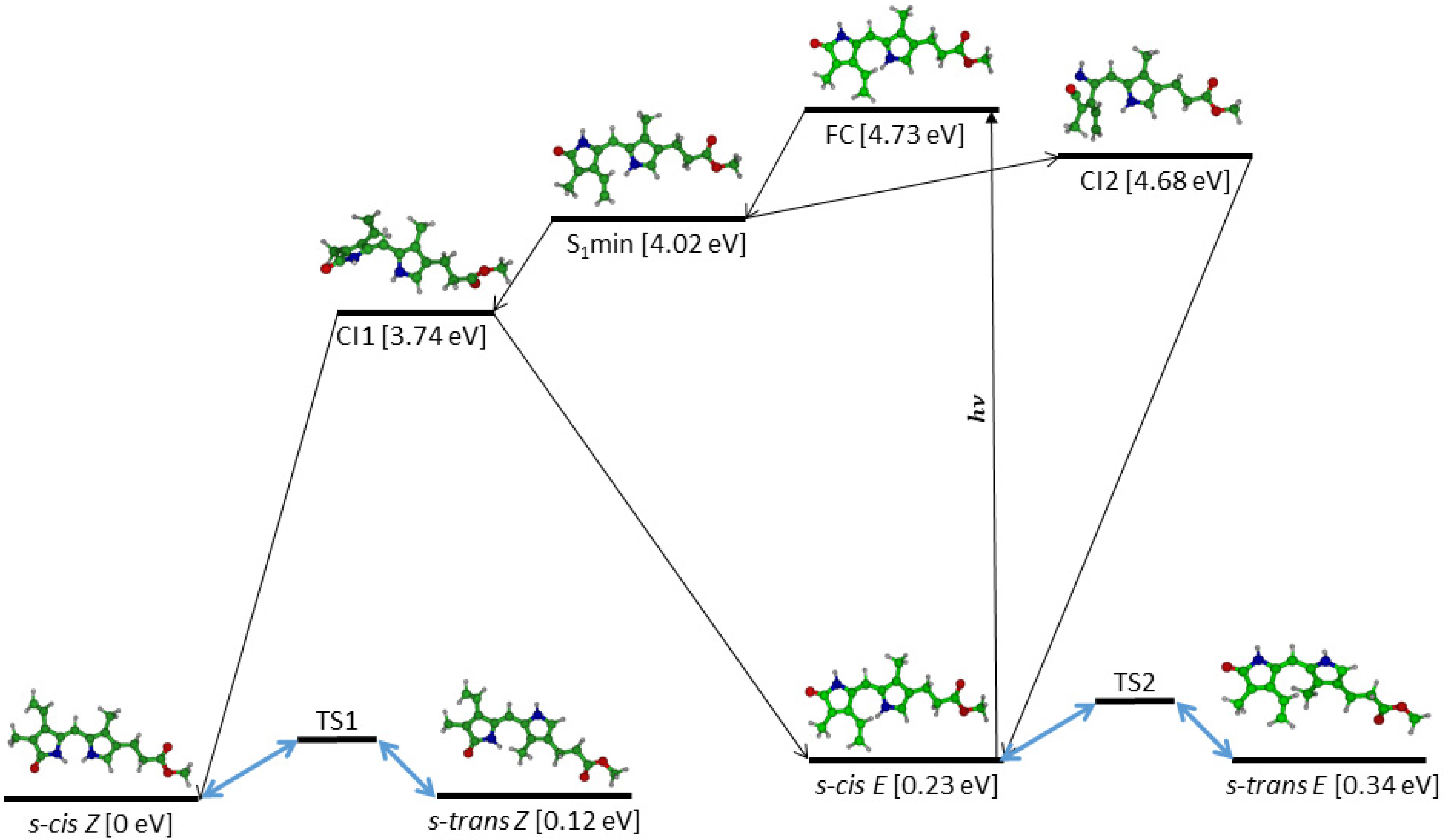


Figure S70. The reaction pathways following the excitation of *s-trans Z*-**1a** and photoisomerization to *s-trans E*-**1a**.

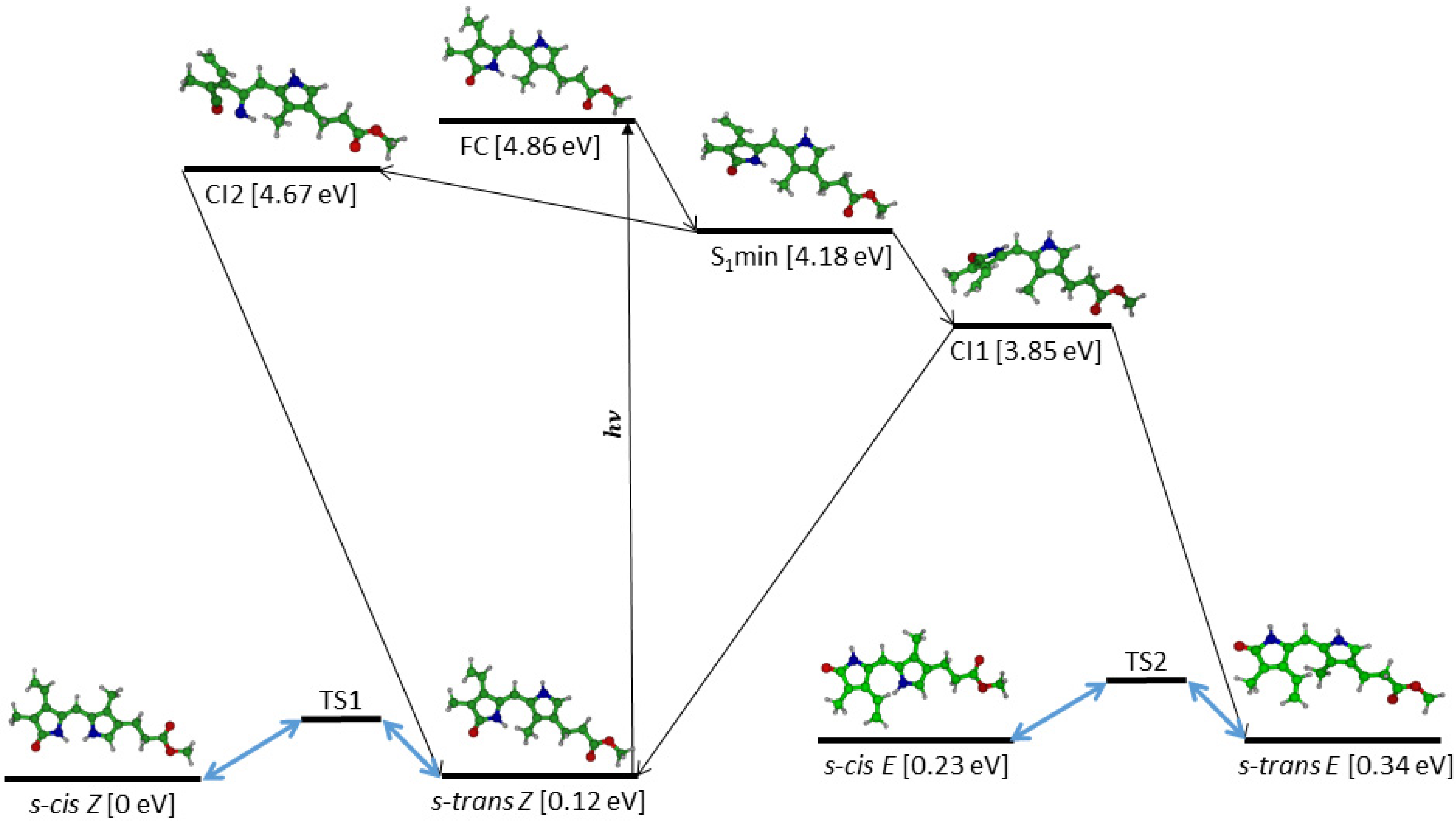


Figure S71. The reaction pathways following the excitation of *s-trans E*-**1a** and photoisomerization to *s-trans Z*-**1a**.

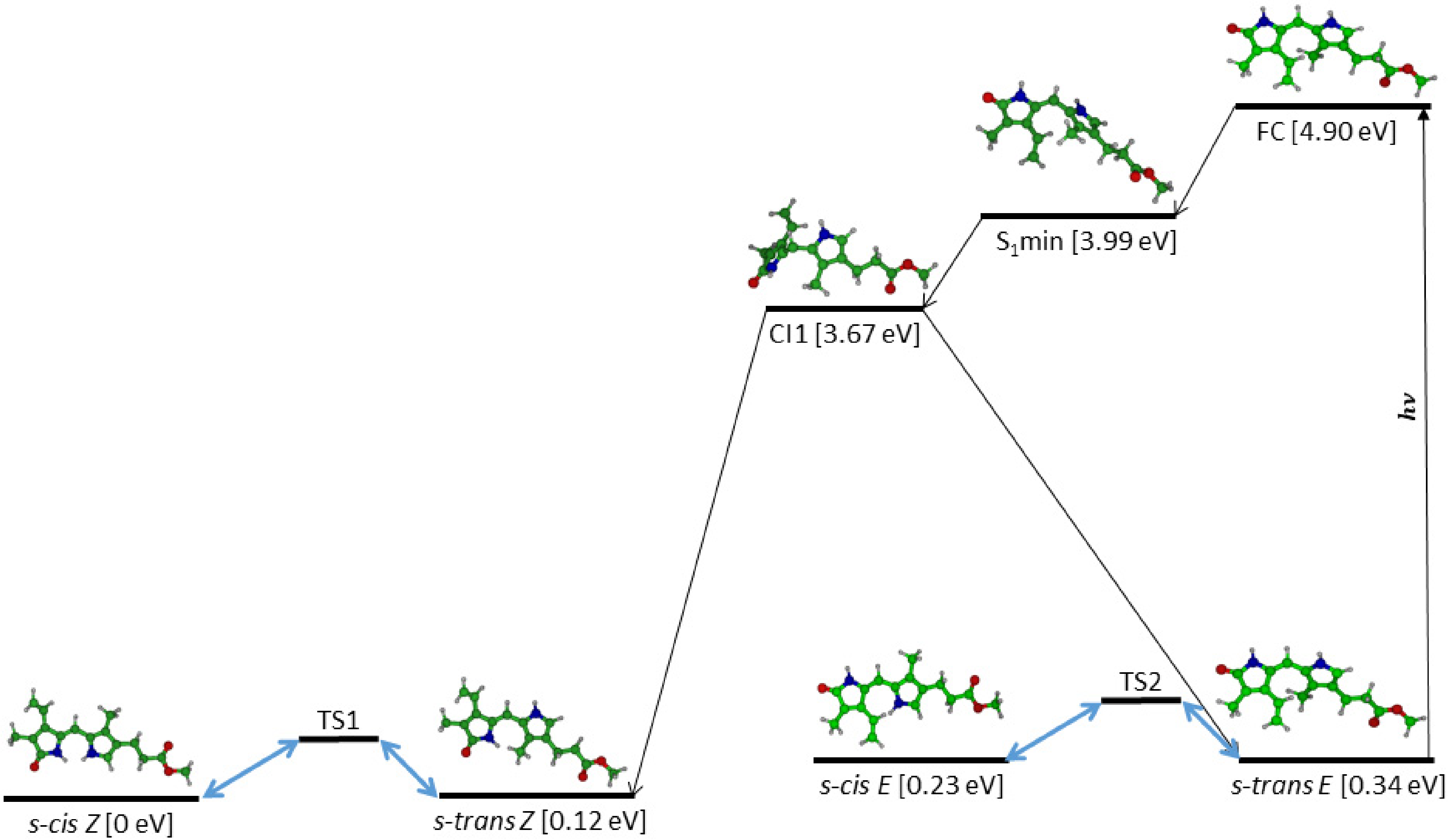
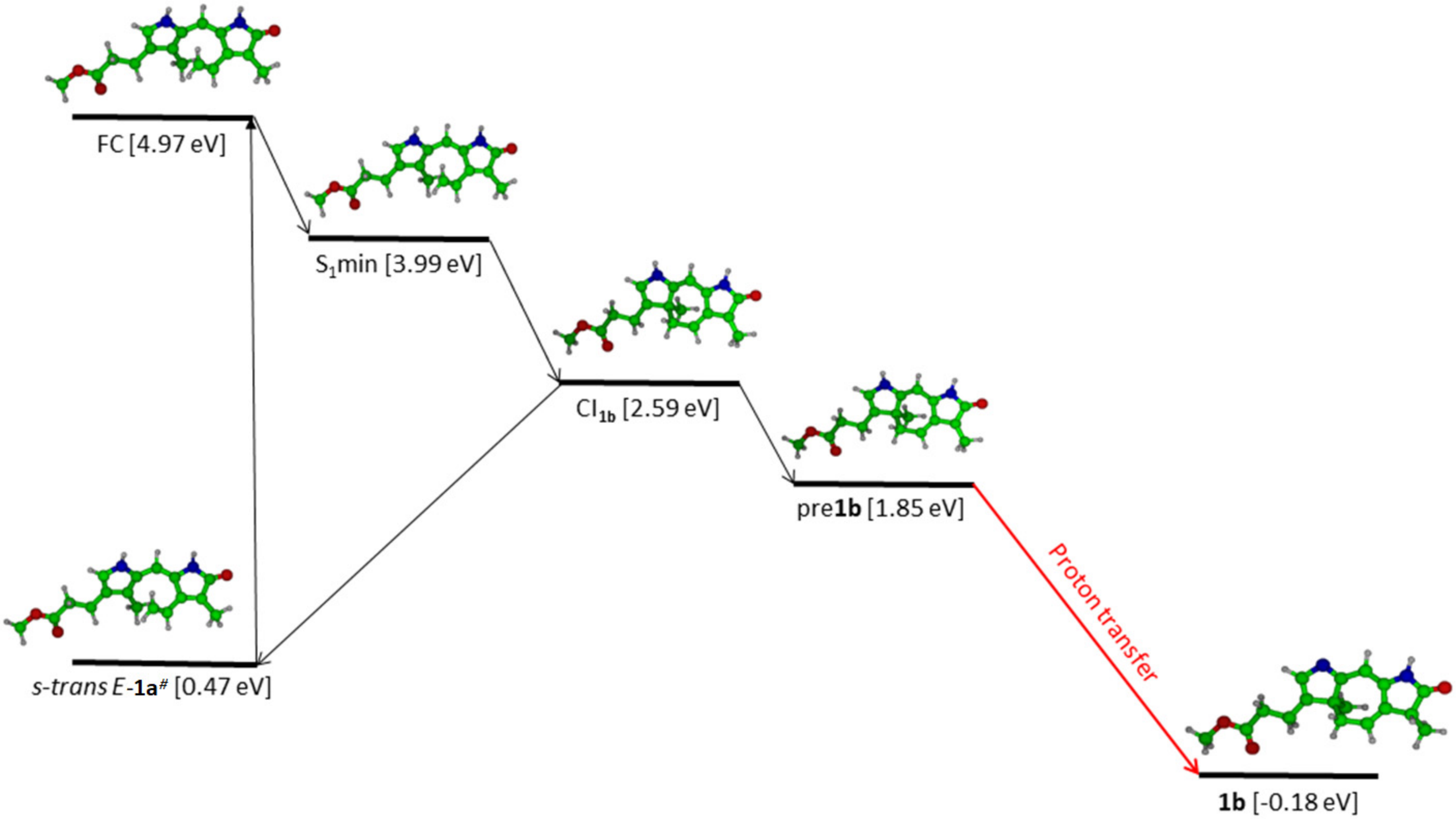


Figure S72. The reaction pathways following the excitation of *s-trans E*-**1a**# and transformation to **1b**.



Cartesian Coordinates of Calculated Structures (in Ansgtrom units)

s-cis Z-**1a:**

N	-0.7182061437	-0.4633376627	-2.6987415078
C	0.6314186794	-0.2032267800	-2.8337615398
C	0.9022484788	-0.0937652675	-4.1690246074
C	-0.3264954060	-0.3284346651	-4.8774060243
C	-1.2746058011	-0.5777417992	-3.9416811746
C	1.5184263471	-0.0710687545	-1.7028621094
C	1.1879636466	0.1928299998	-0.4299426677
N	-0.0896471135	0.4579543713	0.0696557487
C	-0.0384038076	0.7436857862	1.4124232889
C	1.3748124600	0.5143411123	1.8285039829
C	2.0827470314	0.2129505029	0.7352225438
O	-0.9504497545	1.1203660179	2.0864011445
C	1.7831334922	0.6926037319	3.2553539027
C	3.5306894803	-0.0621027600	0.6283950016
C	4.1906262211	-0.9099586721	1.3949810755
C	2.2127056643	0.2529556808	-4.8148640926
C	-0.4778909105	-0.2743235071	-6.3741163577
C	-1.8911647608	-0.5810708920	-6.8562491464
C	-2.0238490137	-0.5258379319	-8.3581490352
O	-1.1447929741	-0.2867592106	-9.1220223107
O	-3.2679361490	-0.7826403368	-8.7386913270
C	-3.5307982484	-0.7634443177	-10.1300731441
H	2.8565841134	0.7906768077	3.3503883585
H	1.3057409411	1.5748761727	3.6656393959
H	1.4608937346	-0.1523864301	3.8573325229
H	4.0578739227	0.4742788511	-0.1425951335
H	5.2470396266	-1.0645482358	1.2712439852
H	3.7025282073	-1.4864226668	2.1599017955
H	2.5625780112	-0.2031472497	-1.9097137311
H	-1.1054133448	-0.8991884593	-1.8933137408
H	-2.3118656229	-0.8177887395	-4.0473392434
H	2.5143461508	-0.5096695444	-5.5273434453
H	2.1500090169	1.1920619447	-5.3582161096
H	3.0084453354	0.3545908810	-4.0867542241
H	-0.1868182634	0.7060301315	-6.7394806633
H	0.2111436249	-0.9735220545	-6.8378918085
H	-2.2101899305	-1.5692548081	-6.5381146180
H	-2.6104312594	0.1176261048	-6.4397829345
H	-4.5798295463	-0.9915495737	-10.2348999111
H	-3.3158739433	0.2113713590	-10.5434587871
H	-2.9329693692	-1.5053080856	-10.6395905652
H	-0.8251558232	0.8259509489	-0.4913367865

S$_1$ min (*s-cis Z*-**1a**):

C	2.0586620205	0.1275881281	0.6978791020
C	1.1478002962	0.3326420195	-0.4569062290
N	-0.0913937661	0.5337835386	0.0350055735
C	-0.0210393660	0.7335469393	1.4634439763
C	1.3373308980	0.4584516385	1.8399396670
C	1.4740561324	0.3567270336	-1.8014545898
C	0.5475392101	0.1763109726	-2.8536033750
N	-0.7403555332	-0.2629620558	-2.7048244983
C	-1.3299332831	-0.3869964600	-3.9233409252
C	-0.4346853093	0.0034652486	-4.9007529634
C	0.7530499216	0.3559837348	-4.2453504454
O	-0.9926314406	1.0651205235	2.0808028951
C	3.3945540221	-0.3604145929	0.5077582573
C	4.4186906211	-0.3518421761	1.3704455447
C	1.7600751798	0.4270563056	3.2727281936
H	3.5742658741	-0.8024565010	-0.4603587373
H	5.3561704839	-0.8047429277	1.1052999198
H	4.3602108986	0.1004821304	2.3416449988
H	2.5068776422	0.4523165864	-2.0668444042
H	-1.1099051528	-0.6280290444	-1.8564703139
H	-2.3400813284	-0.7267766031	-4.0057357176
C	-0.6753184578	0.0605652323	-6.3872862658
C	2.0274091612	0.8540040575	-4.8531849562
H	-0.7701640267	1.0644819167	-0.4677088541
H	2.2259387840	-0.5208866947	3.5292452874
H	2.4784344361	1.2115157550	3.5010870682
H	0.8981160230	0.5717551481	3.9117885434
H	1.8950047917	1.0914007460	-5.9009609711
H	2.3779605007	1.7494789957	-4.3483946786
H	2.8202028987	0.1123415736	-4.7817277205
C	-2.0747169628	-0.3814280416	-6.8026905068
H	-0.5054585133	1.0708970356	-6.7438187568
H	0.0557384543	-0.5585161363	-6.8958338694
C	-2.2805367669	-0.3121020238	-8.2967085043
H	-2.2767329095	-1.4029846348	-6.4942338630
H	-2.8398735309	0.2347399642	-6.3400236895
O	-1.4617230621	0.0329780417	-9.0859228901
O	-3.5049181461	-0.6892672137	-8.6277252903
C	-3.8339388841	-0.6716998275	-10.0071079905
H	-4.8577491119	-1.0045066296	-10.0688260057
H	-3.7386663848	0.3277983452	-10.4055363529
H	-3.1876163140	-1.3390800481	-10.5582136620

CI1 (*s-cis Z*-**1a**):

C	2.0870688217	0.3219737135	0.2934302034
C	0.7976103797	0.1113795118	-0.5307128838
N	-0.1777856843	0.4438196617	0.2673899381
C	0.2639986118	0.8835016267	1.5417050274
C	1.7593635553	0.7827528955	1.4962401555
C	0.5639682234	-0.3572703333	-1.8674395687
C	1.2239981347	0.5975633114	-2.7940373643
N	0.7536235187	1.8940920127	-2.8518093101
C	1.3857484016	2.5737493033	-3.8750453297
C	2.3092242757	1.7529399287	-4.4222428152
C	2.2257014322	0.4909824314	-3.7250288314
C	3.0688687627	-0.7169954994	-4.0199168335
C	3.2850408373	2.0551534559	-5.5270444500
C	3.0677822725	3.4157500102	-6.1795309118
C	4.0363999959	3.6982402792	-7.3003501989
O	3.7648402962	4.8575903066	-7.8887998168
C	4.6021885785	5.2425000965	-8.9623712893
O	-0.4429735153	1.2418894556	2.4096396128
C	2.5817723740	1.1888232714	2.6761471344
C	3.4026607651	0.0076079043	-0.2762828304
C	4.3759776801	-0.5819484676	0.3980309228
O	4.9369273338	2.9977310529	-7.6354009384
H	3.5997812308	1.3981728532	2.3779153924
H	2.1551116484	2.0687291882	3.1421590070
H	2.5961528700	0.4004521280	3.4226994123
H	3.5317496426	0.2645701730	-1.3099922025
H	5.3201820002	-0.7901209723	-0.0702434751
H	4.2643249925	-0.8991662846	1.4192183915
H	1.1030181102	-1.3058209413	-1.9216214441
H	-0.1839848360	2.0888916389	-2.5860705808
H	1.1325721549	3.5907695475	-4.0908571951
H	2.8320911215	-1.1554969320	-4.9873325867
H	4.1311753697	-0.4794095264	-4.0348649511
H	2.9186508640	-1.4902827011	-3.2746424039
H	4.3033604899	2.0017761951	-5.1518611038
H	3.2178163049	1.2847682372	-6.2893498201
H	2.0633324373	3.5008797376	-6.5818702103
H	3.1710482903	4.2194554433	-5.4560356851
H	4.2246400980	6.1932629602	-9.3052720110
H	5.6254603333	5.3439391934	-8.6300834229
H	4.5589106367	4.5134141528	-9.7587715309
H	-1.1274008105	0.3600739804	-0.0340062022

<u>CI2 (*s-cis Z*-**1a**):</u>

C	-1.1275896157	-0.5651617376	-4.1480340361
N	-0.6456226443	-0.5527410287	-2.8716175250
C	0.4620928757	0.2552516133	-2.8048722079
C	0.6569405236	0.7879655578	-4.0595838555
C	-0.3653272034	0.2645915350	-4.9121955250
C	1.2405586181	0.4519441442	-1.6107801201
C	0.8534295494	0.1274445512	-0.3204577510
C	1.9198926828	0.0600302577	0.7405906545
C	3.0603635871	-0.8020877204	0.5503910712
C	4.2510749457	-0.7481526502	1.1519612099
N	-0.3243352751	-0.0856582513	0.2083208304
C	1.6280059791	0.8800532907	1.8136411471
C	0.3798148013	1.4807313104	1.7853432917
O	-0.4670670812	2.2042546043	1.9924145313
C	2.3983856668	1.0690777348	3.1064747480
H	2.9067008934	-1.5534413736	-0.2059039041
H	5.0095872811	-1.4699980965	0.9126766621
H	4.5213469005	0.0101993037	1.8600965147
H	2.2325299318	0.8394761160	-1.7483437523
H	-0.8931569509	-1.2143936717	-2.1735211430
H	-1.9826449155	-1.1569538571	-4.3987063658
C	-0.5447230776	0.5985111619	-6.3702360551
C	1.7352176150	1.7647410967	-4.4408183470
H	-1.0604075024	0.1132664634	-0.4471106459
H	2.7376486332	0.1121329535	3.4842369212
H	3.2616193168	1.7091528812	2.9602556022
H	1.7762869774	1.5267335558	3.8664477671
H	1.6575482234	2.0445622857	-5.4845932229
H	1.6772504212	2.6778705580	-3.8545327699
H	2.7290777271	1.3483880467	-4.2935318650
C	-1.7219010121	-0.1202382255	-7.0202261068
H	-0.6794837294	1.6689732108	-6.4910066453
H	0.3597888354	0.3535668663	-6.9181081915
C	-1.8854580414	0.2195570556	-8.4809119769
H	-1.6136358901	-1.1984163328	-6.9482443568
H	-2.6558805318	0.1238193943	-6.5230860436
O	-2.9234114467	-0.4175164247	-9.0077249561
O	-1.1908249087	0.9566492323	-9.1035205391
C	-3.1893238206	-0.1863971999	-10.3788930083
H	-4.0566377230	-0.7825813456	-10.6156970422
H	-3.3942367599	0.8597836032	-10.5550844850
H	-2.3484808559	-0.4906074691	-10.9855075083

s-cis E-**1a**:

C	2.1024063445	0.2083508074	0.9102524947
C	1.3984842186	0.3272220550	-0.3912730031
N	0.1033661355	0.7358838207	-0.0611548576
C	-0.0215254973	1.0158188165	1.2686643673
C	1.2785284067	0.6179763544	1.8810169577
C	1.7466252869	0.0675786157	-1.6626623209
C	3.0508800583	-0.1291980203	-2.2610226938
N	4.1701087411	0.5695663086	-1.8642673389
C	5.2147610953	0.2477411501	-2.6816493464
C	4.8048308114	-0.6920235652	-3.5683155941
C	3.4092338095	-0.9259094973	-3.3081009903
C	2.5458441675	-1.9133915797	-4.0389749690
C	5.6114689349	-1.3989455176	-4.6245992934
C	7.0552774042	-0.9176802921	-4.7128122247
C	7.8470204382	-1.6242804765	-5.7852144197
O	9.0954948266	-1.1787057345	-5.8306693973
C	9.9509800993	-1.7637182702	-6.7959432388
O	-0.9801143233	1.4783927869	1.8134811018
C	1.4630128825	0.7083904659	3.3617901741
C	3.4380065940	-0.4022116778	1.0980670452
C	3.6585902731	-1.3997151094	1.9348192217
O	7.4314419233	-2.4719273785	-6.5077282603
H	2.5042459065	0.6189001726	3.6393734012
H	1.0751235762	1.6556317252	3.7184417982
H	0.9029517579	-0.0728509495	3.8672978546
H	4.2478108405	-0.0336433237	0.5013407590
H	4.6400250105	-1.8252370974	2.0405783403
H	2.8737409416	-1.8409814576	2.5221945924
H	0.9268245993	0.0433463996	-2.3616583701
H	4.1244669599	1.4102173002	-1.3368045246
H	6.1670275003	0.7182878253	-2.5531044697
H	2.5502916927	-1.7265493992	-5.1092330198
H	2.8933847689	-2.9323824203	-3.8901420076
H	1.5172798725	-1.8727391596	-3.7000523766
H	5.6075928553	-2.4689371119	-4.4387390407
H	5.1390944017	-1.2711088491	-5.5937233769
H	7.1029126849	0.1470500248	-4.9213451488
H	7.5782513366	-1.0652792159	-3.7726388673
H	10.9068751948	-1.2787319947	-6.6749477731
H	10.0452858523	-2.8263762387	-6.6250376219
H	9.5690932706	-1.5965318163	-7.7927157939
H	-0.5642016533	1.0574675238	-0.7246187693

S_1 min (*s-cis E*-**1a**):

C	2.0153376467	-0.0737865288	0.9687661084
C	1.2720686336	-0.1637096910	-0.3300294599
N	0.0559000693	0.3649548561	-0.1166888598
C	0.1066590336	1.1978469512	1.0578735688
C	1.3616140281	0.9090347071	1.7084481099
C	1.6674966240	-0.6089519242	-1.5776374983
C	2.9824774574	-0.7526428837	-2.0777384907
N	4.1535641536	-0.4891543174	-1.4260764216
C	5.1964676358	-0.6355140257	-2.2694529540
C	4.7259778192	-1.0094742611	-3.5186306948
C	3.3354085034	-1.0923527862	-3.4107581223
C	2.3597202689	-1.4539292191	-4.4899874248
C	5.5416475176	-1.2868564859	-4.7553944938
C	7.0430886456	-1.1079037719	-4.5554251227
C	7.8294458171	-1.3829761649	-5.8144459488
O	9.1265027972	-1.2122290626	-5.6144977617
C	9.9843370671	-1.4387483194	-6.7206050254
O	-0.7865772880	1.9453301872	1.3200273356
C	1.6859228194	1.4536204702	3.0612441811
C	3.0563133917	-0.9918173845	1.3106720873
C	3.9890421346	-0.8934259555	2.2767562265
O	7.3623077183	-1.7111261727	-6.8570025565
H	2.6136970383	2.0219579439	3.0583075362
H	0.8930142246	2.1141474071	3.3889134064
H	1.7969350422	0.6605197403	3.7975460663
H	3.0808500329	-1.8833671582	0.7020199274
H	4.6704723467	-1.7043709000	2.4571121742
H	4.0733887355	-0.0378138753	2.9193600427
H	0.8897910084	-0.7281768336	-2.3088745454
H	4.2292911185	-0.2544939763	-0.4611260874
H	6.1967653091	-0.4814712640	-1.9254198711
H	1.7728071379	-0.5936226118	-4.8039184546
H	2.8721776147	-1.8350197552	-5.3641372056
H	1.6639748261	-2.2179008047	-4.1560221921
H	5.3518426748	-2.2985900038	-5.0979270306
H	5.2147776026	-0.6366580358	-5.5597770187
H	7.2839651780	-0.0985792805	-4.2354707558
H	7.4229722421	-1.7715489764	-3.7841826747
H	10.9832969680	-1.2508454065	-6.3606089409
H	9.8946407627	-2.4583633252	-7.0660224868
H	9.7433592633	-0.7650517443	-7.5299539656
H	-0.5299396205	0.6518266429	-0.8710657063

CI1 (*s-cis E*-**1a**):

C	4.2299561941	-1.4094097246	-3.5947175959
C	3.2310277820	-0.7311975143	-2.9431397560
N	3.2764445792	0.5761444245	-3.3835008965
C	4.2341291358	0.7043811828	-4.3700251779
C	4.8529112073	-0.4876101011	-4.5152112276
C	2.1678817760	-1.1221222010	-1.9840997832
C	2.3907573234	-0.3810056480	-0.7742735250
C	3.5622429113	-0.3498775290	0.2304029833
C	3.2839077101	0.5266467631	1.1901737131
C	1.9289212573	1.0958789937	0.8929922160
N	1.5113771964	0.4580709519	-0.3034328662
C	4.7341727928	-1.2139185412	0.0452029493
C	5.3470009977	-1.8458725556	1.0324604925
O	1.3006179741	1.8971788730	1.4800864729
C	4.0545360597	0.9896677979	2.3838991050
C	5.9992575945	-0.8328999737	-5.4259903893
C	6.4413127065	0.3282277371	-6.3265656074
C	7.6129312211	-0.0449739615	-7.1978589183
O	8.7096235119	0.4057784978	-7.0990947369
C	4.6048666760	-2.8547243983	-3.4301075809
O	7.2870654487	-0.9576865121	-8.1052625826
C	8.3169389810	-1.4007278258	-8.9681941860
H	3.6994904085	0.4972053429	3.2841711316
H	5.1072732040	0.7730645598	2.2660116648
H	3.9199530269	2.0554946158	2.5228995097
H	5.0661064033	-1.3318234446	-0.9682960724
H	6.2020394991	-2.4670371016	0.8395857189
H	5.0118914006	-1.7908861362	2.0525279783
H	2.3304432040	-2.1647686082	-1.7034247093
H	2.4529797512	1.1322053829	-3.3669867302
H	4.3999807670	1.6459073390	-4.8502511772
H	4.0834141092	-3.3006568364	-2.5904891664
H	4.3563177337	-3.4451349616	-4.3099834355
H	5.6721596583	-2.9835751441	-3.2563141118
H	5.7236670193	-1.6778354767	-6.0494175007
H	6.8510745690	-1.1599788544	-4.8318980731
H	5.6176573948	0.6249033469	-6.9673459182
H	6.7442865248	1.1794167309	-5.7321874503
H	8.7098329773	-0.5762885696	-9.5456710888
H	9.1196538458	-1.8514473430	-8.4023926085
H	7.8627062545	-2.1308483608	-9.6196575178
H	0.6377372116	0.5907817832	-0.7711205457

CI2 (*s-cis E*-**1a**):

N	-0.2118919542	0.0969250673	-0.1040331683
C	1.0249988851	-0.3013457417	-0.2764222325
C	1.7106040576	-0.2871238257	1.0630543387
C	1.5279246726	0.9604311917	1.6389430258
C	0.5915788742	1.7586502811	0.9888017072
C	1.6333311446	-0.5728858335	-1.4973487599
C	3.0054041376	-0.7942483938	-1.8338696398
C	3.5369702377	-0.9895916203	-3.1011647791
C	4.9492621970	-1.0883953437	-2.9669997863
C	5.2250156864	-0.9608399495	-1.6361110533
N	4.0636013960	-0.7808572726	-0.9600929055
C	2.7967752094	-1.0626336341	-4.4057929451
C	5.9163689203	-1.2955247163	-4.1024553905
C	7.3733226559	-1.3641716612	-3.6583995628
C	8.3289326880	-1.5660126305	-4.8084092783
O	9.5846948892	-1.6144741782	-4.3843535912
C	10.5872058547	-1.8012621696	-5.3671329372
C	2.3255819378	-1.4717232958	1.5995068862
C	3.1628165179	-1.5893365268	2.6377849667
C	2.0034003452	1.4644512131	2.9839713540
O	0.0810856467	2.7380405995	0.7000157513
O	8.0227880681	-1.6710955903	-5.9522070651
H	3.0811050697	1.5884506755	2.9924540150
H	1.5635932324	2.4272432473	3.2134139466
H	1.7325164658	0.7739873691	3.7753831798
H	2.0839626496	-2.3675571606	1.0505787840
H	3.5296942783	-2.5566279912	2.9263066794
H	3.5026091447	-0.7557345069	3.2206068204
H	0.9586706582	-0.6198766695	-2.3316741847
H	3.9925979072	-0.7329725502	0.0277089894
H	6.1568349645	-0.9923890187	-1.1115441591
H	2.9810440488	-0.1831007609	-5.0182737937
H	3.1132422235	-1.9260804569	-4.9836027788
H	1.7263451523	-1.1443203446	-4.2668855326
H	5.6688380285	-2.2085142748	-4.6353899140
H	5.8077765287	-0.4961140695	-4.8290704758
H	7.6719781380	-0.4561296462	-3.1430940317
H	7.5338733751	-2.1773557645	-2.9566315383
H	11.5243951307	-1.8141930384	-4.8332149467
H	10.4390689959	-2.7364841696	-5.8874856767
H	10.5738125943	-0.9909061494	-6.0816345352
H	-0.6868886541	0.2441623106	-0.9796517826

<u>*s-trans Z*-**1a**:</u>

C	2.1229127748	0.2603365579	0.7825585699
C	1.2089503168	0.4325392629	-0.3666275168
N	0.0563402322	0.9933461712	0.1560431766
C	0.1705713966	1.2251644691	1.5000099037
C	1.5232316939	0.7177015715	1.8842865222
C	1.4558917636	0.1242656089	-1.6468949985
C	0.5574907564	0.2458340961	-2.7790122928
N	1.0650180919	0.6397114728	-3.9966309915
C	0.0680232801	0.6754641505	-4.9200190443
C	-1.0825089627	0.2607439039	-4.3333181911
C	-0.7712181973	-0.0237824953	-2.9570359028
C	-1.7377230854	-0.6363259455	-1.9802487733
C	-2.4388729666	0.0819854071	-4.9620856530
C	-2.4943503775	0.5156638102	-6.4225913869
C	-3.8600636572	0.3373895564	-7.0382037471
O	-3.8639381051	0.7103504106	-8.3114054896
C	-5.0904813797	0.5957492337	-9.0095279273
O	-0.6441827136	1.7428604120	2.2032720350
C	1.9954695794	0.8235439884	3.2982738295
C	3.4765436820	-0.3104199912	0.6411449041
C	3.9795925547	-1.2513084973	1.4188857266
O	-4.8229788455	-0.0791744555	-6.4793326241
H	3.0695349062	0.7118752266	3.3656751670
H	1.7083928081	1.7838582707	3.7099418767
H	1.5312364784	0.0610395648	3.9169242862
H	4.0739490153	0.0816349987	-0.1647661020
H	4.9779309337	-1.6203314430	1.2695884986
H	3.4133454289	-1.6940364789	2.2181153915
H	2.4494427329	-0.2243809998	-1.8684209120
H	1.9708016275	1.0228647506	-4.1300391299
H	0.2664915662	0.9921437678	-5.9224488235
H	-2.4757046982	0.0783957886	-1.6207398914
H	-2.2904860388	-1.4443751048	-2.4488342157
H	-1.2287735333	-1.0494848293	-1.1192963975
H	-2.7455675276	-0.9576890045	-4.8941811242
H	-3.1818373028	0.6407893540	-4.4014848632
H	-2.2215565658	1.5610208848	-6.5332057122
H	-1.7896304110	-0.0463423069	-7.0280258008
H	-4.8920976661	0.9398741101	-10.0124397557
H	-5.4241707785	-0.4317098728	-9.0248444319
H	-5.8498138832	1.2089518704	-8.5461775255
H	-0.7126279238	1.3159097547	-0.3846346631

S_1min (*s-trans Z*-**1a**):

C	2.0389694632	0.0911609954	0.7908123137
C	1.2222526885	0.4213702372	-0.4018061223
N	0.1262424133	1.0447569083	0.0295116131
C	0.2075933821	1.3134048319	1.4393849677
C	1.4283020159	0.6955483937	1.8836452804
C	1.5535281642	0.2132176685	-1.7371070192
C	0.6632652273	0.2872309174	-2.8318760809
N	1.1258740820	0.6247767163	-4.0741147487
C	0.1060876757	0.6461006655	-4.9718330358
C	-1.0566952011	0.2765293440	-4.3368450848
C	-0.7279362288	0.0192750588	-2.9913005631
C	-1.6572538561	-0.5742638464	-1.9749616772
C	-2.4247711148	0.1182669504	-4.9471607637
C	-2.4904943682	0.5088656221	-6.4198398692
C	-3.8745426174	0.3447263630	-7.0001793348
O	-3.9027395707	0.6998871754	-8.2749311244
C	-5.1478864647	0.5933377255	-8.9455430937
O	-0.6479710878	1.9380860428	1.9985689635
C	1.8075755999	0.6585811843	3.3285892056
C	3.1916227731	-0.7604620839	0.6822943969
C	4.1826434931	-0.9388274324	1.5629183133
O	-4.8244755940	-0.0509551433	-6.4060095811
H	2.6942879287	1.2556392610	3.5327200528
H	0.9983116569	1.0549716368	3.9292997461
H	2.0188740559	-0.3551834526	3.6588141864
H	3.2375150039	-1.3331952550	-0.2317703152
H	4.9600048659	-1.6551872131	1.3699495682
H	4.2529981722	-0.3873113378	2.4809035845
H	2.5921457242	0.0553180549	-1.9575325522
H	2.0465207676	0.9576983268	-4.2441685907
H	0.2822457450	0.9171612233	-5.9909951806
H	-2.2847600103	0.1717936249	-1.4922681850
H	-2.3234139438	-1.2847689014	-2.4521738547
H	-1.1140168471	-1.0949977561	-1.1985990254
H	-2.7553983092	-0.9097982855	-4.8408166900
H	-3.1399028298	0.7144562167	-4.3905239743
H	-2.1943054074	1.5428693600	-6.5698962755
H	-1.8149602055	-0.0929744042	-7.0207193049
H	-4.9662906662	0.9236342365	-9.9558854421
H	-5.4932816108	-0.4301667528	-8.9407383206
H	-5.8873690485	1.2220238961	-8.4714617998
H	-0.4858189163	1.5690502269	-0.5541085823

CI1 (*s-trans Z*-**1a**):

C	-0.5578948845	-0.1056130580	-2.9988969327
C	0.7885832490	0.1521427506	-2.8848037328
N	1.1930344758	0.6853478039	-4.0735049127
C	0.1432028879	0.7108153944	-4.9735867268
C	-0.9582434187	0.2553983938	-4.3379259073
C	1.7727299789	-0.0906390553	-1.7903572649
C	1.2080696479	0.3408718673	-0.5420804246
C	1.1384144085	-0.5300163811	0.7332909464
C	0.6910335296	0.2145960472	1.7383024408
C	0.3842234781	1.5723818955	1.1807825729
N	0.7427513363	1.5074376223	-0.1953258876
C	1.5820515295	-1.9203329010	0.6509533063
C	1.2271547035	-2.8799276656	1.4925370363
O	-0.0454749657	2.5276386477	1.7094913912
C	0.4806960080	-0.0744842209	3.1889450258
C	-2.3560532117	0.1308209393	-4.8809829406
C	-2.4862260225	0.5658934734	-6.3361438104
C	-3.8887340309	0.4345551395	-6.8738934877
O	-4.8369937569	0.0555233220	-6.2644041596
C	-1.4328435821	-0.7262401384	-1.9470246452
O	-3.9507559355	0.8037400897	-8.1487224022
C	-5.2159700177	0.7276936606	-8.7765575508
H	1.2291402402	-0.7684829487	3.5498144936
H	0.5328882369	0.8400198829	3.7653388590
H	-0.4982018830	-0.5141638200	3.3537863748
H	2.1982123183	-2.1198299239	-0.2049022910
H	1.5916303810	-3.8814325684	1.3575388801
H	0.5542756609	-2.7255135231	2.3155774889
H	2.5181060210	0.7147418903	-1.9126668632
H	2.1492193642	0.7832318266	-4.3217406282
H	0.2904509650	1.0682767289	-5.9707751602
H	-1.9528826702	-0.0022749648	-1.3153754516
H	-2.2025484398	-1.3513786634	-2.3892044652
H	-0.8538665180	-1.3765374142	-1.2931634900
H	-2.6955366859	-0.8971647137	-4.7922730490
H	-3.0434879275	0.7156895490	-4.2761838439
H	-2.1853475993	1.6015631862	-6.4636251852
H	-1.8338945743	-0.0174781152	-6.9786004380
H	-5.0632163386	1.0623020111	-9.7909117232
H	-5.5843633870	-0.2882030460	-8.7692934536
H	-5.9291461221	1.3665051795	-8.2753492390
H	0.6185005513	2.2607578199	-0.8414657489

CI2 (*s-trans Z*-**1a**):

C	-0.6127834892	-0.1792502310	-3.2233866454
C	0.6270523337	0.3673182118	-2.9816444949
N	0.9372206956	1.1552131369	-4.0615027578
C	-0.0920098806	1.1534537443	-4.9532056998
C	-1.0704688212	0.3362699066	-4.4811357211
C	1.5858495039	0.2254096470	-1.9031299291
C	1.2827586439	0.1051489175	-0.5586206428
C	2.3834813950	-0.2914412423	0.3876674057
C	2.5164432900	0.5795638786	1.4570364091
C	1.5806055316	1.5900969421	1.5387667824
N	0.1773749823	0.3308001410	0.0989314323
C	3.1420420843	-1.4892007257	0.1180397332
C	4.3438845048	-1.8366505142	0.5846362405
O	1.0585084240	2.5623775043	1.7922103021
C	3.4434057687	0.4768898873	2.6545989467
C	-2.3819081023	-0.0158551415	-5.1315737468
C	-2.6250944936	0.7153109508	-6.4471436980
C	-3.9444330773	0.3590144694	-7.0858279646
O	-4.7388298393	-0.4126330918	-6.6537688535
C	-1.3385804828	-1.2083745123	-2.4029871685
O	-4.1225002844	1.0244539005	-8.2203698622
C	-5.3261772628	0.7805405641	-8.9243292173
H	4.4554637484	0.7690074731	2.3974094489
H	3.1115592672	1.1225450326	3.4588980138
H	3.4612198806	-0.5393556817	3.0288564977
H	2.6586622991	-2.1508822820	-0.5807419096
H	4.7827125658	-2.7739632008	0.2971723563
H	4.9337985655	-1.2115728555	1.2254128057
H	2.6270463432	0.2283015028	-2.1768133846
H	1.7240920860	1.7588367466	-4.1003650052
H	-0.0358955574	1.7310422593	-5.8520728449
H	-2.1761143968	-0.7852434550	-1.8521025109
H	-1.7418720135	-1.9905544707	-3.0393126811
H	-0.6798299861	-1.6758126805	-1.6829312415
H	-2.4315448541	-1.0857537134	-5.3111788166
H	-3.1996479631	0.2023182603	-4.4514643293
H	-2.6106864644	1.7921386056	-6.3076164743
H	-1.8457181175	0.4940066349	-7.1704036287
H	-5.2852002531	1.4041560473	-9.8036770185
H	-5.3975297326	-0.2601768301	-9.2060428766
H	-6.1810103220	1.0435152064	-8.3180049615
H	-0.5390845194	0.6847190580	-0.5116962892

<u>*s-trans E*-**1a**:</u>

N	0.0522652559	0.7874517658	-0.0577979356
C	1.3407141221	0.3264763305	-0.3230707719
C	1.9311620543	0.0390619782	1.0067611619
C	1.0401885220	0.3675110092	1.9500457875
C	-0.1750568342	0.9181055969	1.2842995619
C	1.7857446977	0.1427276828	-1.5756991430
C	3.1220593156	-0.1363621221	-2.0615933233
C	4.3398850734	0.4336331617	-1.8184410007
C	5.2833572764	-0.1778802361	-2.7153445004
C	4.5917382353	-1.0745582483	-3.4642325439
N	3.2840266126	-1.0302719309	-3.0983977467
C	4.6604380857	1.5810517404	-0.9050252550
C	6.7465886104	0.1692700943	-2.7885883677
C	7.5165576223	-0.6511028669	-3.8173657102
C	8.9830204598	-0.3011108658	-3.8721529613
O	9.6142814909	-1.0251952182	-4.7872368754
C	11.0029715833	-0.7955041729	-4.9412342956
C	3.2193614446	-0.6530901498	1.1931919849
C	4.0761420523	-0.4063005494	2.1679736627
C	1.0694777935	0.2062103404	3.4363458858
O	-1.1576484907	1.3654979888	1.7966382286
O	9.5274384486	0.5108068509	-3.1956603838
H	1.3851209765	1.1264280864	3.9198226297
H	0.0739768352	-0.0190289270	3.7983563742
H	1.7477020885	-0.5825786686	3.7346869236
H	3.4494169197	-1.4090467232	0.4648082206
H	4.9877333734	-0.9687072055	2.2557352495
H	3.9178780047	0.3723963055	2.8913399270
H	1.0329482326	0.2277678893	-2.3460600051
H	2.5913725835	-1.6755698559	-3.3968279804
H	4.9200691404	-1.7454898071	-4.2302299042
H	5.3217490763	1.2844498098	-0.0969869257
H	5.1556385769	2.3780039879	-1.4528040477
H	3.7651099713	1.9953444484	-0.4593407699
H	6.8661265183	1.2233769225	-3.0209212414
H	7.2069395322	0.0334195977	-1.8146904447
H	7.4445313243	-1.7142483598	-3.6072313008
H	7.1115243367	-0.5123726392	-4.8152651915
H	11.3284468330	-1.4678193722	-5.7195016770
H	11.1887680379	0.2291838673	-5.2291292983
H	11.5272246791	-1.0063588880	-4.0202802392
H	-0.5282624720	1.2356843521	-0.7295487572

S_1min (*s-trans E*-**1a**):

N	0.1420366544	0.9572491990	0.1419113821
C	1.3222737608	0.4097933569	-0.2871576326
C	1.9657897468	-0.1062282609	0.8805905206
C	1.1508038591	0.1599906672	1.9838824216
C	-0.0311093977	0.8339328774	1.5174350024
C	1.6828485825	0.4529277022	-1.6311359018
C	2.9956737879	0.0952850975	-2.1141803333
C	4.2485929979	0.8380174608	-2.1275703696
C	5.2158565789	0.0511980341	-2.7323691395
C	4.5752577791	-1.1331342282	-3.0885444144
N	3.2739622709	-1.0808504110	-2.7181221418
C	4.3911082247	2.1880478793	-1.5143756687
C	6.6650652899	0.4111942138	-2.9474529616
C	7.4910070380	-0.7024813775	-3.5836996096
C	8.9325376740	-0.2965484251	-3.7847768155
O	9.6359601964	-1.2837324296	-4.3095225575
C	11.0132341460	-1.0373368947	-4.5532021417
C	3.2510909145	-0.8030893569	0.8629088892
C	4.1694511260	-0.8280917852	1.8227399076
C	1.3317411050	-0.2059435908	3.4232051307
O	-1.0135532330	1.2355663972	2.1065069497
O	9.3824036692	0.7686251030	-3.5127363490
H	2.0065023145	0.4690411412	3.9499214321
H	0.3732090907	-0.1554063537	3.9260772602
H	1.7300148538	-1.2107509645	3.5383506161
H	3.4641323926	-1.3841139277	-0.0210197750
H	5.0656517271	-1.4135483009	1.7152069769
H	4.0570521791	-0.2829431614	2.7409718847
H	1.1078738806	1.0646819557	-2.3068028979
H	2.5873590085	-1.7929833514	-2.8370746644
H	4.9683650393	-1.9983287002	-3.5798591151
H	4.4646630910	2.0870864551	-0.4352204744
H	5.2744821188	2.6978590412	-1.8753995393
H	3.5154975710	2.7908185407	-1.7193541481
H	6.7279390557	1.2973035208	-3.5688931254
H	7.1091733690	0.6818361565	-1.9967420418
H	7.4874913994	-1.6014471385	-2.9743868082
H	7.0994519884	-0.9871485723	-4.5563559009
H	11.4036068243	-1.9500719467	-4.9734123144
H	11.1318468949	-0.2204542004	-5.2495964826
H	11.5216274357	-0.7991173048	-3.6307448955
H	-0.5392450056	1.3845588822	-0.4406531543

CI1 (*s-trans E*-**1a**):

N	-0.0900346109	0.6798281207	0.1971842420
C	1.0396302721	0.4514783783	-0.4159351744
C	1.9637418481	-0.1668686223	0.6458764440
C	1.2923226616	-0.2803817705	1.7885648437
C	-0.0824442129	0.2677979632	1.5512524399
C	1.2521278695	0.7621539112	-1.8009783193
C	1.4807467777	-0.5332026640	-2.4775860774
C	0.6857241546	-1.6567167492	-2.5764421960
C	1.3831739781	-2.6163959684	-3.3941942689
C	2.5540231813	-2.0462290569	-3.7632781018
N	2.6320073712	-0.8056607152	-3.1711622189
C	-0.7140852123	-1.8018544155	-2.0498093527
C	0.8649110736	-3.9809843638	-3.7623120775
C	1.7846868073	-4.7481458157	-4.7056943892
C	1.2560322486	-6.1126668398	-5.0704232850
O	2.0561207187	-6.7205311071	-5.9388963555
C	1.6736361140	-8.0143129197	-6.3654776880
C	3.3487667855	-0.5277416661	0.3184560805
C	4.3731339990	-0.3485864652	1.1359013602
C	1.6659302951	-0.8354333980	3.1247684598
O	-0.9933014059	0.3635857028	2.2897210191
O	0.2601928356	-6.6085616183	-4.6506073383
H	1.9319923767	-0.0373250612	3.8115201321
H	0.8250956487	-1.3658158021	3.5547557993
H	2.5080416600	-1.5083351105	3.0378664297
H	3.5028002820	-0.9394565186	-0.6611352821
H	5.3665742548	-0.6356808273	0.8441573097
H	4.2685052758	0.1045982711	2.1050537308
H	2.1835488484	1.3318353681	-1.8326928453
H	3.3058850265	-0.1127276342	-3.3988686937
H	3.3427210356	-2.3997942940	-4.3936672610
H	-1.2967518191	-2.4730530600	-2.6723628986
H	-0.7689638176	-2.1990240005	-1.0351545508
H	-1.2182385006	-0.8396761351	-2.0554519441
H	0.7057830101	-4.5730406766	-2.8657642309
H	-0.1122261065	-3.8905953411	-4.2272214956
H	1.9437519236	-4.2006937447	-5.6294062665
H	2.7680365256	-4.8901035108	-4.2665386337
H	2.4331078034	-8.3318749805	-7.0629180644
H	1.6281709874	-8.6939186003	-5.5264916990
H	0.7085645885	-7.9851712280	-6.8506572422
H	-0.8602715526	1.0946159662	-0.2860123399

<u>*s-trans E*-**1a**#</u>:

C	4.3672498519	0.3577561647	-1.7936452007
C	3.1359547309	-0.1518974979	-2.0959582954
N	3.2821663738	-0.9422873169	-3.2162174497
C	4.5890129643	-0.9827411892	-3.5814657668
C	5.2989189153	-0.1825711421	-2.7435083628
C	1.8032077078	0.1022646637	-1.5950092328
C	1.3368562572	0.2660707532	-0.3466180287
C	1.8892130898	-0.0037975863	1.0017296778
C	1.0054823545	0.4009415722	1.9160939905
C	-0.1910720122	0.9482084961	1.2180066600
N	0.0407699368	0.7405981204	-0.1136880226
C	3.1528996378	-0.7203493634	1.3086653095
C	3.3988235085	-1.9658631741	0.9574324501
O	-1.1606888216	1.4530023431	1.7013981393
C	1.0472420399	0.3207230571	3.4074773493
C	6.7712684453	0.1304073213	-2.7768768789
C	7.5246112071	-0.5990269975	-3.8835063599
C	9.0000944509	-0.2849544967	-3.8979304925
O	9.5624018399	0.4371514707	-3.1391953428
C	4.7157364918	1.3805855887	-0.7526315090
O	9.6167451999	-0.9265442690	-4.8819585062
C	11.0117262657	-0.7192077971	-5.0080417743
H	0.9371006551	1.3098115536	3.8394884529
H	0.2211422472	-0.2796235539	3.7745045094
H	1.9730894902	-0.1157258052	3.7582827344
H	3.8730429856	-0.1790575701	1.8969845409
H	4.3165391415	-2.4507495058	1.2357372542
H	2.7050162435	-2.5405628041	0.3703616009
H	1.0550462372	0.2062133126	-2.3679413068
H	2.5732324744	-1.5304721844	-3.5856771742
H	4.9046441527	-1.5791514277	-4.4116948591
H	5.3249274508	0.9586133420	0.0420324280
H	5.2831691072	2.1973101106	-1.1893075714
H	3.8283049371	1.8056124986	-0.3002541313
H	6.9204588155	1.1992653772	-2.8983324803
H	7.2228831673	-0.1185090035	-1.8213451289
H	7.4231448778	-1.6758807631	-3.7853447579
H	7.1286192287	-0.3462896077	-4.8624837165
H	11.3234416414	-1.3157698524	-5.8510144174
H	11.2257996391	0.3244662406	-5.1878125640
H	11.5255964592	-1.0381049751	-4.1126688534
H	-0.5024293867	1.2078438969	-0.8039229129

S$_1$ min (*s-trans E*-**1a**$^{\#}$):

C	4.2141256054	0.2976069670	-1.7793267810
C	2.9273731597	-0.2032711188	-2.1865749409
N	3.1465325082	-0.9045086132	-3.3268331181
C	4.4899276944	-0.9344723561	-3.6234498872
C	5.1744266654	-0.2092054488	-2.7029593938
C	1.6243973884	-0.0405257427	-1.6744935012
C	1.2545605879	0.1402993467	-0.3461098111
C	1.9615292543	-0.0953009732	0.9276120728
C	1.1706050385	0.4601558822	1.9404048454
C	-0.0637823476	0.9001882265	1.3698361242
N	0.0372197875	0.5977128756	-0.0243051085
C	3.1708693690	-0.8263625815	1.0996206554
C	3.7886695760	-1.6736769141	0.2443759404
O	-1.0455835834	1.4201181107	1.8279087466
C	1.4457456497	0.4852933031	3.4088257507
C	6.6529805599	0.0701039605	-2.6479954937
C	7.4470582268	-0.6213366308	-3.7508506705
C	8.9257112215	-0.3272694135	-3.6694111556
O	9.4424003272	0.3707415011	-2.8583528228
C	4.4570190170	1.4226175660	-0.8295668592
O	9.5900477521	-0.9513349780	-4.6292496751
C	10.9947071624	-0.7601541847	-4.6689939773
H	2.3383507434	1.0618403947	3.6476815392
H	0.6105750209	0.9370660251	3.9295326434
H	1.5942125492	-0.5154260461	3.8121335324
H	3.6514246467	-0.6671197889	2.0519497434
H	4.7168091877	-2.1347377694	0.5292259841
H	3.3204282531	-2.0610052128	-0.6366500701
H	0.8252435839	-0.0921253152	-2.3939472446
H	2.4567649798	-1.4781178695	-3.7545346082
H	4.8363740847	-1.4677111575	-4.4833344448
H	5.4540521041	1.3678000650	-0.4105184295
H	4.3736570719	2.3690727913	-1.3625158000
H	3.7418022393	1.4400901589	-0.0218547197
H	6.8279451157	1.1393231964	-2.7034792901
H	7.0393011293	-0.2430609293	-1.6839270483
H	7.3263263246	-1.6997783438	-3.7099519108
H	7.1101129759	-0.3129988491	-4.7363093299
H	11.3465843484	-1.3420179575	-5.5059482449
H	11.2300530331	0.2844264240	-4.8116754183
H	11.4493098009	-1.1066085976	-3.7524145357
H	-0.5944778131	1.0013779973	-0.6794292874

CI$_{1b}$:

C	4.1136754483	0.1307880892	-1.5118659974
C	2.7791812931	-0.1605420373	-2.1883192958
N	3.0365651615	-0.4270341467	-3.5127922515
C	4.4170912717	-0.5984999844	-3.6935930763
C	5.1008950595	-0.3017027741	-2.6029314419
C	1.5342097816	-0.1642846629	-1.6556278096
C	1.2208554848	-0.0045589690	-0.2895676052
C	2.0840994746	-0.0453079209	0.8715902246
C	1.1926741026	0.2609951913	2.0009801029
C	-0.1599992537	0.4210104601	1.4924072406
N	-0.0968346363	0.1539744854	0.1270963033
C	3.3930054143	-0.3131494257	0.9435926877
C	4.3009603227	-0.6783093038	-0.2003615770
O	-1.1594006602	0.7280477979	2.0766467504
C	1.5625902354	0.3630435611	3.4337489648
C	6.5913072589	-0.2945907484	-2.4098090059
C	7.3751196561	-0.6575536977	-3.6665083988
C	8.8677560565	-0.6475750268	-3.4424674295
O	9.4087077627	-0.3819998391	-2.4179076293
C	4.2508592528	1.6459122919	-1.2495344152
O	9.5193167923	-0.9772801501	-4.5478205462
C	10.9345075471	-1.0051333161	-4.4760324324
H	2.3337710662	1.1158090876	3.5874488103
H	0.6957820936	0.6281841517	4.0247936364
H	1.9615875369	-0.5796761693	3.8057112445
H	3.8513380840	-0.2892166418	1.9161848262
H	5.3259266645	-0.5373964632	0.1282818294
H	4.2088482147	-1.7352883559	-0.4434274795
H	0.7032132138	-0.3098261565	-2.3268741175
H	2.3803867485	-0.9364478930	-4.0606282020
H	4.7721621942	-0.8971711199	-4.6592391077
H	5.2115618611	1.8619428891	-0.7933370554
H	4.1814239470	2.2013333465	-2.1785122706
H	3.4775864127	1.9960532023	-0.5802438844
H	6.9146959859	0.6822828714	-2.0642158223
H	6.8629690572	-0.9857460432	-1.6183294319
H	7.1077249818	-1.6459196022	-4.0278908895
H	7.1626439375	0.0314692295	-4.4783102908
H	11.2732850938	-1.2877662623	-5.4601494832
H	11.3195474368	-0.0310106724	-4.2116151755
H	11.2622948939	-1.7286553767	-3.7437669757
H	-0.8125022505	0.4985041041	-0.4726595231

pre**1b**:

C	4.1052956673	0.1209694998	-1.5256077186
C	2.7727190075	-0.1832098780	-2.1987868505
N	3.0336211201	-0.4635838528	-3.4876008717
C	4.4182784964	-0.5984968479	-3.7047177576
C	5.0995268837	-0.3099451109	-2.6115715921
C	1.5178571123	-0.1536724891	-1.6700593400
C	1.2057139401	0.0498687452	-0.3082682584
C	2.0620916647	0.0177515565	0.9271957149
C	1.2039440280	0.2984197728	2.0184281088
C	-0.0999916822	0.4403416962	1.5702098686
N	-0.0033634396	0.2553954737	0.1110396633
C	3.3706757041	-0.3095814952	0.9292984699
C	4.2812922343	-0.6620179241	-0.2174177577
O	-1.1938907339	0.6571019808	2.0413422873
C	1.6110920463	0.3589069177	3.4571108075
C	6.5879847071	-0.3083085352	-2.4094300761
C	7.3778640928	-0.6668460395	-3.6636336923
C	8.8688286687	-0.6583683073	-3.4251762264
O	9.3948695874	-0.4019908474	-2.3908481709
C	4.2204765989	1.6487261692	-1.3081537911
O	9.5302897676	-0.9757521520	-4.5260876194
C	10.9460863911	-1.0047608101	-4.4414440212
H	2.3634257733	1.1247011852	3.6495210229
H	0.7451470179	0.5930464582	4.0651230715
H	2.0193430868	-0.5851048477	3.8218474007
H	3.8336513814	-0.3816542082	1.8976368885
H	5.3008173204	-0.5011140838	0.1167134804
H	4.2103924812	-1.7291082797	-0.4402789055
H	0.6842445050	-0.2798242431	-2.3398722015
H	2.3416626878	-0.7882435635	-4.1236594304
H	4.7586965704	-0.8898537913	-4.6767134293
H	5.1904147087	1.8868782703	-0.8864974783
H	4.1203251583	2.1751823655	-2.2506391373
H	3.4637498896	2.0079198733	-0.6258252042
H	6.9098085680	0.6658855958	-2.0561256825
H	6.8494880790	-1.0041649747	-1.6190218541
H	7.1124639990	-1.6536832491	-4.0305235217
H	7.1725785542	0.0266611308	-4.4733837797
H	11.2930967438	-1.2794187000	-5.4247362351
H	11.3278313389	-0.0326912376	-4.1655578717
H	11.2658477385	-1.7344923880	-3.7120698919
H	-0.8128564651	0.3258371653	-0.4676154172

1b:

C	4.2422999725	0.2774048103	-2.4032158727
C	2.9426673789	0.1492852536	-1.7005662542
N	3.2216378223	-0.4991644110	-0.5023709482
C	4.5378935935	-0.7769015653	-0.2775393027
C	5.3201489220	-0.2742813786	-1.4788134141
C	1.7034947708	0.4876152496	-2.0734056917
C	1.3456048641	1.1767203807	-3.3000708075
N	0.1544443241	1.1495763372	-3.7460124931
C	0.1466674357	1.8844645512	-4.9533344379
C	1.3261625929	2.3934870896	-5.2737126813
C	2.2847843917	2.0185954860	-4.1480360645
C	1.7243685349	3.2269641235	-6.4582045170
C	0.5736426006	3.5120502547	-7.4170408242
C	0.9997858544	4.3394703535	-8.6046531169
O	-0.0231695181	4.5847435214	-9.4101372256
C	0.2407930086	5.3540053171	-10.5699180740
O	4.9758893919	-1.3057277560	0.6971564828
C	6.3865138656	0.7380282203	-1.0468971151
C	4.4683559061	0.7052581207	-3.6354443889
C	3.4978116277	1.2322082828	-4.6632492790
O	2.1035020996	4.7307428427	-8.8127211026
H	6.9654976199	1.0686703991	-1.9015244218
H	5.9320984443	1.6107058089	-0.5896887942
H	7.0578501521	0.2839771100	-0.3286310016
H	5.4872364478	0.6393448297	-3.9824754978
H	0.8749220282	0.2064821557	-1.4480336317
H	-0.7789367355	1.9593804533	-5.4892806029
H	2.1432752250	4.1716791877	-6.1236435450
H	2.5230449986	2.7367977428	-7.0079069394
H	0.1407801305	2.5922272794	-7.7977949676
H	-0.2323897867	4.0415455564	-6.9191714865
H	-0.7024467349	5.4421317707	-11.0854859905
H	0.6136028760	6.3314369497	-10.2998685403
H	0.9664710004	4.8571557429	-11.1974949448
H	2.5262214801	-0.7325521960	0.1717295963
C	2.7103444210	3.2773537655	-3.3643651181
H	4.0552706351	1.8742207668	-5.3380675389
H	3.1536247194	0.3943315946	-5.2684828328
H	3.2841087499	3.0249623136	-2.4817458627
H	3.3211978403	3.9227107777	-3.9875875476
H	1.8362640236	3.8375664376	-3.0523483803
H	5.8081330251	-1.1334925299	-1.9280358234

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