Supplementary Information

Diporphyrin tweezer for multichannel spectroscopic analysis of enantiomeric excess

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Contents

1. Additional Data

Table S1. Summary of overall binding constants (β_4)[a] for (*R*)-CSA and (*S*)-CSA as obtained from a range of analytical techniques for complexation with (*R*)-**1** in chloroform.

(*R*)-**1**		
	(*R*)-CSA	(*S*)-CSA
Method	β_4 / M^{-4}	β_4 / M^{-4}
UV-vis[b]	$(1.22 \pm 0.31) \times 10^{21}$	$(2.31 \pm 0.58) \times 10^{22}$
FI[b]	$(9.27 \pm 2.32) \times 10^{21}$	$(1.98 \pm 0.65) \times 10^{21}$

[a] The overall binding constant is defined as $\beta_4 = K_1K_2K_3K_4$. [b] [(*R*)-**1**] = 1.0×10^{-6} M.

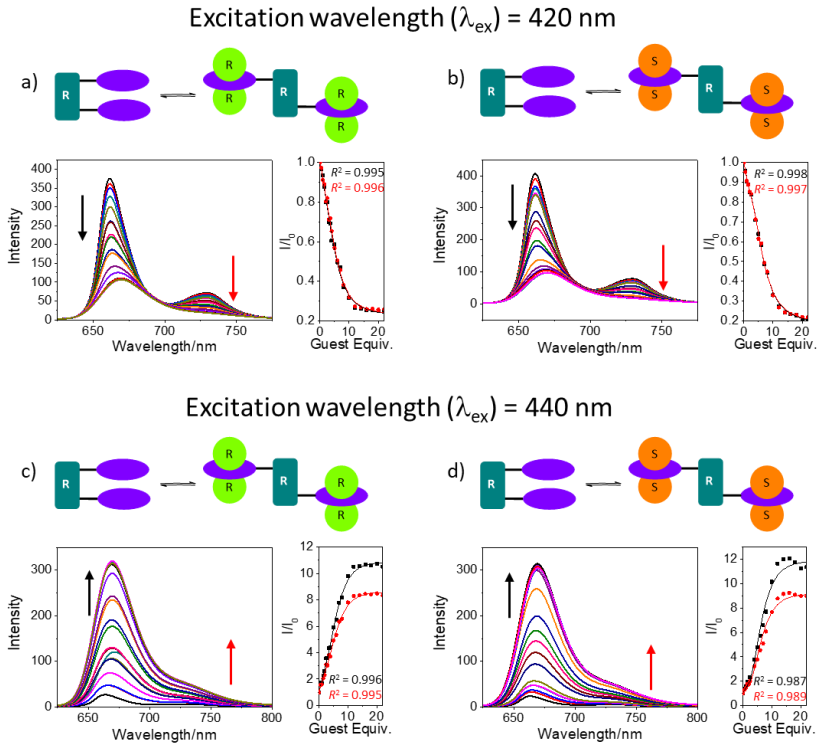


Fig. S1. Titrations of (*R*)-**1** monitored using fluorescence spectroscopy. (a) Titration of (*R*)-**1** (1.0 x 10^{-6} M) with 0-22 equiv. of (*R*)-CSA (3.5 x 10^{-4} M) in chloroform monitored using fluorescence spectroscopy at λ_{Ex} = 420 nm and binding isotherms for the titration constructed from normalized fluorescence at 662 nm (black) and 730 nm (red) and fitted simultaneously (solid lines) using 1:4 host-guest binding model. (b) Titration of (*R*)-**1** (1.0 x 10^{-6} M) with 0-24 equiv. of (*S*)-CSA (3.5 x 10^{-4} M) in chloroform monitored using fluorescence spectroscopy at λ_{Ex} = 420 nm and binding isotherms for the titration constructed from normalized fluorescence at 662 nm (black) and 730 nm (red) and fitted simultaneously (solid lines) using 1:4 host-guest binding model. (c) Titration of (*R*)-**1** (1.0 x 10^{-6} M) with 0-22 equiv. of (*R*)-CSA (3.5 x 10^{-4} M) in chloroform monitored using fluorescence spectroscopy at λ_{Ex} = 440 nm and binding isotherms for the titration constructed from normalized fluorescence at 662 nm (black) and 730 nm (red) and fitted simultaneously (solid lines) using 1:4 host-guest binding model. (d) Titration of (*R*)-**1** (1.0 x 10^{-6} M) with 0-24 equiv. of (*S*)-CSA (3.5 x 10^{-4} M) in chloroform monitored using fluorescence spectroscopy at λ_{Ex} = 440 nm and binding isotherms for the titration constructed from normalized fluorescence at 662 nm (black) and 730 nm (red) and fitted simultaneously (solid lines) using 1:4 host-guest binding model. For actual binding constants see Table S1.

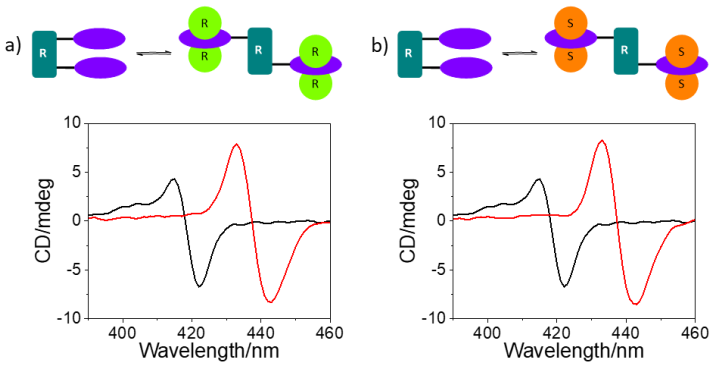


Fig. S2. CD spectra of (*R*)-**1** with 30 equiv. of CSA. (a) CD spectra of (*R*)-**1** (1.0×10^{-6} M) before addition (black) and after addition (red) of 30 equiv. of (*R*)-CSA. (b) CD spectra of (*R*)-**1** (1.0×10^{-6} M) before addition (black) and after addition (red) of 30 equiv. of (*S*)-CSA.

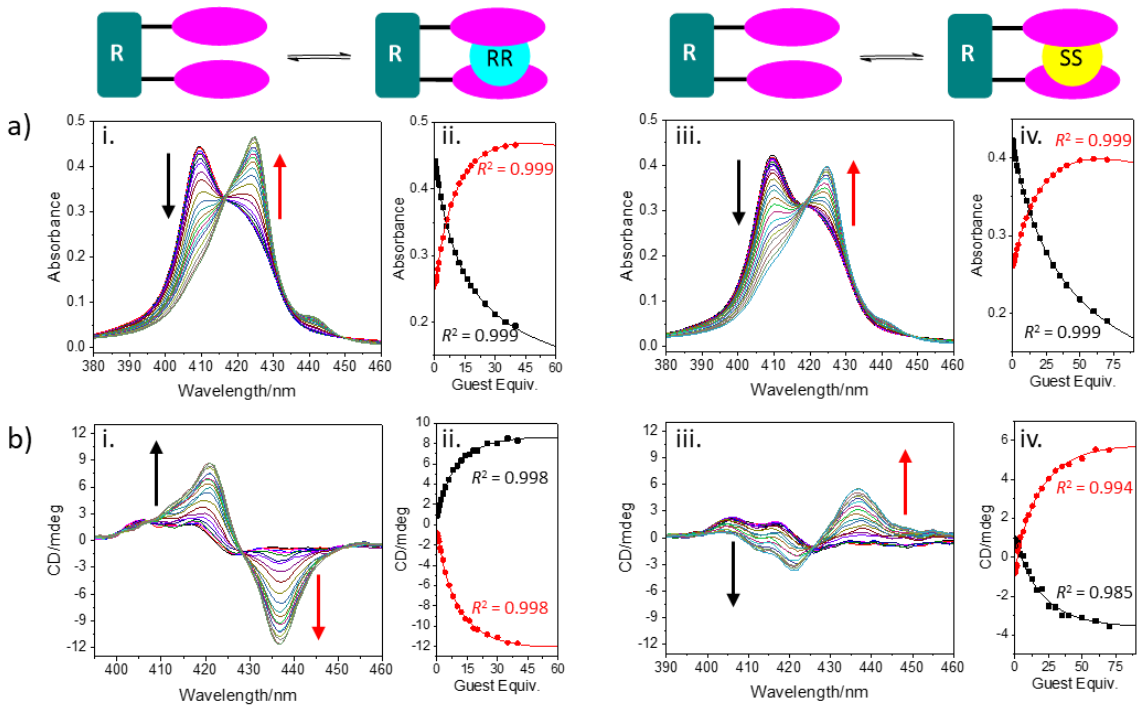


Fig. S3. Titrations of (*R*)-**2** monitored using UV-vis and CD spectroscopy. (a) Titrations monitored using UV-vis spectroscopy. i. (*R*)-**2** (1.0 x 10^{-6} M) with up to 40 equiv. of (*R*,*R*)-CHDA (3.5 x 10^{-4} M) in chloroform. ii. 1:1 host-guest binding isotherms for the titration of (*R*)-**2** with (*R*,*R*)-CHDA constructed from absorbances at 410 nm (black) and 425 nm (red) and fitted simultaneously. iii. (*R*)-**2** (1.0 x 10^{-6} M) with up to 70 equiv. of (*S*,*S*)-CHDA (3.5 x 10^{-4} M) in chloroform. iv. 1:1 host-guest binding isotherms for the titration of (*R*)-**2** with (*S*,*S*)-CHDA constructed from absorbances at 410 nm (black) and 425 nm (red) and fitted simultaneously. (b) Titrations monitored using CD spectroscopy. i. (*R*)-**2** (1.0 x 10^{-6} M) with up to 40 equiv. of (*R*,*R*)-CHDA (3.5 x 10^{-4} M) in chloroform. ii. 1:1 host-guest binding isotherms for the titration of (*R*)-**2** with (*R*,*R*)-CHDA constructed from CD signals at 421 nm (black) and 437 nm (red) and fitted simultaneously. iii. (*R*)-**2** (1.0 x 10^{-6} M) with up to 70 equiv. of (*S*,*S*)-CHDA (3.5 x 10^{-4} M) in chloroform. iv. 1:1 host-guest binding isotherms for the titration of (*R*)-**2** with (*S*,*S*)-CHDA constructed from CD signals at 410 nm (black) and 425 nm (red) and fitted simultaneously. For the binding constants see Table 1.

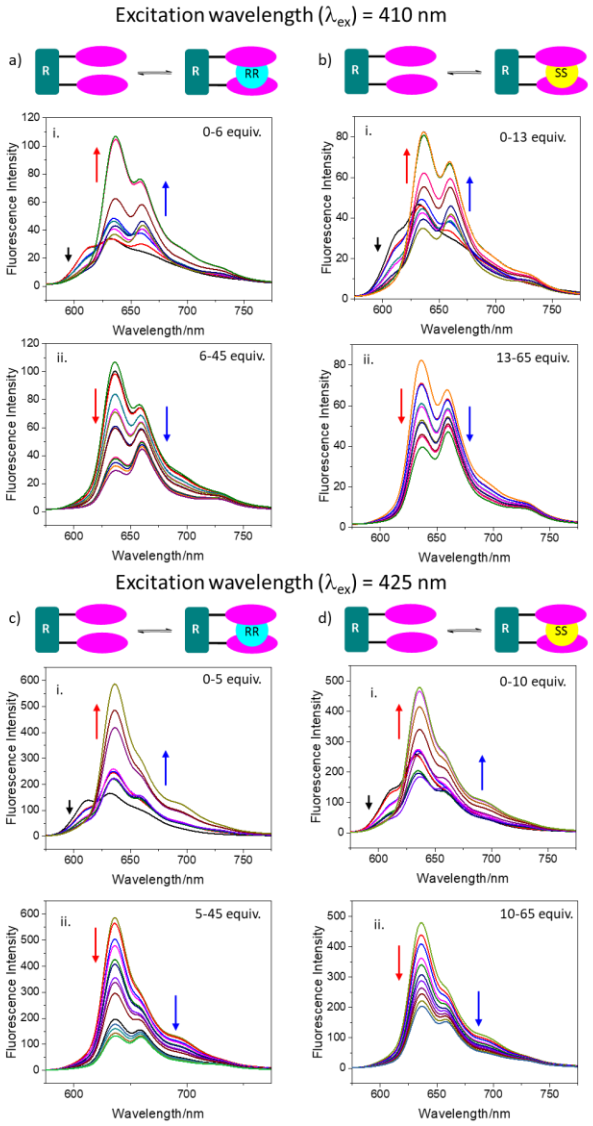


Fig. S4. Titrations of (*R*)-**2** monitored by fluorescence spectroscopy. (a) Titration of (*R*)-**2** (1.0 x 10^{-6} M) with (*R*,*R*)-CHDA (3.5 x 10^{-4} M) in chloroform monitored by fluorescence spectroscopy at λ_{Ex} = 410 nm. i. Addition of 0-6 equiv. of (*R*,*R*)-CHDA. ii. Addition of 06-45 equiv. of (*R*,*R*)-CHDA. (b) Titration of (*R*)-**2** (1.0 x 10^{-6} M) with (*S*,*S*)-CHDA (3.5 x 10^{-4} M) in chloroform monitored by fluorescence spectroscopy at λ_{Ex} = 410 nm. i. Addition of 0-13 equiv. of (*S*,*S*)-CHDA. ii. Addition of 13-65 equiv. of (*S*,*S*)-CHDA. (c) Titration of (*R*)-**2** (1.0 x 10^{-6} M) with (*R*,*R*)-CHDA (3.5 x 10^{-4} M) in chloroform monitored by fluorescence spectroscopy at λ_{Ex} = 425 nm. i. Addition of 0-5 equiv. of (*R*,*R*)-CHDA. ii. Addition of 05-45 equiv. of (*R*,*R*)-CHDA. (d) Titration of (*R*)-**2** (1.0 x 10^{-6} M) with (*S*,*S*)-CHDA (3.5 x 10^{-4} M) in chloroform monitored by fluorescence spectroscopy at λ_{Ex} = 410 nm. i. Addition of 0-10 equiv. of (*S*,*S*)-CHDA. ii. Addition of 10-65 equiv. of (*S*,*S*)-CHDA.

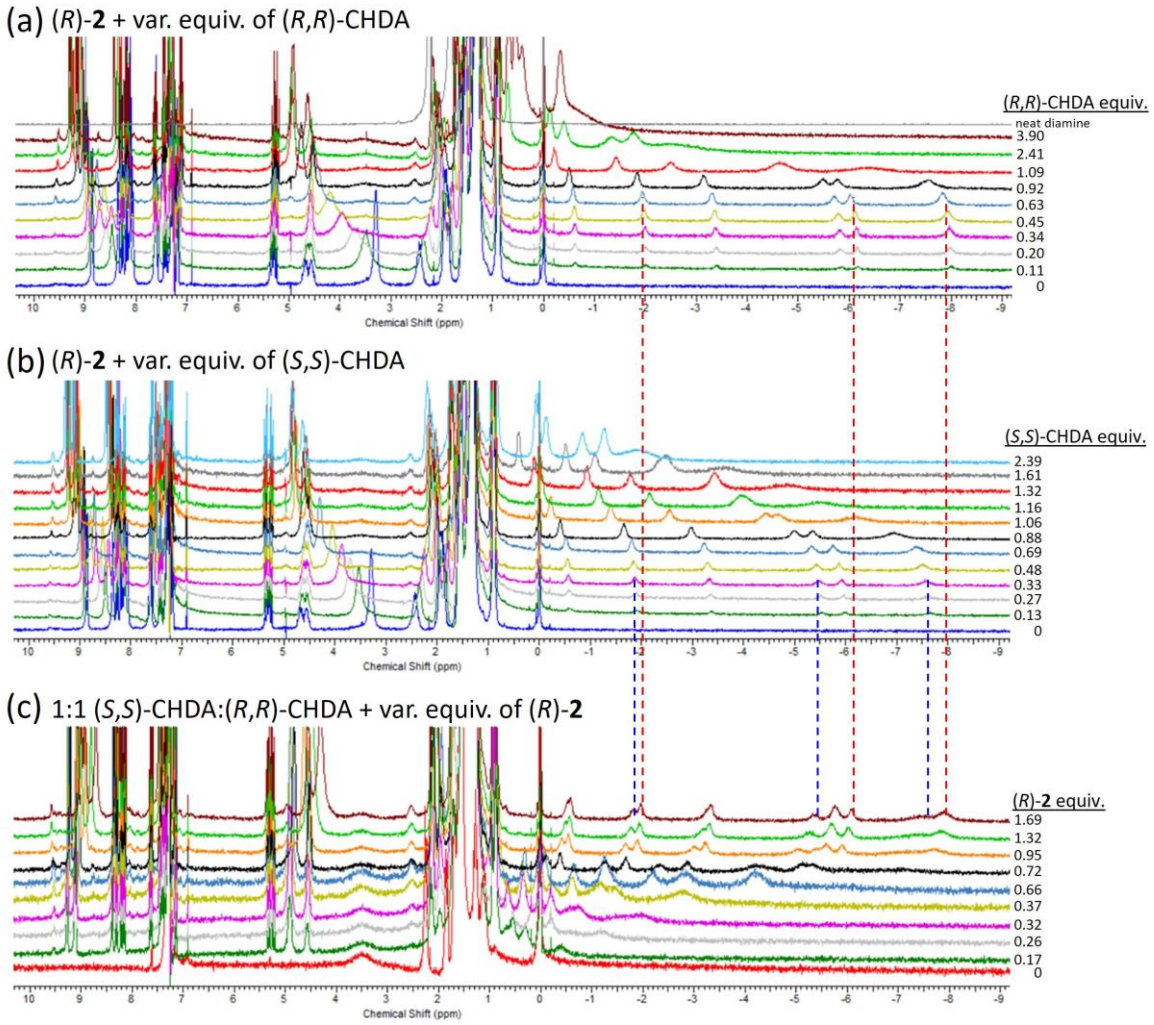


Fig. S5. Titrations of (*R*)-**2** monitored using ^{1}H NMR spectroscopy (a) ^{1}H NMR spectra of (*R*)-**2** (1.87 mM, $CDCl_3$, 25 °C) during the titration with (*R*,*R*)-CHDA. (b) ^{1}H NMR spectra of (*R*)-**2** (1.87 mM, $CDCl_3$, 25 °C) during the titration with (*S*,*S*)-CHDA. (c) ^{1}H NMR spectra of 1:1 (rac.) (*R*,*R*)-CHDA:(*S*,*S*)-CHDA (1.78 mM, $CDCl_3$, 25 °C) during the titration with (*R*)-**2**. Numbers of equivalents are denoted at right.

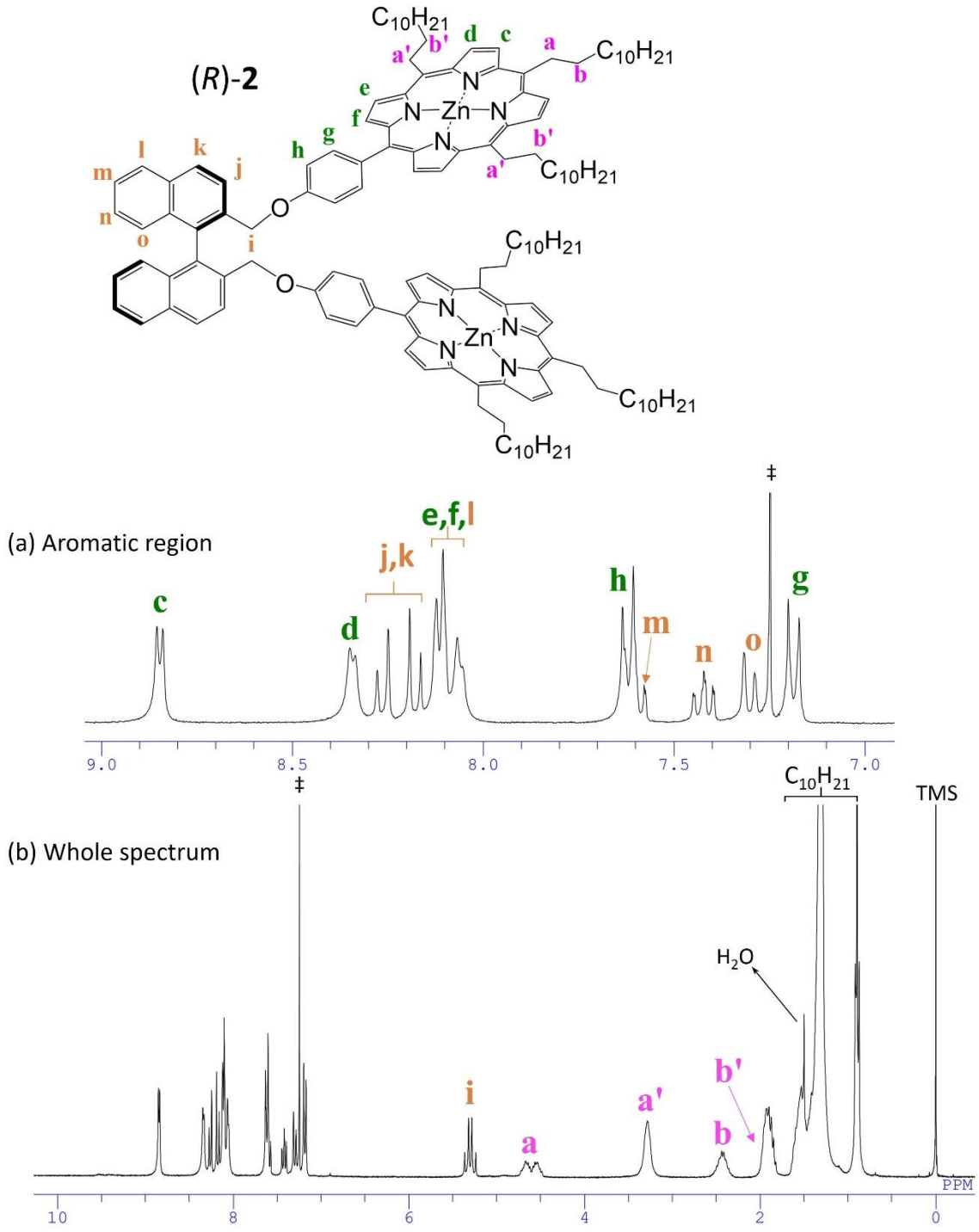


Fig. S6. ^{1}H NMR spectra assignment [S1] of (*R*)-**2** (~5 × 10^{-3} M, $CDCl_3$, 25 °C). (a) Aromatic portion of spectrum. (b) Whole spectrum. Double dagger symbol (‡) denotes residual $CHCl_3$.

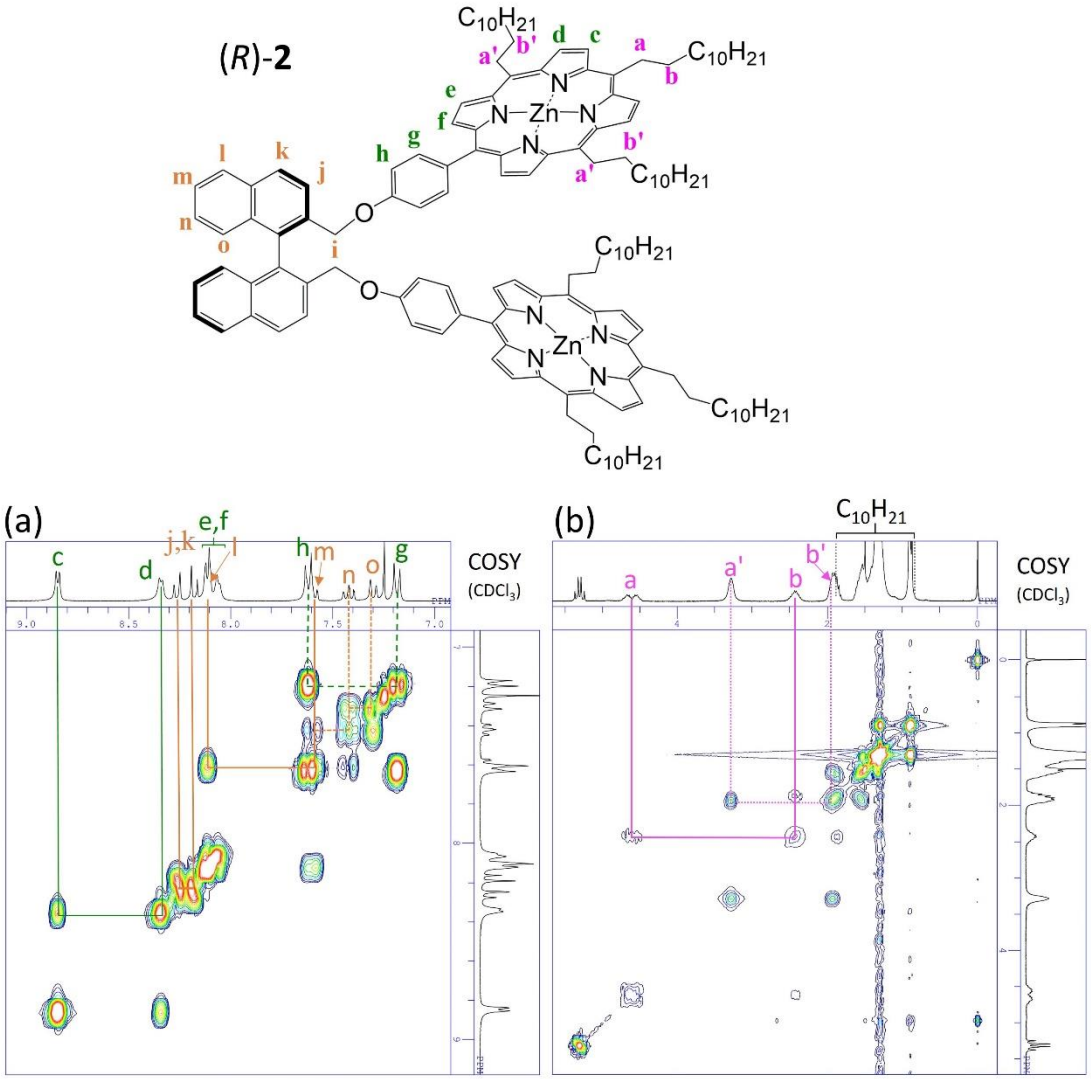


Fig. S7. (a, b) ^{1}H-^{1}H COSY NMR spectra of (*R*)-**2** (~5 × 10^{-3} M, $CDCl_3$, 25 °C).

2. Binding Studies

1:4 host-guest binding model. This model was used for analysis of UV-vis and fluorescence spectroscopic titration data of host molecule **1** with camphorsulfonic acid guest.

This model is described by the equilibrium equations S1:

$$\begin{aligned} \mathrm{H} + \mathrm{G} &\overset{K_1}{\rightleftharpoons} \mathrm{HG} \\ \mathrm{HG} + \mathrm{G} &\overset{K_2}{\rightleftharpoons} \mathrm{HG_2} \\ \mathrm{HG_2} + \mathrm{G} &\overset{K_3}{\rightleftharpoons} \mathrm{HG_3} \\ \mathrm{HG_3} + \mathrm{G} &\overset{K_4}{\rightleftharpoons} \mathrm{HG_4} \end{aligned} \tag{S1}$$

Where K_1, K_2, K_3 and K_4 are equilibrium binding constants. The following formulas hold for binding constants and mass balance equations.

$$K_1 = \frac{[\mathrm{HG}]}{[\mathrm{H}][\mathrm{G}]} \tag{S2}$$

$$K_2 = \frac{[\mathrm{HG_2}]}{[\mathrm{HG}][\mathrm{G}]} \tag{S3}$$

$$K_3 = \frac{[\mathrm{HG_3}]}{[\mathrm{HG_2}][\mathrm{G}]} \tag{S4}$$

$$K_4 = \frac{[\mathrm{HG_4}]}{[\mathrm{HG_3}][\mathrm{G}]} \tag{S5}$$

$$[\mathrm{H}]_\mathrm{t} = [\mathrm{H}] + [\mathrm{HG}] + [\mathrm{HG_2}] + [\mathrm{HG_3}] + [\mathrm{HG_4}] \tag{S6}$$

$$[\mathrm{G}]_\mathrm{t} = [\mathrm{G}] + [\mathrm{HG}] + 2[\mathrm{HG_2}] + 3[\mathrm{HG_3}] + 4[\mathrm{HG_4}] \tag{S7}$$

Where $[\mathrm{H}]_\mathrm{t}$ and $[\mathrm{G}]_\mathrm{t}$ is the total concentration of host H and guest G, respectively. [H] and [G] are the concentration of free H and G, respectively. [HG], [HG_2], [HG_3] and [HG_4] are the concentrations of 1:1 HG complex, 1:2 HG_2 complex, 1:3 HG_3 complex and 1:4 HG_4 complex, respectively.

Combination of Equations S2-S7 yields system of two non-linear equations in the following form, which is solved for [H] and [G] using two-dimensional Newton iterative method (actual implementation of this method can be seen elsewhere [10]).

$$[\mathrm{H}] + K_1[\mathrm{H}][\mathrm{G}] + K_1K_2[\mathrm{H}][\mathrm{G}]^2 + K_1K_2K_3[\mathrm{H}][\mathrm{G}]^3 + K_1K_2K_3K_4[\mathrm{H}][\mathrm{G}]^4 - [\mathrm{H}]_\mathrm{t} = 0 \tag{S8}$$

$$[\mathrm{G}] + K_1[\mathrm{H}][\mathrm{G}] + 2K_1K_2[\mathrm{H}][\mathrm{G}]^2 + 3K_1K_2K_3[\mathrm{H}][\mathrm{G}]^3 + 4K_1K_2K_3K_4[\mathrm{H}][\mathrm{G}]^4 - [\mathrm{G}]_\mathrm{t} = 0 \tag{S9}$$

[HG], [HG_2], [HG_3] and [HG_4] can be then obtained from equations S2-S5.

The general binding isotherm has a form of equation S10.

$$Y = Y_\mathrm{H}[\mathrm{H}] + Y_\mathrm{HG}[\mathrm{HG}] + Y_\mathrm{HG2}[\mathrm{HG_2}] + Y_\mathrm{HG3}[\mathrm{HG_3}] + Y_\mathrm{HG4}[\mathrm{HG_4}] \tag{S10}$$

Where Y corresponds to observed physical property (i.e. absorbance A or fluorescence F). Y_H, Y_{HG}, Y_{HG2}, Y_{HG3} and Y_{HG4} then denote corresponding quantity for each experimental technique. For UV-vis: $Y_H = \varepsilon_H d$, $Y_{HG} = \varepsilon_{HG} d$, $Y_{HG2} = \varepsilon_{HG2} d$, $Y_{HG3} = \varepsilon_{HG3} d$, $Y_{HG4} = \varepsilon_{HG4} d$, where ε_H, ε_{HG}, ε_{HG2}, ε_{HG3} and ε_{HG4} are molar extinction coefficients of H, HG, HG_2, HG_3 and HG_4 species, respectively, and d is path length (in cm). For fluorescence: $Y_H = k_H$, $Y_{HG} = k_{HG}$, $Y_{HG2} = k_{HG2}$, $Y_{HG3} = k_{HG3}$, $Y_{HG4} = k_{HG4}$, where k_H, k_{HG}, k_{HG2}, k_{HG3} and k_{HG4} are proportionality constants for H, HG, HG_2, HG_3 and HG_4 species, respectively.

In order to evaluate the binding constants, the experimental data were fitted using theoretical binding isotherms (typically constructed at two different wavelengths) using a non-linear least squares fitting procedure.

Singular value decomposition (SVD) and determination of number of absorbing species

During titration experiment only a few absorbing species are present in the measured spectrum (e. g. free porphyrin, complex 1:1, complex 1:2, etc.). Measured spectra (absorbance values) from a titration experiment could be arranged into a $N_{res} \times N_{exp}$ matrix **A**, where N_{exp} is number of titration steps and N_{res} is number of discrete points each spectrum consists of.

Assuming spectral shape of these absorbing species is constant during the whole experiment, matrix **A** can be viewed as linear combination of matrix of absorbing species' spectra. This linear combination is expressed as a matrix product:

$$\mathbf{A}_{\lambda n} = \sum_{i=1}^{N_{spec}} \mathbf{Z}_{\lambda i}\, \mathbf{F}_{in} \tag{S11}$$

where $\lambda = 1, 2 \ldots N_{res}$ and $n = 1, 2, \ldots N_{exp}$.

Columns of **Z** contain spectral shapes of absorbing species and rows of **F** contain their fractions during experiment (each column of **F** sums to 1). N_{spec} stands for number of present absorbing species (for example: N_{spec} =3 if only free porphyrin, complex 1:1 and complex 1:2 are present). Correct number of N_{spec} can be deduced from *singular value* decomposition [28-31] (SVD) procedure applied to the matrix **A**:

$$\mathbf{A}_{\lambda n} = \sum_{\mu=1}^{N_{res}} \sum_{m=1}^{N_{exp}} \mathbf{U}_{\lambda\mu} \mathbf{W}_{\mu m}\, \mathbf{V}_{mn} \tag{S12}$$

where again $\lambda = 1, 2 \ldots N_{res}$ and $n = 1, 2, \ldots N_{exp}$.

Columns of the square orthonormal $N_{res} \times N_{res}$ matrix **U** are called basis spectra. **W** is a rectangular diagonal $N_{res} \times N_{exp}$ matrix. These numbers are denoted as singular values and are sorted in descending order. Rows of the square orthonormal $N_{res} \times N_{res}$ matrix **V** are called amplitude vectors. A convenient compact form of SVD is **A** = **UK** (where **K** = **WV**), where rows of **K** are called *combination coefficients*.

In the presence of N_{spec} absorbing species in the titration experiment, first N_{spec} basis spectra carry the information about spectral shape of the absorbing species, first N_{spec} amplitude vectors (or combination coefficients) carry the information about their fraction in the sample. Remaining parts of the matrices **U** and **V** or **K** represent noise. Using approximate transformation matrix basis spectra can be transformed into the matrix of absorbing spectra **Z** and amplitude vectors/combination coeff. into the matrix of fractions **F** [28,30,32].

The presence of N_{spec} absorbing species causes first N_{spec} singular values to be substantially higher than the rest (holds for sufficiently high signal/noise ratio, N_{spec} is often denoted as the factor dimension). Another indicator is a plot of residuals that describes average standard error of the SVD approximation of measured spectra for given factor dimension. Residuals are defined as follows[29]:

$$\mathrm{residual}(i) = \sqrt{\sum_{j=i+1}^{N_{exp}} \mathbf{W}_{jj}^2 \Big/ N_{res}(N_{exp} - i)} \tag{S13}$$

For $i = N_{spec}$ the value of the residual drops significantly since all relevant spectra of absorbing species are included in SVD approximation of **A**. For $i > N_{spec}$ the value of residual does not change much since only basis vectors which consists mostly of noise are added into SVD approximation. Signal containing basis and amplitude vectors also tend to have higher autocorrelation compared to noise containing vectors. The simplest case $N_{spec} = 2$ can be easily identified observing plot of mutual dependence of the first two combination coefficients which should be linear [33].

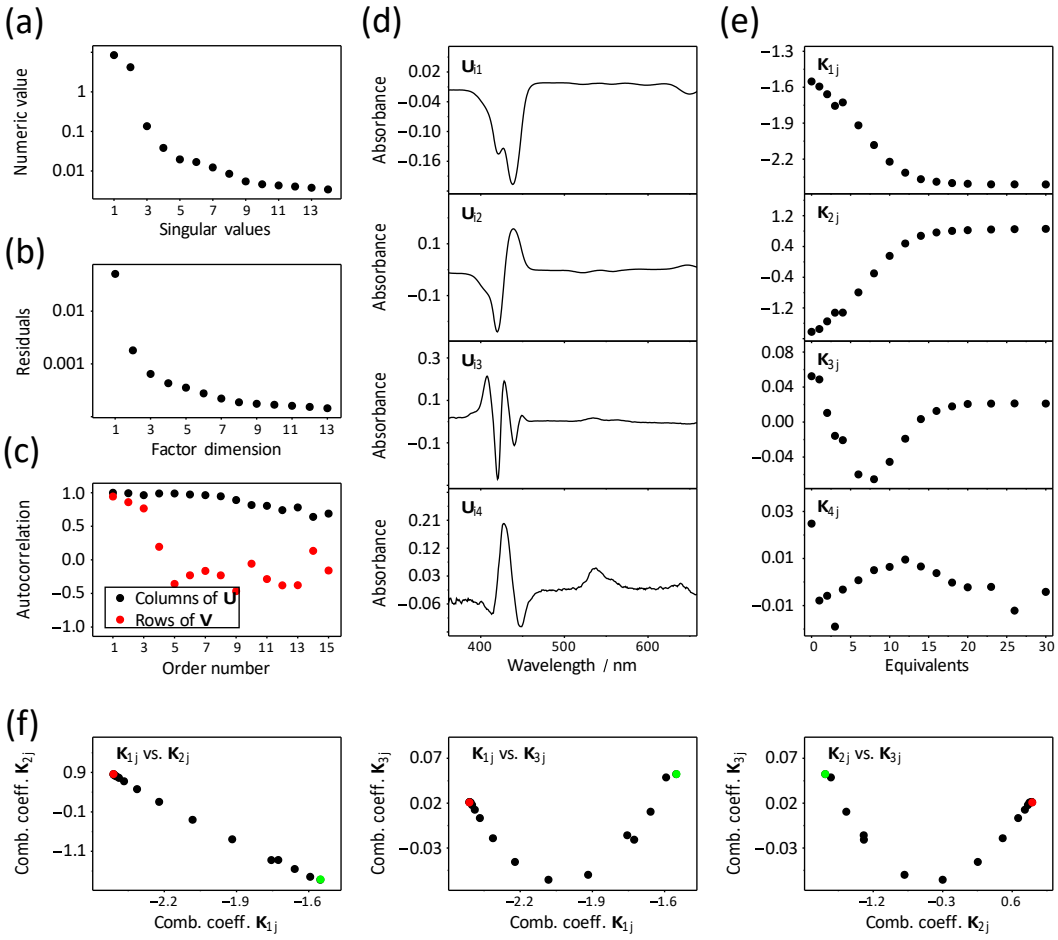


Fig. S8. SVD decomposition of titration of (*R*)-**1** with (*R*)-CSA in chloroform. For actual UV-vis spectra see Fig. 2 in the main manuscript. (a) Singular values (indicating the presence of only two species, i.e. H and HG_4 based on Job's plot for this system). (b) Residuals (significant drop can be seen at factor dimension = 2). (c) Autocorrelations of basis **U** and amplitude vectors **V**, respectively. (d) First four basis vectors **U**. (e) First four amplitude vectors **V**. (f) Mutual dependence of first three combination coefficients (red and green dots denote first and last measured spectrum, respectively).

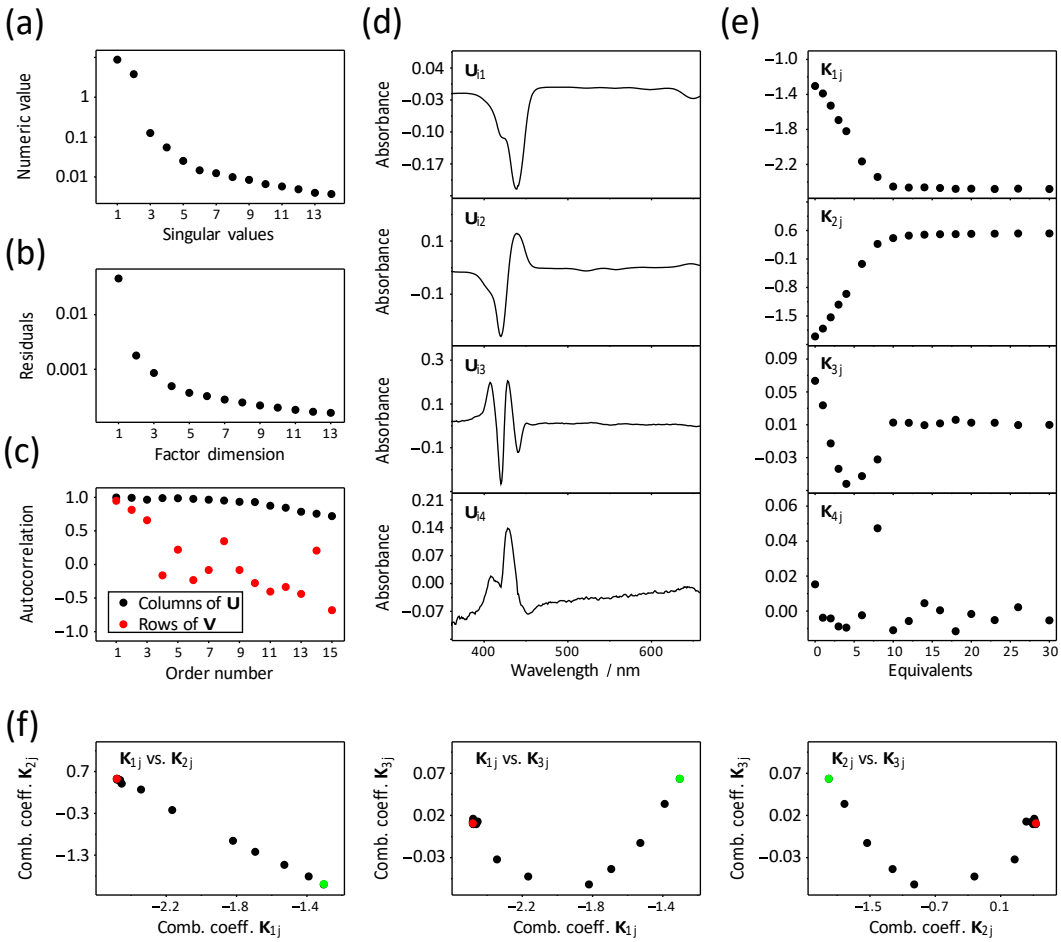


Fig. S9. SVD decomposition of UV-vis titration of (*R*)-**1** with (*S*)-CSA in chloroform. For actual UV-vis spectra see Fig. 2 in the main manuscript. (a) Singular values (indicating the presence of only two species, i.e. H and HG_4 based on Job's plot for this system). (b) Residuals (significant drop can be seen at factor dimension = 2). (c) Autocorrelations of basis **U** and amplitude vectors **V**, respectively. (d) First four basis vectors **U**. (e) First four amplitude vectors **V**. (f) Mutual dependence of first three combination coefficients (red and green dots denote first and last measured spectrum, respectively).

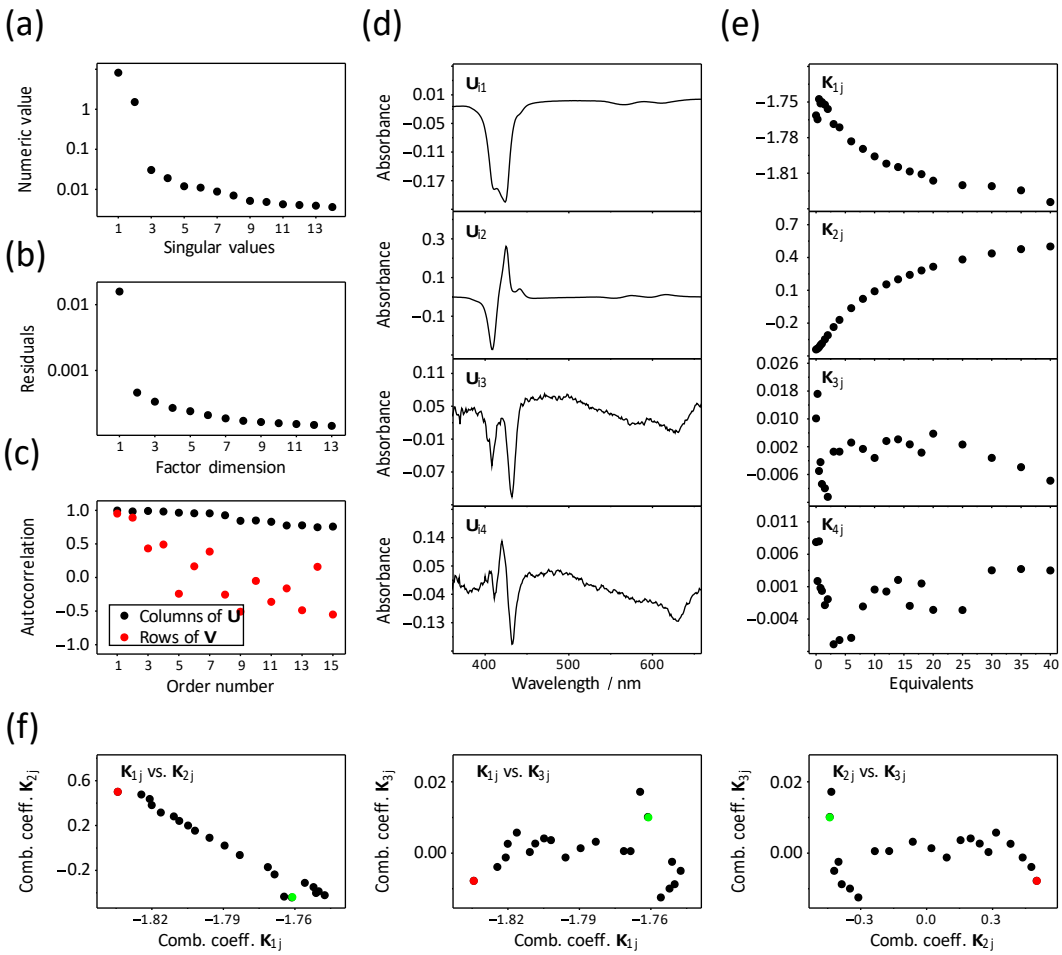


Fig. S10. SVD decomposition of UV-vis titration of (*R*)-**2** with (*R*,*R*)-CHDA in chloroform. For actual UV-vis spectra see Fig. S3. (a) Singular values (indicating the presence of only two species, i.e. H and HG based on Job's plot for this system). (b) Residuals (significant drop can be seen at factor dimension = 2). (c) Autocorrelations of basis **U** and amplitude vectors **V**, respectively. (d) First four basis vectors **U**. (e) First four amplitude vectors **V**. (f) Mutual dependence of first three combination coefficients (red and green dots denote first and last measured spectrum, respectively).

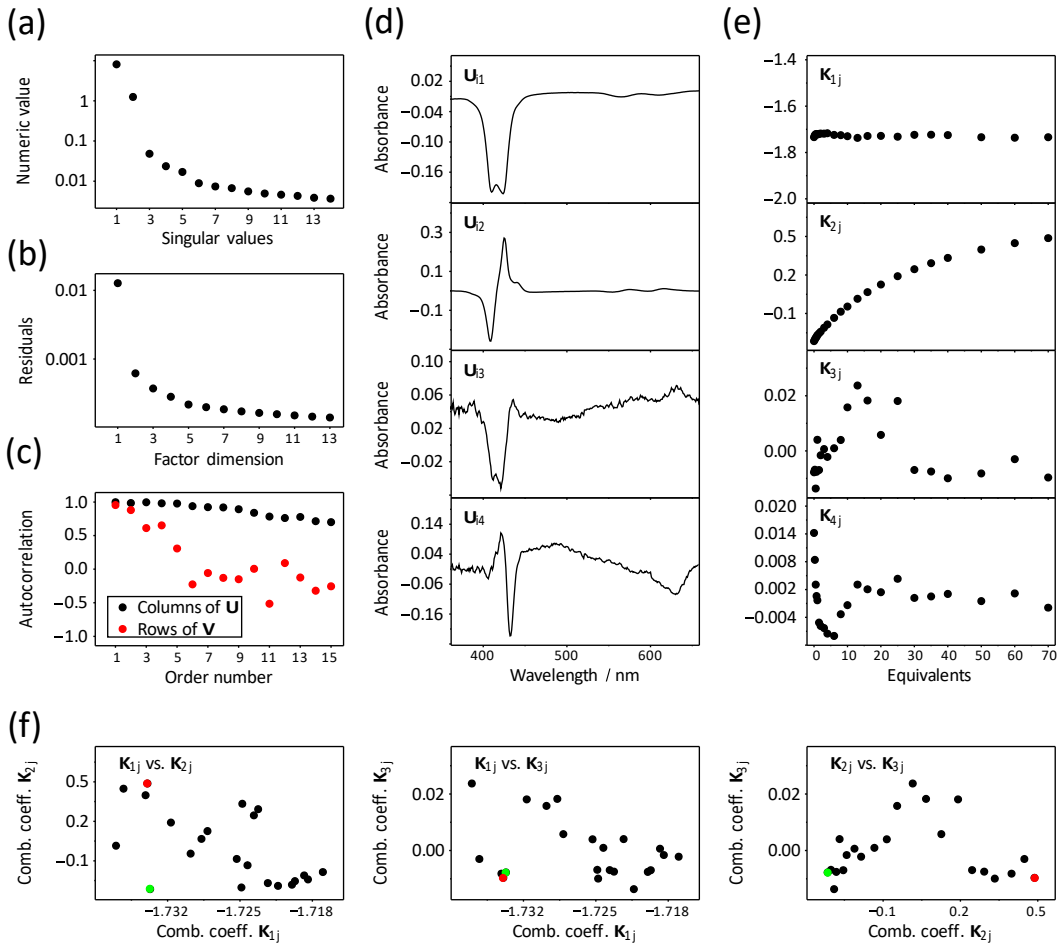
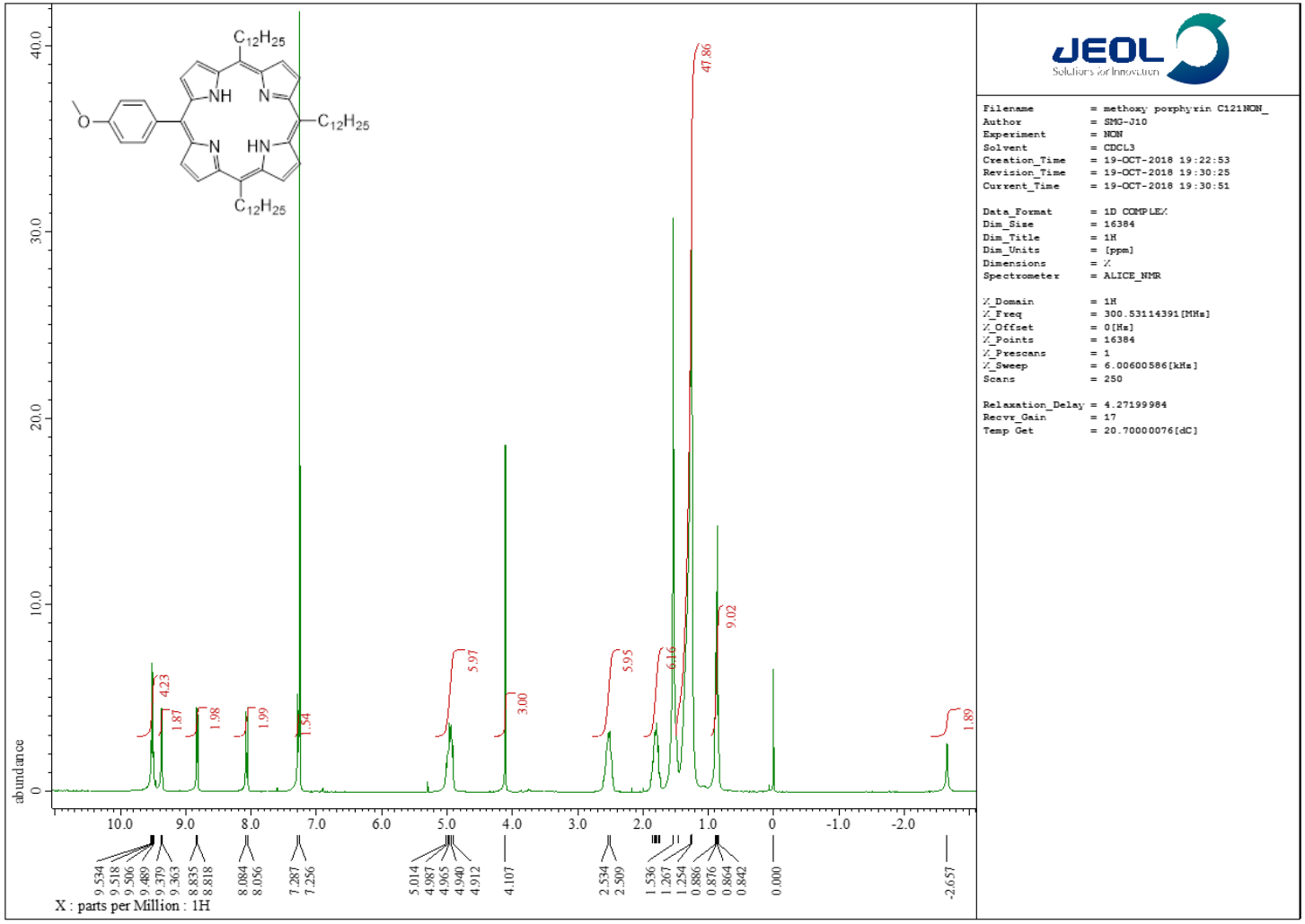


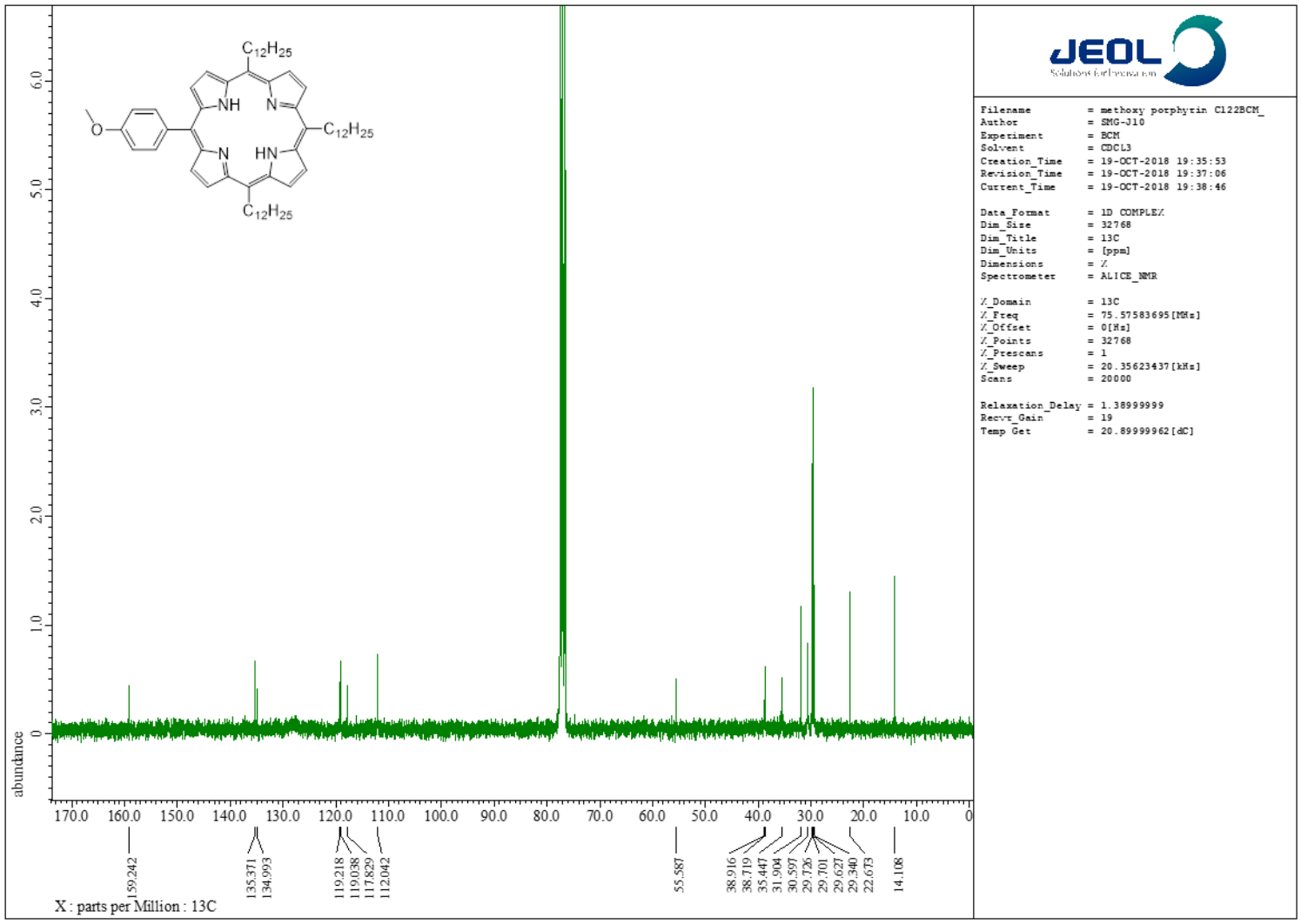
Fig. S11. SVD decomposition of UV-vis titration of (*R*)-**2** with (*S*,*S*)-CHDA in chloroform. For actual UV-vis spectra see Fig. S3. (a) Singular values (indicating the presence of only two species, i.e. H and HG based on Job's plot for this system). (b) Residuals (significant drop can be seen at factor dimension = 2). (c) Autocorrelations of basis **U** and amplitude vectors **V**, respectively. (d) First four basis vectors **U**. (e) First four amplitude vectors **V**. (f) Mutual dependence of first three combination coefficients (red and green dots denote first and last measured spectrum, respectively). $\mathbf{K}_{1j}$ is almost constant, therefore the expected linearity of $\mathbf{K}_{1j}$ vs. $\mathbf{K}_{2j}$ plot is obscured by noise.

3. NMR and Mass Spectra

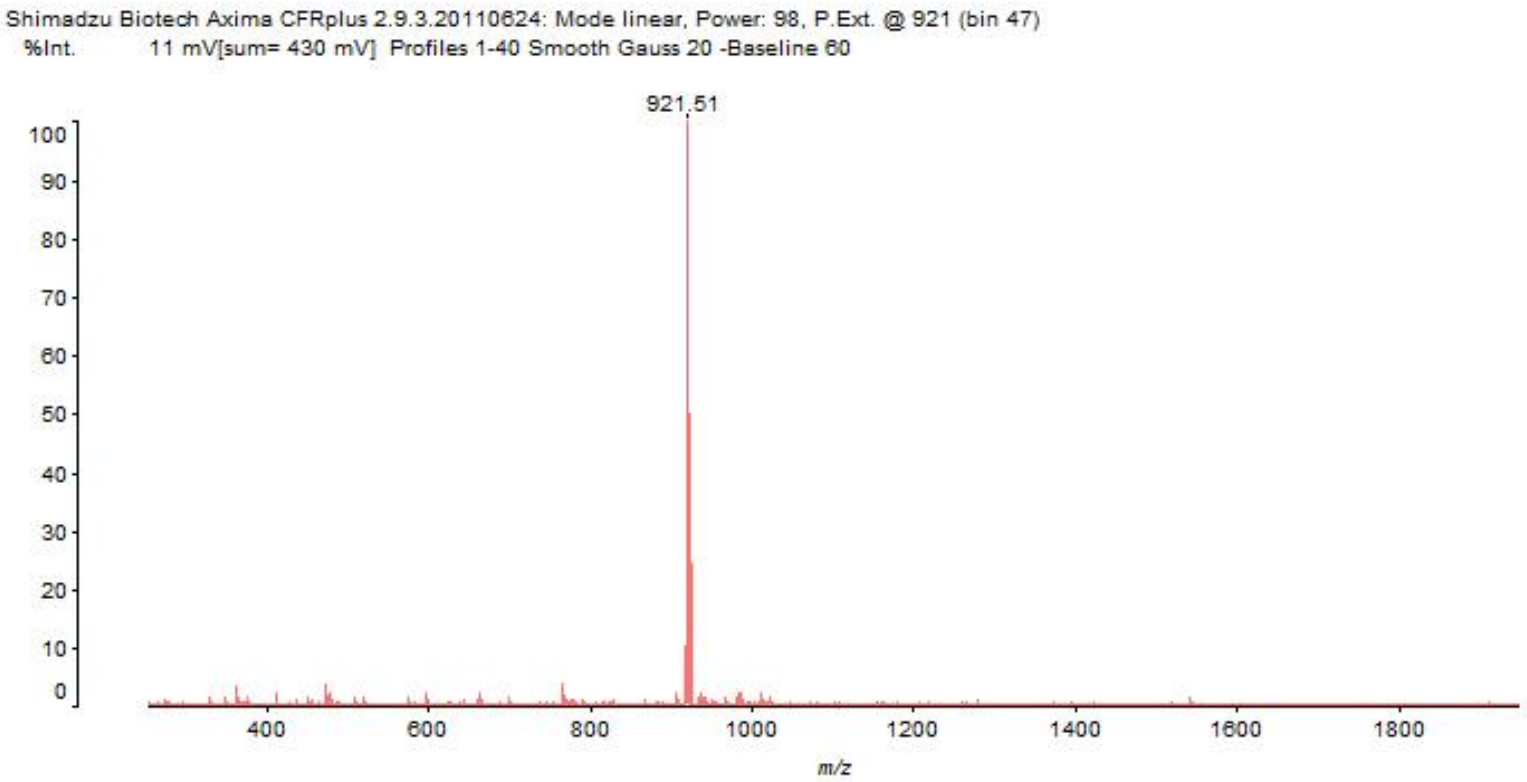
3 ^{1}H NMR Spectrum



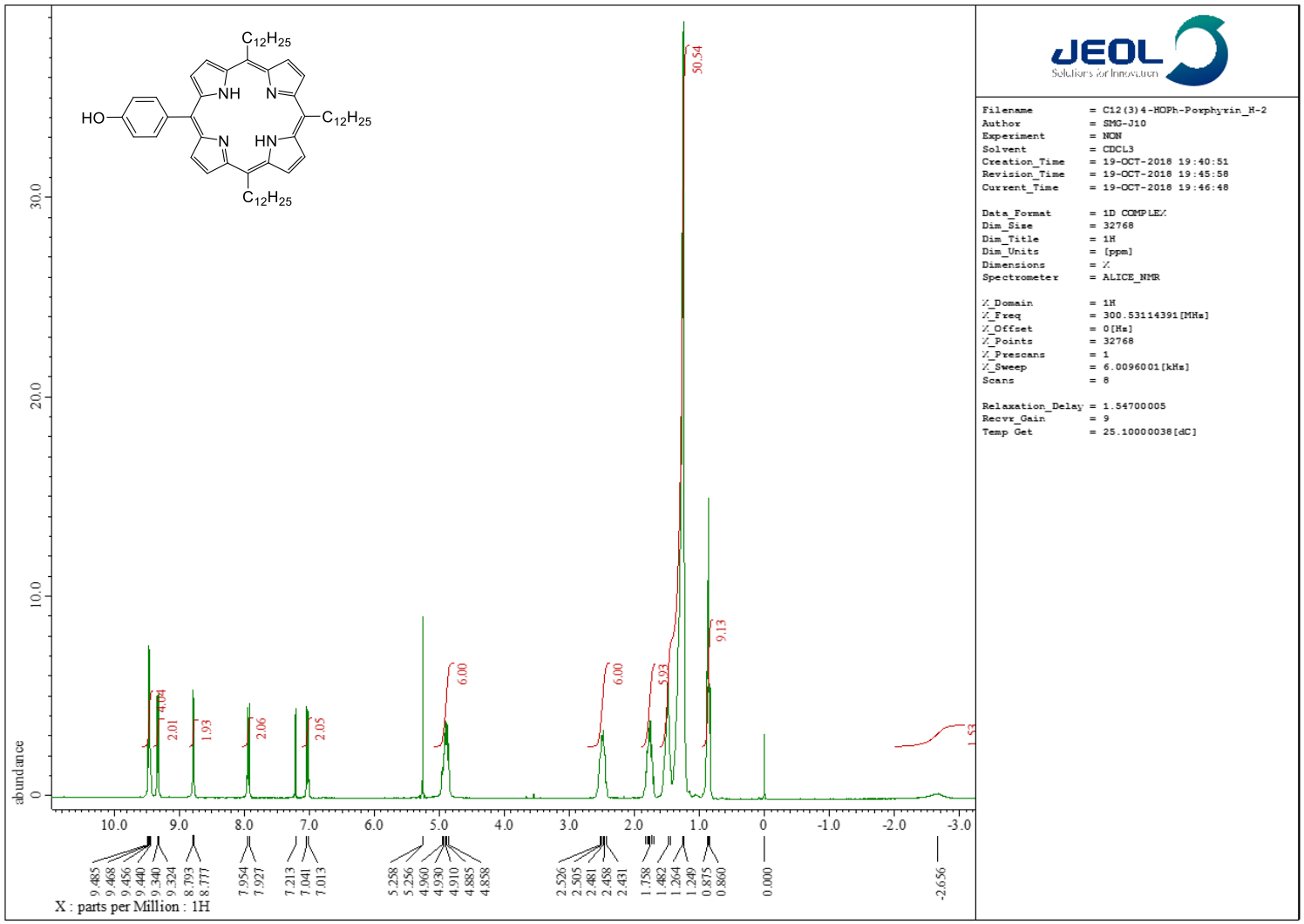
3 ^{13}C NMR Spectrum



3 MALDI-TOF Mass Spectrum



4 ^{1}H NMR Spectrum



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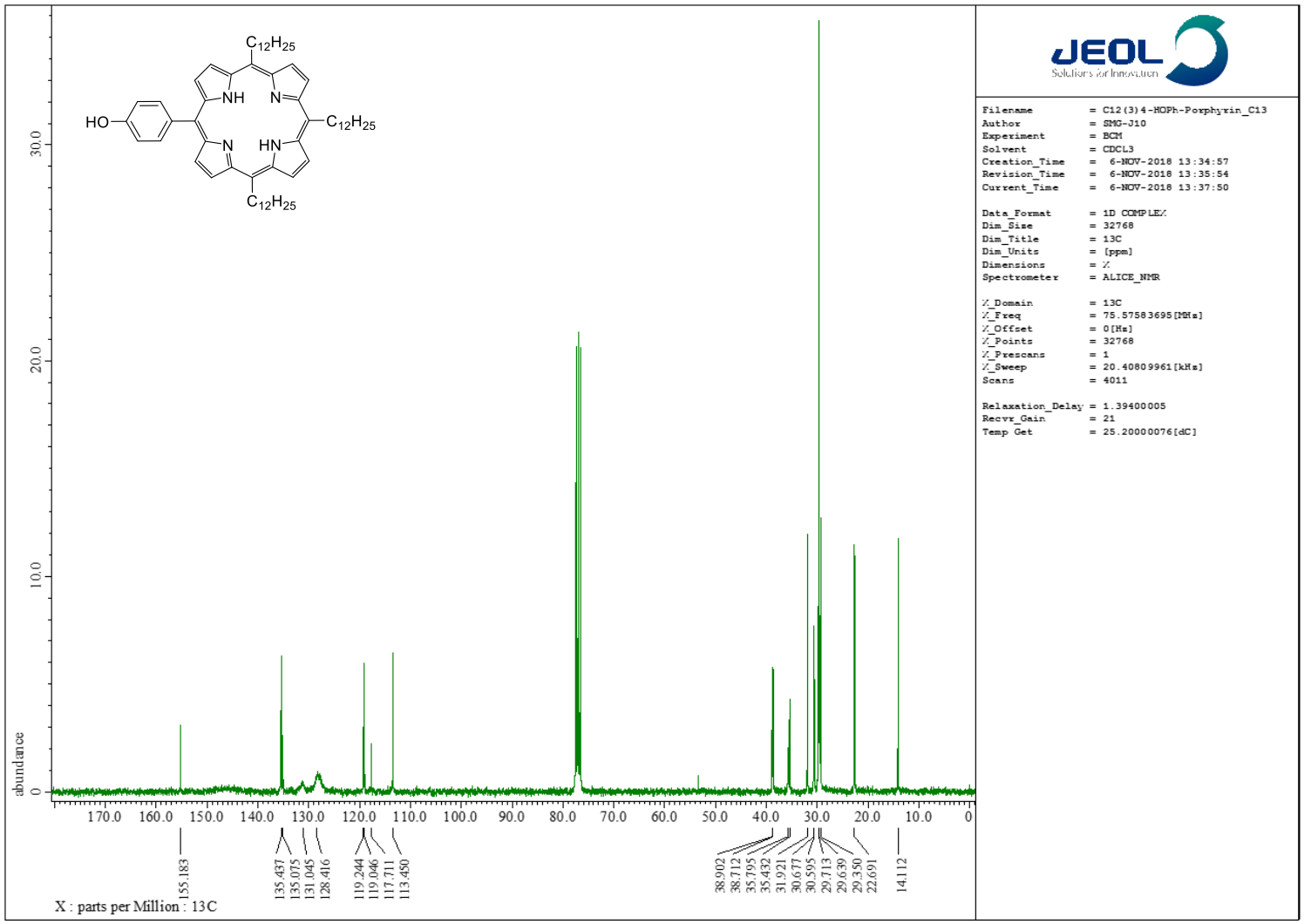
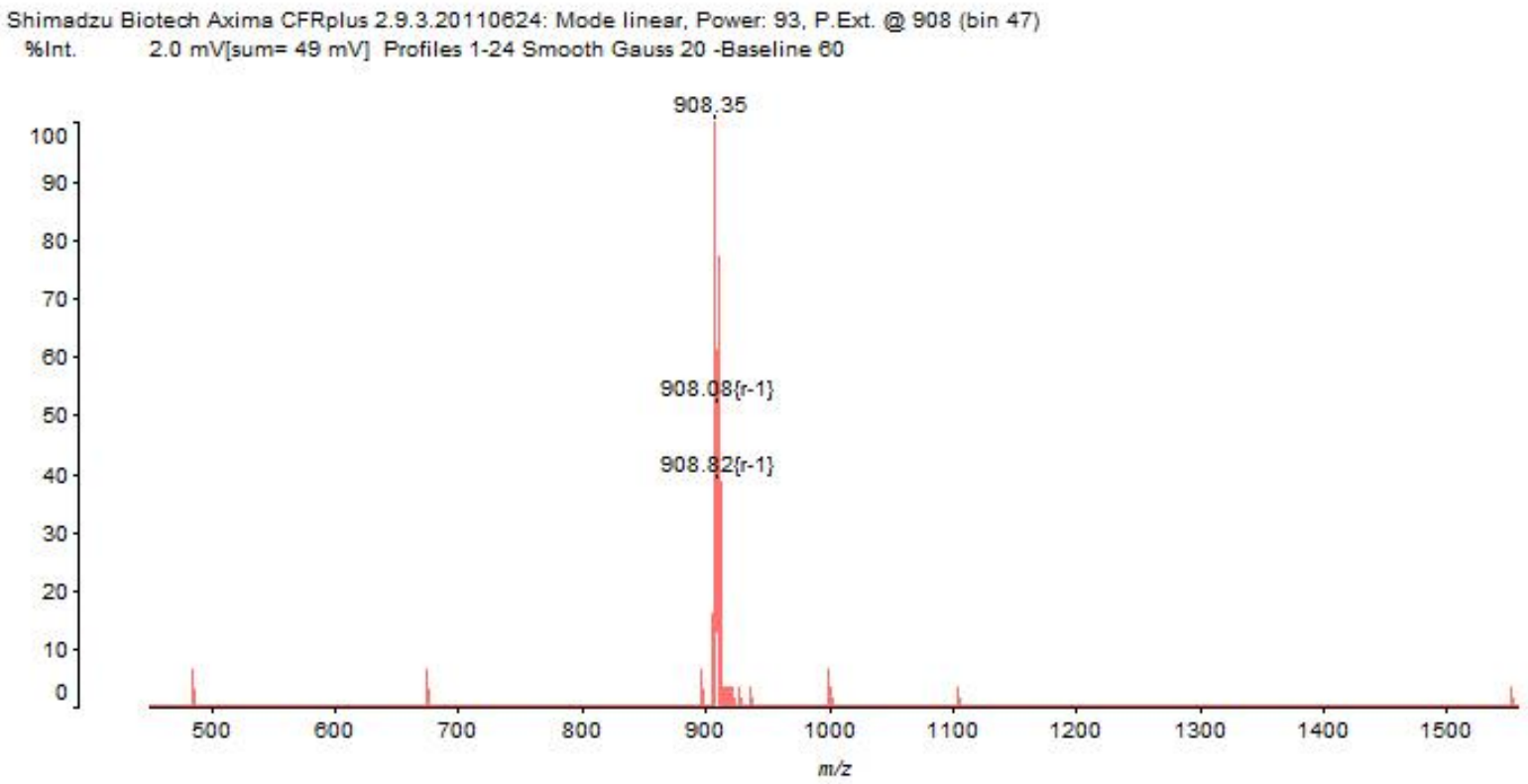
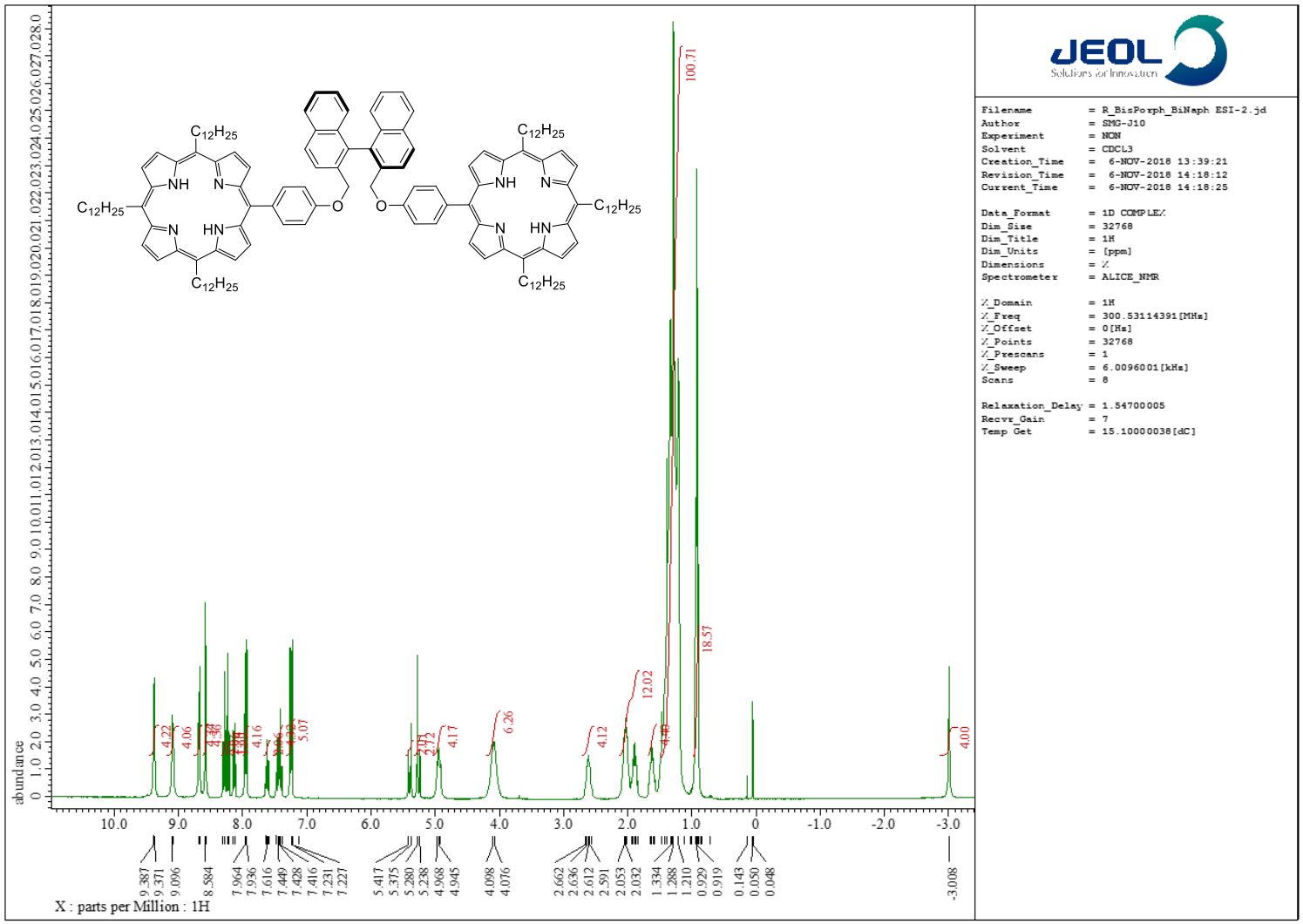


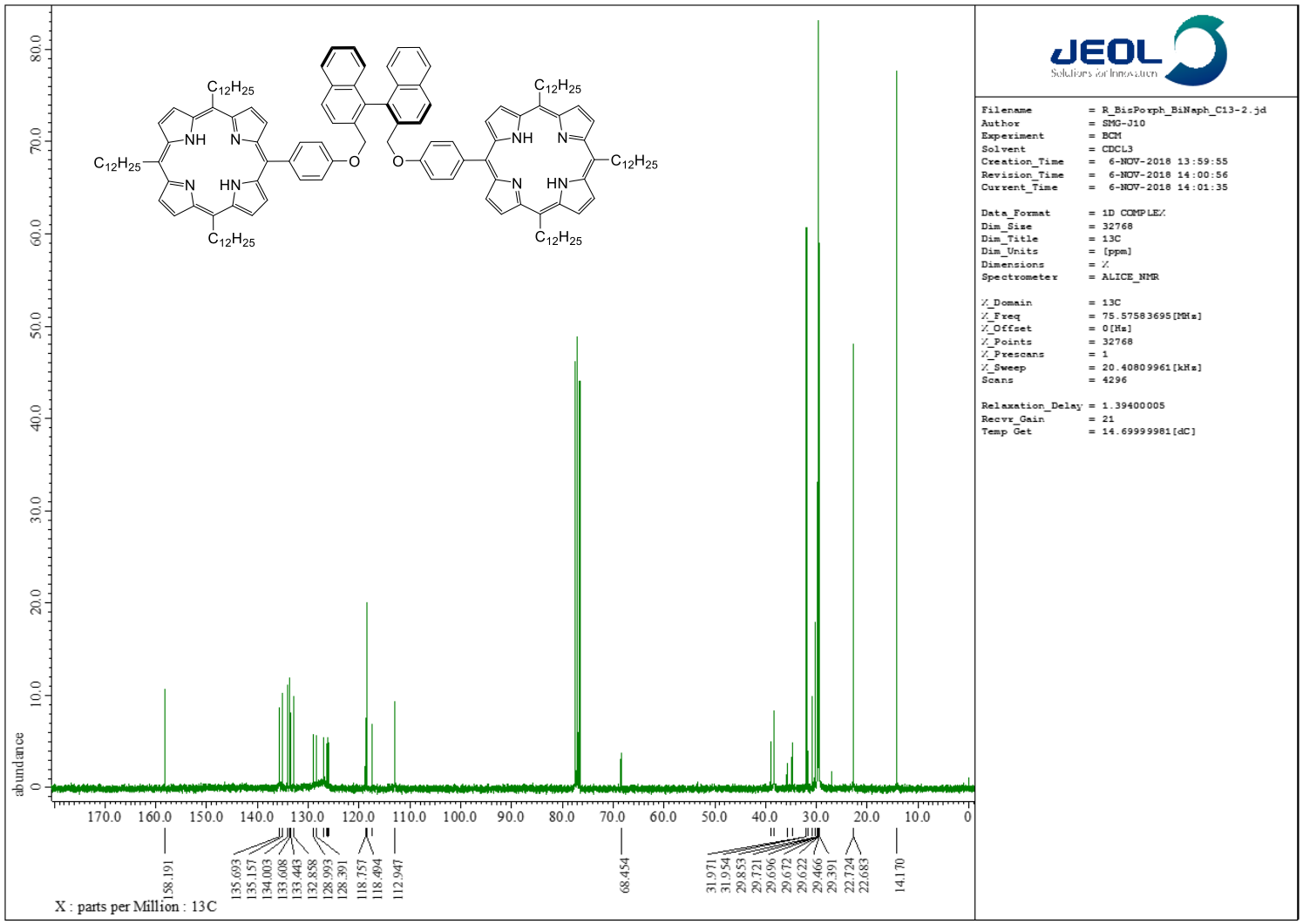
4 MALDI-TOF Mass Spectrum



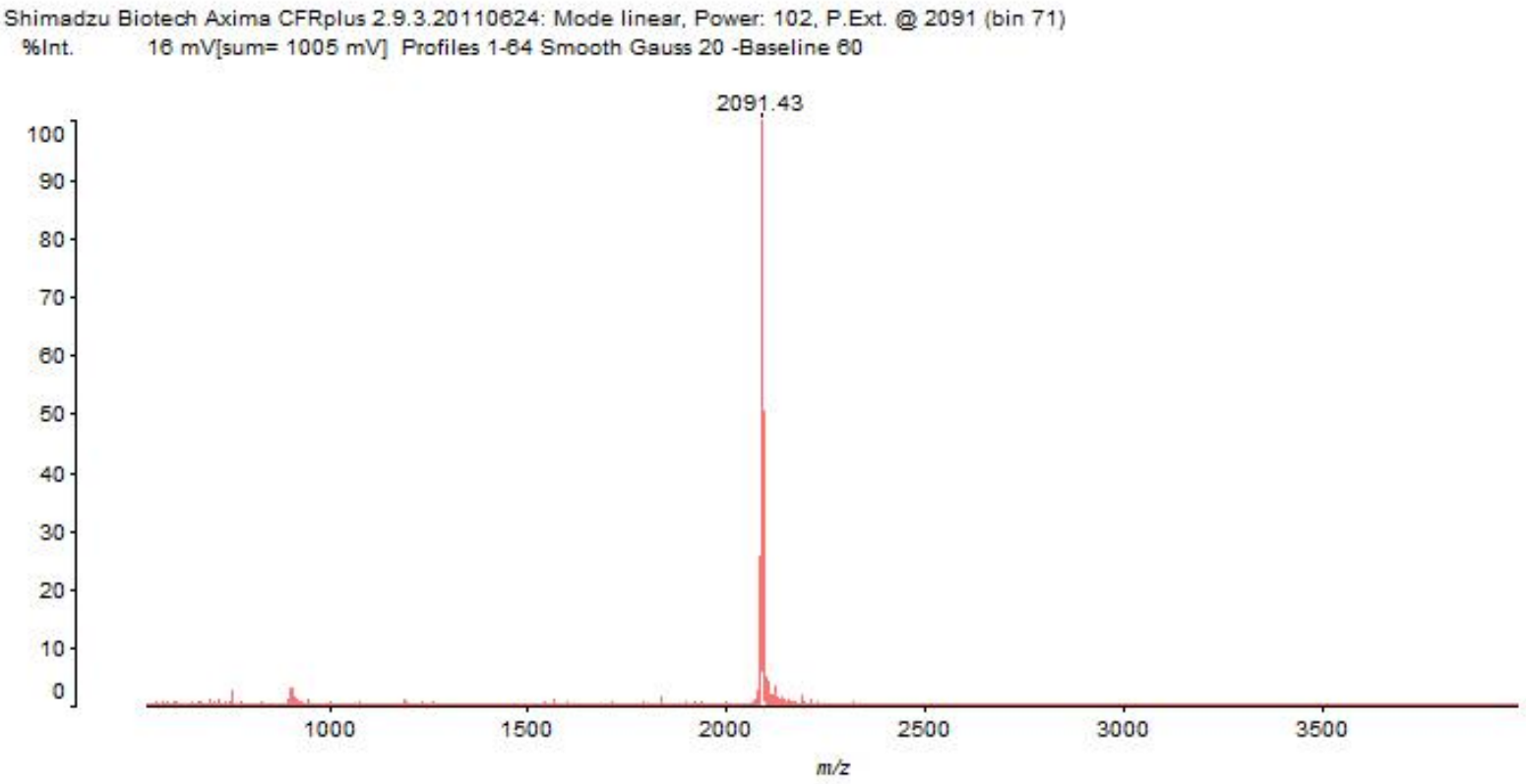
(*R*)-**1** ^{1}H NMR Spectrum



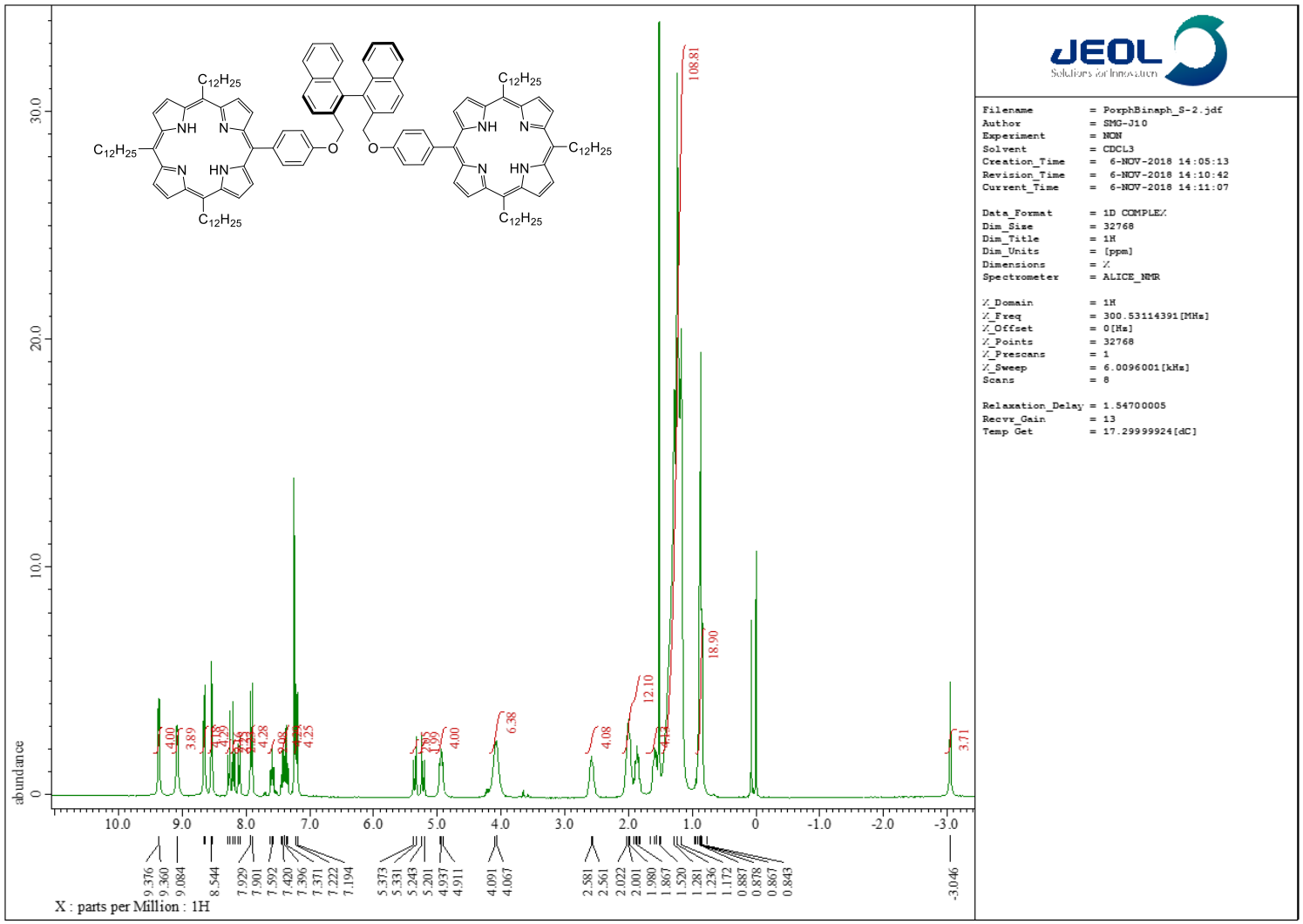
(*R*)-**1** ^{13}C NMR Spectrum



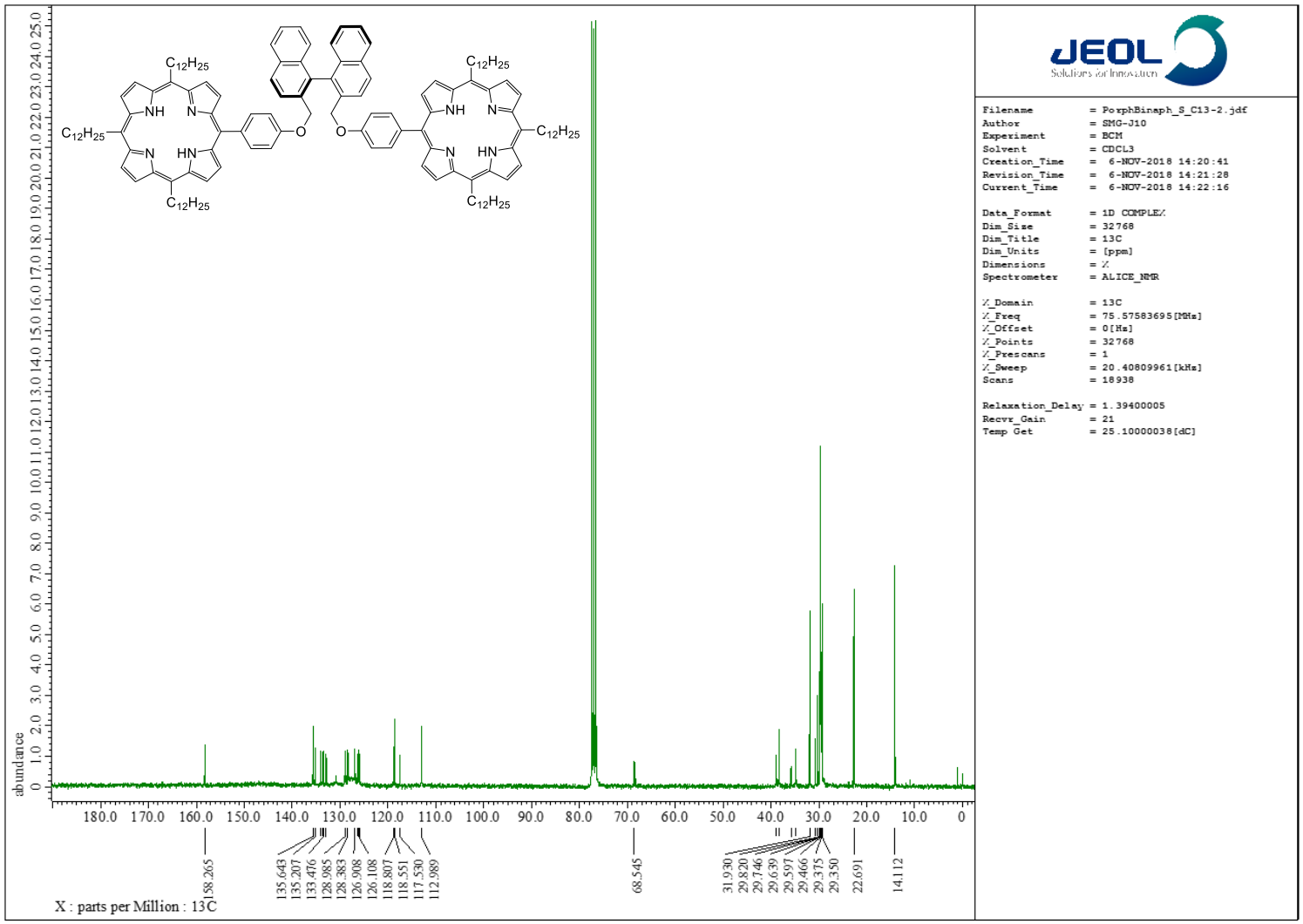
(*R*)-**1** MALDI-TOF Mass Spectrum



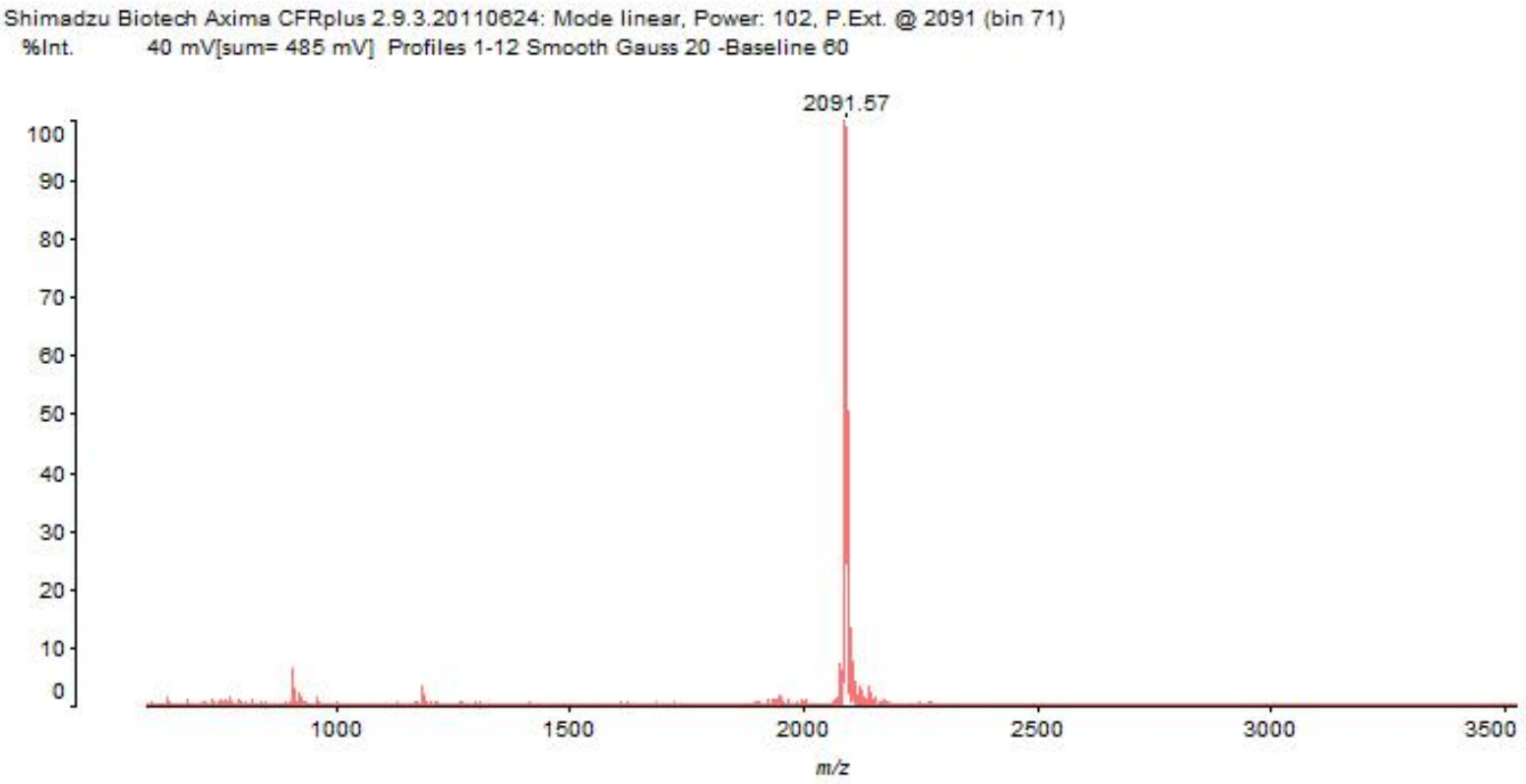
(*S*)-**1** ^{1}H NMR Spectrum



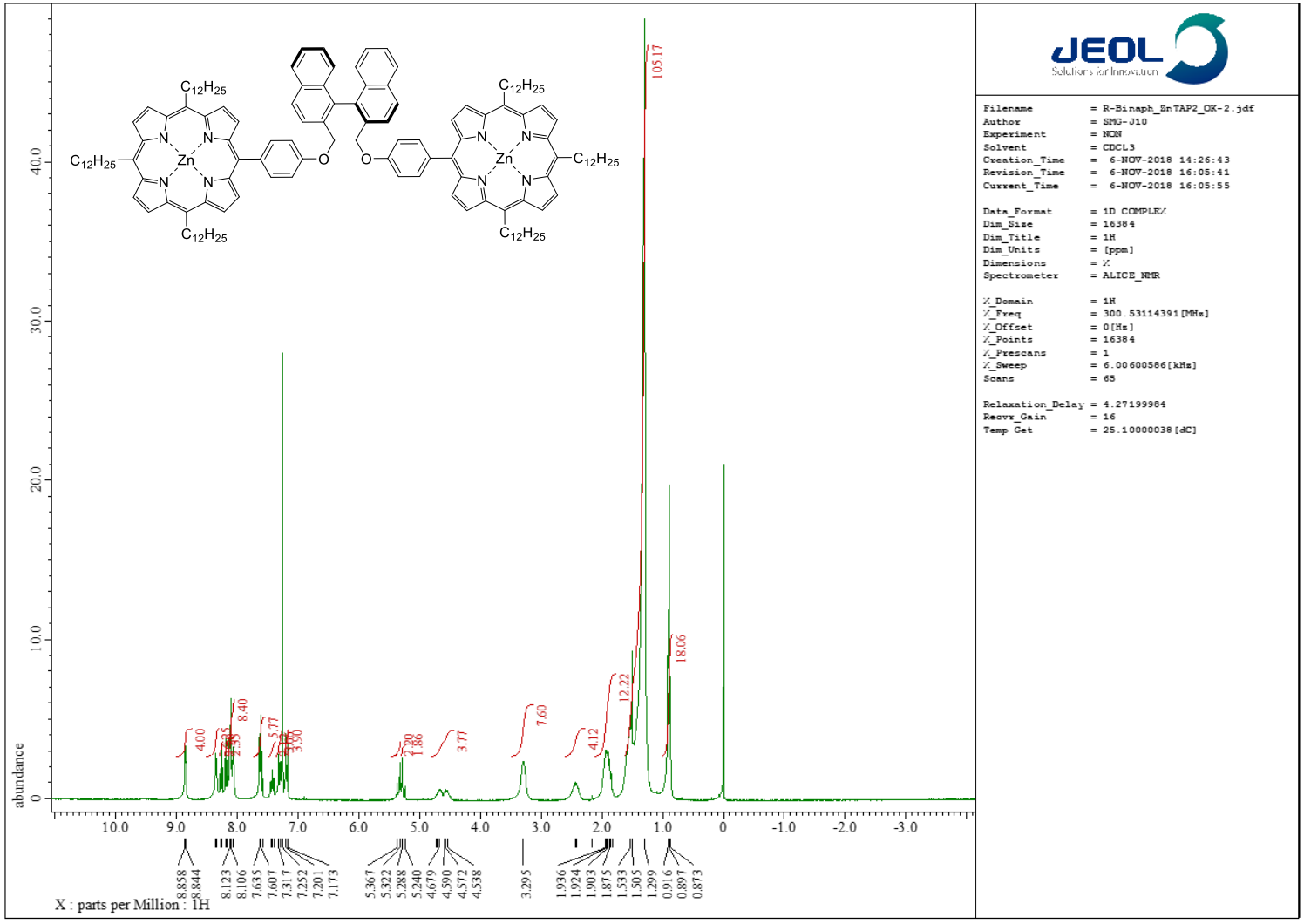
(*S*)-**1** ^{13}C NMR Spectrum



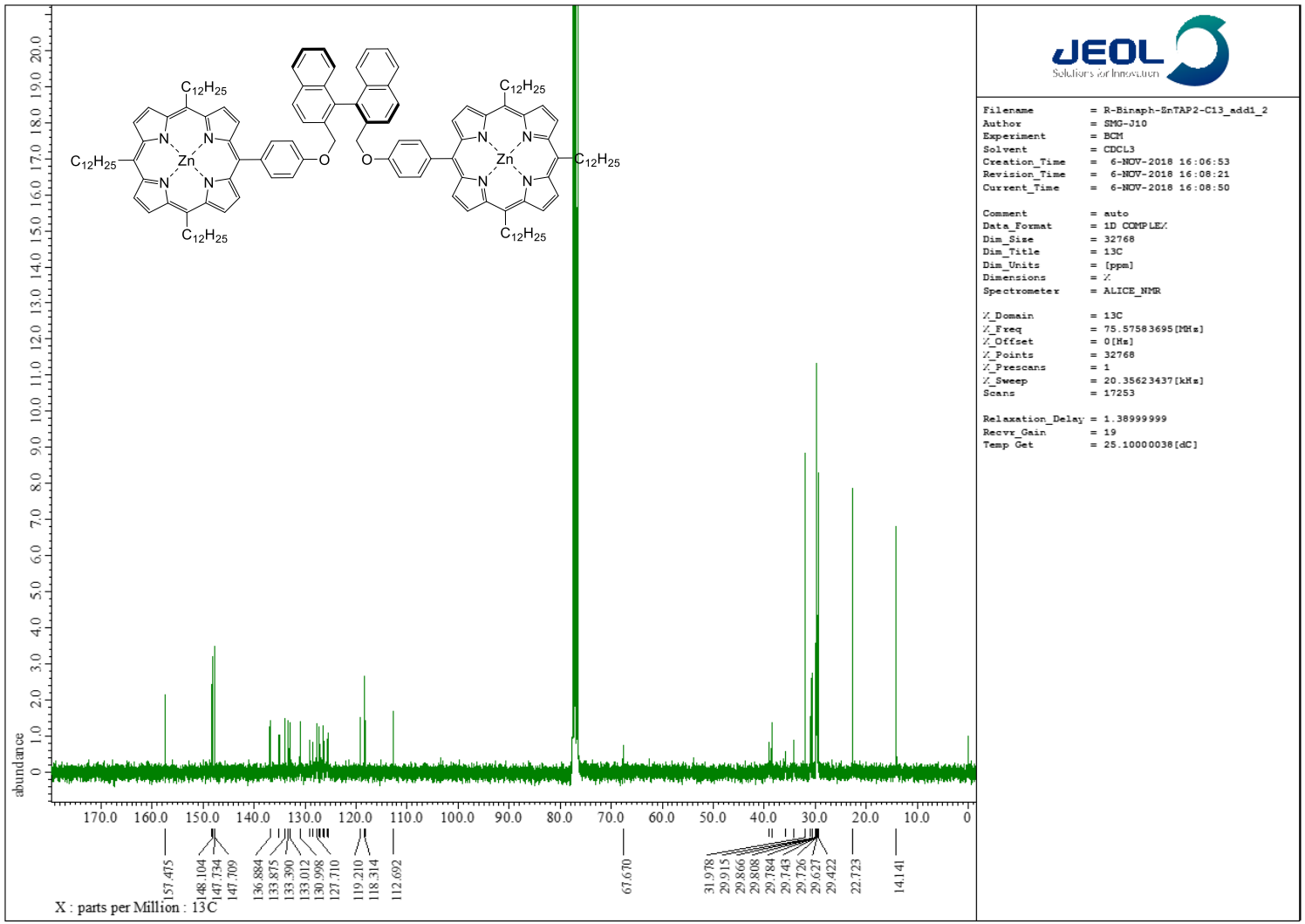
(*S*)-**1** MALDI-TOF Mass Spectrum



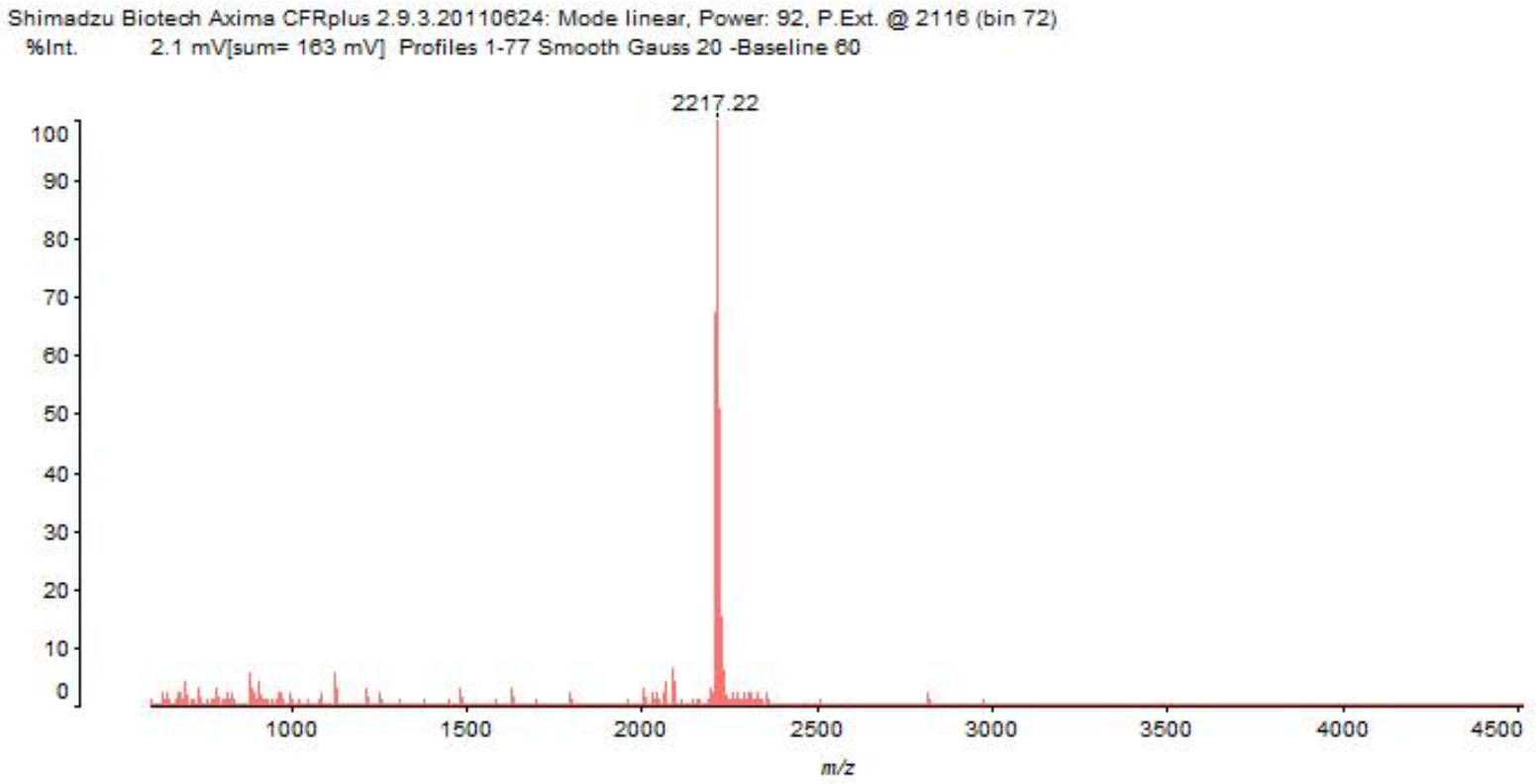
(*R*)-**2** ^{1}H NMR Spectrum



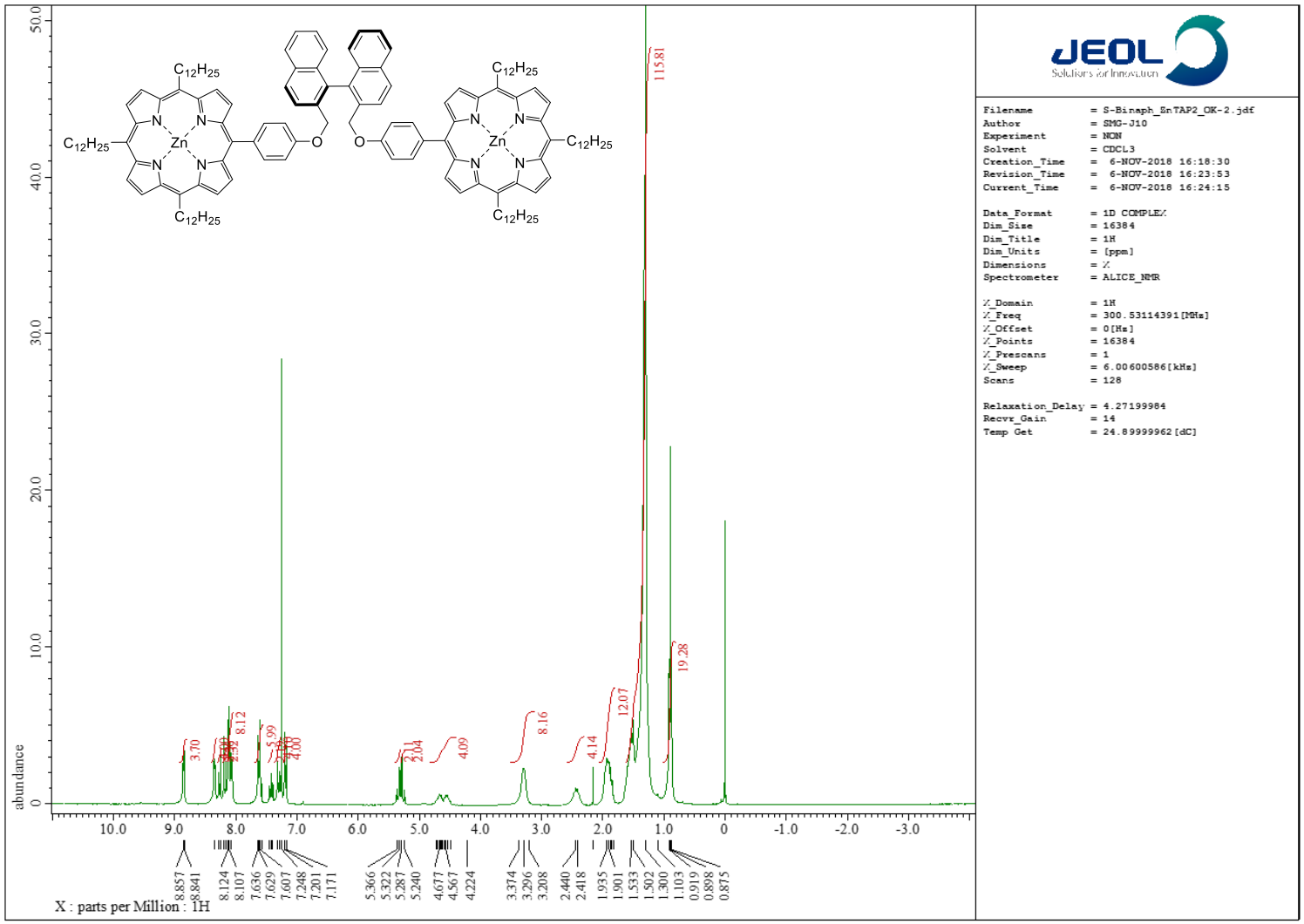
(*R*)-**2** ^{13}C NMR Spectrum



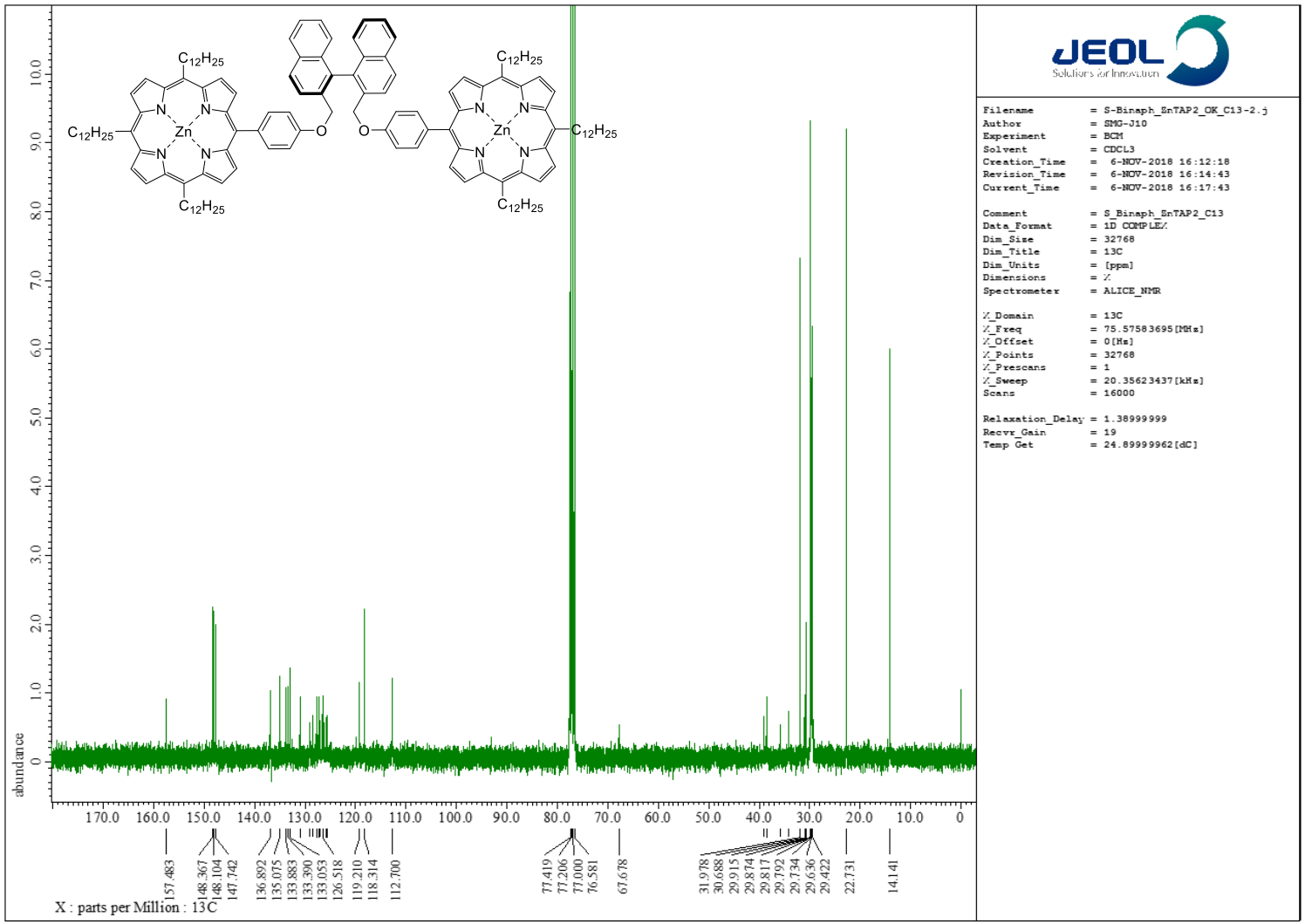
(*R*)-**2** MALDI-TOF Mass Spectrum



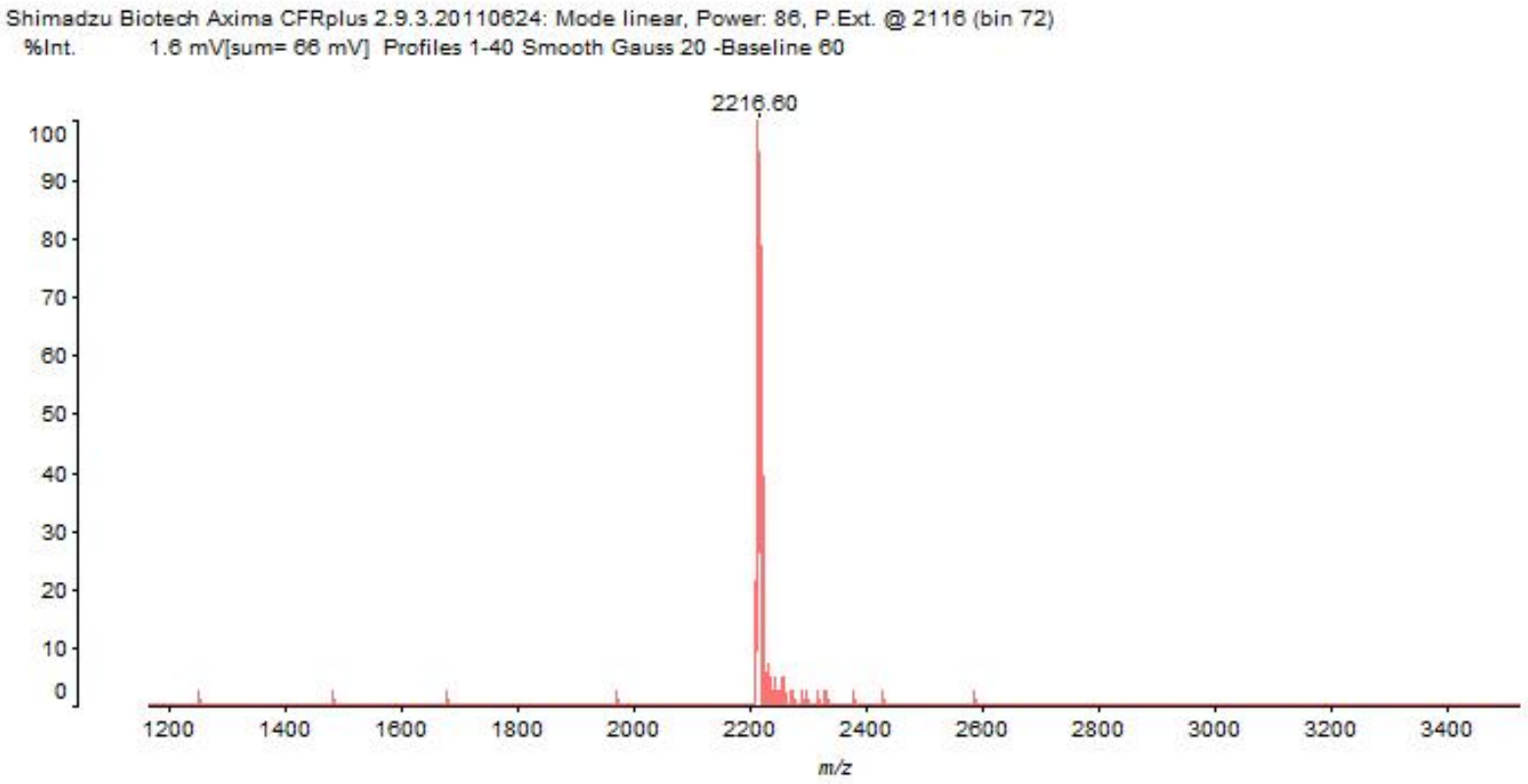
(*S*)-**2** ^{1}H NMR Spectrum



(*S*)-**2** ^{13}C NMR Spectrum



(*S*)-**2** MALDI-TOF Mass Spectrum



4. References

S1. Eckenroad, K. W., Thompson, L. E., Strein, T. G., Rovnyak, D. Proton NMR assignments for *R*,*S*-1,1'-binaphthol (BN) and *R*,*S*-1,1'-binaphthyl-2,2'-diyl hydrogen phosphate (BNDHP) interacting with bile salt micelles. *Magn. Reson. Chem.* 2007, 45, 72–75.