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Supporting Information

Tryptophan association in water driven by charge-transfer interactions with electron-deficient aromatic haptens

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1. General information

Reagents

Reagents were purchased and used without further purification unless otherwise noted. The solvents used were purified and dried following the standard methods. [1]

Purification of reaction crudes

Reactions were monitored by analytical thin layer chromatography using pre-coated aluminium-backed plates (0.2 mm silica gel 60 F254, Merck®) and visualized by UV light. Purification of compounds was performed using silica gel column chromatography (Chromagel 60A SdS. C.C. 70-200 µm) with solvent mixtures of increasing polarity as eluents and crystallization using different solvent mixtures.

Melting Points (m.p.)

Melting points were measured in a Leica Galen III microscope and are reported in ºC.

IR spectroscopy

IR spectra were recorded using a Nicolet IR100 with Nujol as a suspension.

UV-vis spectrometry

UV-vis spectra were recorded on a UNICAM (Heλios) spectrophotometer.

pH

pH was measured using the pH-meter Crison Basic 20.

NMR spectroscopy

^{1}H and ^{13}C NMR spectra were recorded at room temperature using Bruker models WP-200-SY, Varian 200 Mercury VS 2000 (200 MHz to ^{1}H and 50 MHz to ^{13}C) and Bruker Advance NEO 400 MHz with a Prodigy CPPBBO BB-H&F z-gradient cryo-probe (400 MHz to ^{1}H and 100 MHz to ^{13}C) spectrometers. Chemical shifts were reported in ppm with the solvent signal ($^{1}H/^{13}C$: deuterated chloroform $CDCl_3$ 7.26/77.2 ppm, dimethylsulfoxide DMSO-d_6 2.50/39.5 ppm or water D_2O-d_2 4.79 ppm) and tetramethylsilane (TMS 0.00 ppm) as an internal standard using reported shifts. [2] Coupling constants (*J*) were reported in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; quin, quintet; sext, sextet; m, multiplet; br, broad.

Mass spectrometry

Mass spectra were recorded on a quadrupole-TOF Applied Biosystems QSTAR XL and Waters ZQ 4000 spectrometers using electrospray ionization (ESI) or electronic impact (EI).

X-ray diffraction studies

- *Procedure for the single crystal preparation*
  Single crystals suitable for X-ray diffraction measurements were obtained by slowly evaporating solutions of stoichiometric mixtures of L-tryptophan and the receptor (**3**, **4**, **5** or **6**). 30 mg of L-tryptophan (0.15 mmol) and the equimolar amount of the corresponding receptor were dissolved in 2.5 mL of a water/methanol or water/THF mixture in a clean and dry 10 mL glass vial. The mouth of the glass vial was covered with a cap having a small hole and kept it for slow evaporation at room temperature. At the end of the process, single crystals were obtained after around 5-6 days.

- *X-Ray Crystallography*

  Suitable single crystals of complexes of L-tryptophan with receptors **3**, **4**, **5** and **6** were mounted on glass fibre for data collection on a Bruker Kappa APEX II diffractometer. Data were collected at 298(2) K using Cu K_α radiation (λ = 1.54178 Å) and *ω* scan technique, and were corrected for Lorentz and polarization effects. The detector was placed at a distance of approximately 37.5 mm from the crystal.
  A series of narrow frames of data were collected with a scan width of 0.5º in *ω* and an exposure time of 10 s per frame. The data were integrated with SAINT [3] to a resolution of 0.78 Å using a narrow-frame algorithm. Data were corrected for absorption effects using the multi-scan method using SADABS. [4]
  Subsequent structure solution and refinement were carried out with SHELXT and SHELXL, respectively. [5, 6] The structures were solved by direct methods combined with difference Fourier synthesis and refined by full-matrix least-squares procedures, with anisotropic thermal parameters in the last cycles of refinement for all non-hydrogen atoms. The refinement was based on F^2 for all reflections, weighted R factors (*wR*) and goodness-of-fit (GoF) values are based on F^2, while conventional R factors (R) are based on F. The $Fo^2 > 2\sigma(Fo^2)$ criterion was used only for calculating R factors and it is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F. Scattering factors were taken from the International Tables for Crystallography. [7] Hydrogen atom positions were calculated by geometrical methods and refined as a riding model. Complex of L-tryptophan and 2,4,6-trinitrobenzene sulfonic acid (**3**) crystallizes with three molecules of water. Complex of L-tryptophan and 3,5-dinitrobenzoic acid (**4**) crystallizes with one methanol solvent molecule in the asymmetric unit. Complex of L-tryptophan and *N,N´*-bis(glycinyl)pyromellitic diimide (**6**) crystallizes with two water solvent molecules; it should be noticed that hydrogen atoms of water molecules are not shown in the structural formula of the complex, as they were not located by X-ray diffraction.
  Mercury 4.2.0 program was used for analysis and molecular and crystal structure drawings preparation. [8]

  The CCDC numbers assigned for the crystal structures are: 2179406 (complex Trp-2,4,6-trinitrobenzene sulfonic acid), 2179399 (complex Trp-3,5-dinitrobenzoic acid), 2179404 (complex Trp-2,4,6-trinitrobenzoic acid) and 2179405 (complex Trp- *N,N´*-bis(glycinyl)pyromellitic diimide).

^{1}H NMR titration experiments

A typical procedure for ^{1}H NMR titrations is described. A solution of the receptor (5 mM, 1.5 mL) in H_2O or DMSO-d_6 was prepared and a volume of 500 µL was added to a standard NMR tube. The ^{1}H NMR spectrum of the sample was collected at 298 K. A solution of the guest (0.05 M) was prepared by dissolving the required amount of guest in the remaining solution (1.0 mL) of receptor. Aliquots of this solution were then added to the NMR tube, mixing well after each addition, and recording the corresponding ^{1}H NMR spectrum. The concentration of the receptor was thus kept constant during the titration as the guest solution also contained the receptor at its initial concentration. During the course of the titration, some of the proton signals of the receptor are shifted and these chemical shifts (δ ppm) were plotted against the ratio of concentrations [Guest]/[Host]. Data were fitted using the online fitting tool Bindfit. [9] Dioxane was used as internal standard.

UV-vis titration experiments

A typical procedure for UV-vis titrations is described. Two stock solutions (30 mM, 10 mL) in H_2O of receptor and guest were prepared. For the UV-vis titration experiments, samples were prepared adding 1.0 mL of the stock solution of the receptor (30 mM) in the optical cell and diluting three times to a final host concentration 10 mM. The 2.0 mL added volume comes from mixing calculated volumes of water and guest stock solution, to achieve different ratio of concentrations [Guest]/[Host. Thus, the concentration of the receptor was kept constant during the titration (10mM) while the concentration of the guest was gradually increased. Data were fitted using the online fitting tool Bindfit. [9]

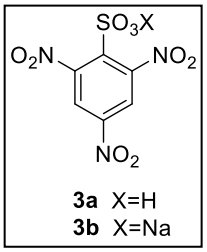
Modelling studies

Theorical studies were carried out using GAMESS interface for Chem3D 19.1 software [10] using the semiempirical method AM1 and theoretical Hartree-Fock.

2. Synthesis and Characterization

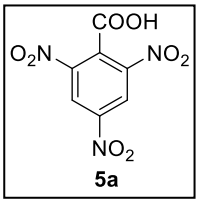
2.1. Synthesis of receptors

- **Sodium 2,4,6-trinitrobenzene sulfonate (3b) and 2,4,6-trinitrobenzene sulfonic acid (3a)**



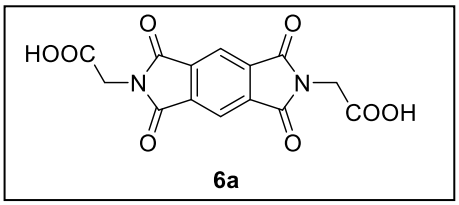
These compounds were prepared according to published literature. [11]. Anhydrous sodium bisulfite (1.0 g, 7.9 mmol) was added to a solution of 2-chloro-1,3,5-trinitrobenzene (1.0 g, 4.0 mmol) in 10 mL of absolute ethanol and refluxed for 8 h. The reaction mixture was then filtered under vacuum, the salts were discarded, and the filtrate was evaporated and crystallized from methanol yielding compound **3b** (1.1 g; 87%) as orange crystals. 2,4,6-trinitrobenzene sulfonic acid (**3a**) was obtained when **3b** was dissolved in hot concentrated HCl. The precipitate formed immediately upon cooling was removed and **3b** was obtained as white crystals after 2 hours in the cold.

- **2,4,6-trinitrobenzoic acid (5a)**



A suspension of 2,4,6-trinitrotoluene (4.0 g, 18 mmol), boric acid (0.2 g, 3.2 mmol) and 98% sulfuric acid (20 mL) was mixed in a two-necked flask equipped with a magnetic stirrer and a thermometer and was heated at 45 ºC in a closed system. After the suspension became homogenous, CrO_3 (5.0 g, 50 mmol) was gradually added for one hour and the mixture was maintained at that temperature for 2 h. The reaction mixture was then poured in an Erlenmeyer flask with ice and filtered, yielding compound **5a** (3.5 g, 75%). The spectroscopic properties of compound **5** were in agreement with the published data. [12]

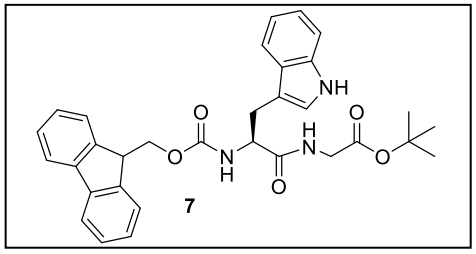
- ***N,N´*-bis(glycinyl)pyromellitic diimide (6a)**



Freshly sublimed 1,2,4,5-benzenetetracarboxylic acid anhydride (1.0 g, 4.6 mmol) and glycine (1.0 g, 13 mmol) were dissolved in 20 mL of acetic acid under reflux. After refluxing the solution for 90 minutes, the reaction mixture was added over 10 mL of water and the resulting precipitate was filtered off affording compound **6a** (1.5 g, 98%) as a white solid whose spectroscopic properties were in agreement with the published data. [13]

2.2. Synthesis of Trp-Gly-Trp (10)

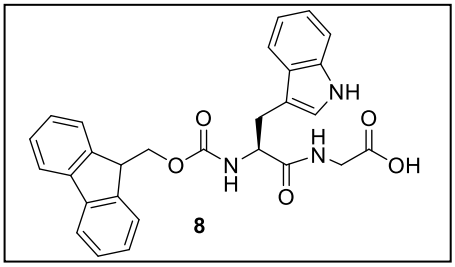
- ***N*-Fmoc-Trp-Gly-OtBu (7)**



Fmoc-Trp-OH (1.0 g, 2.3 mmol) and Gly-OtBu • HCl (393 mg, 2.3 mmol) were suspended in 20 mL of CH_2Cl_2 at room temperature and *N*-ethyldiisopropylamine (303 mg; 2.3 mmol) and DCC (531 mg, 2.53 mmol) were added consecutively. After 10 minutes the reaction was filtered, and the filtrate was evaporated under reduced pressure. The crude reaction mixture was purified by column chromatography over silica gel, eluting with CH_2Cl_2:EtOAc mixtures of increasing polarity. Compound **7** (1.08 g, 85%) was obtained as a white solid. m.p.: 93 ºC. IR (nujol, υ in cm^{-}

^{1}): 3410, 3306, 2916, 1716, 1658, 1229, 1158, 730.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (br s, NH), 7.76 (d, *J* = 7.6 Hz, 2H), 7.53 (m, 2H), 7.43 – 7.34 (m, 3H), 7.29 (m, 4H), 7.23 – 7.17 (t, *J* = 7.2 Hz, 1H), 7.14 (t, *J* = 7.3 Hz, 1H), 6.20 (br s, NH), 5.49 (br s, NH), 4.54 (m, 1H), 4.41 (m, 2H), 4.19 (t, *J* = 7.0 Hz, 1H), 3.91 – 3.72 (m, 2H), 3.37 (m, 1H), 3.21 (dd, *J* = 14.6, 7.1 Hz, 1H), 1.42 (s, 9H).^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4 (2C), 168.5 (C), 143.9 (C), 143.9 (C), 141.5 (2C), 141.4 (C), 136.3 (C), 127.9 (2CH), 127.2 (2CH), 125.3 (2CH), 123.4 (CH), 122.5 (CH), 120.1 (2CH), 120.1 (CH), 118.9 (CH), 111.4 (CH), 111.4 (C) 82.5 (C), 67.3 (CH_2), 55.6 (CH), 47.3 (CH), 42.2 (CH_2), 28.5 (CH_2), 28.1 ($3CH_3$).HRMS (ESI+): Calculated for $C_{32}H_{34}N_3O_5$ $[M + H]^+$ 540.2493, found 540.2492.

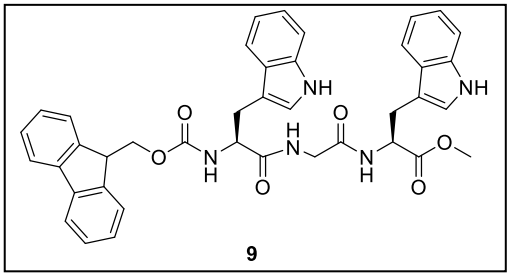
- ***N*-Fmoc-Trp-Gly-OH (8)**



8

Compound **7** (1.1 g, 2.0 mmol) was treated with trifluoroacetic acid (0.8 mL, 10.5 mmol) in a round bottom flask equipped with a gas bubbler and heated at 70 ºC for 10 minutes. After this time, the solvent was evaporated under reduced pressure and then, ethyl acetate (5 mL) was added to the crude and again concentrated under vacuum to remove possible traces of remaining acid. Compound **8** (0.9 g, 94%) was obtained as a brownish solid which was used without further purification in the next step. m.p.: 108 ºC; IR (nujol, υ in cm^{-1}): 3397, 3312, 2916, 1716, 1658, 1190, 736. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (br s, NH), 7.73 (d, *J* = 7.8 Hz, 2H), 7.48 (m, 2H), 7.40 – 7.33 (m, 3H), 7.29 – 7.19 (m, 4H), 7.10 (m, 2H), 6.94 (br s, NH), 6.60 (br s, NH), 4.60 (m, 1H), 4.47 – 4.24 (m, 2H), 4.12 (t, *J* = 7.0 Hz, 1H), 3.98 – 3.70 (m, 2H), 3.42 – 3.06 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6 (C), 172.2 (2C), 143.8 (C), 143.7 (C), 141.4 (C),141.4 (C), 136.3 (C), 127.9 (2CH), 127.5 (C), 127.3 (2CH), 125.2 (2CH), 123.8 (CH),122.4 (CH), 120.2 (2CH), 119.9 (CH), 118.6 (CH), 111.5 (C), 111.5 (CH), 55.6 (CH), 47.1 (CH), 41.4 (CH_2), 33.3 (CH_2), 24.8 (CH_2). HRMS (ESI+): Calculated for $C_{28}H_{26}N_3O_5$ $[M + H]^+$ 484.1867, found 484.1864.

- ***N*-Fmoc-Trp-Gly-Trp-OMe (9)**

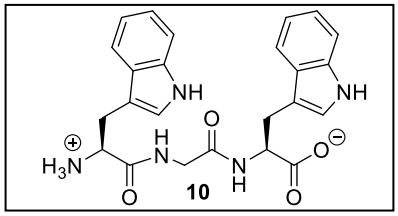


9

First, Trp-OMe • HCl (1.0 g, 3.9 mmol) was treated with an aqueous solution of sodium carbonate (883 mg, 8.3 mmol; dissolved in the minimum amount of water) and ethyl acetate (10 mL). After stirring for 10 minutes, the phases were separated, the organic layer was dried over anhydrous sodium sulfate, filtered, and the solvent was evaporated under reduced pressure yielding Trp-OMe (820 mg, 95%) as a white solid. Then, compound **8** (300 mg, 0.6 mmol) and Trp-OMe (135 mg, 0.6 mmol) were dissolved in 15 mL of CH_2Cl_2 and DCC (141 mg, 0.7 mmol) was slowly added. The reaction mixture was maintained in a covered flask, stirring at room temperature for 30 minutes. Then, the resultant mixture was filtered to eliminate N,N′-diciclohexylurea (DCU) and the filtrate acidified with 10 mL of HCl 1M. The organic layer was basified with Na_2CO_3, dried over anhydrous sodium sulfate, filtered, and the solvent was evaporated under reduced pressure. The crude reaction mixture was then purified by column chromatography over silica gel, eluting with CH_2Cl_2:EtOAc mixtures of increasing polarity (starting with 90:10) and the deep yellow fraction was collected. Compound **9** (273 mg, 64%) was obtained as a pale-yellow solid. m.p.: 115 ºC**.** IR (nujol, υ in cm^{-1}): 3390, 3299, 2916, 1729, 1651, 1262, 749. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (br s, NH), 7.92 (s, NH),

7.75 (d, *J* = 7.6 Hz, 2H), 7.53 – 7.46 (d, *J* = 7.5 Hz, 2H), 7.45 – 7.34 (m, 3H), 7.33 – 7.22 (m, 6H), 7.22 – 7.03 (m, 4H), 6.89 (d, *J* = 2.3 Hz, 1H), 6.56 (d, NH), 6.21 (br s, NH), 5.38 (d, NH), 4.81 (dd, *J* = 13.0, 5.5 Hz, 1H), 4.50 – 4.25 (m, 3H), 4.17 – 4.07 (t, *J* = 7.5 Hz, 1H), 3.77 (dd, *J* = 16.7, 5.6 Hz, 1H), 3.70 – 3.60 (m, 4H), 3.34 – 3.18 (m, 3H), 3.10 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3 (C), 172.1 (2C), 168.4 (C), 143.9 (C), 143.8 (C), 141.5 (3C), 136.3 (C), 136.2 (C), 127.9 (2CH), 127.6 (C), 127.2 (2CH), 125.2 (2CH), 123.5 (2CH), 122.5 (CH), 122.4 (CH), 120.2 (2CH), 120.0 (CH), 119.8 (CH), 118.7 (CH), 118.5 (CH), 111.6 (CH), 111.6 (C), 111.5 (CH), 109.7 (C), 67.2 (CH_2), 55.7 (CH), 52.8 (CH_3), 52.6 (CH), 47.2 (CH), 43.3 (CH_2), 28.1 (CH_2), 27.4 (CH_2). HRMS (ESI+): Calculated for $C_{40}H_{38}N_5O_6$ $[M + H]^+$ 684.2817, found 684.2814.

- **Trp-Gly-Trp (10)**



A solution of NaOH (142 mg, 3.6 mmol) in 10 mL of MeOH was added to compound **9** (973 mg, 1.4 mmol) at room temperature. After 5 minutes the reaction mixture was concentrated under vacuum and partitioned with 10 mL of H_2O and 10 mL of CH_2Cl_2. The organic layer was discarded, and potassium dihydrogen phosphate was added to the aqueous layer and the solvent was evaporated under vacuum. After addition of absolute EtOH and sonication, the solid was filtered off and the filtrate evaporated under reduced pressure yielding compound **10** (450 mg, 71%) as an orange-yellowish solid.m.p.: 156 ºC. IR (nujol, υ in cm^{-1}): 3591, 3468, 2923, 1761, 1690, 723. ^{1}H NMR (400 MHz, D_2O) δ 7.54 (m, 2H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.22 – 7.12 (m, 2H), 7.09 (m, 4H), 4.49 (dd, *J* = 7.5, 4.9 Hz, 1H), 3.60 – 3.45 (m, 3H), 3.31 (dd, *J* = 14.8, 4.8 Hz, 1H), 3.10 (dd, *J* = 14.8, 7.6 Hz, 1H), 2.99 (d, *J* = 6.7 Hz, 2H).^{13}C NMR (100 MHz, D_2O) δ 178.1 (C), 175.5 (C), 169.9(C), 136.1 (C), 136.0 (C), 127.3 (C), 126.8 (C), 124.6 (CH), 124.1 (CH), 121.9 (CH), 121.7 (CH), 119.3 (CH), 119.2 (CH), 118.4 (CH), 118.4 (CH), 111.8 (CH), 111.8 (CH), 110.0 (C), 108.6 (C), 55.7 (CH), 54.7 (CH), 42.4 (CH_2), 29.0 (CH_2), 27.2 (CH_2). HRMS (ESI+): Calculated for $C_{24}H_{26}N_5O_4$ $[M + H]^+$ 448.1979, found 448.1977.

2.3. NMR spectra

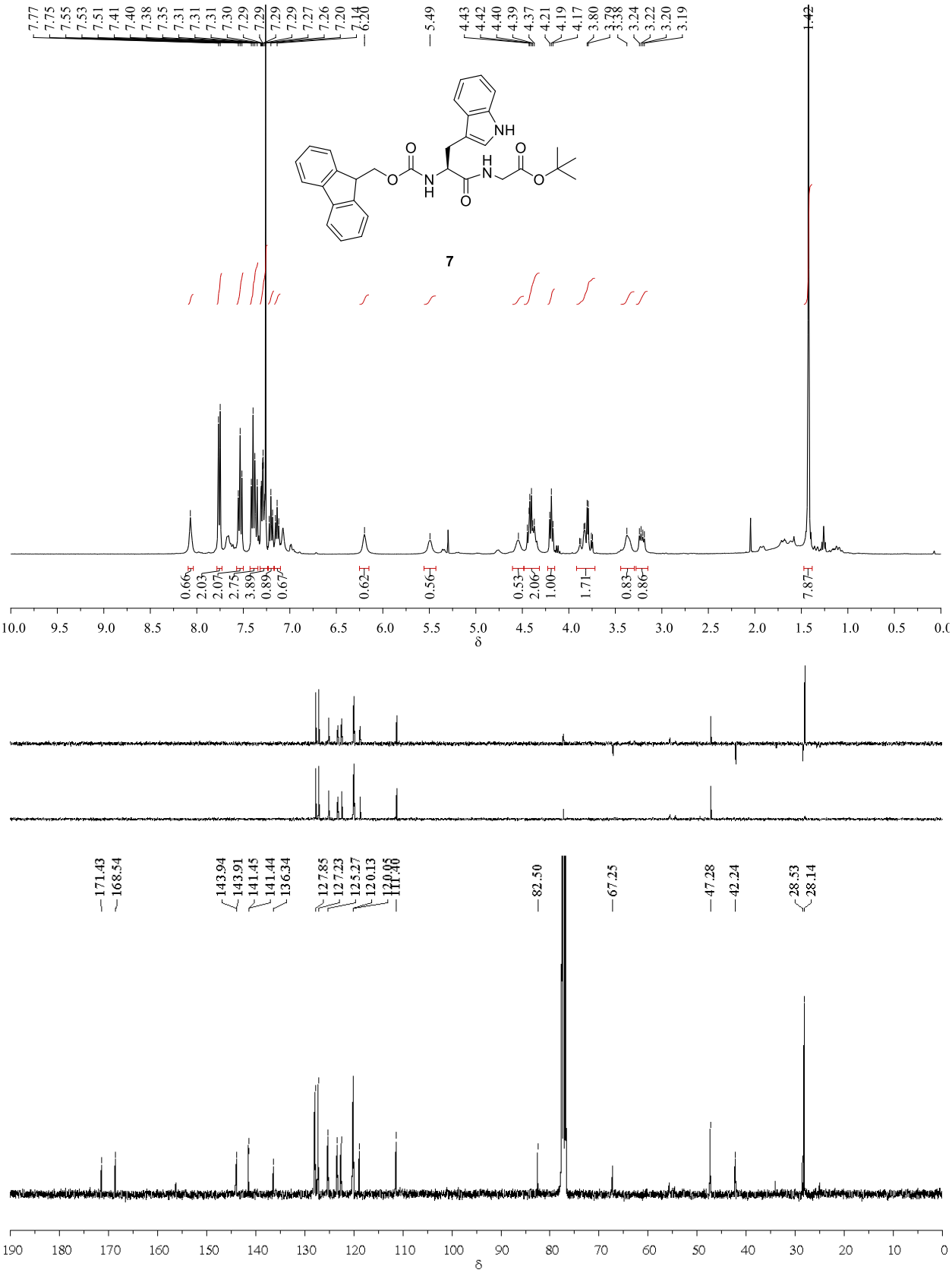
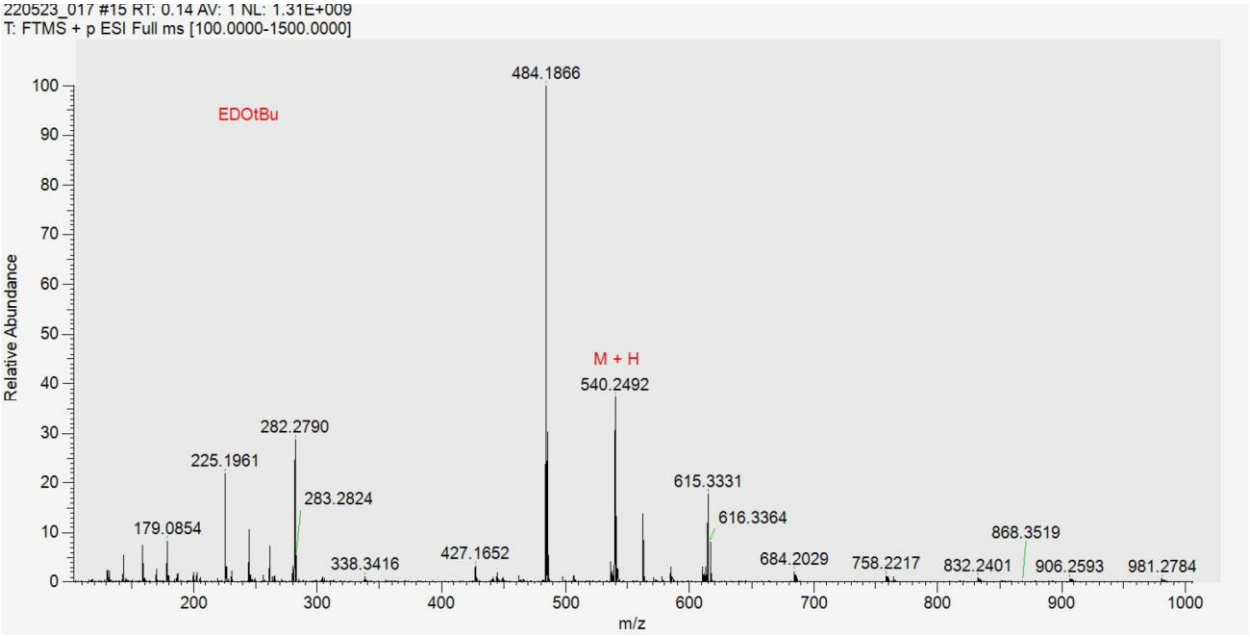


Figure S1. *^{1}H and ^{13}C spectra of N-Fmoc-Trp-Gly-OtBu (**7**) in $CDCl_3$.*



Display Formula	S Fit	RDB	Delta [mmu]	Theo. mass	Combined Score	# Matched Iso.
$C_{32}H_{34}O_5N_3$	52,62	17,5	-0,09	540,2493	96,9	4

Figure S2. *Mass spectrum of N-Fmoc-Trp-Gly-OtBu (**7**).*

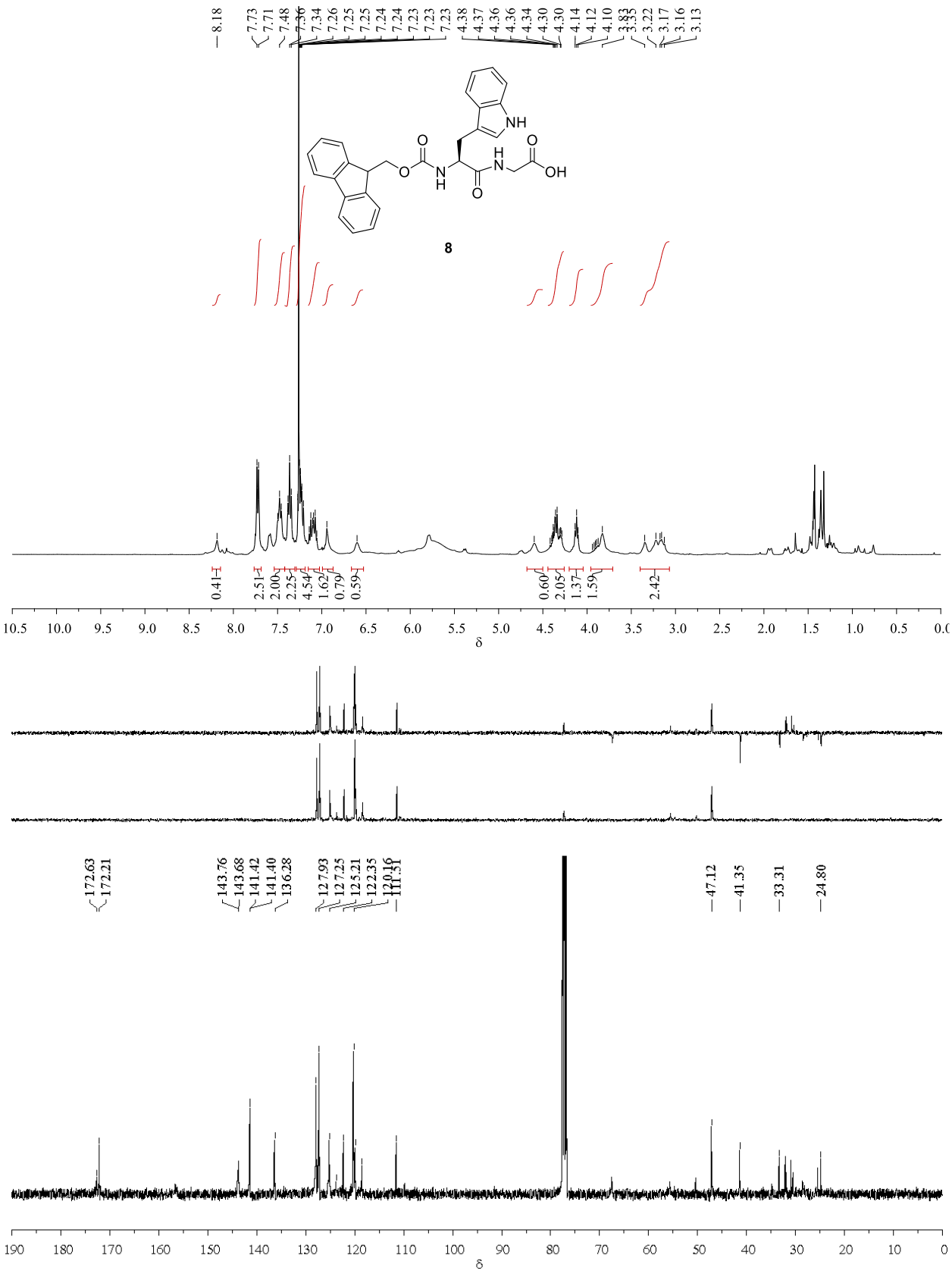
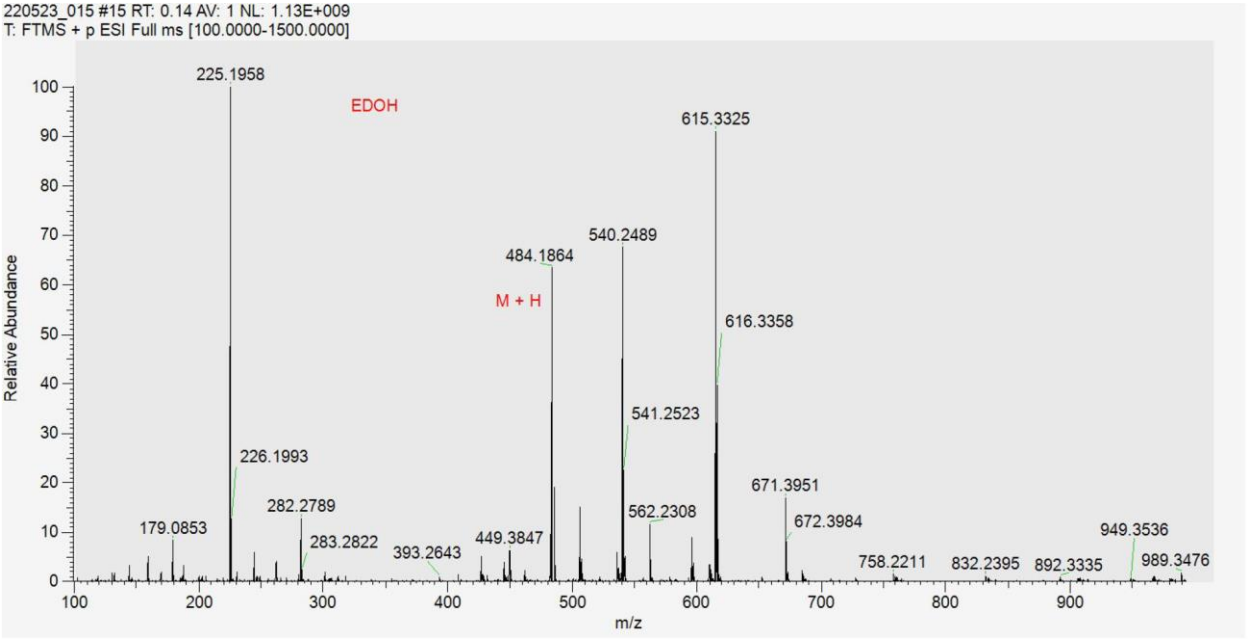


Figure S3. *^{1}H and ^{13}C spectra of N-Fmoc-Trp-Gly-OH (**8**) in $CDCl_3$.*



Display Formula	S Fit	RDB	Delta [ppm]	Theo. mass	Combined Score	# Matched Iso.
$C_{28}H_{26}O_5N_3$	76,09	17,5	-0,61	484,1867	94,02	4

Figure S4. *Mass spectrum of N-Fmoc-Trp-Gly-OH (**8**).*

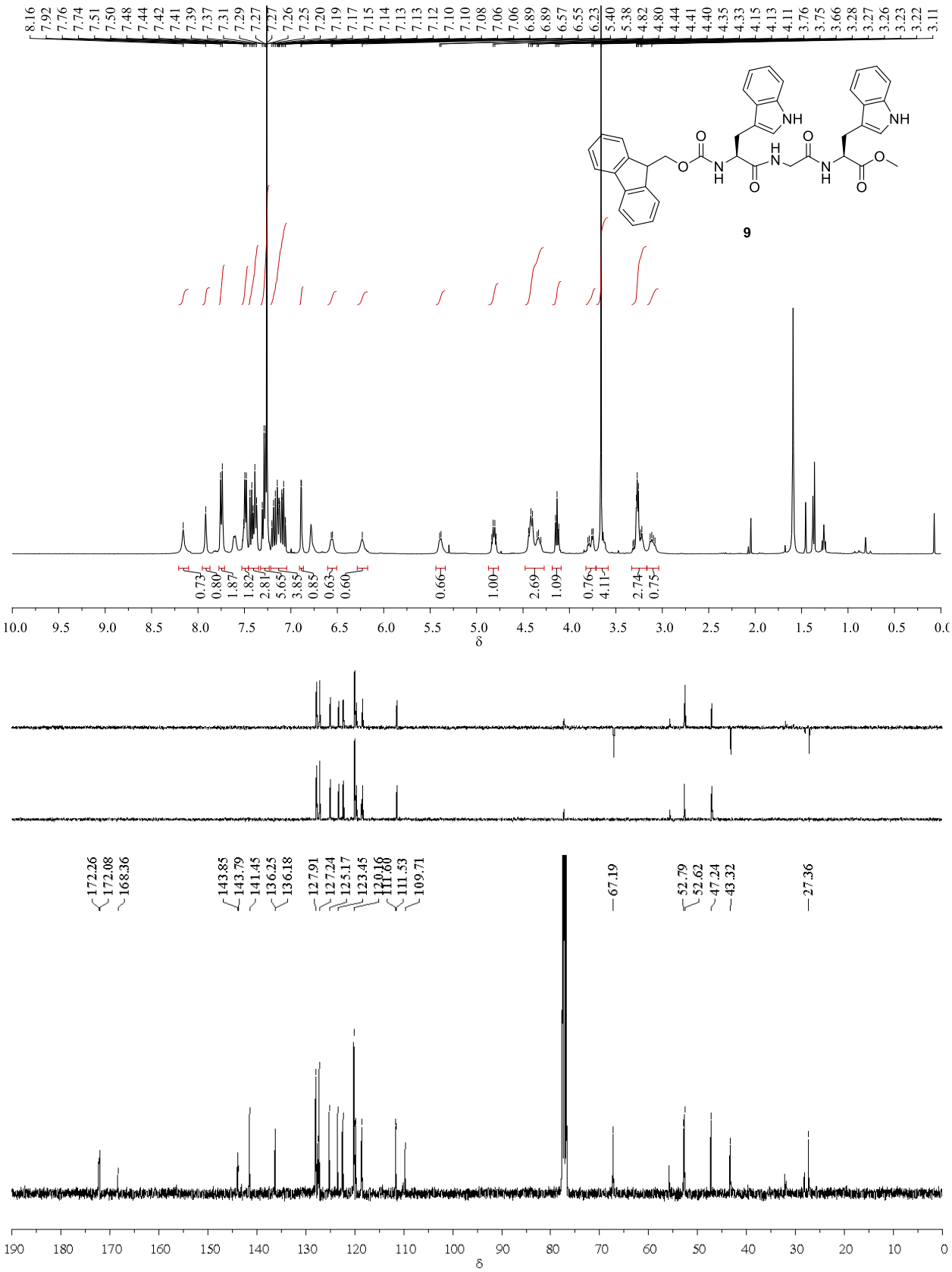
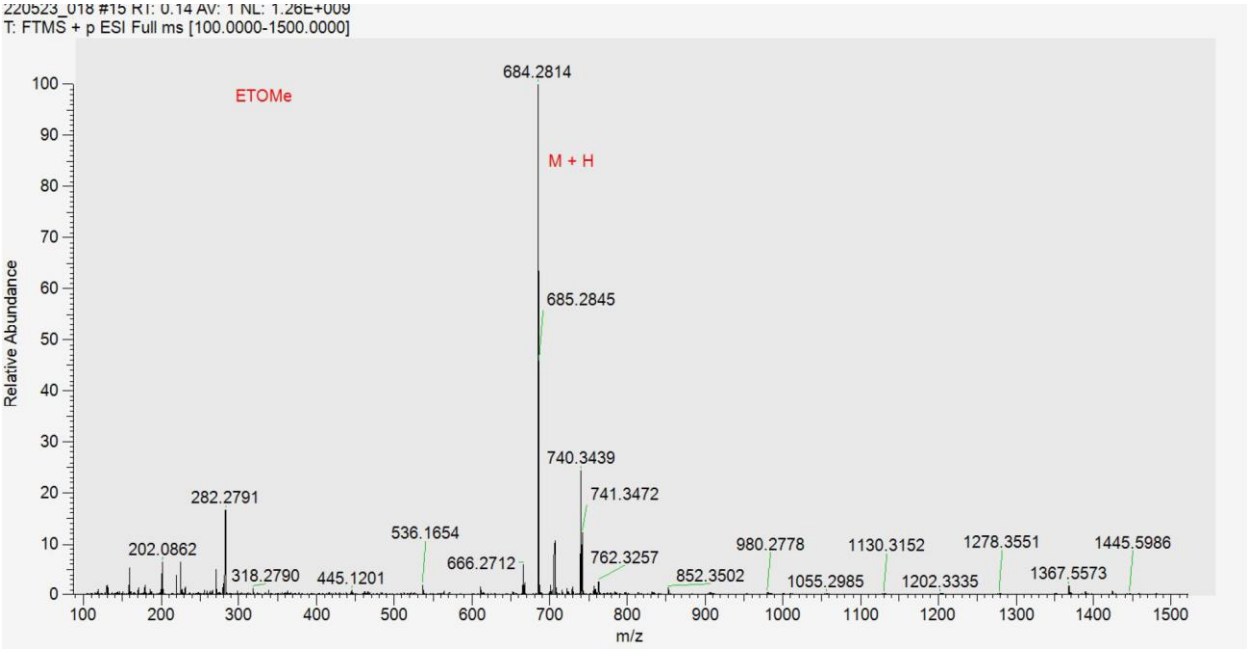


Figure S5. *^{1}H and ^{13}C spectra of N-Fmoc-Trp-Gly-Trp-OMe (**9**) in $CDCl_3$.*



Display Formula	S Fit	RDB	Delta [ppm]	Theo. mass	Combined Score	# Matched Iso.
$C_{40}H_{38}O_6N_5$	92,34	24,5	-0,42	684,28166	98,49	5

Figure S6. *Mass spectrum of N-Fmoc-Trp-Gly-Trp-OMe (**9**).*

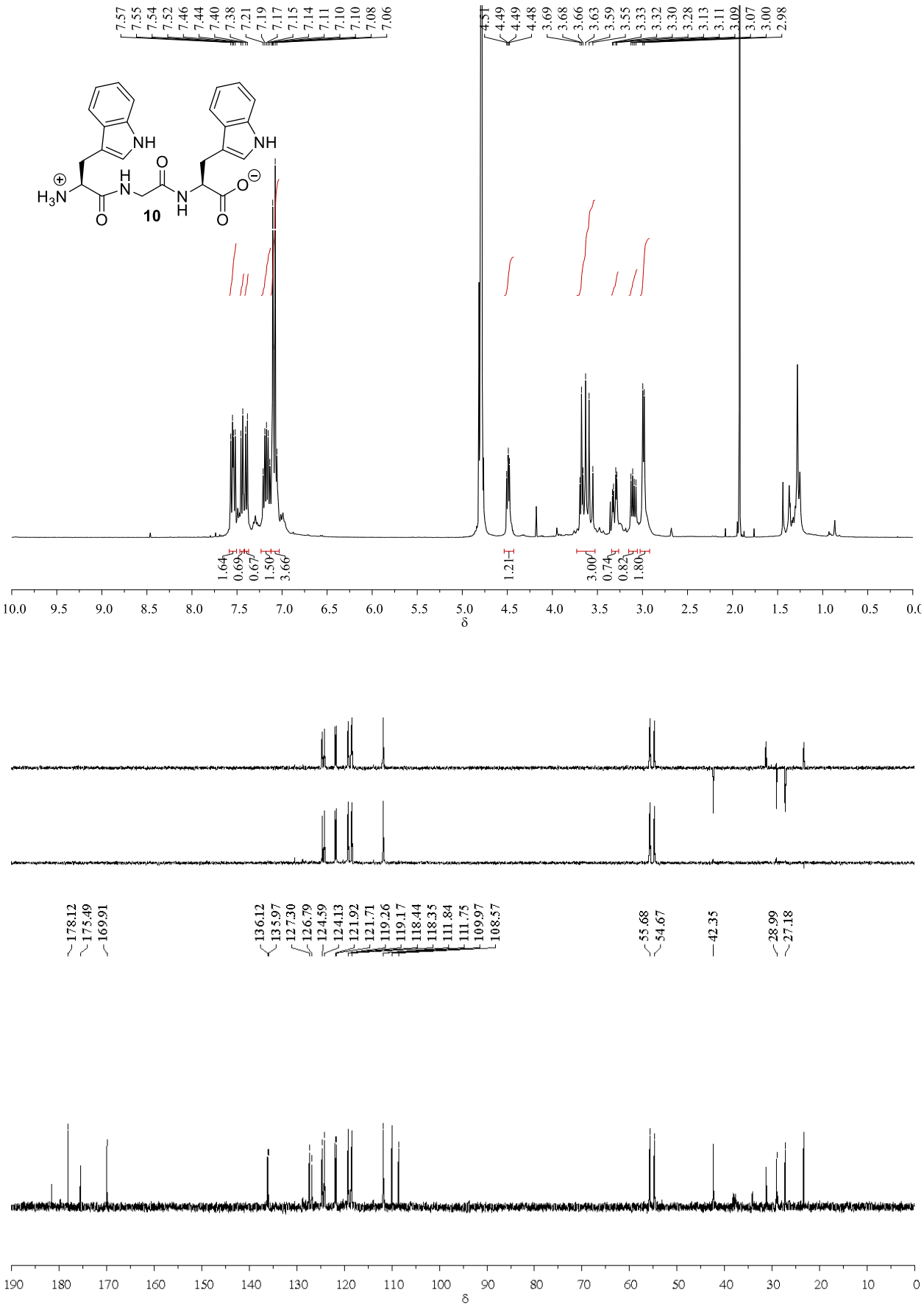


Figure S7. *^{1}H and ^{13}C spectra of Trp-Gly-Trp (**10**) in D_2O.*

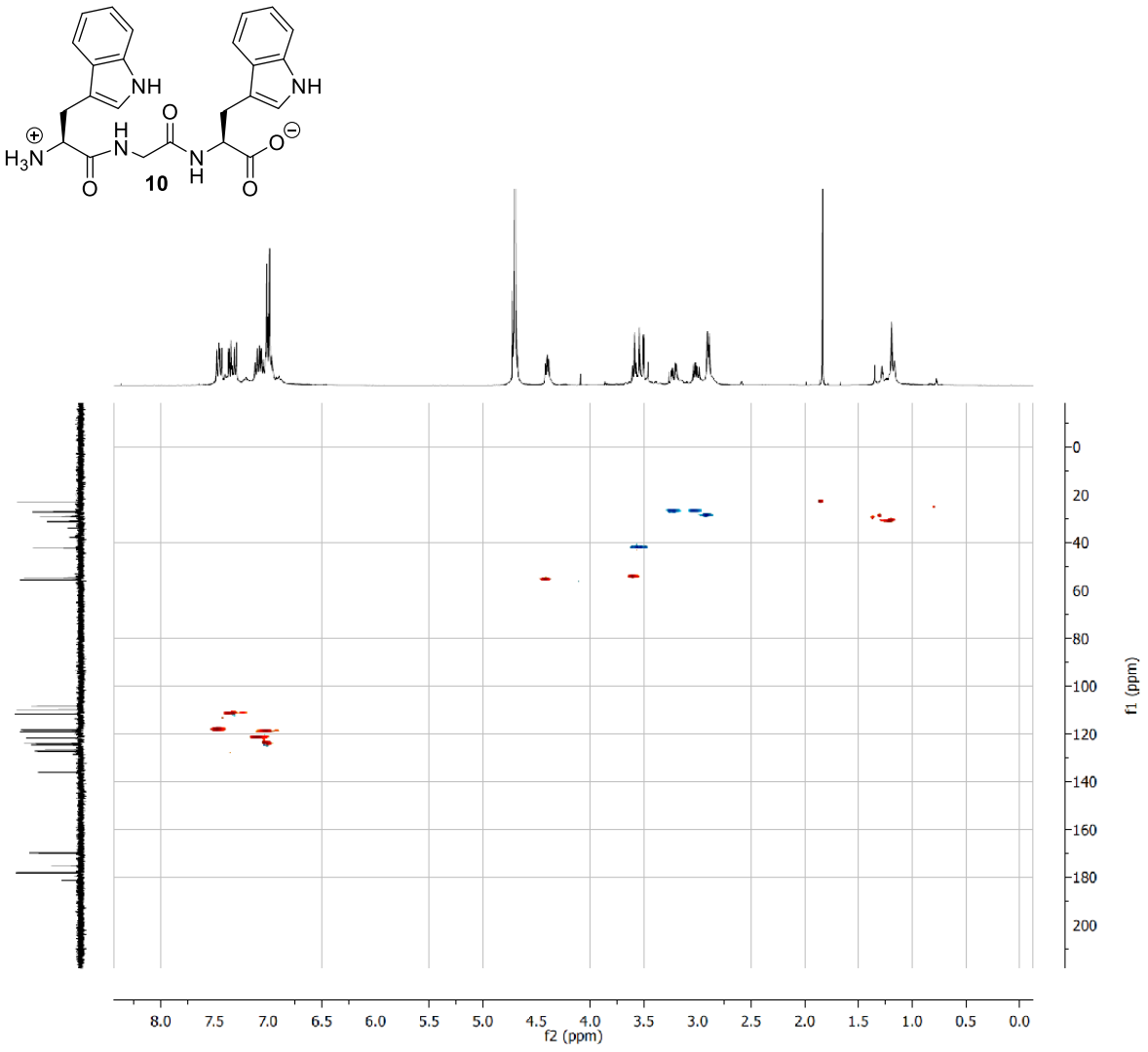


Figure S8. *HSQC 145 Hz of Trp-Gly-Trp (**10**) in D_2O.*

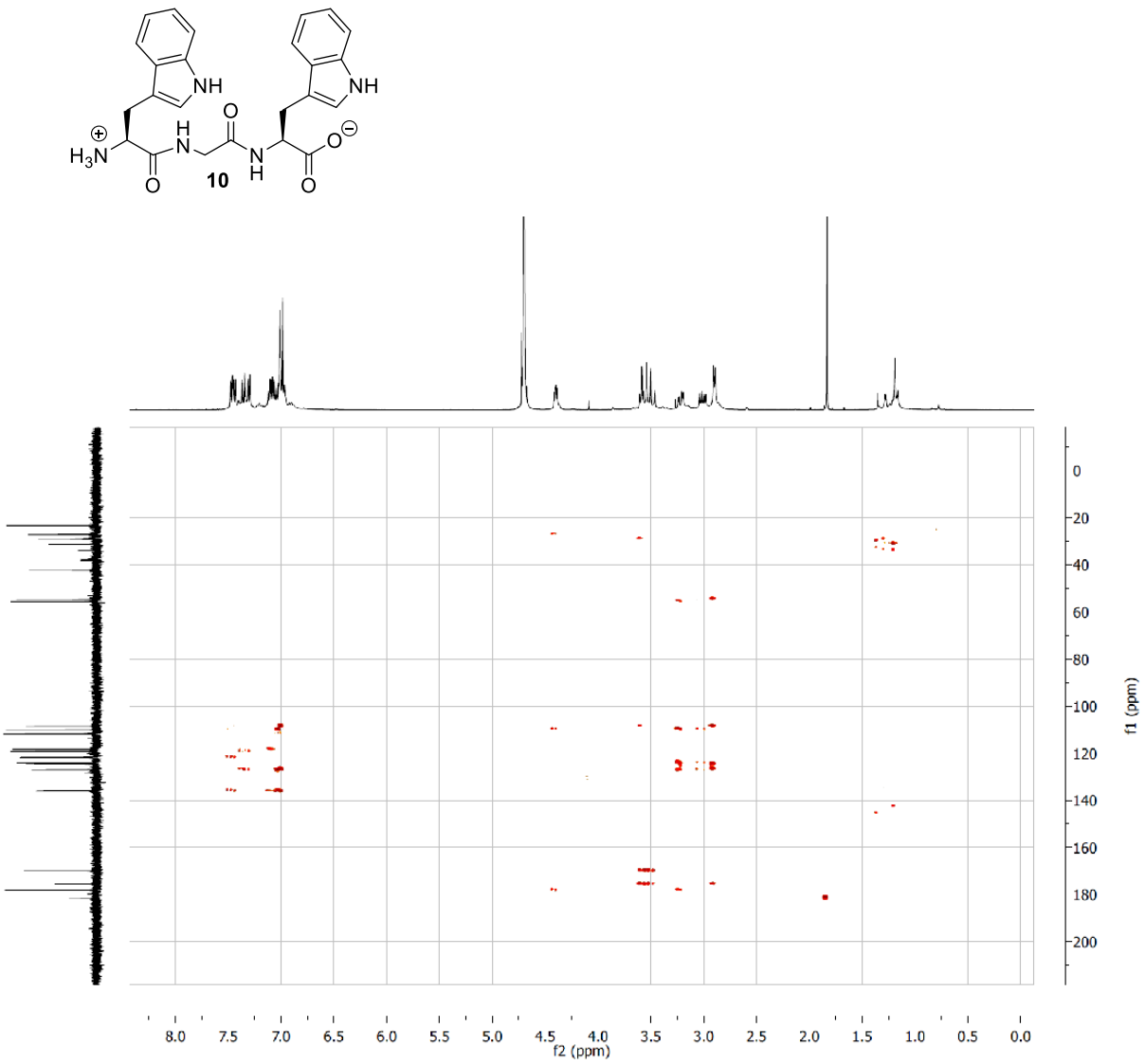


Figure S9. *HMBC CIGAR of Trp-Gly-Trp (**10**) in D_2O.*

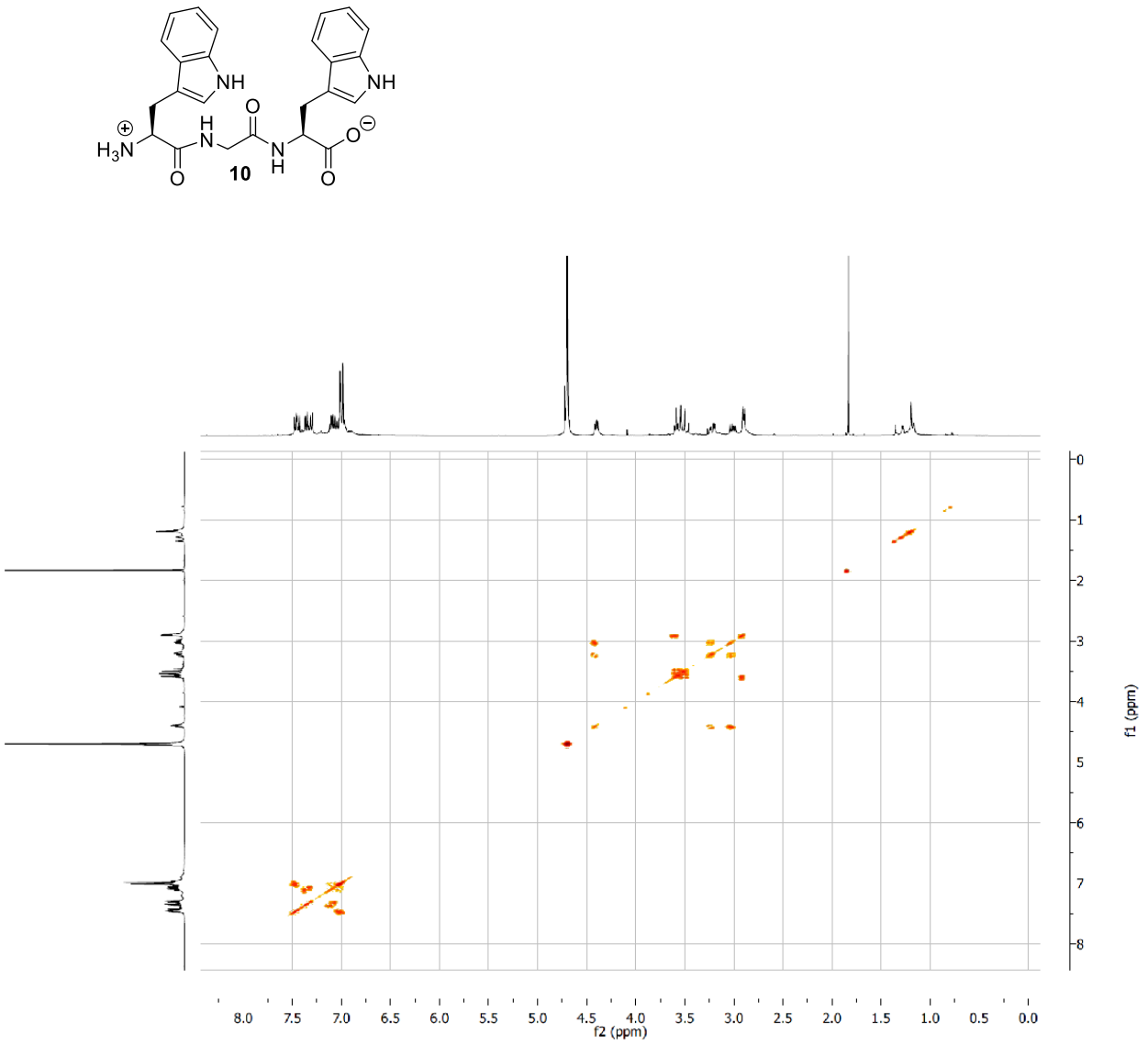


Figure S10. *COSY spectrum of Trp-Gly-Trp (**10**) in D_2O.*

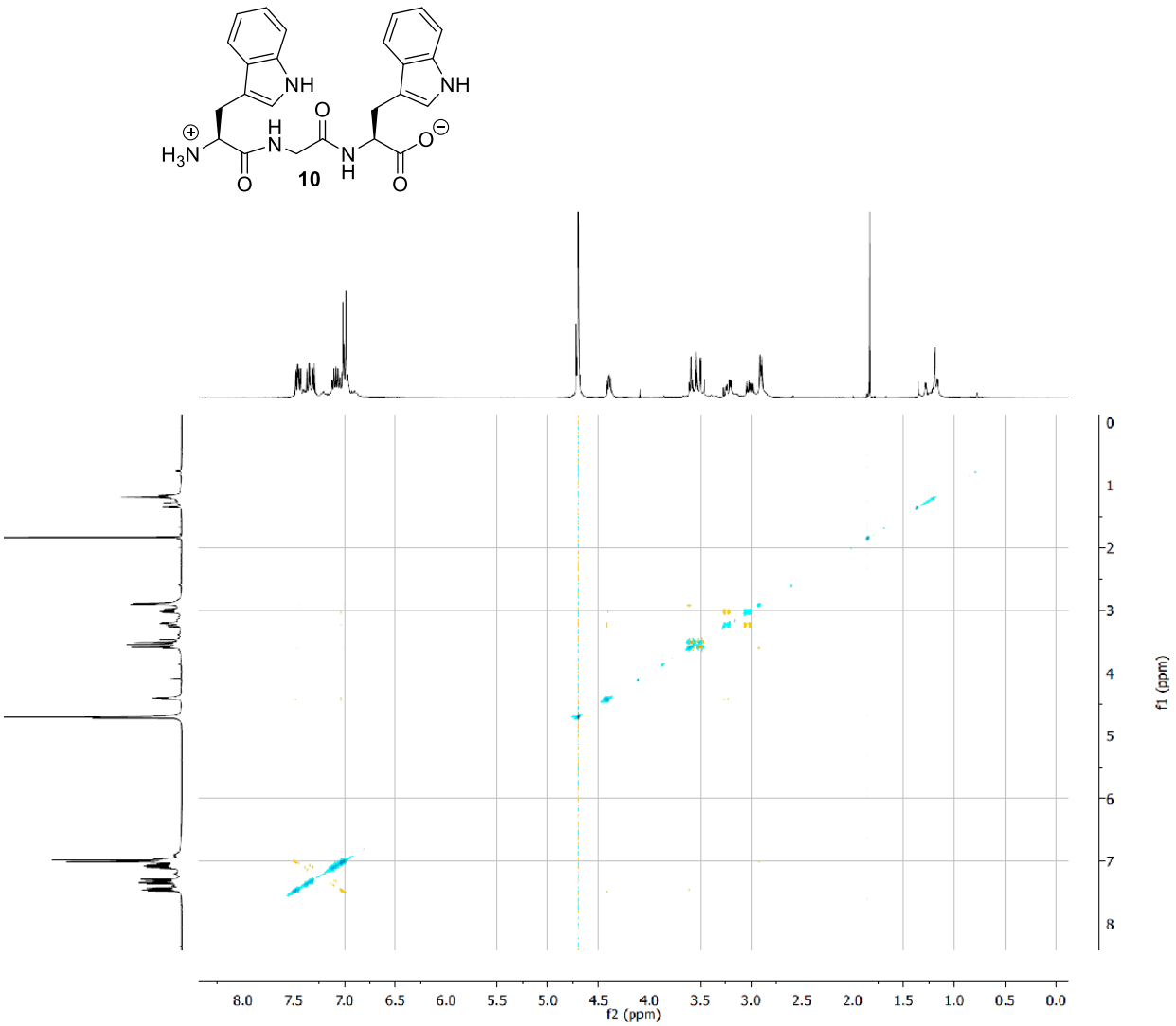


Figure S11. *ROESY of Trp-Gly-Trp (**10**) in D_2O.*

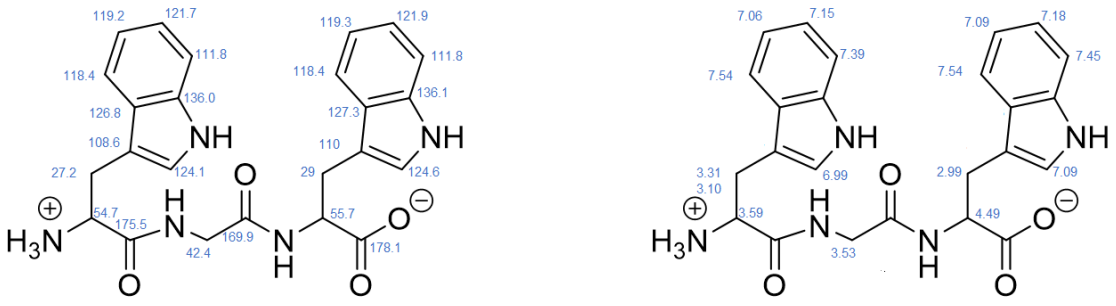


Figure S12. *Assignments of NMR signals for Trp-Gly-Trp (**10**) in D_2O.*

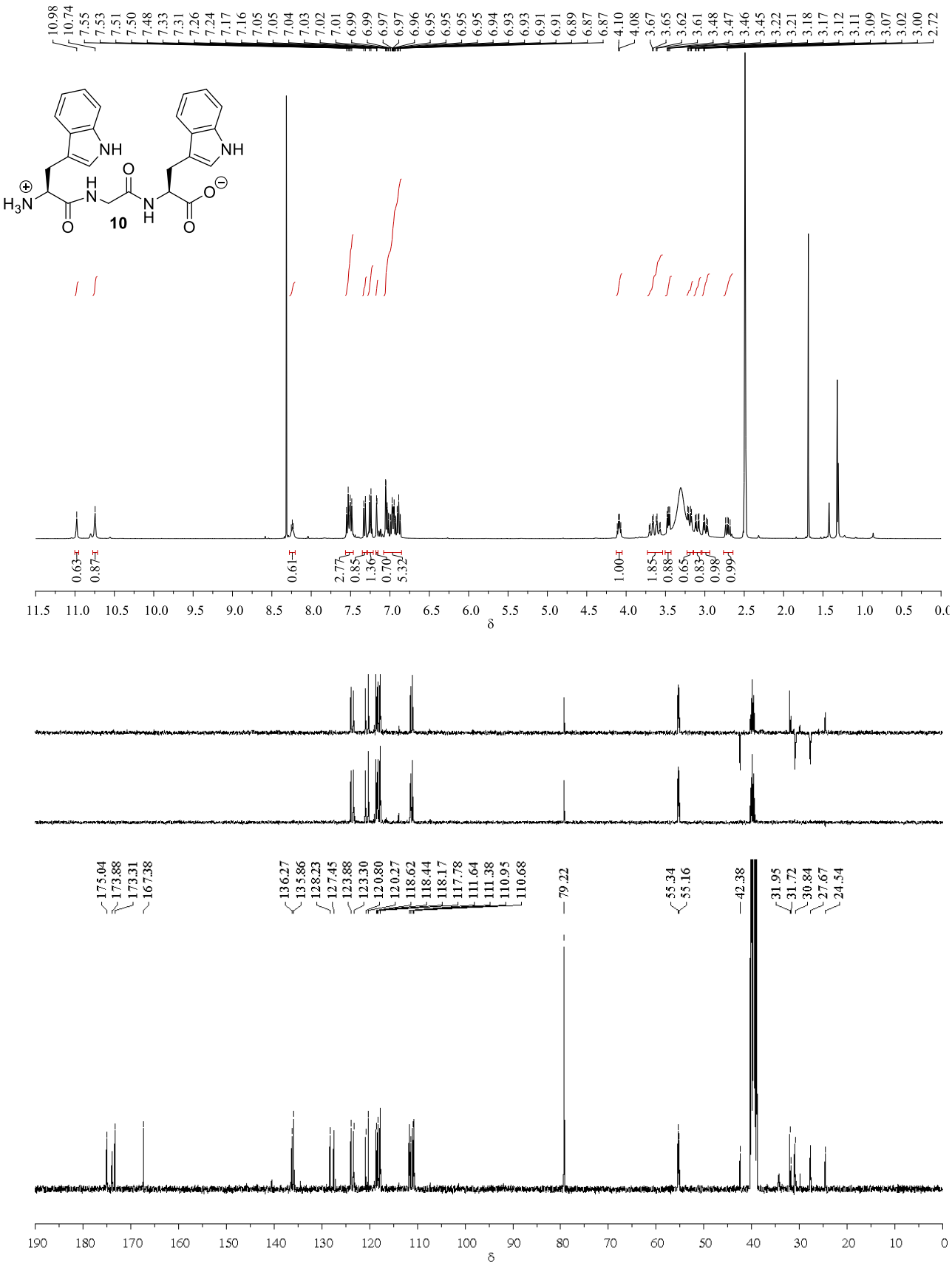


Figure S13. *^{1}H and ^{13}C spectra of Trp-Gly-Trp (**10**) in DMSO-d_6.*

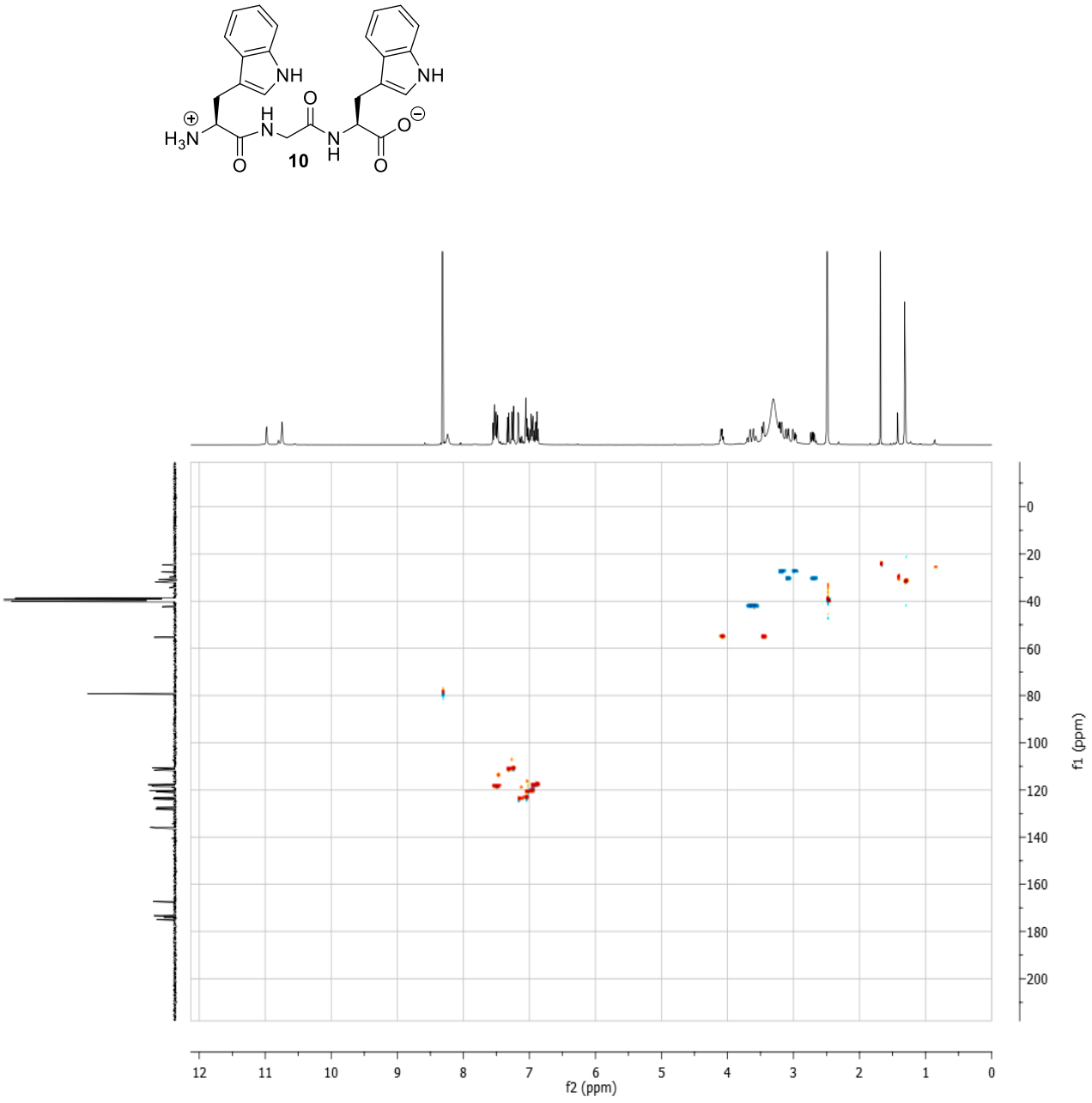


Figure S14. *HSQC 145 Hz of Trp-Gly-Trp (**10**) in DMSO-d_6.*

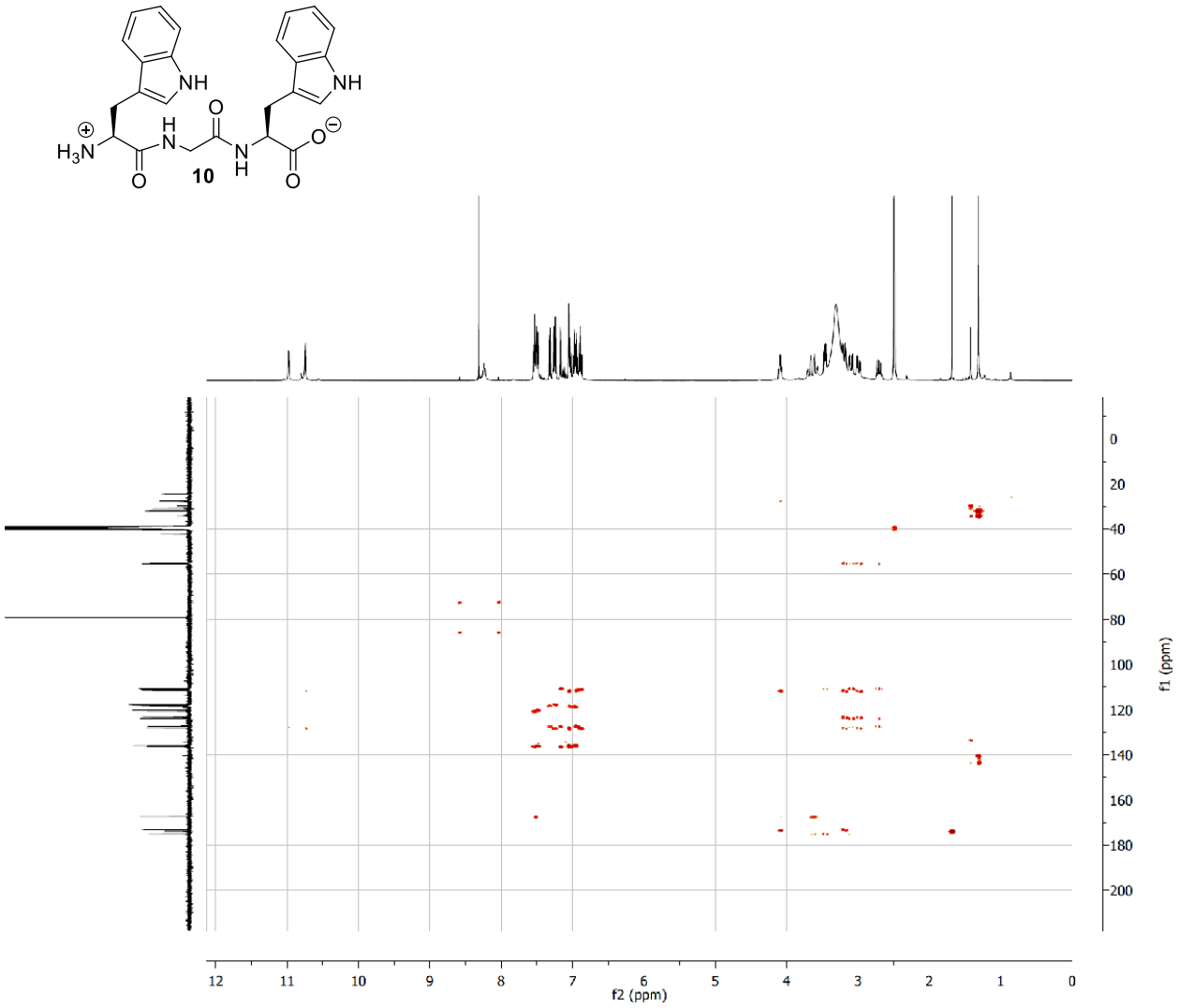


Figure S15. *HMBC CIGAR of Trp-Gly-Trp (**10**) in DMSO-d_6.*

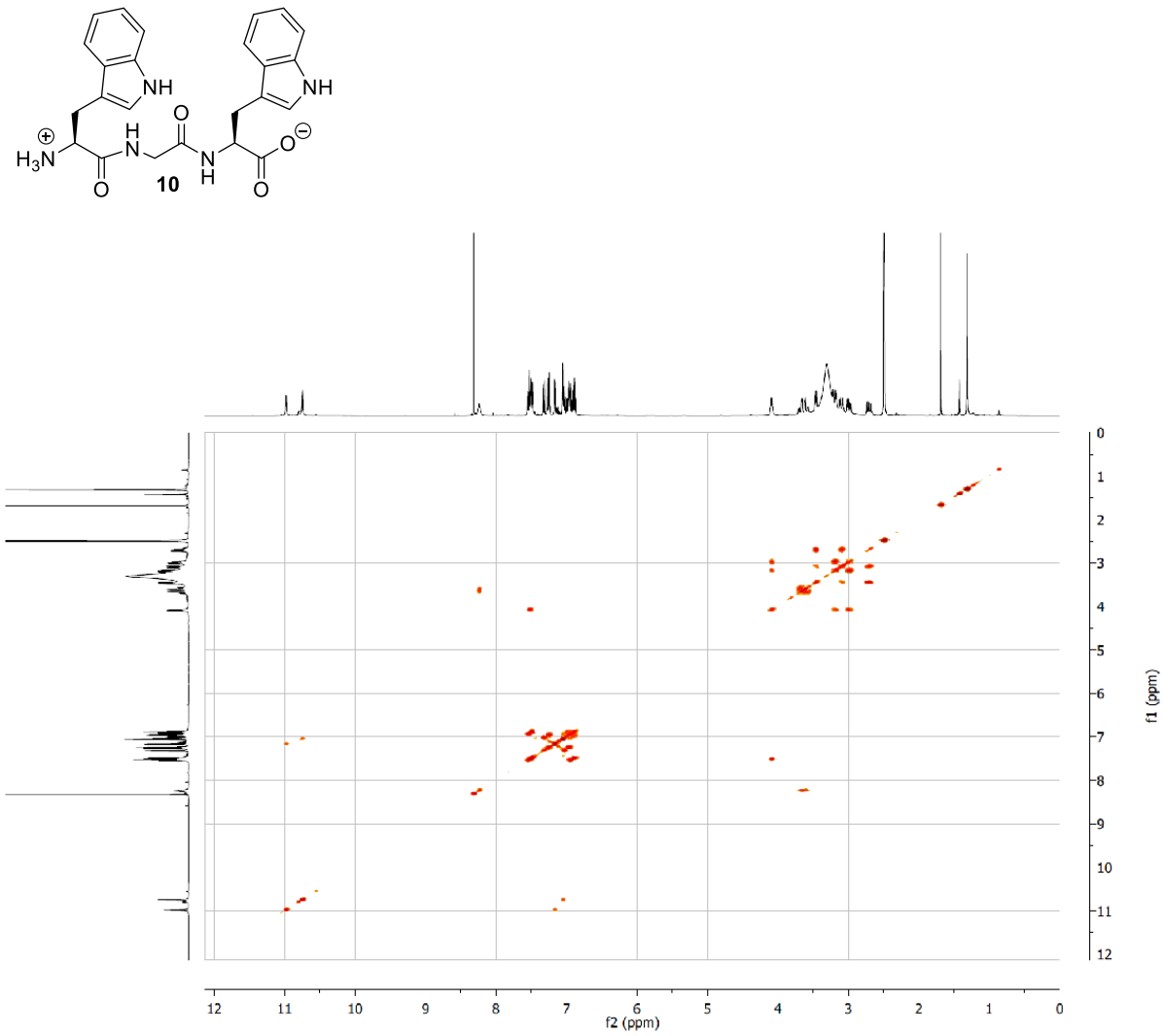


Figure S16. *COSY spectrum of Trp-Gly-Trp (**10**) in DMSO-d_6.*

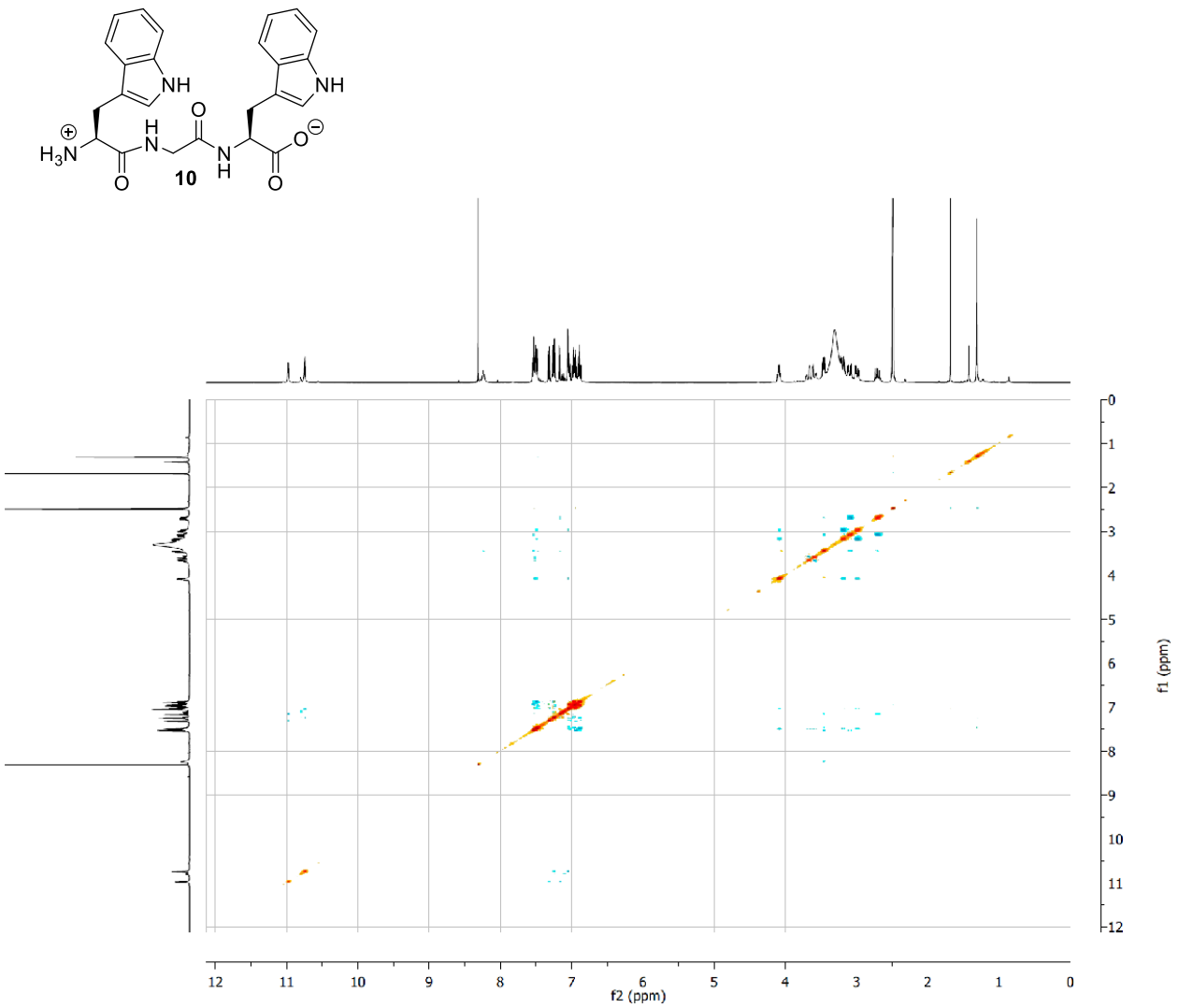
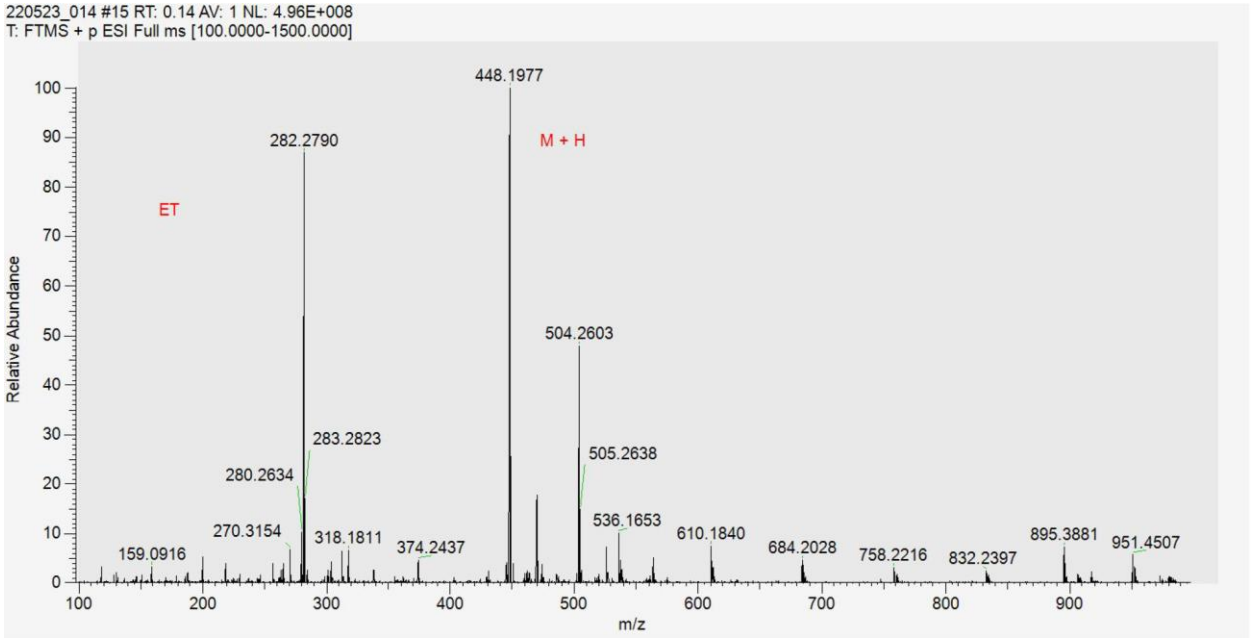


Figure S17. *ROESY of Trp-Gly-Trp (**10**) in DMSO-d_6.*



Display Formula	S Fit	RDB	Delta [ppm]	Theo. mass	Combined Score	# Matched Iso.
$C_{25}H_{22}N_9$	54,37	19,5	-3,45	448,19927	97,25	4
$C_{23}H_{23}N_9{}^{23}Na$	54,08	16,5	1,92	448,19686	97,23	4
$C_{24}H_{26}O_4N_5$	48,56	14,5	-0,46	448,19793	96,73	4

Figure S18. *Mass spectrum of Trp-Gly-Trp (**10**).*

3. Crystallographic data

3.1. Complex of 2,4,6-trinitrobenzenesulfonic acid (3a) with L-tryptophan

Table S1. *Crystal data and structure refinement for the complex of 2,4,6-trinitrobenzenesulfonic acid (**3a**) with L-tryptophan (CCDC* 2179406).

Empirical formula	$C_{17}H_{21}N_5O_{14}S$
Molecular weight	551.45
Temperature	298(2) K
Wavelength	1.54178 Å
Crystal system, space group	monoclinic, $P2_1/n$
Unit cell dimensions	a = 7.0718(2) Å α = 90.00 deg.
	b = 27.8784(8) Å β = 106.641(2) deg.
	c = 12.1169(4) Å γ = 90.00 deg.
Volume	2288.80(12) $Å^3$
Z, Calculated density	4, 1.600 Mg/m^3
Absorption coefficient	2.033 mm^{-1}
F(000)	1144
Crystal size	0.12 x 0.10 x 0.08 mm
Theta range for data collection	3.17 to 67.23 deg.
Limiting indexes	$-8 \le h \le 7$, $-32 \le k \le 32$, $-12 \le l \le 14$
Reflections collected / unique	15152 / 3866 (R_{int} = 0.0397)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3866 / 0 / 360
Goodness-of-fit on F^2	1.059
Final R indexes [I>2σ(I)]	R1 = 0.0488, wR2 = 0.1292
R indexes (all data)	R1 = 0.0577, wR2 = 0.1399
Largest diff. peak and hole	0.396 and -0.358 e. $Å^{-3}$
Diffractometer model	Bruker Kappa Appex II

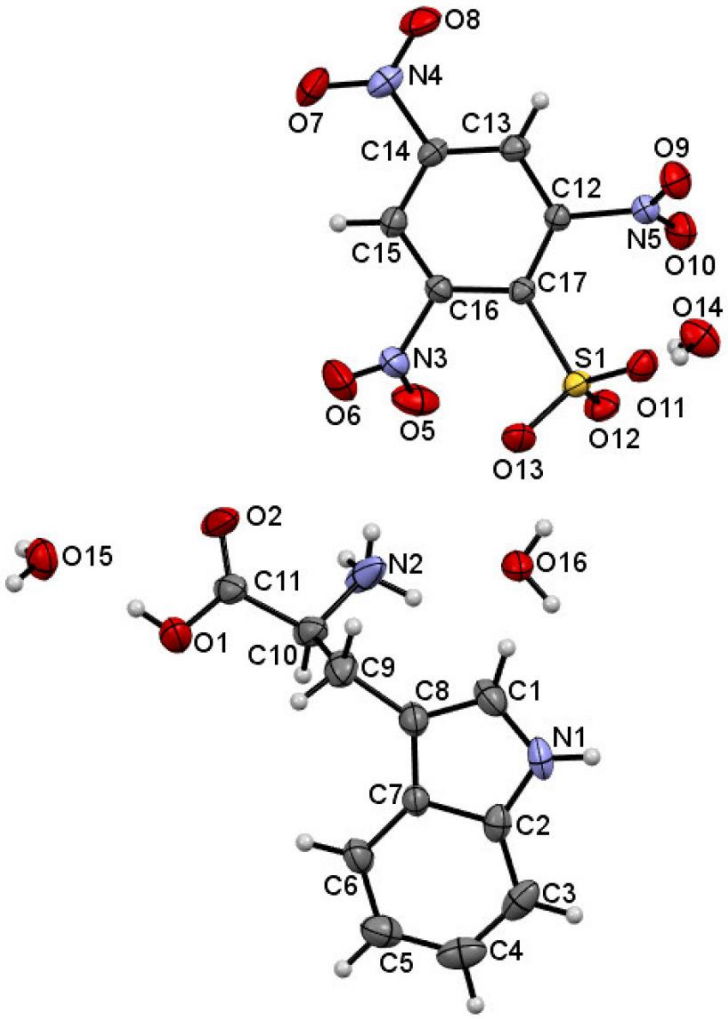


Figure S19. *ORTEP representation for the associate of 2,4,6-trinitrobenzene sulfonic acid (**3a**) with L-tryptophan (CCDC* 2179406).

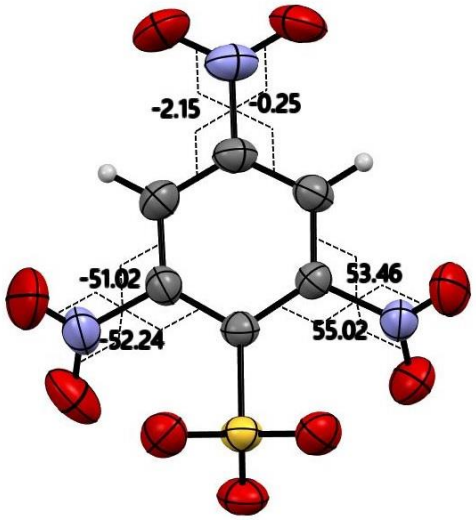


Figure S20. *2,4,6-trinitrobenzene sulfonic acid (**3a**) torsion angles.*

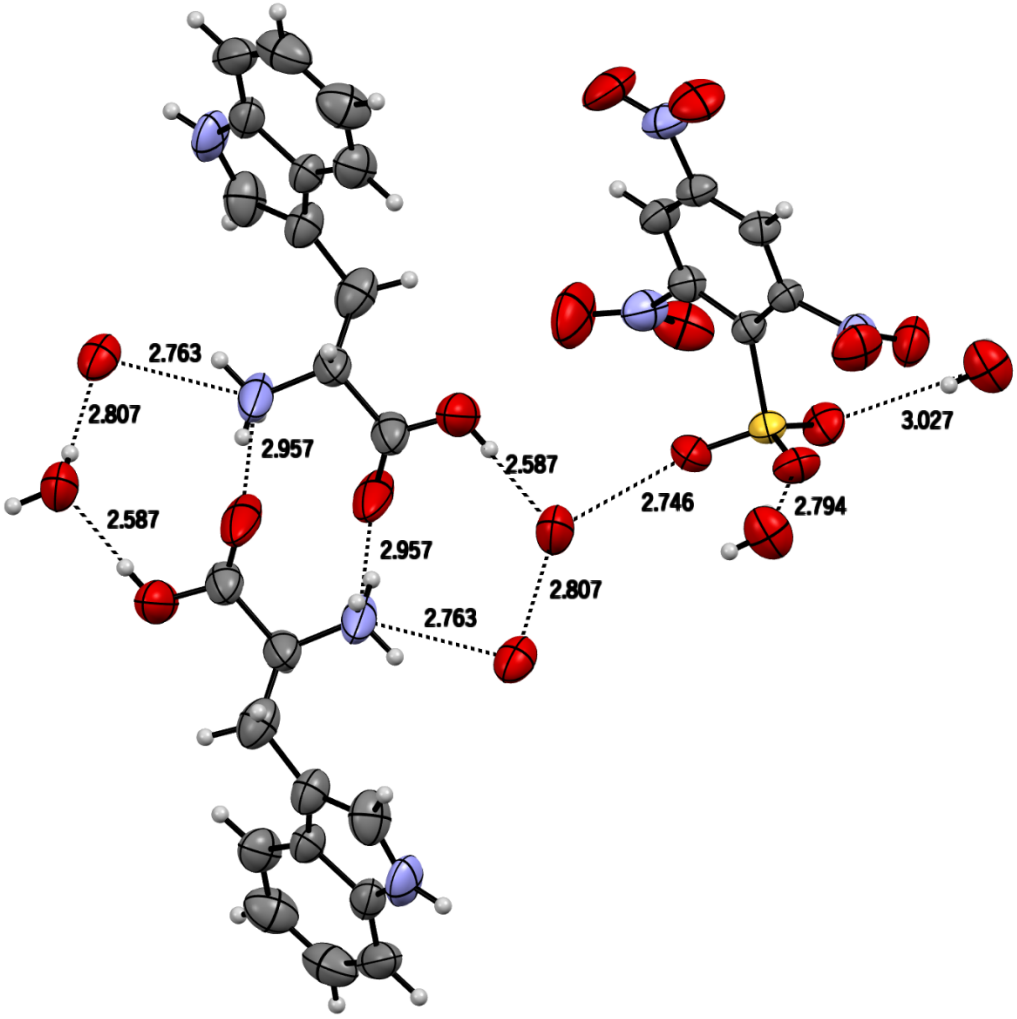


Figure S21. *Crystal structure for the complex showing hydrogen bonds by dotted lines and including crystallization water molecules.*

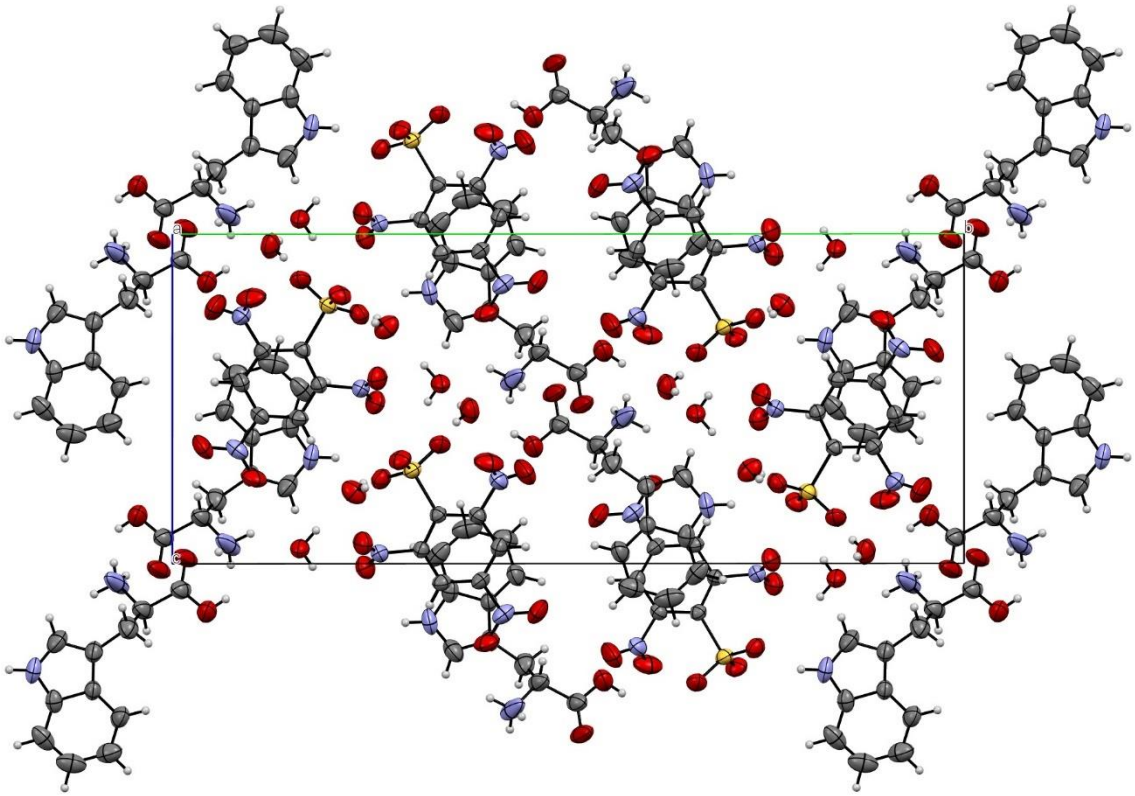


Figure S22. *Crystal packing of the complex viewed along the [100] direction of the unit cell.*

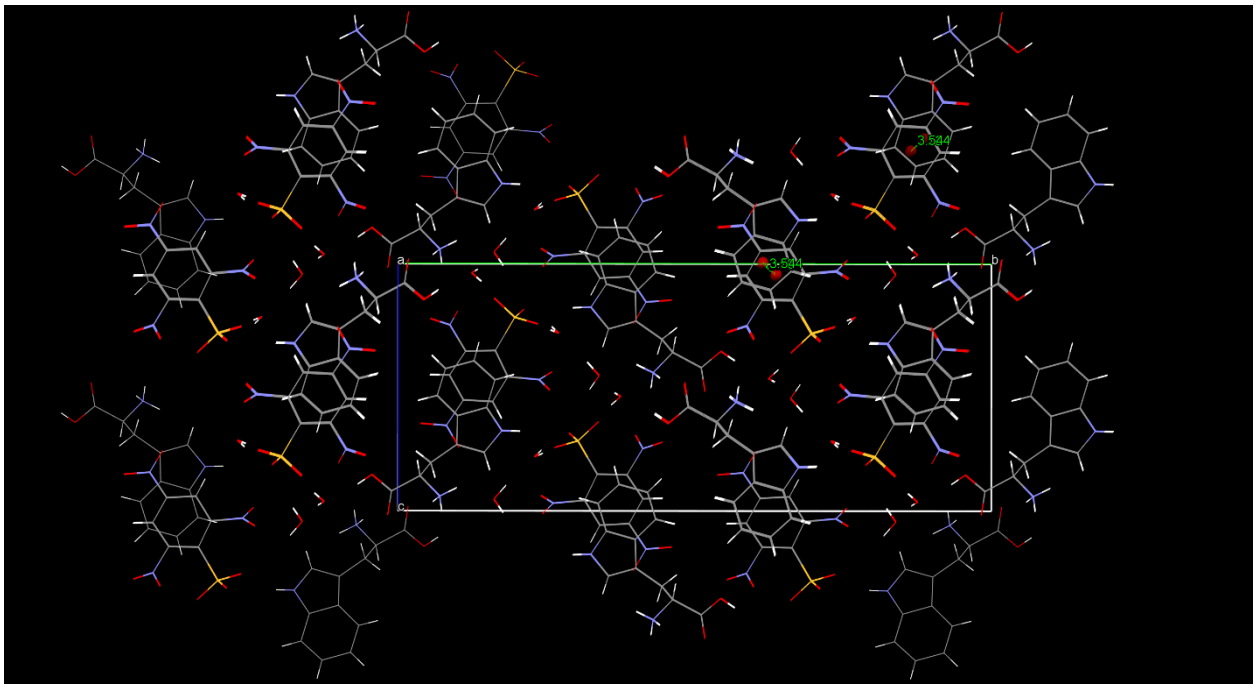


Figure S23. *Crystal packing of the complex viewed along the [100] direction of the unit cell, showing distance between centroids.*

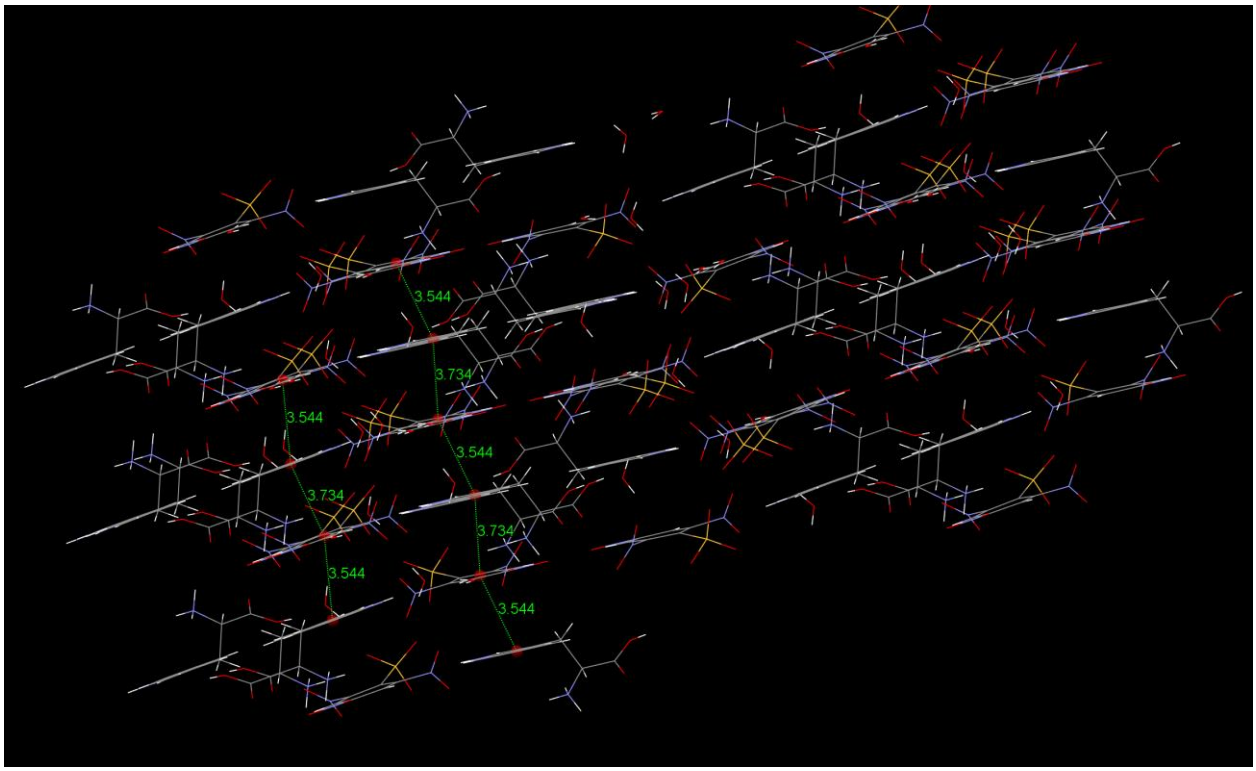


Figure S24. *Crystal packing of the complex showing the nearly parallel stacking and the distance between centroids.*

3.2. Complex of 3,5-dinitrobenzoic acid (4a) with L-tryptophan

Table S2. *Crystal data and structure refinement for 3,5-dinitrobenzoic acid (**4a**) with L-tryptophan.*

Empirical formula	$C_{19}H_{20}N_4O_9$
Molecular weight	448.39
Temperature	298(2) K
Wavelength	1.54178 Å
Crystal system, space group	monoclinic, $P2_1/n$
Unit cell dimensions	a = 7.2094(4) Å α = 90.00 deg.
	b = 7.5386(3) Å β = 98.214(3) deg.
	c = 19.1587(8) Å γ = 90.00 deg.
Volume	1030.57(8) $Å^3$
Z, Calculated density	2, 1.445 Mg/m^3
Absorption coefficient	0.999 mm^{-1}
F(000)	468
Crystal size	0.15 x 0.12 x 0.10 mm
Theta range for data collection	2.33 to 66.72 deg.
Limiting indexes	$-8 \le h \le 8$, $-8 \le k \le 6$, $-22 \le l \le 22$
Reflections collected / unique	7296 / 2586 (R_{int} = 0.0291)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2586 / 2 / 283
Goodness-of-fit on F^2	1.060
Final R indexes [$I>2\sigma(I)$]	R1 = 0.0528, wR2 = 0.1483
R indexes (all data)	R1 = 0.0565, wR2 = 0.1521
Largest diff. peak and hole	0.614 and -0.354 e. $Å^{-3}$
Diffractometer model	Bruker Kappa Appex II

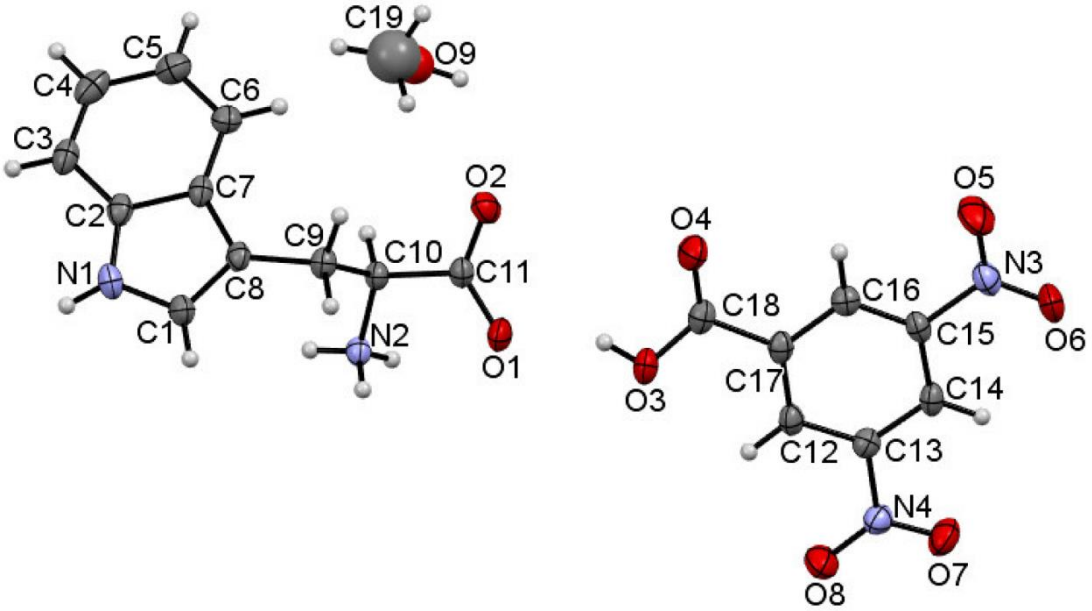


Figure S25. *ORTEP representation for the associate of 3,5-dinitrobenzoic acid (**4a**) with L-tryptophan (CCDC* 2179399).

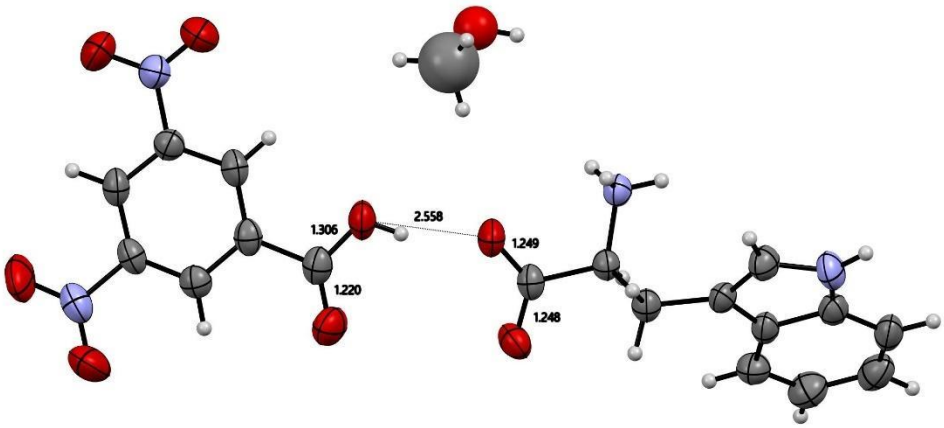


Figure S26. *Crystal structure of the complex showing C-O bond lengths and the intermolecular H-bond between Trp and **4a**.*

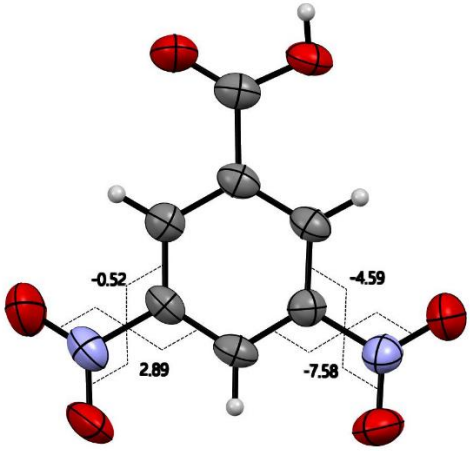


Figure S27. *3,5-dinitrobenzenoic acid (**4a**) torsion angles.*

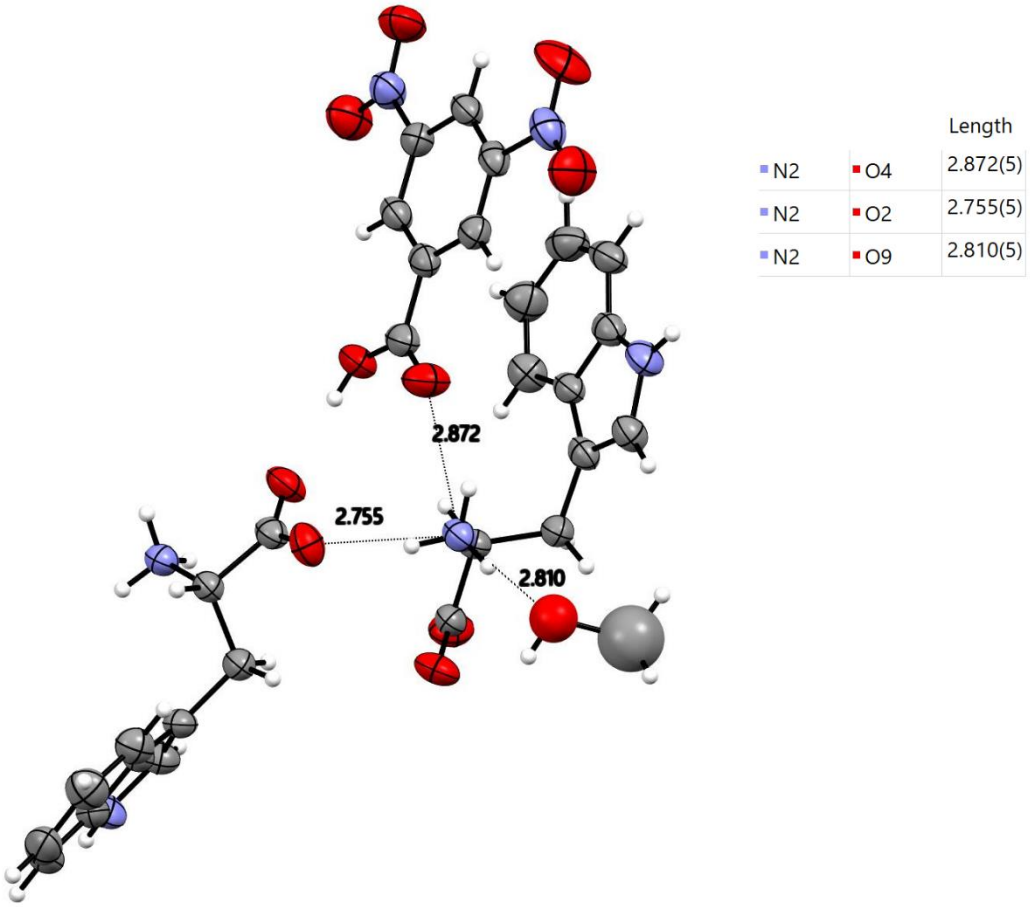


Figure S28. *H-bonds around the ammonium group indicated by dotted lines.*

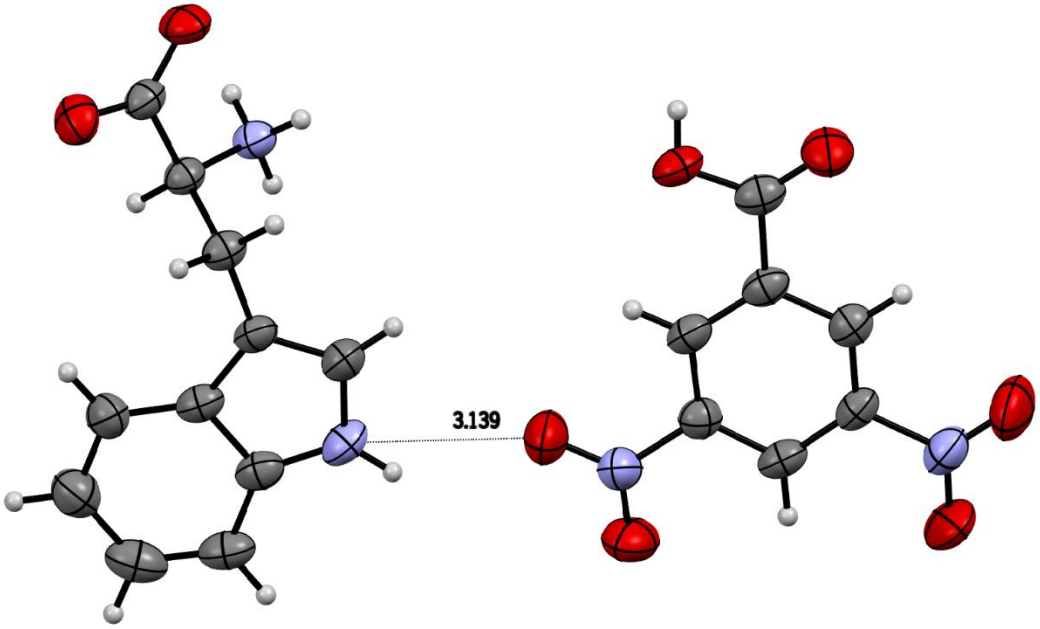


Figure S29. *H-bond between indole NH and one of the nitro groups (3.139 Å) indicated by dotted lines.*

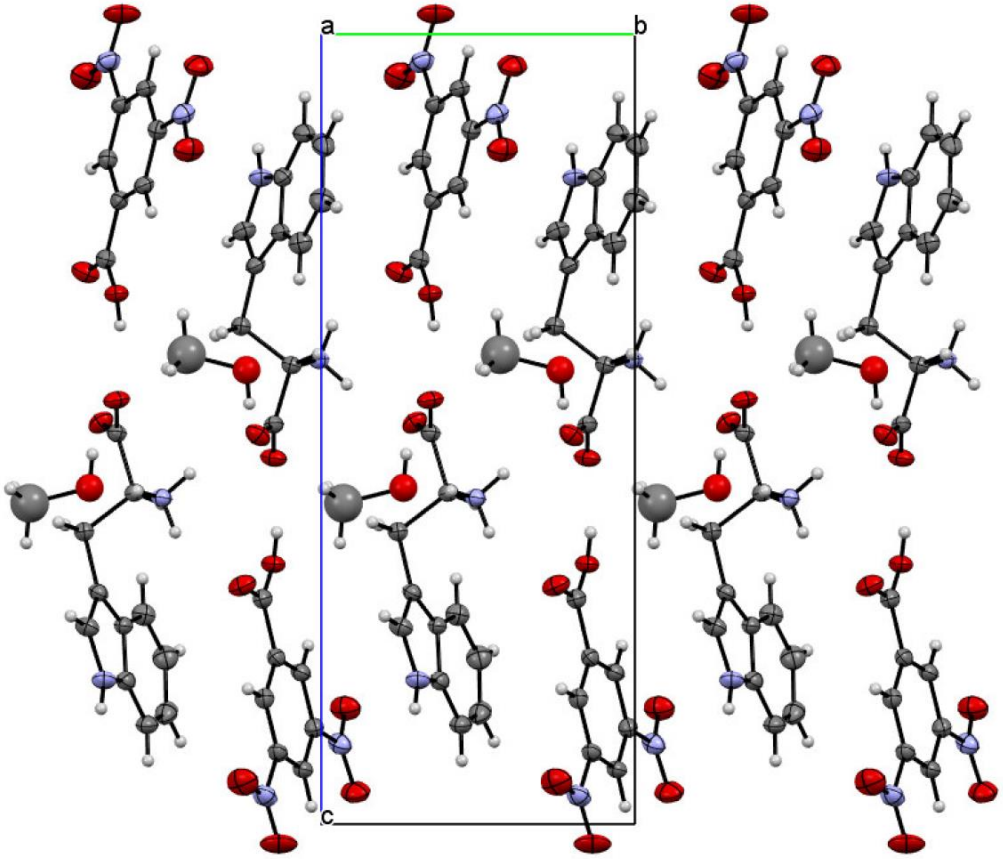


Figure S30. *π-π stacking interactions between L-tryptophan and 3,5-dinitrobenzoic acid (**4a**).*

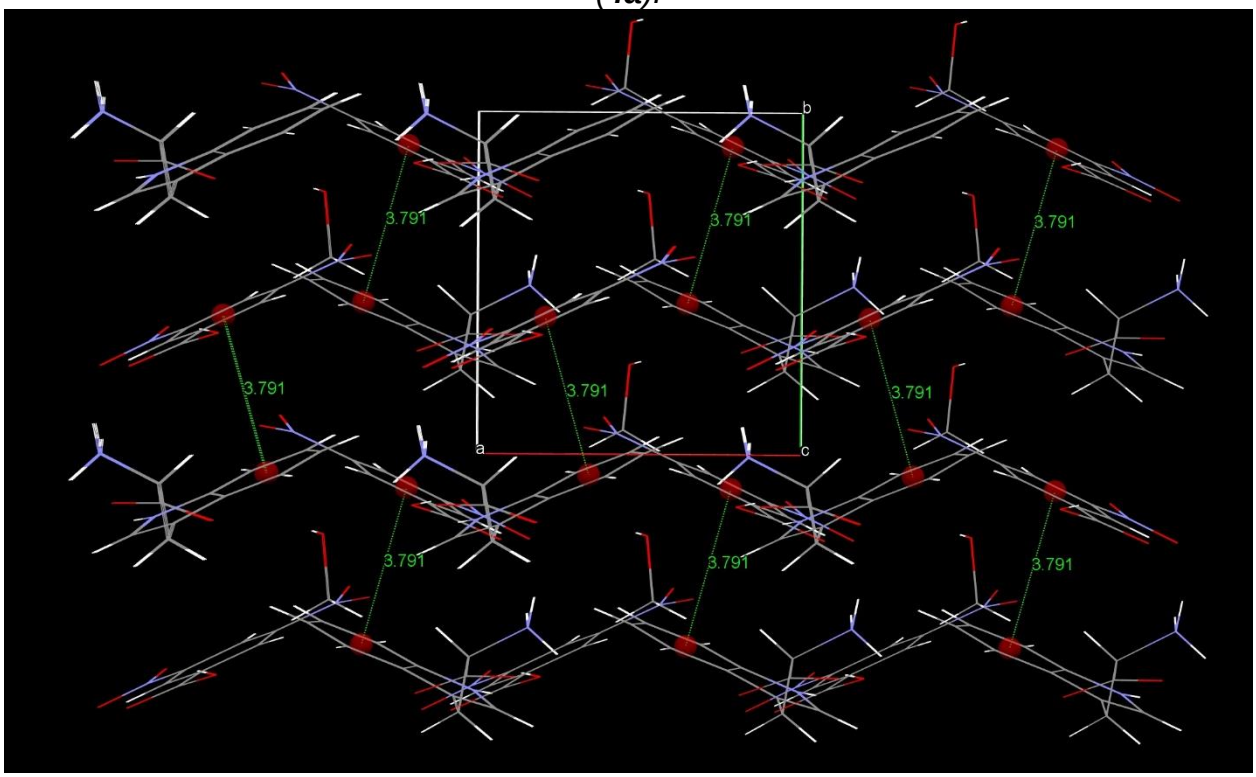


Figure S31. *Crystal packing of the complex showing the π-π stacking and the distance between centroids.*

3.3. Complex of 2,4,6-trinitrobenzoic acid (5a) with L-tryptophan

Table S3. *Crystal data and structure refinement for 2,4,6-trinitrobenzoic acid (**5a**) with L-tryptophan.*

Empirical formula	$C_{18}H_{15}N_5O_{10}$
Molecular weight	461.35
Temperature	298(2) K
Wavelength	1.54178 Å
Crystal system, space group	monoclinic, $P2_1/n$
Unit cell dimensions	a = 6.9989(2) Å α = 90.00 deg.
	b = 9.8927(3) Å β = 97.0060(10) deg.
	c = 28.2400(7) Å γ = 90.00 deg.
Volume	1940.68(9) $Å^3$
Z, Calculated density	2, 1.579 Mg/m^3
Absorption coefficient	1.140 mm^{-1}
F(000)	952
Crystal size	0.16 x 0.14 x 0.12 mm
Theta range for data collection	3.15 to 67.10 deg.
Limiting indexes	$-8 \le h \le 5$, $-11 \le k \le 11$, $-33 \le l \le 31$
Reflections collected / unique	13813 / 3262 (R_{int} = 0.0267)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3262 / 0 / 301
Goodness-of-fit on F^2	1.042
Final R indexes [I>2σ(I)]	R1 = 0.0378, wR2 = 0.1001
R indexes (all data)	R1 = 0.0411, wR2 = 0.1028
Largest diff. peak and hole	0.237 and -0.261 e. $Å^{-3}$
Diffractometer model	Bruker Kappa Appex II

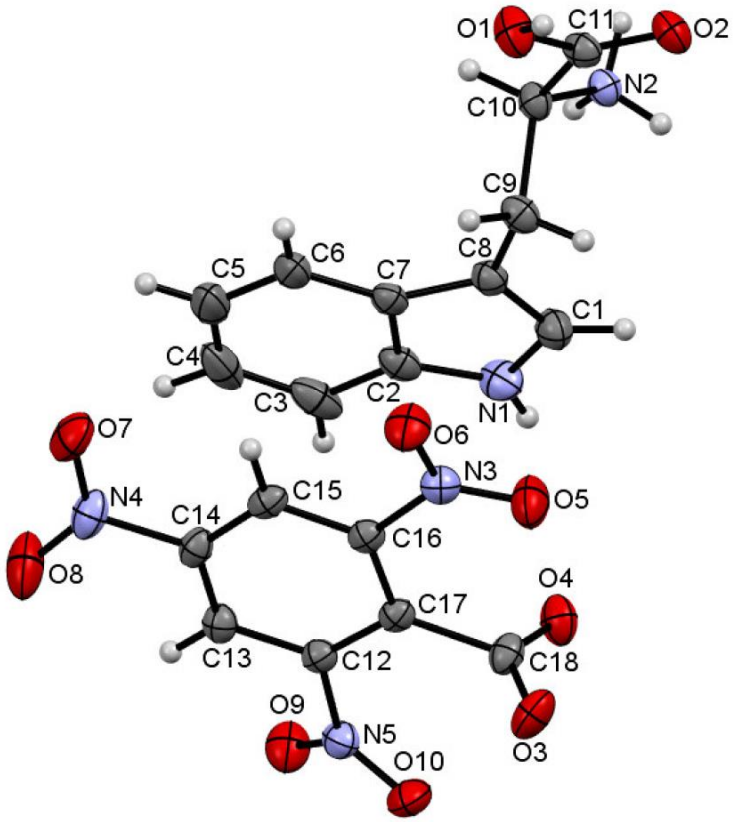


Figure S32. *ORTEP representation for the associate of 2,4,6-trinitrobenzoic acid (**5a**) with L-tryptophan (CCDC* 2179404).

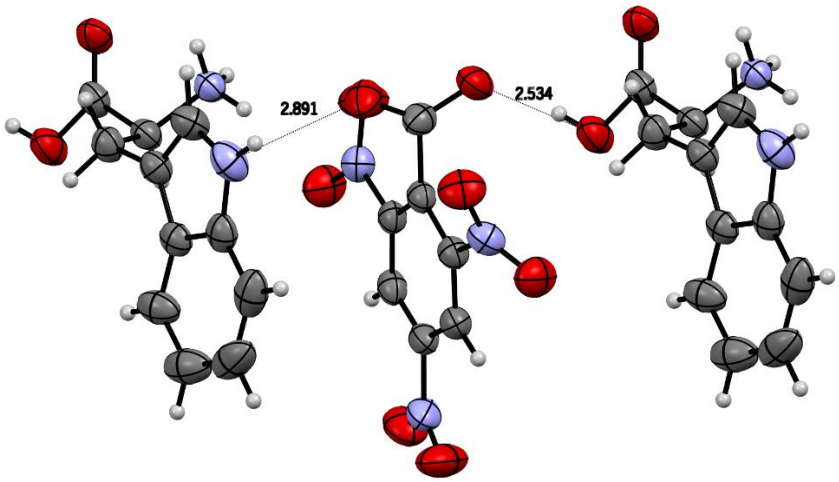


Figure S33. *H-bond interactions between trinitrobenzoic acid carboxylate with two tryptophan molecules.*

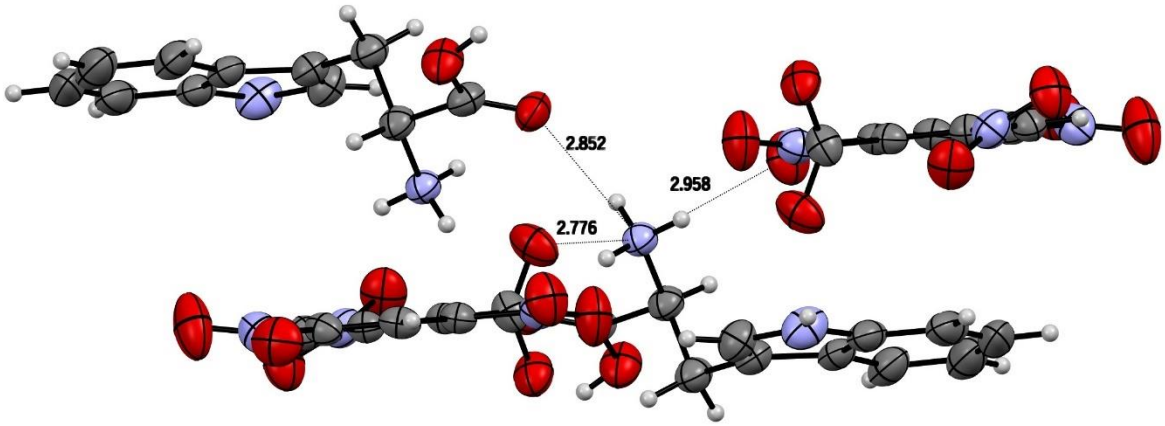


Figure S34. *Three H-bonds around the ammonium group indicated by dotted lines.*

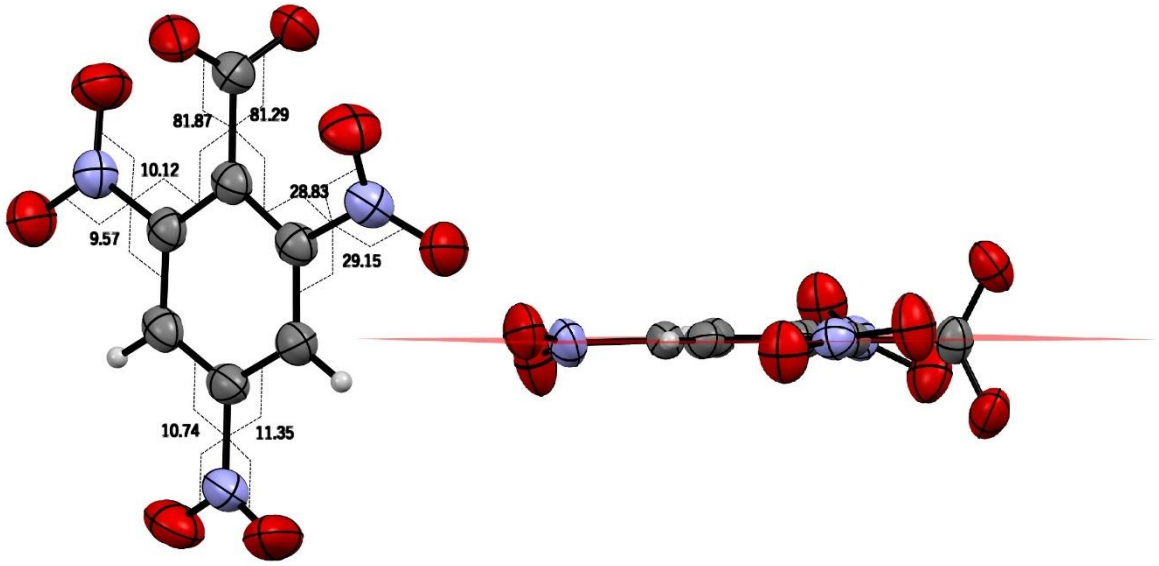


Figure S35. *Torsion angles of 2,4,6-trinitrobenzoic acid (**5a**).*

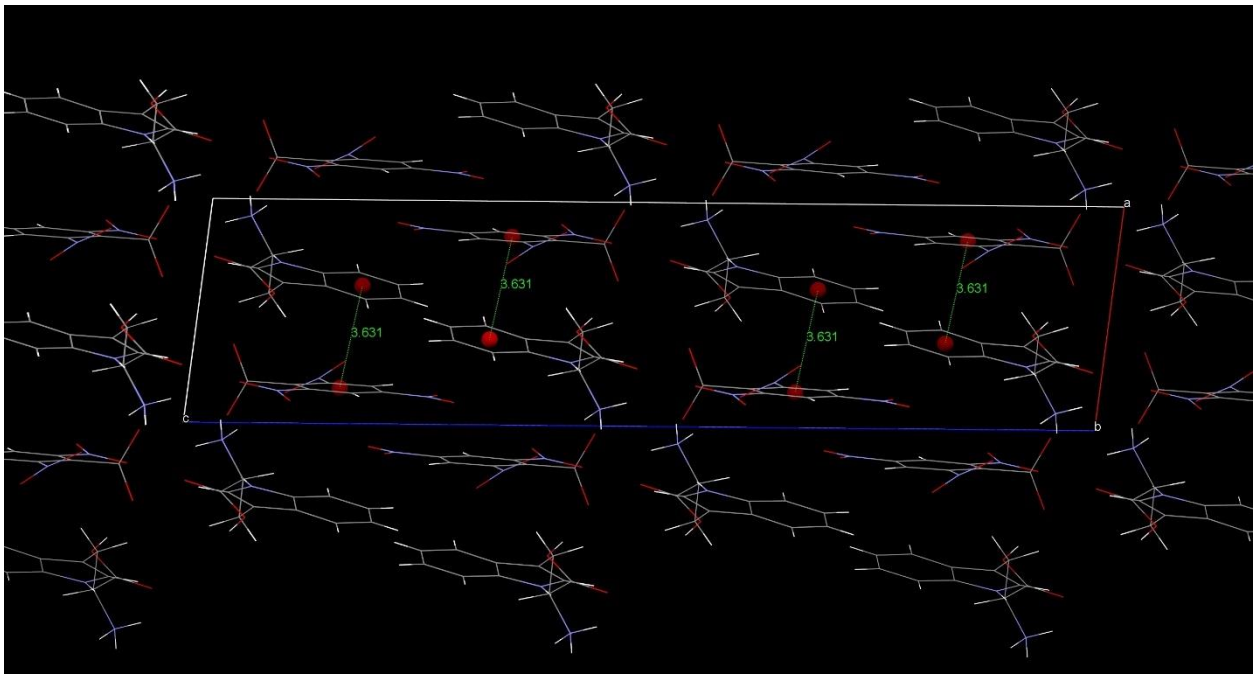


Figure S36. *Crystal packing of the complex showing the π-π stacking and the distance between centroids. Crystallization solvent molecules have been omitted for clarity.*

3.4. Complex of *N,N´*-bis(glycinyl)pyromellitic diimide (6a) with L-tryptophan

Table S4. *Crystal data and structure refinement for receptor **6a** with L-tryptophan.*

Empirical formula	$C_{36}H_{32}N_6O_{14}$
Molecular weight	772.68
Temperature	298(2) K
Wavelength	1.54178 Å
Crystal system, space group	triclinic, P1
Unit cell dimensions	a = 8.3904(3) Å α = 77.406(2) deg.
	b = 9.2903(3) Å β = 89.956(2) deg.
	c = 11.4586(4) Å γ = 77.501(2) deg.
Volume	850.03(5) $Å^3$
Z, Calculated density	1, 1.509 Mg/m^3
Absorption coefficient	1.006 mm^{-1}
F(000)	402
Crystal size	0.15 x 0.14 x 0.10 mm
Theta range for data collection	3.96 to 66.66 deg.
Limiting indexes	$-9 \le h \le 8$, $-10 \le k \le 10$, $-12 \le l \le 13$
Reflections collected / unique	5774 / 3144 (R_{int} = 0.0209)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3144 / 3 / 510
Goodness-of-fit on F^2	1.106
Final R indexes [I>2σ(I)]	R1 = 0.0369, wR2 = 0.1091
R indexes (all data)	R1 = 0.0382, wR2 = 0.1107
Largest diff. peak and hole	0.438 and -0.166 e. $Å^{-3}$
Diffractometer model	Bruker Kappa Appex II

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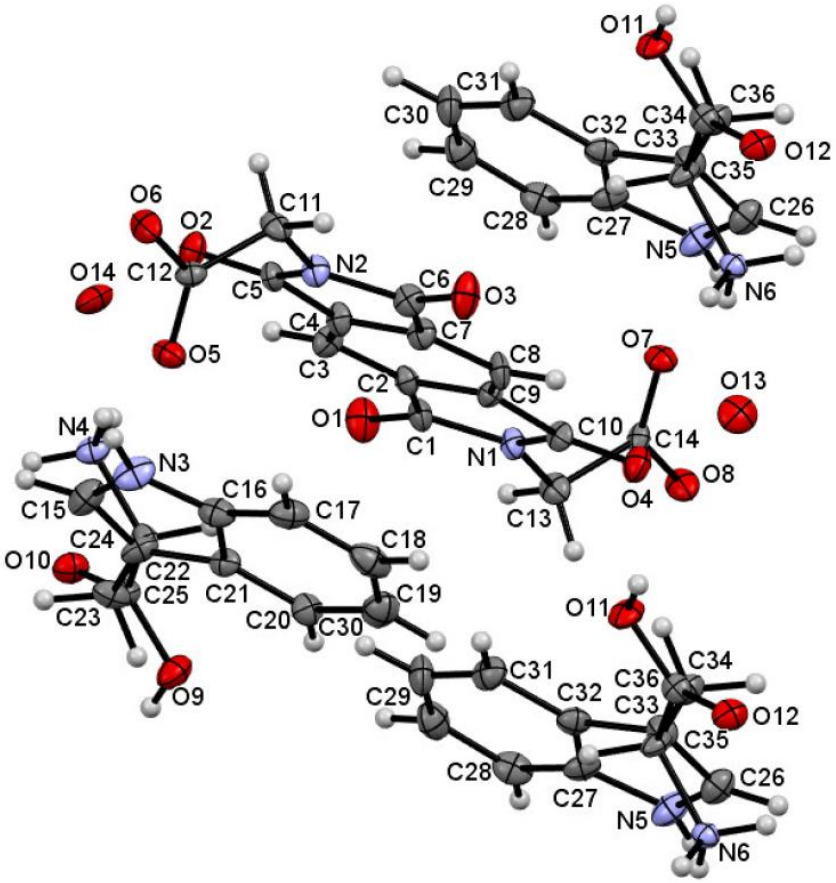


Figure S37. *ORTEP representation for the associate of N,N´-bis(glycinyl)pyromellitic diimide (**6a**) with L-tryptophan (CCDC* 2179405).

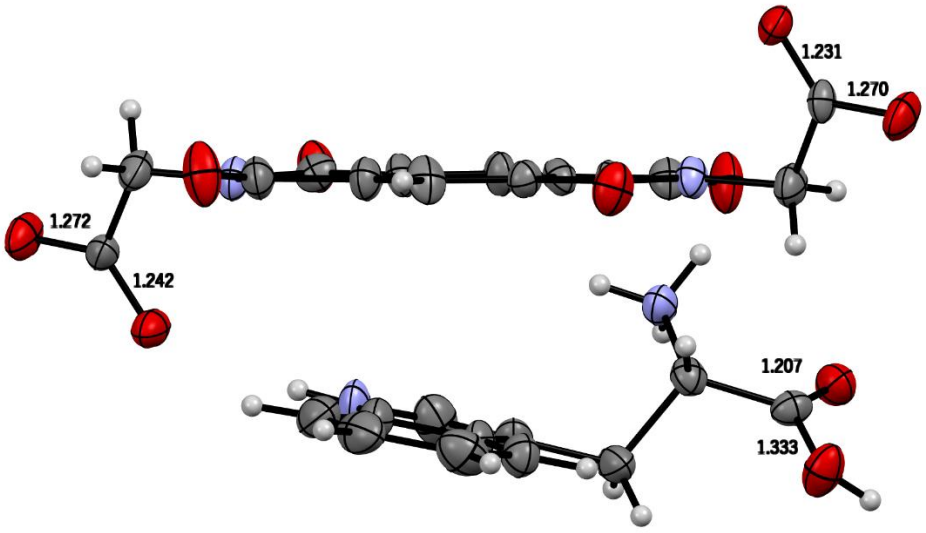


Figure S38. *C-O bond lengths for the Trp carboxyl and receptor **6** carboxylate groups.*

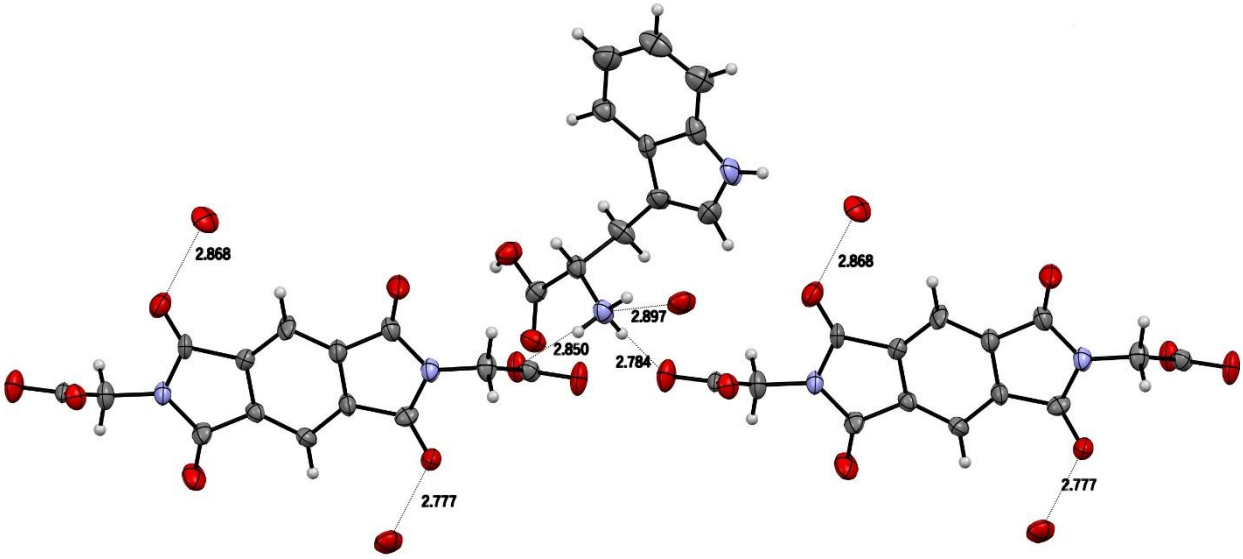


Figure S39. *H-bonds around the Trp ammonium group and diimide carbonyl groups indicated by dotted lines.*

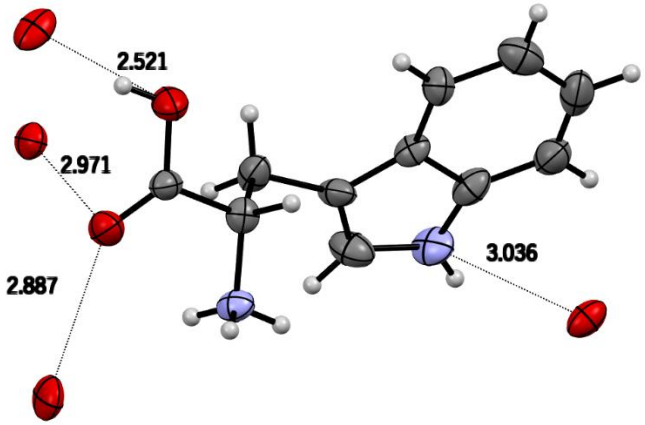


Figure S40. *H-bonds around the Trp carboxylic group and indole NH indicated by dotted lines.*

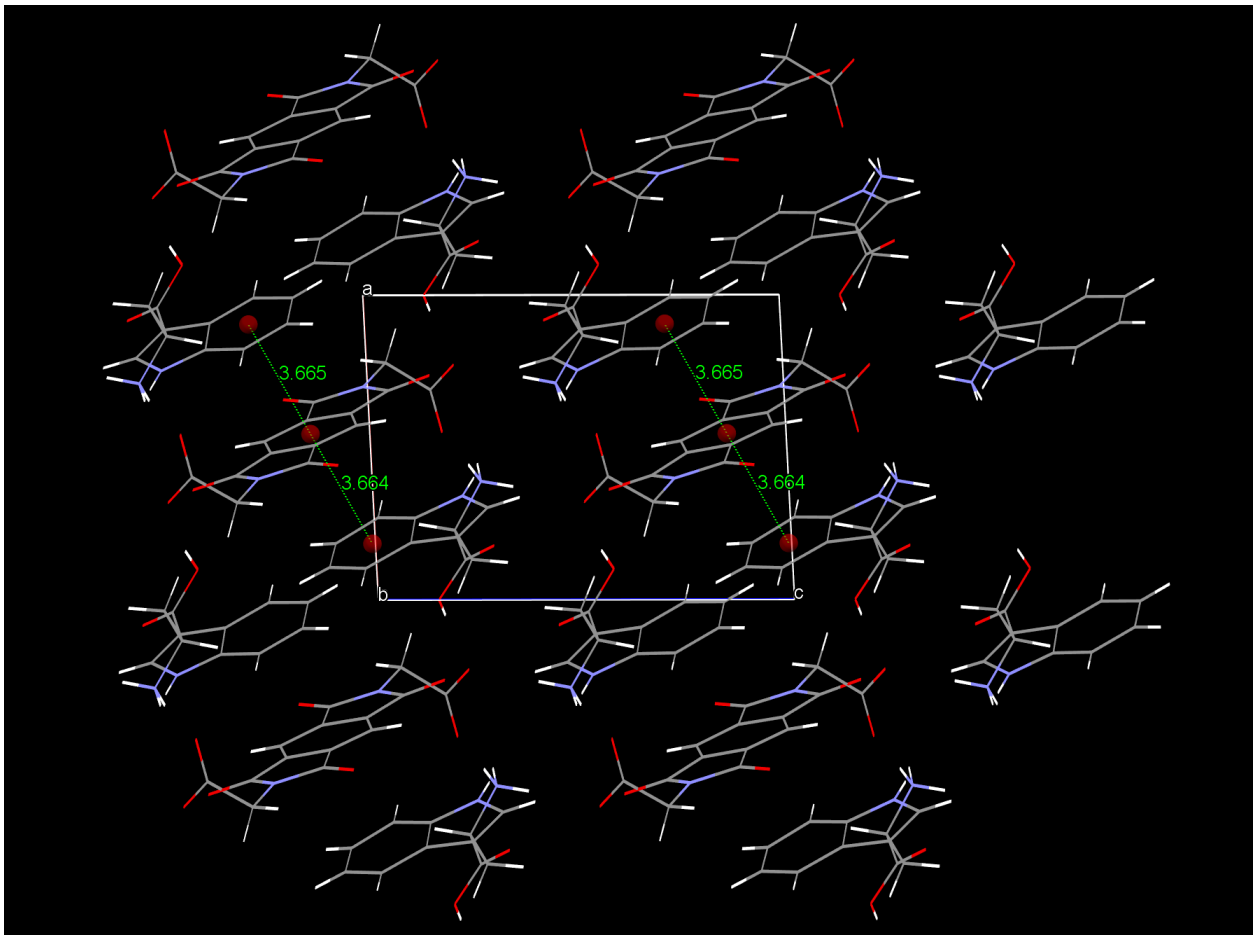


Figure S41. *Crystal packing of the complex showing the π-π stacking and the distance between centroids. Crystallization water molecules have been omitted for clarity.*

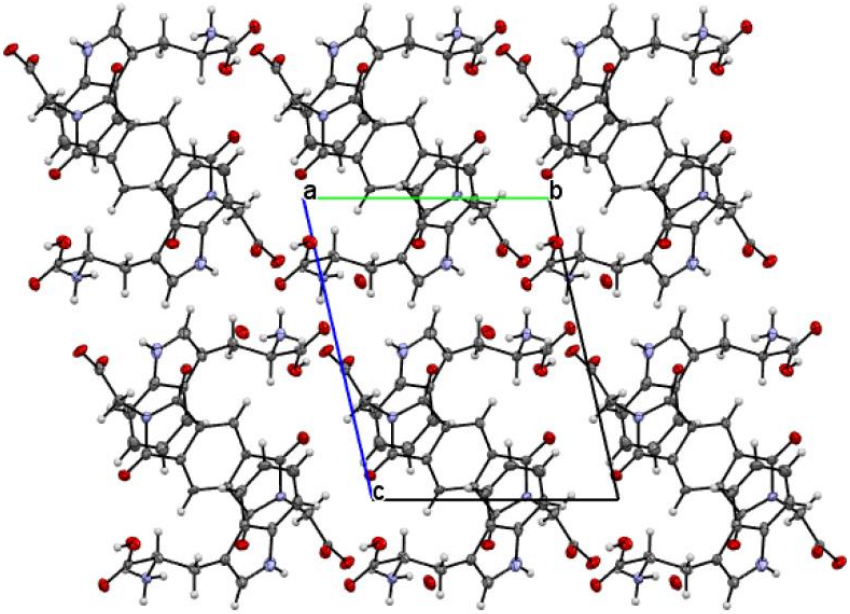


Figure S42. *Crystal packing of the complex viewed along the [100] direction of the unit cell.*

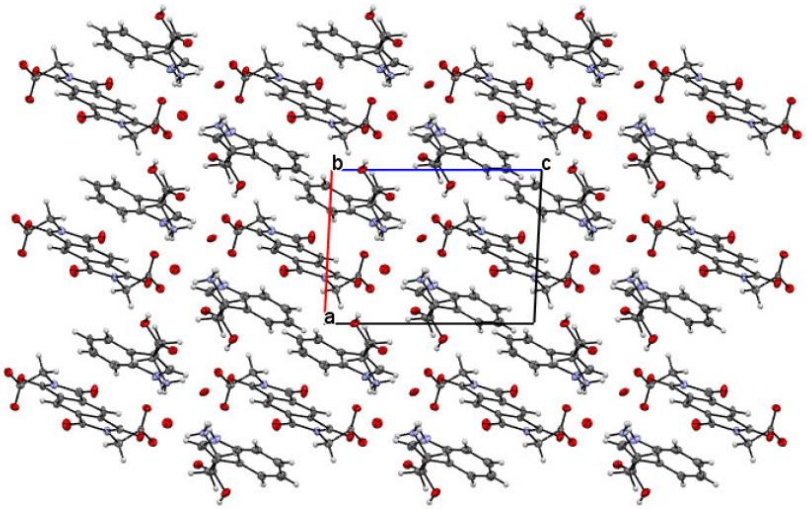
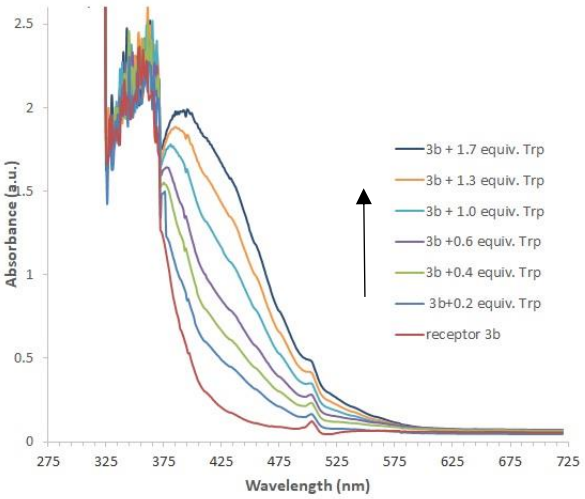
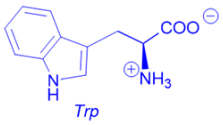


Figure S43. *Crystal packing of the complex viewed along the [010] direction of the unit cell.*

4. UV-vis studies with tryptophan

4.1. Sodium 2,4,6-trinitrobenzene sulfonate (3b)





Trp

[3b] mol/L	[Trp] mol/L	[Trp]/[3b]
0.010	0.000	0.0
0.010	0.002	0.2
0.010	0.004	0.4
0.010	0.006	0.6
0.010	0.010	1.0
0.010	0.013	1.3
0.010	0.017	1.7

Figure S44. *UV-vis spectra (250-725 nm) corresponding to the titration of sodium 2,4,6-trinitrobenzenesulfonate (**3b**) with L-Trp.*

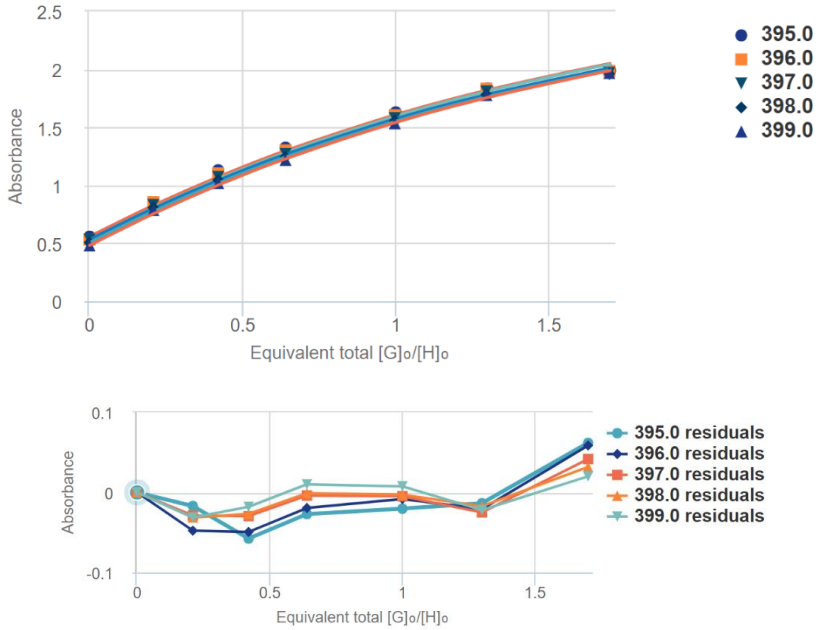


Figure S45. *Binding isotherm for the 1:1 receptor **3b**:Trp binding and the residual error obtained from fitting using Bindfit*

UV 1:1 *(λ = 375-445 nm)*
K_a=87(±1.2%) M^{-1}
Covariance=4.8309e-3

http://app.supramolecular.org/bindfit/view/9845d3a9-fb69-4025-bb0b-b1050235e3b1

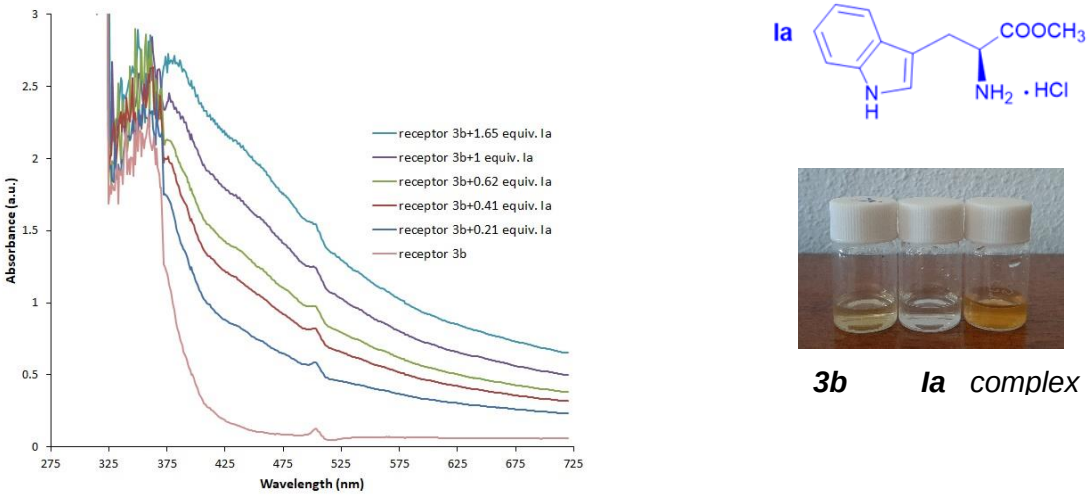


Figure S46. *UV-vis spectra (250-725 nm) corresponding to the titration of sodium 2,4,6-trinitrobenzenesulfonate (**3b,** 0.01M**) with L-Trp methyl ester hydrochloride(**Ia**).*

Figure S47. *Left: solution of receptor **3b** (0.01M) in H_2O. Middle: solution of tryptophan methyl ester (**Ib**, (0.01M)) in H_2O. Right: complex in H_2O.*

4.2. 3,5- dinitrobenzoic acid (4a)

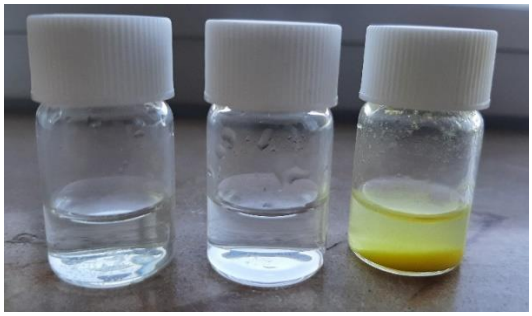
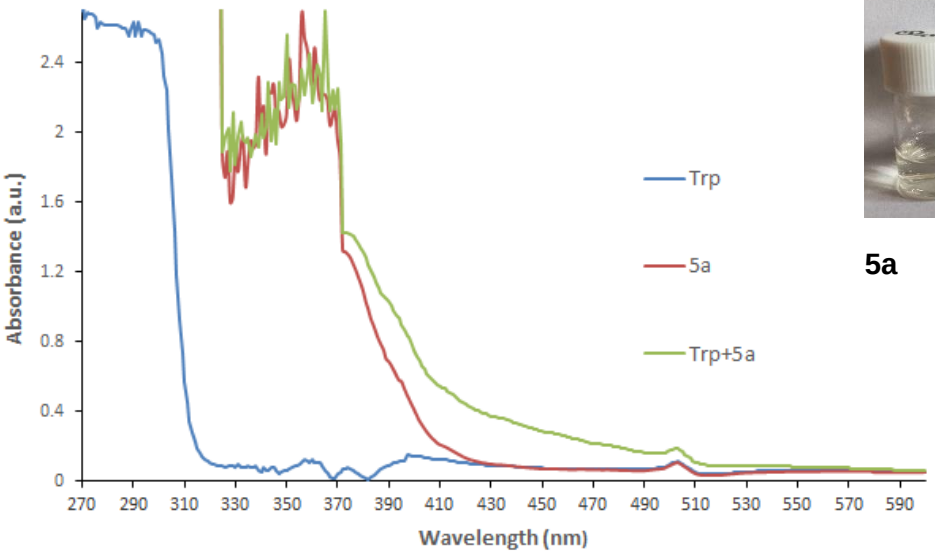
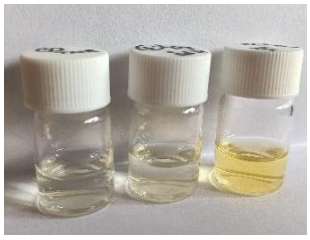


Figure S48. *Left: solution of receptor **4a** (0.01M) in H_2O. Middle: solution of L-Trp (0.01M) in H_2O. Right: solution of complex in H_2O.*

4.3. 2,4,6- trinitrobenzoic acid (5a)

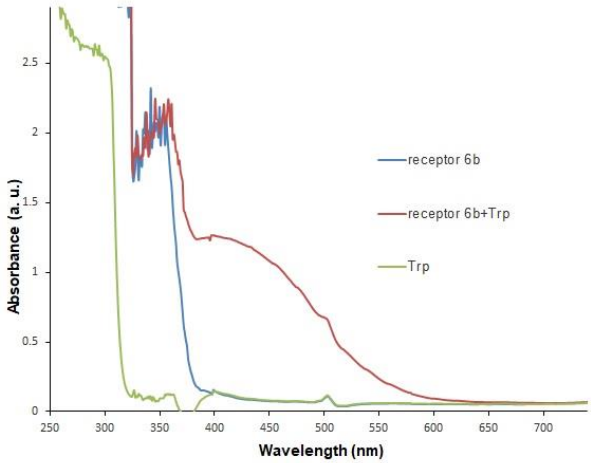




5a ***Trp*** *complex*

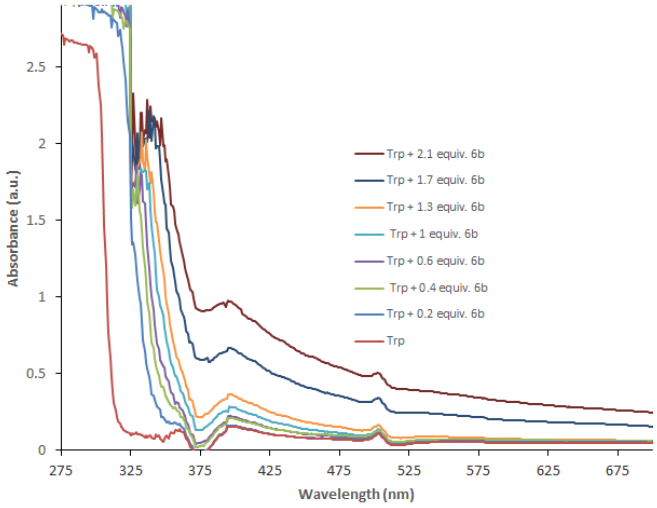
Figure S49. *UV-Vis spectra (250-600 nm) of 2,4,6-trinitrobenzoic acid (**5a**,* 0.01M, *red line), L-Trp (0.01M, blue line) and the complex between 2,4,6-trinitrobenzoic acid (**5a**) and L-Trp (green line).*

4.4. *N,N´*-bis(glycinyl)pyromellitic diimide (6b)



6b *Trp* *complex*

Figure S50. *UV-Vis spectra (250-700 nm) of diimide **6b**,* 0.01M, *blue line), L-Trp (0.01M, green line) and the complex between 2,4,6-trinitrobenzoic acid (**5a**) and L-Trp (red line).*



[**6b**] mol/L	[Trp] mol/L
0.010	0.000
0.010	0.002
0.010	0.004
0.010	0.006
0.010	0.010
0.010	0.013
0.010	0.017
0.010	0.021

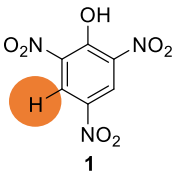
Figure S51. *UV-vis spectra (250-725 nm) corresponding to the titration of diimide **6b** with L-Trp.*

5. NMR titrations with tryptophan

5.1. Picric acid (1)

^{1}H NMR titration between picric acid and L-tryptophan in D_2O. The shift of the proton of the receptor (H-3(5)) was followed.

[Receptor **1**] (M)	[L-Trp] (M)	[G]/[H]	chemical shift (δ, ppm)
0.0049	0.0000	0.00	8.7518
0.0049	0.0016	0.33	8.7300
0.0049	0.0031	0.63	8.7108
0.0049	0.0044	0.90	8.6979
0.0049	0.0057	1.16	8.6826
0.0049	0.0069	1.41	8.6749
0.0049	0.0090	1.84	8.6544
0.0049	0.0109	2.22	8.6390
0.0049	0.0126	2.57	8.6211
0.0049	0.0172	3.51	8.5980
0.0049	0.0196	4.00	8.5877
0.0049	0.0217	4.43	8.5749



1

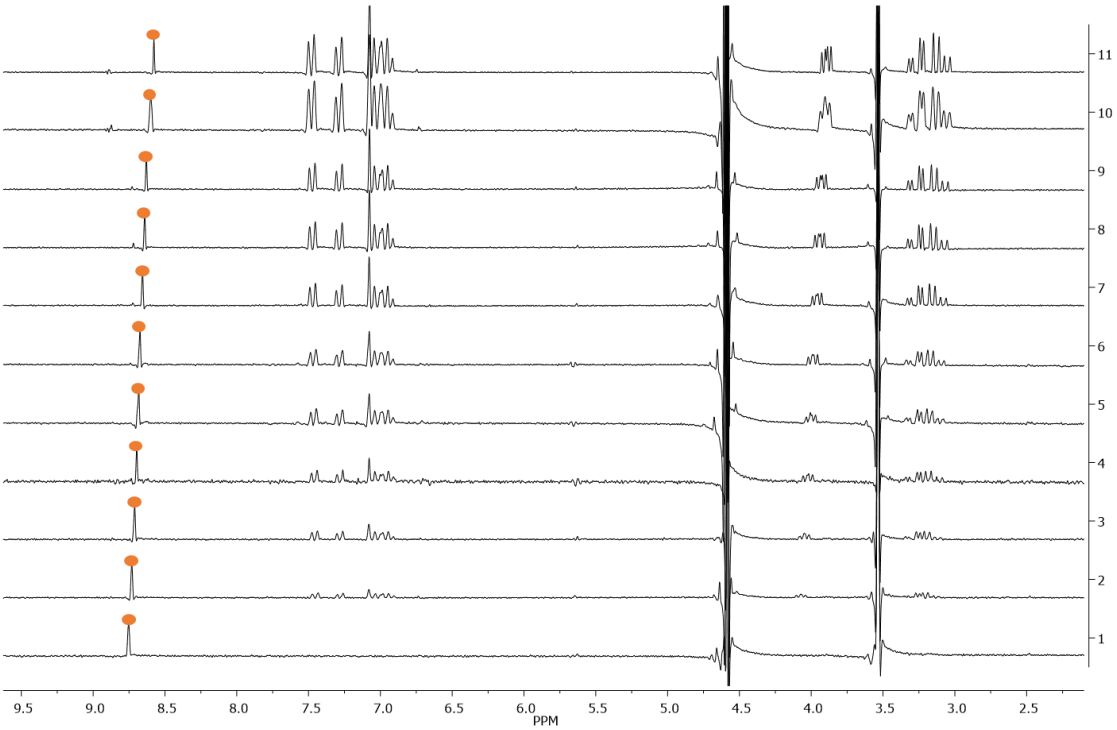


Figure S52. *^{1}H NMR spectra (2.5-9.5 ppm) corresponding to titration of picric acid (**1**) and L-Trp.*

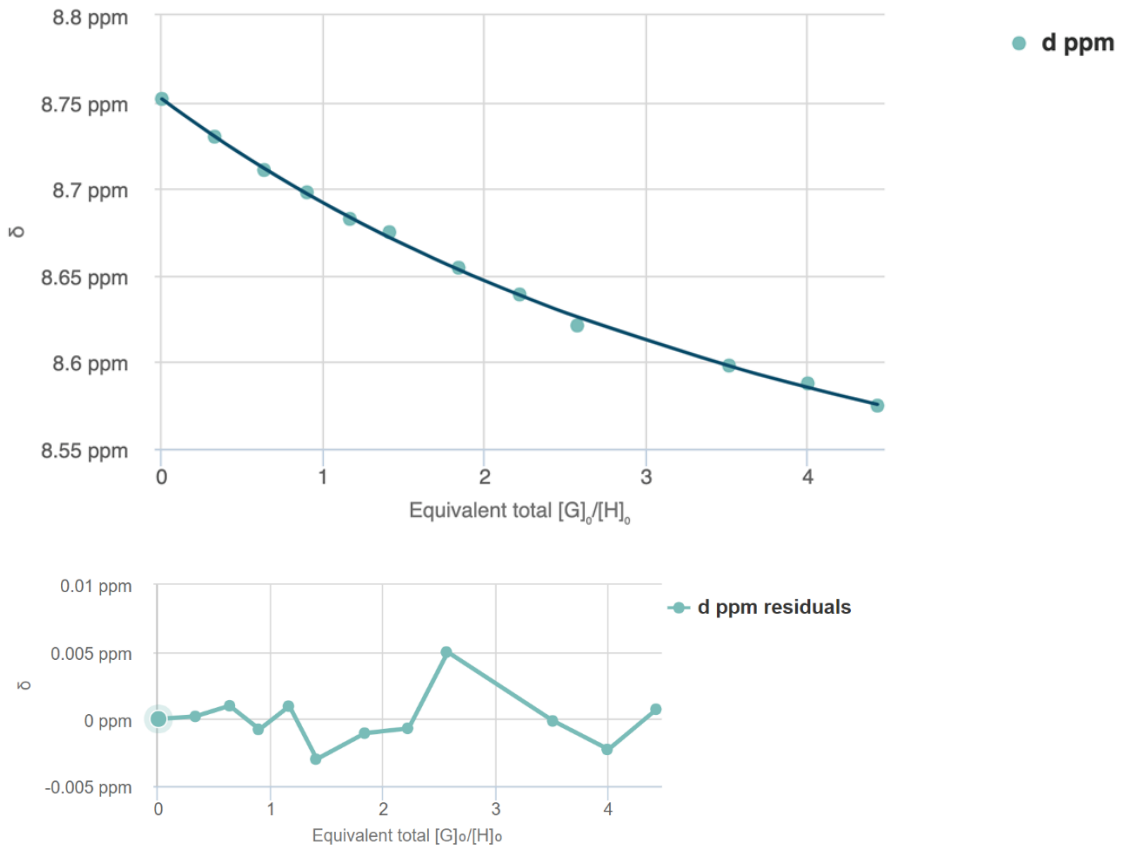


Figure S53. *Binding isotherm corresponding to titration of picric acid (**1**) and L-Trp (supramolecular.org).*

NMR 1:1
K_a=47.7(±2.4%) M^{-1}
Covariance=1.1982e-3

http://app.supramolecular.org/bindfit/view/5782103f-30e4-4c3d-aa88-abbd087367b6

5.2. Sodium 2,4,6-trinitrobenzenesulfonate (3b)

^{1}H NMR titration between sodium 2,4,6-trinitrobenzenesulfonate and L-tryptophan in D_2O. The shift of the H-13 proton of the L-Trp was followed.

[L-Trp] (M)	[Sodium 2,4,6-trinitrobenzenesulfonate] (M)	[G]/[H]	chemical shift (δ, ppm)
0.0049	0.0000	0.00	7.5319
0.0049	0.0016	0.33	7.5242
0.0049	0.0030	0.61	7.5216
0.0049	0.0043	0.88	7.5170
0.0049	0.0068	1.39	7.5098
0.0049	0.0089	1.82	7.5037
0.0049	0.0107	2.18	7.5011
0.0049	0.0124	2.53	7.4960
0.0049	0.0158	3.22	7.4909
0.0049	0.0185	3.78	7.4883
0.0049	0.0207	4.22	7.4857

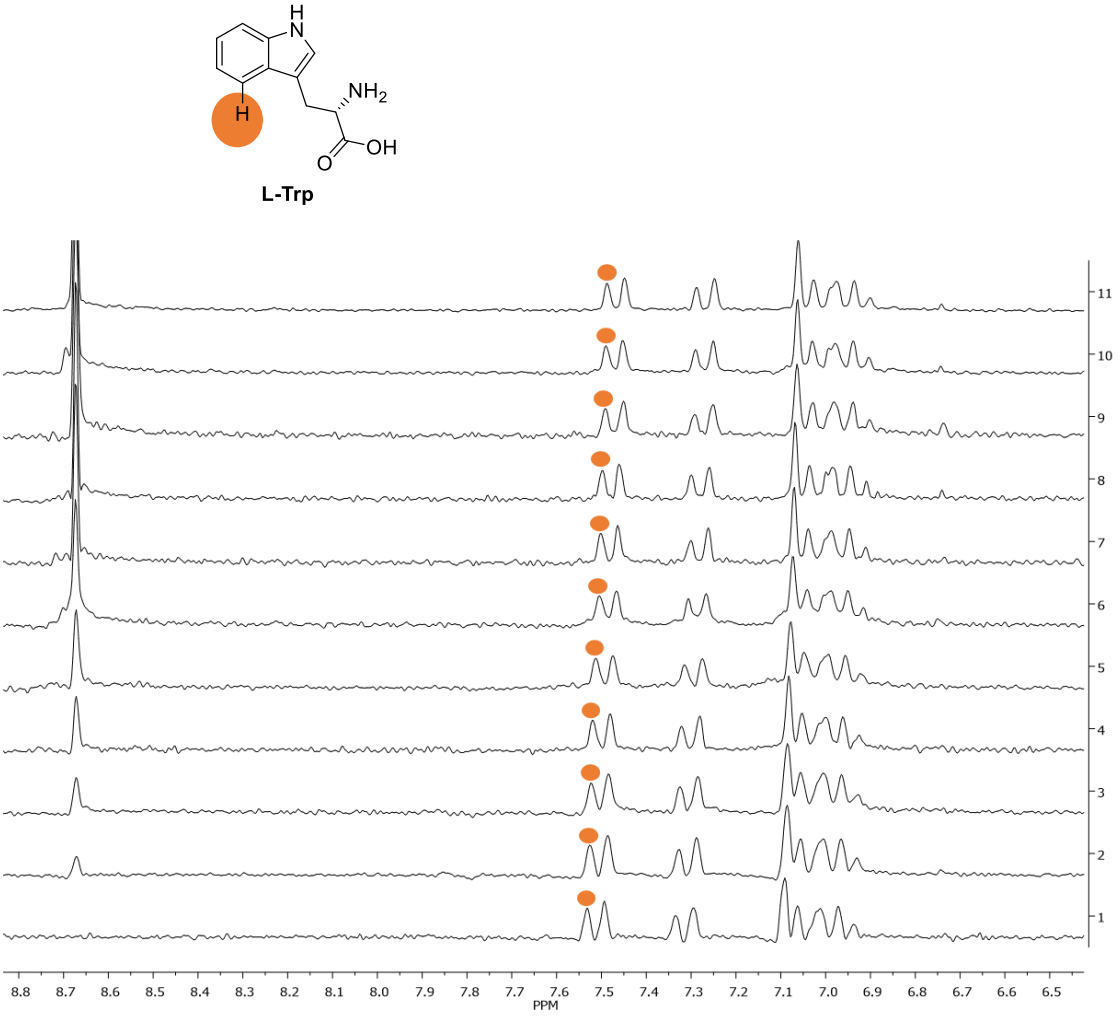


Figure S54. *^{1}H NMR spectra (6.4-8.8 ppm) corresponding to titration of **3b** and L-Trp.*

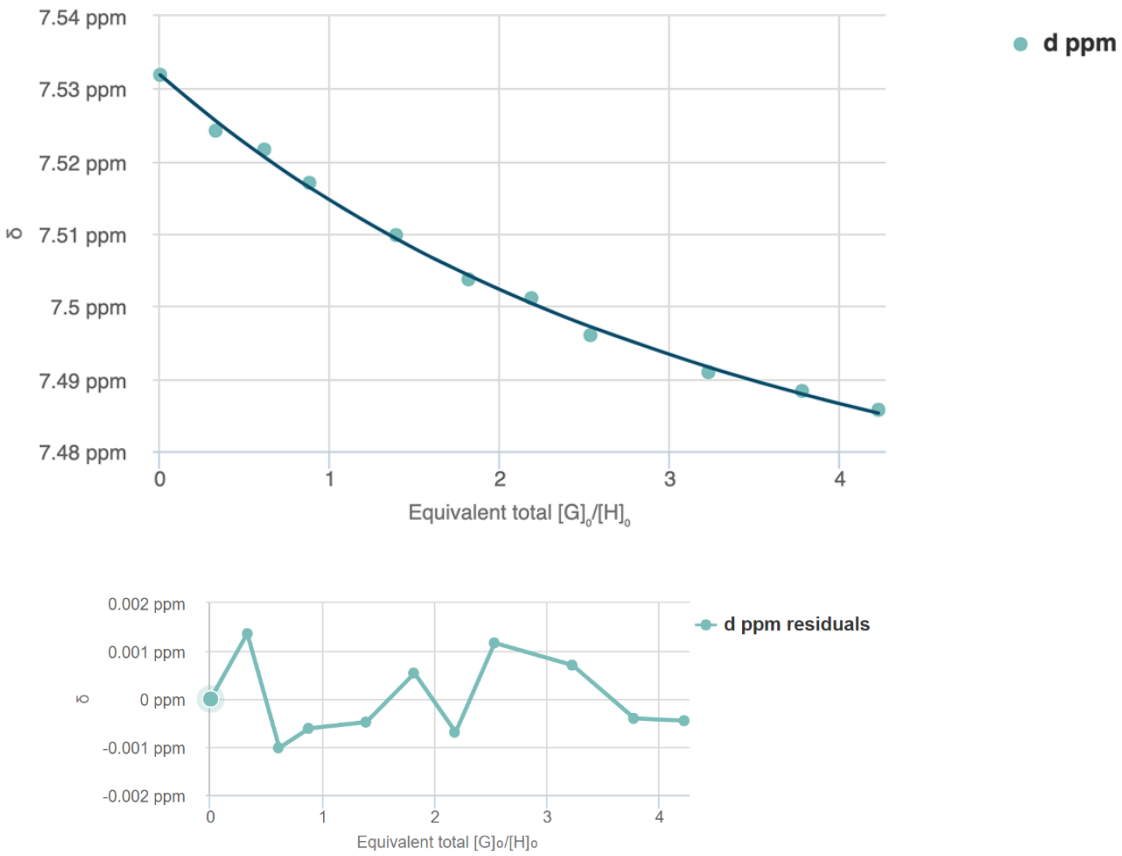


Figure S55. *Binding isotherm corresponding to titration of L-Trp and sodium 2,4,6-trinitrobenzenesulfonate (**3b**) (supramolecular.org).*

NMR 1:1
K_a= 62(±3.9%) M^{-1}
Covariance=2.6343e-3

http://app.supramolecular.org/bindfit/view/b94c31e5-2975-4b65-8269-999959445314

5.3. 3,5-dinitrobenzoic acid (4a)

^{1}H NMR titration between 3,5-dinitrobenzoic acid and *L*-tryptophan was carried out in D_2O. The shift of the H-2 proton of the receptor was followed.

[Receptor **4a**] (M)	[L-Trp] (M)	[G]/[H]	chemical shift (δ, ppm)
0.0052	0.0000	0.00	8.8927
0.0052	0.0018	0.35	8.8671
0.0052	0.0034	0.65	8.8440
0.0052	0.0049	0.94	8.8184
0.0052	0.0063	1.21	8.7902
0.0052	0.0077	1.48	8.7723
0.0052	0.0100	1.92	8.7543
0.0052	0.0122	2.35	8.7364
0.0052	0.0141	2.71	8.7287
0.0052	0.0180	3.46	8.7005

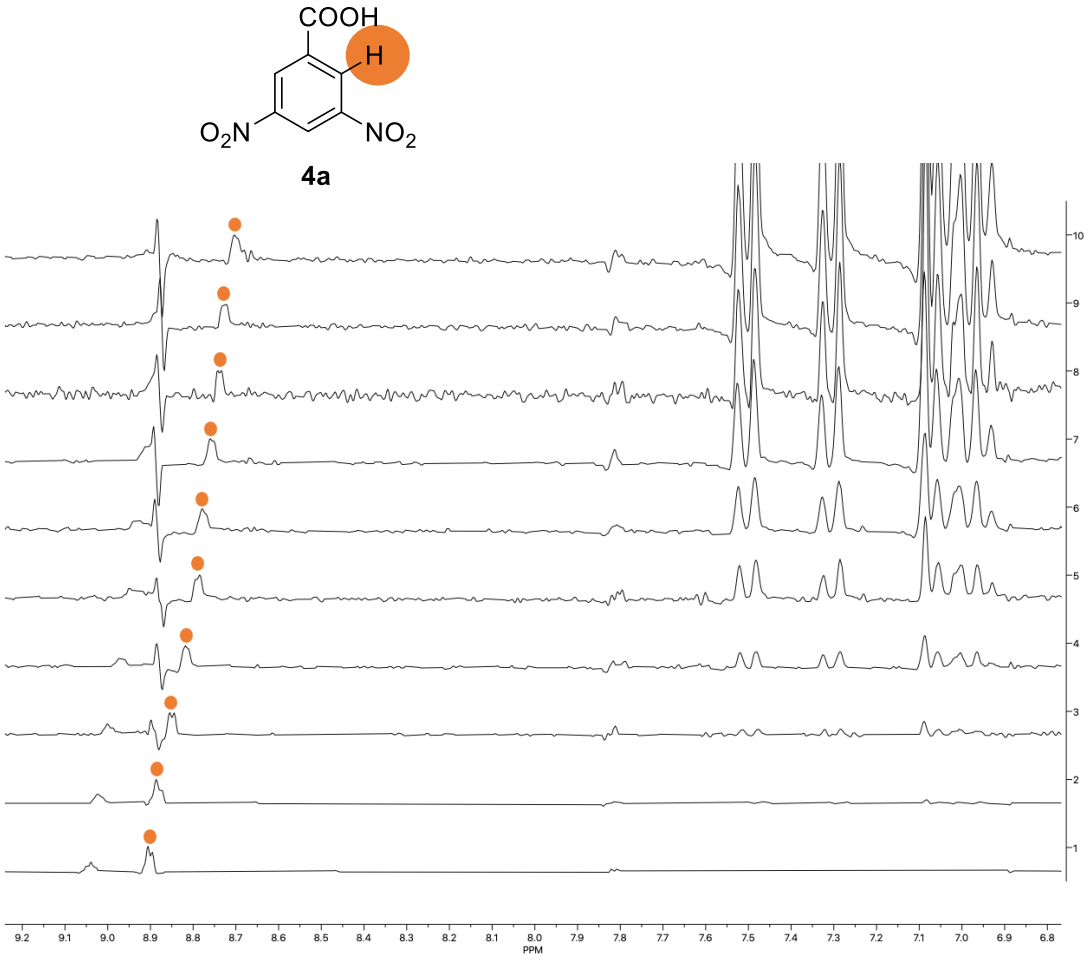


Figure S56. *^{1}H NMR spectra (6.8-9.2 ppm) corresponding to titration of **4a** and L-Trp.*

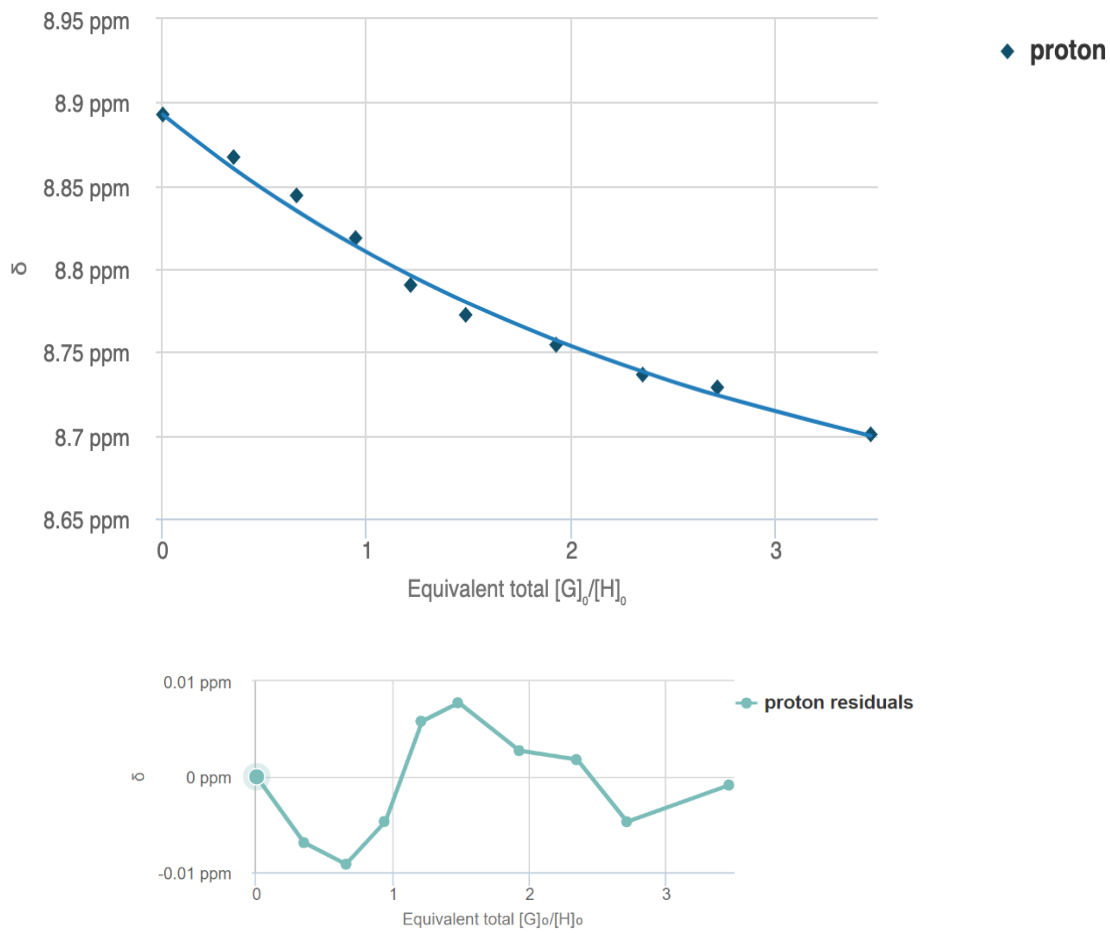


Figure S57. *Binding isotherm corresponding to titration of 3,5-dinitrobenzoic acid (**4a**) and L-Trp (supramolecular.org).*

NMR 1:1
K_a= 72(±7.4%) M^{-1}
Covariance=7.5124e-3

http://app.supramolecular.org/bindfit/view/75dac39e-6317-46cd-86db-b244b288e852

5.4. Lithium 3,5-dinitrobenzoate (4b)

^{1}H NMR titration between 3,5-dinitrobenzoate and *L*-tryptophan was carried out in D_2O. The shift of the H-2 proton of the receptor was followed.

[Receptor **4b**] (M)	[L-Trp] (M)	[G]/[H]	chemical shift (δ, ppm)
0.0063	0.000	0.00	8.8466
0.0063	0.0014	0.22	8.8338
0.0063	0.0033	0.52	8.8235
0.0063	0.0048	0.76	8.8105
0.0063	0.0062	0.98	8.7928
0.0063	0.0075	1.18	8.7800
0.0063	0.0098	1.55	8.7646
0.0063	0.0118	1.87	8.7543
0.0063	0.0136	2.16	8.7418
0.0063	0.0174	2.76	8.7236
0.0063	0.0204	3.24	8.7056

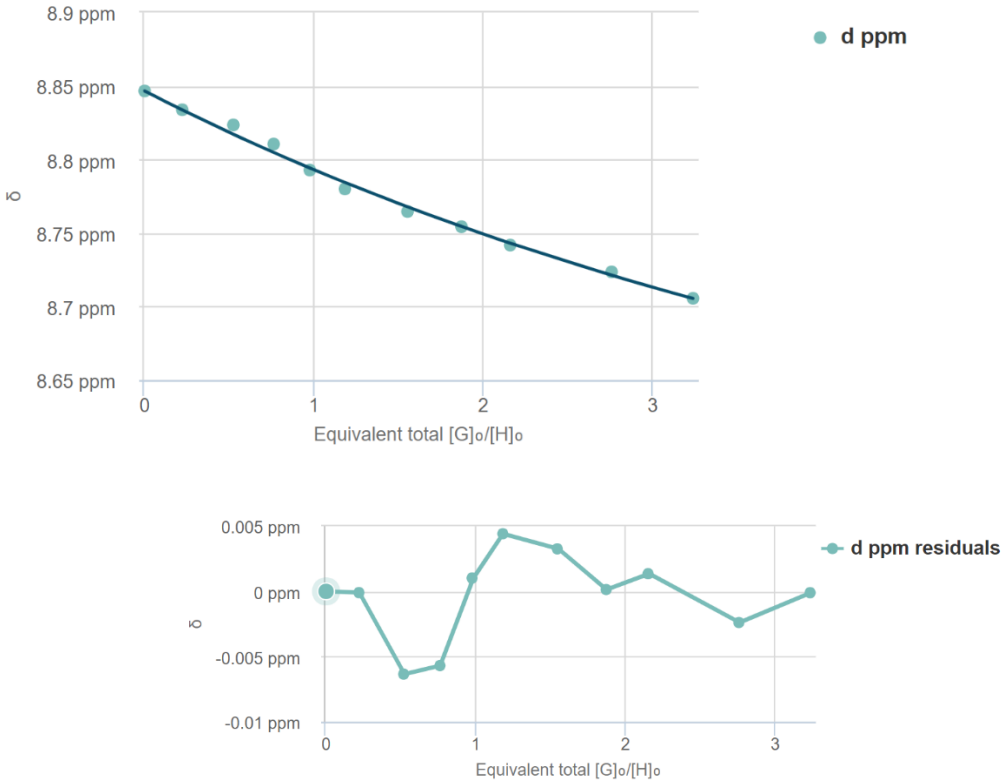


Figure S58. *Binding isotherm corresponding to titration of 3,5-dinitrobenzoate (**4b**) and L-Trp (supramolecular.org).*

NMR 1:1
K_a= 22.4 (±4.4%) M^{-1}
Covariance= 5.1248e-3

http://app.supramolecular.org/bindfit/view/e8bd196c-a60b-4695-a1e1-4fc88deee2a8

5.5. 2,4,6-trinitrobenzoic acid (5a)

The shift of the proton of 2,4,6-trinitrobenzoic acid in the ^{1}H NMR titration with *L*-tryptophan in D_2O was evaluated.

**Warning: 2,4,6-trinitrobenzoic acid is a potentially explosive compound.*

[Receptor **5a**] (M)	[L-Trp] (M)	[G]/[H]	chemical shift (δ, ppm)
0.0049	0.0000	0.00	9.1131
0.0049	0.0030	0.61	9.0952
0.0049	0.0043	0.88	9.0875
0.0049	0.0056	1.14	9.0834
0.0049	0.0078	1.59	9.0772
0.0049	0.0098	2.00	9.0670
0.0049	0.0115	2.35	9.0619
0.0049	0.0138	2.82	9.0567
0.0049	0.0157	3.20	9.0516
0.0049	0.0184	3.76	9.0491
0.0049	0.0205	4.18	9.0465

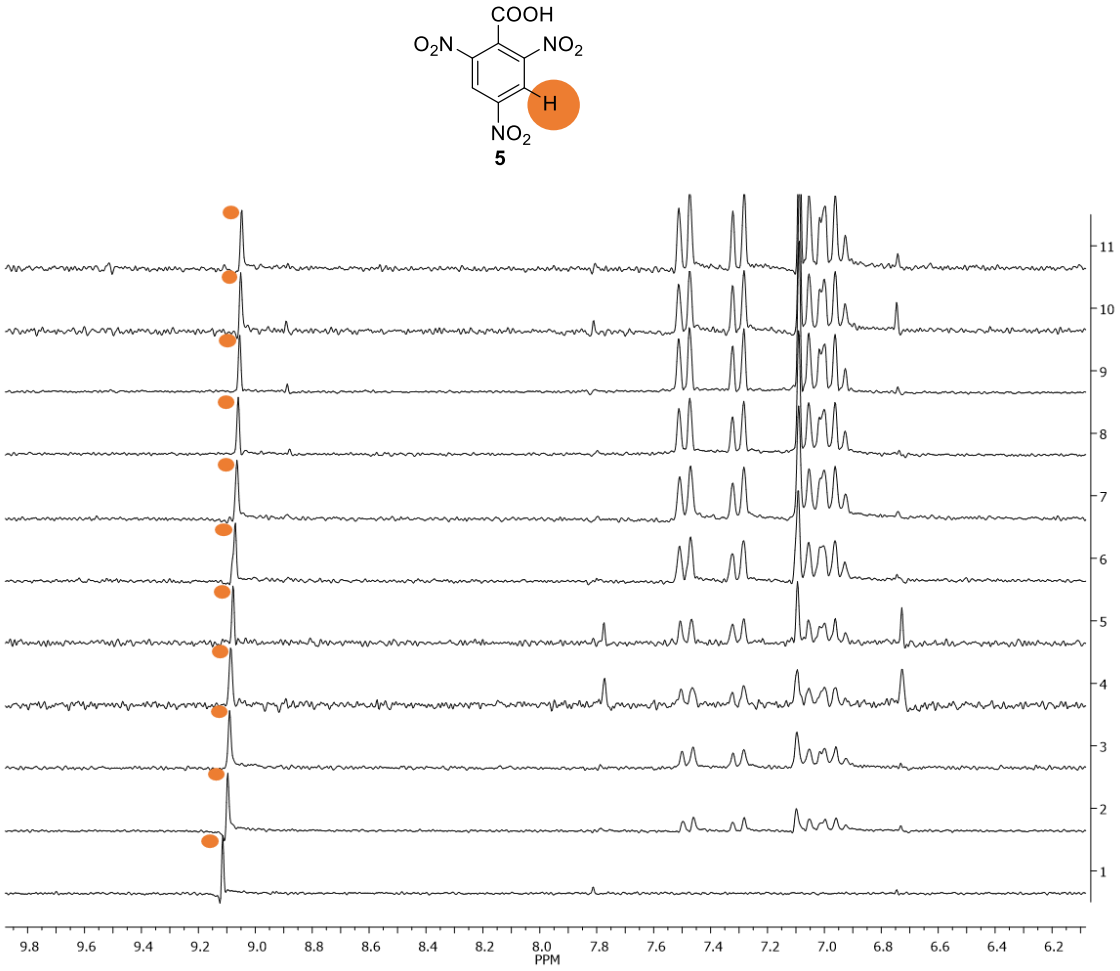


Figure S59. *^{1}H NMR spectra (6.2-9.8 ppm) corresponding to titration of **5a** and L-Trp.*

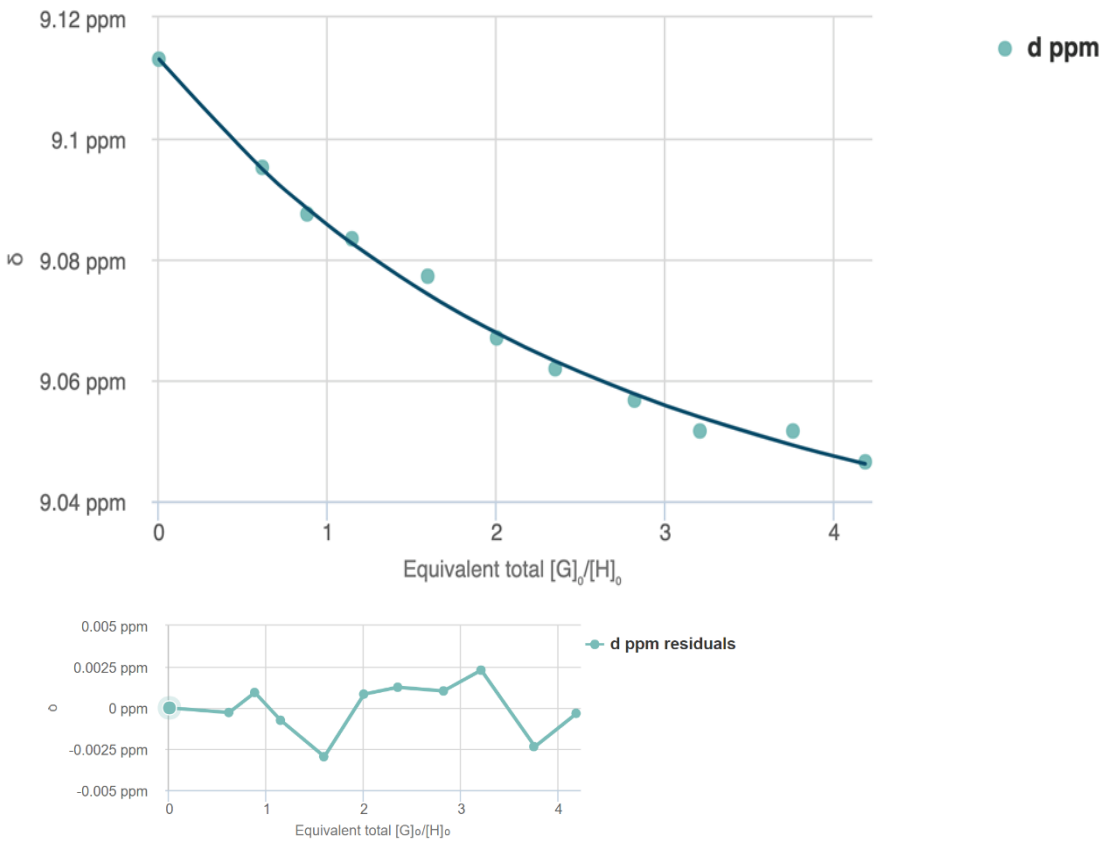


Figure S60. *Binding isotherm corresponding to titration of 2,4,6-trinitrobenzoic acid (**5a**) and L-Trp (supramolecular.org).*

NMR 1:1
K_a= 92.7 (±5.8%) M^{-1}
Covariance= 5.4835e-3

http://app.supramolecular.org/bindfit/view/69061afa-c4c4-4113-b879-b876979844c2

5.6. Lithium 2,4,6-trinitrobenzoate (5b)

The shift of the proton of 2,4,6-trinitrobenzoate in the ^{1}H NMR titration with *L*-tryptophan in D_2O was evaluated.

**Warning: 2,4,6-trinitrobenzoic acid is a potentially explosive compound.*

[Receptor **5b**] (M)	[L-Trp] (M)	[G]/[H]	chemical shift (δ, ppm)
0.0063	0.0000	0.00	9.106
0.0063	0.0018	0.29	9.1003
0.0063	0.0034	0.54	9.0926
0.0063	0.0049	0.78	9.0875
0.0063	0.0063	1.00	9.0824
0.0063	0.0077	1.22	9.0798
0.0063	0.0101	1.60	9.0721
0.0063	0.0122	1.94	9.0644
0.0063	0.0141	2.24	9.0593
0.0063	0.018	2.86	9.0465

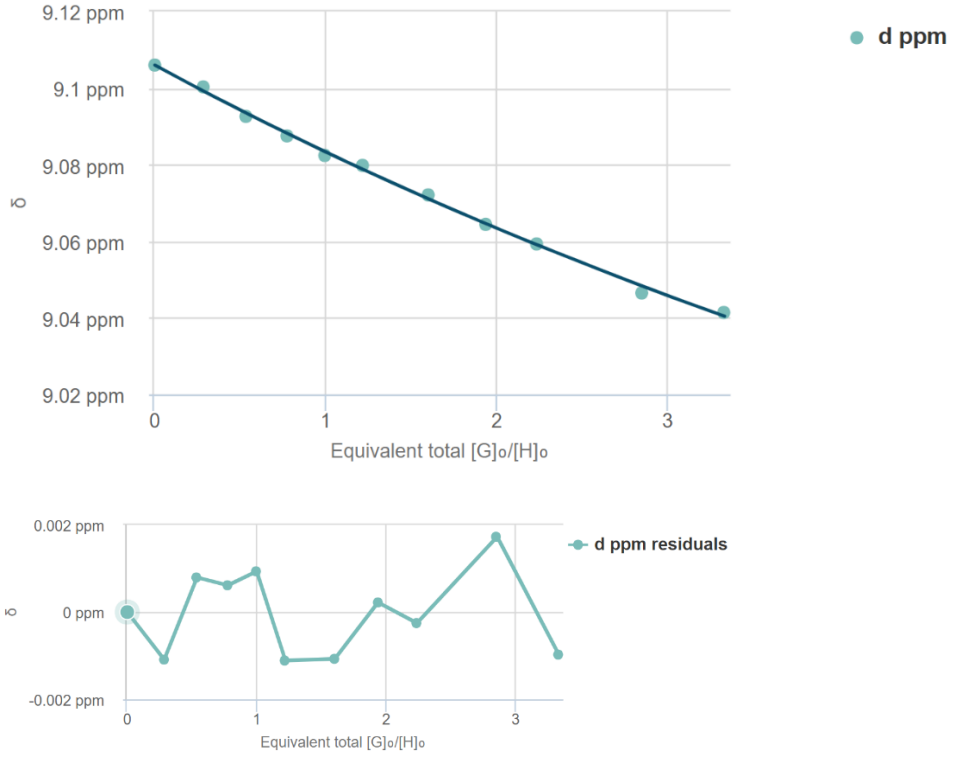


Figure S61. *Binding isotherm corresponding to titration of 2,4,6-trinitrobenzoate (**5b**) and L-Trp (supramolecular.org).*

NMR 1:1
***K*$_a$= 12.7(±2.5%) M^{-1}**
Covariance= 2.1310e-3

http://app.supramolecular.org/bindfit/view/92415c68-4dc7-442e-8aa6-ed59e8f4f4ca

5.7. *N,N´*-bis(glycinyl)pyromellitic diimide (6b)

The shift of the aromatic proton of the receptor **6b** was evaluated.

[Receptor **6b**] (M)	[L-Trp] (M)	[G]/[H]	chemical shift (δ, ppm)
0.0054	0.0000	0.00	8.1495
0.0054	0.0016	0.27	8.1188
0.0054	0.0032	0.59	8.0931
0.0054	0.0046	0.85	8.0701
0.0054	0.0059	1.09	8.0521
0.0054	0.0072	1.33	8.0316
0.0054	0.0094	1.74	8.0009
0.0054	0.0110	2.04	7.9753
0.0054	0.0131	2.43	7.9493
0.0054	0.0147	2.72	7.9317
0.0054	0.0180	3.33	7.9115
0.0054	0.0206	3.82	7.8932

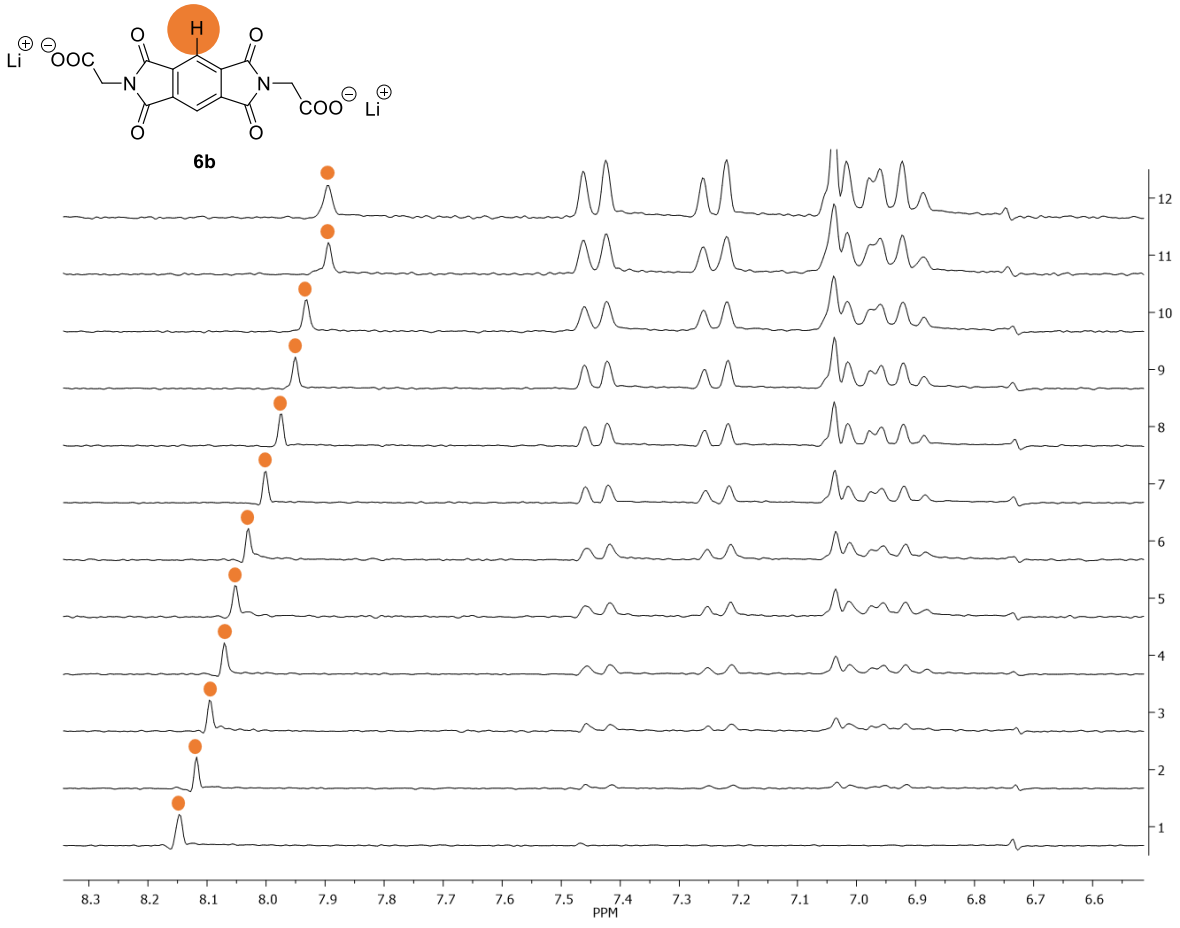


Figure S62. *^{1}H NMR spectra (6.5-8.3 ppm) corresponding to titration of **6b** and L-Trp.*

1:1Binding model (1 molecule diimide **6b** + 1molecule Trp)

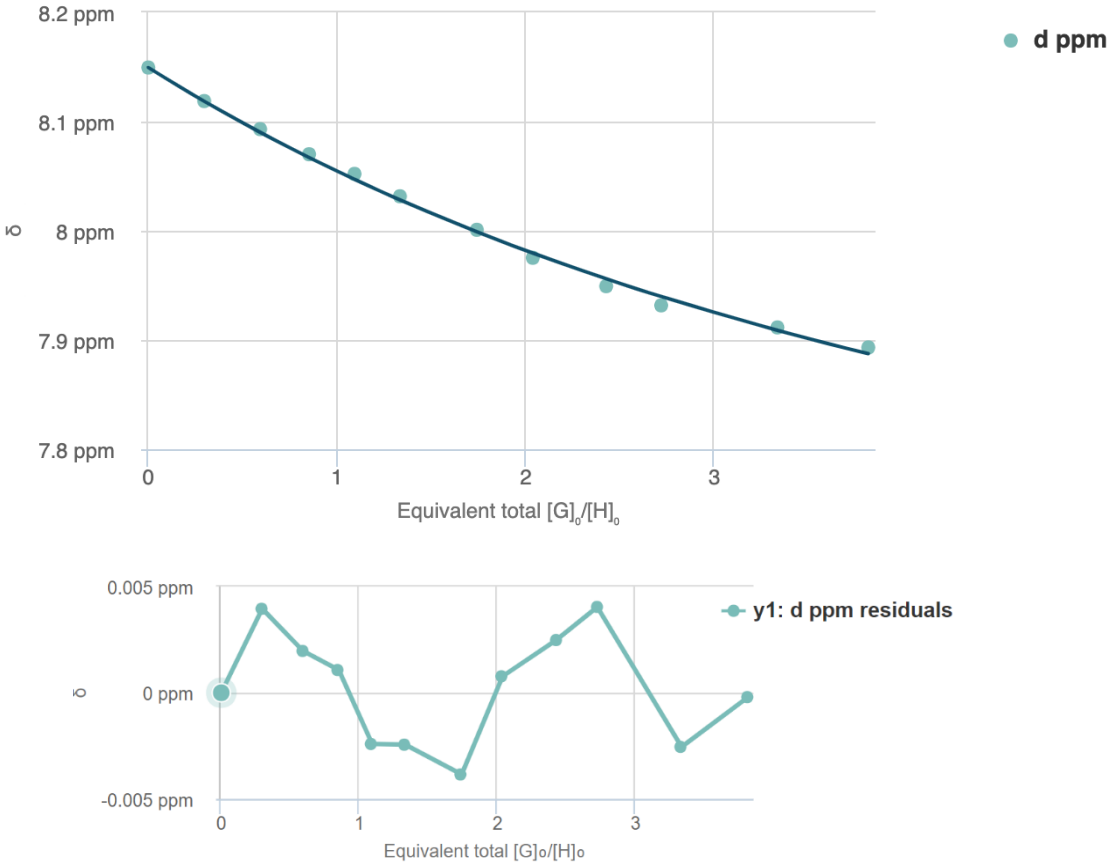


Figure S63. *Binding isotherm corresponding to titration of receptor **6b** and L-Trp (supramolecular.org).*

NMR 1:1
K_a= 38 (±3.3%) M^{-1}
Covariance= 2.8205e-3

http://app.supramolecular.org/bindfit/view/09640114-d841-4d40-aedb-b367890a45c0

Comparison of the different binding models *(online web-applet BindFit[9])*

Different binding models were considered:

- 1:1 Binding model (1 molecule diimide **6b** + 1 molecule Trp)
- 1:2 Binding model (1 molecule diimide **6b** + 2 molecules Trp)
- 2:1 Binding model (2 molecules diimide **6b** + 1 molecule Trp)

Association constants are shown in table S5. Models converging on negative values for the association constants have not been included.

Table S5. Association constants for the binding of diimide 6b with Trp

Binding model	$cov_{fit}\ (10^{-3})^a$	cov_{fit} *factor*	$K_1(M^{-1})$	$K_2(M^{-1})$
1:1	2.8205	1	38 (±3.3%)	
Full 1:2	0.97299	2.9	137.5 (±22.3%)	214.3 (±25.9%)
Non cooperative 1:2	1.0134	2.8	471.9(±4%)	118(±4%)
Additive 1:2	0.97471	2.9	188 (±22.7%)	179 (±19.8%)
Non cooperative 2:1	1.5765	1.8	128 (±8.6%)	32 (±8.6%)
Statistical 2:1	2.9417	0.9	30 (±2.9%)	7.5 (±2.9%)

[a] cov_{fit} factor = cov_{fit} for the **1:1** model divided by the cov_{fit} for the binding model under study

Table S6 analyses chemical shifts of the diimide aromatic proton, in the free receptor (H) and in the complexes formed with tryptophan (HG_2 or H_2G):

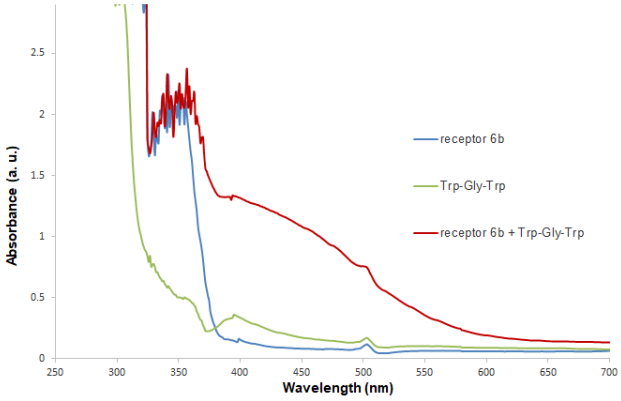
Table S6. Chemical shifts for the binding of diimide 6b with Trp

Binding model	δ_H	δ_{HG}	δ_{HG_2}	δ_{H_2G}
1:1	8.1495	7.5130		
Full 1:2		7.9485	7.8169	
Non cooperative 1:2		8.0260	7.7730	
Additive 1:2		7.9781	7.8066	
Non cooperative 2:1		7.6664		8.9210
Statistical 2:1		7.4766		6.8036

Models 2:1 are not considered due to the poor quality of fit or illogical chemical shifts. Three 1:2 models allow better fitting than the 1:1 model *(cov_{fit} factor close to 3),* with the non cooperative model showing lower errors in the estimation of association constants. The stoichiometry 1:2 also agrees with the one in crystal structure for diimide and Trp.

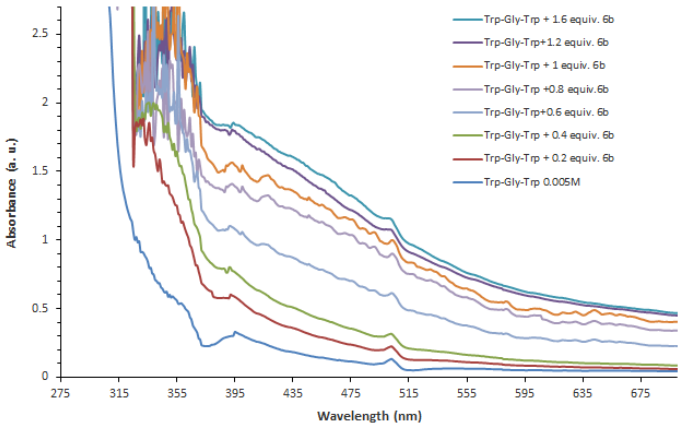
6. Binding to Tripeptide Trp-Gly-Trp (10)

6.1. UV-vis titration with diimide 6b



6b *Trp-Gly-Trp* complex

Figure S64. *UV-Vis spectra (250-700 nm) of diimide **6b**, 0.01M, blue line), Trp-Gly-Trp (0.01M, green line) and the complex between diimide (**6b**) and tripeptide **10**.*



[6b] mol/L	[10] mol/L	[10]/[6b]
0.005	0.000	0.0
0.005	0.001	0.2
0.005	0.002	0.4
0.005	0.003	0.6
0.005	0.004	0.8
0.005	0.005	1.0
0.005	0.006	1.2
0.005	0.008	1.6

Figure S65. *UV-vis spectra (275-700 nm) corresponding to the titration of diimide **6b** with tripeptide **10**.*

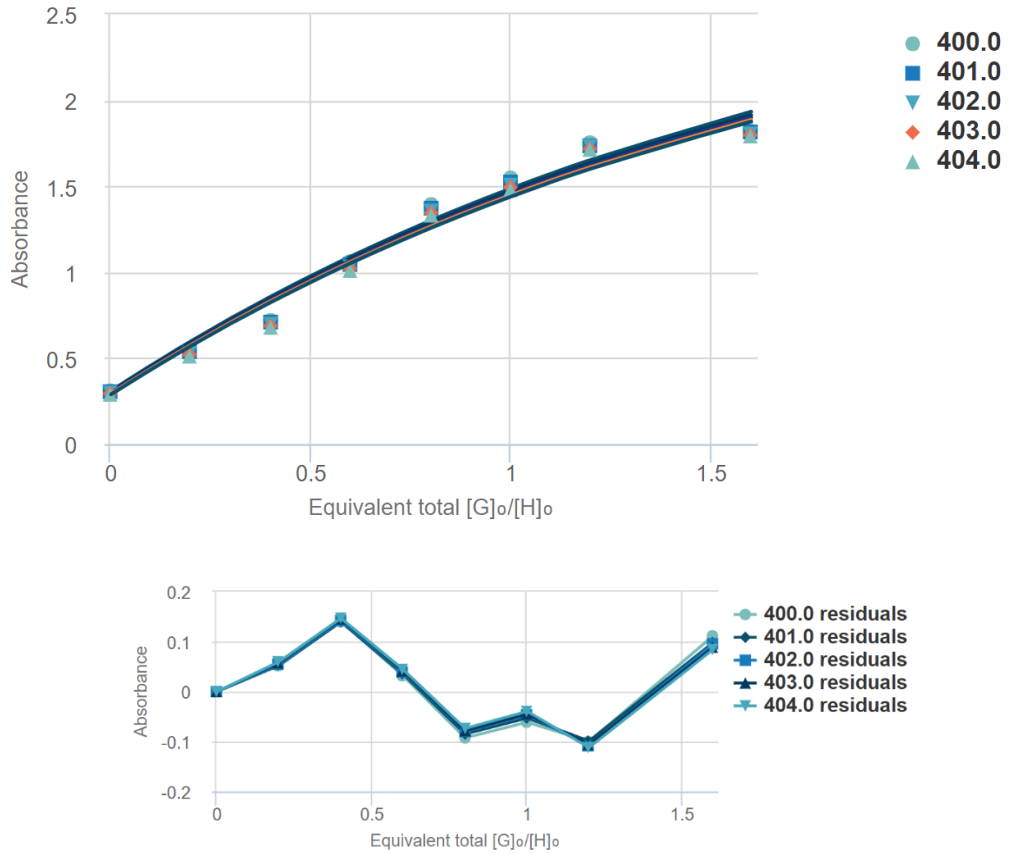


Figure S66. *Binding isotherm for the 1:1 receptor **6b**:Trp-Gly-Trp (**10**) binding and the residual error obtained from fitting using Bindfit.*

UV 1:1 (λ = 400-410 nm)
K_a= 156 (±4.1%) M^{-1}
Covariance= 2.3573e-2

http://app.supramolecular.org/bindfit/view/0b368567-2bf6-4d12-91c2-cc2f1311d2ba

6.2. NMR titration in D_2O with diimide 6b

The shift of the aromatic proton of the receptor **6b** was evaluated in D_2O.

[Receptor **6b**] (M)	[Trp-Gly-Trp] (M)	[G]/[H]	chemical shift (δ, ppm)
0.0048	0.0000	0.00	8.1469
0.0048	0.0011	0.23	8.1162
0.0048	0.0021	0.44	8.0854
0.0048	0.0030	0.63	8.0598
0.0048	0.0039	0.81	8.0414
0.0048	0.0054	1.13	8.0085
0.0048	0.0068	1.42	7.9804
0.0048	0.0080	1.67	7.9624
0.0048	0.0090	1.88	7.9445
0.0048	0.0120	2.50	7.9137
0.0048	0.0150	3.13	7.8855

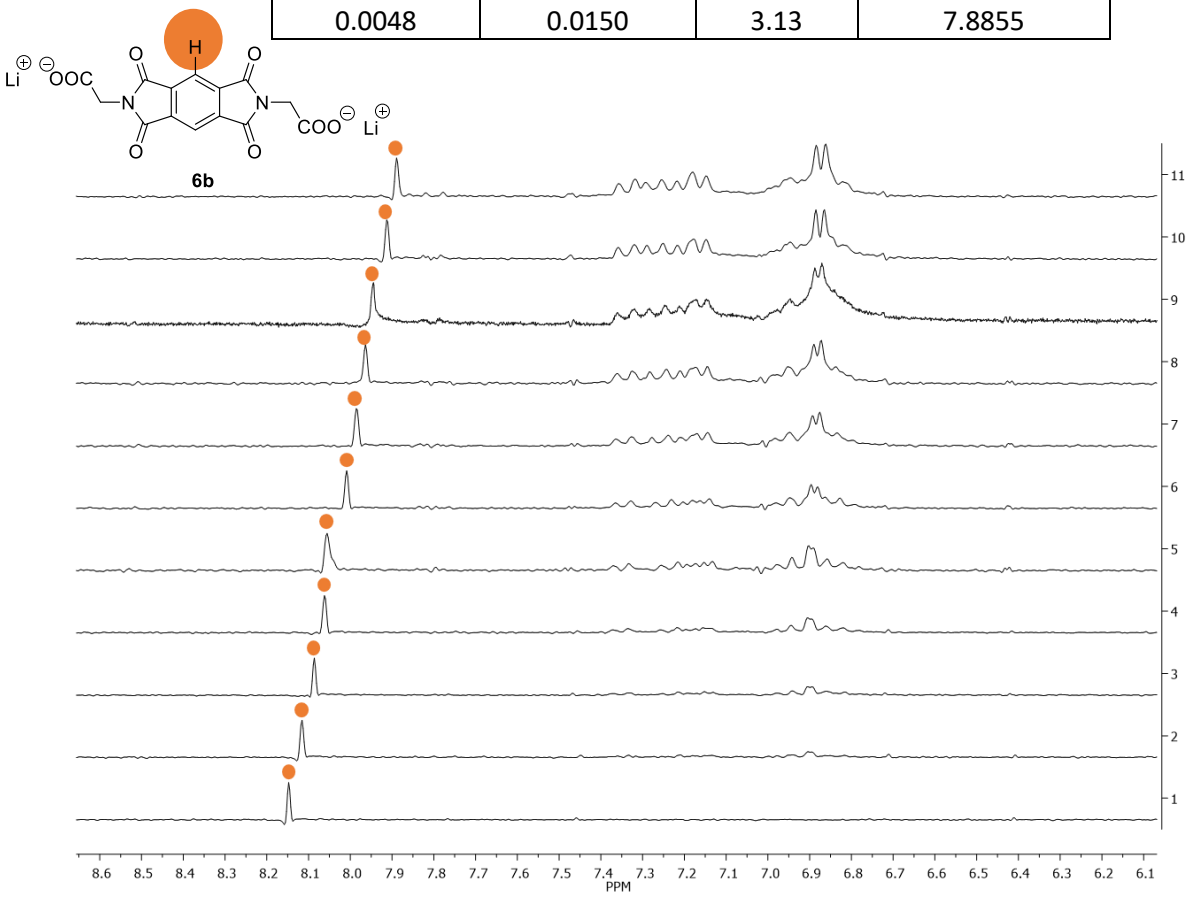


Figure S67. *^{1}H NMR spectra (6.1-8.6 ppm) corresponding to titration of **6b** and Trp-Gly-Trp (**10**).*

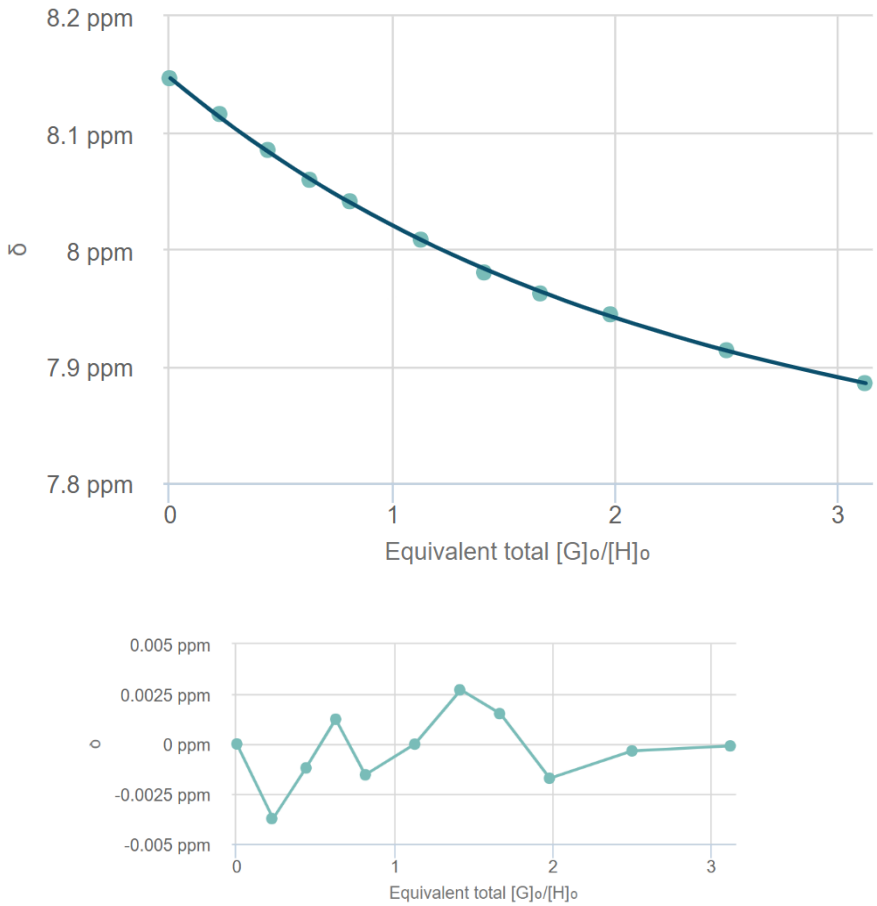


Figure S68. *Binding isotherm for the 1:1 receptor **6b**:Trp-Gly-Trp binding and the residual error obtained from fitting using Bindfit.*

NMR 1:1
K_a=112.3 (±1.9%) M^{-1}
Covariance=4.3630e-4

http://app.supramolecular.org/bindfit/view/5888ba20-4d52-4054-8fbf-f584df512711

Comparison of the different binding models *(online web-applet BindFit[9])*

Different binding models were considered:

- 1:1 Binding model (1 molecule diimide **6b** + 1 molecule tripeptide **10**)
- 1:2 Binding model (1 molecule diimide **6b** + 2 molecule tripeptide **10**)
- 2:1 Binding model (2 molecules diimide **6b** + 1 molecule tripeptide **10**)

Association constants are shown in table S7. Models converging on negative values (or not converging) for the association constants have not been included.

Table S7. Association constants for the binding of diimide 6b with tripeptide 10

Binding model	$cov_{fit}\ (10^{-4})^a$	cov_{fit} *factor*	$K_1(M^{-1})$	$K_2(M^{-1})$
1:1	4.3630	1	112.3 (±1.9%)	
Full 1:2	2.6375	1.6	1662 (±15%)	48 (±5.7%)
Non cooperative 1:2	4.2224	1.0	82 (±1.9%)	20.5 (±1.9%)
Additive 1:2	3.4458	1.2	484.6 (±8.4%)	63 (±10.3%)
Statistical 1:2	14.816	0.3	826 (±7.2%)	206.5(±7.2%)
Non cooperative 2:1	3.2135	1.3	190(±3%)	47.5 (±3%)
Statistical 2:1	5.8675	0.7	70 (±1.5%)	17.5 (±1.5%)

[a] cov_{fit} factor = cov_{fit} for the **1:1** model divided by the cov_{fit} for the binding model under study

Table S8 analyses chemical shifts of the diimide aromatic proton, in the free receptor (H) and in the formed complexes with tripeptide (HG_2 or H_2G):

Table S8. Chemical shifts for the binding of diimide 6b with tripeptide 10

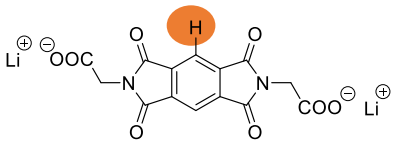
Binding model	δ_H	δ_{HG}	δ_{HG_2}	δ_{H_2G}
1:1	8.1469	7.6949		
Full 1:2		7.9845	7.6181	
Non cooperative 1:2		7.5919	7.9926	
Additive 1:2		7.9295	7.7122	
Statistical 1:2		7.9754	7.8038	
Non cooperative 2:1		7.7089		8.3586
Statistical 2:1		7.6517		7.1566

Binding models 2:1 are not considered, either nonsense chemical shifts or bad quality of fitting. Among all the 1:2 binding models, full model 1:2 shows the better cov_{fit} *factor*, cov_{fit} *factor=1.6*. But as more parameters are involved in fitting, when comparing binding 1:2 to 1:1, the quality of fitting should be significantly improved, which means cov_{fit} *factor* >3. This is not the case.

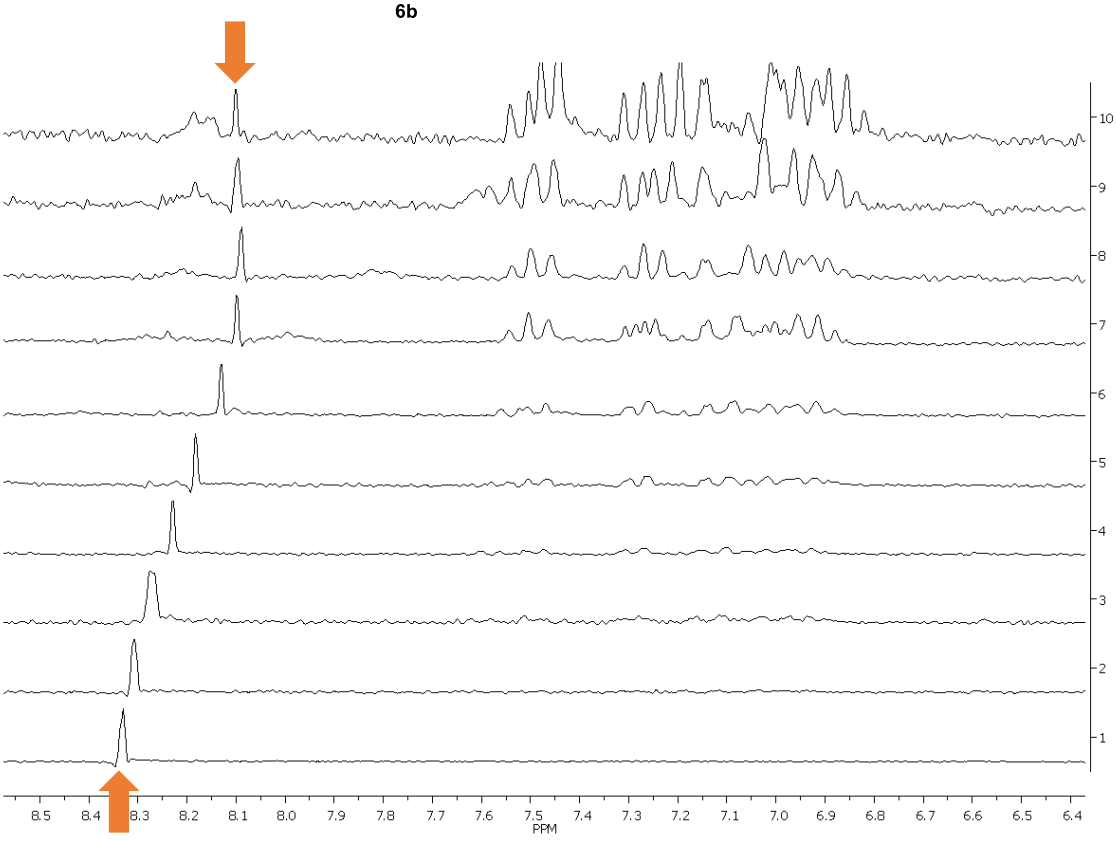
Job plot analysis

Job plot experiments were carried out to get more information about the stoichiometry of the complex formed between receptor **6b** and Trp-Gly-Trp (**10**).

$X_{\text{Receptor 6b}}$	[Receptor **6b**]	[Trp-Gly-Trp, **10**]	chemical shift (δ, ppm)	Δδ	Δδ[Receptor **6b**]
1.0	0.0048	0.0000	8.3289	0.0000	0.000000
0.9	0.0043	0.0005	8.3084	0.0205	0.000089
0.8	0.0038	0.0011	8.2725	0.0564	0.000217
0.7	0.0034	0.0016	8.2264	0.1025	0.000344
0.6	0.0029	0.0021	8.1802	0.1487	0.000428
0.5	0.0024	0.0027	8.1290	0.1999	0.000480
0.4	0.0019	0.0032	8.0983	0.2306	0.000443
0.3	0.0014	0.0037	8.0880	0.2409	0.000347
0.2	0.0010	0.0042	8.0957	0.2332	0.000224
0.1	0.0005	0.0048	8.1008	0.2281	0.000109



6b



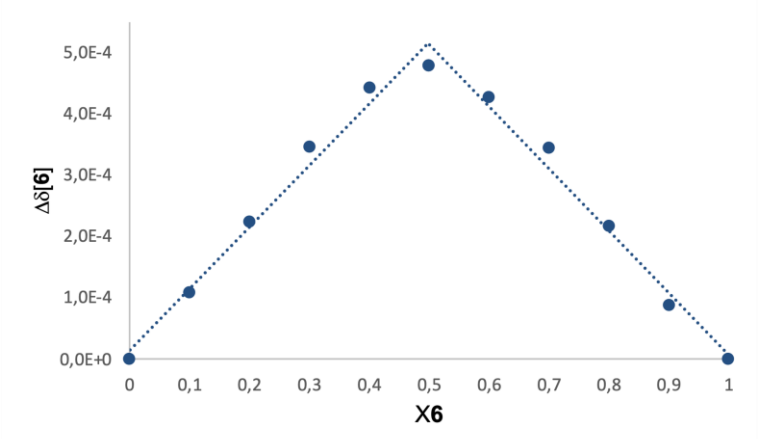


Figure S69. *Job plot showing a 1:1 binding stoichiometry for a (**6b**)$_1$(Trp-Gly-Trp)$_1$ complex.*

Dilution experiments

Dilution experiments with decreasing concentrations of Trp-Gly-Trp (**10**) in D_2O were carried out proving Trp-Gly-Trp fragments self-association does not exist in the concentration range for titrations.

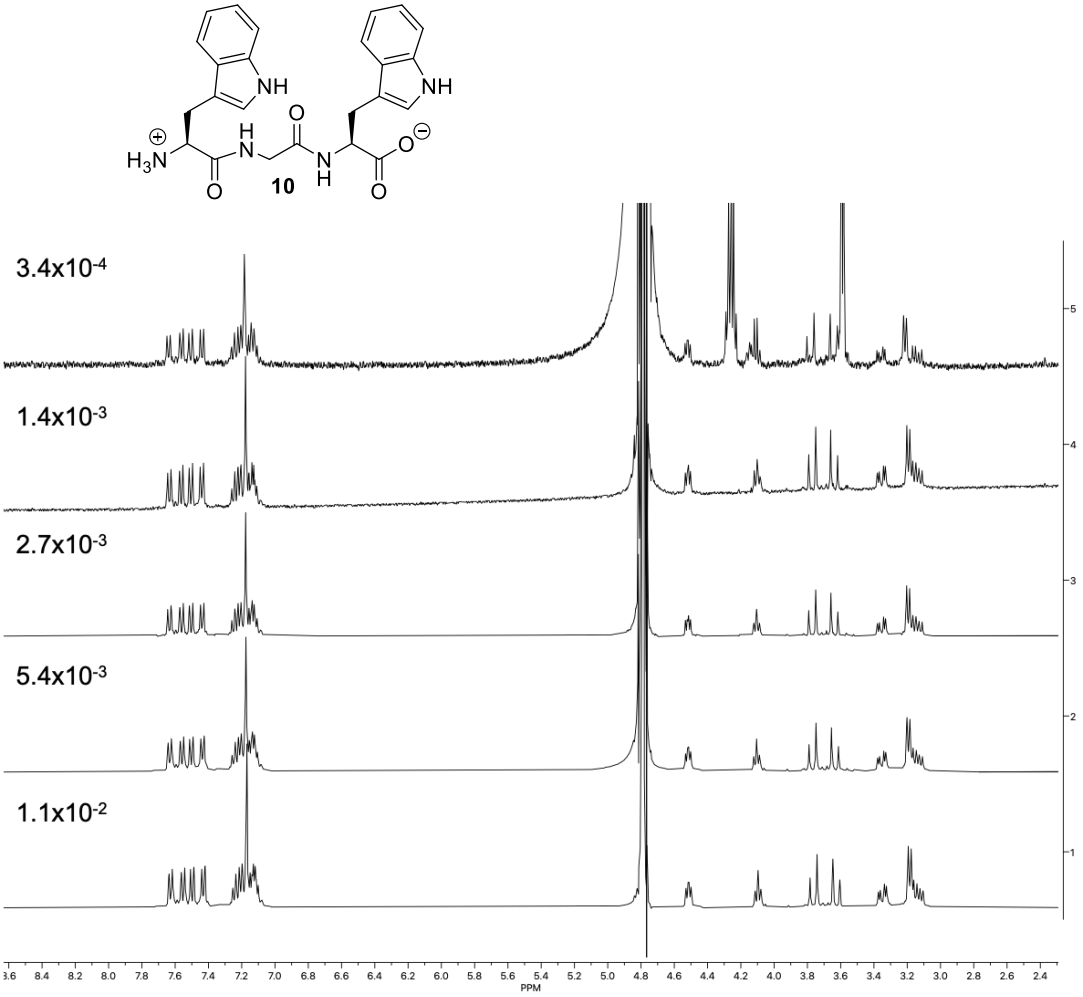


Figure S70. *^{1}H NMR spectra of Trp-Gly-Trp (**10**) in D_2O at different concentrations.*

6.3. 2D NMR studies of the complexes (6b:10) formed in D_2O

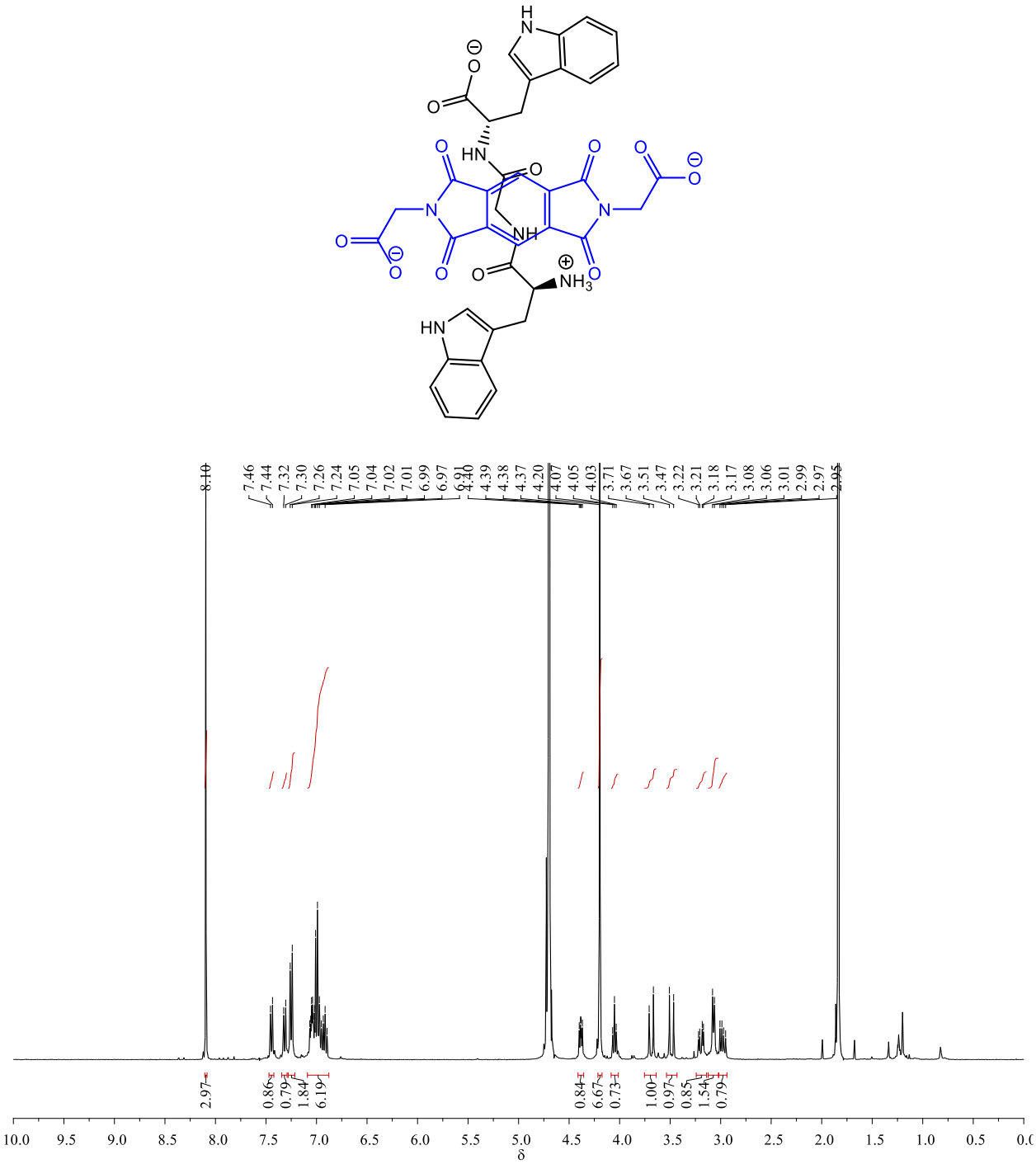


Figure S71. *^{1}H NMR spectrum of associate between receptor* **6b** *and Trp-Gly-Trp* ***10*** *in D_2O.*

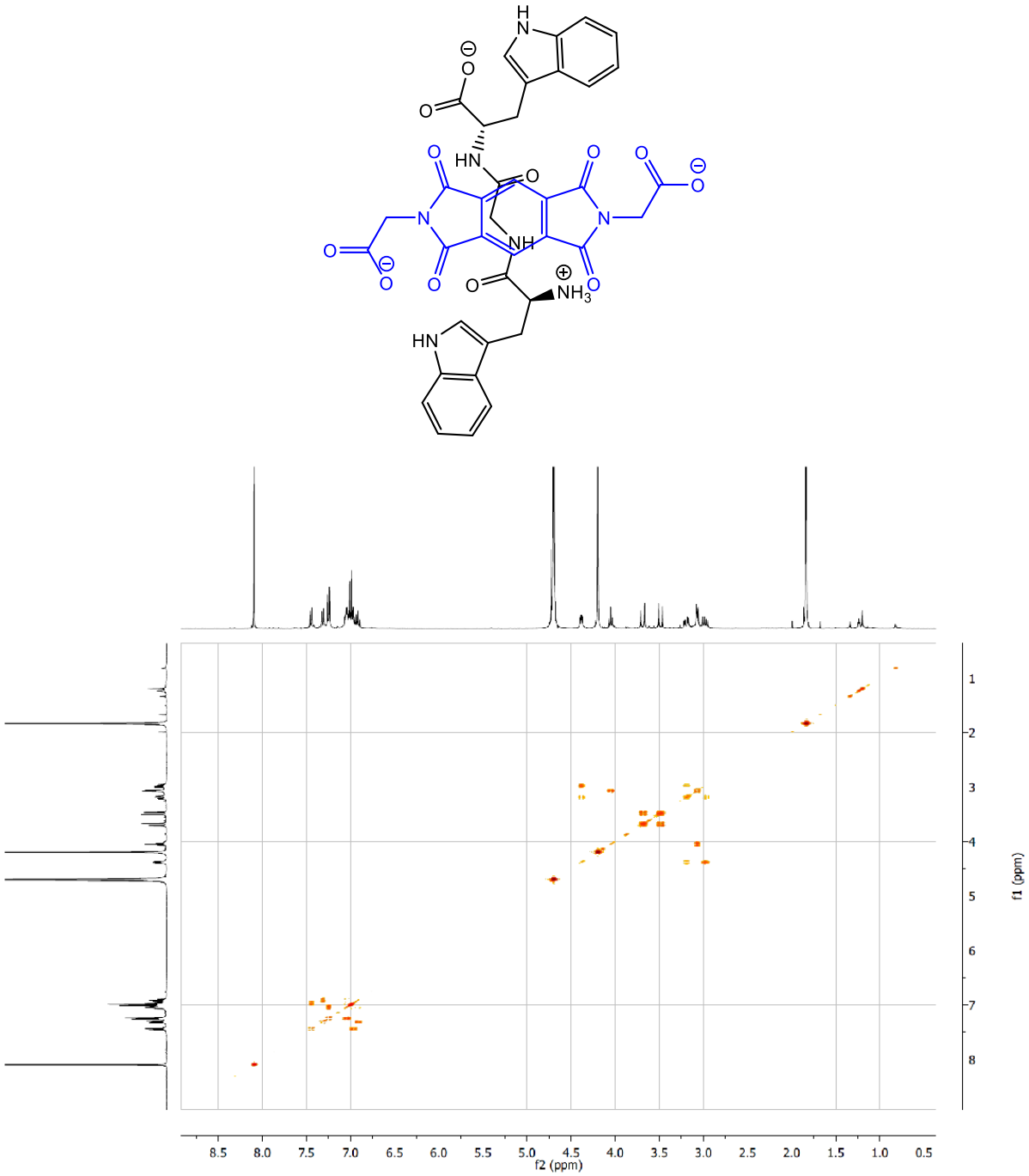


Figure S72. *COSY spectrum of associate between receptor* **6b** *and Trp-Gly-Trp* ***10*** *in* D_2O.

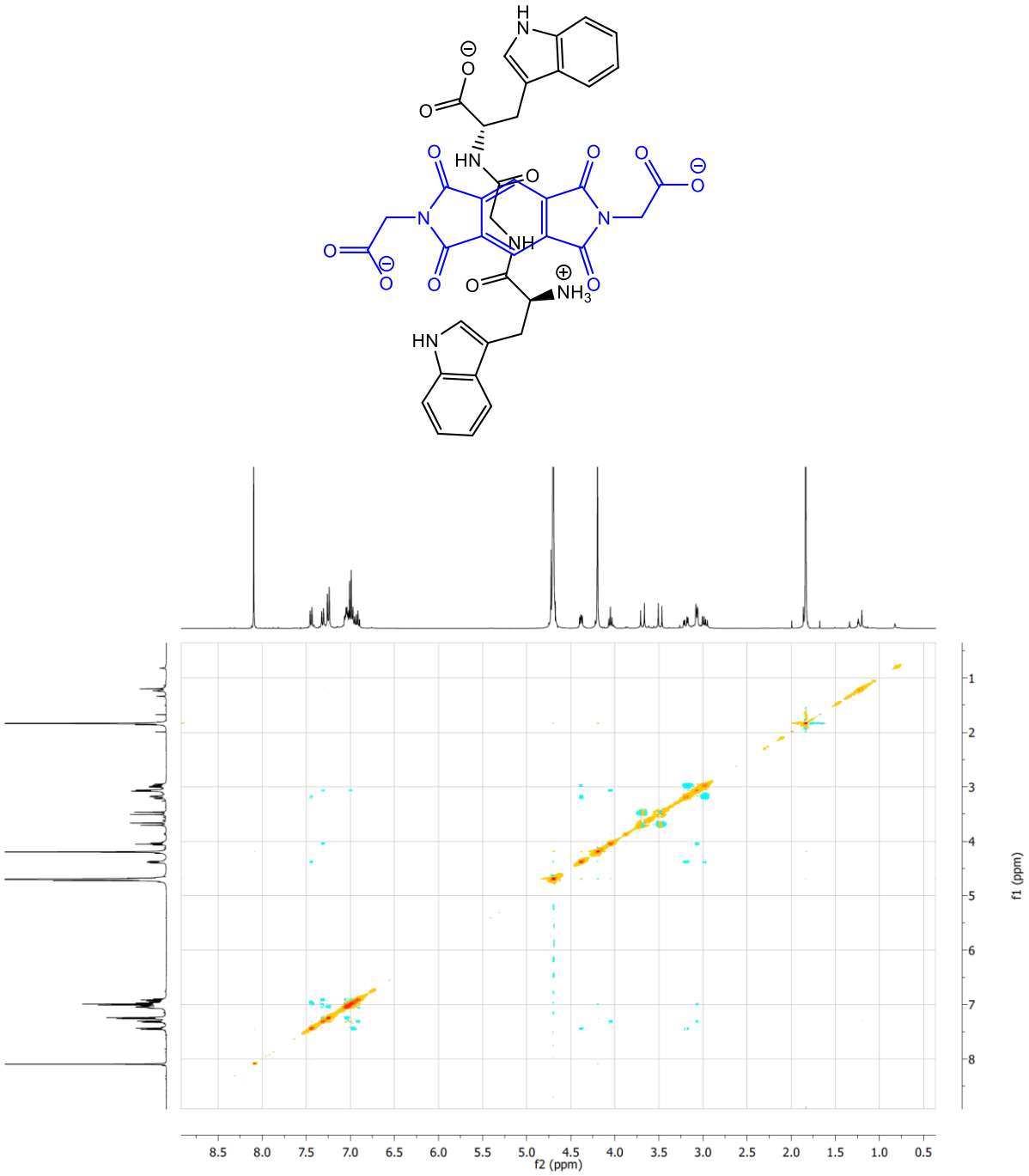


Figure S73. *ROESY spectrum of associate between receptor* **6b** *and Trp-Gly-Trp* ***10*** *in* D_2O.

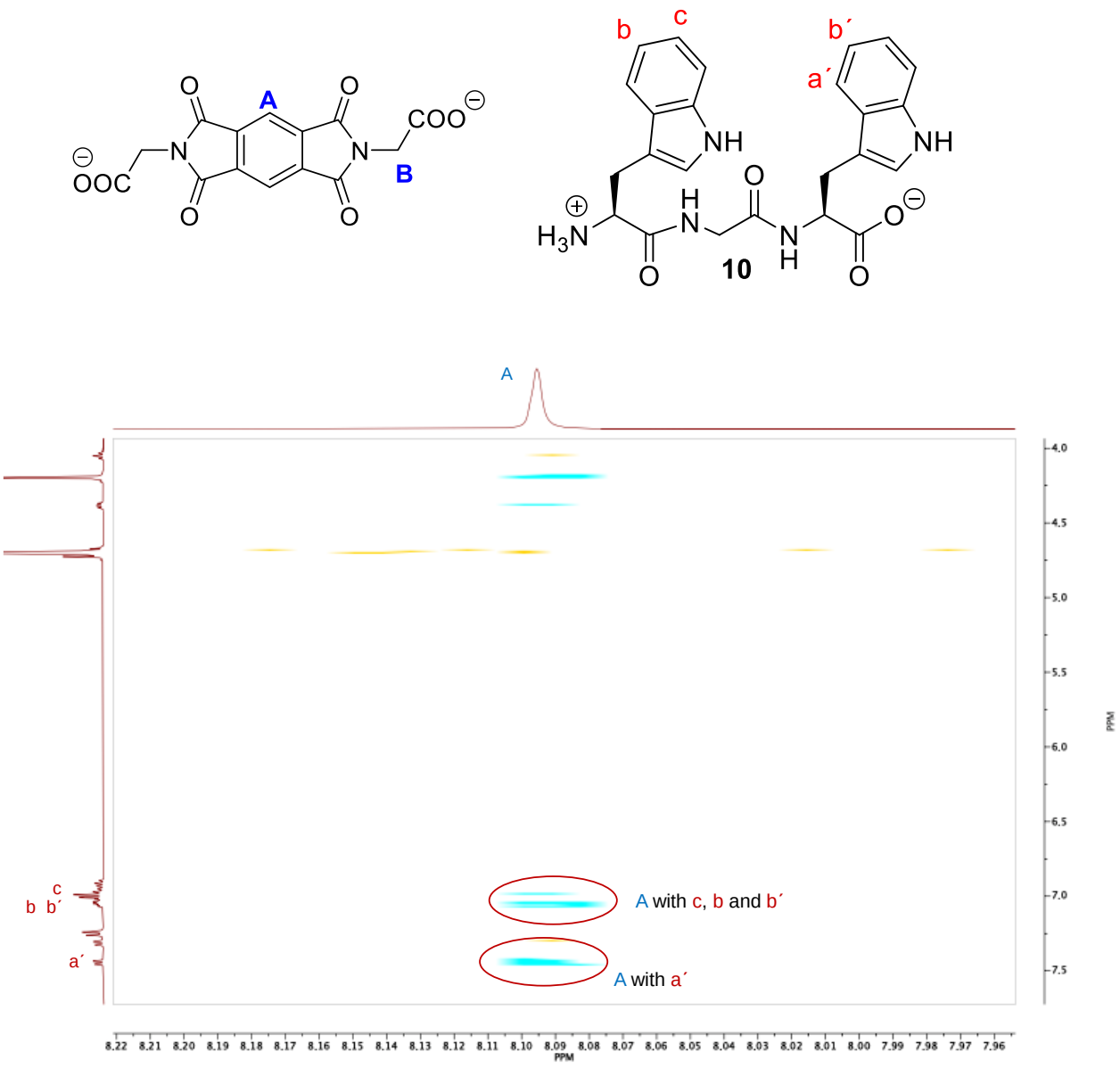


Figure S74. *ROESY spectrum (aromatic region) of associate between receptor* **6b** *and Trp-Gly-Trp* ***10*** *in* D_2O.

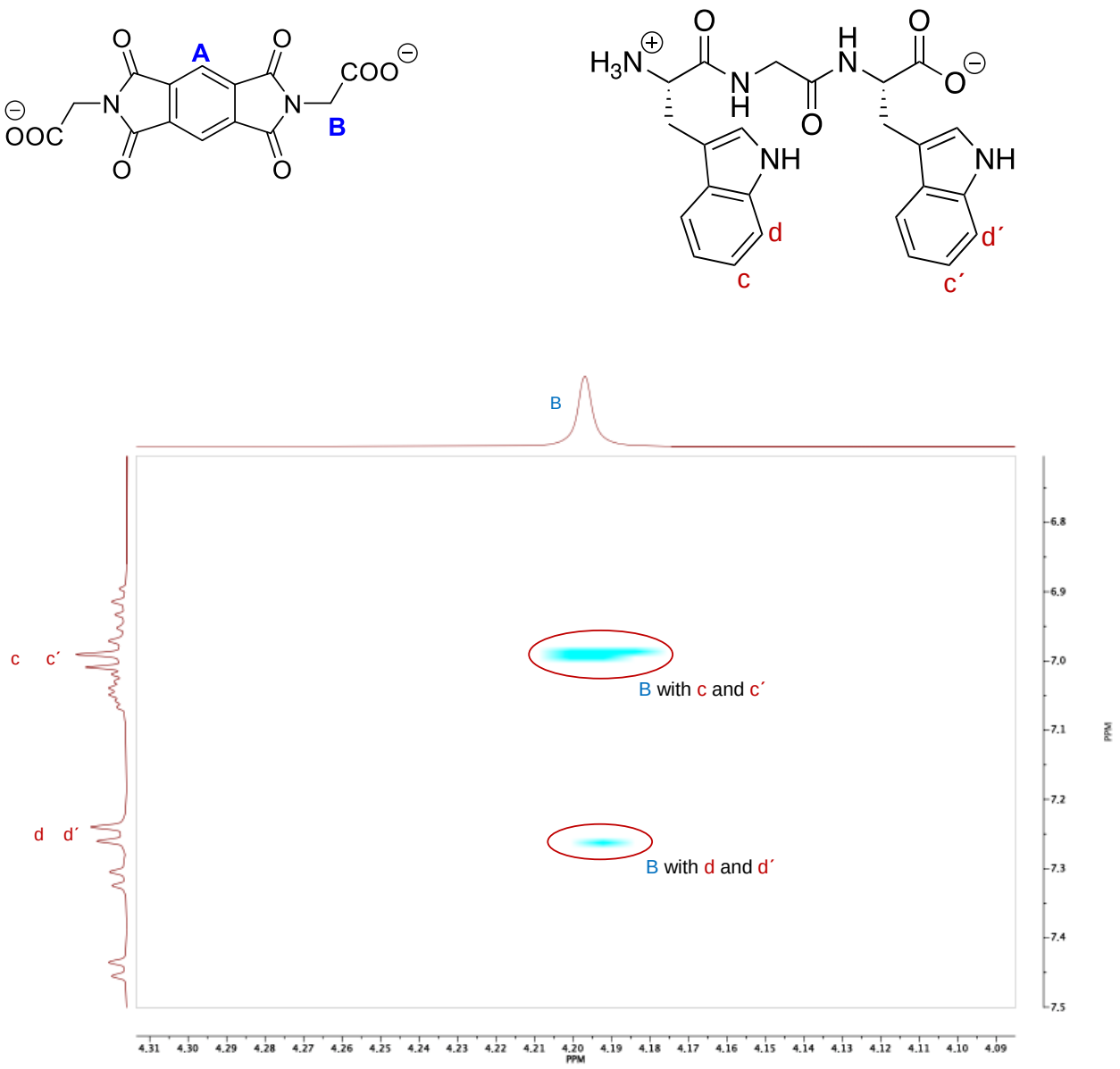


Figure S75. *ROESY spectrum (4.10-4.30 ppm) of associate between receptor* **6b** *and Trp-Gly-Trp* ***10*** *in* D_2O.

6.4. NMR titration in DMSO (d_6) with diimide 6a

The shift of the aromatic protons of receptor **6a** was evaluated.

[Receptor **6a**] (M)	[Trp-Gly-Trp, **10**] (M)	[G]/[H]	chemical shift (δ, ppm)
0.0051	0.0000	0.00	8.3263
0.0051	0.0012	0.24	8.2636
0.0051	0.0023	0.45	8.2085
0.0051	0.0033	0.65	8.1597
0.0051	0.0043	0.84	8.1322
0.0051	0.0052	1.02	8.1103
0.0051	0.0068	1.33	8.0751
0.0051	0.0082	1.61	8.0598
0.0051	0.0095	1.86	8.0522
0.0051	0.0120	2.35	8.0521

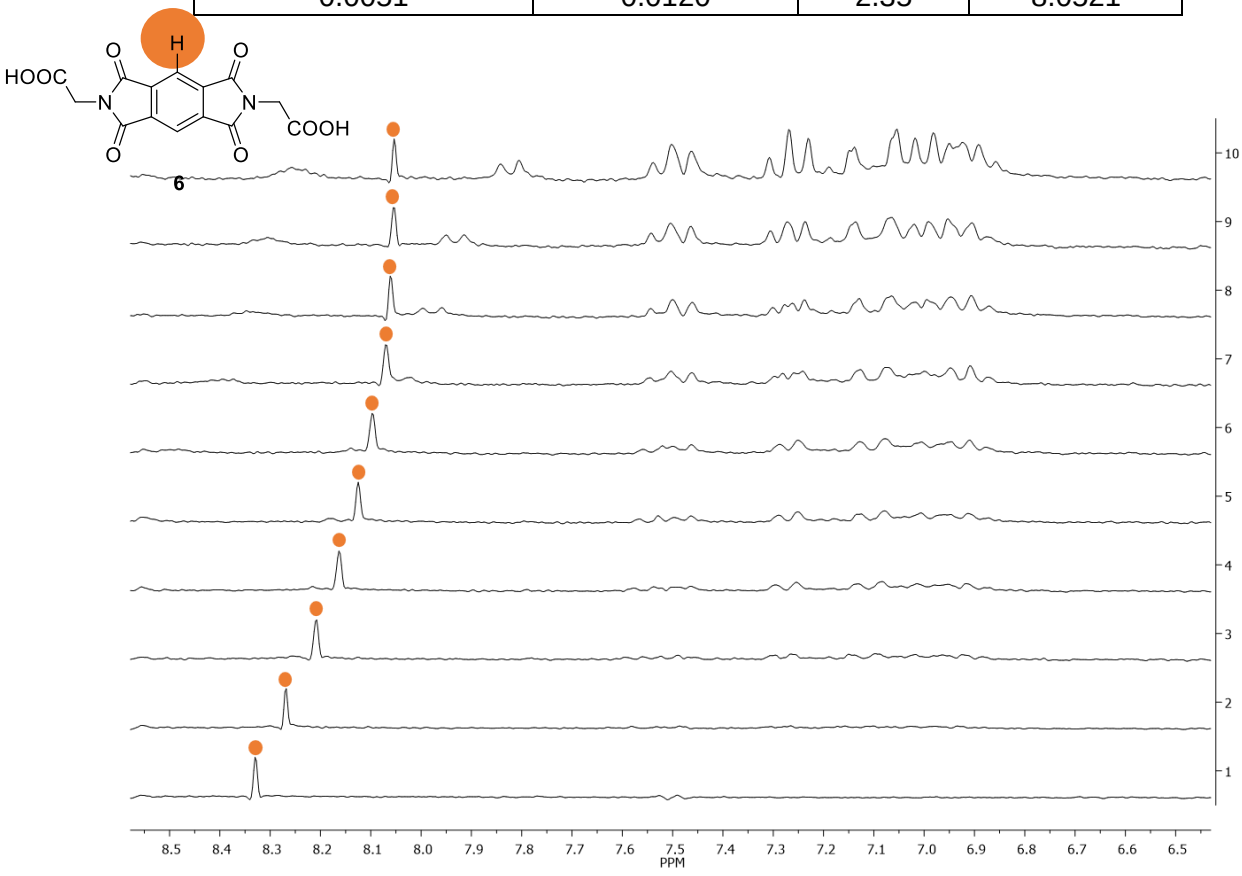


Figure S76. *^{1}H NMR spectra (6.4-8.6 ppm) corresponding to titration of **6a** and Trp-Gly-Trp (**10**).*

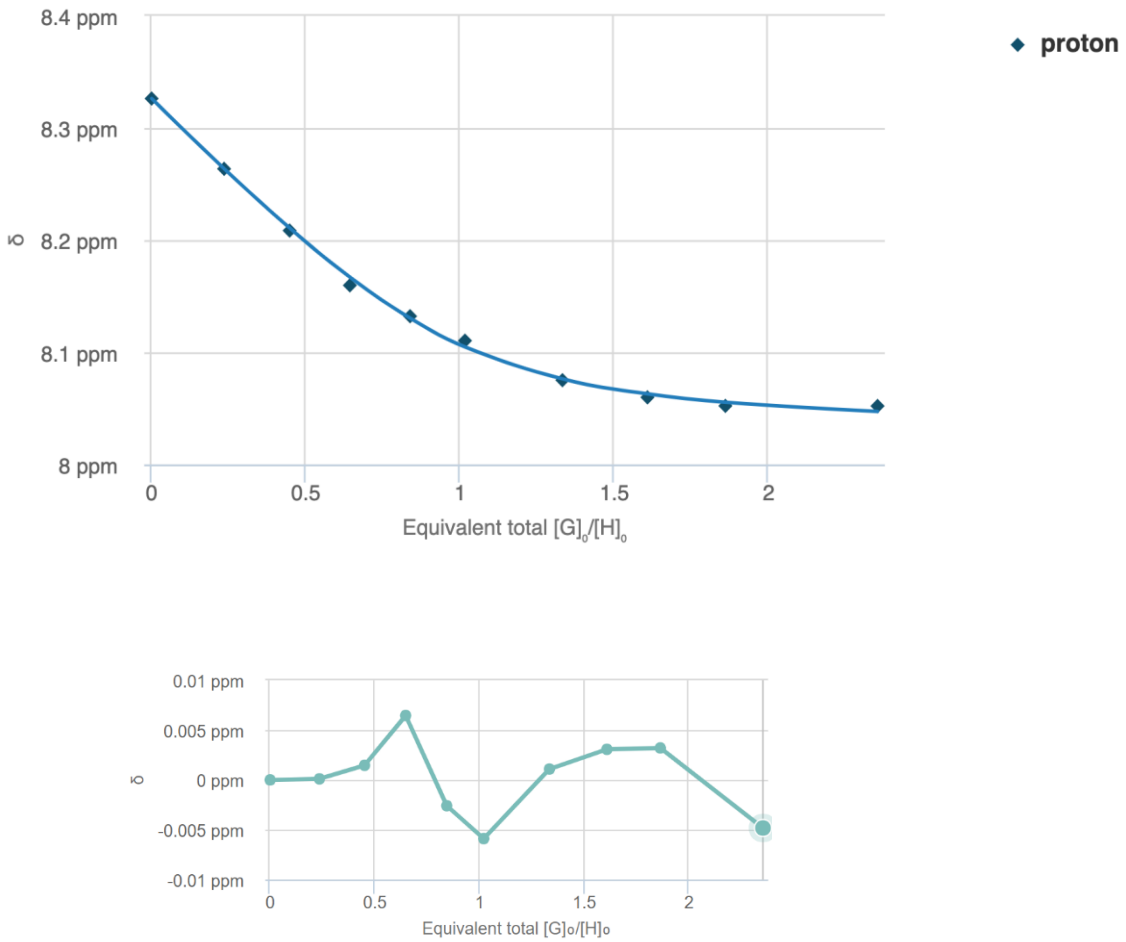


Figure S77. *Binding isotherm corresponding to titration of receptor* **6a** *and Trp-Gly-Trp (**10**).*

NMR 1:1
K_a=2108 (±13.8%) M^{-1}
Covariance=1.5744e-3

http://app.supramolecular.org/bindfit/view/e648dd2e-6d83-4fd9-baa8-b72a56055c17

Comparison of the different binding models *(online web-applet BindFit[9])*

Different binding models were considered:

- 1:1 Binding model (1 molecule diimide **6a** + 1 molecule tripeptide **10**)
- 1:2 Binding model (1 molecule diimide **6a** + 2 molecule tripeptide **10**)
- 2:1 Binding model (2 molecules diimide **6a** + 1 molecule tripeptide **10**)

Association constants are shown in table S9. Models converging on negative values (or not converging) for the association constants have not been included.

Table S9. Association constants for the binding of diimide 6a with tripeptide 10

Binding model	$cov_{fit}\ (10^{-3})^a$	cov_{fit} *factor*	$K_1(M^{-1})$	$K_2(M^{-1})$
1:1	1.5744	1	2108 (±13.8%)	
Non cooperative 1:2	0.8806	1.8	6430.13(±52.2%)	1671(±52.2%)
Statistical1:2	113.3	0.01	886 (±61%)	221 (±61%)
Non cooperative 2:1	2.5589	0.6	4430 (±69%)	1107.5(±69%)
Additive 2:1	1.4787	1	1894(±26.7%)	2.5 (±360%)
Statistical 2:1	8.0149	0.2	241 (±7%)	60.2 (±7%)

[a] cov_{fit} factor = cov_{fit} for the **1:1** model divided by the cov_{fit} for the binding model under study

Table S10 analyses chemical shifts of the diimide aromatic proton, in the free receptor (H) and in the formed complexes with tripeptide (HG_2 or H_2G):

Table S10. Chemical shifts for the binding of diimide 6a with tripeptide 10

Binding model	δ_H	δ_{HG}	δ_{HG_2}	δ_{H_2G}
1:1	8.3263	8.0289		
Non cooperative 1:2		8.0123	8.0570	
Statistical 1:2		8.0822	7.9926	
Non cooperative 2:1		7.9924		8.2043
Additive 1:2		8.0274		7.7284
Statistical 2:1		7.9736		7.6208

None of the 1:2 or 2:1 binding models show better quality of fitting than the 1:1 model.

6.5. 2D NMR studies complexes 6a:10 in DMSO(d_6)

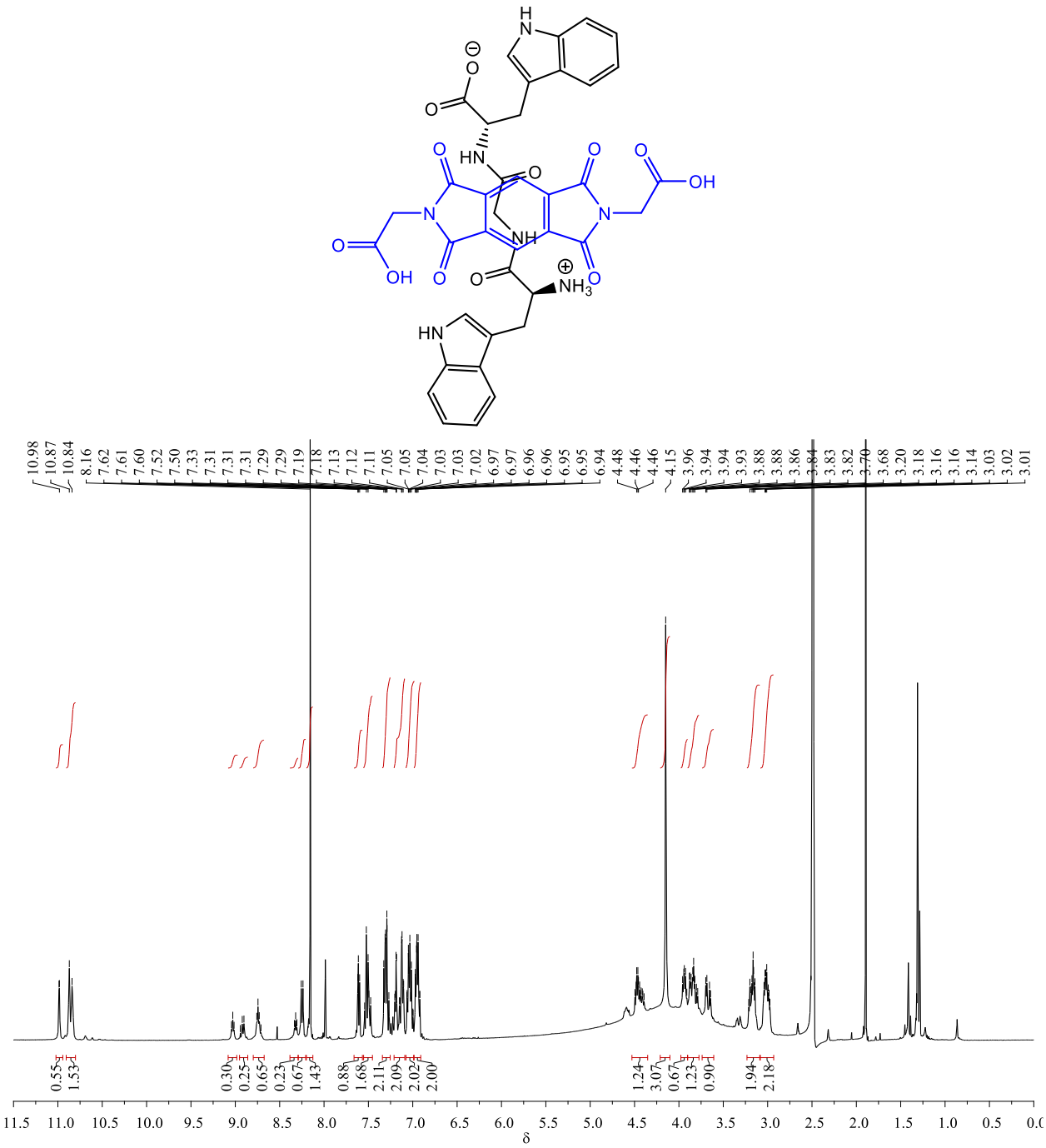


Figure S78. *^{1}H NMR spectrum of associate between receptor* **6a** *and Trp-Gly-Trp* ***10*** *in DMSO-d_6.*

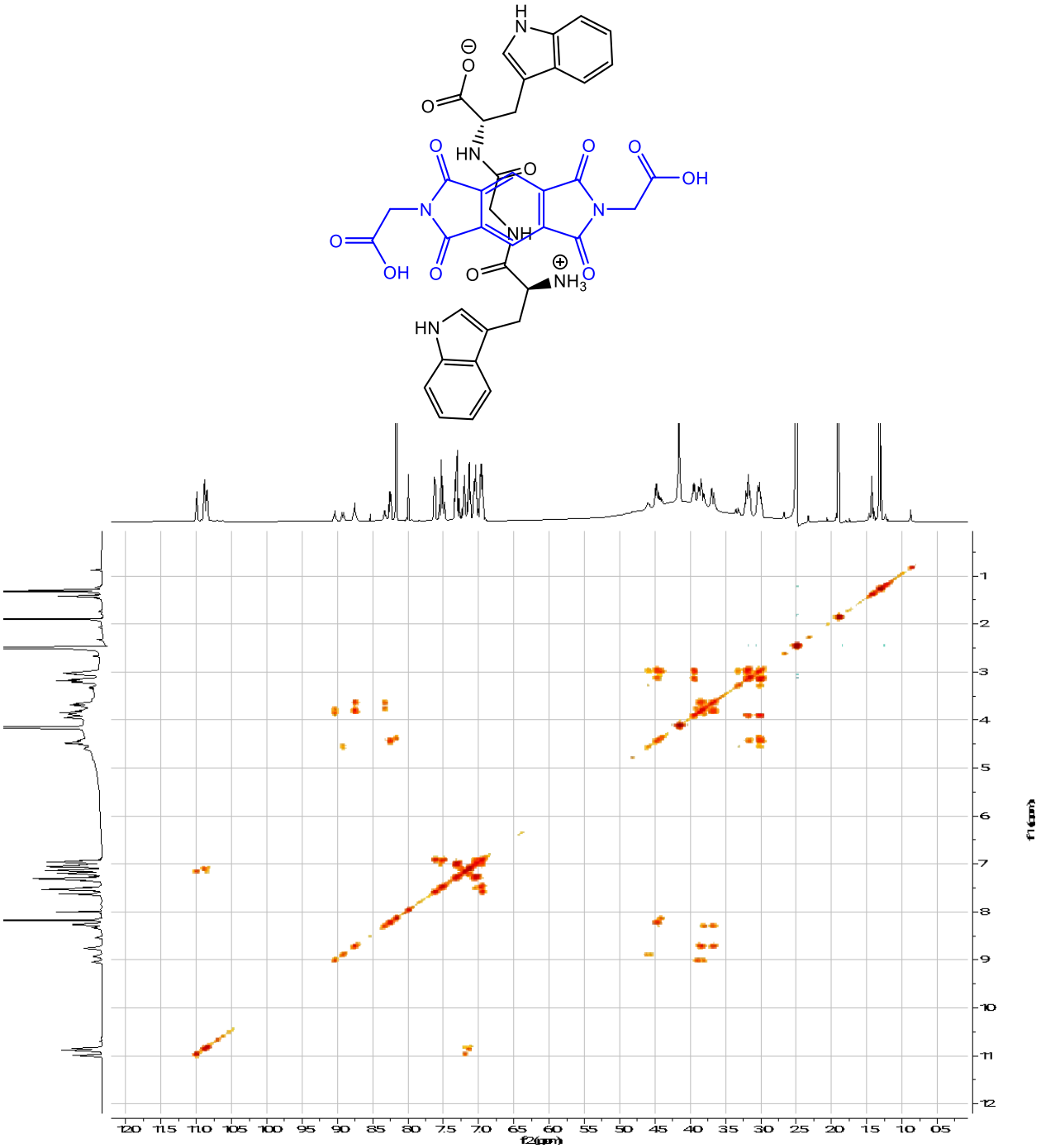


Figure S79. *COSY spectrum of associate between receptor* **6a** *and Trp-Gly-Trp* ***10*** *in DMSO-d_6.*

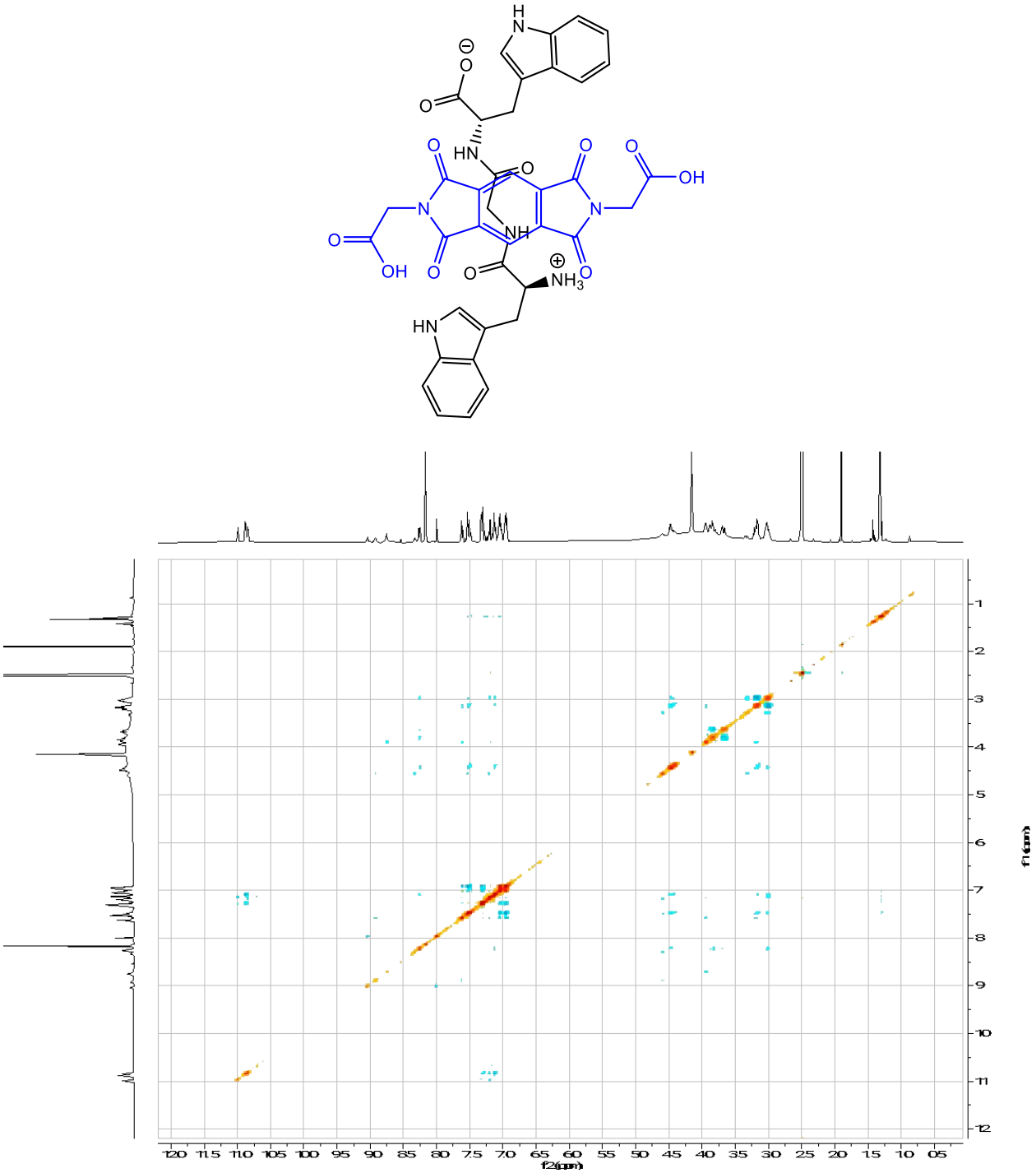


Figure S80. *ROESY spectrum of associate between receptor* **6a** *and Trp-Gly-Trp* ***10*** *in DMSO-d_6.*

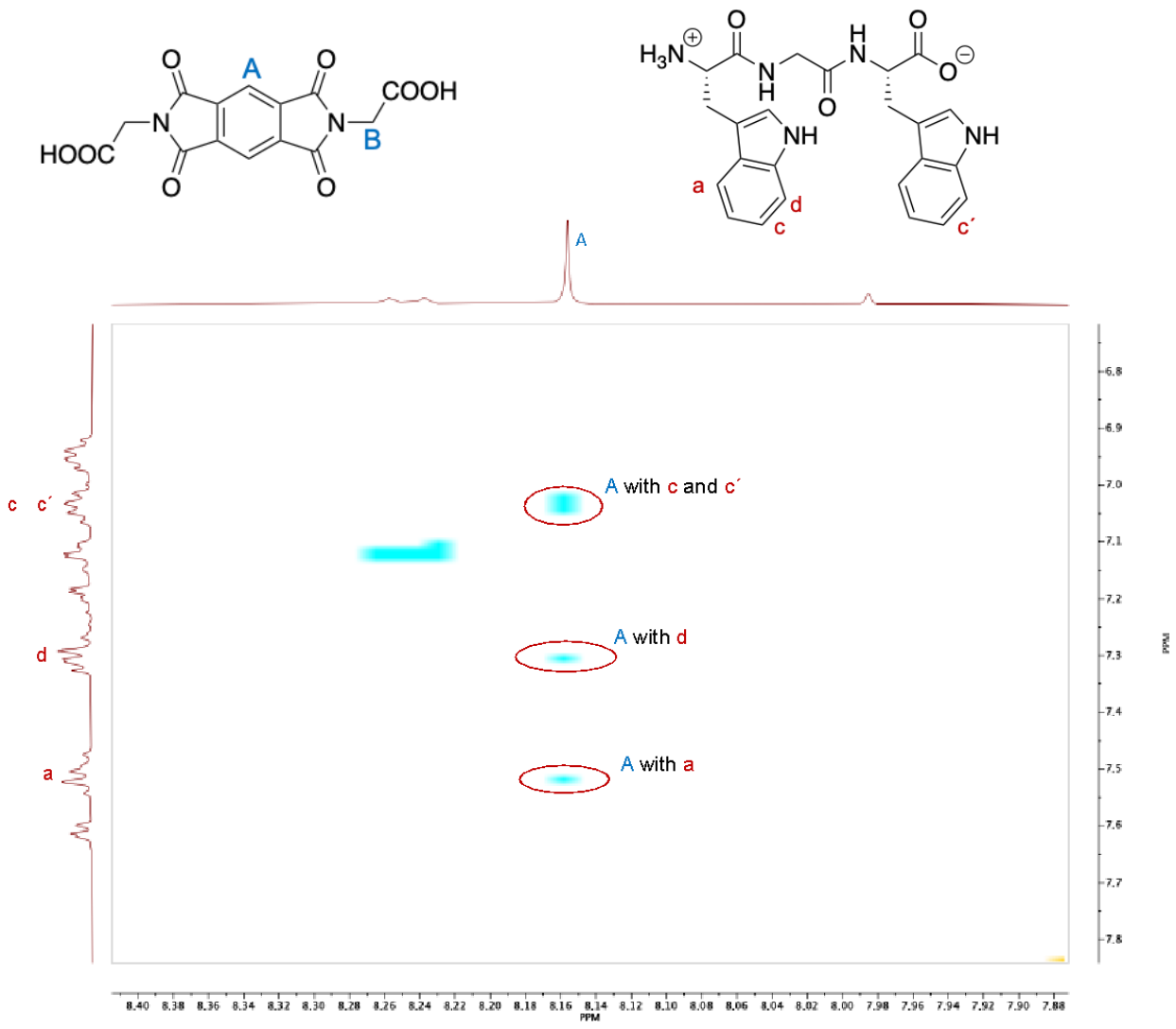


Figure S81. *ROESY spectrum (7.80-8.40 ppm) of associate between receptor* **6a** *and Trp-Gly-Trp* ***10*** *in DMSO-d_6.*

7. Modelling studies

Table S11. Coordinates for the model of the associate of receptor 6 with tripeptide Trp-Gly-Trp (10).

Atom	X	Y	Z	Atom	X	Y	Z
N(1)	3.042	-1.686	-1.250	H(46)	8.846	0.193	5.852
C(2)	2.011	-0.680	-1.012	H(47)	7.804	1.938	4.476
C(3)	1.400	-0.844	0.372	H(48)	5.031	-3.259	-1.617
N(4)	2.284	-1.079	1.372	H(49)	3.266	-3.583	-3.937
C(5)	1.835	-1.233	2.739	H(50)	3.993	-4.797	-3.072
C(6)	1.049	-0.027	3.196	H(51)	5.475	-2.081	-4.374
O(7)	1.060	1.089	2.752	H(52)	6.208	-3.594	-3.876
O(8)	0.326	-0.371	4.289	H(53)	8.662	0.708	-2.044
C(9)	3.032	-1.450	3.699	H(54)	6.575	0.203	-3.361
O(10)	0.205	-0.740	0.575	H(55)	7.728	-4.562	-1.917
C(11)	4.084	-0.366	3.668	H(56)	9.708	-4.916	-0.509
C(12)	5.359	-0.443	4.365	H(57)	11.169	-3.045	0.087
C(13)	6.034	0.767	4.132	H(58)	10.662	-0.763	-0.665
N(14)	5.224	1.541	3.333	C(59)	8.399	3.672	0.269
C(15)	4.055	0.843	3.064	H(60)	6.853	-6.013	2.178
C(16)	5.968	-1.429	5.140	H(61)	4.498	-6.815	4.574
C(17)	7.217	-1.185	5.668	O(62)	4.985	-6.717	3.741
C(18)	7.875	0.027	5.428	H(63)	5.321	-5.742	1.346
C(19)	7.297	1.010	4.657	O(64)	4.904	-4.498	4.109
C(20)	3.895	-1.595	-2.301	C(65)	5.241	-5.431	3.430
O(21)	3.993	-0.596	-2.996	C(66)	5.984	-5.376	2.119
C(22)	4.674	-2.885	-2.562	C(67)	7.541	-2.052	1.751
N(23)	3.668	-3.846	-3.056	C(68)	6.314	-1.846	1.152
C(24)	5.845	-2.634	-3.521	C(69)	5.938	-0.638	0.616
C(25)	6.973	-1.881	-2.873	C(70)	6.879	0.355	0.724
C(26)	8.050	-2.445	-2.082	C(71)	8.108	0.153	1.317
C(27)	8.884	-1.377	-1.706	C(72)	8.484	-1.059	1.849
N(28)	8.336	-0.221	-2.211	C(73)	7.613	-3.473	2.195
C(29)	7.178	-0.545	-2.902	N(74)	6.382	-4.028	1.819
C(30)	8.353	-3.734	-1.643	C(75)	5.549	-3.118	1.212
C(31)	9.468	-3.933	-0.862	C(76)	6.793	1.770	0.277
C(32)	10.305	-2.862	-0.521	N(77)	8.030	2.327	0.601
C(33)	10.026	-1.581	-0.938	C(78)	8.887	1.418	1.218
H(34)	2.937	-2.586	-0.830	O(79)	8.496	-4.072	2.744
H(35)	2.456	0.302	-1.089	O(80)	4.418	-3.352	0.845
H(36)	1.202	-0.751	-1.727	O(81)	10.014	1.660	1.568
H(37)	3.213	-1.363	1.157	O(82)	5.885	2.366	-0.238
H(38)	1.165	-2.076	2.837	H(83)	4.995	-0.481	0.140
H(39)	-0.186	0.374	4.638	H(84)	9.436	-1.214	2.310
H(40)	2.622	-1.529	4.699	C(85)	9.059	3.823	-1.083
H(41)	3.486	-2.405	3.464	H(86)	9.090	4.054	1.006

H(42)	5.406	2.473	3.041	H(87)	7.513	4.293	0.263
H(43)	3.280	1.286	2.485	O(88)	9.469	4.867	-1.507
H(44)	5.486	-2.374	5.297	H(89)	9.581	2.832	-2.655
H(45)	7.699	-1.931	6.268	O(90)	9.154	2.670	-1.799

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9. UV/Vis data

Table S12. UV-vis absorption spectroscopic titration of 3b with tryptophan

Wavelength (nm)	Absorbance (a.u.) receptor **3b** 10mM	Absorbance (a.u.) receptor **3b** 10mM/Trp 2.1 mM	Absorbance (a.u.) receptor **3b** 10mM/Trp 4.2 mM	Absorbance (a.u.) receptor **3b** 10mM/Trp 6.4 mM	Absorbance (a.u.) receptor **3b** 10mM/Trp 10mM	Absorbance (a.u.) receptor **3b** 10mM/Trp 13mM	Absorbance (a.u.) receptor **3b** 10mM/Trp 17mM
375	1.20271169	1.49695875	1.55027483	1.62811974	1.70507108	1.7581548	1.80423868
376	1.16950116	1.48457658	1.53902702	1.63406298	1.71892117	1.78206882	1.81695804
377	1.12773879	1.47246031	1.53615178	1.64189374	1.74936047	1.79945041	1.85010379
378	1.08812892	1.45863298	1.5200362	1.63863109	1.74867821	1.81721456	1.87202103
379	1.04834684	1.4404644	1.50562276	1.63887682	1.76457257	1.84236195	1.88625715
380	1.00756137	1.42066237	1.48247424	1.62064008	1.76621727	1.84378411	1.90917783
381	0.95567588	1.38413408	1.44957594	1.60225113	1.77642619	1.86270921	1.92558586
382	0.91416021	1.35621186	1.42445423	1.58146671	1.75995025	1.87270078	1.93081309
383	0.87142306	1.32181863	1.38836163	1.55648667	1.76472412	1.8703101	1.95565625
384	0.83999092	1.29675163	1.36520041	1.5416795	1.75266517	1.87968936	1.9491178
385	0.80654427	1.26578444	1.33652523	1.51279091	1.74550024	1.88472242	1.97835598
386	0.77529608	1.23423461	1.30695052	1.49442951	1.73118809	1.8790972	1.95876527
387	0.75262336	1.21036994	1.28585473	1.46871272	1.72611944	1.87351144	1.97699459
388	0.72624892	1.18625224	1.26480045	1.44988175	1.70745598	1.87530018	1.96094299
389	0.67942794	1.16726762	1.24178475	1.43122352	1.7048509	1.86366001	1.97835598
390	0.66823268	1.15598284	1.23098475	1.42102862	1.69169174	1.86305759	1.9772006
391	0.64829642	1.13503826	1.2105039	1.40637064	1.6818949	1.85936627	1.97526811
392	0.62882313	1.11269786	1.18960619	1.38282137	1.66643184	1.85001155	1.98560549
393	0.60476973	1.09024611	1.14178775	1.33849967	1.64835828	1.84178832	1.9730992
394	0.58351095	1.06425602	1.15806521	1.35003265	1.60957717	1.8127896	1.94657581
395	0.557047	1.01246778	1.12986543	1.32484514	1.6294314	1.83508233	1.98957281
396	0.53163643	1.02307715	1.10276894	1.30128197	1.60544326	1.83321479	1.98640448
397	0.53232089	0.99390638	1.0721576	1.26990441	1.57895577	1.80958427	1.97049446
398	0.50590667	0.96684977	1.04535718	1.24401849	1.5556741	1.78138575	1.96106208
399	0.48136898	0.94200697	1.01891568	1.21833797	1.53485517	1.77871622	1.9683896
400	0.45861797	0.91750188	0.99473793	1.1931013	1.51156211	1.76300954	1.94877028
401	0.43869105	0.89109687	0.968737	1.16965516	1.48711557	1.73617464	1.92922355
402	0.41585089	0.84952292	0.94163853	1.13877035	1.46450335	1.72195558	1.91346221
403	0.3985876	0.82868026	0.92204736	1.11982113	1.44071597	1.70193329	1.90745479
404	0.37659978	0.80879777	0.88413996	1.09960008	1.41996504	1.67927229	1.8993538
405	0.36079251	0.78931235	0.86656324	1.07599484	1.40049901	1.67021578	1.87634432
406	0.34771399	0.77349031	0.85052531	1.06009157	1.3830836	1.64737375	1.87279797
407	0.33478873	0.75667173	0.83418908	1.04369227	1.36413441	1.6359934	1.85176764
408	0.3231921	0.74446219	0.82149498	1.03046295	1.34999378	1.61962592	1.84847694
409	0.31297875	0.73093792	0.80825564	1.01580134	1.33619547	1.60705695	1.82988504
410	0.30465055	0.72135156	0.79763154	1.0036547	1.32626047	1.59954836	1.82725116
411	0.30067054	0.71506419	0.79274272	0.99927967	1.3157293	1.58752265	1.81950137
412	0.2963347	0.71073889	0.7855907	0.97750977	1.31280111	1.58685117	1.81996019
413	0.28835471	0.69975025	0.77605264	0.96824019	1.30046578	1.57136315	1.80068374
414	0.28227375	0.69106869	0.76758841	0.95621344	1.28934963	1.5615526	1.79822063
415	0.27438562	0.68266179	0.75755049	0.94818014	1.27875839	1.55321437	1.78122823
416	0.26769875	0.67287412	0.74814772	0.93841559	1.26564829	1.53979398	1.77863793
417	0.25854661	0.66128061	0.73779341	0.92561147	1.25282912	1.5300455	1.76117637
418	0.24981572	0.65099657	0.72709372	0.91409964	1.2409822	1.51355536	1.75202674
419	0.24373903	0.64242532	0.71835542	0.90494578	1.22695263	1.50452502	1.73743027

420	0.23565943	0.63244657	0.7070111	0.8930446	1.21670399	1.48969633	1.72778696
421	0.22970408	0.62305277	0.6988962	0.88395043	1.20276712	1.47655271	1.71356597
422	0.22207391	0.61402751	0.68916018	0.87272667	1.19130298	1.46701643	1.70427898
423	0.21731743	0.60669511	0.68007404	0.86475604	1.18082471	1.45268077	1.69117955
424	0.21066397	0.59356882	0.6719447	0.85311573	1.1679959	1.43783805	1.6750594
425	0.20641356	0.58620084	0.66303219	0.8454817	1.158334	1.42903696	1.66665349
426	0.20084493	0.57711485	0.65468706	0.83447969	1.14336169	1.41375034	1.64853225
427	0.1951269	0.57056107	0.644673	0.82685164	1.12300899	1.40264491	1.64118982
428	0.19138667	0.56263953	0.63668891	0.81807073	1.11454267	1.39206268	1.6242267
429	0.18635299	0.55588179	0.62867534	0.8071511	1.10056256	1.37824229	1.61207655
430	0.18340543	0.54967851	0.62315852	0.80205817	1.09313182	1.36792755	1.60143506
431	0.17865682	0.54270865	0.61561432	0.7918866	1.08192249	1.35392972	1.58913846
432	0.1779091	0.53843845	0.61089776	0.78705636	1.0755553	1.3469709	1.57477562
433	0.1759497	0.53668942	0.60946582	0.78424351	1.07176808	1.34355679	1.57857708
434	0.17460571	0.53198813	0.60390359	0.77757489	1.06310442	1.33322938	1.56258241
435	0.1703798	0.52539769	0.59709927	0.76899454	1.05330216	1.32370887	1.55229944
436	0.16710867	0.51792861	0.58926158	0.76098849	1.041962	1.3085295	1.53564459
437	0.16343981	0.51224955	0.58314486	0.75304864	1.0323023	1.29519768	1.52651302
438	0.15974959	0.50345224	0.5747316	0.74343858	1.01817235	1.28156474	1.50645831
439	0.15539115	0.4956175	0.56573777	0.72867194	1.00622	1.26383464	1.49012572
440	0.15171478	0.48653067	0.55647258	0.71669877	0.98861989	1.24648589	1.46924976
441	0.14796796	0.47838338	0.54723864	0.70683861	0.97523118	1.21898464	1.44908711
442	0.14483111	0.47018481	0.53893988	0.69580037	0.96034007	1.2028225	1.42810494
443	0.14052904	0.46053999	0.5284443	0.6829191	0.94420896	1.1828182	1.40635954
444	0.13656768	0.4516499	0.51946989	0.67086665	0.92803335	1.16248732	1.38432344
445	0.13378655	0.44263236	0.51006119	0.6600817	0.91412458	1.14554213	1.36375288

Table S13. UV-vis absorption spectroscopic titration of 3b with tryptophan methyl ester hydrochloride

Wavelength (nm)	Absorbance (a.u.) receptor **3b** 10mM	Absorbance (a.u.) **3b** 10mM + **Ia** 2.2 mM	Absorbance (a.u.) receptor **3b** 10mM + **Ia** 4.1 mM	Absorbance (a.u.) receptor **3b** 10mM +**Ia** 6.2 mM	Absorbance (a.u.) receptor **3b** 10mM + **Ia** 10mM	Absorbance (a.u.) receptor **3b** 10mM+ **Ia** 16.5 mM
375	1.19887769	1.73652964	1.99430483	2.12848544	2.391795	2.59550838
376	1.16574466	1.72556501	2.01193181	2.12563415	2.39728908	2.72216167
377	1.12355701	1.70867557	1.979473	2.12691201	2.45456918	2.65521486
378	1.08243675	1.68598522	1.96577272	2.12096149	2.39394127	2.68193666
379	1.04089657	1.65728131	1.96433017	2.10835105	2.39566591	2.67243676
380	0.9991496	1.63891465	1.93930216	2.091247	2.39115318	2.65777477
381	0.94677936	1.58762345	1.89408126	2.07150174	2.33847128	2.71354352
382	0.90296146	1.56224944	1.88988188	2.05888625	2.35085994	2.6595559
383	0.85636387	1.52134693	1.84639852	2.01313874	2.34765695	2.66474275
384	0.82467956	1.49238696	1.82576569	2.01161945	2.3183066	2.66514432
385	0.79160972	1.46620252	1.80531919	1.9696027	2.32102664	2.64073384
386	0.75686763	1.44021302	1.77327125	1.96814736	2.30918395	2.67860874
387	0.73375653	1.41337894	1.7490192	1.94469812	2.27474194	2.65975426
388	0.706401	1.39228771	1.72367609	1.92350519	2.29047563	2.60067247
389	0.65856151	1.37420411	1.71192972	1.90685858	2.2798407	2.6178028
390	0.64647998	1.36369269	1.69656633	1.90069927	2.25080495	2.6147513
391	0.62570634	1.34202677	1.68202021	1.88071112	2.2478747	2.59277909
392	0.60278499	1.32456997	1.66717792	1.8715361	2.21438548	2.56304265
393	0.58014666	1.30079553	1.64435696	1.83612334	2.18862609	2.55940573
394	0.55746064	1.27466837	1.61939084	1.83537952	2.19178902	2.51970555
395	0.53027809	1.22947198	1.57191382	1.77905552	2.13324021	2.50445565
396	0.50277032	1.24482668	1.58073837	1.79083366	2.16889844	2.53670439
397	0.50357409	1.2175417	1.55770841	1.76212964	2.13035767	2.48161769
398	0.47608714	1.19270178	1.53745228	1.73608	2.10463271	2.49498577
399	0.45083607	1.16937282	1.50949373	1.7224137	2.08144546	2.46699099
400	0.4311989	1.1504086	1.48940135	1.69842748	2.07283502	2.4285241
401	0.40982717	1.12674335	1.46485784	1.67489502	2.05789271	2.44141141
402	0.38543075	1.10422395	1.44006944	1.65686725	2.02849223	2.39793999
403	0.364469	1.08617556	1.42402743	1.6341939	2.01732181	2.37716454
404	0.34612498	1.06699382	1.40656991	1.61557489	1.99216692	2.38310456
405	0.33187978	1.05043925	1.38939308	1.60310354	1.96948125	2.35369432
406	0.31871984	1.03885901	1.37454351	1.5845592	1.94973629	2.35723878
407	0.30521321	1.02491301	1.36224015	1.57471038	1.95557785	2.32771738
408	0.29562037	1.01325514	1.34901292	1.56594233	1.92959267	2.32697909
409	0.28465278	1.003392	1.33779009	1.54645234	1.91257353	2.32651832
410	0.27601843	0.9951844	1.32778204	1.54193654	1.9181848	2.29277057
411	0.27258806	0.98998852	1.32305047	1.53713802	1.90689364	2.29370906
412	0.26873526	0.98612255	1.31959195	1.53323614	1.89575195	2.30338155
413	0.26082256	0.97211653	1.31223924	1.52065508	1.8905902	2.27010658
414	0.2539959	0.95681462	1.30325056	1.51426438	1.89255258	2.27711939
415	0.24684989	0.94853105	1.29429875	1.50260036	1.87729275	2.25696086
416	0.23968536	0.94242518	1.28843741	1.49833836	1.86883061	2.26568033
417	0.23207719	0.93245676	1.27597822	1.48695563	1.85319003	2.23777173
418	0.22373113	0.9261204	1.26883044	1.47474781	1.85118149	2.24169383
419	0.21838249	0.91829991	1.26019039	1.46988998	1.84055313	2.21331956
420	0.21122515	0.91101388	1.25249498	1.45963296	1.82988504	2.22592119

421	0.20547359	0.90386545	1.24408705	1.45386466	1.81981675	2.19907682
422	0.19947811	0.8975869	1.23668434	1.44268533	1.81157778	2.20391158
423	0.19426676	0.89167183	1.23160612	1.43867198	1.80294009	2.18098281
424	0.18972511	0.88603327	1.22386567	1.42904865	1.79792057	2.19158646
425	0.18531565	0.88038452	1.21843849	1.4271981	1.78871924	2.16310649
426	0.17920301	0.87458056	1.21082839	1.41573664	1.78196369	2.17659097
427	0.17541215	0.87060017	1.20756628	1.41077669	1.77634831	2.15045776
428	0.17206689	0.86579102	1.20132174	1.40635954	1.77029258	2.15745315
429	0.16761246	0.85989439	1.19637902	1.40119856	1.76187861	2.13774932
430	0.16436649	0.85745723	1.1907636	1.39792914	1.75451202	2.1412824
431	0.16066153	0.8514868	1.18654578	1.39072583	1.75151179	2.13996161
432	0.15889842	0.85044527	1.18504691	1.38857411	1.75131578	2.1170772
433	0.15761358	0.84832988	1.18234209	1.38537696	1.74119518	2.12790202
434	0.15566513	0.84517449	1.18072594	1.3813976	1.74620178	2.12813529
435	0.15219605	0.84095344	1.1739122	1.3792603	1.73463964	2.11855828
436	0.14968344	0.8372385	1.16110684	1.37261367	1.72450435	2.10160394
437	0.14682944	0.83242274	1.15764667	1.36689529	1.72799586	2.10835105
438	0.14305854	0.8281946	1.15104768	1.35961796	1.71853483	2.0871936
439	0.14003175	0.82167641	1.14518403	1.35606396	1.70546763	2.07826151
440	0.13668667	0.8171661	1.13727244	1.34707713	1.70219575	2.08539244
441	0.13327858	0.81128521	1.13326381	1.33996028	1.6890519	2.0627831
442	0.13070958	0.80697007	1.12666776	1.33300494	1.68085229	2.05675285
443	0.12670381	0.79975431	1.11784562	1.32648148	1.67786342	2.05983226
444	0.12447862	0.79442214	1.11162952	1.31869543	1.66316019	2.03692082
445	0.12136332	0.78857507	1.10568946	1.30939642	1.66092637	2.02728818

Table S14. UV-vis absorption spectroscopic titration of tryptophan with 6b

Wavelength (nm)	Absorbance (a.u.) Trp 10mM	Absorbance (a.u.) Trp 10mM+ **6b** 2.1mM	Absorbance (a.u.) Trp 10mM+ **6b** 4.2 mM	Absorbance (a.u.) Trp 10mM+ **6b** 6.4mM	Absorbance (a.u.) Trp 10mM+ **6b** 10mM	Absorbance (a.u.) Trp 10mM+ **6b** 13mM	Absorbance (a.u.) Trp 10mM+ **6b** 17mM	Absorbance (a.u.) Trp 10mM+ **6b** 21mM
375	-0.0484837	-0.0414748	0.0261008	0.04462449	0.12794169	0.21663603	0.58901875	0.90918842
376	-0.0411265	-0.0340145	0.03043872	0.0502388	0.13055704	0.21738549	0.58639346	0.90423804
377	-0.0330046	-0.0282934	0.02682456	0.05459741	0.13688185	0.21944005	0.58723547	0.9038933
378	-0.0238087	-0.0169891	0.03504964	0.06194284	0.14110925	0.22569476	0.58887715	0.90431119
379	-0.0116119	-0.0068086	0.0447299	0.06256387	0.1506574	0.2331843	0.59364381	0.90860389
380	-0.0037715	0.00164431	0.05433648	0.06991533	0.157082	0.2383232	0.60356876	0.90963614
381	0.00480328	0.0109486	0.06206909	0.07829376	0.16307361	0.24345363	0.57137774	0.90975255
382	0.01589999	0.02024909	0.07063984	0.08703702	0.17054764	0.25013466	0.57649854	0.91385739
383	0.02836099	0.03394653	0.0848905	0.09848063	0.1818236	0.26253782	0.5847845	0.91862388
384	0.03959107	0.04569138	0.09677814	0.11139766	0.19157631	0.27190441	0.5910244	0.92531151
385	0.0535492	0.05953681	0.10792211	0.12410683	0.20357349	0.28170183	0.60165713	0.93204062
386	0.06701565	0.07300967	0.12146442	0.13542959	0.21479052	0.29401578	0.61010599	0.93795982
387	0.07765346	0.08359027	0.13258616	0.14716269	0.22461824	0.30260064	0.61856724	0.94510365
388	0.0869065	0.09273112	0.14159695	0.1536895	0.23243972	0.30915207	0.62361651	0.94892084
389	0.09274938	0.0989898	0.14795268	0.16148523	0.23819918	0.31597285	0.62912806	0.95263166
390	0.09721521	0.10313717	0.15161993	0.16633662	0.24226851	0.32005089	0.63106262	0.95496273
391	0.10200806	0.10954543	0.15825461	0.17171464	0.24688056	0.32460208	0.63368725	0.95784996
392	0.10874752	0.11539832	0.16352524	0.17649444	0.25098916	0.32982559	0.63840436	0.95755052
393	0.12421553	0.12092825	0.16822618	0.18209698	0.25582284	0.33306382	0.64096936	0.93430455
394	0.14589082	0.15729654	0.20543806	0.18645371	0.24940755	0.33595349	0.64174717	0.96077233
395	0.15047126	0.15675224	0.20424019	0.22102289	0.2525835	0.36591288	0.66411704	0.97422731
396	0.15284948	0.15946675	0.2065896	0.21903929	0.2855688	0.36212217	0.66762821	0.96978899
397	0.15279641	0.16069484	0.20762163	0.2188775	0.27993002	0.36204223	0.66477283	0.96747793
398	0.15391166	0.15997424	0.20626128	0.21793247	0.2800335	0.35974321	0.66138814	0.96174157
399	0.15305023	0.15993534	0.206033	0.21725442	0.27827097	0.35743854	0.65634332	0.95677139
400	0.15214919	0.15723604	0.20353879	0.21500634	0.27483844	0.34970122	0.65277148	0.94840762
401	0.1508061	0.15649064	0.20063464	0.21265645	0.27183053	0.34691102	0.64608954	0.94117176
402	0.14802474	0.15416554	0.1992245	0.20879304	0.26628283	0.34145348	0.64014934	0.93140975
403	0.14591451	0.15124757	0.19544897	0.20591437	0.26391841	0.33739418	0.63201082	0.92283567
404	0.14324876	0.1487343	0.19378064	0.20207216	0.26020146	0.33246302	0.62745988	0.91758808
405	0.14051344	0.14615702	0.18981387	0.19831923	0.25581425	0.3268786	0.62056939	0.89118139
406	0.1386568	0.14409698	0.18804246	0.19582853	0.25155536	0.32264857	0.61491951	0.88321964
407	0.13663727	0.14166015	0.18496977	0.19399986	0.24827527	0.31799128	0.60940045	0.87703093
408	0.13454186	0.13959254	0.18164474	0.19093816	0.24600276	0.3150317	0.6039123	0.87009431
409	0.13221561	0.13703663	0.17938021	0.18644437	0.24178624	0.3100495	0.59785043	0.86335867
410	0.13133439	0.13469641	0.17738018	0.18458695	0.23809773	0.30742802	0.59333042	0.85742908
411	0.13032309	0.13478527	0.17606822	0.18286781	0.23595766	0.30505452	0.59008209	0.85424127
412	0.12930354	0.13395735	0.17495059	0.18207119	0.23526358	0.30344005	0.58825236	0.849947
413	0.12686141	0.13246653	0.1721934	0.18070423	0.23196085	0.29870752	0.58244194	0.84466702
414	0.12525563	0.12971847	0.17062999	0.17714241	0.22924959	0.29545402	0.57845859	0.83947144
415	0.12364186	0.127821	0.16858393	0.17456349	0.22557504	0.29139811	0.57239381	0.83248478
416	0.12107399	0.12540165	0.16583624	0.17170107	0.22307738	0.28867201	0.56700507	0.82536752
417	0.11742196	0.12106307	0.16235666	0.16805027	0.21809963	0.28353838	0.55970503	0.81765671
418	0.11602247	0.11873347	0.16015069	0.16383165	0.21387351	0.27790679	0.55417167	0.80874465
419	0.11305151	0.11702603	0.15642028	0.16223486	0.21104298	0.27377011	0.54488701	0.80102693
420	0.1118475	0.11402284	0.15343837	0.15876195	0.20721131	0.27009528	0.53770084	0.79274003
421	0.10926609	0.11216788	0.15005325	0.15432908	0.20329945	0.26471334	0.53229572	0.78615037

422	0.10772448	0.11020095	0.14763712	0.15182936	0.19990527	0.26084078	0.52633058	0.77759572
423	0.10649347	0.10816548	0.14593273	0.14921045	0.19678673	0.25771803	0.52071845	0.77141742
424	0.10370091	0.10576148	0.14308269	0.1461838	0.19311287	0.25261226	0.51449008	0.7634174
425	0.1021937	0.10413067	0.14108339	0.14323246	0.18937638	0.24920473	0.50971838	0.75678331
426	0.10040984	0.10211018	0.13837601	0.14105634	0.18592629	0.24407715	0.50396061	0.74882671
427	0.0998241	0.10165883	0.13703961	0.13920638	0.18293467	0.24208722	0.49927926	0.74298175
428	0.09831939	0.09914095	0.1349784	0.13687944	0.18094588	0.23954585	0.4950876	0.73787891
429	0.09728966	0.0977327	0.13301834	0.13501397	0.17809427	0.23519791	0.4899727	0.73159055
430	0.09569081	0.09688341	0.13143195	0.1339958	0.17601938	0.23207794	0.48702623	0.72608939
431	0.09492711	0.09588087	0.13011033	0.13164126	0.17371394	0.22865948	0.48222631	0.7211961
432	0.09420572	0.09555928	0.12994508	0.13060631	0.17261779	0.22701708	0.48072343	0.71778585
433	0.09432388	0.09535475	0.12989882	0.13078234	0.17234323	0.22731311	0.47919956	0.71603426
434	0.09367517	0.0951325	0.12901702	0.12921583	0.17017027	0.22492941	0.47588963	0.71200802
435	0.09266552	0.09419061	0.12732114	0.12788803	0.16823194	0.22269499	0.47281621	0.70787246
436	0.09216476	0.09322605	0.12631383	0.12633707	0.16631114	0.2206893	0.46877407	0.6992133
437	0.09136167	0.09251555	0.12478821	0.12507658	0.16448764	0.21838031	0.46605518	0.6942339
438	0.09006437	0.09083082	0.12301244	0.12291211	0.16245576	0.21550036	0.46125166	0.68760471
439	0.08902894	0.08935797	0.12216062	0.12166953	0.15879449	0.21238936	0.45777354	0.68273291
440	0.08765517	0.08860907	0.1203159	0.11936016	0.15733521	0.20888787	0.45221791	0.67534102
441	0.08678396	0.08743255	0.11884482	0.11806441	0.15513967	0.2066113	0.44840361	0.66965524
442	0.08545268	0.0863228	0.11797548	0.11607468	0.15292115	0.20357763	0.44437842	0.664813
443	0.08415661	0.08535594	0.11549973	0.11414311	0.15024474	0.20054089	0.43925549	0.65866442
444	0.08326188	0.08400849	0.11473208	0.11294222	0.14789773	0.19803476	0.43610854	0.65308399
445	0.08229917	0.08328452	0.11315916	0.11107785	0.14604276	0.19504658	0.4321576	0.64738148

Table S15. UV-vis absorption spectroscopic titration of Trp-Gly-Trp with 6b

Wavelength (nm)	**Trp-Gly-Trp** 5mM	**Trp-Gly-Trp** 5mM + **6b** 1mM	**Trp-Gly-Trp** 5mM + **6b** 2mM	**Trp-Gly-Trp** 5mM + **6b** 3mM	**Trp-Gly-Trp** 5mM + **6b** 4mM	**Trp-Gly-Trp** 5mM + **6b** 5mM	**Trp-Gly-Trp** 5mM + **6b** 6mM	**Trp-Gly-Trp** 5mM+ **6b** 10mM
375	0.22917521	0.65375268	0.87271697	1.17313321	1.42671796	1.63531769	1.86053021	1.90861444
376	0.22979401	0.64327257	0.8585283	1.15073713	1.43244674	1.6016259	1.86512195	1.90066471
377	0.23042404	0.63520333	0.84682563	1.13853286	1.42195259	1.58723714	1.85449282	1.88917468
378	0.23324373	0.62985714	0.83388675	1.12756194	1.40567854	1.57672135	1.83884171	1.87703091
379	0.23999015	0.62495674	0.82637675	1.11947136	1.40465246	1.56693456	1.83929143	1.87195632
380	0.24104346	0.59077045	0.81669314	1.10944123	1.39267858	1.5551748	1.82628938	1.85589304
381	0.24310993	0.58379733	0.80515556	1.09605614	1.38690094	1.53809647	1.82070679	1.84939705
382	0.24907834	0.58139713	0.79864111	1.08438648	1.3815369	1.51966242	1.8112121	1.84233173
383	0.25571251	0.577576	0.79310669	1.07243869	1.38253035	1.49965375	1.80857694	1.83959149
384	0.26322913	0.57804421	0.79193233	1.07064794	1.38168743	1.49699965	1.8072932	1.84212034
385	0.27169168	0.5788075	0.79050108	1.07340761	1.3728293	1.50433079	1.79986117	1.83797356
386	0.28029759	0.57899859	0.78762857	1.07428864	1.37154926	1.50908685	1.80238869	1.83962152
387	0.28746391	0.58054984	0.78983672	1.0783616	1.36402763	1.51558626	1.80156289	1.84317838
388	0.29166327	0.57949138	0.78634679	1.07053228	1.35210415	1.50233795	1.80443241	1.83908151
389	0.29486786	0.57816414	0.76169539	1.08030923	1.39310228	1.54789142	1.80010774	1.83812312
390	0.29752549	0.57928859	0.76183842	1.07804405	1.38861512	1.54290569	1.79263497	1.83902153
391	0.30078513	0.5776499	0.79818245	1.10120636	1.40047219	1.55608021	1.76850493	1.83262359
392	0.30296605	0.60365244	0.79579045	1.10394671	1.40789771	1.56433079	1.77944738	1.82024718
393	0.3045831	0.59741709	0.77467004	1.09655606	1.41268569	1.56965077	1.80606883	1.84402665
394	0.30639965	0.59330144	0.7708457	1.09118666	1.40579632	1.56199591	1.79772972	1.85726648
395	0.33474931	0.58702568	0.7634073	1.08147612	1.39380676	1.54867418	1.79650474	1.84402665
396	0.32855223	0.58065564	0.75448733	1.07371408	1.38689978	1.54099975	1.77926447	1.84049298
397	0.32501676	0.57249764	0.74607106	1.06419282	1.37615451	1.52906056	1.77549285	1.83929143
398	0.31787749	0.56519169	0.73811885	1.04980971	1.35563689	1.50626321	1.77065098	1.83812312
399	0.31432185	0.55483188	0.72737876	1.04404442	1.35420994	1.50467771	1.75639154	1.8305019
400	0.30953367	0.5467826	0.71897348	1.06052699	1.39348889	1.54832099	1.75291093	1.82182911
401	0.30455596	0.53741933	0.7090821	1.04461002	1.37176523	1.52418359	1.73478109	1.8155073
402	0.29733429	0.52754489	0.69713465	1.03060676	1.35557418	1.50619353	1.73167948	1.80429404
403	0.29355789	0.51932775	0.68711419	1.02001158	1.34420636	1.49356262	1.71749118	1.79783875
404	0.28869818	0.51118286	0.67875173	1.00941968	1.33135265	1.47928073	1.71372323	1.79169302
405	0.28400001	0.50338995	0.66911364	0.99872877	1.3194565	1.46606277	1.70304978	1.78502378
406	0.27914802	0.49595754	0.6622114	0.98885519	1.30667071	1.45185635	1.69695523	1.78375491
407	0.27390637	0.48727558	0.65468901	0.98356763	1.30326705	1.4480745	1.68621713	1.77528571
408	0.27102562	0.47826973	0.64732364	0.97513961	1.29367948	1.43742165	1.68327502	1.76664846
409	0.2667666	0.47206478	0.63919651	0.97062748	1.2923121	1.43590234	1.67670666	1.7544133
410	0.26201902	0.46702152	0.63349485	0.96430241	1.28527349	1.42808165	1.66302024	1.75195312
411	0.26127728	0.46496426	0.63041681	0.96391598	1.2873002	1.43033355	1.6647628	1.75187956
412	0.25938153	0.46154694	0.62720395	0.9672079	1.29652577	1.44058419	1.66562669	1.74960441
413	0.25572422	0.457248	0.62157122	0.97214718	1.31109891	1.45677656	1.65327548	1.74227345
414	0.25189112	0.45145338	0.61545662	0.97306117	1.31836068	1.4648452	1.646103	1.73511139
415	0.24899819	0.44749602	0.60968145	0.97246797	1.32241694	1.46935216	1.64677641	1.7310478
416	0.24511908	0.44170675	0.60347113	0.97090241	1.32499394	1.47221549	1.63292376	1.72264296
417	0.23994715	0.4345028	0.59548787	0.96841943	1.32740134	1.47489038	1.62718002	1.71213113
418	0.23645448	0.42919444	0.58943701	0.96623283	1.32863987	1.47626653	1.62267555	1.70665953
419	0.23101651	0.42311641	0.57902161	0.95665954	1.31959373	1.46621525	1.61177443	1.69568183
420	0.2279924	0.41744806	0.57184737	0.94536067	1.30431032	1.44923369	1.60479596	1.6904763
421	0.22363374	0.41194801	0.56500502	0.93954804	1.29928433	1.44364925	1.59328954	1.67914777
422	0.21965175	0.40629311	0.55876532	0.9323915	1.29113014	1.43458904	1.58611375	1.66985014
423	0.21620927	0.40090547	0.55432731	0.92195295	1.27503949	1.41671054	1.58292709	1.66641169

424	0.21248072	0.39607978	0.54760934	0.91248315	1.26286477	1.40318307	1.57118513	1.66011149
425	0.20951494	0.39168367	0.5422997	0.90475793	1.25277931	1.39197701	1.5630903	1.64831962
426	0.20600787	0.38683178	0.53645339	0.89972707	1.24836108	1.38706786	1.56223358	1.64600689
427	0.20158074	0.38258233	0.53185065	0.89828862	1.24973583	1.38859537	1.55470723	1.63812113
428	0.19973323	0.37867516	0.52775858	0.89556103	1.24817051	1.38685613	1.54313314	1.63513022
429	0.19668289	0.37559411	0.52372062	0.88913902	1.23944806	1.37716451	1.54243599	1.62937588
430	0.19407727	0.37222566	0.51964517	0.88608857	1.23724658	1.37471842	1.53742233	1.62517836
431	0.19209239	0.36951113	0.51485658	0.88335345	1.23629366	1.37365962	1.52840029	1.61995165
432	0.19157498	0.3670156	0.51343494	0.8829624	1.23682072	1.37424525	1.52537585	1.61648983
433	0.19061877	0.3660591	0.51160442	0.8815827	1.23581348	1.37312609	1.52303801	1.61825335
434	0.18856104	0.36397271	0.50925094	0.87777082	1.23059716	1.36733018	1.51931771	1.61214764
435	0.18643502	0.3601053	0.50563807	0.87413555	1.2268541	1.36317122	1.51578559	1.6079893
436	0.18482352	0.35786704	0.50182593	0.86848914	1.21942075	1.35491194	1.50606817	1.60188629
437	0.18316568	0.3542742	0.49879692	0.86507221	1.21557233	1.35063592	1.50302884	1.59698248
438	0.18020479	0.35090183	0.4935031	0.85852893	1.20774681	1.3419409	1.49165887	1.5879765
439	0.17740176	0.34680194	0.48845486	0.85088874	1.1975897	1.33065522	1.48714225	1.58603004
440	0.17523851	0.34280357	0.48387067	0.84222149	1.18503877	1.31670974	1.47627956	1.57613182
441	0.17260292	0.33770881	0.47921134	0.83830986	1.18170578	1.31300642	1.4705825	1.56770431
442	0.17020302	0.33366737	0.47477634	0.8341041	1.17760497	1.30844997	1.46007123	1.56629415
443	0.16705064	0.32904392	0.46884565	0.82853081	1.17221898	1.30246554	1.45497758	1.55511244
444	0.16472554	0.32524631	0.4631664	0.82699842	1.17438184	1.30486871	1.4427094	1.54282991
445	0.16303503	0.32173391	0.45880905	0.82048075	1.16576277	1.29529197	1.43784994	1.54245114