

SUPPORTING INFORMATION

New approach for post-functionalization of *meso*-formylporphyrins

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1. General remarks

Phenanthrene-1,10-dione, ^[1] phenanthroline-1,10-dione, ^[2] **1Cu**, ^[3] **2Cu** ^[3] were prepared according to published procedures.

POCl₃ (Aldrich, 99%), DMF (Sigma-Aldrich, >99%), 1,2-dichloroethane (DCE, Fluka, >99%), AcOH (Sigma-Aldrich, >99%), CH₂Cl₂ (reagent grade, 99%), TFA (Sigma-Aldrich, 99%), H₂SO₄ (reagent grade, 93-95%), NH₄OAc (Merck, >98%), NaHCO₃ (reagent grade, >99%) were used without purification. Reagent grade CHCl₃ was dried over CaCl₂ and distilled over K₂CO₃ prior to use.

TLC was performed at Silica gel 60 F₂₅₄ plates (Merck). Column chromatography was performed at glass columns with silica 60 (0.063-0.2 mm) and neutral alumina (Macherey-Nagel).

NMR spectra were acquired at Bruker Avance II 300 MHz and Bruker Avance III 600 MHz spectrometers in CDCl₃ or CDCl₃/MeOD mixture, CHCl₃ residual signal (7.24 ppm) was used as internal reference. UV-Vis spectra were recorded at Unicam UV-4 spectrophotometer in CHCl₃ in rectangular quartz cells with 1 cm optical path. MALDI-TOF mass-spectra were obtained on Bruker Ultraflex mass-spectrometer in positive ion mode without application of matrix.

Geometry optimization and molecular orbitals analysis were performed at the density functional theory (DFT) level with SPARTAN'14 software (Wavefunction Inc.). The Becke's three parameter hybrid functional with the Lee-Yang-Parr correlation functional (B3LYP) method was employed to do the calculations using 6-31G* basis set.

2. Synthetic procedures and characterization

3Cu and 4Cu. The modification to published procedure [3,4] was applied for formylation. POCl₃ (1.75 ml) was added to solution of DMF (1.75 ml) in DCE (5 ml) upon stirring at ambient temperature and kept for 0.5 hours. The obtained solution was added to solution of **1Cu** or **2Cu** (0.7 mmol) in DCE (95 ml) and the obtained mixture was heated at 60°C under dry argon until complete consumption of starting material was revealed by TLC (*ca.* 6 hours). The mixture was cooled to room temperature and water (50 ml) was added. The water phase was neutralized with solid NaHCO₃, organic phase was separated, dried over Na₂SO₄ and evaporated to dryness. The residue was passed through a pad of silica with CHCl₃ and the resulting solution was evaporated to give pure **3Cu** (92%) or **4Cu** (98%). The physico-chemical characteristics of the obtained compounds are equal to published ones. [3,4]

7Cu. Mixture of **4Cu** (0.2 mmol, 128 mg), **A** (0.2 mmol, 42 mg) and NH₄OAc (2 mmol, 154 mg) was gently refluxed in CHCl₃ (34 ml) and AcOH (6 ml) for 24 hours. As a second step the same amount of **A** and NH₄OAc were added and reflux was continued for additional 24 hours. Afterwards, this procedure was repeated once more for further 24 hours. The mixture was cooled to ambient temperature, diluted with CHCl₃ (50 ml) and extracted with water (50 ml). Organic layer was separated, dried over Na₂SO₄, evaporated and applied in CH₂Cl₂ to silica column packed in hexane. The column was eluted with CH₂Cl₂/hexane (50→100% of CH₂Cl₂) and then CH₂Cl₂/acetone mixtures (0→0.6% of acetone). The obtained fraction of **7Cu** was evaporated to give 90% (147 mg) of pure compound.

MALDI TOF MS: m/z calculated for C₅₃H₄₀CuN₆ [M]⁺ 823.26, found 823.21.

UV-Vis (CHCl₃; λ, nm; rel. int): 255 (0.260), 283 (0.091), 306 (0.087), 411 (1.000), 535 (0.067), 561 (sh, 0.018).

8Cu. Mixture of **4Cu** (0.1 mmol, 64 mg), **B** (0.2 mmol, 42 mg) and NH₄OAc (2 mmol, 154 mg) was gently refluxed in CHCl₃ (17 ml) and AcOH (3 ml) for 24 hours. As a second step the same amount of **B** and NH₄OAc were added and reflux was continued for additional 24 hours. Afterwards, this procedure was repeated once more for further 24 hours. The mixture was cooled to ambient temperature, diluted with CHCl₃ (50 ml) and extracted with water (50 ml). Organic layer was separated and stirred with 200 mg of solid K₂CO₃ for 0.5 hour, then dried over Na₂SO₄, evaporated and applied in CHCl₃ to silica column packed in CHCl₃. The column was eluted with CHCl₃/MeOH mixtures (0→10% of MeOH). The obtained fraction of **8Cu** was evaporated to give 62% (51 mg) of pure compound.

MALDI TOF MS: m/z calculated for C₅₁H₃₈CuN₈ [M]⁺ 825.25, found 825.23.

UV-Vis (CHCl₃; λ, nm; rel. int): 277 (0.129), 411 (1.000), 534 (0.050), 564 (sh, 0.012).

9Cu. Mixture of **3Cu** (0.1 mmol, 55 mg), **A** (0.1 mmol, 21 mg) and NH₄OAc (1 mmol, 77 mg) was gently refluxed in CHCl₃ (17 ml) and AcOH (3 ml) for 24 hours. As a second step the same amount of **A** and NH₄OAc were added and reflux was continued for additional 24 hours. Afterwards this procedure was repeated once more for further 24 hours. The mixture was cooled to ambient temperature, diluted with CHCl₃ (50 ml) and extracted with water (50 ml). Organic layer, containing a fine suspension of **5Cu**, was separated and evaporated to dryness. DMF (10 ml), 1-bromobutane (0.5 mmol, 54 μl) and K₂CO₃ (0.6 mmol, 83 mg) were added and the mixture was heated at 100°C for 24 h under argon atmosphere. Then the mixture was cooled to ambient temperature, diluted with CHCl₃ (50 ml) and extracted with water (50 ml). The organic layer was dried over Na₂SO₄ evaporated with silica and applied to silica column packed in hexane. The

column was eluted with CHCl₃/hexane mixtures (0→40% of CHCl₃) and CHCl₃/hexane/acetone mixture (40% of CHCl₃ and 0.1% of acetone). The obtained fraction of **9Cu** was evaporated to give 83% (66 mg) of pure compound (for 2 steps from **3Cu**).

MALDI TOF MS: m/z calculated for C₅₁H₃₆CuN₆ [M]⁺ 795.23, found 795.20.

UV-Vis (CHCl₃; λ, nm; rel. int): 285 (0.095), 308 (0.085), 338 (0.048), 411 (1.000), 534 (0.074), 566 (0.029).

10Cu. Mixture of **3Cu** (0.1 mmol, 55 mg), **B** (0.2 mmol, 42 mg) and NH₄OAc (2 mmol, 154 mg) was gently refluxed in CHCl₃ (17 ml) and AcOH (3 ml) for 24 hours. As a second step the same amount of **B** and NH₄OAc were added and reflux was continued for additional 24 hours. Afterwards, this procedure was repeated once more for further 24 hours. The mixture was cooled to ambient temperature, diluted with CHCl₃ (50 ml) and extracted with water (50 ml). Organic layer, containing a fine suspension of **6Cu**, was separated and evaporated to dryness. DMF (10 ml), 1-bromobutane (0.5 mmol, 54 μl) and K₂CO₃ (0.6 mmol, 83 mg) were added and the mixture was heated at 100°C for 24 h under argon atmosphere. Then the mixture was cooled to ambient temperature, diluted with CHCl₃ (50 ml) and extracted with water (50 ml). The organic layer was dried over Na₂SO₄ evaporated with silica and applied to silica column packed in hexane. The column was eluted with CHCl₃/hexane mixtures (0→40% of CHCl₃) and CHCl₃/hexane/acetone mixture (40% of CHCl₃ and 0.1% of acetone). The obtained fraction of **10Cu** was evaporated to give 58% (46 mg) of pure compound (for 2 steps from **3Cu**).

MALDI TOF MS: m/z calculated for C₄₉H₃₅CuN₈ [M+H]⁺ 798.23, found 798.13.

UV-Vis (CHCl₃; λ, nm; rel. int): 285 (0.136), 410 (1.000), 534 (0.053), 566 (0.016).

Demetallation of 3Cu, 7Cu-10Cu. The copper(II) porphyrin was dissolved or suspended in TFA (4 ml per 0.1 mmol) and H₂SO₄ was added (0.6 ml per 0.1 mmol) upon intense stirring. The mixture was stirred at ambient temperature for 15 min, afterwards CHCl₃ (20 ml per 0.1 mmol) and water (20 ml per 0.1 mmol) were added. The water phase was neutralized with solid NaHCO₃ at vigorous stirring and organic layer was separated. The CHCl₃ solution was stirred with K₂CO₃ for 15 min, dried over Na₂SO₄ and evaporated. The residue was passed through a plug of silica with CHCl₃ (**3H₂**, **7H₂**, **9H₂**), 1% of MeOH in CHCl₃ (**10H₂**) or alumina (Brockman III grade) with 2% of MeOH in CH₂Cl₂ (**8H₂**), followed by size-exclusion chromatography with 4% EtOH in CHCl₃.

3H₂. Yield 94%. The characteristics are equal to published ones. [3]

7H₂. Yield 88%. MALDI TOF MS: m/z calculated for C₅₃H₄₂N₆ [M]⁺ 762.35, found 762.28.

¹H NMR (600 MHz; CDCl₃; δ, ppm; *J*, Hz): 10.77 (s, 1H, NH), 10.21 (s, 1H, H_{meso}), 9.30 (d, 2H, ³*J* = 4.6, H_β), 9.20 (d, 2H, ³*J* = 4.8, H_β), 9.08 (d, 1H, ³*J* = 7.9, H_{Ar}), 8.94-8.86 (m, 2H, H_{Ar}), 8.84 (d, 2H, ³*J* = 4.6, H_β), 8.81 (d, 2H, ³*J* = 4.8, H_β), 8.13 (d, 1H, ³*J* = 7.8, H_{Ar}), 7.82 (t, 1H, ³*J* = 7.6, H_{Ar}), 7.78-7.64 (m, 3H, H_{Ar}), 7.29 (s, 4H, H_{Mes}), 2.62 (s, 6H, H_{p-Me}), 1.84 (s, 12H, H_{o-Me}), -2.83 (s, 2H, NH_{Por}).

UV-Vis (CHCl₃; λ, nm; rel. int): 254 (0.315), 305 (0.106), 415 (1.000), 510 (0.078), 550 (0.037), 584 (0.032), 642 (0.019).

8H₂. Yield 87%. MALDI TOF MS: m/z calculated for C₅₁H₄₀N₈ [M]⁺ 764.34, found 764.30.

¹H NMR (300 MHz; CDCl₃; δ, ppm; *J*, Hz): 10.20 (s, 1H, H_{meso}), 9.28 (d, 2H, ³*J* = 4.6, H_β), 9.14 (br.s, 2H, H_{Ar}), 9.11 (d, 2H, ³*J* = 4.8, H_β), 8.81 (d, 2H, ³*J* = 4.6, H_β), 8.77 (d, 2H, ³*J* = 4.8, H_β), 8.53 (br.s, 1H, H_{Ar}), 7.83-7.48 (br.m, 3H, H_{Ar}), 2.61 (s, 6H, H_{p-Me}), 1.80 (s, 12H, H_{o-Me}), -2.90 (s, 2H, NH_{Por}).

UV-Vis (CHCl₃; λ, nm; rel. int): 284 (0.119), 415 (1.000), 509 (0.070), 549 (0.025), 582 (0.027), 642 (0.014).

9H₂. Yield 97%. MALDI TOF MS: m/z calculated for C₅₁H₃₈N₆ [M]⁺ 734.32, found 734.71.

¹H NMR (600 MHz; CDCl₃; δ, ppm; J, Hz): 10.31 (s, 1H, H_{meso}), 9.37 (d, 2H, ³J = 4.7, H_β), 9.07-8.99 (m, 4H, 2H_β+2H_{Ar}), 8.94 (d, 2H, ³J = 4.8, H_β), 8.46-8.40 (m, 1H, H_{Ar}), 8.33-8.25 (m, 2H, H_{Ar}), 8.22-8.15 (m, 2H, H_{Ar}), 7.83-7.69 (m, 10H, H_{Ph}), 4.36 (t, 2H, ³J = 8.0, CH₂), 1.71 (quint, 2H, ³J = 7.8, CH₂), 0.66 (sext, 2H, ³J = 7.4, CH₂), 0.24 (t, 3H, ³J = 7.4, CH₃), -2.90 (s, 2H, NH_{Por}).

UV-Vis (CHCl₃; λ, nm; rel. int): 256 (0.272), 414 (1.000), 510 (0.080), 546 (0.039), 582 (0.037), 640 (0.020).

10H₂. Yield 95%. MALDI TOF MS: m/z calculated for C₄₉H₃₇N₈ [M+H]⁺ 737.31, found 737.31

¹H NMR (600 MHz; CDCl₃; δ, ppm; J, Hz): 10.34 (s, 1H, H_{meso}), 9.39 (d, 2H, ³J = 4.6, H_β), 9.33-9.27 (br.m, 3H, H_{Ar}), 9.05 (d, 2H, ³J = 4.5, H_β), 8.97 (d, 2H, ³J = 4.8, H_β), 8.86 (d, 2H, ³J = 4.8, H_β), 8.71 (d, 1H, ³J = 8.2, H_{Ar}), 8.34-8.26 (m, 2H, H_{Ar}), 8.24-8.16 (m, 2H, H_{Ar}), 7.84-7.74 (m, 10H, H_{Ph}), 4.36 (t, 2H, ³J = 7.7, CH₂), 0.87 (quint, 2H, ³J = 7.2, CH₂), 0.68 (sext, 2H, ³J = 7.4, CH₂), 0.25 (t, 3H, ³J = 7.3, CH₃), -2.89 (s, 2H, NH_{Por}).

UV-Vis (CHCl₃; λ, nm; rel. int): 253 (0.136), 286 (0.106), 414 (1.289), 510 (0.054), 540 (0.019), 581 (0.020), 635 (0.009).

5H₂. Route 1. Demetallation of 5Cu. Suspension of **5Cu** in CHCl₃, obtained as described in the preparation of **9Cu** from **3Cu** (0.1 mmol, 55 mg), was evaporated to dryness and suspended in TFA (2 ml). H₂SO₄ (0.6 ml) was slowly added upon vigorous stirring and the mixture was stirred at ambient temperature for 15 min. Afterwards CHCl₃ (20 ml) and water (20 ml) were added and water phase was neutralized with solid Na₂CO₃. Organic layer was separated and evaporated to dryness. The residue was suspended in MeOH, filtered and washed successively with MeOH. The solid was washed from filter with CHCl₃/MeOH mixture (1/1) and evaporated to give 41 mg (61%) of **5H₂**.

Route 2. The procedure for preparation of **5Cu** was applied with **3H₂** (0.1 mmol, 49 mg) as starting material. The obtained reaction mixture containing suspension of **5H₂** was extracted with water (50 ml) and evaporated to dryness. The residue was suspended in MeOH, filtered and washed with MeOH successively. The obtained solid was dissolved and washed off from filter with CHCl₃/MeOH (1/1) mixture. The evaporation of the obtained solution gave 64 mg (95%) of **5H₂**.

MALDI TOF MS: m/z calculated for C₄₇H₃₀N₆ [M]⁺ 678.25, found 677.62.

¹H NMR (300 MHz; 20% MeOD in CDCl₃; δ, ppm; J, Hz): 10.22 (s, 1H, H_{meso}), 9.26 (br.d, 2H, ³J = 4.3, H_β), 8.99 (br.d, 2H, ³J = 4.3, H_β), 8.89 (d, 2H, ³J = 4.4, H_β), 8.81 (d, 2H, ³J = 4.4, H_β), 8.69-8.78 (br.s, 3H, H_{Ar}), 8.21 (br.s, 1H, H_{Ar}), 8.03-8.11 (m, 4H, H_{o-Ph}), 7.69-7.61 (m, 6H, H_{m+p-Ph}), 7.61-7.50 (br.m, 4H, H_{Ar}). NH-protons are not observed because of exchange with MeOD.

UV-Vis (CHCl₃; λ, nm; rel. int): 258 (0.310), 414 (1.000), 512 (0.114), 550 (0.063), 584 (0.062), 644 (0.045).

Alkylation of 5H₂ to give 9H₂. Following the procedure for **9Cu** and **10Cu**, alkylation of **5H₂** (0.075 mmol, 51 mg) afforded 89% (49 mg) of **9H₂**. The characteristics are equal to described above compound.

References

1. Linstead R. P., Doering W. E., *J. Am. Chem. Soc.*, **1942**, 64, 1991–2003.
2. Zheng R. H., Guo H. C., Jiang H. J., Xu K. H., Liu B. B., Sun W. L., Shen Z. Q., *Chin. Chem. Lett.*, **2010**, 21, 1270–1272.

- Morotti T., Pizzotti M., Ugo R., Quici S., Bruschi M., Mussini P., Righetto S., *Eur. J. Inorg. Chem.*, **2006**, 2006, 1743–1757.
- Carcel C. M., Laha J. K., Loewe R. S., Thamyongkit P., Schweikart K.-H., Misra V., Bocian D. F., Lindsey J. S., *J. Org. Chem.*, **2004**, 69, 6739–6750.

3. Self-condensation of phenanthredione

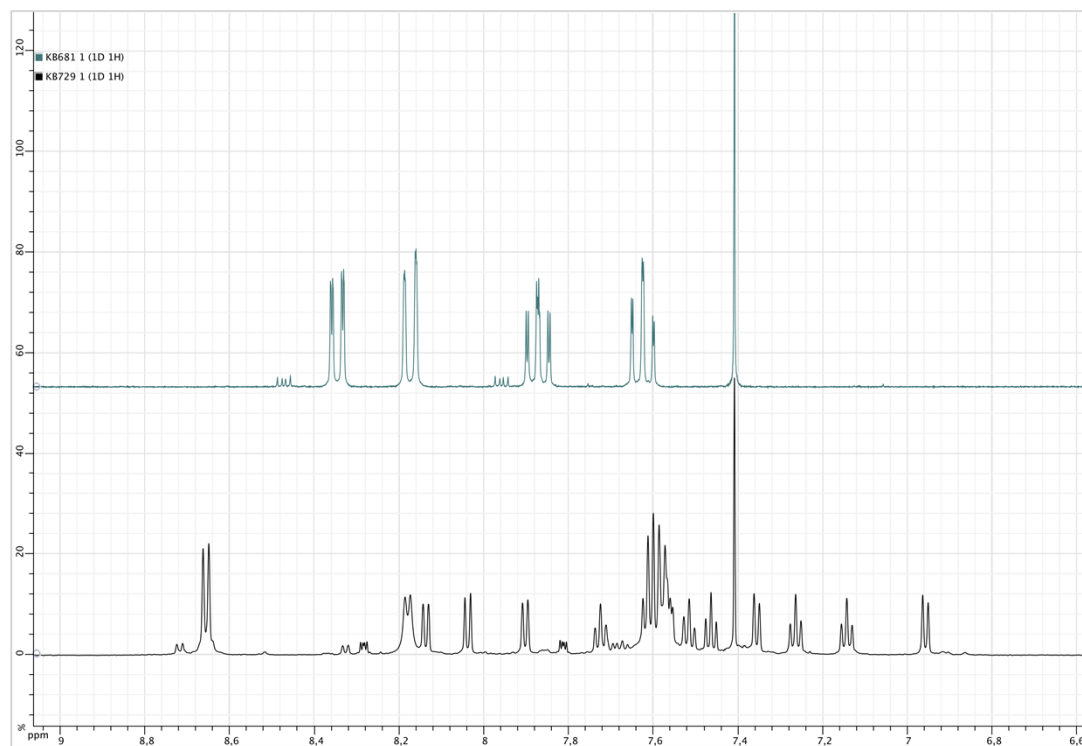


Fig. S1. ¹H NMR spectra of 5,6-phenanthredione (top, CDCl₃) and the condensation product (bottom, CDCl₃/MeOD = 1/1), obtained after 24 hours of reflux in CHCl₃/AcOH in the presence of excess of NH₄OAc. The spectra are referenced by residual solvent signal.

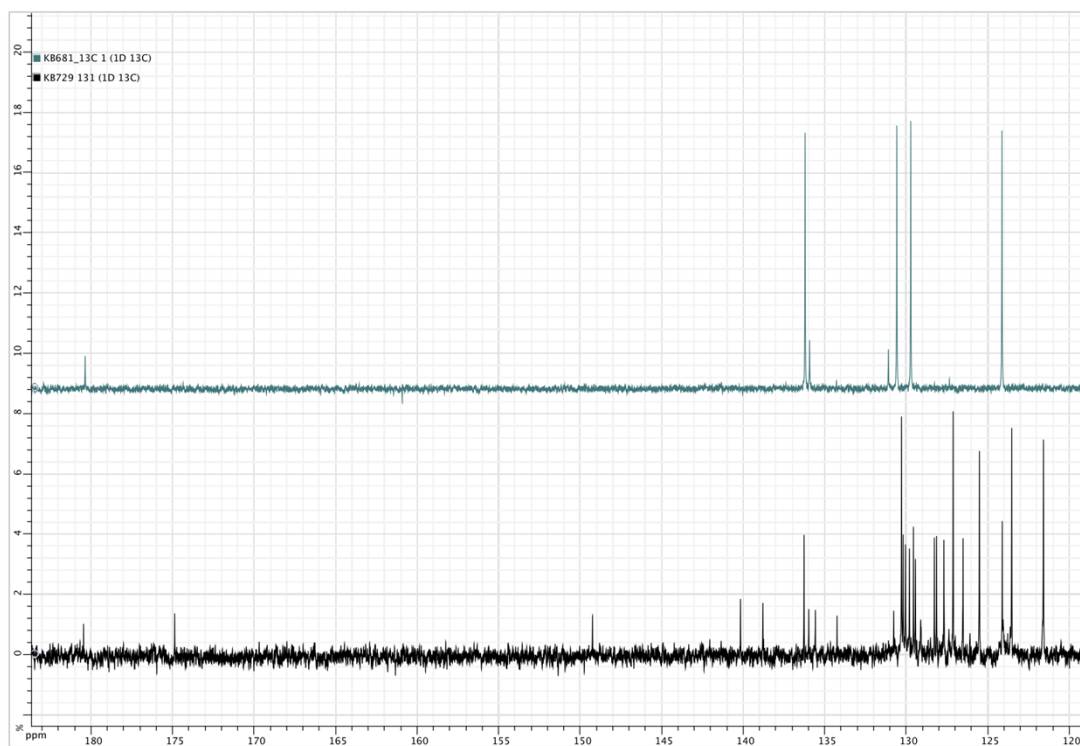


Fig. S2. ^{13}C NMR spectra of 5,6-phenanthrenedione (top, CDCl_3) and the condensation product (bottom, $\text{CDCl}_3/\text{MeOD} = 1/1$), obtained after 24 hours of reflux in $\text{CHCl}_3/\text{AcOH}$ in the presence of excess of NH_4OAc . The spectra are referenced by residual solvent signal.

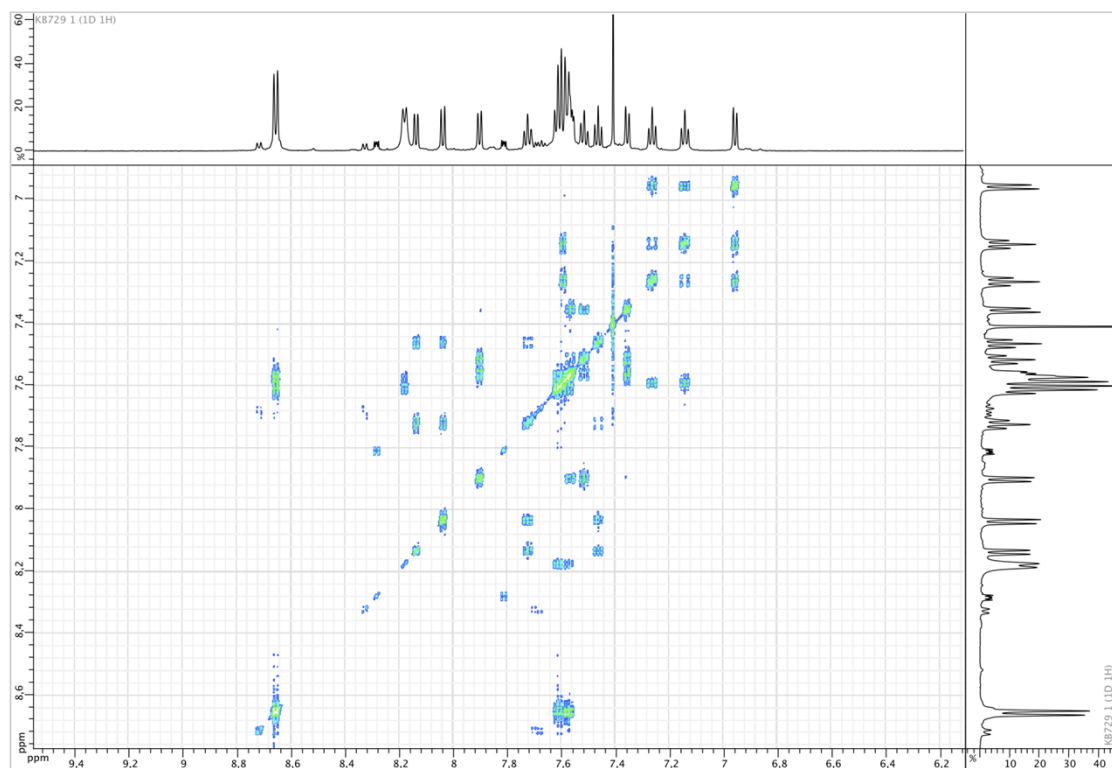


Fig. S3. ^1H - ^1H COSY spectrum ($\text{CDCl}_3/\text{MeOD} = 1/1$) of the condensation product, obtained after 24 hours of reflux in $\text{CHCl}_3/\text{AcOH}$ in the presence of excess of NH_4OAc .

4. Spectra of the synthesized compounds

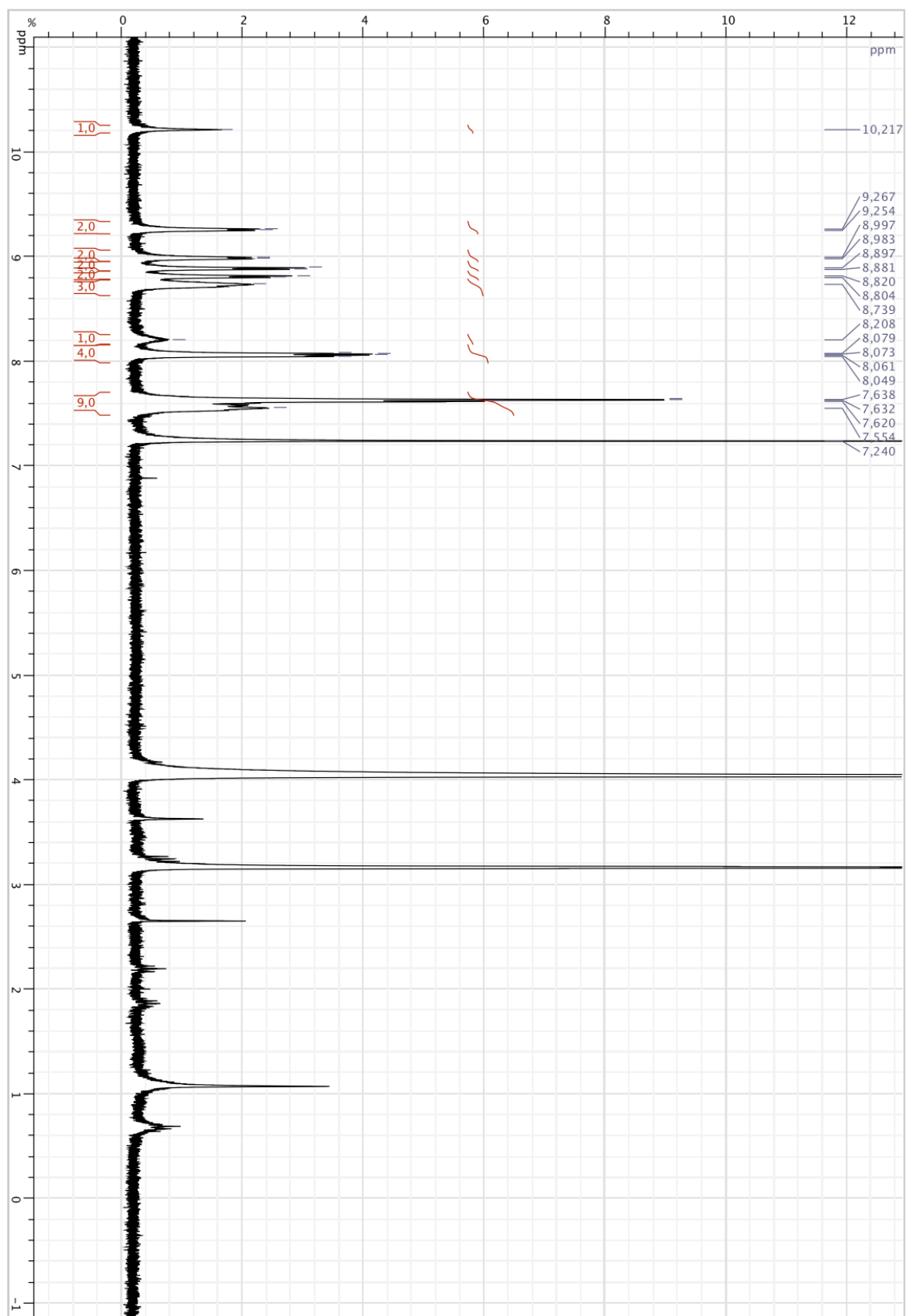


Fig. S4. $^1\text{H-NMR}$ spectrum of 5H_2 (300 MHz, 20% of MeOD in CDCl_3).

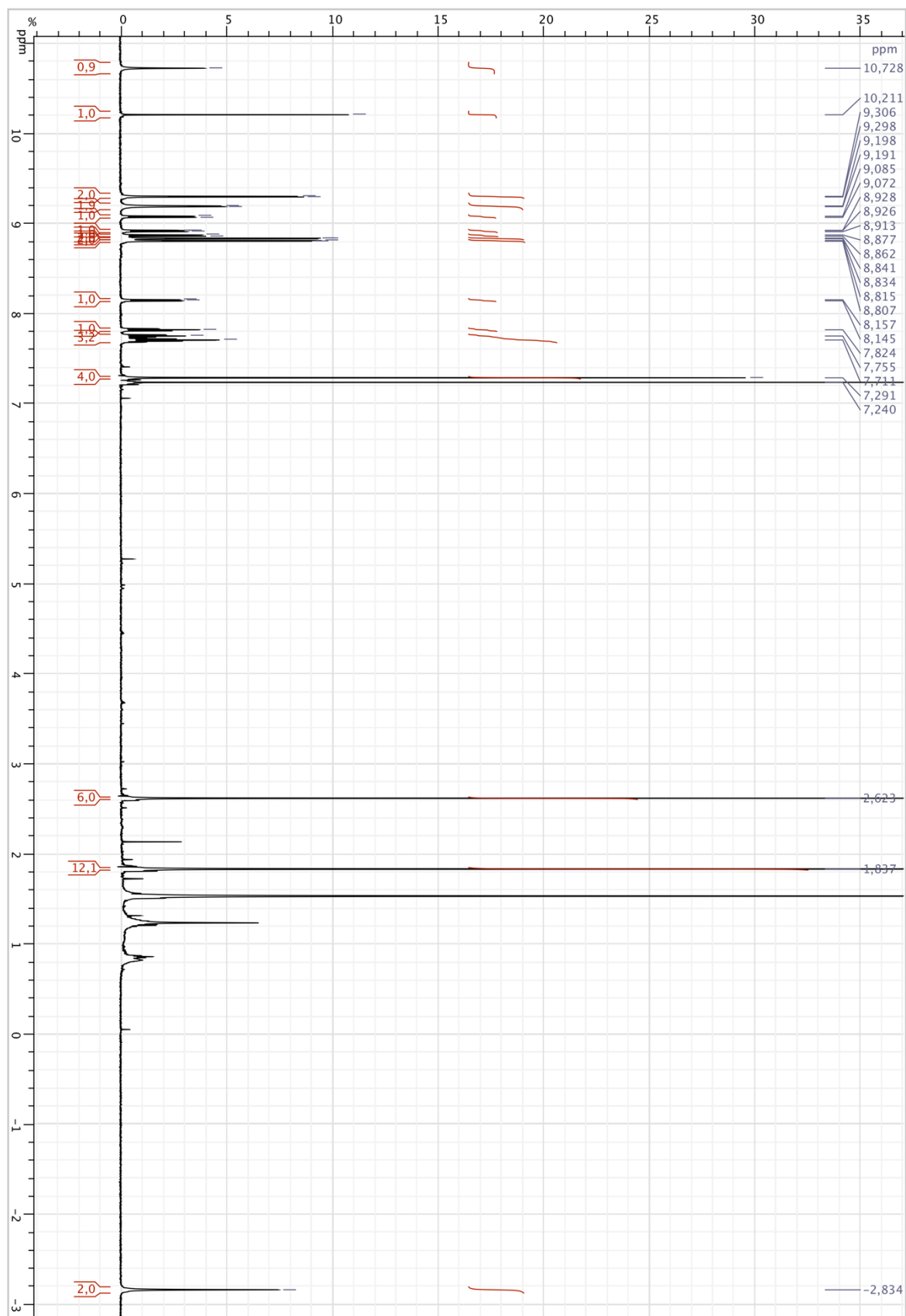


Fig. S5. ¹H-NMR spectrum of 7H₂ (600 MHz, CDCl₃).

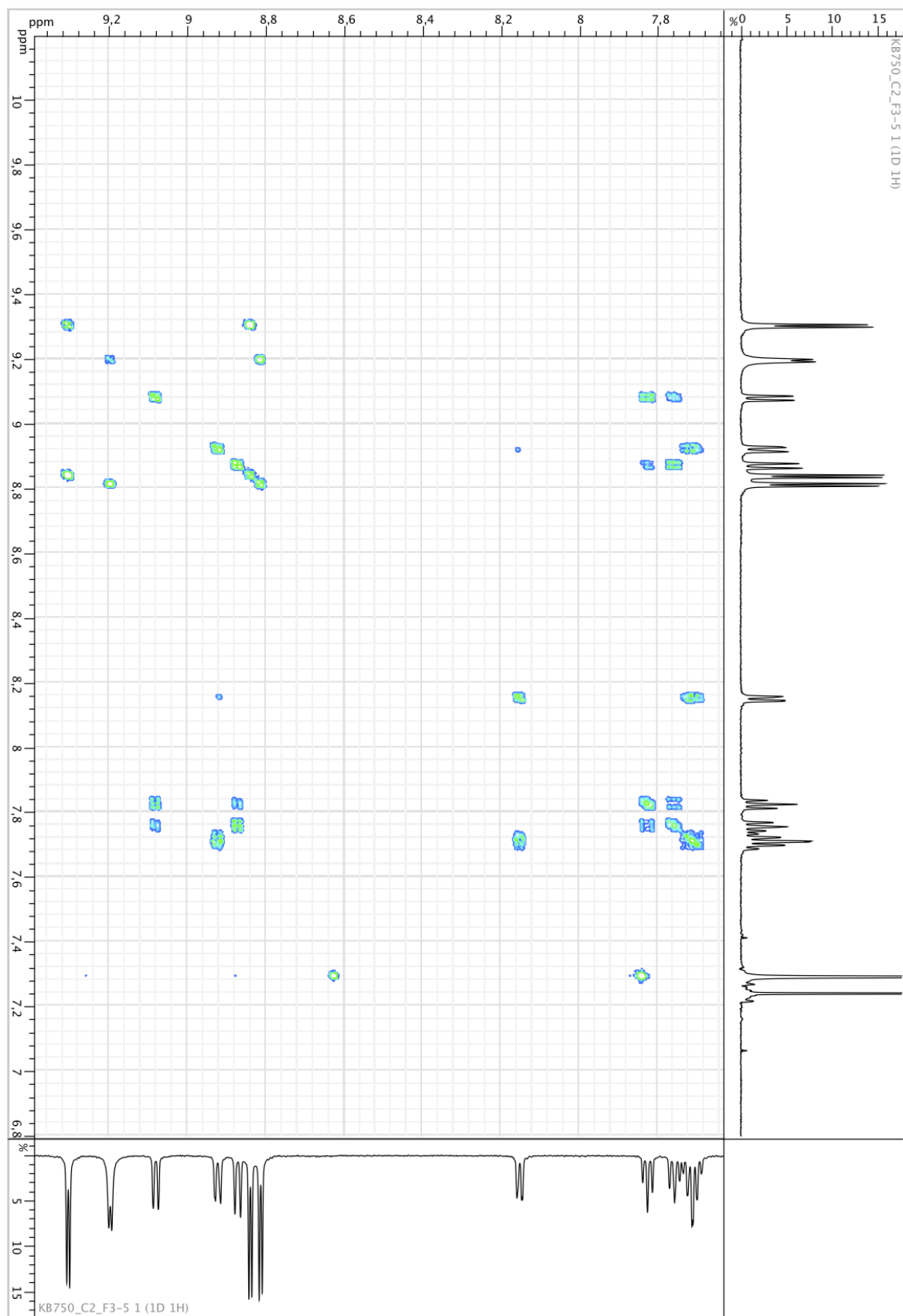


Fig. S6. ^1H - ^1H COSY spectrum of **7H₂** in aromatic region (600 MHz, CDCl_3).

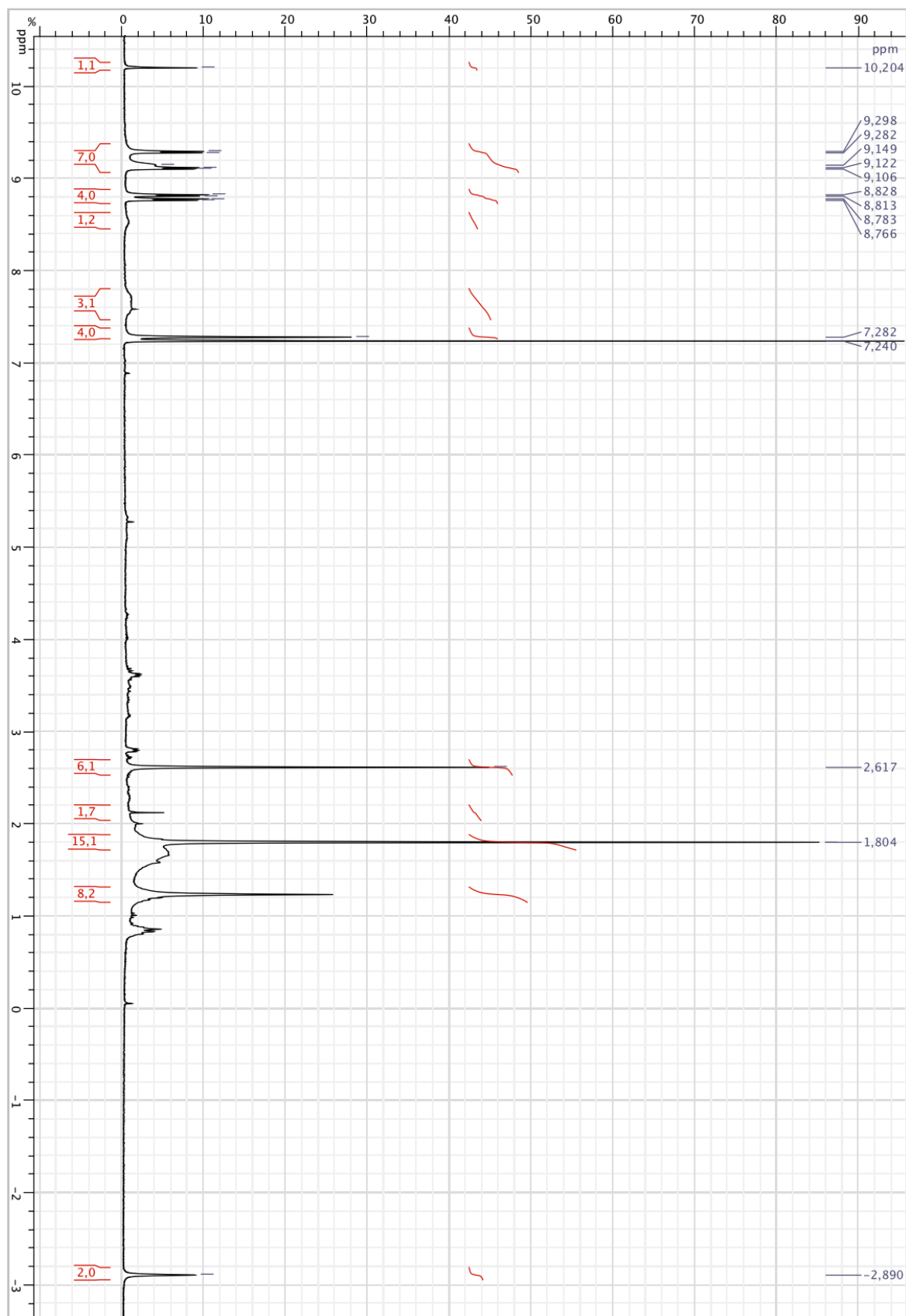


Fig. S7. $^1\text{H-NMR}$ spectrum of 8H_2 (300 MHz, CDCl_3).

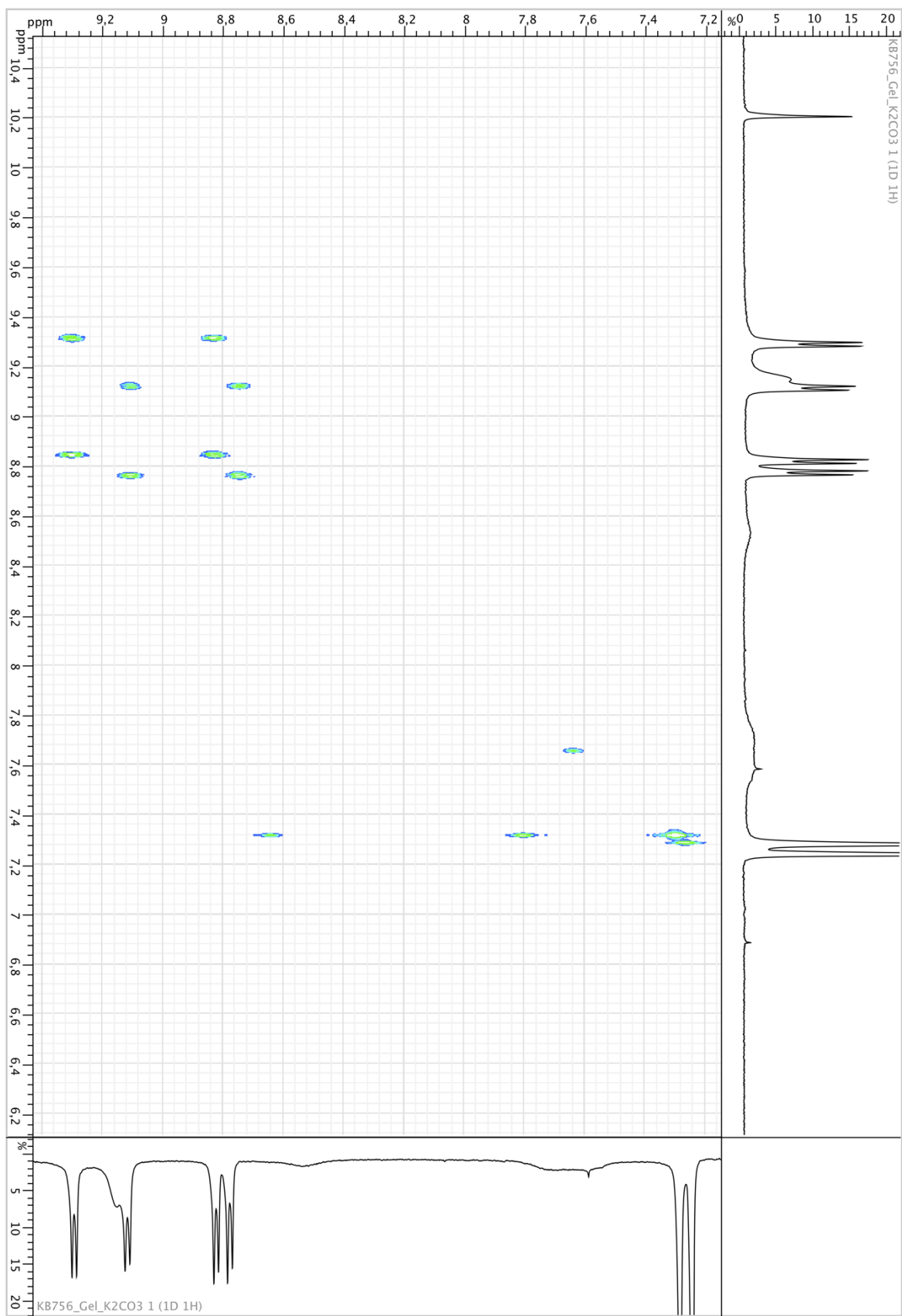


Fig. S8. ^1H - ^1H COSY spectrum of **8H₂** in aromatic region (600 MHz, CDCl_3).

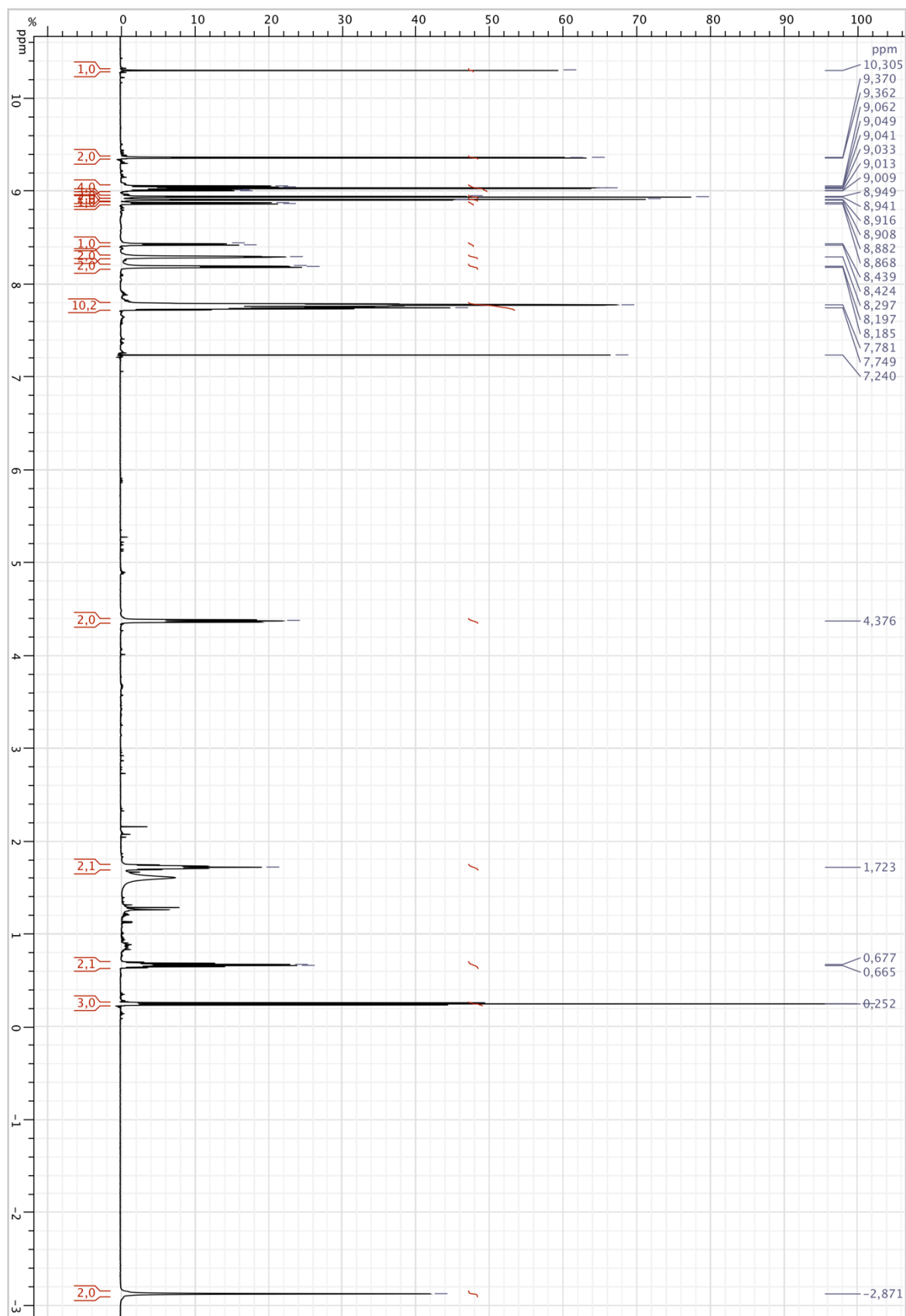


Fig. S9. ^1H -NMR spectrum of 9H_2 (600 MHz, CDCl_3).

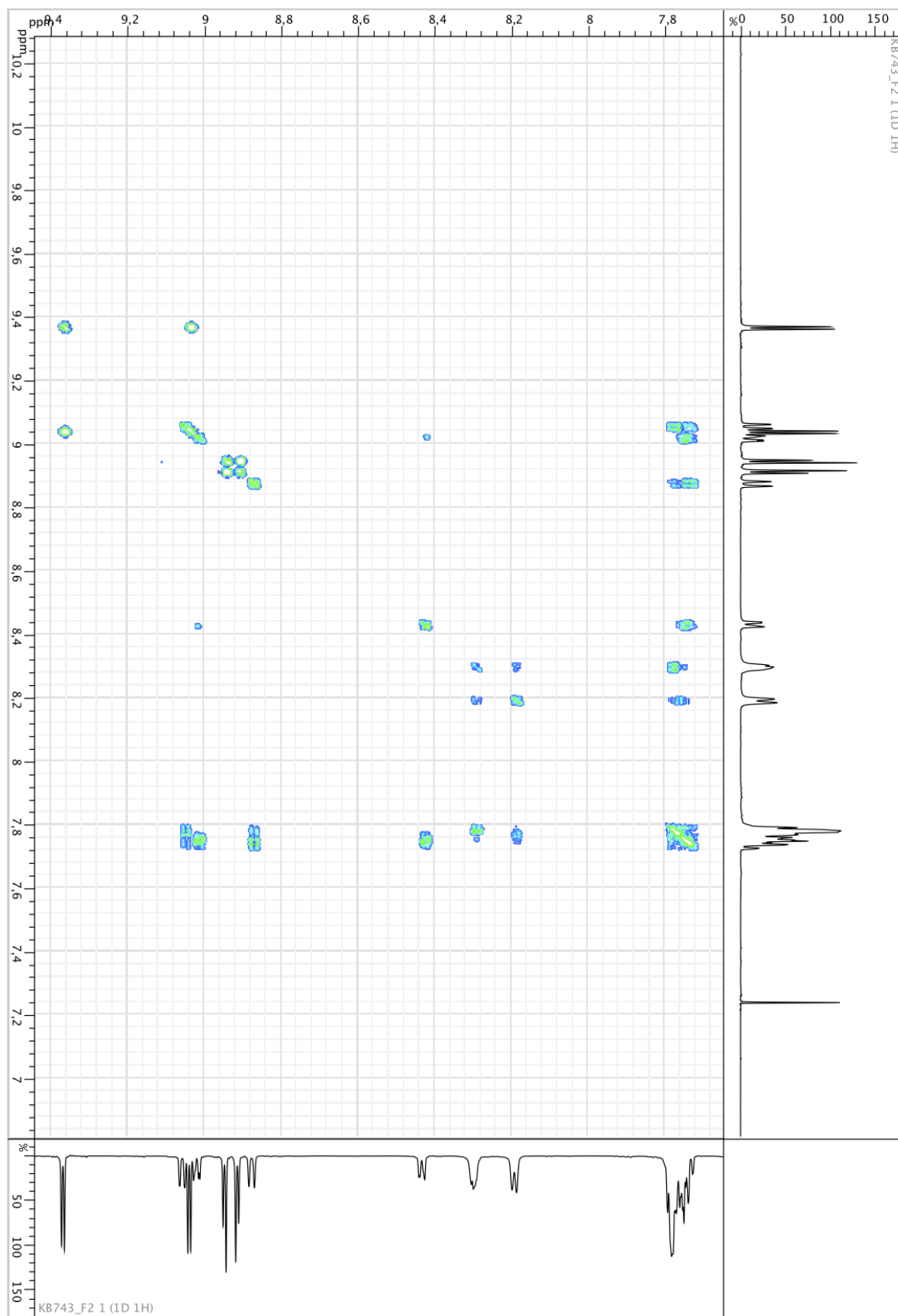


Fig. S10. ¹H-¹H COSY spectrum of **9H₂** in aromatic region (600 MHz, CDCl₃).

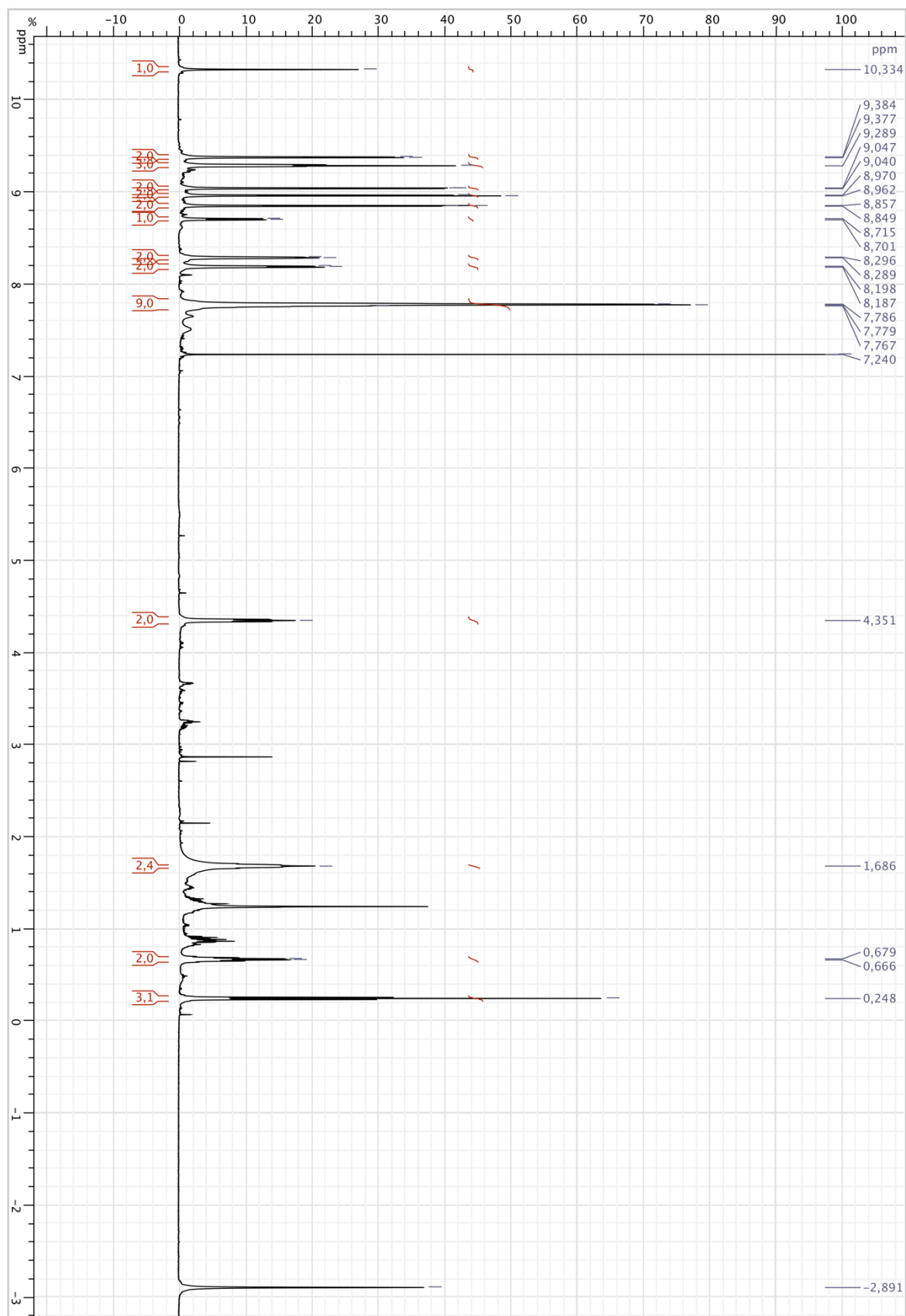


Fig. S11. ¹H-NMR spectrum of 10H₂ (600 MHz, CDCl₃).

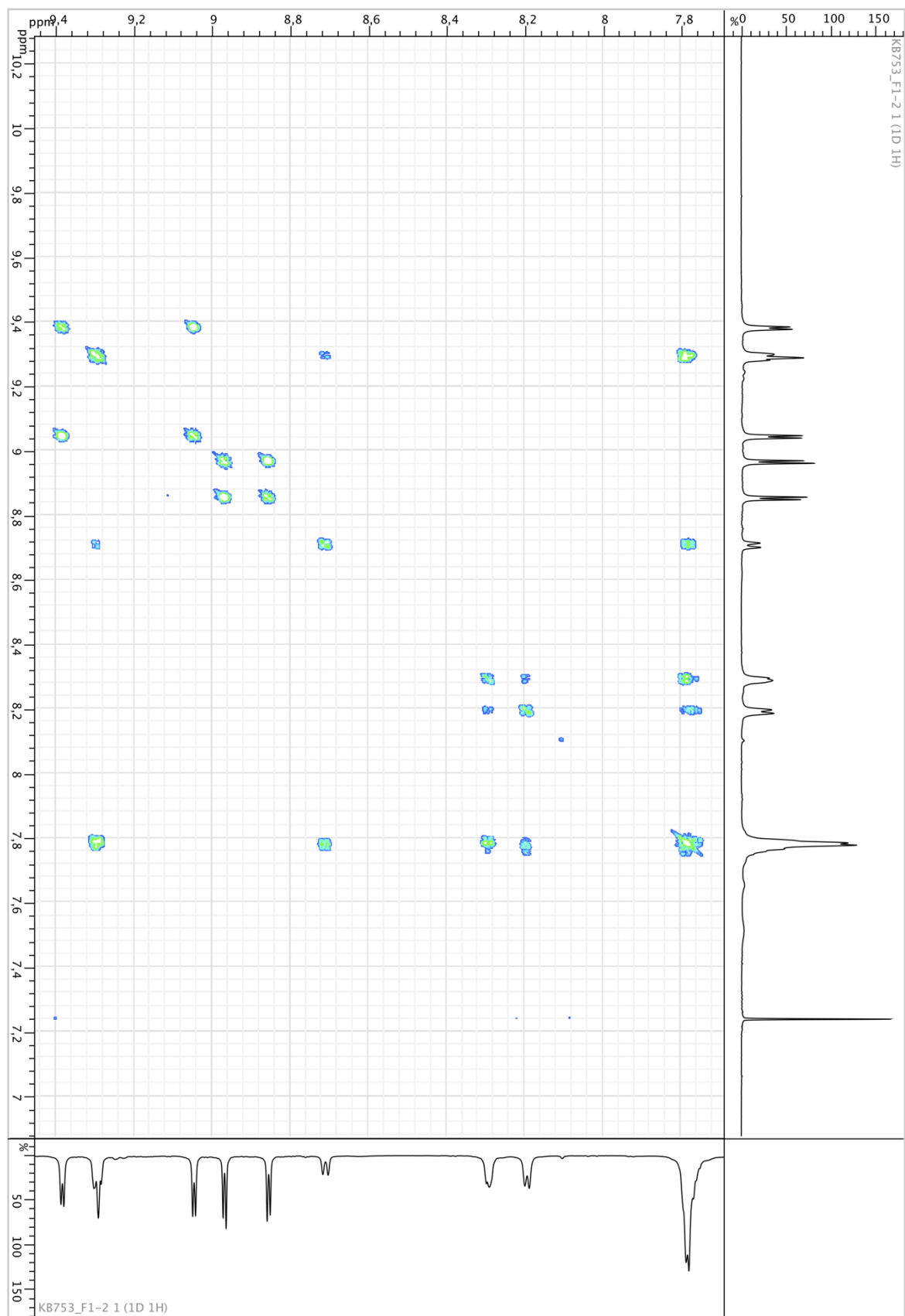


Fig. S12. ^1H - ^1H COSY spectrum of **10H₂** in aromatic region (600 MHz, CDCl_3).

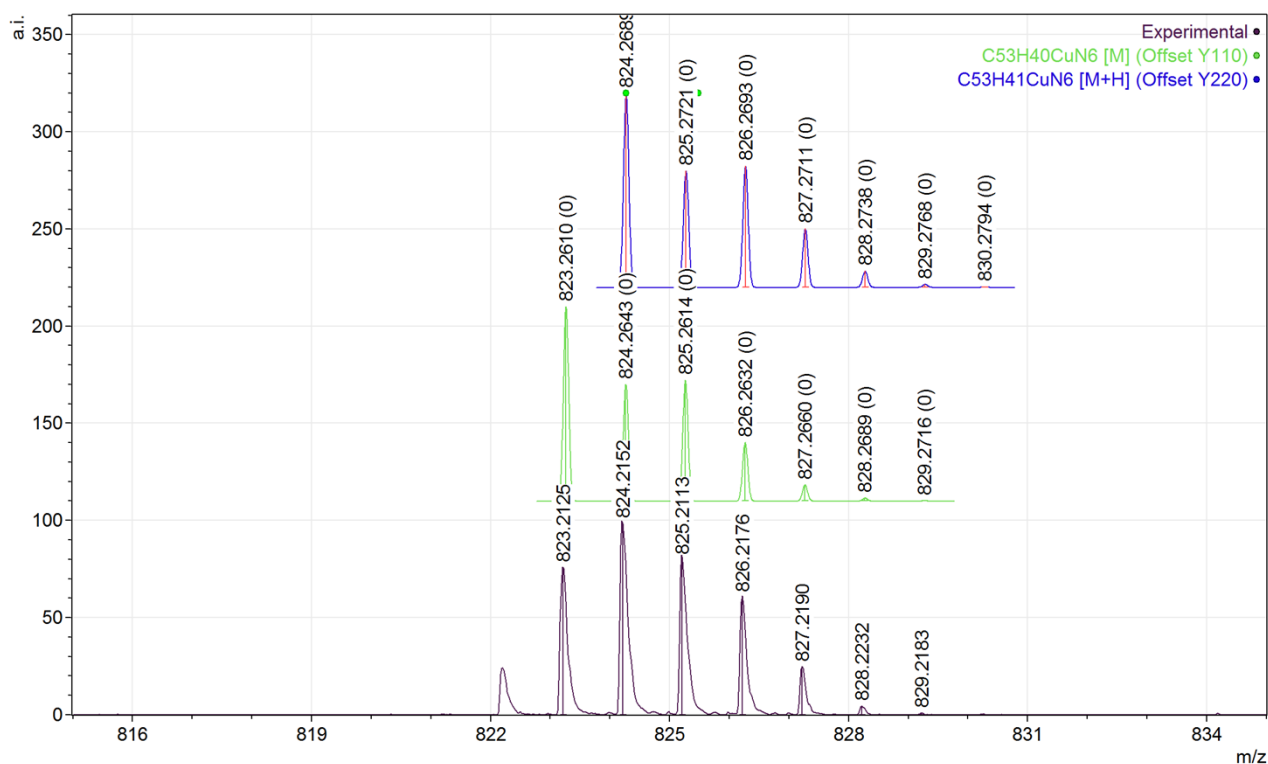


Fig. S13. MALDI-TOF MS spectrum of ${}^7\text{Cu}$.

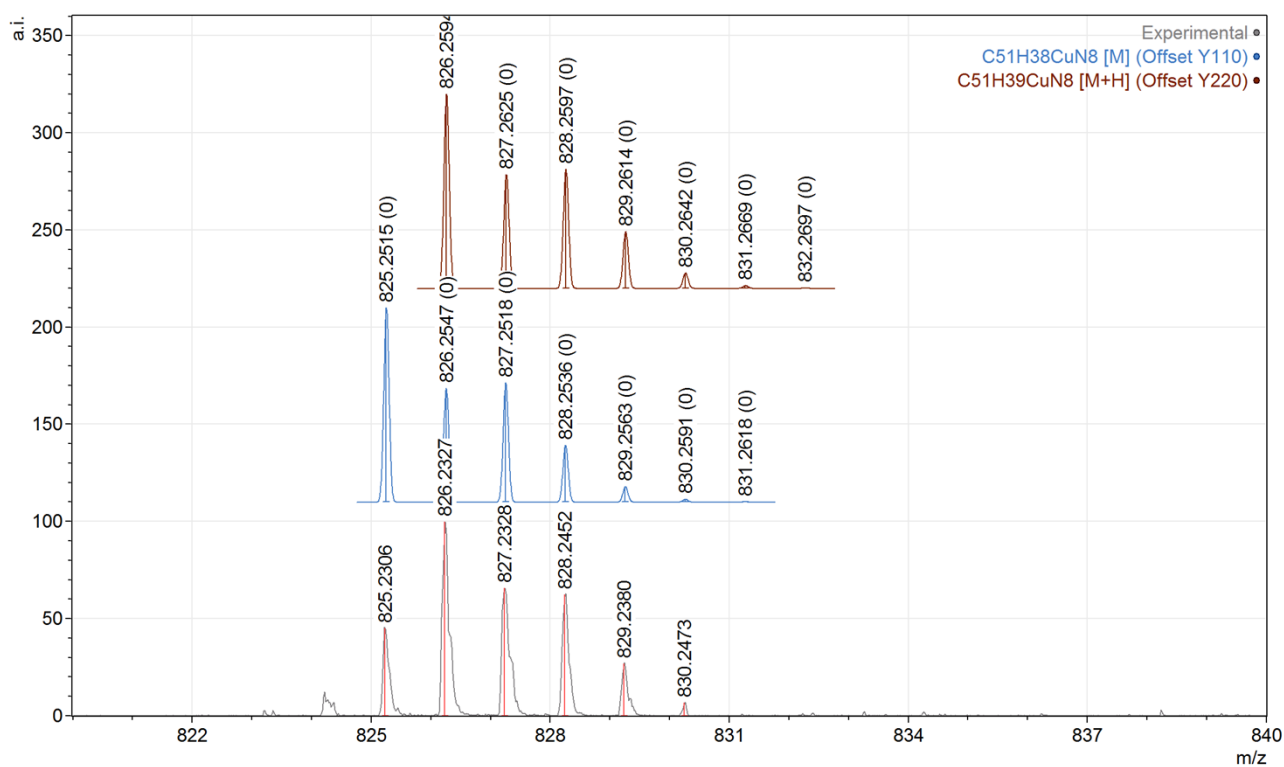


Fig. S14. MALDI-TOF MS spectrum of ${}^8\text{Cu}$.

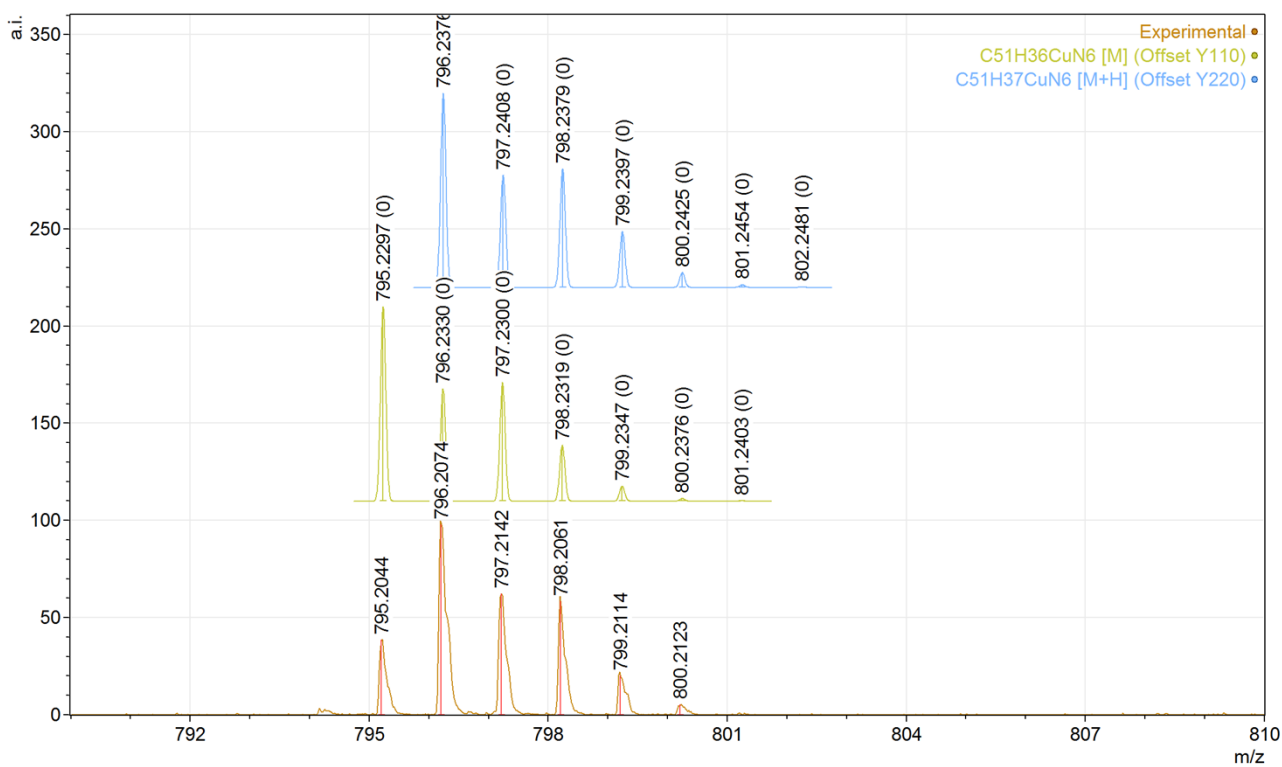


Fig. S15. MALDI-TOF MS spectrum of **9Cu**.

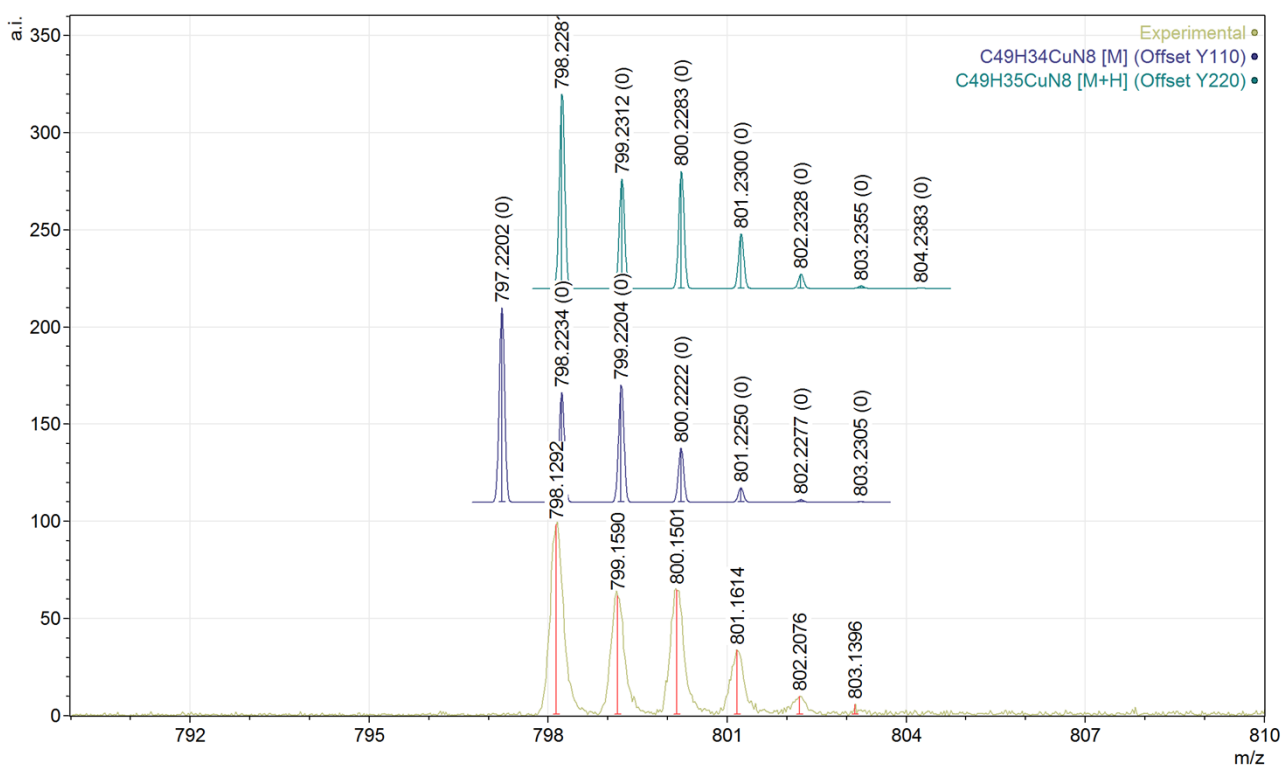


Fig. S16. MALDI-TOF MS spectrum of **10Cu**.

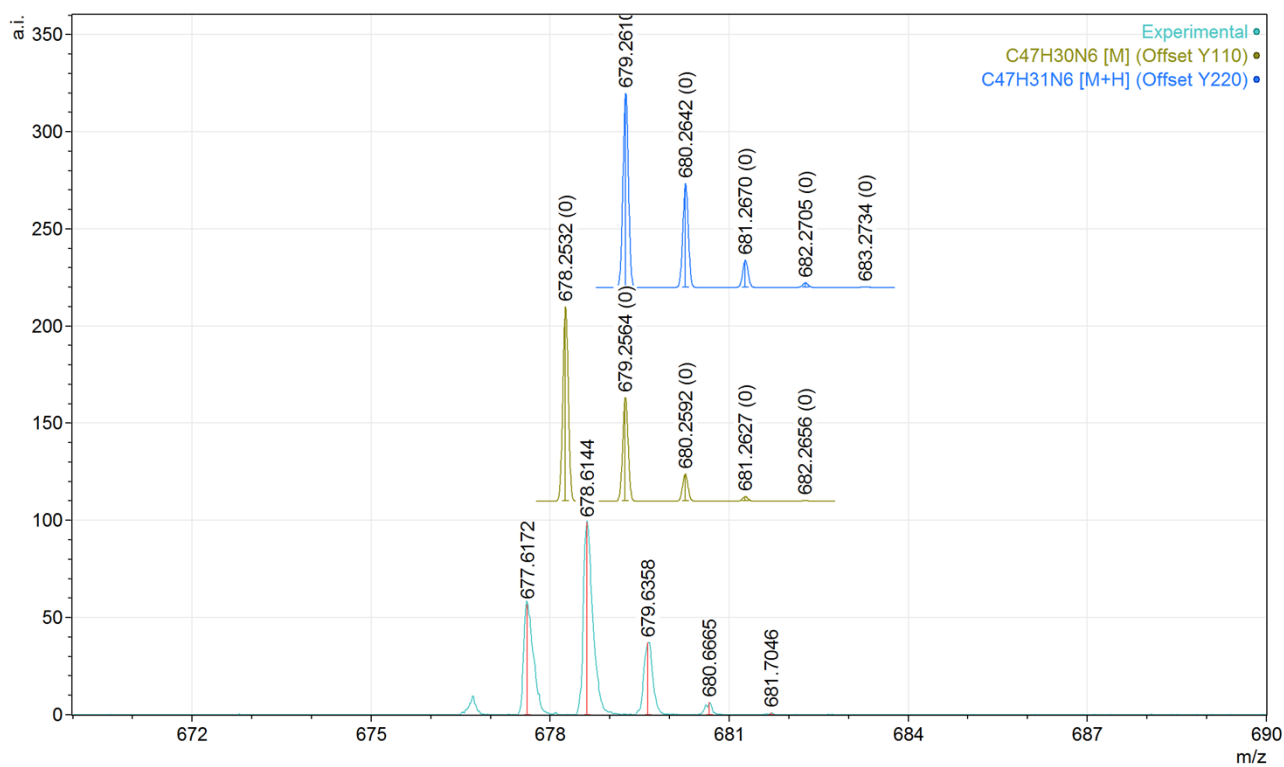


Fig. S 17. MALDI-TOF MS spectrum of 5H₂.

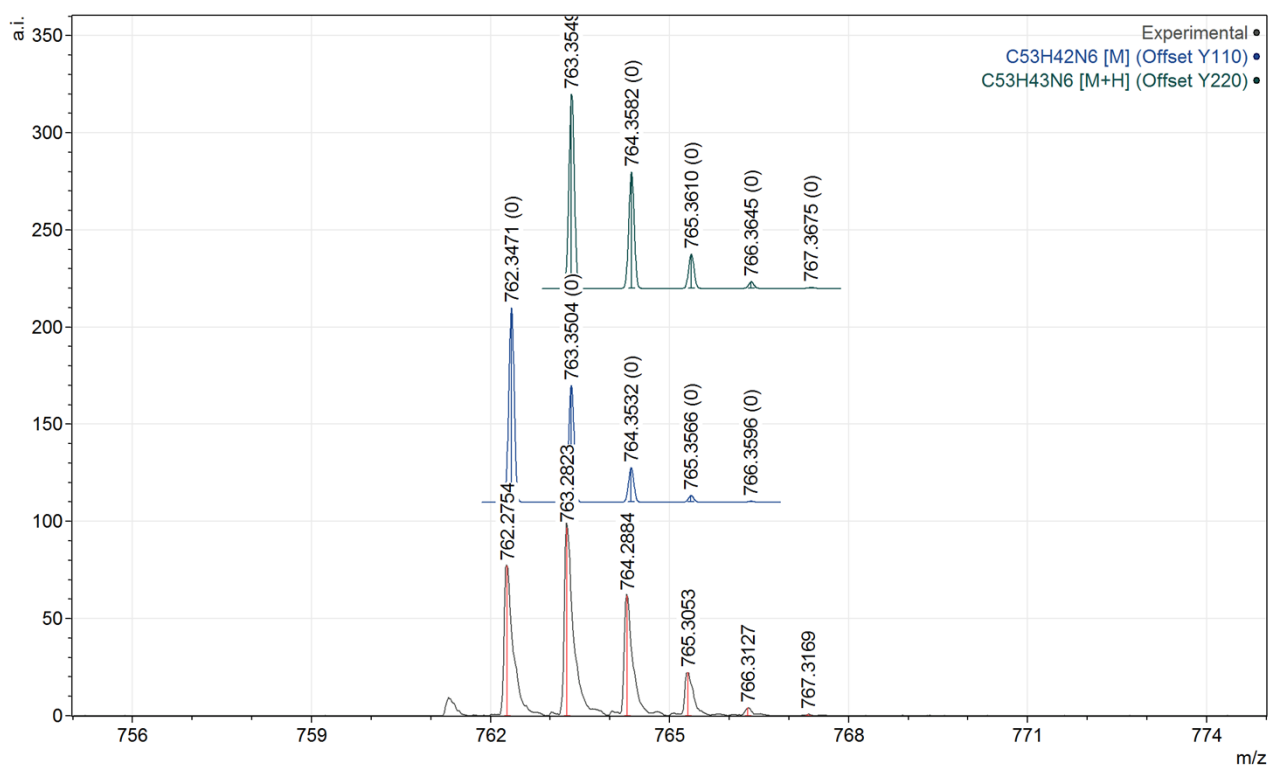


Fig. S 18. MALDI-TOF MS spectrum of 7H₂.

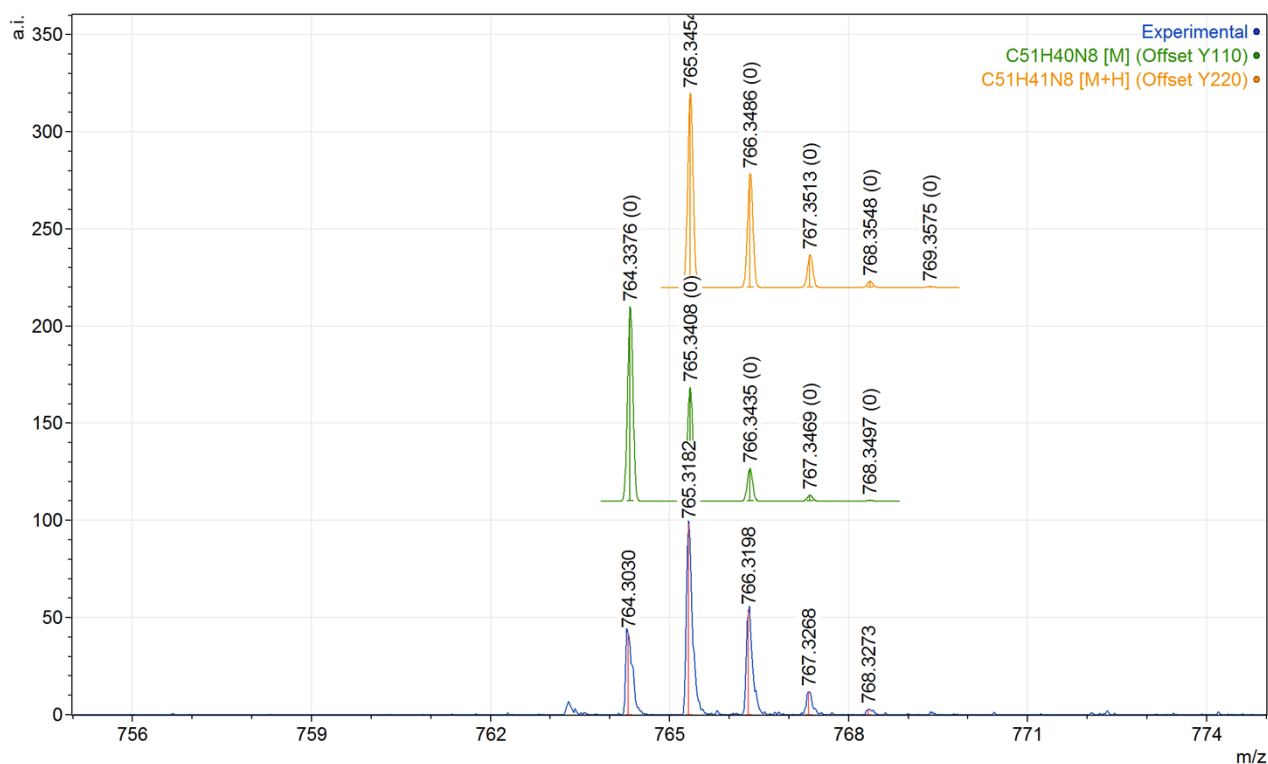


Fig. S19. MALDI-TOF MS spectrum of $8H_2$.

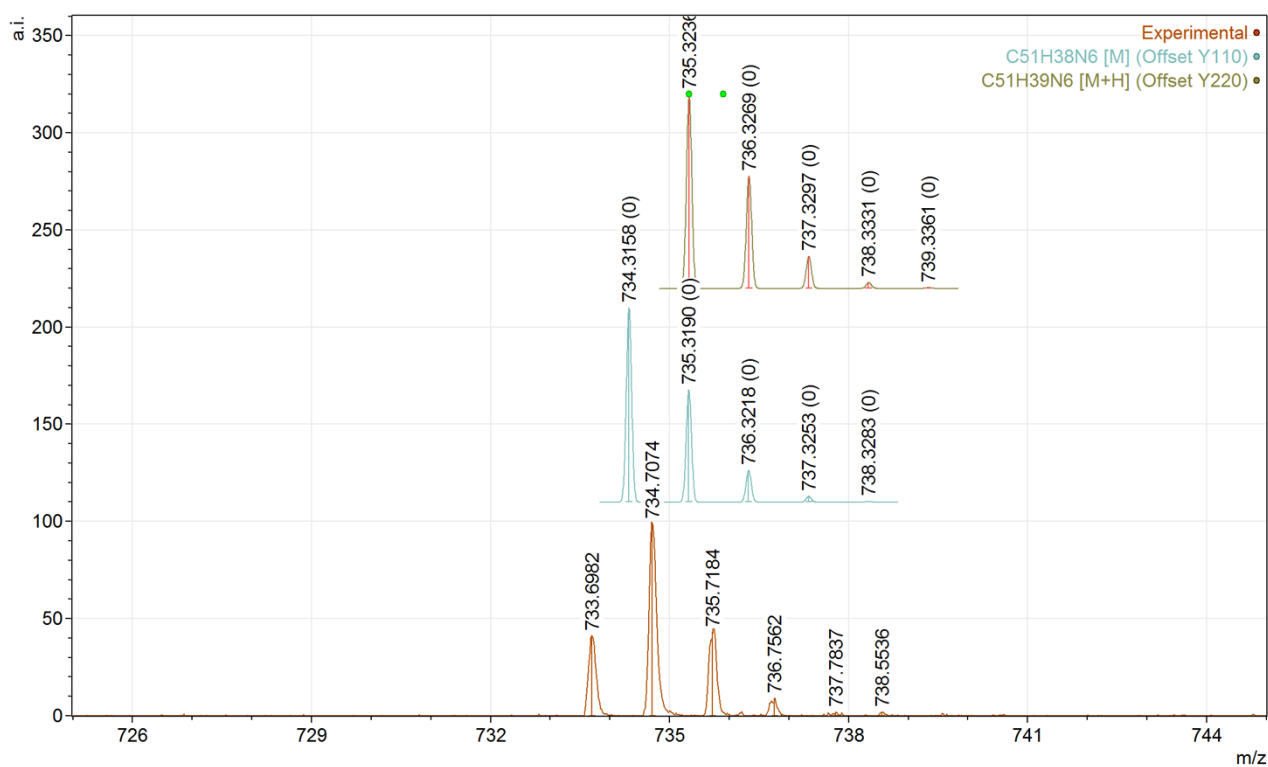


Fig. S 20. MALDI-TOF MS spectrum of $9H_2$.

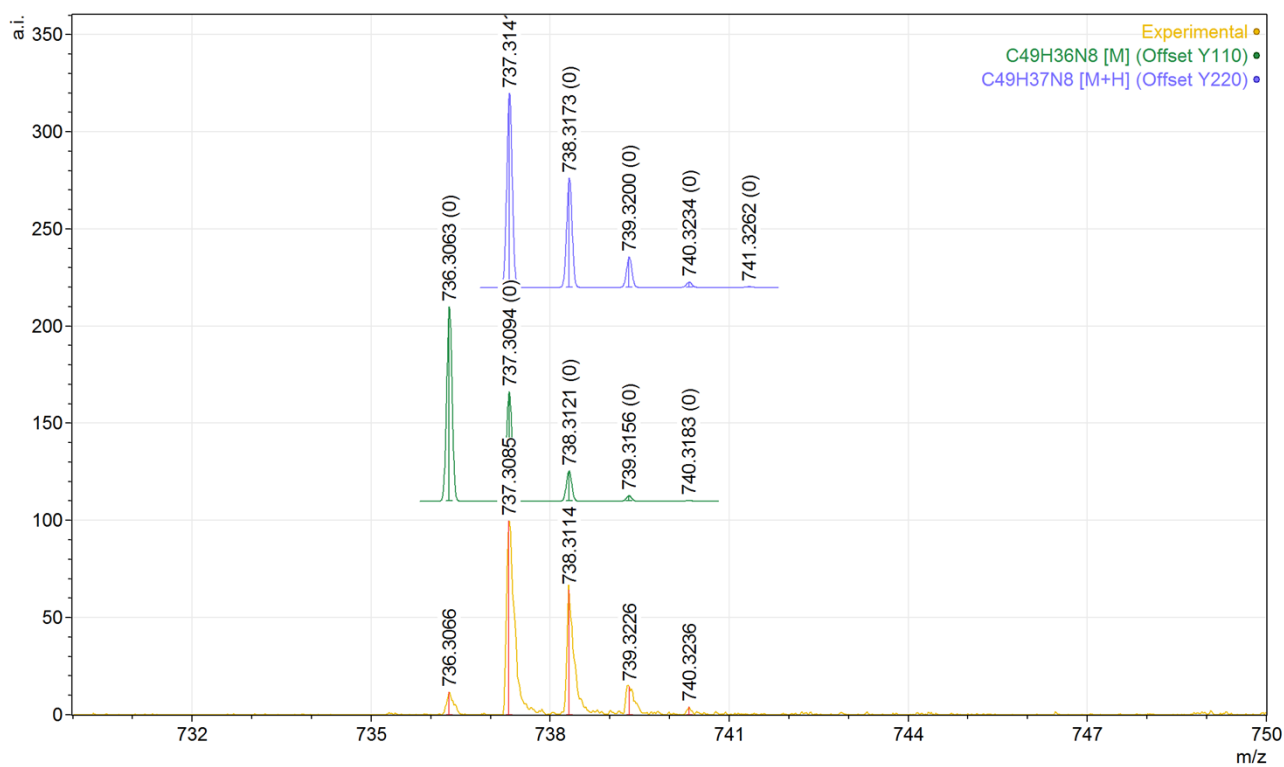


Fig. S21. MALDI-TOF MS spectrum of 10H₂.

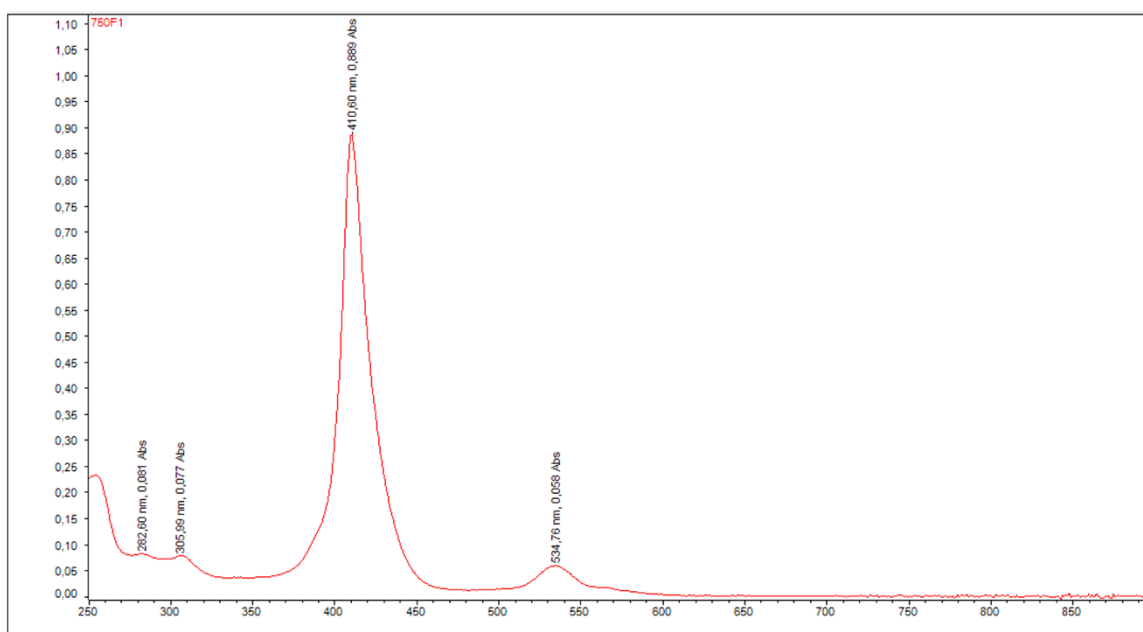


Fig. S22. UV-Vis spectrum of 7Cu (CHCl₃).

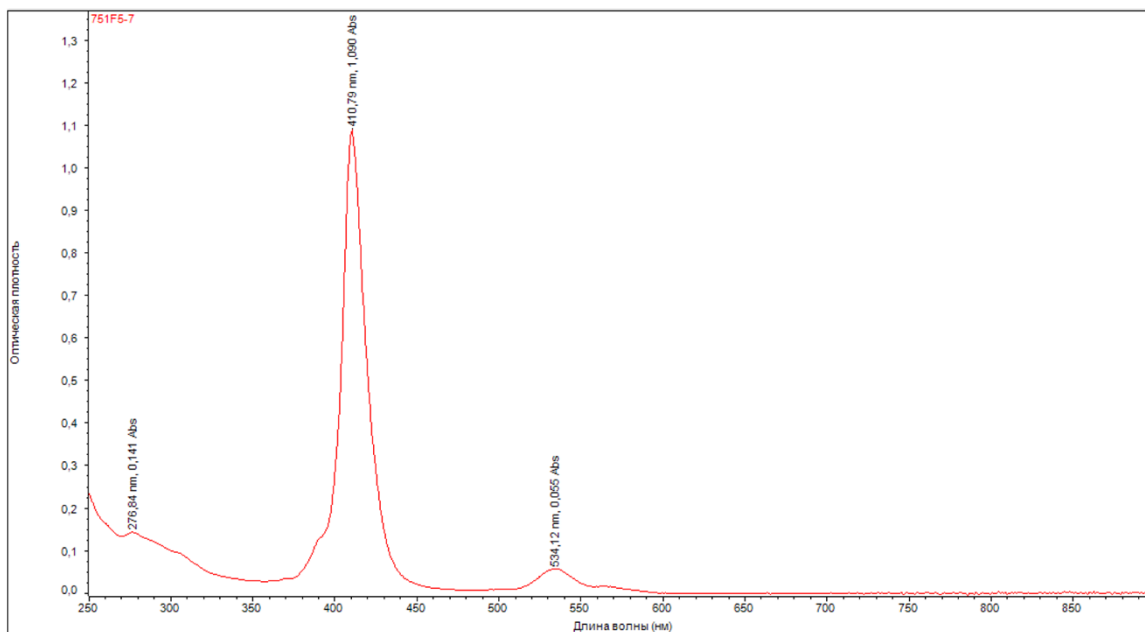


Fig. S23. UV-Vis spectrum of **8Cu** (CHCl_3).

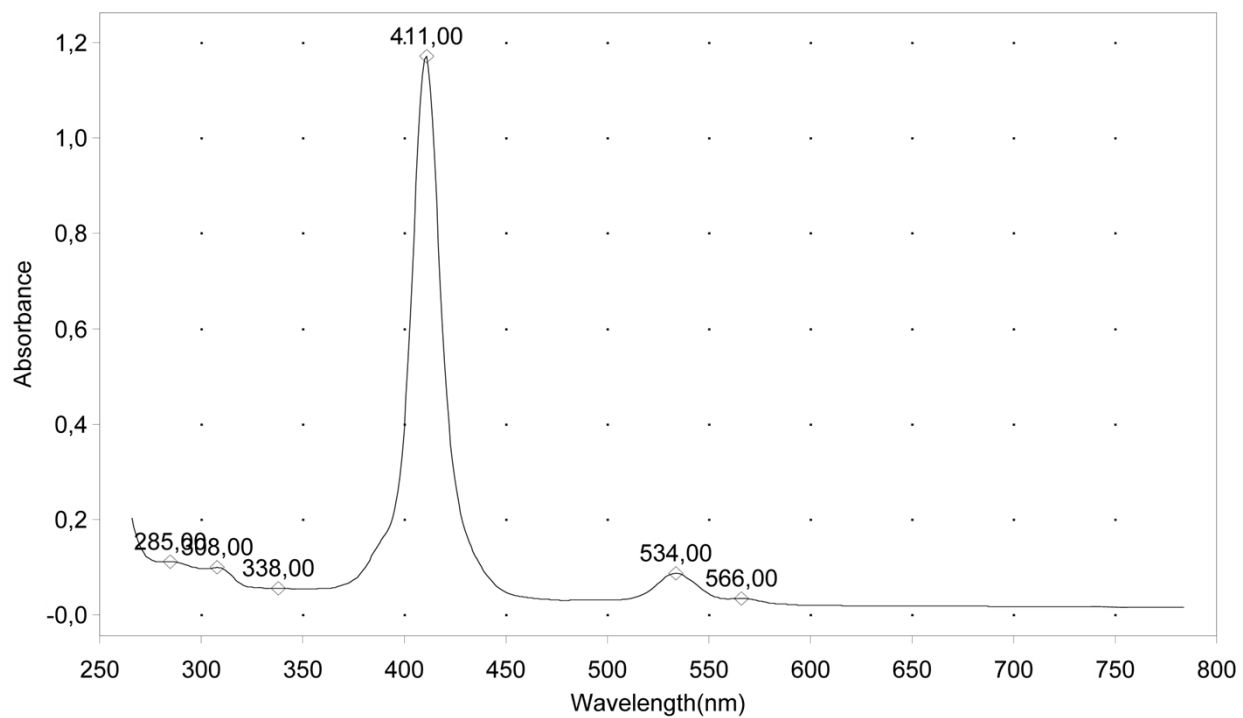


Fig. S24. UV-Vis spectrum of **9Cu** (CHCl_3).

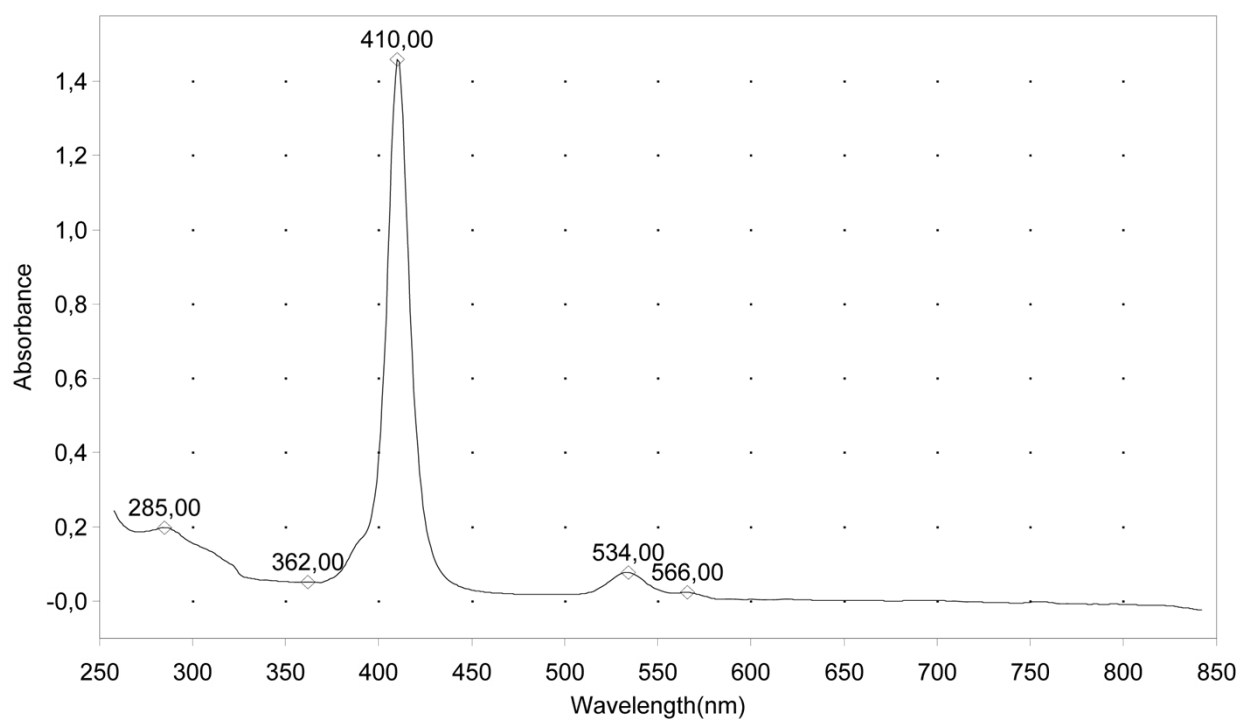


Fig. S25. UV-Vis spectrum of **10Cu** (CHCl₃).

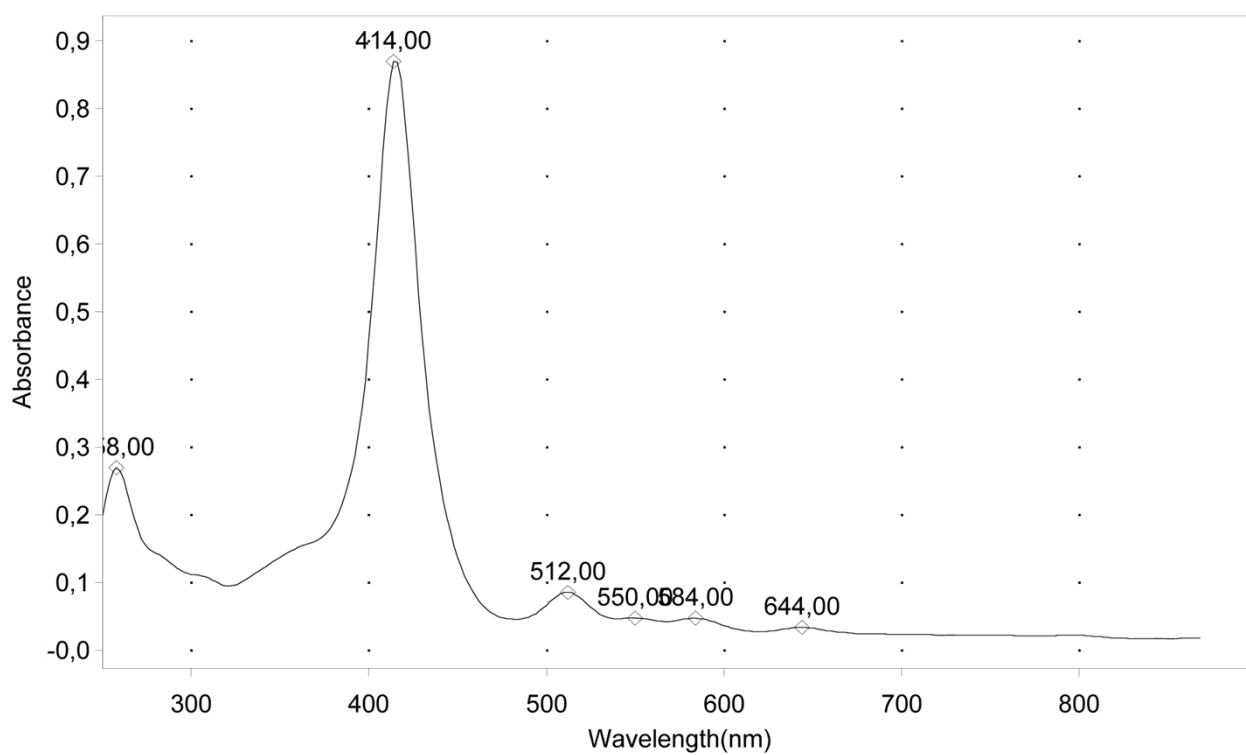


Fig. S26. UV-Vis spectrum of **5H₂** (CHCl₃).

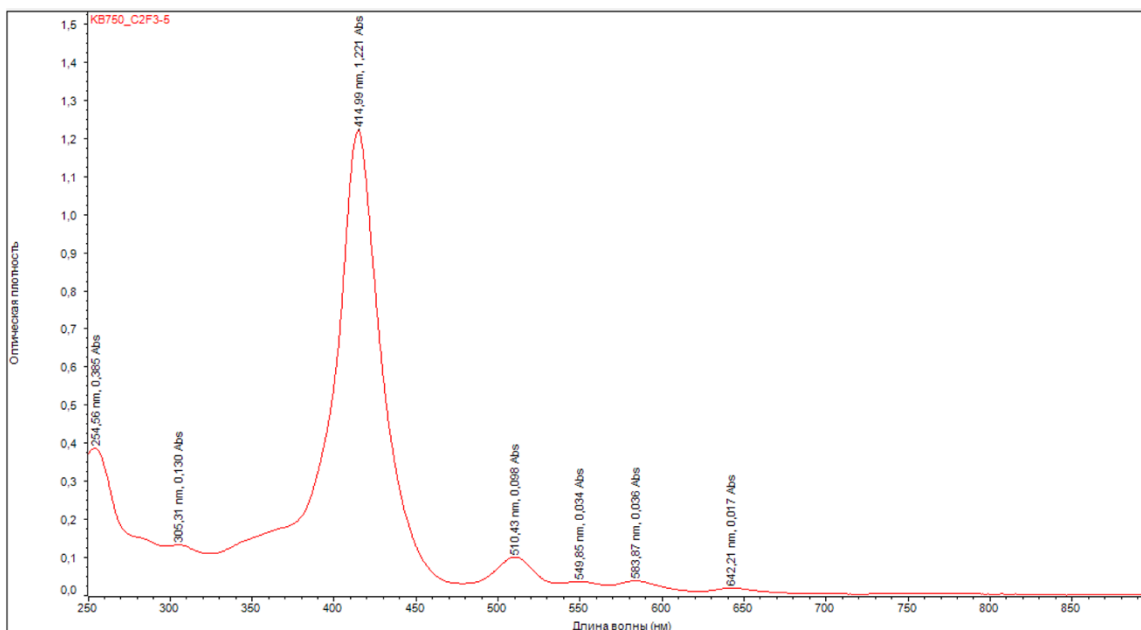


Fig. S27. UV-Vis spectrum of **7H₂** (CHCl₃).

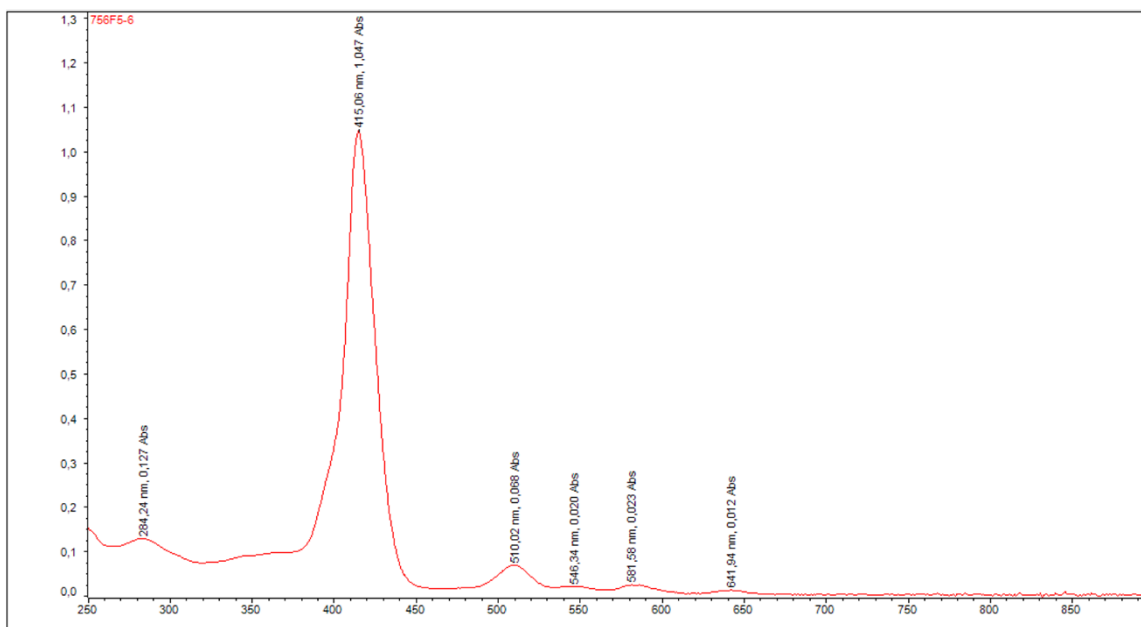


Fig. S28. UV-Vis spectrum of **8H₂** (CHCl₃).

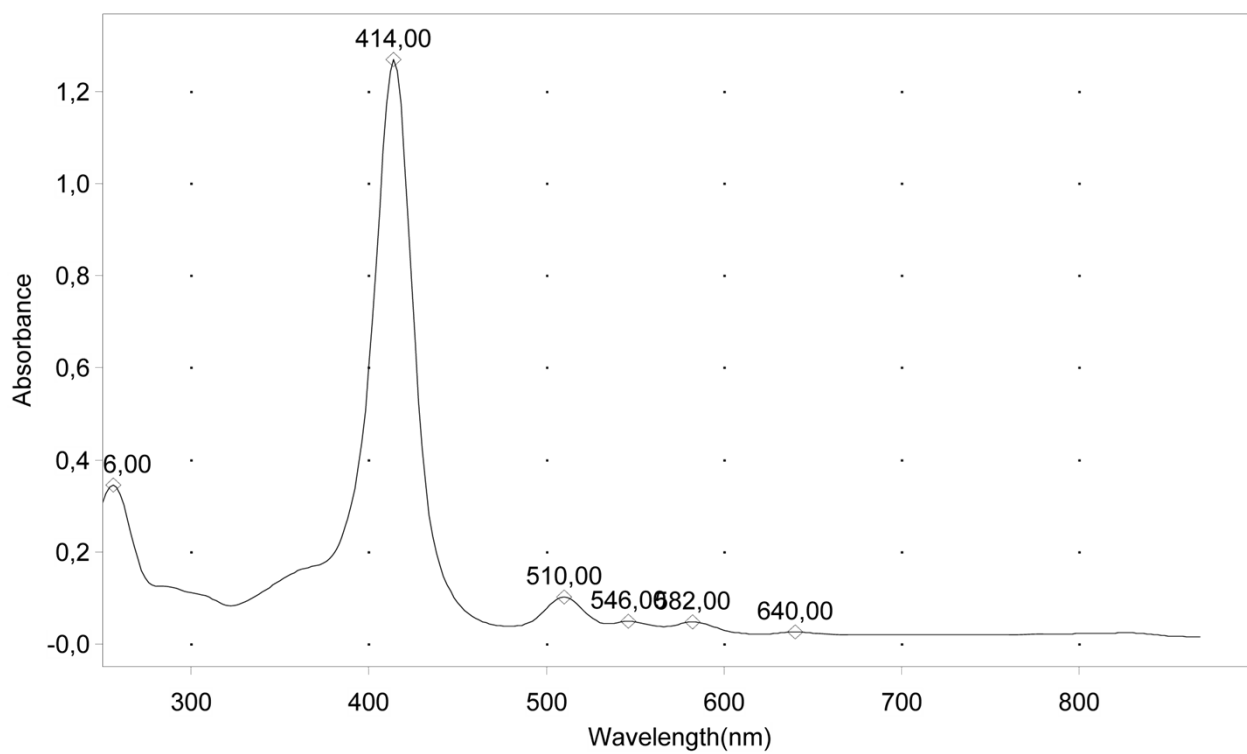


Fig. S29. UV-Vis spectrum of **9H₂** (CHCl₃).

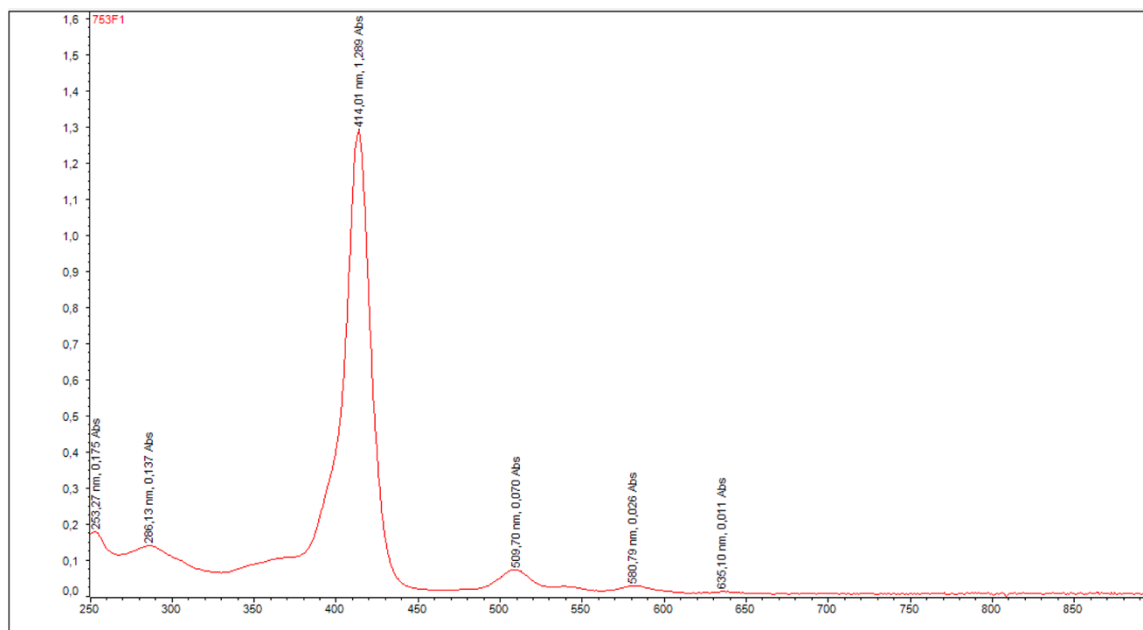


Fig. S30. UV-Vis spectrum of **10H₂** (CHCl₃).