Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Exocyclic π-System Extension of Phenanthriporphyrin Framework: Towards Azaaceneporphyrinoids

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Electronic Supplementary Information

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Experimental Section

Instrumentation

NMR spectroscopy: The ^{1}H NMR and ^{13}C NMR spectra were recorded on high-field spectrometers (^{1}H: 700, 600 and 500 MHz, ^{13}C: 151 and 176 MHz), equipped with a broadband inverse gradient probe head. The spectra were referenced to the residual solvent signal ($CDCl_3$: δ=7.24 ppm, CD_2Cl_2: δ=5.32 ppm). Two-dimensional NMR spectra were recorded with 2048 data points in the t_2 domain and up to 1024 points in the t_1 domain, with a 1 s recovery delay.

UV/Vis spectroscopy: UV-Vis absorption spectra were recorded on a Varian Carry-60 Bio spectrophotometer and a JASCO V-730 spectrophotometer. All characterizations were carried out at room temperature.

X‑ray diffraction data: Monocrystals suitable for the XRD experiments were obtained by slow evaporation of the respective solutions in dichloromethane (**3** – **5**) or chloroform (**6**). The X‑ray diffraction data for **3** and **4** were collected on an Xcalibur diffractometer with an Onyx and Atlas detector, respectively (CuKα radiation, λ= 1.54175 Å) and for **5** and **6** were collected on an Xcalibur diffractometer with a Sapphire2 and Ruby detector, respectively (MoKα radiation, λ=0.71073 Å). The data were collected at 100(2) K by using an Oxford Cryosystem device. Data reduction and analysis were carried out with the CrysAlis programs.[1] The space groups were determined, based on systematic absences and intensity statistics. The structures were solved by direct methods by using the SHELXS program and refined by using all F^2 data as implemented within the SHELXL program.[2]

In **3**, one of the phenyl group reveals two positional disorder. The anisotropic displacements of the disordered atoms of the phenyl group were restrained by SIMU and ISOR command. The occupancy factors of the disordered components were refined assuming that the sum of the disordered components is equal to 1. The occupancy factor of the major component of the disorder is equal to 0.56.

In **5** and **6**, solvent molecules (chloroform in **5** and dichloromethane in **6**) reveal two positional disorder. The occupancy factors of the disordered atoms were refined assuming that the sum of the disordered components is equal to 1. The occupancy factor of the major component of the disorder in **5** and **6** is equal to 0.53 and 0.80, respectively.

Crystal data for compound **3**: $C_{45}H_{28}N_4$, triclinic, $P\bar{1}$, a = 13.475(3) Å, b = 13.847(3) Å, c = 18.641(4) Å, α = 71.11(3) °, β = 70.17(4) °, γ = 89.04(3) °, V = 3078.8(15) Å^3, Z = 4, d_c = 1.348 g/cm^3, T = 100(2) K, R = 0.079, wR = 0.212 [4987 reflections with I > 2σ(I)] for 929 variables.

Crystal data for compound **4**: $C_{47}H_{26}N_6 \cdot CH_2Cl_2$, monoclinic, $P2_1/c$, a = 6.880(2) Å, b = 25.608(3) Å, c = 20.540(3) Å, β = 91.74(3) °, V = 3617.1(13) Å^3, Z = 4, d_c = 1.395 g/cm^3, T = 100(2) K, R = 0.110, wR = 0.290 [4447 reflections with I > 2σ(I)] for 509 variables.

Crystal data for compound **5**: $C_{49}H_{30}N_4 \cdot CHCl_3$, triclinic, $P\bar{1}$, a = 9.756(2) Å, b = 13.125(3) Å, c = 14.877(3) Å, α = 96.16(3) °, β = 94.46(3) °, γ = 101.42(2) °, V = 1846.9(7) Å^3, Z = 2, d_c = 1.428 g/cm^3, T = 100(2) K, R = 0.052, wR = 0.104 [4333 reflections with I > 2σ(I)] for 545 variables.

Crystal data for compound **6**: $C_{48}H_{29}N_5 \cdot 0.898CH_2Cl_2$, triclinic, $P\bar{1}$, a = 9.955(2) Å, b = 12.581(3) Å, c = 15.888(3) Å, α = 107.70(2) °, β = 98.52(2) °, γ = 93.85(2) °, V = 1861.4(7) Å^3, Z = 2, d_c = 1.342 g/cm^3, T = 100(2) K, R = 0.067, wR = 0.152 [6658 reflections with I > 2σ(I)] for 533 variables.

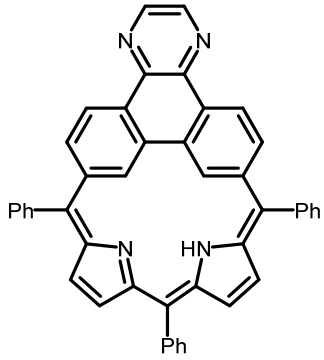
DFT studies: Geometry optimizations were carried out within unconstrained C_1 symmetry in vacuo using Gaussian software.[3] Starting coordinates were derived from preoptimized models taking into account all imposed geometrical restrictions. Harmonic frequencies were calculated using analytical second derivatives as a verification of local minimum achievement, with no imaginary frequencies observed. Optimizations were performed at B3LYP/6-31G(d,p) level of theory.[4] NICS values (determined in the central point between six meso C atoms) and NMR shifts were calculated for optimized models using the GIAO method with TMS shieldings as a reference for NMR.[5] Good qualitative agreement for each set of experimental and calculated chemical shifts has been demonstrated. Electronic spectra were obtained from TD-DFT calculations with number of states equal to 60. All properties were calculated for optimized models at B3LYP/6-31G(d,p)[6] level of theory.

Synthesis

$CDCl_3$ was prepared directly before use by running through a basic alumina column. Reagents not listed here were used as received.

Characterization

Compound 3



3

In a dry 25 mL round-bottom flask equipped with a magnetic stirrer 5,6-dioxophenanthriporphyrin **2** (10 mg, 0.017 mmol) was dissolved in a freshly distilled pyrridine (5 mL). Anhydrous 1,2-diaminoethane (5.6 µL, 0.083 mmol) was added to the solution in the flask which was then refluxed for 1 hour under nitrogen atmosphere. After this time the solvent was removed on a rotary evaporator, and the solid residue was subjected to column chromatography on basic alumina (4 g of water per 100 g of active alumina) with dichloromethane as the eluent. The crude product eluted as the first light-green fraction which, after washing with methanol yielded **3** as a light-green solid. Yield: 3.5 mg (34%).

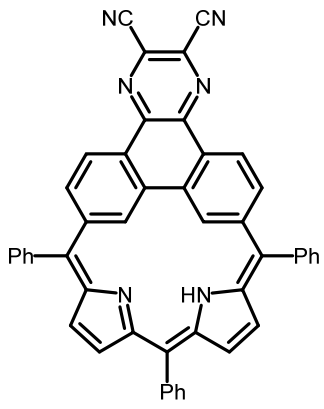
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 14.15 (b, 1H, 26-NH), 13.61 (s, 2H, 22,25-H), 8.34 (s, 2H, 5',6'-H), 8.12 (d, 2H, ^{3}J = 8.6 Hz, 3,8-H), 7.41 – 7.35 (m, 6H, *meso*-Ph), 7.33 – 7.29 (m, 2H, *meso*-Ph), 7.29 – 7.26 (m, 5H, *meso*-Ph), 7.19 – 7.17 (m, 2H, *meso*-Ph), 6.59 (dd, 2H, ^{3}J = 8.6 Hz, ^{4}J = 1.7 Hz, 2,9-H), 6.14 (d, 2H, ^{3}J = 5.2 Hz, 13,19/14,18-H), 5.82 (d, 2H, ^{3}J = 5.2 Hz, 13,19/14,18-H).

^{13}C NMR (176 MHz, CDCl3, 300 K): δ 145.1, 143.9, 140.3, 139.3, 138.5, 134.6 (b), 134.0, 131.2, 131.0, 129.1, 128.6, 128.3, 128.2, 128.0, 127.2, 125.1, 111.4.

HR-MS (ESI+, TOF) *m/z*: $[M+H]^+$ 625.2400, calcd. for $C_{45}H_{29}N_4^+$ 625.2387.

UV-Vis (CH_2Cl_2, 298 K): λ_{max} (log ε) 359 (4.7), 476 (3.9), 726 (3.9), 785 (3.8).

Compound 4



4

In a dry 25 mL round-bottom flask equipped with a magnetic stirrer 5,6-dioxophenanthriporphyrin **2** (10 mg, 0.017 mmol) and diaminomaleonitrile (9.0 mg, 0.083 mmol, 5 equiv.) were dissolved in a freshly distilled pyrridine (5 mL). The solution was refluxed for 1 hour under nitrogen atmosphere. After this time the solvent was removed on a rotary evaporator, and the solid residue was subjected to column chromatography on basic alumina (4 g of water per 100 g of active alumina) with dichloromethane as the eluent. The crude product eluted as the first emerald-green fraction which, after washing with methanol yielded **3** as a emerald-green solid. Yield: 7.7 mg (69%).

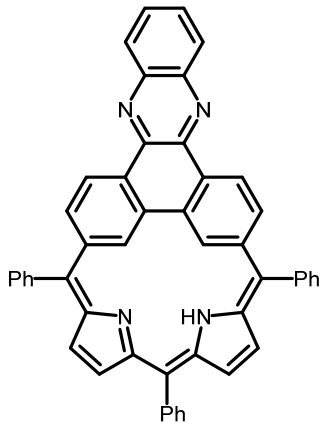
^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 13.25 (b, 2H, 22,25-H), 8.01 (d, 2H, ^3J = 8.7 Hz, 3,8-H), 7.45 – 7.39 (m, 6H, *meso*-Ph), 7.35 – 7.28 (m, 3H, *meso*-Ph), 7.28 – 7.24 (m, 4H, *meso*-Ph), 7.20 – 7.18 (m, 2H, *meso*-Ph), 6.67 (dd, 2H, ^3J = 8.7 Hz, ^4J = 1.6 Hz, 2,9-H), 6.19 (d, 2H, ^3J = 5.2 Hz, 13,19/14,18-H), 5.91 (d, 2H, ^3J = 5.2 Hz, 13,19/14,18-H).

^{13}C NMR (176 MHz, $CDCl_3$, 300 K): δ 147.5, 143.1, 138.6, 137.9, 135.6, 131.2, 131.1, 130.8, 129.9, 129.4, 128.45, 128.41, 128.3, 127.6, 126.3, 125.9, 115.8, 113.6.

HR-MS (ESI+, TOF) *m/z*: $[M+H]^+$ 675.2282, calcd. for $C_{47}H_{27}N_6^+$ 675.2292.

UV-Vis (CH_2Cl_2, 298 K): λ_{max} (log ε) 379 (4.8), 425 (4.4), 445 (4.3), 597 (4.2), 758 (3.8), sh. ca. 840.

Compound 5



5

In a dry 25 mL round-bottom flask equipped with a magnetic stirrer 5,6-dioxophenanthriporphyrin **2** (10 mg, 0.017 mmol) and 1,2-diaminobenzene (9.0 mg, 0.083 mmol, 5 equiv.) were dissolved in a freshly distilled pyrridine (5 mL). The solution was refluxed for 1 hour under nitrogen atmosphere. After this time the solvent was removed on a rotary evaporator, and the solid residue was subjected to column chromatography on basic alumina (4 g of water per 100 g of active alumina) with dichloromethane as the eluent. The crude product eluted as the first green fraction which, after washing with methanol yielded **3** as a green solid. Yield: 3.4 mg (30%).

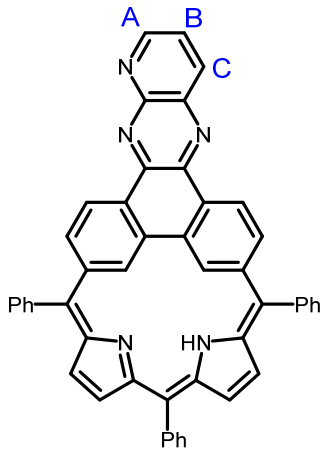
^{1}H NMR (600 MHz, $CDCl_3$, 300 K): δ 12.01 (b, 2H, 22,25-H), 8.51 (d, 2H, ^3J = 8.6 Hz, 3,8-H), 7.95 (m, 2H, 4',7'/23',24'-H), 7.60 (m, 2H, 4',7'/23',24'-H), 7.46 – 7.41 (m, 6H, *meso*-Ph), 7.39 – 7.34 (m, 6H, *meso*-Ph), 7.32 (m (t), 1H, *meso*-*p*-Ph), 7.28 (m (d), 2H, *meso*-*o*-Ph), 6.87 (dd, 2H, ^3J = 8.7 Hz, ^4J = 1.2 Hz, 2,9-H), 6.41 (d, 2H, ^3J = 5.2 Hz, 13,19/14,18-H), 6.10 (d, 2H, ^3J = 5.2 Hz, 13,19/14,18-H).

^{13}C NMR (151 MHz, $CDCl_3$, 300 K): δ 145.6, 143.0, 140.6, 139.6, 138.8, 134.8 (b), 133.7, 131.5, 131.3, 129.8, 129.4, 129.2, 128.8, 128.2, 128.1, 128.0, 127.3, 125.8, 111.6.

HR-MS (ESI+, TOF) *m/z*: $[M+H]^+$ 675.2596, calcd. for $C_{49}H_{31}N_4^+$ 675.2543.

UV-Vis (CH_2Cl_2, 298 K): λ_{max} (log ε) 363 (4.7), 374 (4.7), 394 (4.7), 417 (4.6), 438 (4.5), 527 (4.1), 701 (4.1), 760 (4.0).

Compound 6



6

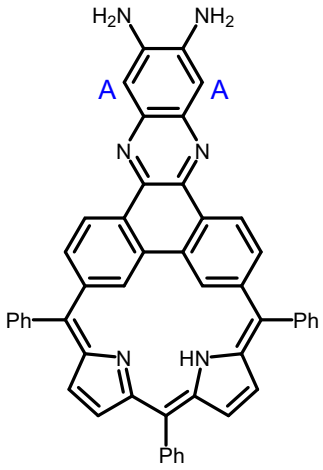
In a dry 25 mL round-bottom flask equipped with a magnetic stirrer 5,6-dioxophenanthriporphyrin **2** (10 mg, 0.017 mmol) and 2,3-diaminopyridine (9.1 mg, 0.083 mmol, 5 equiv.) were dissolved in a freshly distilled pyrridine (5 mL). The solution was refluxed for 1 hour under nitrogen atmosphere. After this time the solvent was removed on a rotary evaporator, and the solid residue was subjected to column chromatography on basic alumina (4 g of water per 100 g of active alumina) with dichloromethane as the eluent. The crude product eluted as the first blue fraction which, after washing with methanol yielded **3** as a blue solid. Yield: 9.6 mg (86%).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 12.41 (b, 1H, 26-NH), 11.89 (s, 1H, 22,25-H), 11.85 (s, 1H, 22,25-H), 8.99 (dd, 1H, ^{3}J = 4.1 Hz, ^{4}J = 1.9 Hz, A/C-H), 8.66 (d, 1H, ^{3}J = 8.6 Hz, 3/8-H), 8.47 (d, 2H, ^{3}J = 8.6 Hz, 3/8-H), 8.28 (dd, 1H, ^{3}J = 8.4 Hz, ^{4}J = 1.9 Hz, A/C-H) 7.52 (dd, 1H, ^{3}J = 8.4 Hz, ^{4}J = 4.0 Hz, B-H) 7.48 – 7.42 (m, 6H, *meso*-Ph), 7.38 – 7.31 (m, 7H, *meso*-Ph), 7.30 – 7.27 (m, 2H, 16-*o*-Ph), 6.92 – 6.89 (2 dd, 2H, ^{3}J = 8.6 Hz, ^{4}J = 1.7 Hz, 2/9-H), 6.43 – 6.41 (2 d, 2H, ^{3}J = 5.2 Hz, 13,19-H), 6.13 (2 d, 2H, ^{3}J = 5.2 Hz, 14,18-H). **^{13}C NMR** (151 MHz, $CDCl_3$, 300 K): δ 154.2, 151.3, 148.6, 147.0, 141.4, 141.2, 139.5, 139.4, 138.7, 138.4, 138.2, 134.9 (b), 134.1, 133.9, 131.6, 131.32, 131.31, 129.5, 129.0, 128.9, 128.5, 128.4, 128.24, 128.23, 128.2, 128.1, 128.0, 127.4, 126.8, 126.0, 124.9, 112.0.

HR-MS (ESI+, TOF) *m/z*: $[M+H]^+$ 676.2501, calcd. for $C_{48}H_{30}N_5^+$ 676.2496.

UV-Vis (CH_2Cl_2, 298 K): λ_{max} (log ε) 370 (4.7), 420 (4.3), 440 (4.2), 581 (4.1), 698 (4.0), 760 (3.9).

Compound 7



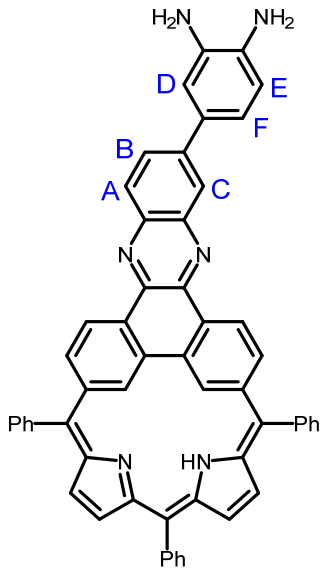
7

In a dry 25 mL round-bottom flask equipped with a magnetic stirrer 5,6-dioxophenanthriporphyrin **2** (20 mg, 0.034 mmol) and 1,2,4,5-tetraaminebenzene tetrahydrochloride (186 mg, 0.66 mmol, 20 equiv.) were dissolved in a freshly distilled pyrridine (10 mL). The solution was refluxed for 48 hours under nitrogen atmosphere. After this time the solvent was removed on a rotary evaporator, and the solid residue was subjected to column chromatography on basic alumina (4 g of water per 100 g of active alumina) with dichloromethane as the eluent. Once the first fraction was eluted the solvent system was changed for 1% MeOH/DCM and the crude product was collected as the second, orange band. The crude product was recrystallized from dichloromethane/*n*-hexane yielding **7** as an orange solid. Yield: 7 mg (29%).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 12.65 (s, 2H, 22,25-H), 8.33 (d, 2H, ^{3}J = 8.6 Hz, 3,8-H), 7.43 – 7.37 (m, 7H, *meso*-Ph), 7.08 (s, 2H, A-H) 6.72 (dd, 2H, ^{3}J = 8.6 Hz, ^{4}J = 1.7 Hz, 2,9-H), 6.28 (d, 2H, ^{3}J = 5.2 Hz, 13,19/14,18-H), 5.97 (d, 2H, ^{3}J = 5.2 Hz, 13,19/14,18-H), 3.93 (s, 4H, NH_2).

^{13}C NMR (176 MHz, $CDCl_3$, 300 K): δ 142.6, 140.6, 140.5, 139.7, 139.5, 138.8, 134.7, 133.2, 131.4, 131.2, 130.1, 129.2, 128.5, 128.2, 128.0, 127.8, 127.2, 125.1, 111.2, 110.3. **HR-MS** (ESI+, TOF) *m/z*: $[M+H]^+$ 705.2757, calcd. for $C_{49}H_{33}N_6^+$ 705.2761. **UV-Vis** (CH_2Cl_2, 298 K): λ_{max} (log ε) 359 (4.1), 447 (4.4), 750 (3.4).

Compound 8



8

In a dry 25 mL round-bottom flask equipped with a magnetic stirrer 5,6-dioxophenanthriporphyrin **2** (10 mg, 0.017 mmol) and 3,3'-diaminobenzidine (17.8 mg, 0.083 mmol, 5 equiv.) were dissolved in a freshly distilled pyrridine (5 mL). The solution was refluxed for 1 hour under nitrogen atmosphere. After this time the solvent was removed on a rotary evaporator, and the solid residue was subjected to column chromatography on basic alumina (4 g of water per 100 g of active alumina) with dichloromethane/*n*-hexane (4/1, v/v) as the eluent. Once the first fraction was eluted the solvent system was changed for 1% MeOH/DCM and the crude product

was collected as the second, orange band. The crude product was washed with methanol yielding **7** as an orange solid. Yield: 4.1 mg (32%).

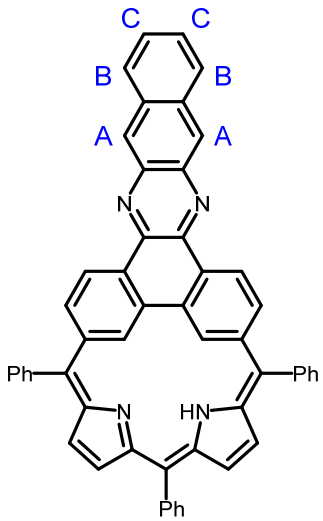
^{1}H NMR (500 MHz, $CDCl_3$, 300 K) δ 12.12 (b, 2H, 22,25-H), 8.51 – 8.48 (m (2d), 2H, 3,8-H), 8.06 (d, 1H, ^4J = 1.7 Hz, C-H), 7.94 (d, 1H, ^3J = 8.7 Hz, A-H), 7.84 (dd, 1H, ^3J = 8.7 Hz, ^4J = 1.8 Hz, B-H), 7.46 – 7.41 (m, 6H, *meso*-Ph), 7.38 – 7.31 (m, 7H, *meso*-Ph), 7.28 – 7.27 (m, 2H, *meso*-Ph), 7.16 – 7.14 (m (dd and s), 2H, D,F-H), 6.87 – 6.85 (m (2 dd), 2H, 2,9-H),6.80 (d, 1H, ^3J = 7.7 Hz, E-H), 6.40 – 6.08 (m (2 d), 2H, ^3J = 5.1 Hz, 13,19-H), 6.08 (m (2d), 2H, ^3J ~ 5.2 Hz, 14,18-H), 3.51 (b, 4H, -NH_2).

^{13}C NMR (176 MHz, $CDCl_3$, 300 K) δ 145.8, 144.9, 143.3, 142.6, 142.1, 140.5, 140.3, 139.6, 138.8, 135.4, 134.9, 134.8, 133.7, 133.5, 131.6, 131.5, 131.3, 129.5, 129.43, 129.41, 129.38, 129.3, 128.8, 128.2, 128.1, 127.9, 127.3, 125.7, 125.6, 125.2, 119.5, 116.9, 115.6, 111.6.

HR-MS (ESI+, TOF) *m/z*: $[M+H]^+$ 781.3100, calcd. for $C_{55}H_{37}N_6^+$ 781.3074.

UV-Vis (CH_2Cl_2, 298 K): λ_{max} (log ε) 359 (4.6), 420 (4.5), 445 (4.6), 526 (4.2), 705 (4.0), 770 (3.9).

Compound 9



9

In a dry 25 mL round-bottom flask equipped with a magnetic stirrer 5,6-dioxophenanthriporphyrin **2** (10 mg, 0.017 mmol) and 3,3'-diaminobenzidine (17.8 mg, 0.083 mmol, 5 equiv.) were dissolved in a freshly distilled pyrridine (5 mL). The solution was refluxed for 1 hour under nitrogen atmosphere. After this time the solvent was removed on a rotary evaporator, and the solid residue was subjected to column chromatography on basic alumina (4 g of water per 100 g of active alumina) with dichloromethane/*n*-hexane (4/1, v/v) as the eluent. Once the first fraction was eluted the solvent system was changed for 1% MeOH/DCM and the crude product was collected as the second, orange band. . The crude product was washed with methanol yielding **7** as an orange solid. Yield: 4.1 mg (32%). The product is very poorly soluble in organic solvents. It's solubility increases after acidification with gaseous HCl.

^{1}H NMR (700 MHz, $CDCl_3$, 300 K): δ 11.14 (b, 2H, 22,25-H), 8.69 (d, 2H, ^3J = 8.5 Hz, 3,8-H), 8.54 (s, 2H, A-H), 7.99 (m, 2H, A/B-H) 7.49 – 7.32 (m, 17H, *meso*-Ph, A/B-H), 7.05 (dd, 2H, ^3J = 8.7 Hz, ^4J = 1.5 Hz, 2,9-H), 6.56 (d, 2H, ^3J = 5.2 Hz, 13,19/14,18-H), 6.26 (d, 2H, ^3J = 5.2 Hz, 13,19/14,18-H).

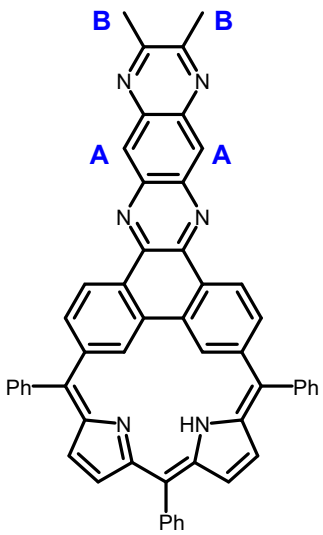
HR-MS (ESI+, TOF) *m/z*: $[M+H]^+$ 725.2674, calcd. for $C_{53}H_{33}N_4^+$ 725.2700.

UV-Vis (CH_2Cl_2, 298 K): λ_{max} (log ε) 360 (4.1), 440 (3.8), 463 (4.0), 492 (3.9), 662 (3.6), 747 (3.4).

Compound 9·HCl

^{1}H NMR (700 MHz, $CDCl_3$, 300 K): δ 14.94 (s, 2H, NH), 10.94 (s, 2H, 22,25-H), 8.78 (d, 2H, ^3J = 8.3 Hz, 3,8-H), 8.58 (s, 2H, A-H), 8.01 – 7.99 (m, 2H, B/C-H), 7.53 – 7.39 (m, 15H, *meso*-Ph, B/C-H), 7.34 (d, 2H, ^3J = 7.4 Hz, *meso-o*-Ph), 7.09 (d, 2H, ^3J = 8.2 Hz, 2,9-H), 6.08 (d, 2H, ^3J = 5.1 Hz, 13,19/14,18-H), 6.25 (d, 2H, ^3J = 5.2 Hz, 13,19/14,18-H). **^{13}C NMR** (176 MHz, $CDCl_3$, 300 K): δ 158.6, 146.3, 146.1, 139.7, 139.3, 139.1, 138.6, 137.4, 134.7, 134.6, 133.9, 132.1, 131.7, 131.28, 131.26, 129.69, 129.67, 129.35, 128.9, 128.6, 128.4, 128.2, 127.8, 127.1, 126.8, 110.3.

Compound 10



10

In a dry 50 mL round-bottom flask equipped with a magnetic stirrer compound **7** (30 mg, 0.04 mmol) and butane-2,3-dione (200 µL, 2.3 mmol, 57 equiv.) were dissolved in a freshly distilled pyrridine (15 mL). The solution was refluxed for 1 hour under nitrogen atmosphere. After this time the solvent was removed on a rotary evaporator, and the solid residue was subjected to column chromatography on basic alumina (4 g of water per 100 g of active alumina) with dichloromethane as the eluent. The crude product was recrystallized from DCM/MeOH solvent system yielding **10** as a dark green solid. Yield: 7.5 mg (23%).

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 11.11 (b, 2H, 22,25-H), 8.69 (d, 2H, ^3J = 8.6 Hz, 3,8-H), 8.57 (s, 2H, A-H), 7.49 – 7.42 (m, 10H, *meso*-Ph), 7.41 – 7.33 (m, 15H, *meso*-Ph), 7.05 (dd, 2H, ^3J = 8.5 Hz, ^4J = 1.7 Hz, 2,9-H), 6.56 (d, 2H, ^3J = 5.2 Hz, 13,19/14,18-H), 6.26 (d, 2H, ^3J = 5.2 Hz, 13,19/14,18-H), 2.75 (s, 6H, B-CH_3).

Due to aggregation of **10** in solution and poor S/N ration in the spectrum not all of the signals were identified.

^{13}C NMR (75.5 MHz, $CDCl_3$, 300 K): δ 155.6, 147.0 141.5, 141.1, 140.8, 139.6, 138.8, 134.9, 133.4, 131.7, 131.5, 129.7, 129.0, 128.7, 128.2, 128.1, 128.0, 127.5, 127.3, 126.3, 124.8, 23.7.

HR-MS (ESI+, TOF) *m/z*: $[M+H]^+$ 755.2854, calcd. for $C_{53}H_{35}N_6^+$ 755.2918.

UV-Vis (CH_2Cl_2, 298 K): λ_{max} (log ε) 275 (4.4), 365 (4.4), 449 (4.3), sh. 473, 653 (4.0), 755 (3.8).

The ^{1}H NMR and 2D NMR spectra

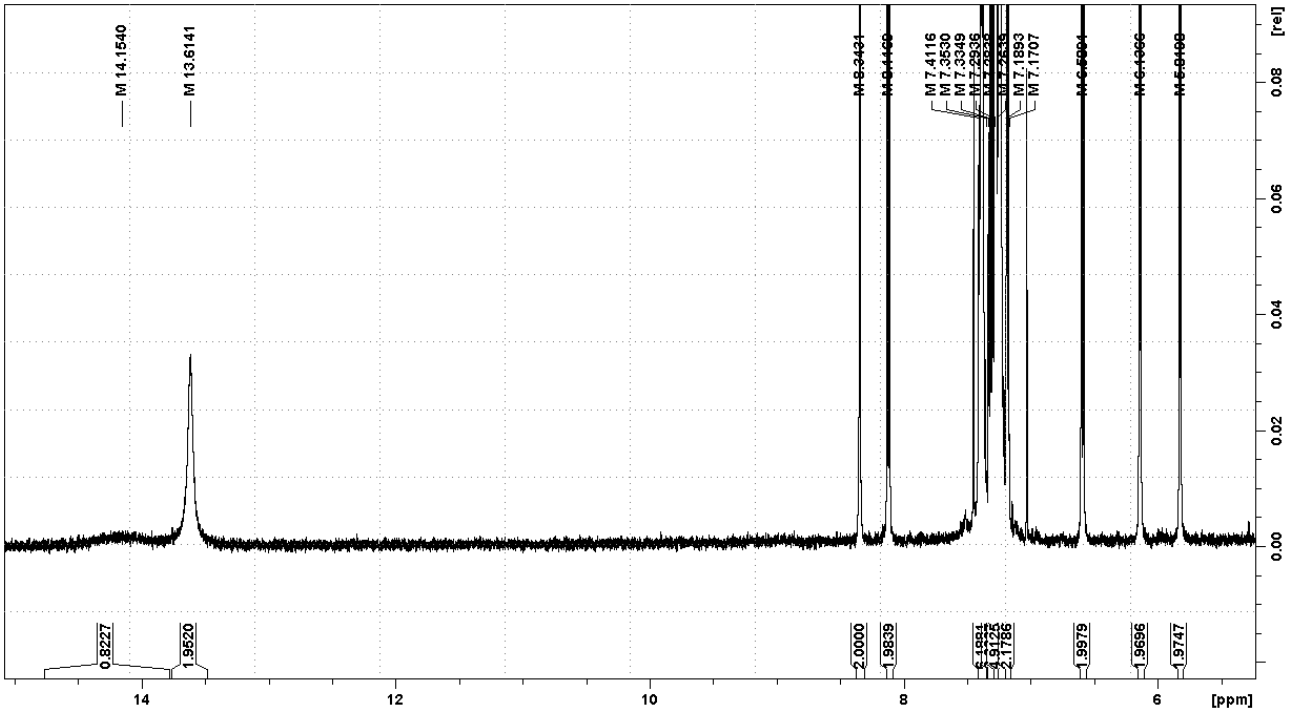


Figure S 1. The ^{1}H NMR spectrum of **3** ($CDCl_3$, 300 K, 500 MHz).

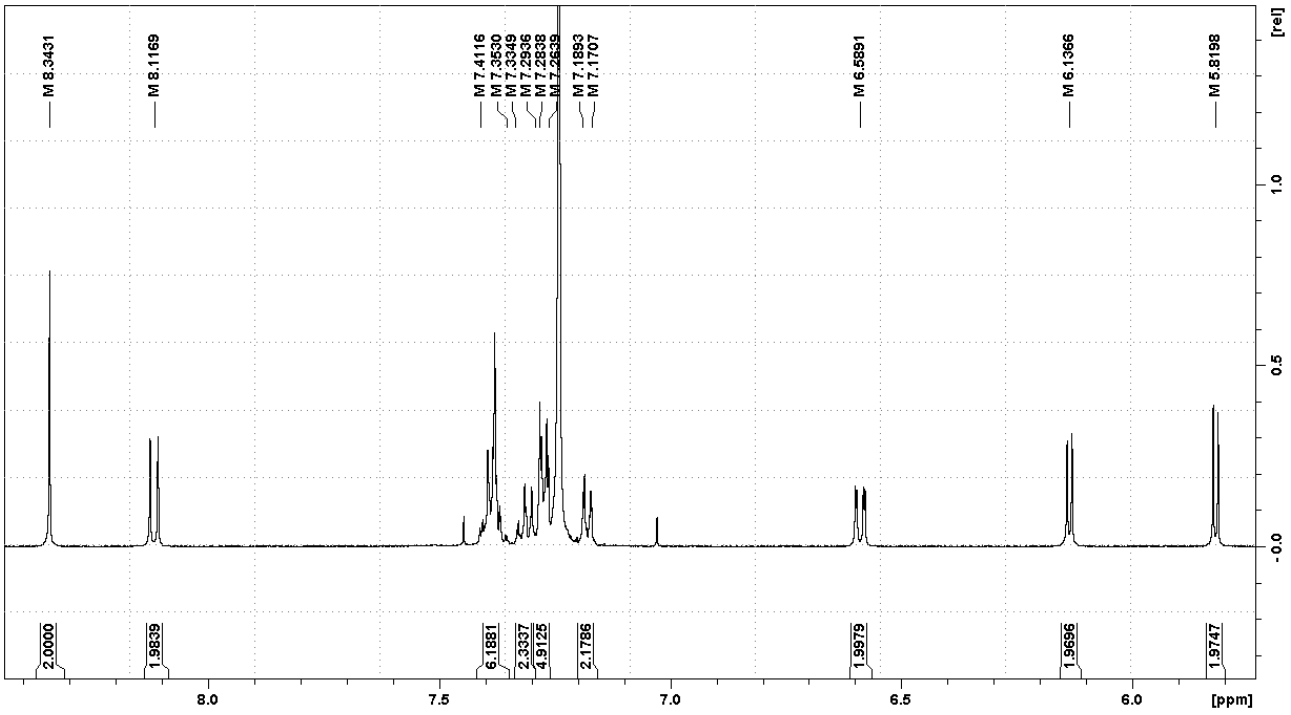


Figure S 2. The aromatic region of the ^{1}H NMR spectrum of **3** ($CDCl_3$, 300 K, 500 MHz).

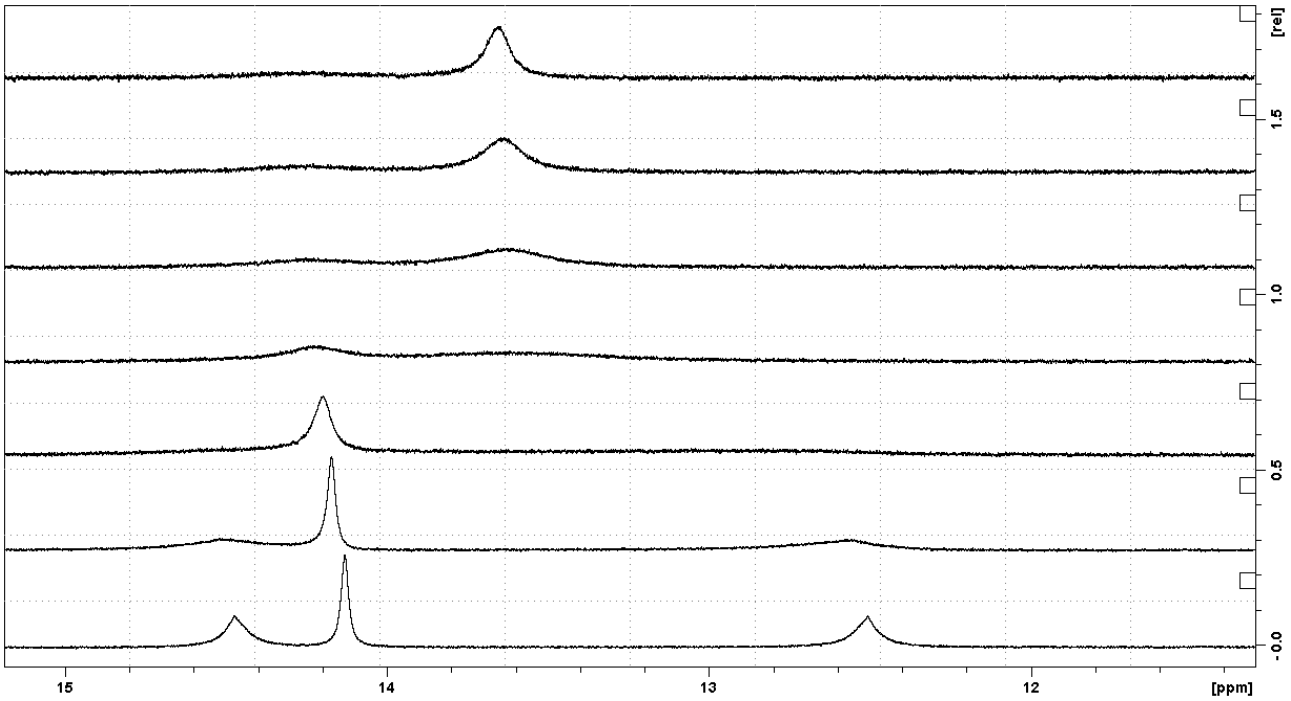


Figure S 3. The downfield region of the ^{1}H NMR spectra of **3** recorded in 300 K (top) – 180 K (bottom) temperature range every 20 K (600 MHz, CD_2Cl_2).

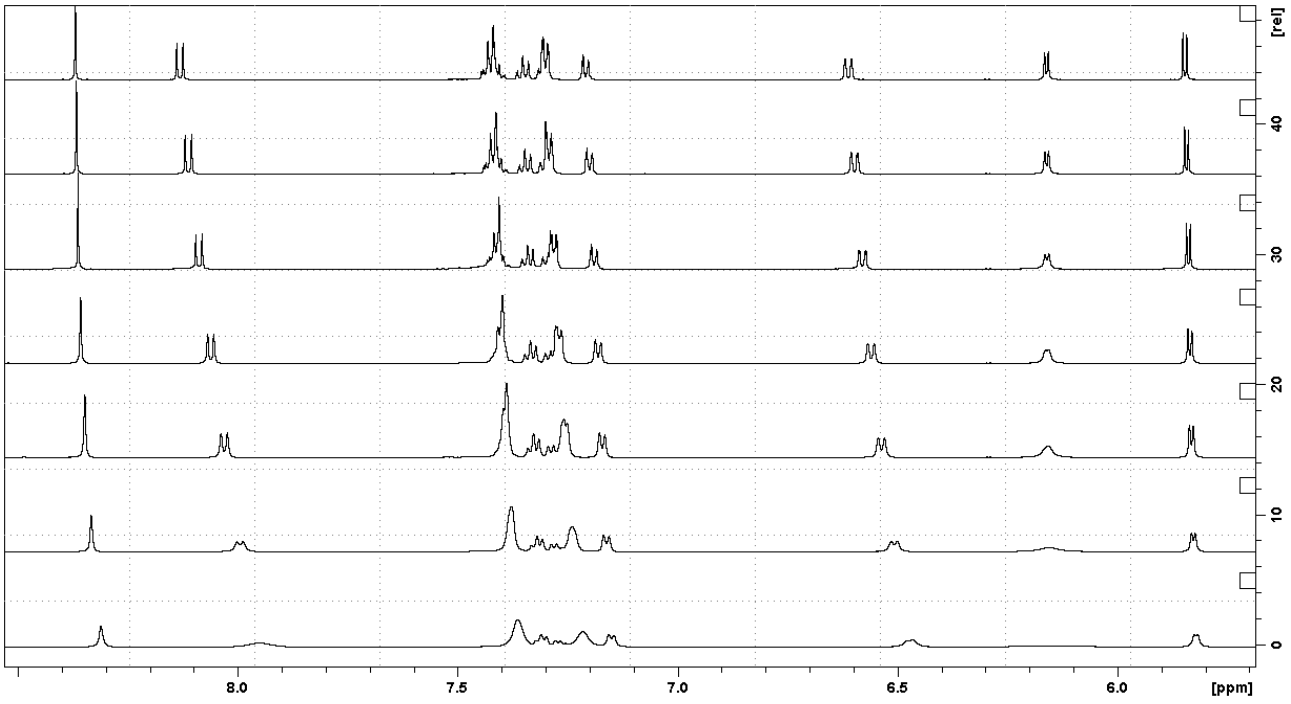


Figure S 4. The aromatic region of the ^{1}H NMR spectra of **3** recorded in 300 K (top) – 180 K (bottom) temperature range every 20 K (600 MHz, CD_2Cl_2).

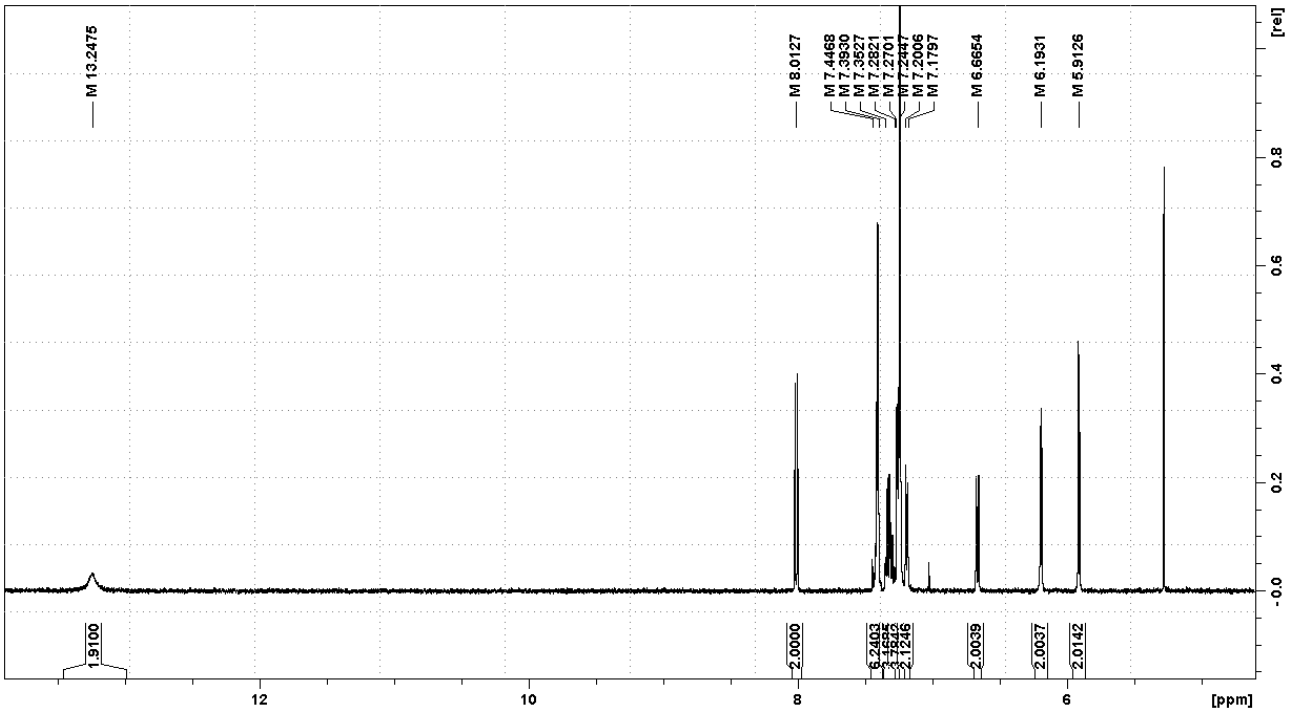


Figure S 5. The ^{1}H NMR spectrum of **4** ($CDCl_3$, 300 K, 500 MHz).

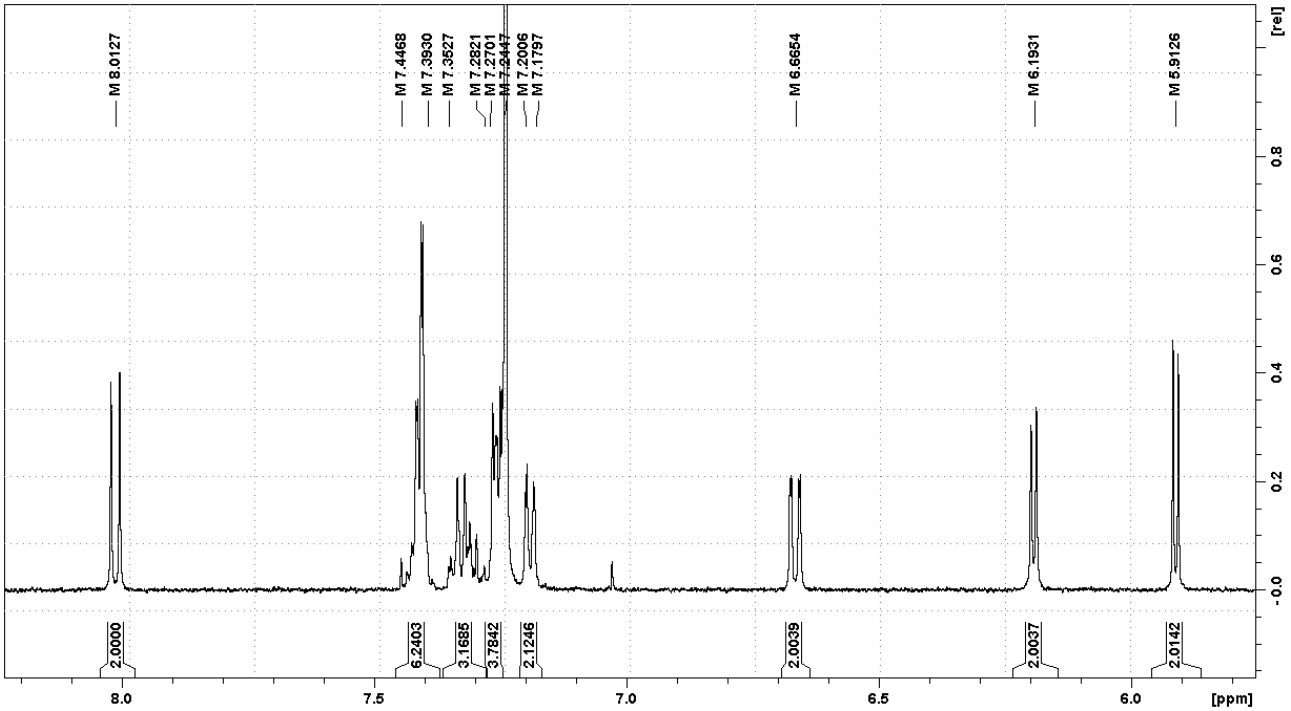


Figure S 6. The aromatic region of the ^{1}H NMR spectrum of **4** ($CDCl_3$, 300 K, 500 MHz).

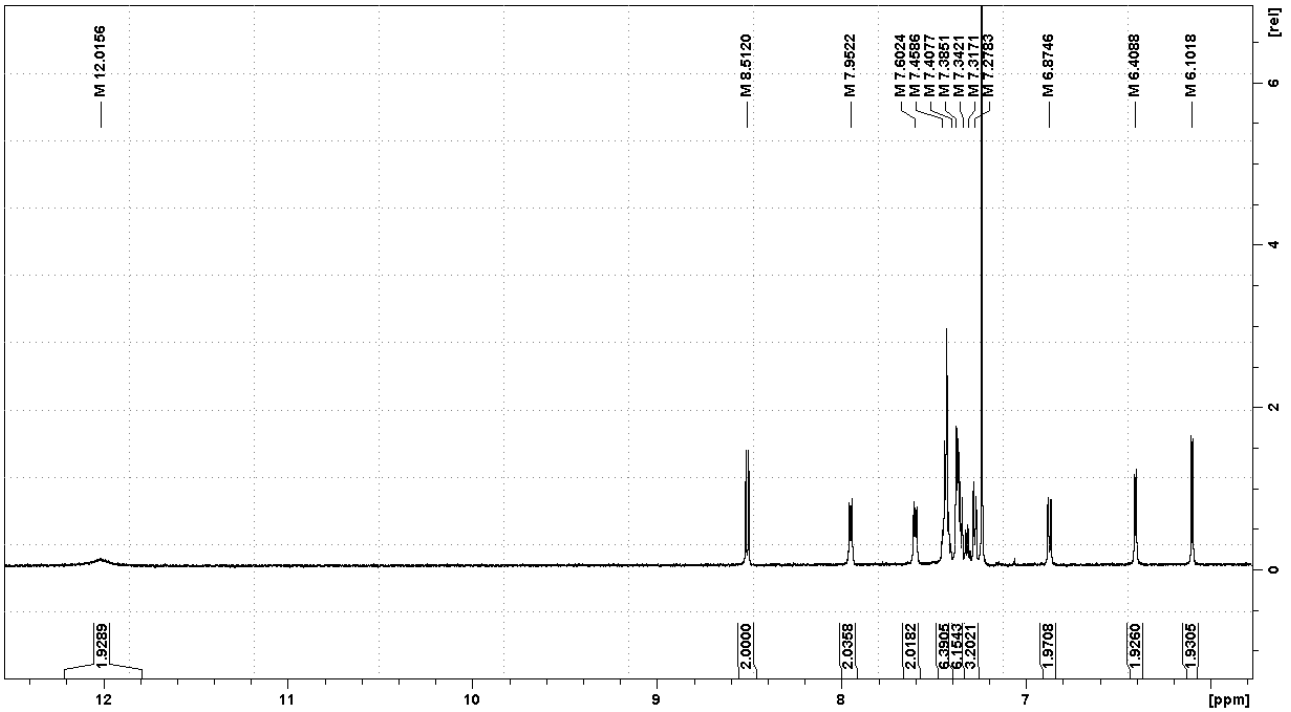


Figure S 7. The ^{1}H NMR spectrum of **5** ($CDCl_3$, 300 K, 500 MHz).

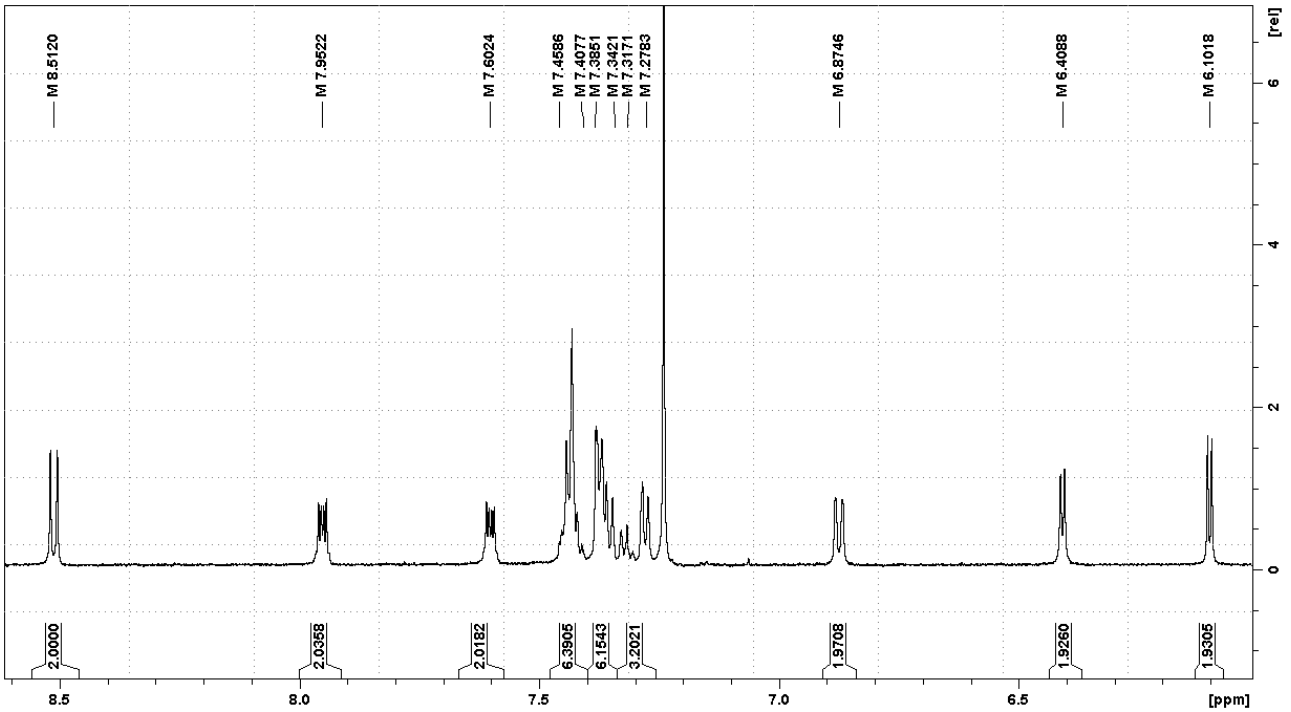


Figure S 8. The aromatic region of the ^{1}H NMR spectrum of **5** ($CDCl_3$, 300 K, 500 MHz).

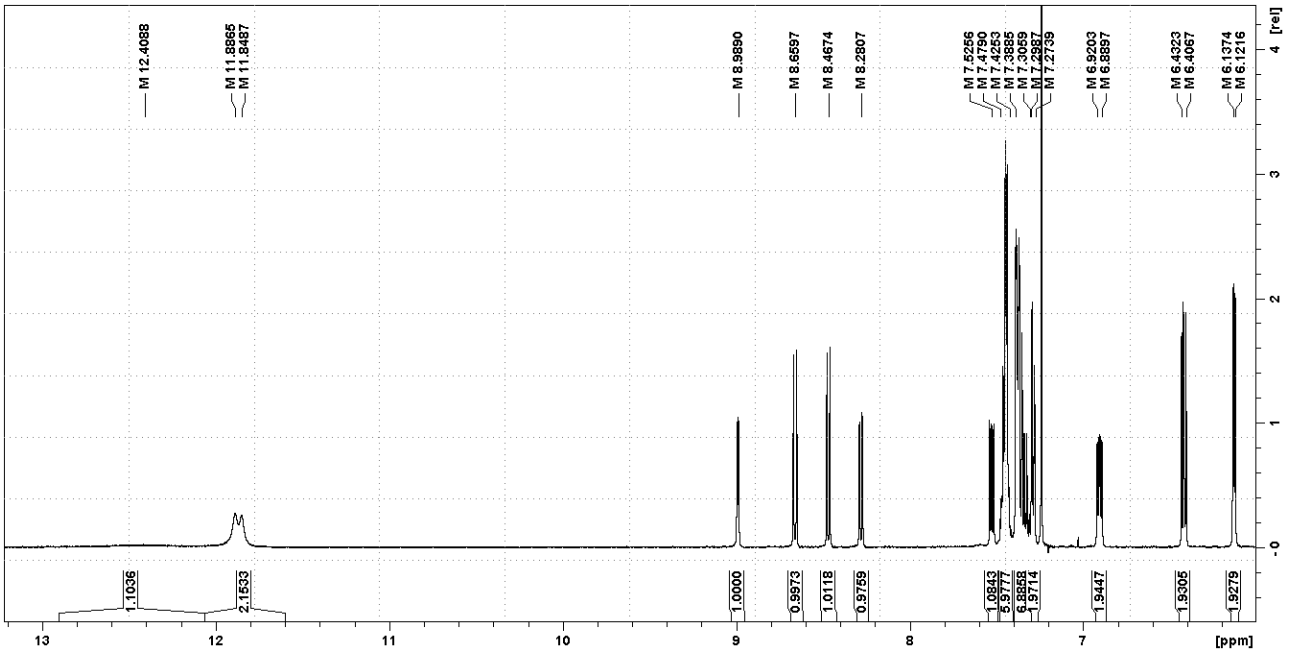


Figure S 9. The ^{1}H NMR spectrum of **6** ($CDCl_3$, 300 K, 500 MHz).

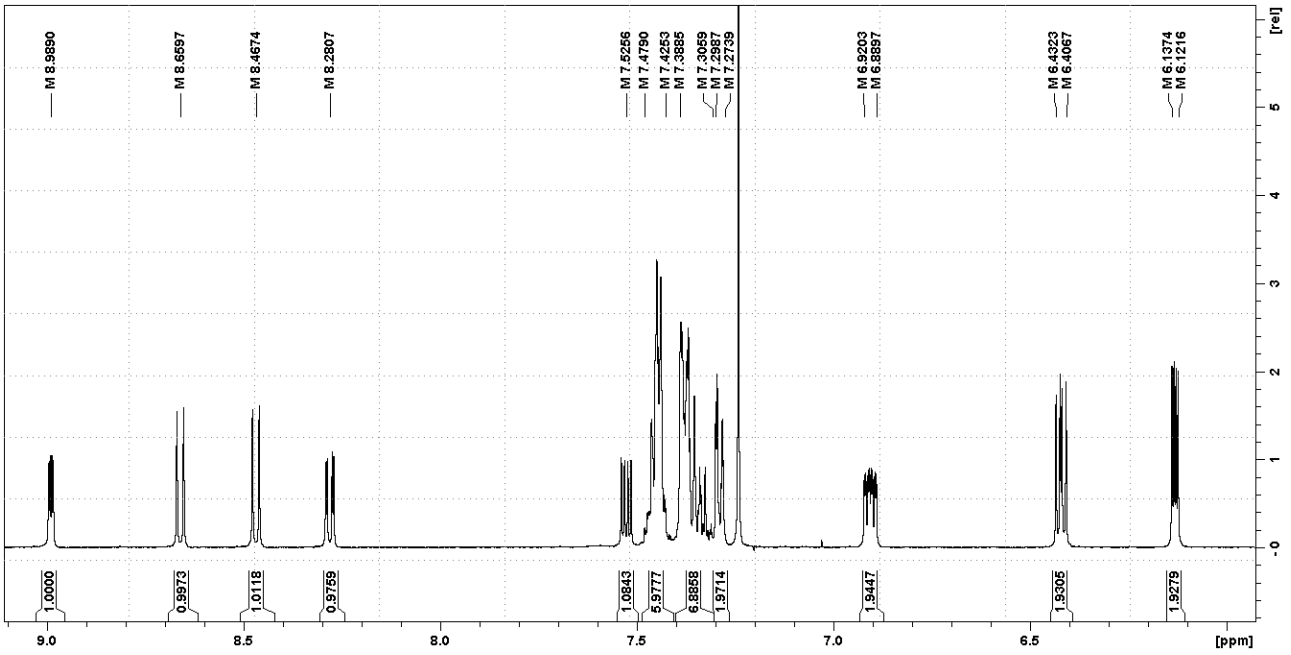


Figure S 10. The aromatic region of the ^{1}H NMR spectrum of **6** ($CDCl_3$, 300 K, 500 MHz).

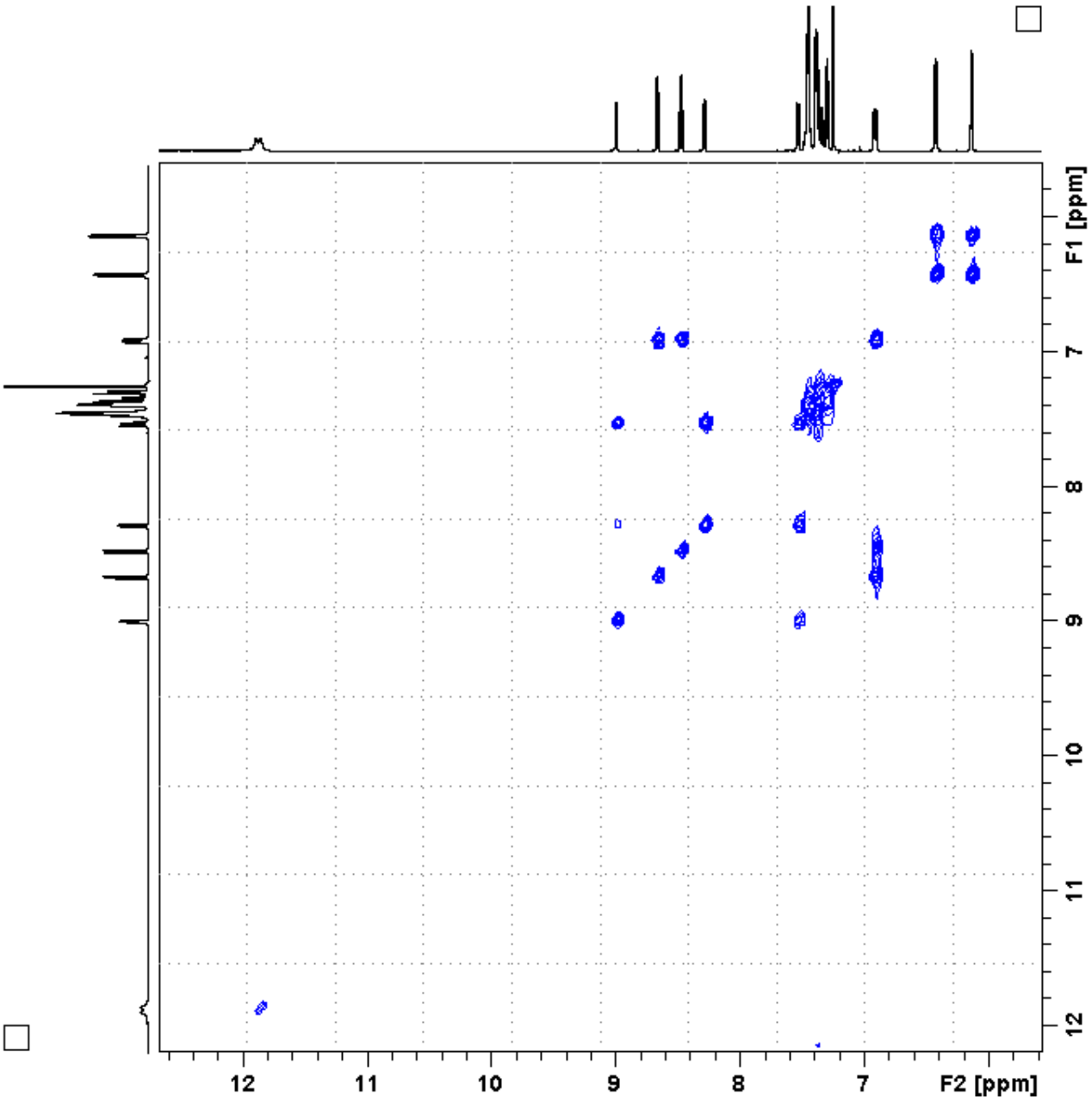


Figure S 11. The ^{1}H-^{1}H COSY spectrum of **6** ($CDCl_3$, 300 K, 500 MHz).

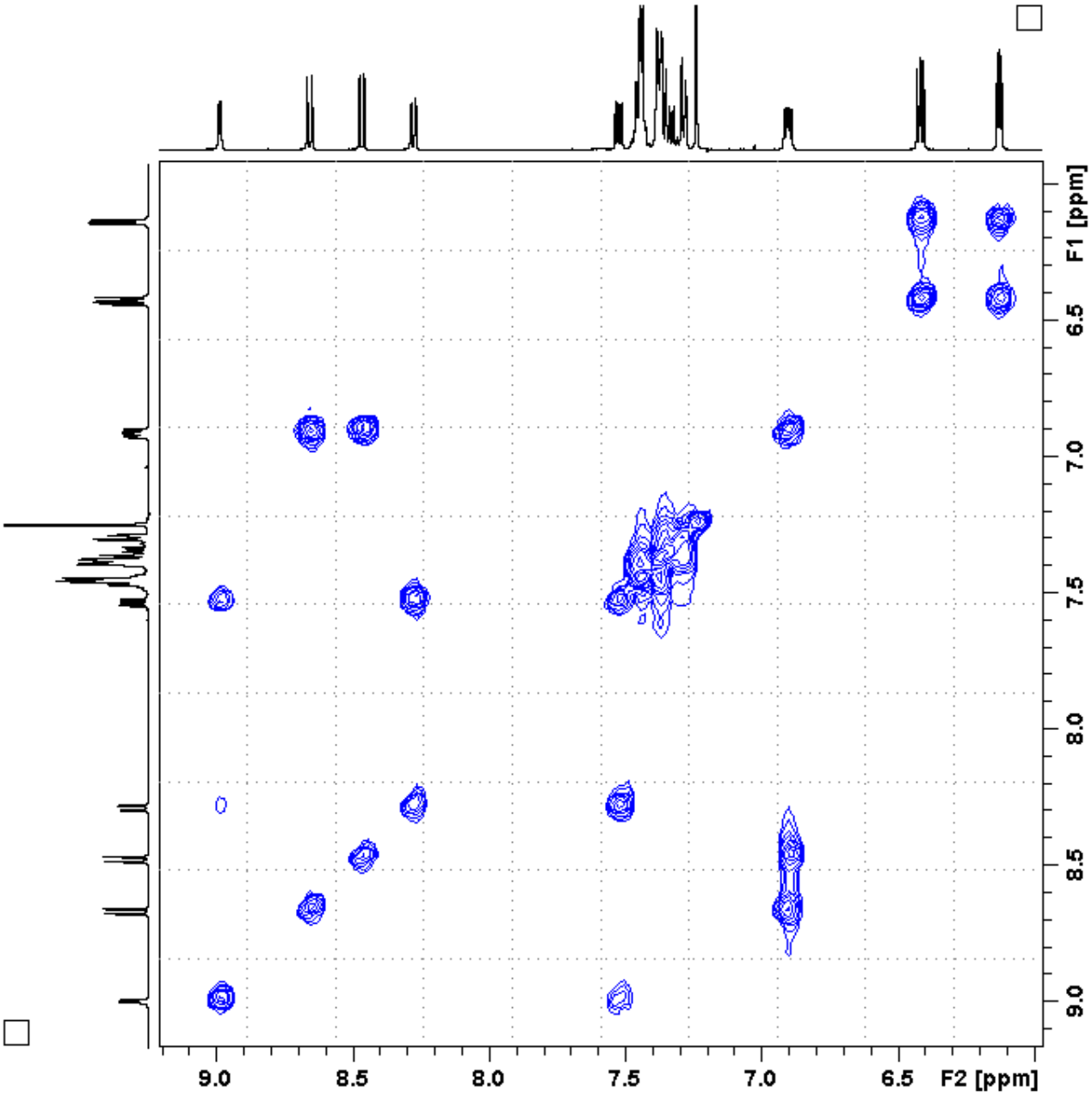


Figure S 12. The aromatic part of the ^{1}H-^{1}H COSY spectrum of **6** ($CDCl_3$, 300 K, 500 MHz).

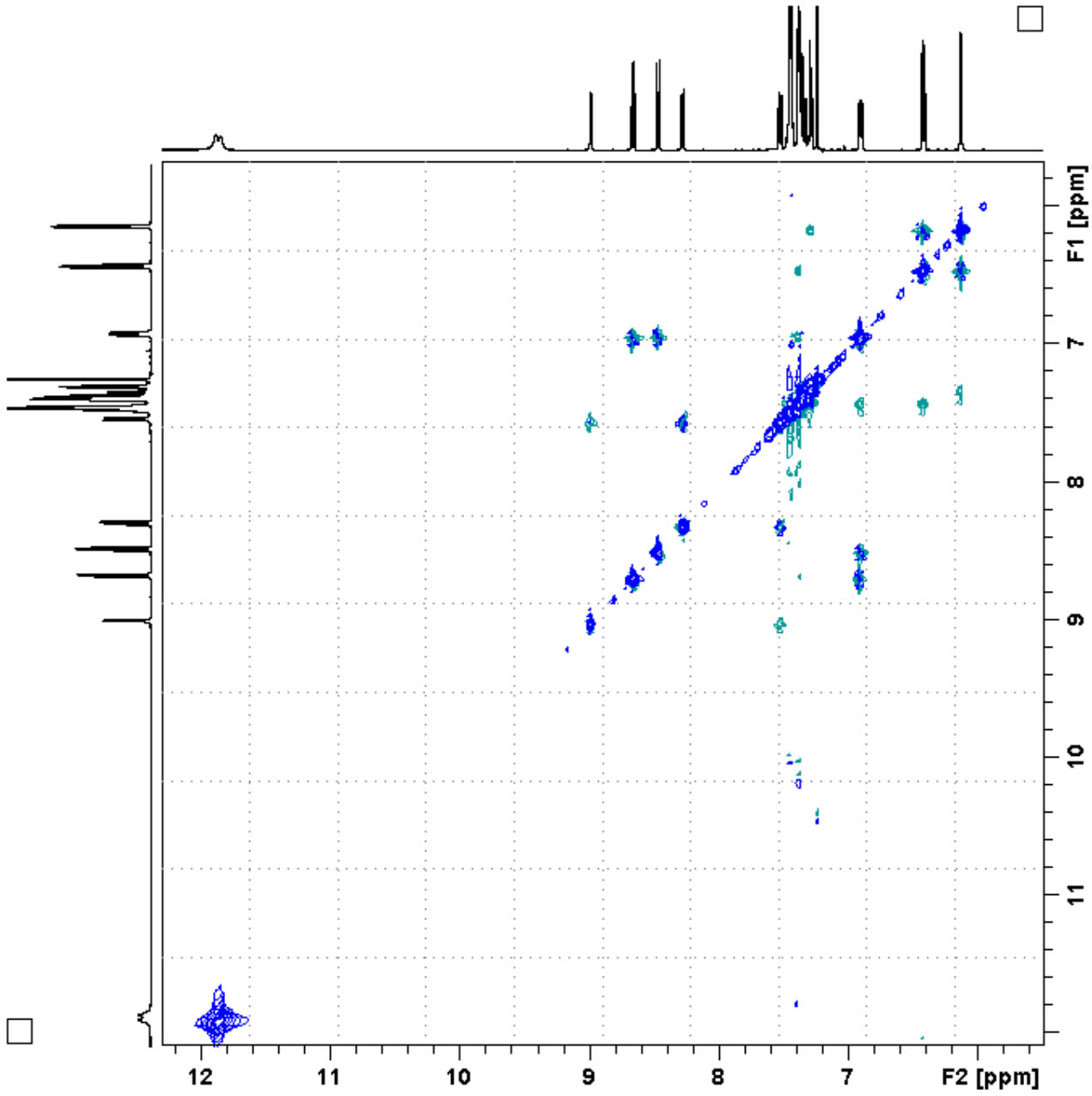


Figure S 13. The ^{1}H-^{1}H NOESY spectrum of of **6** ($CDCl_3$, 300 K, 500 MHz).

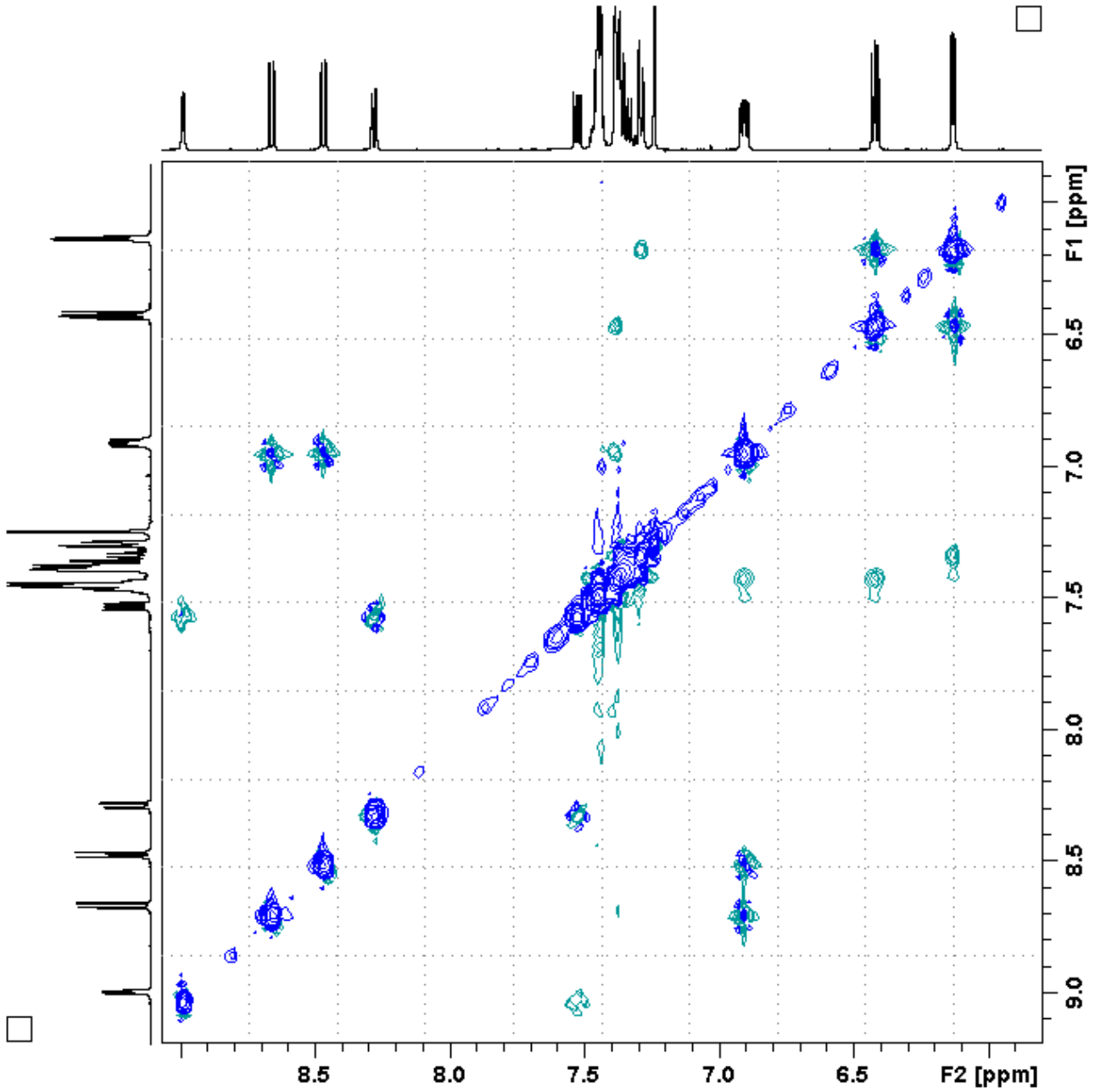


Figure S 14. A part of the ^{1}H-^{1}H NOESY spectrum of of **6** ($CDCl_3$, 300 K, 500 MHz).

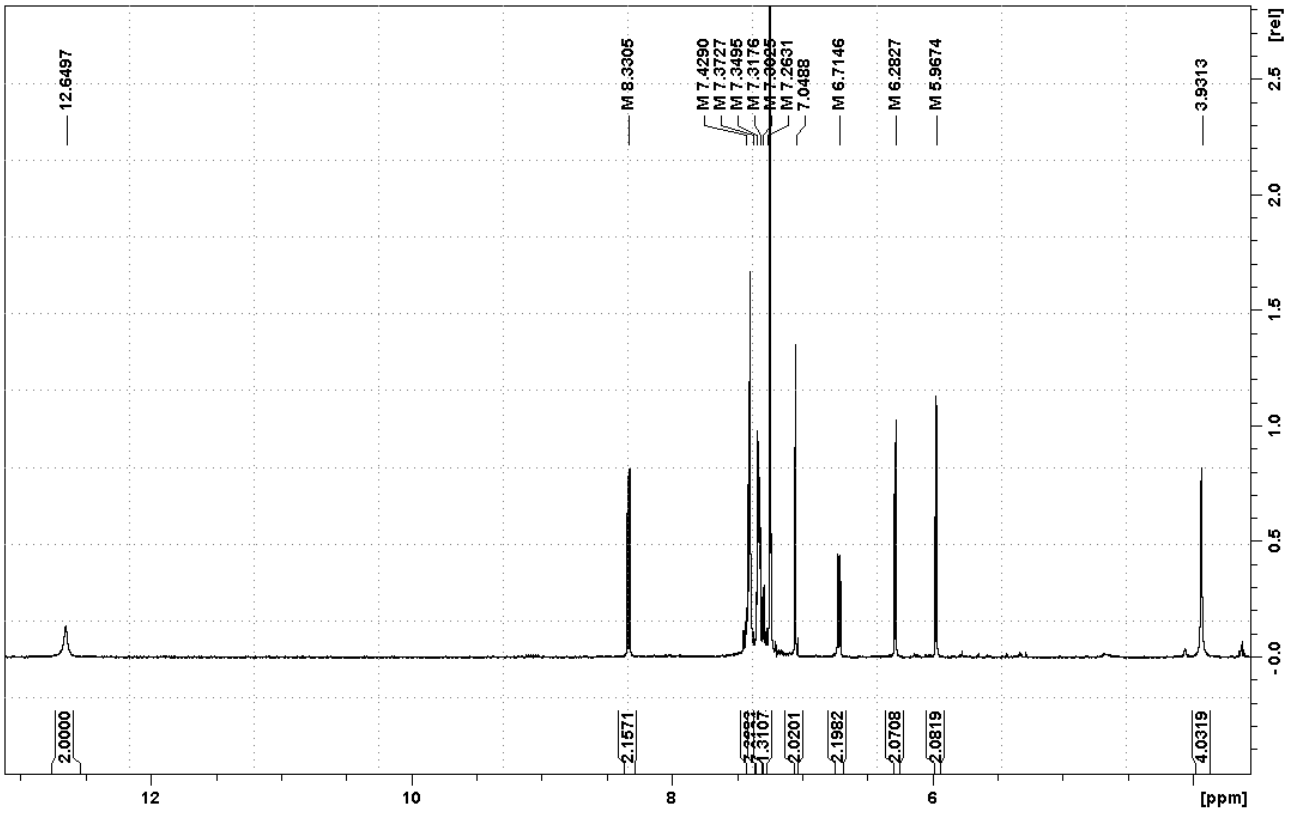


Figure S 15. The ^{1}H NMR spectrum of **7** ($CDCl_3$, 300 K, 500 MHz).

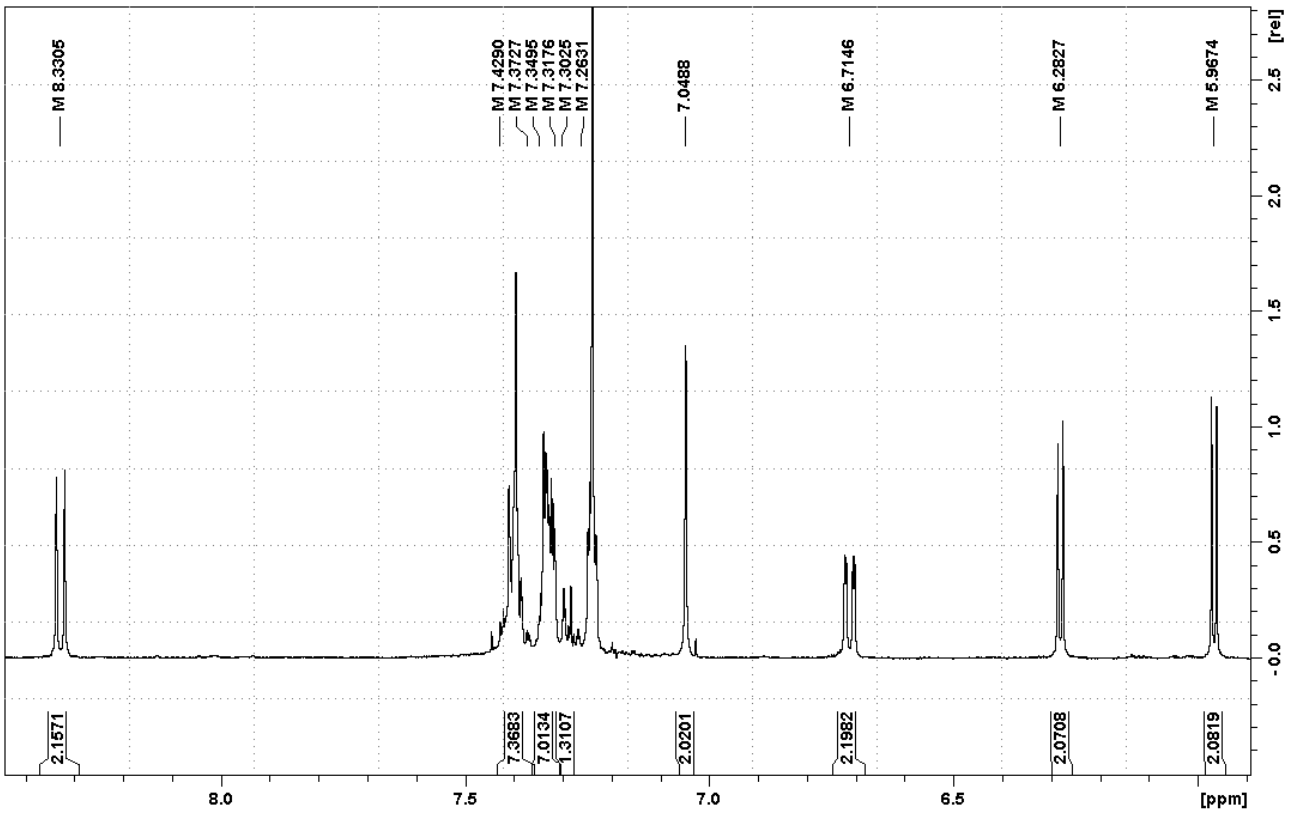


Figure S 16. The aromatic region of the ^{1}H NMR spectrum of **7** ($CDCl_3$, 300 K, 500 MHz).

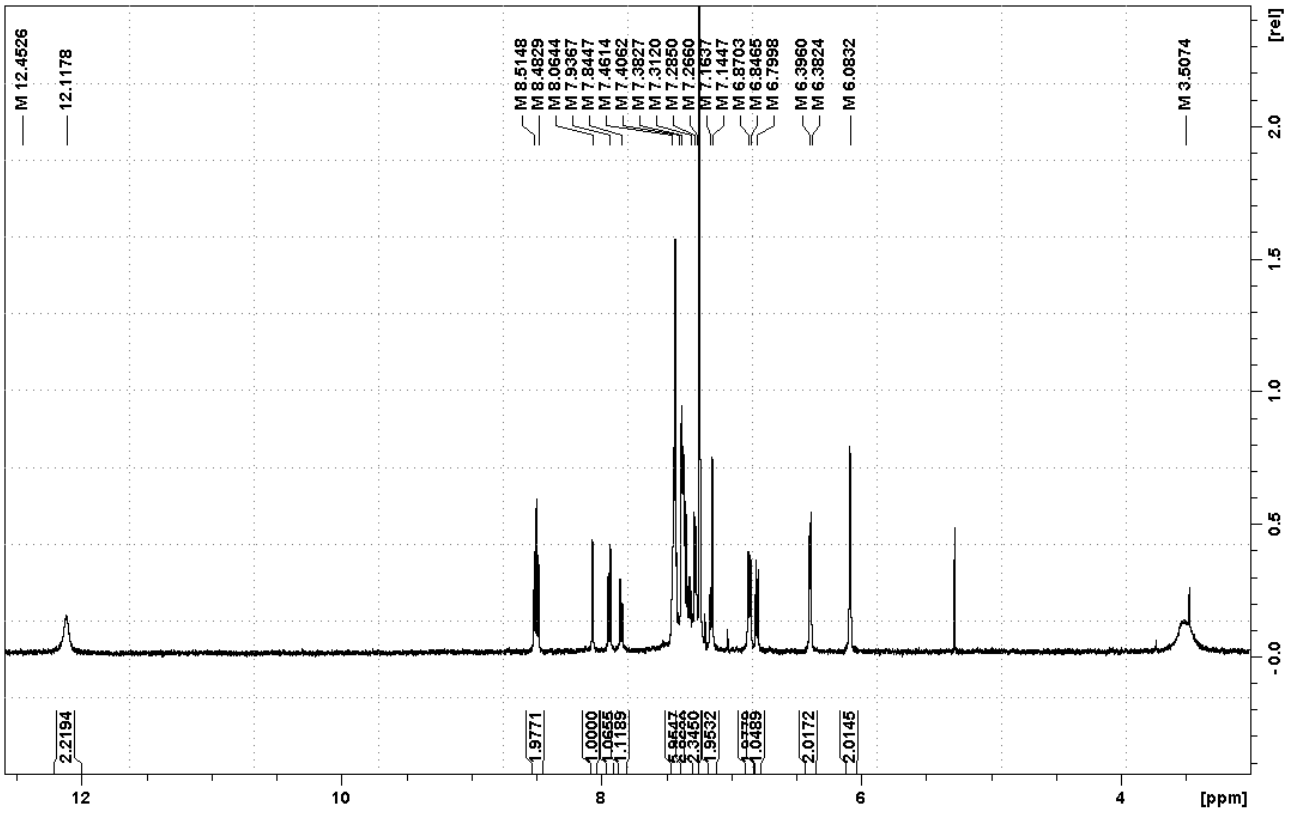


Figure S 17. The ^{1}H NMR spectrum of **8** ($CDCl_3$, 300 K, 500 MHz).

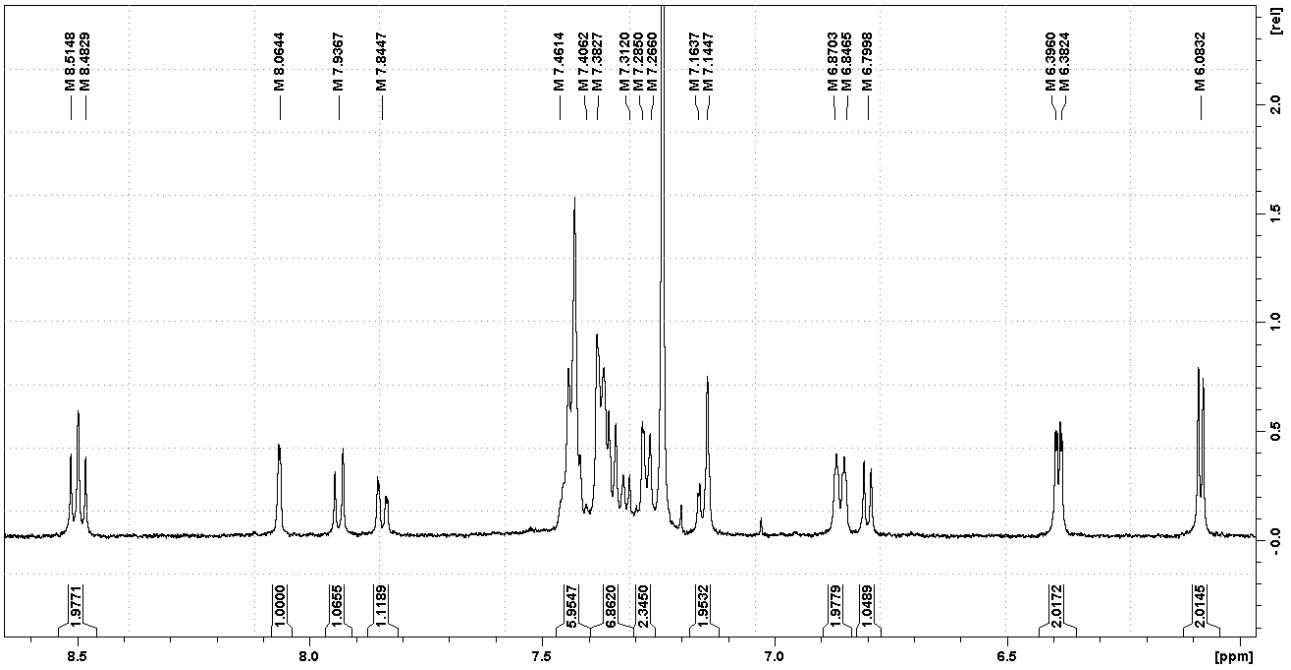


Figure S 18. The aromatic region of the ^{1}H NMR spectrum of **8** ($CDCl_3$, 300 K, 500 MHz).

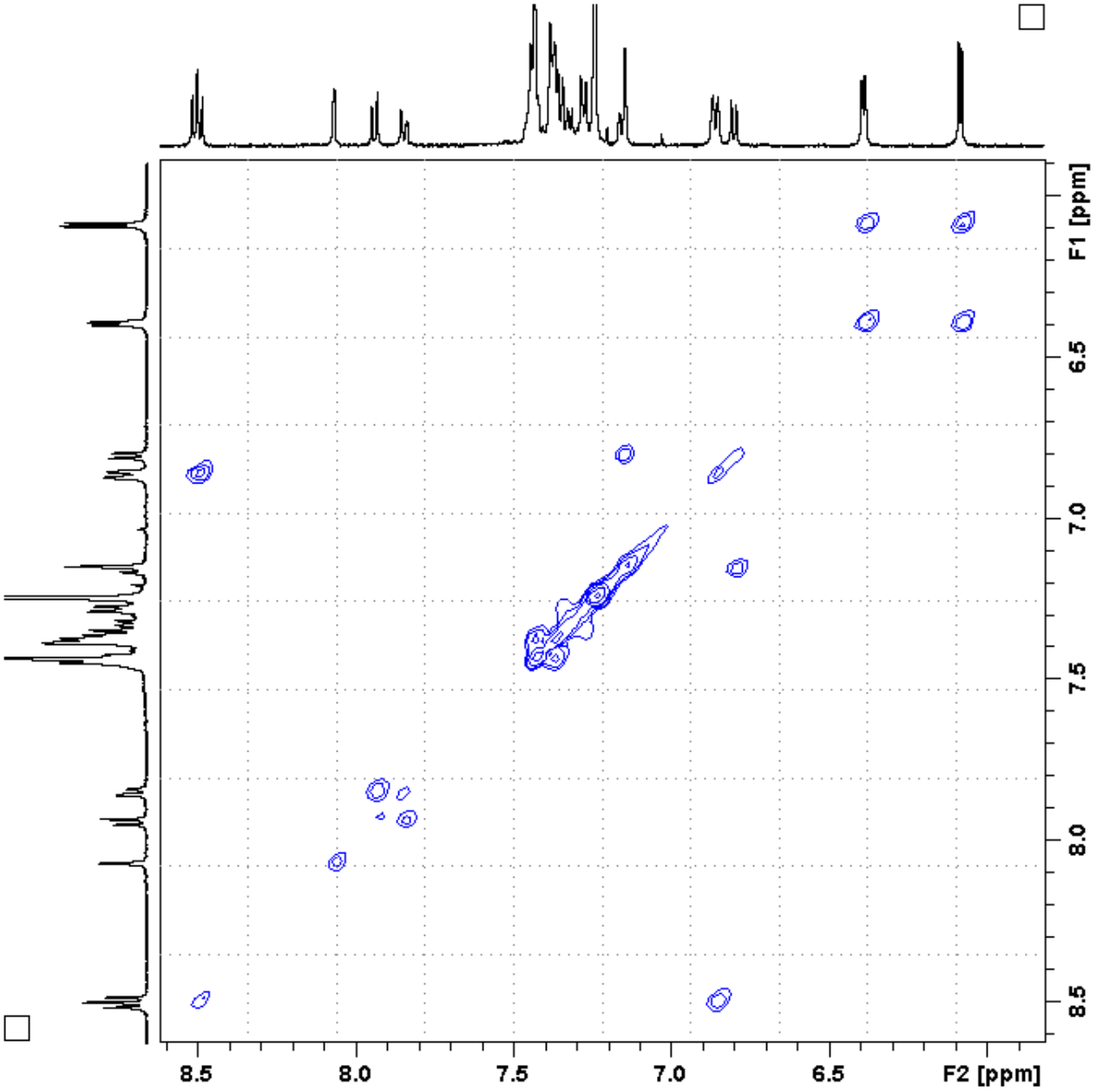


Figure S 19. The ^{1}H-^{1}H COSY spectrum of **8** ($CDCl_3$, 300 K, 500 MHz).

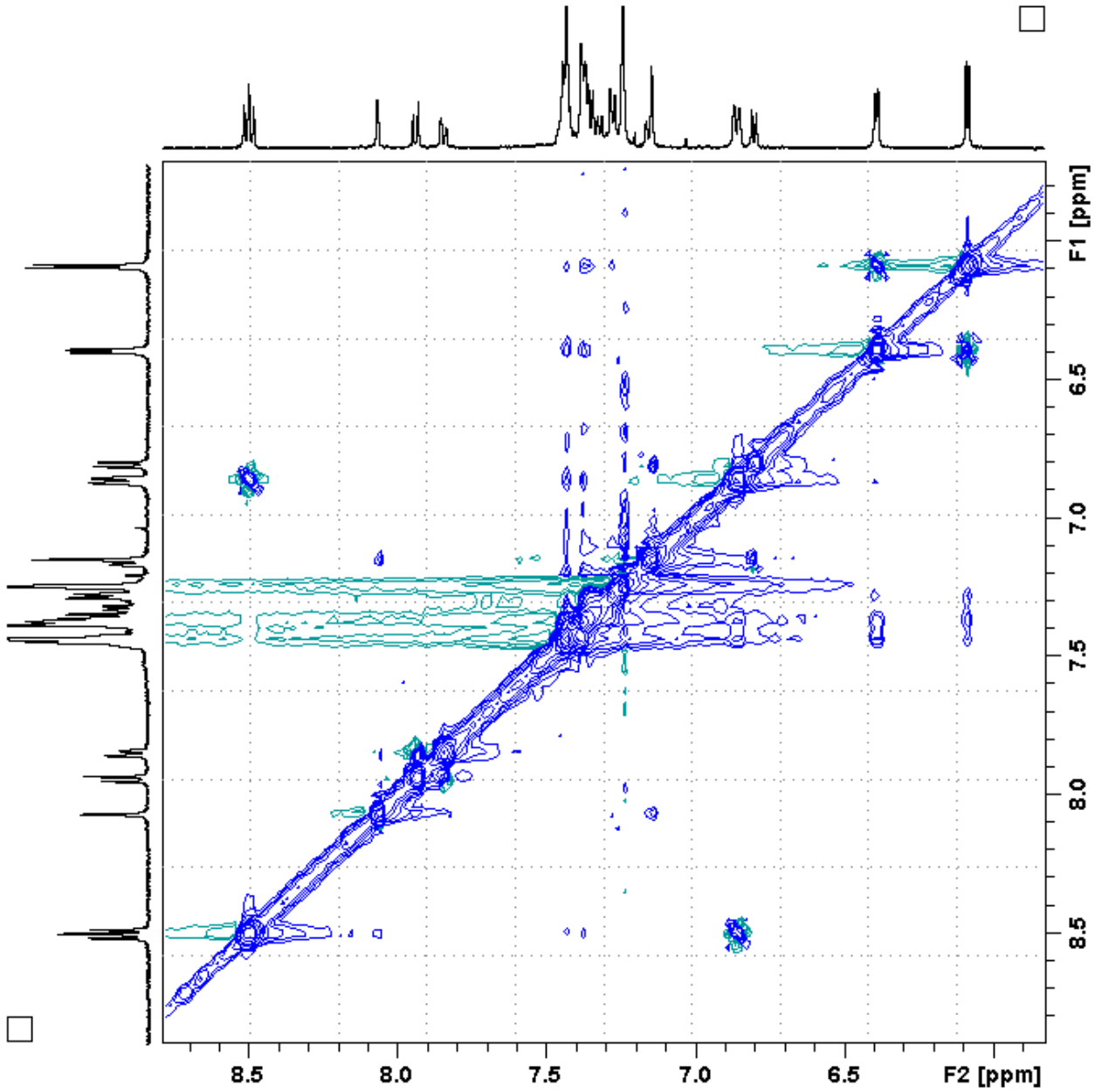


Figure S 20. A part of the ^{1}H-^{1}H NOESY spectrum of **8** ($CDCl_3$, 300 K, 500 MHz).

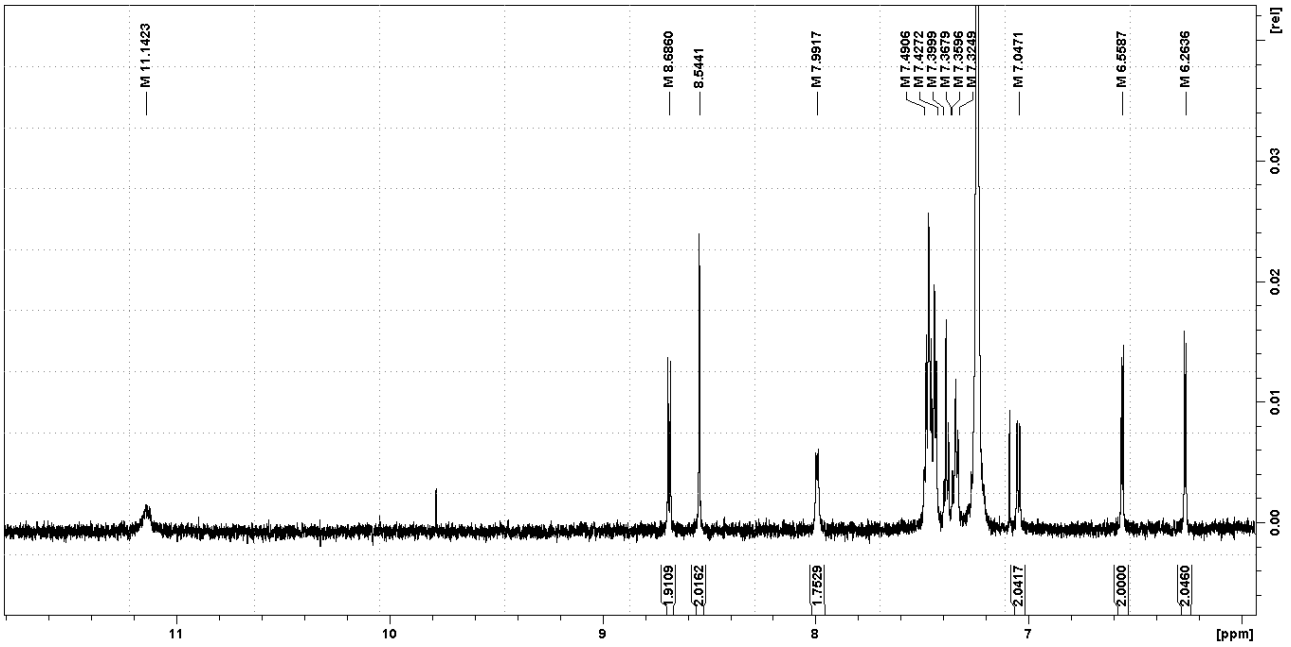


Figure S 21. The ^{1}H NMR spectrum of **9** ($CDCl_3$, 300 K, 700 MHz).

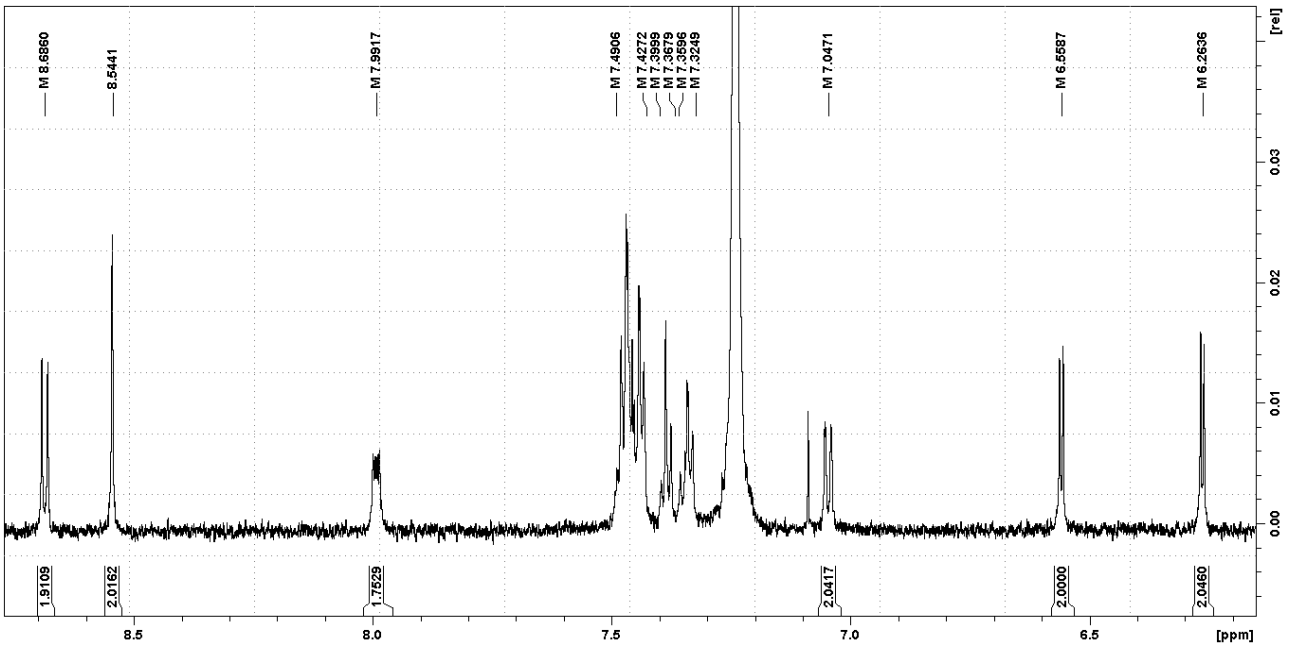


Figure S 22. The aromatic region of the ^{1}H NMR spectrum of **9** ($CDCl_3$, 300 K, 700 MHz).

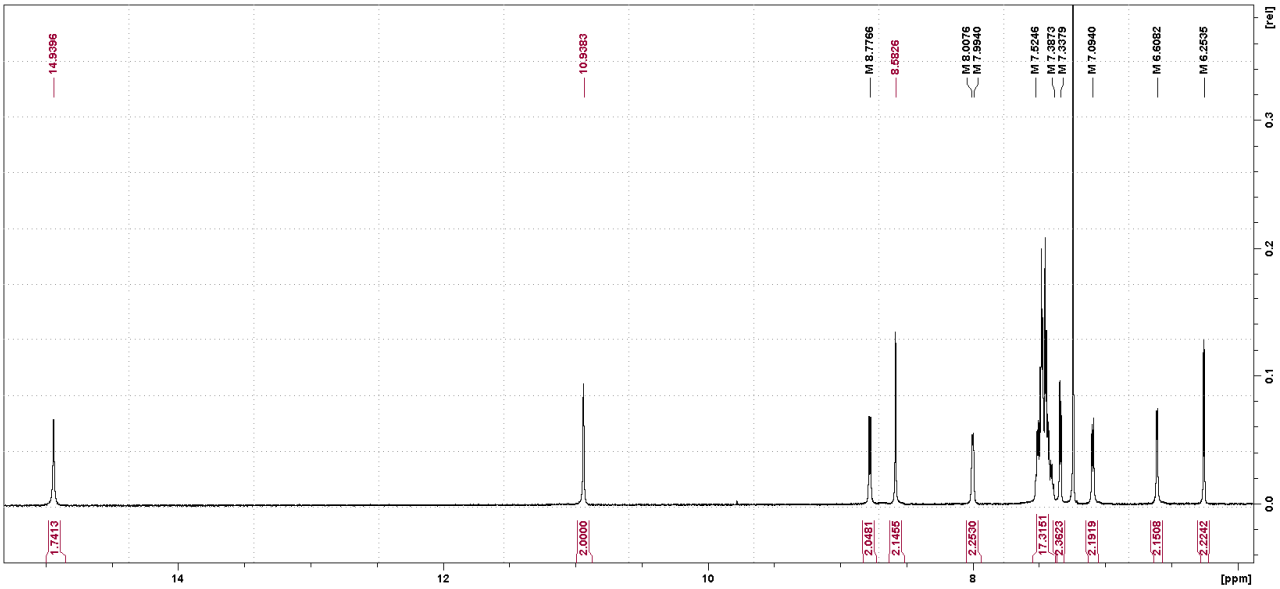


Figure S 23. The ^{1}H NMR spectrum of **9·HCl** ($CDCl_3$, 300 K, 700 MHz).

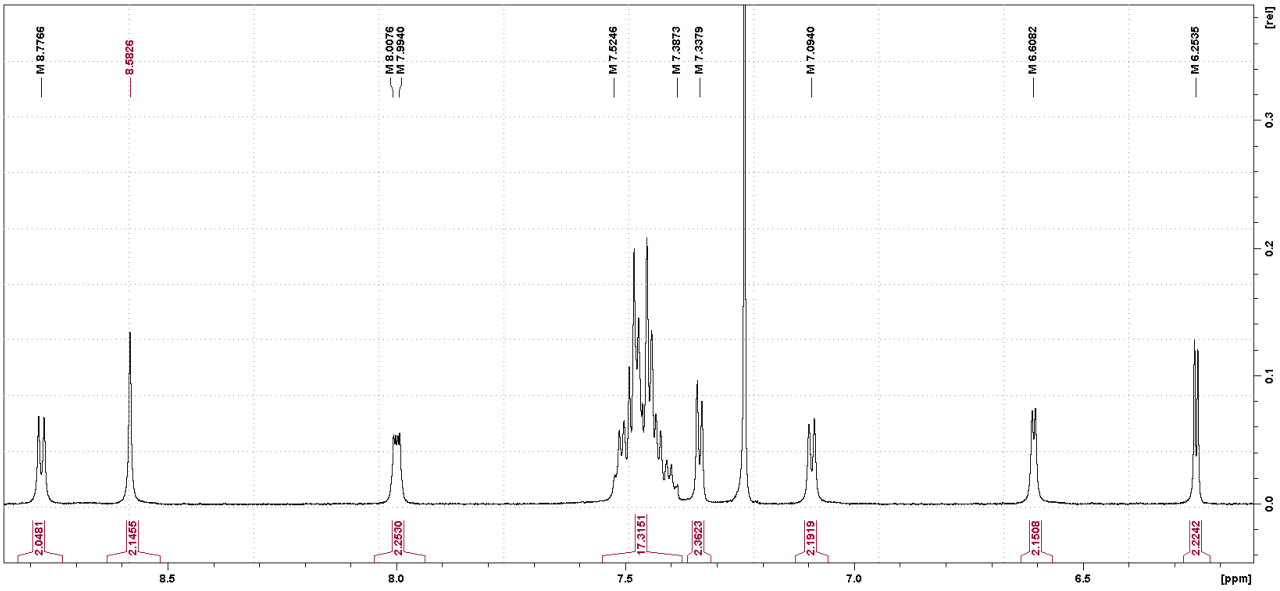


Figure S 24. The aromatic region of the ^{1}H NMR spectrum of **9·HCl** ($CDCl_3$, 300 K, 500 MHz).

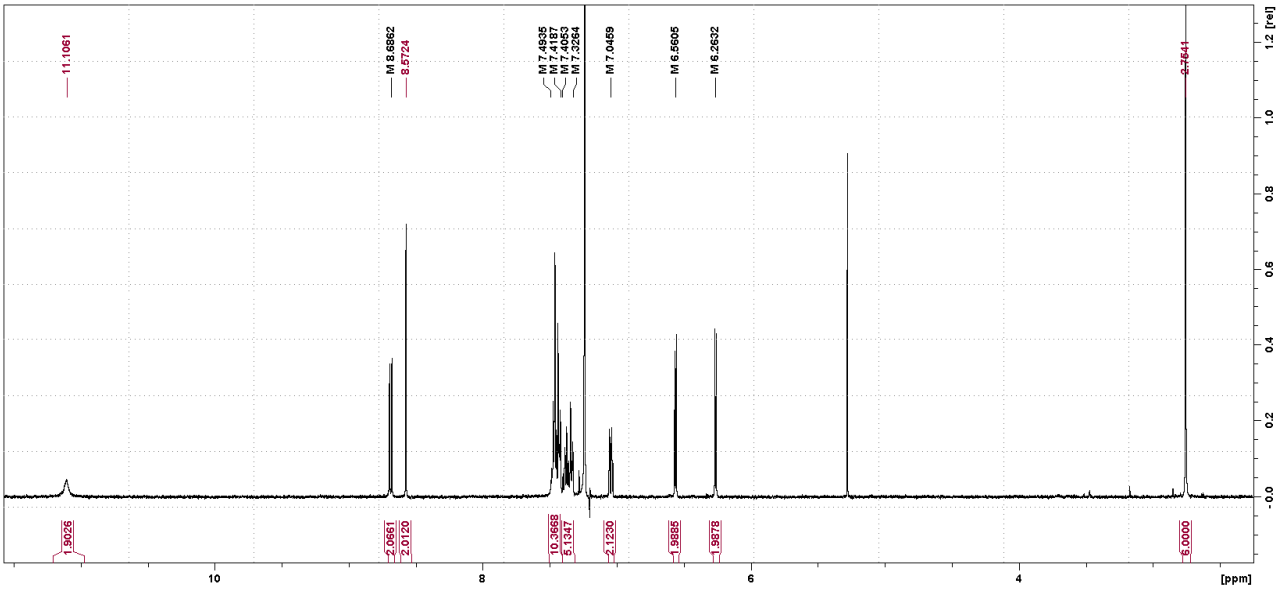


Figure S 25. The ^{1}H NMR spectrum of **10** ($CDCl_3$, 300 K, 500 MHz).

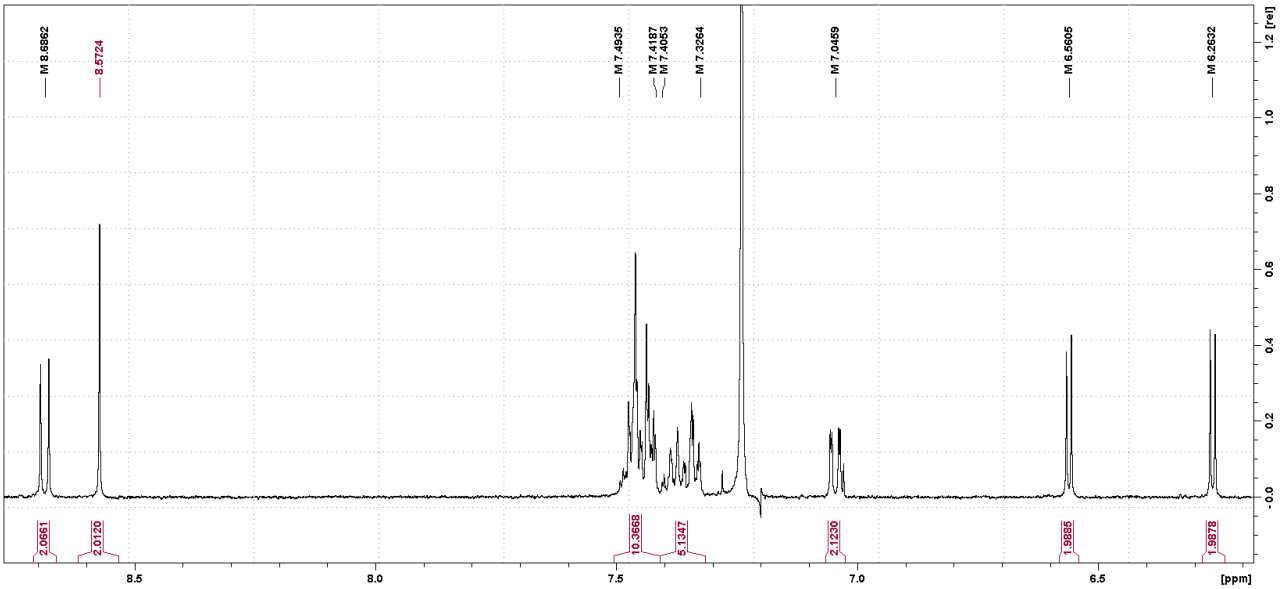


Figure S 26. The aromatic region of the ^{1}H NMR spectrum of **10** ($CDCl_3$, 300 K, 500 MHz).

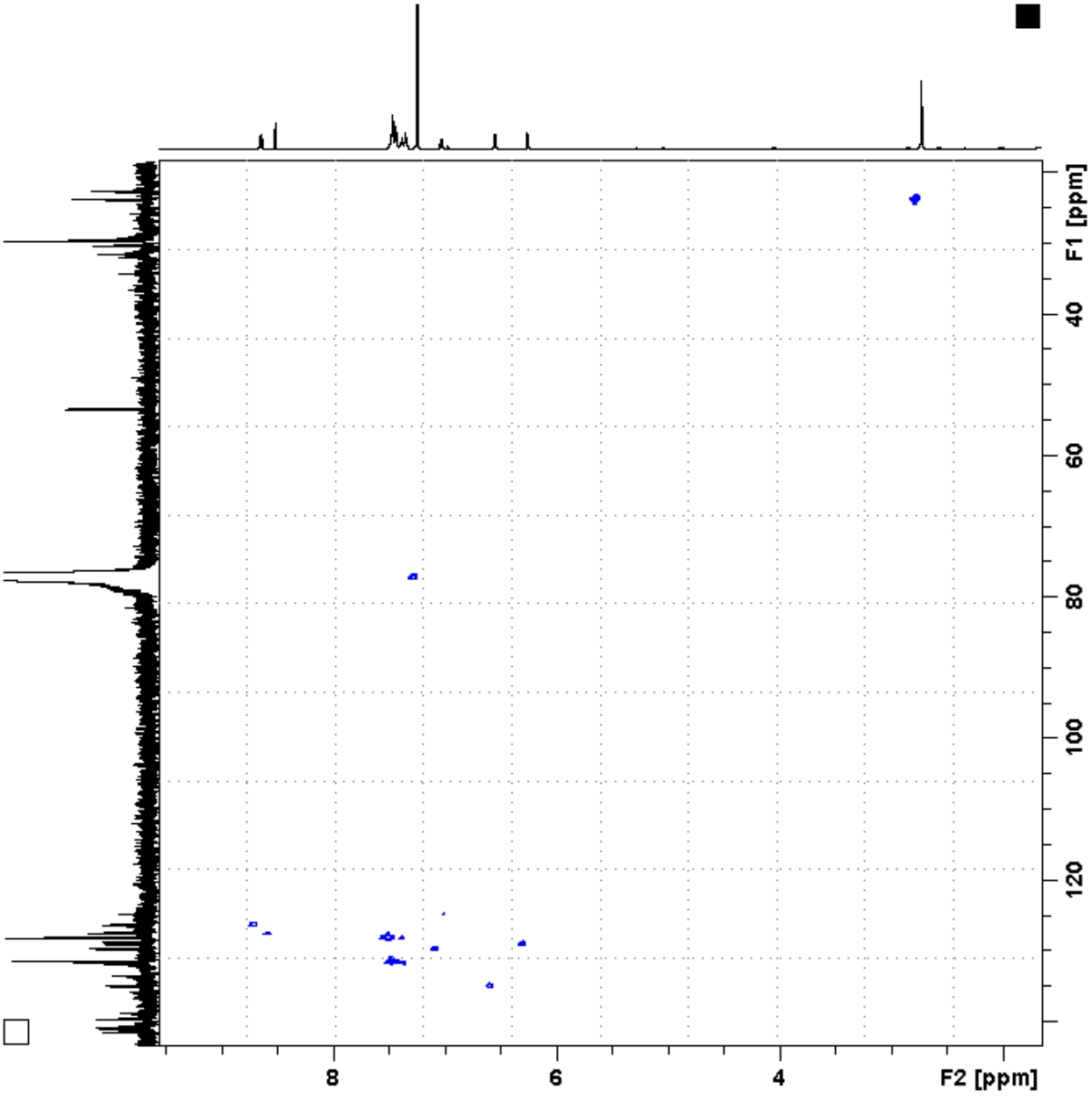


Figure S 27. The ^{1}H-^{13}C HMQC spectrum of **10** ($CDCl_3$, 300 K, 500 MHz).

The ^{13}C NMR spectra

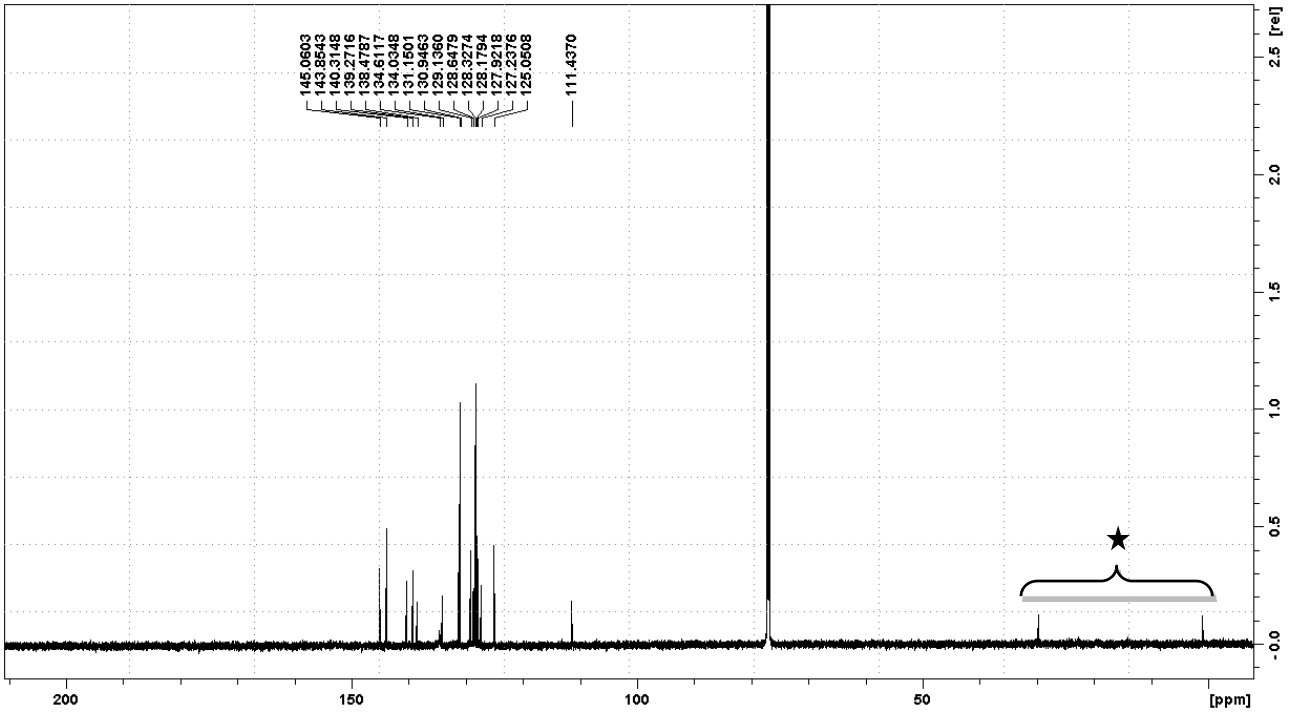


Figure S 28. ^{13}C NMR spectrum of **3** (176 MHz, $CDCl_3$, 300 K). Signals corresponding to residual solvents and impurities are marked with asterisks.

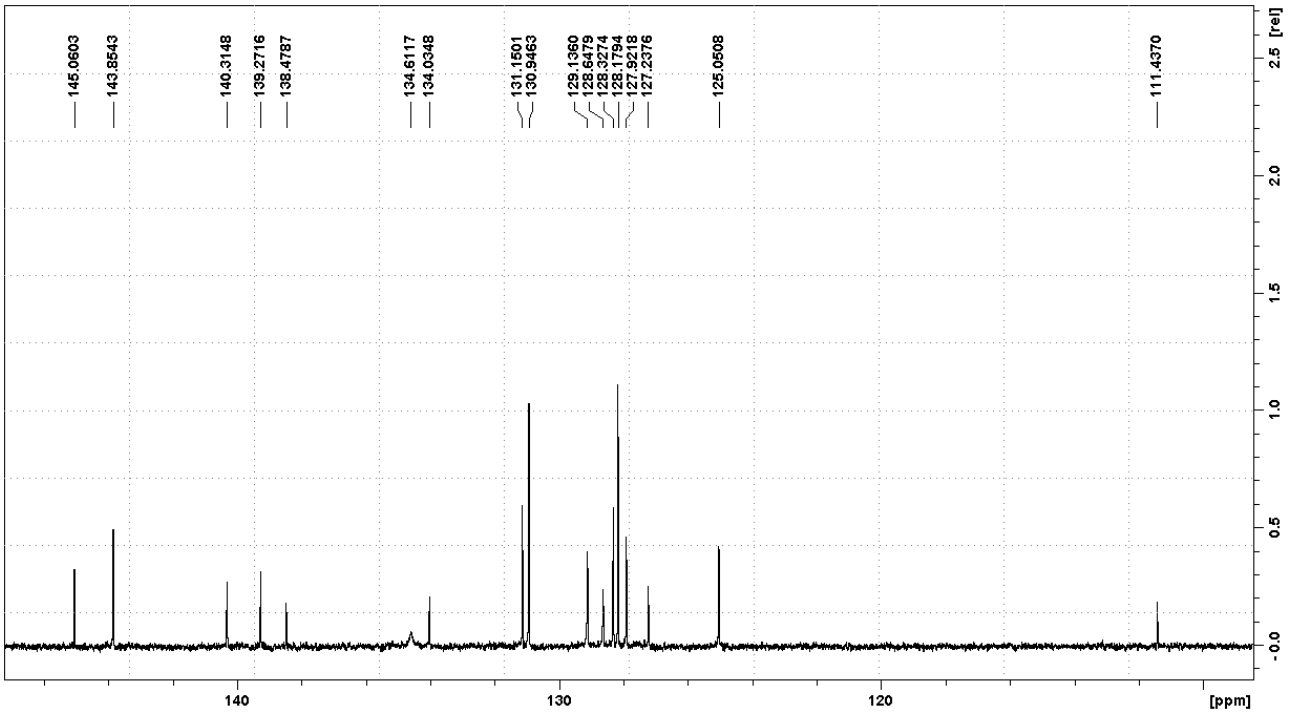


Figure S 29. Part of the ^{13}C NMR spectrum of **3** (176 MHz, $CDCl_3$, 300 K).

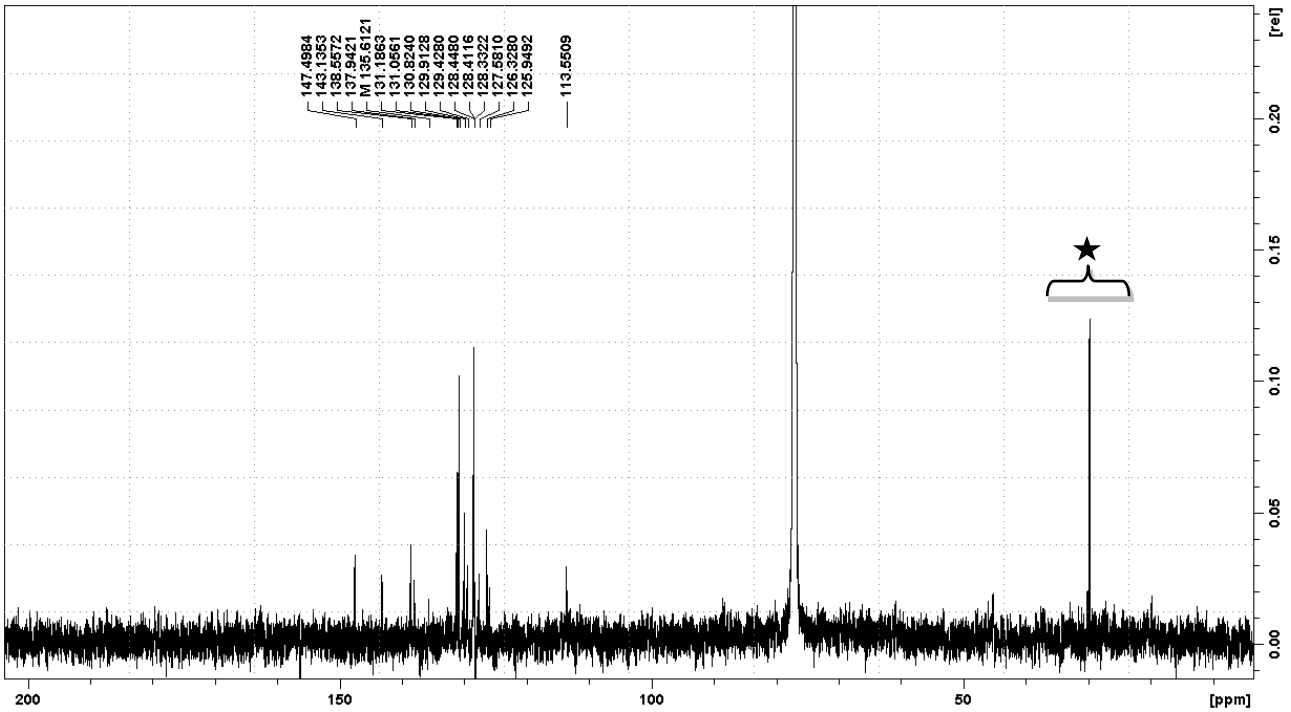


Figure S 30. ^{13}C NMR spectrum of **4** (176 MHz, $CDCl_3$, 300 K). Signals corresponding to residual solvents and impurities are marked with asterisks.

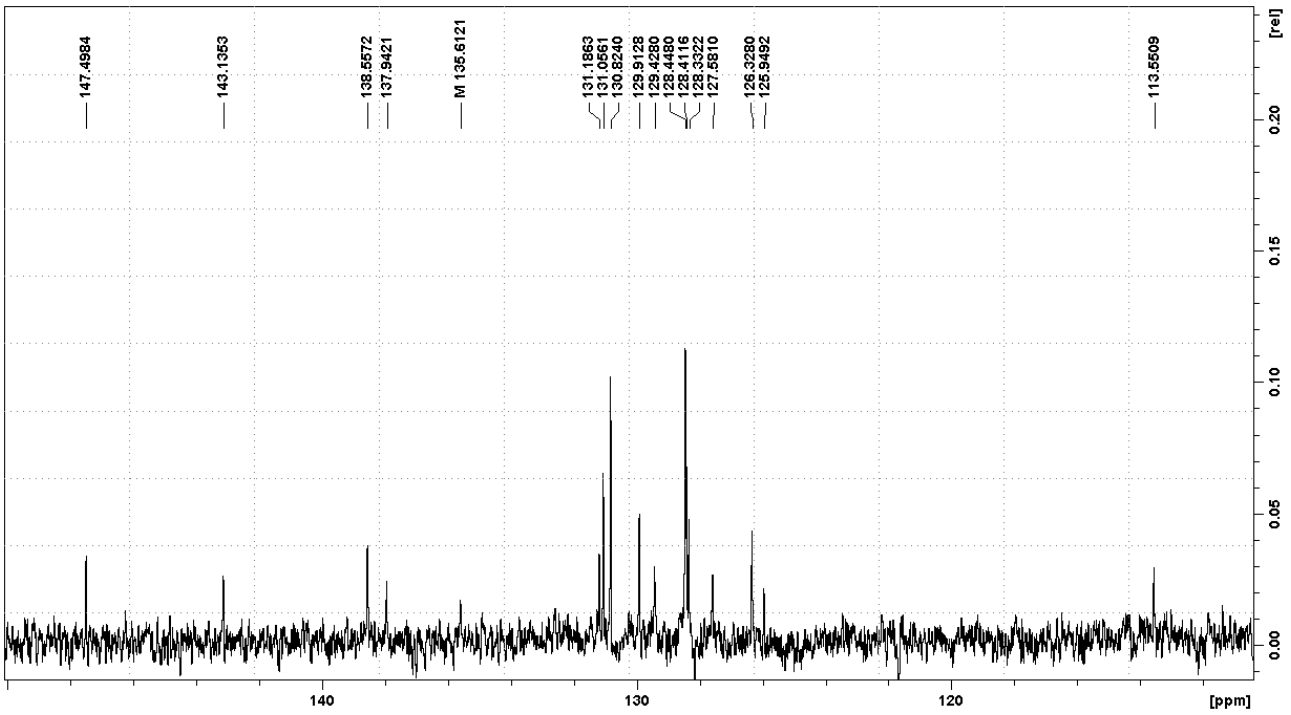


Figure S 31. Part of the ^{13}C NMR spectrum of **4** (176 MHz, $CDCl_3$, 300 K).

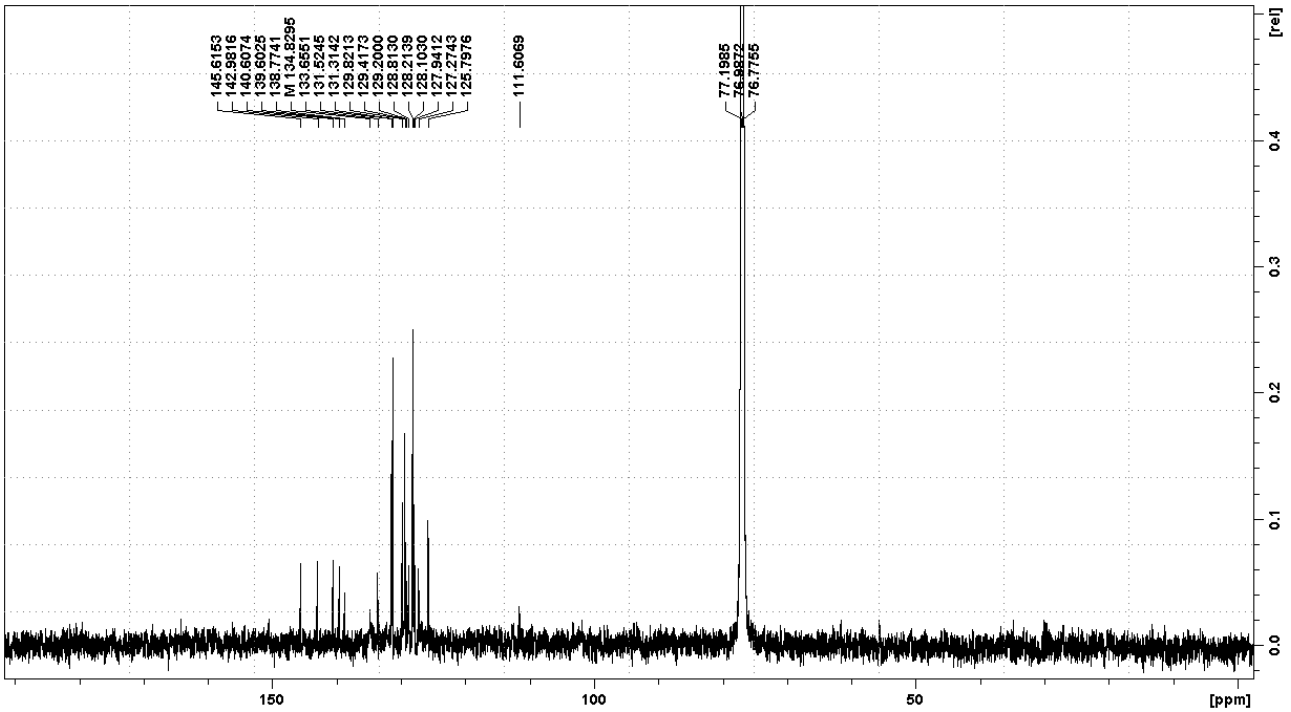


Figure S 32. ^{13}C NMR spectrum of **5** (176 MHz, $CDCl_3$, 300 K).

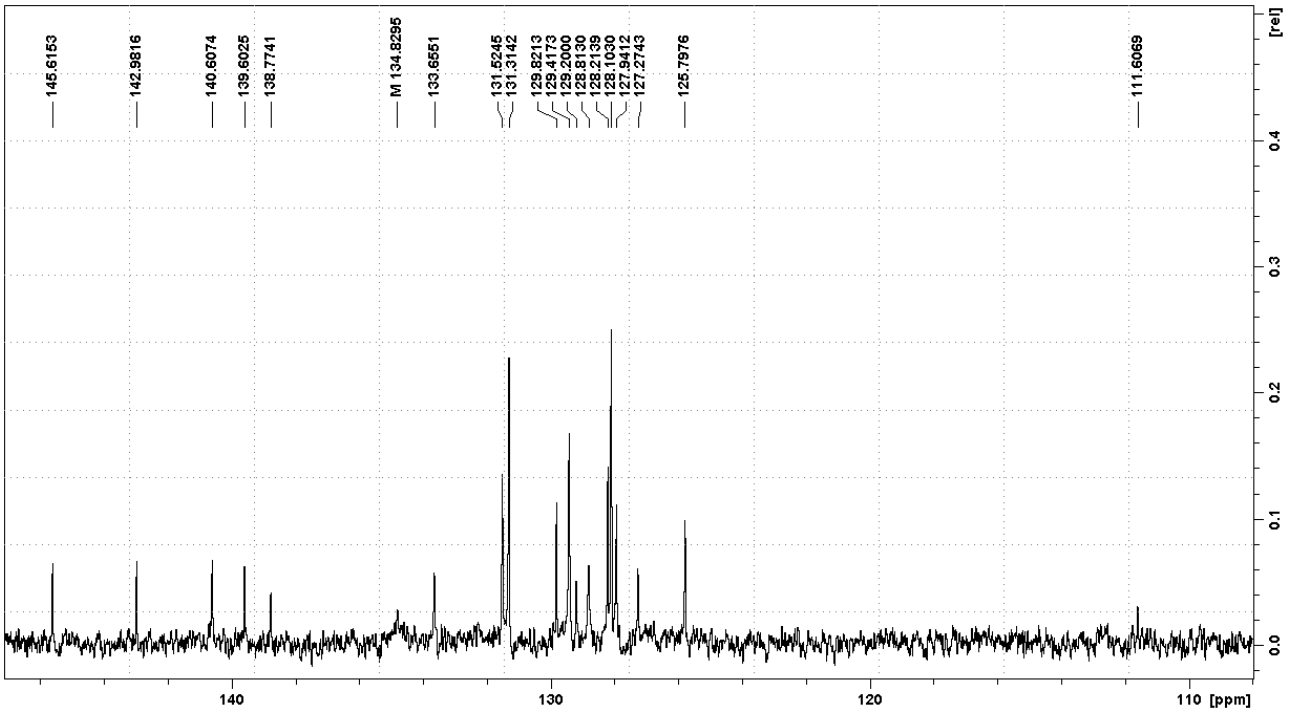


Figure S 33. Part of the ^{13}C NMR spectrum of **5** (176 MHz, $CDCl_3$, 300 K).

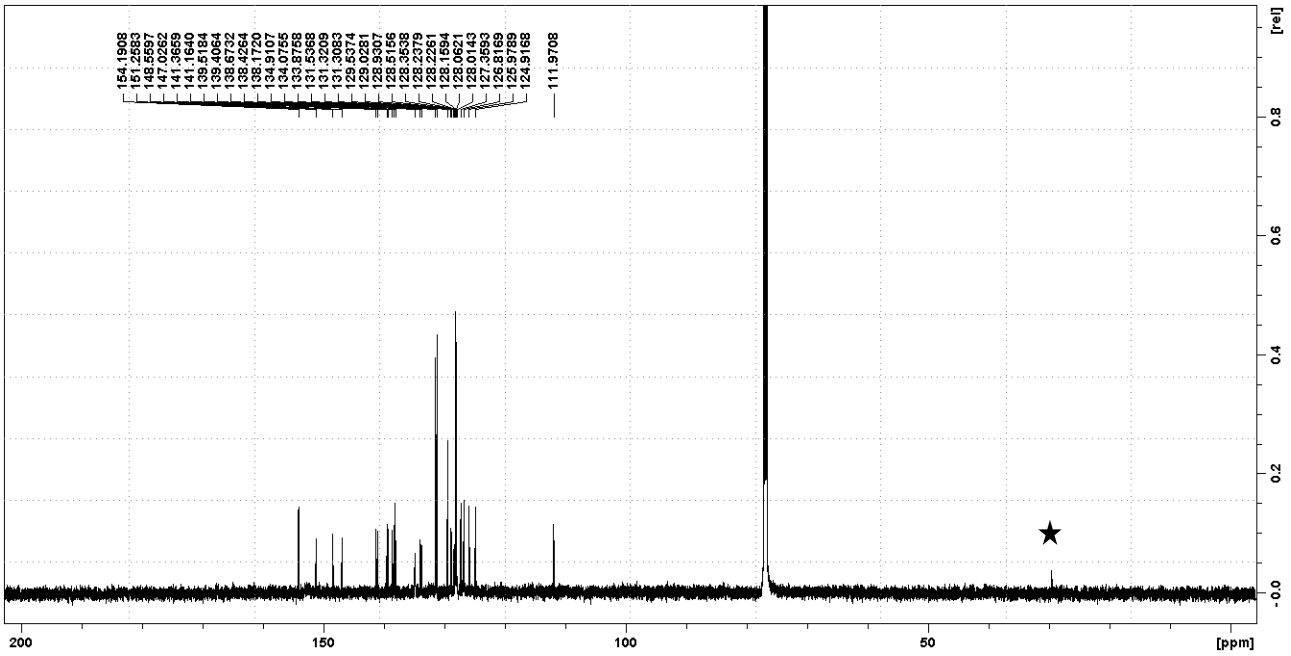


Figure S 34. ^{13}C NMR spectrum of **6** (151 MHz, $CDCl_3$, 300 K). Signals corresponding to residual solvents and impurities are marked with asterisks.

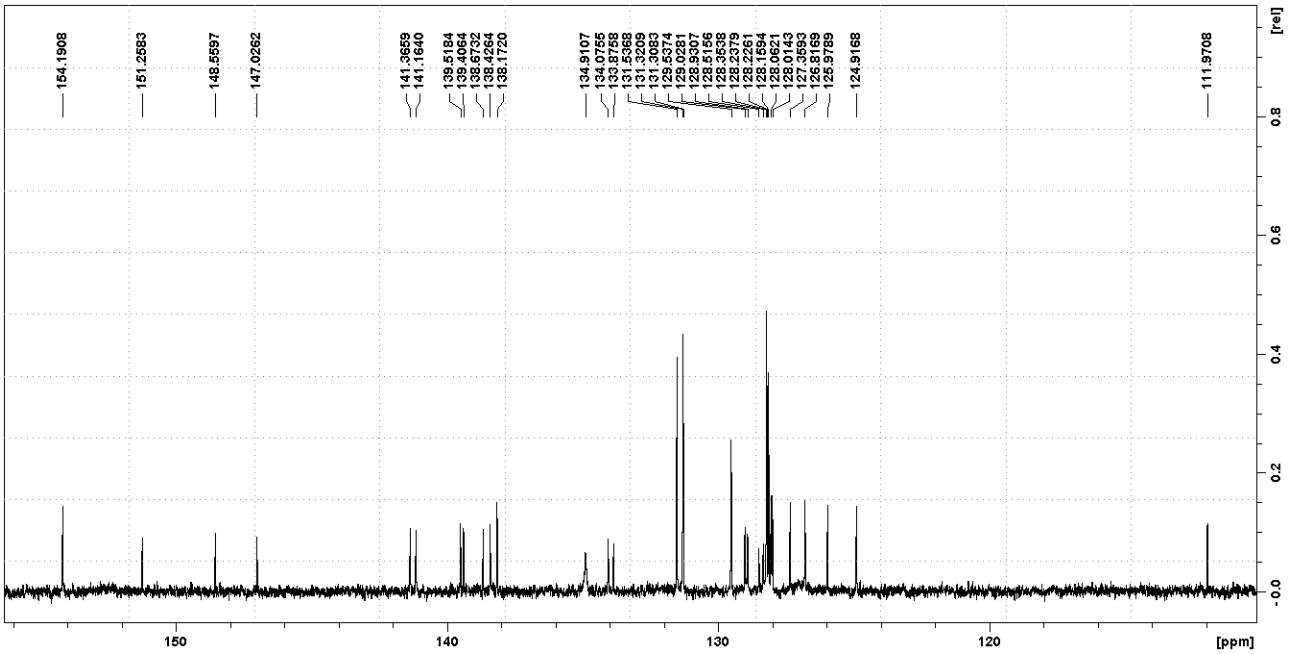


Figure S 35. Part of the ^{13}C NMR spectrum of **6** (151 MHz, $CDCl_3$, 300 K).

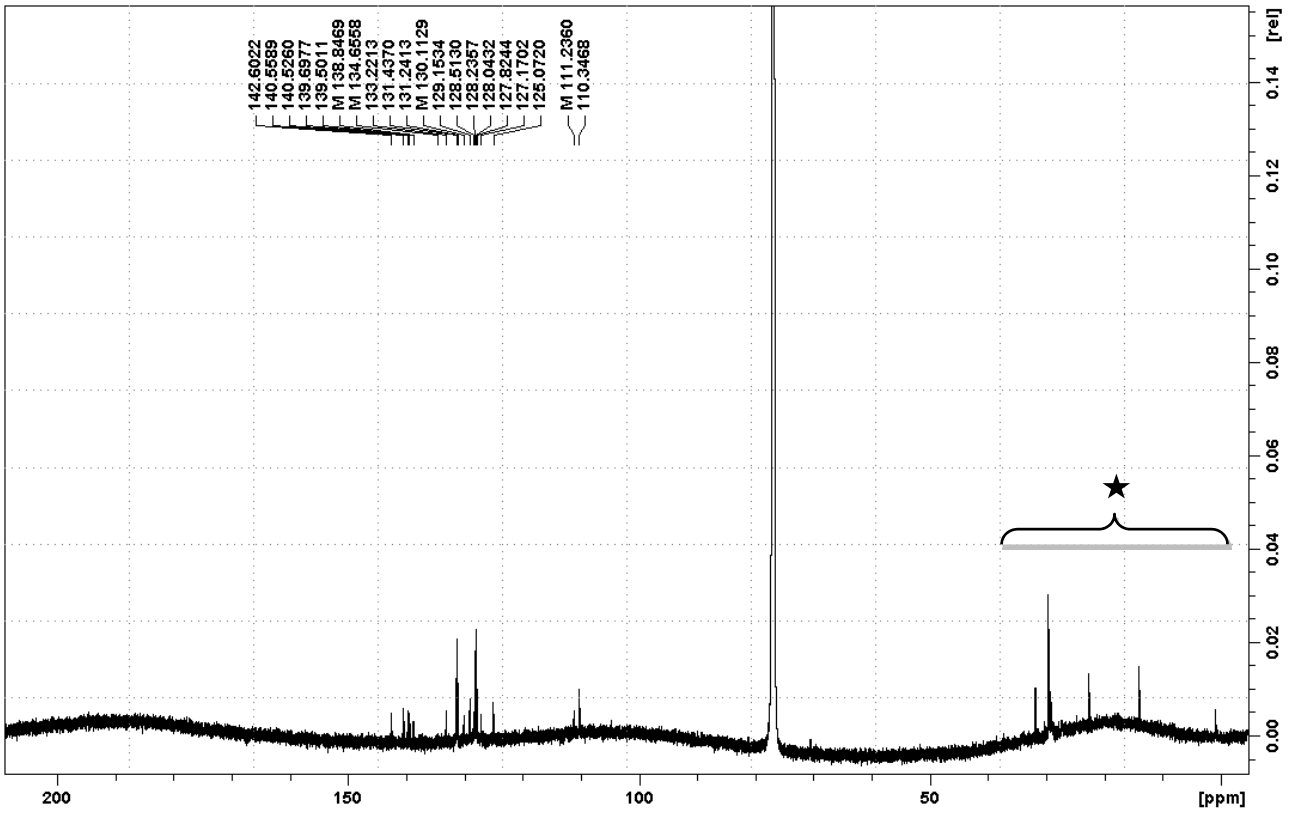


Figure S 36. ^{13}C NMR spectrum of **7** (176 MHz, $CDCl_3$, 300 K). Signals corresponding to residual solvents and impurities are marked with asterisks.

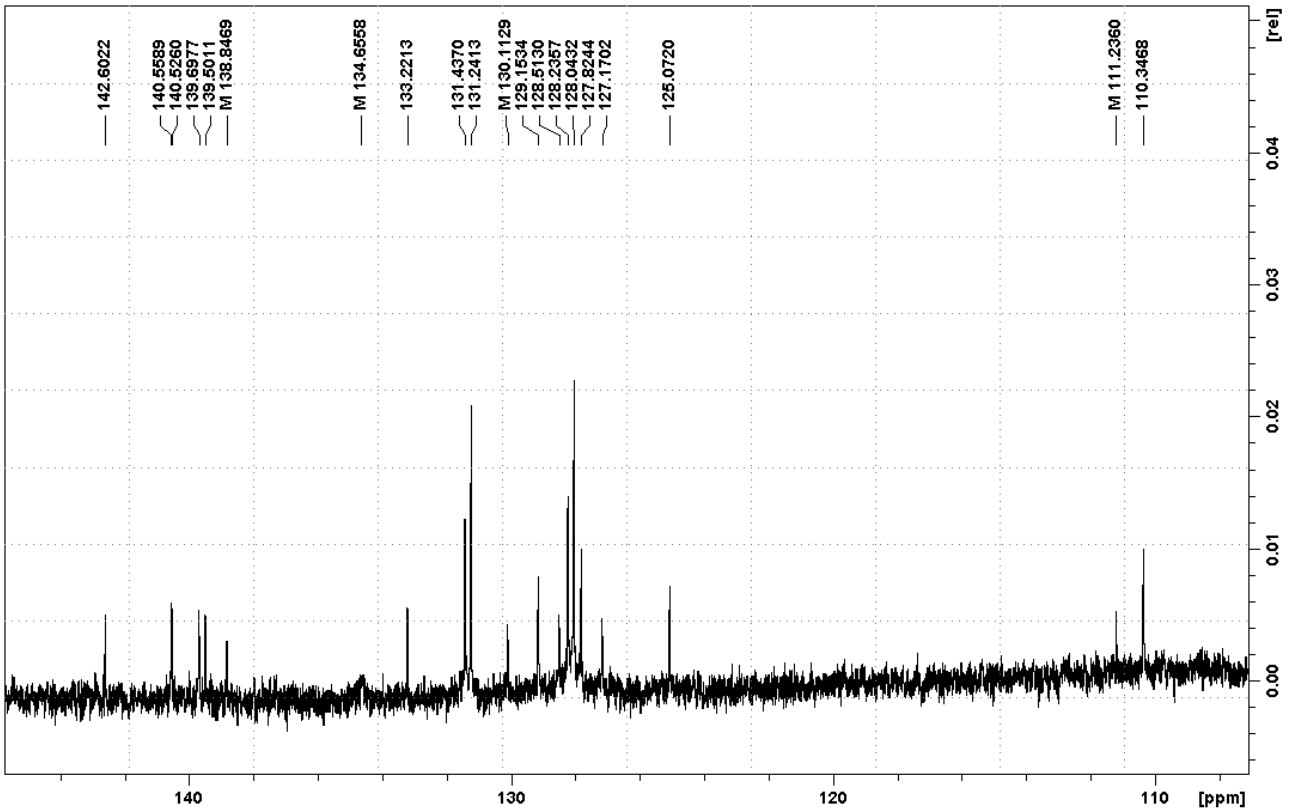


Figure S 37. Part of the ^{13}C NMR spectrum of **7** (176 MHz, $CDCl_3$, 300 K).

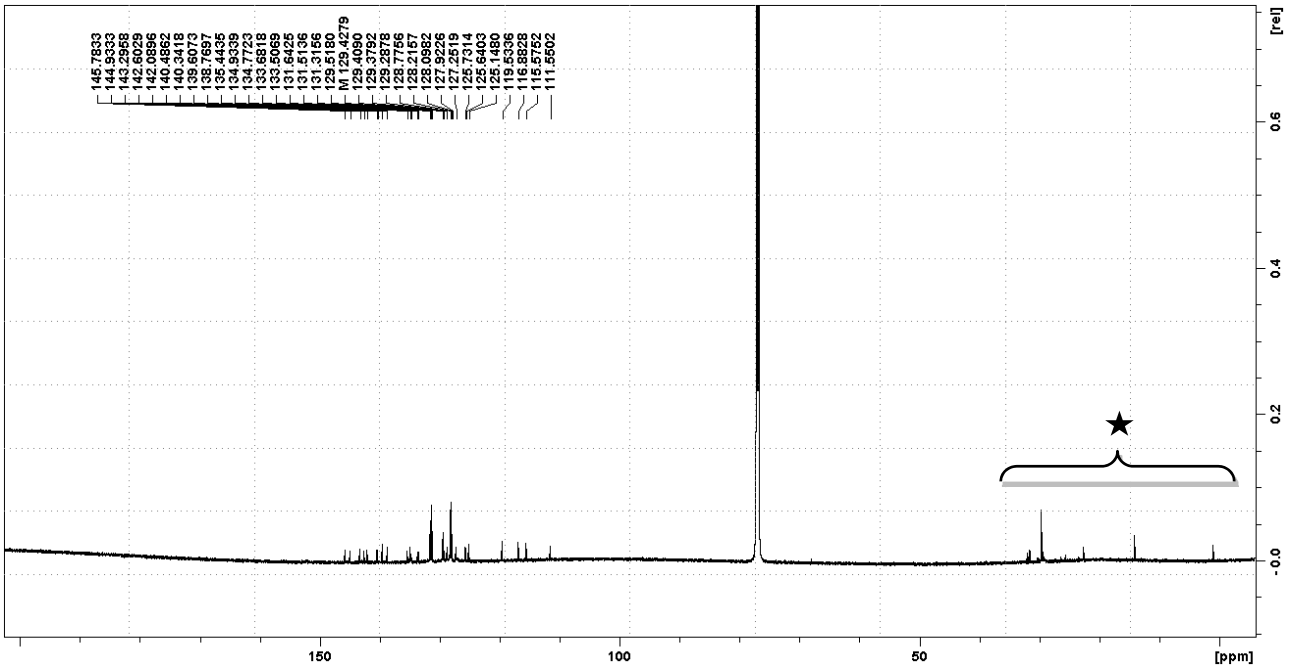


Figure S 38. ^{13}C NMR spectrum of **8** (176 MHz, $CDCl_3$, 300 K). Signals corresponding to residual solvents and impurities are marked with asterisks.

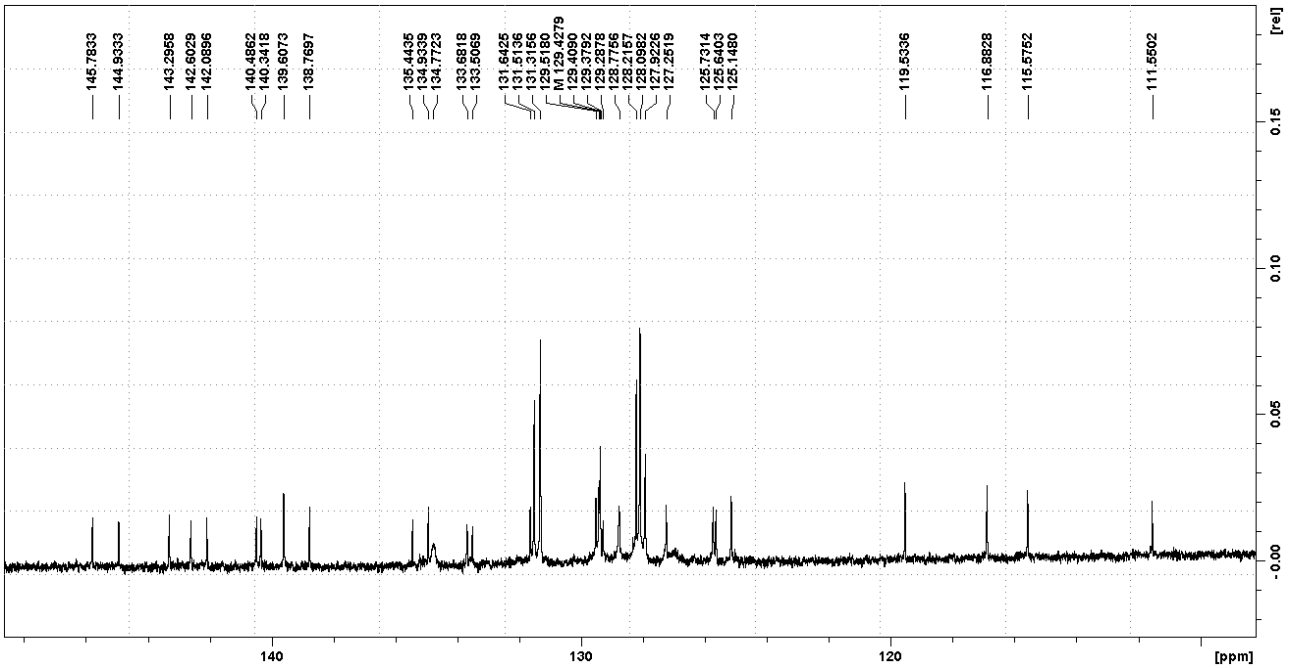


Figure S 39. Part of the ^{13}C NMR spectrum of **8** (176 MHz, $CDCl_3$, 300 K).

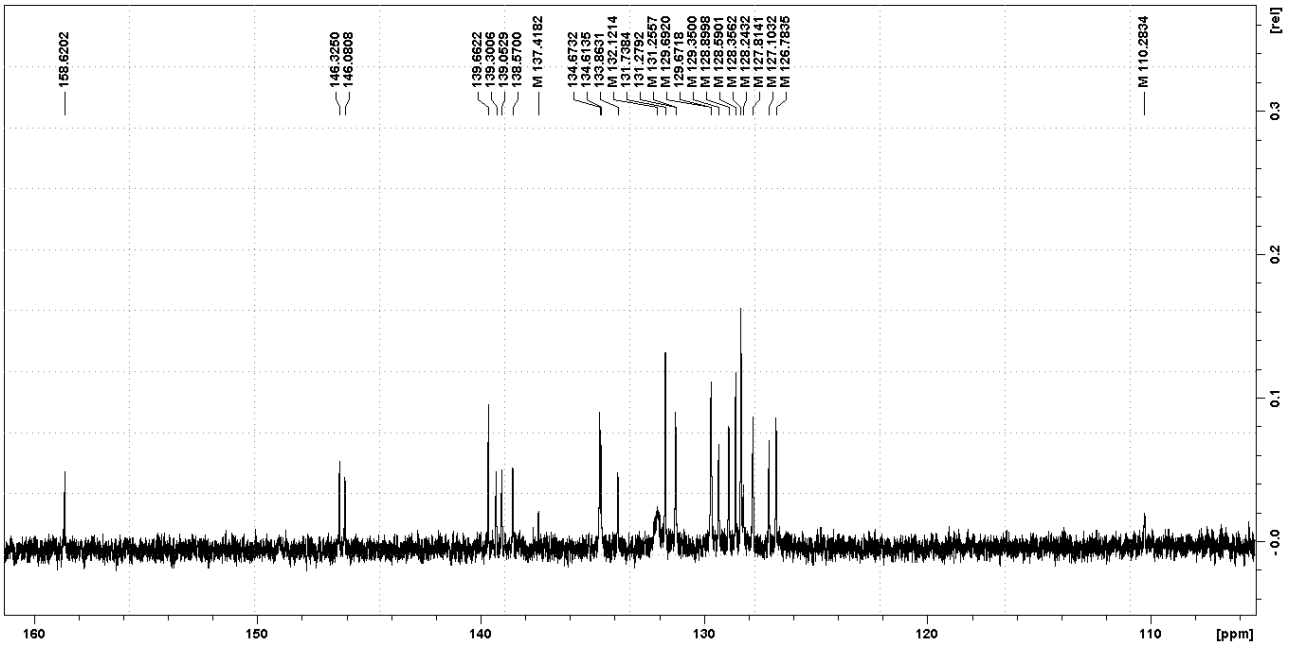


Figure S 40. The ^{13}C NMR spectrum of **9·HCl** (176 MHz, $CDCl_3$, 300 K).

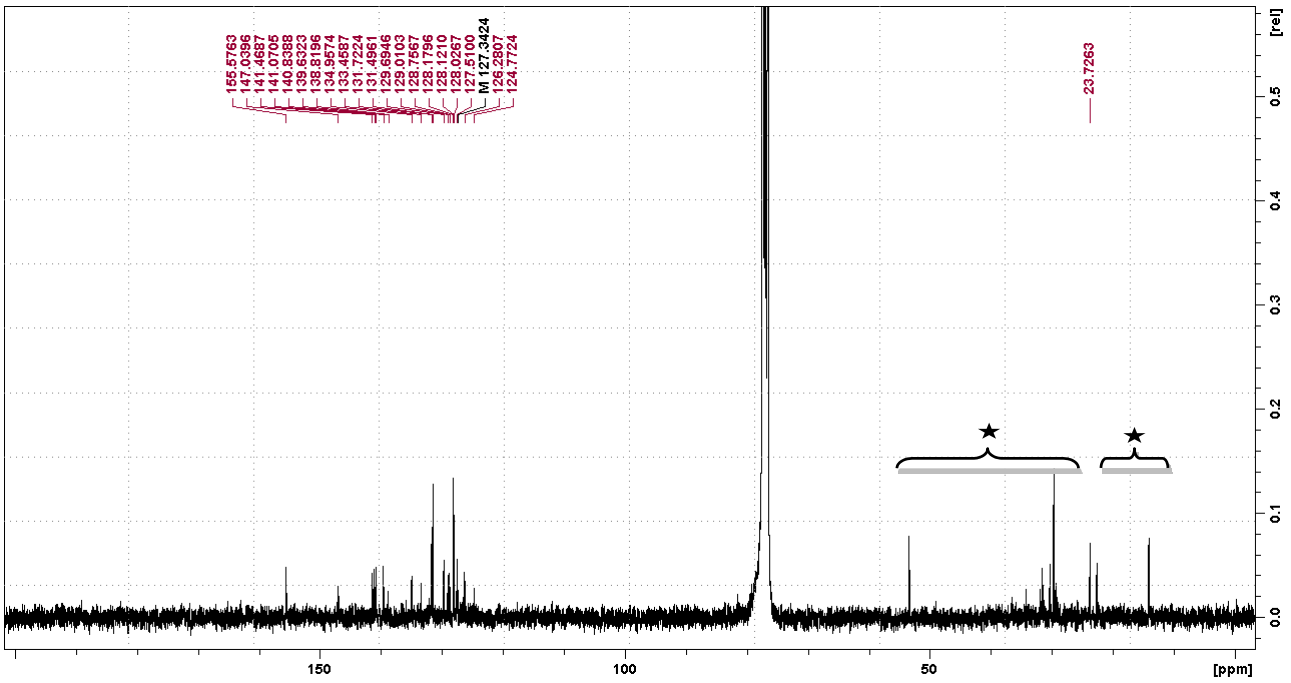


Figure S 41. ^{13}C NMR spectrum of 10 (75.5 MHz, $CDCl_3$, 300 K). Signals corresponding to residual solvents and impurities are marked with asterisks.

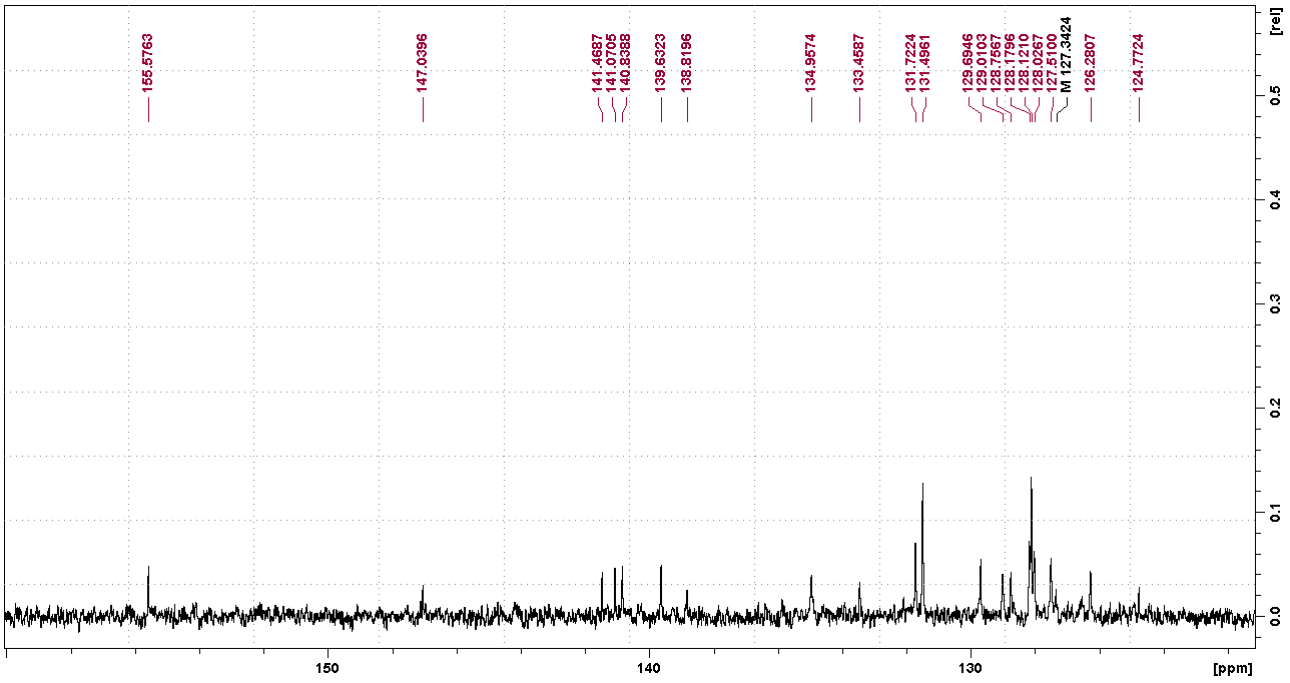


Figure S 42. Part of the ^{13}C NMR spectrum of **10** (75.5 MHz, $CDCl_3$, 300 K).

High-resolution mass spectra

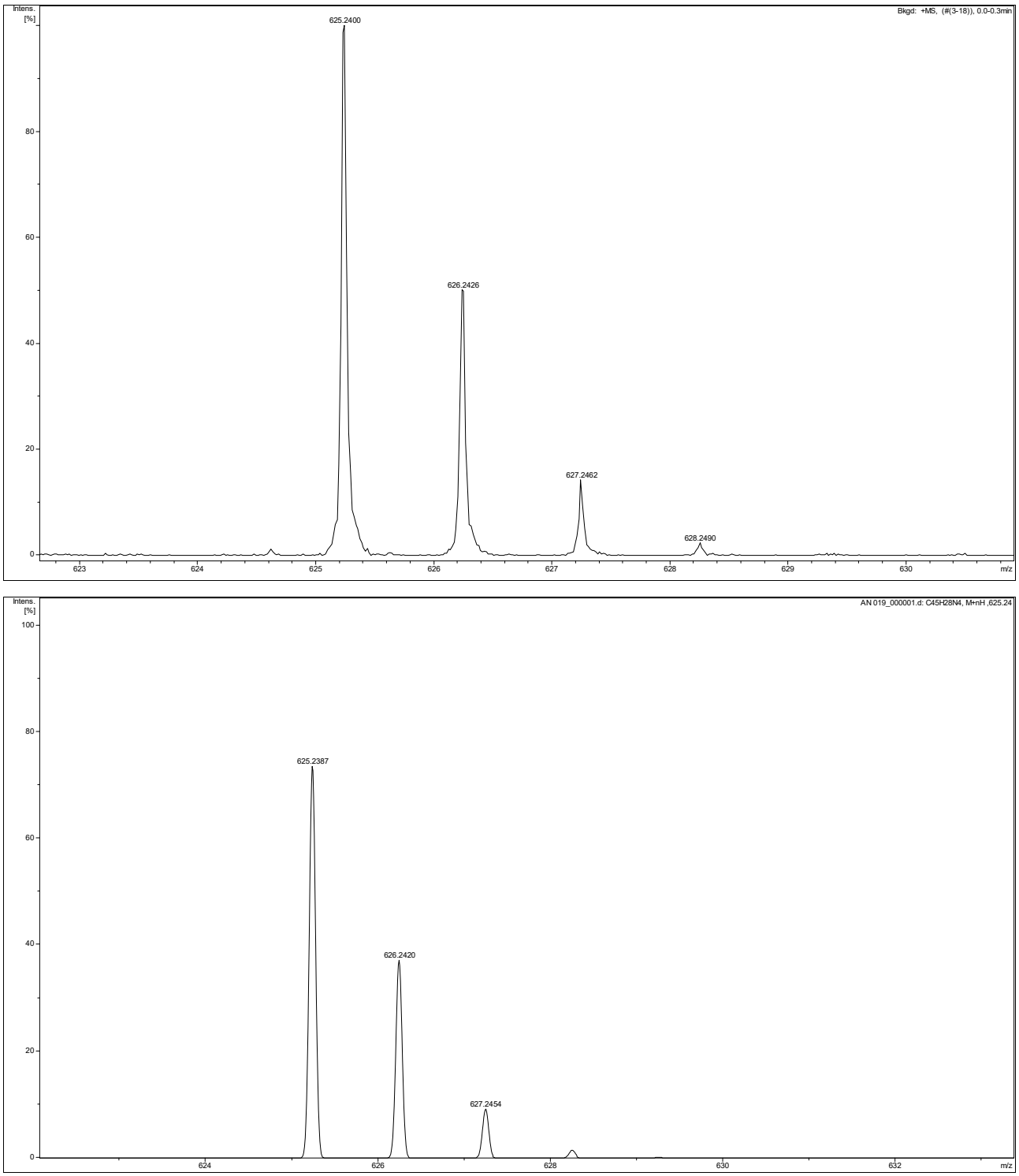


Figure S 43. HR-MS spectrum of **3** (ESI+, TOF, $[M+H]^+$) (top) and simulated pattern (bottom).

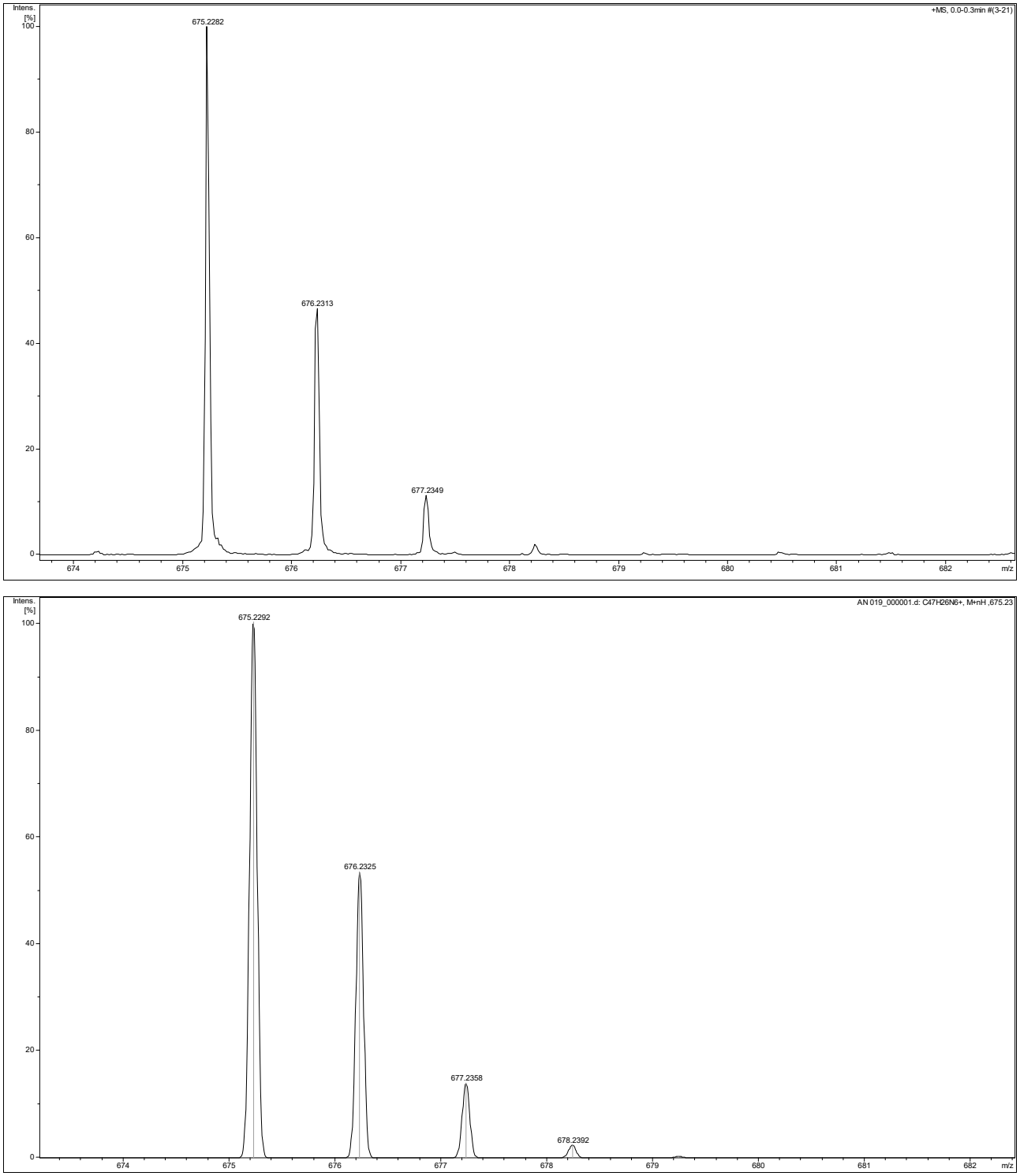


Figure S 44. HR-MS spectrum of **4** (ESI+, TOF, $[M+H]^+$) (top) and simulated pattern (bottom).

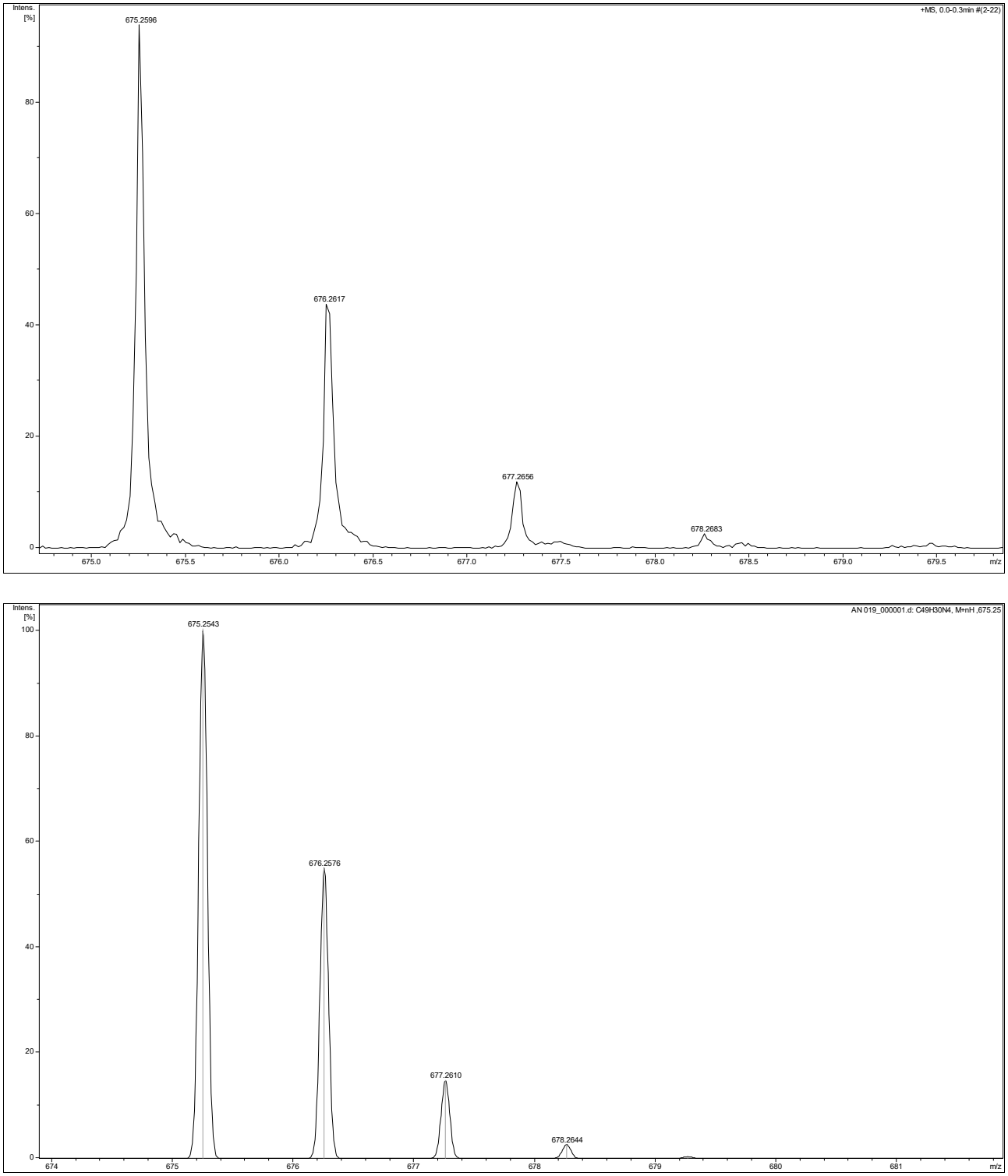


Figure S 45. HR-MS spectrum of **5** (ESI+, TOF, $[M+H]^+$) (top) and simulated pattern (bottom).

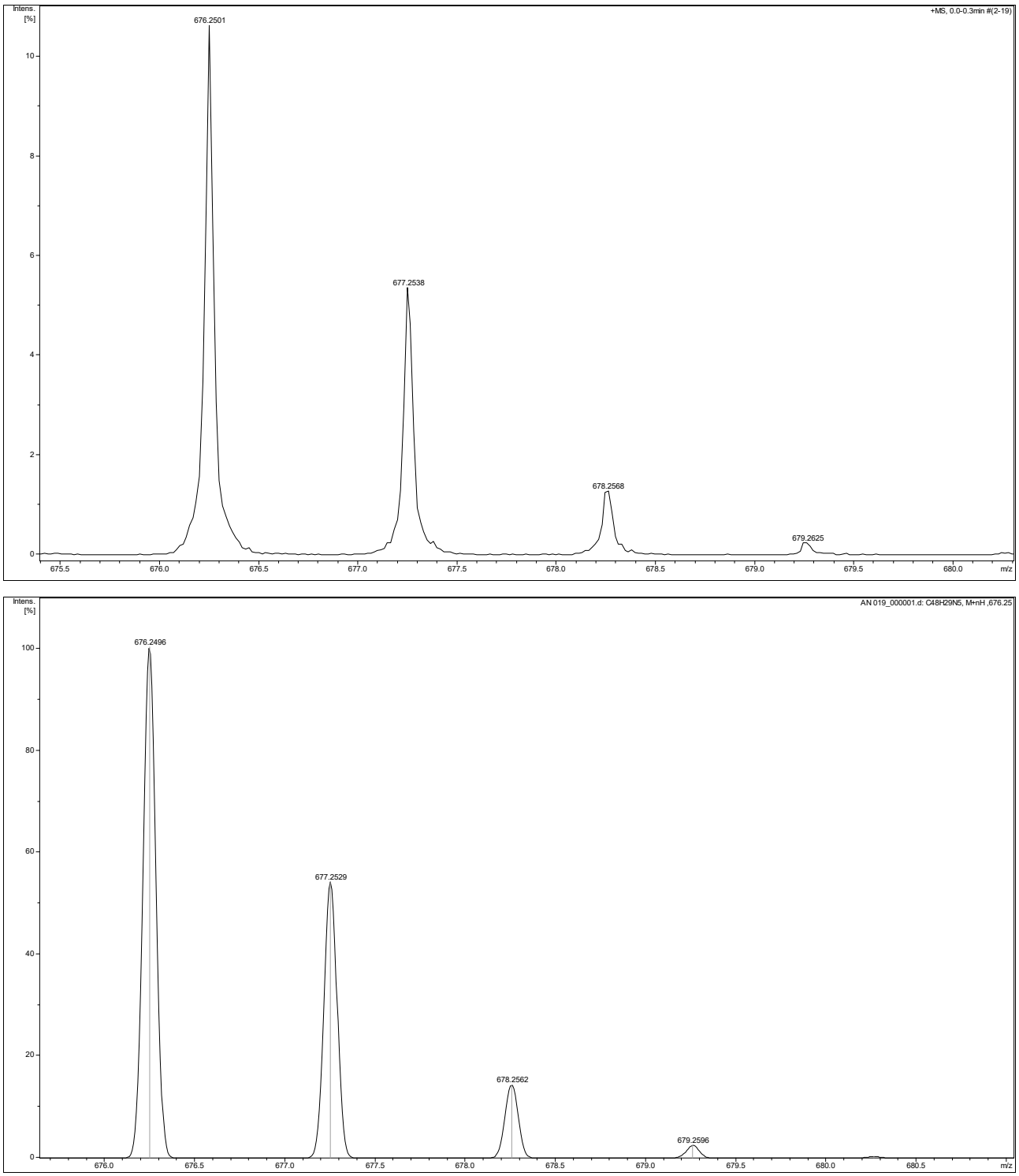


Figure S 46. HR-MS spectrum of **6** (ESI+, TOF, $[M+H]^+$) (top) and simulated pattern (bottom).

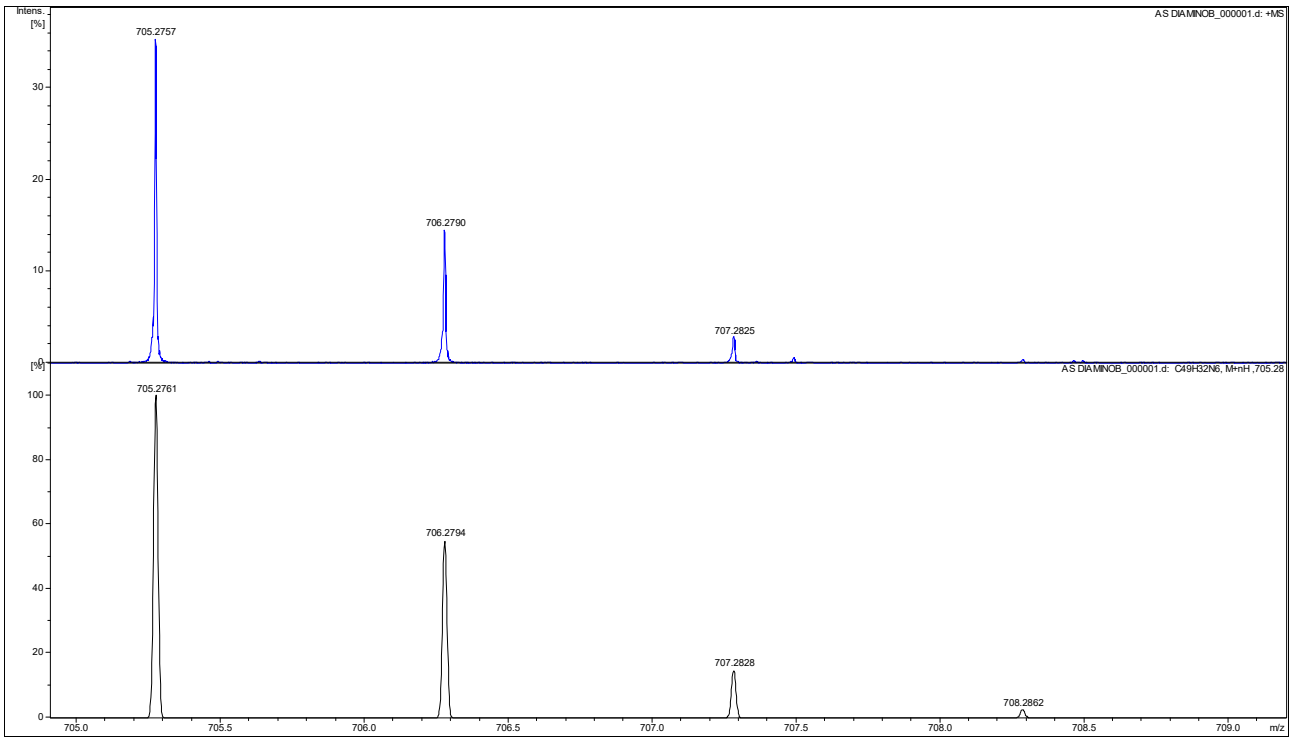


Figure S 47. HR-MS spectrum of **7** (ESI+, TOF, $[M+H]^+$) (top) and simulated pattern (bottom).

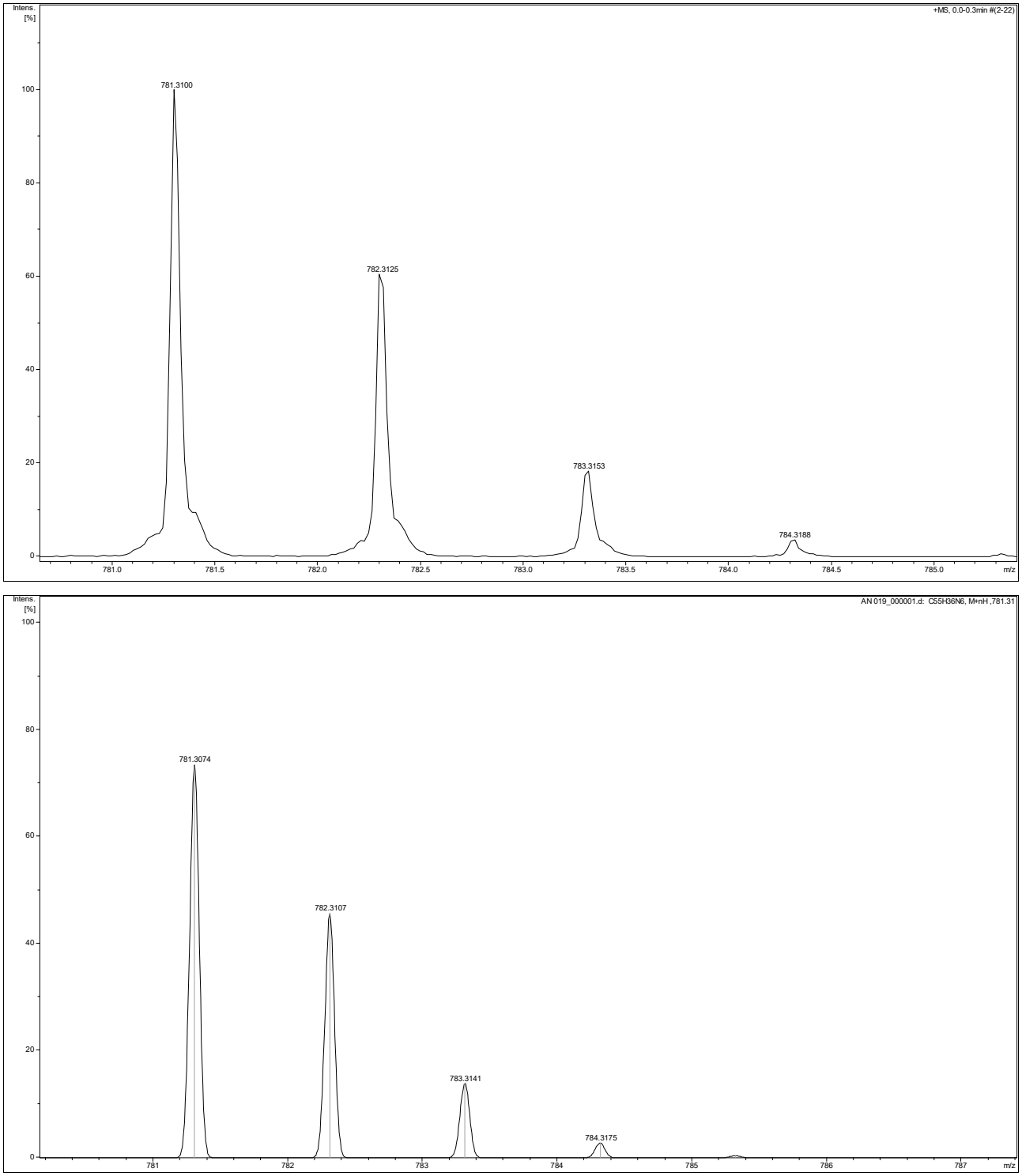


Figure S 48. HR-MS spectrum of **8** (ESI+, TOF, $[M+H]^+$) (top) and simulated pattern (bottom).

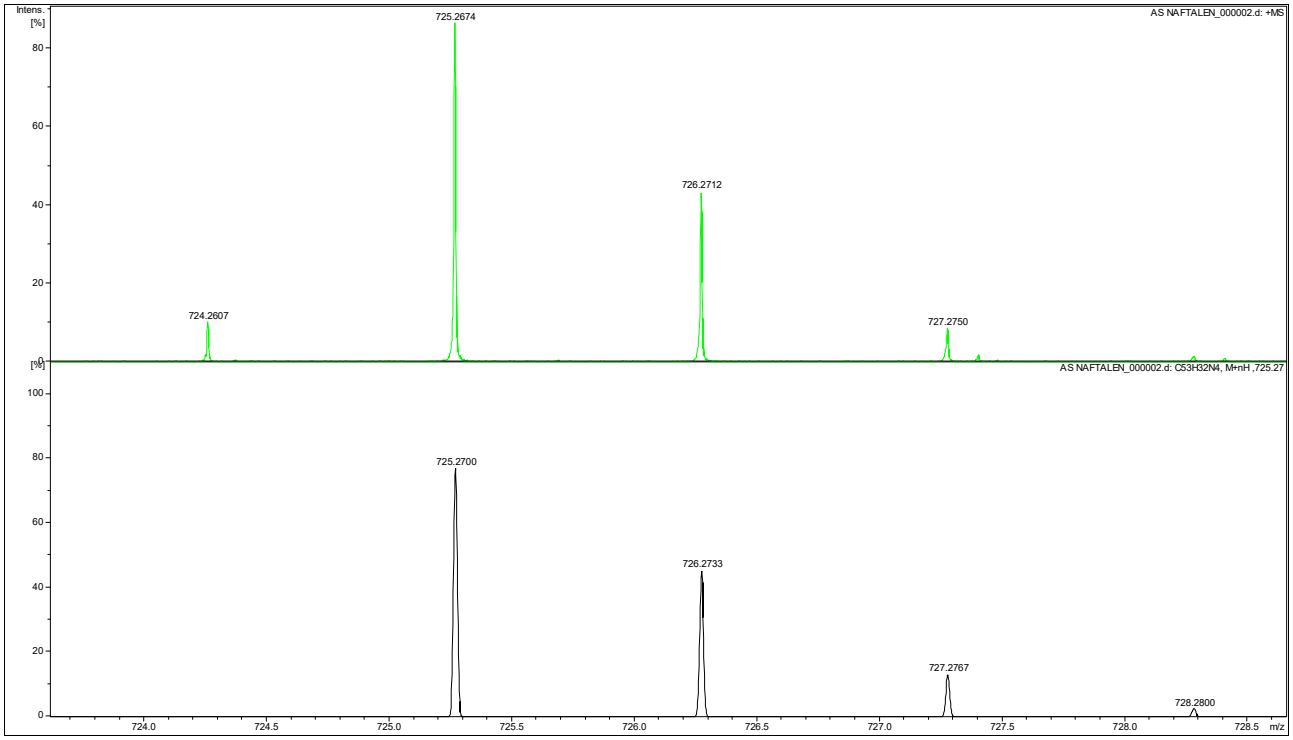


Figure S 49. HR-MS spectrum of **9** (ESI+, TOF, $[M+H]^+$) (top) and simulated pattern (bottom).

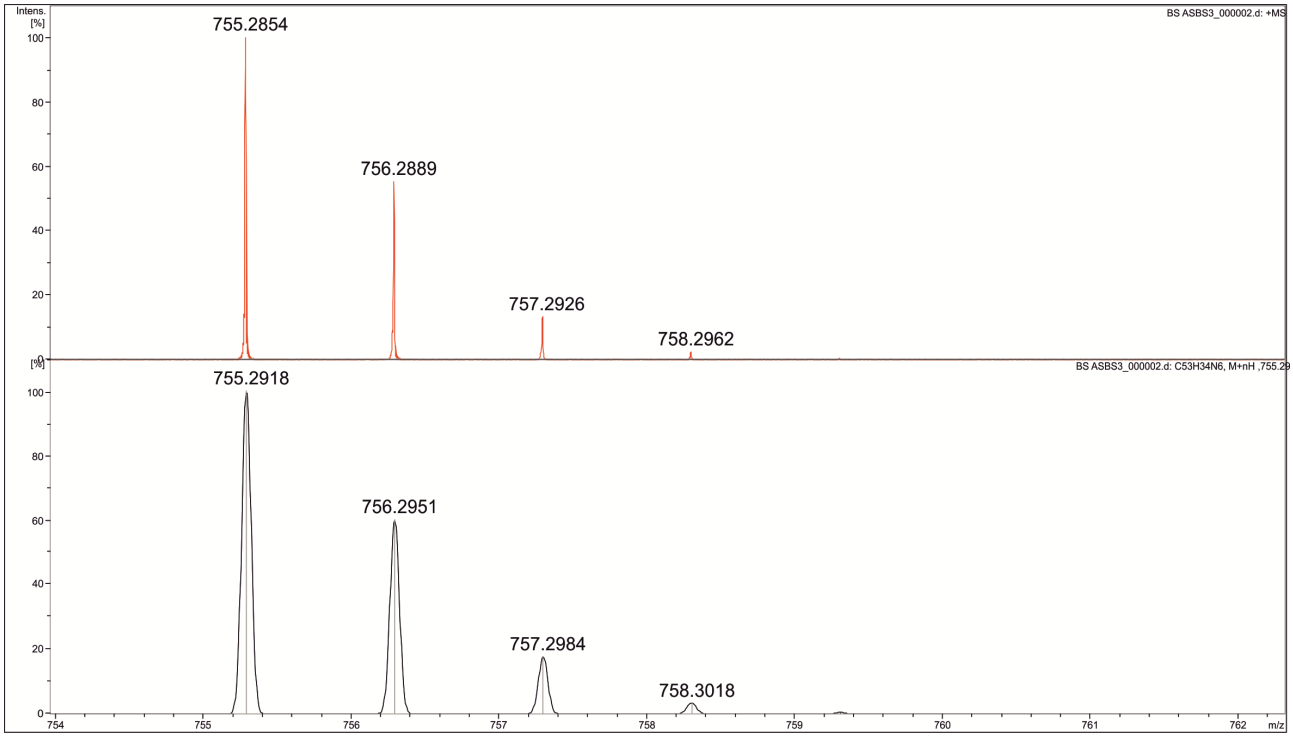


Figure S 50. HR-MS spectrum of **10** (ESI+, TOF, $[M+H]^+$) (top) and simulated pattern (bottom).

Absorption spectra in DCM

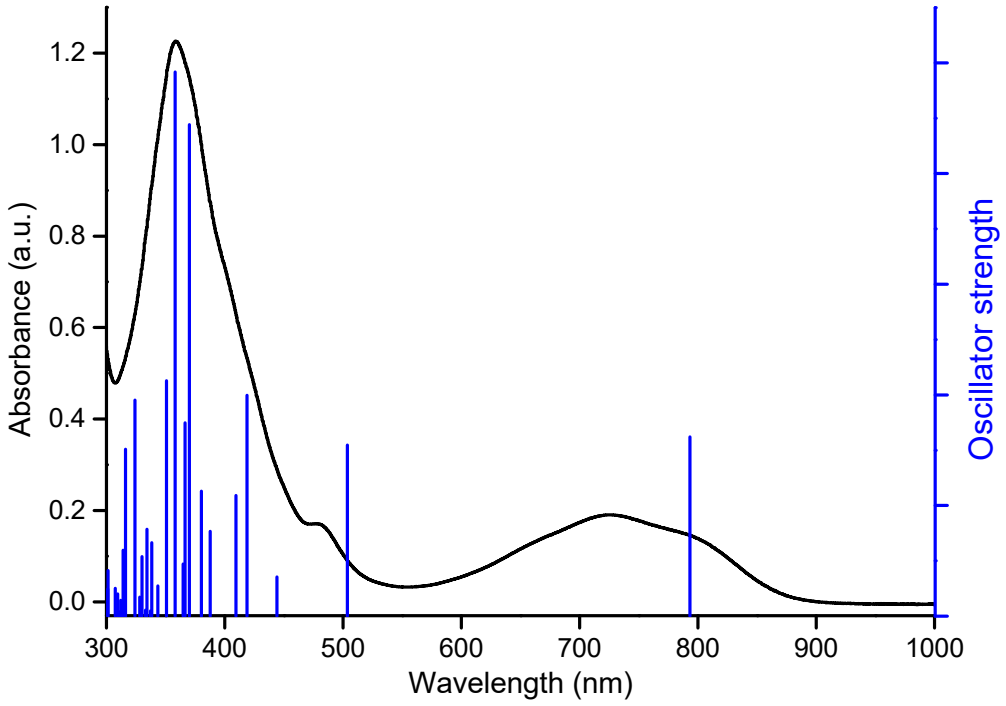


Figure S 51. UV-vis absorption spectrum of **3** (dichloromethane, 298 K) and calculated oscillator strength.

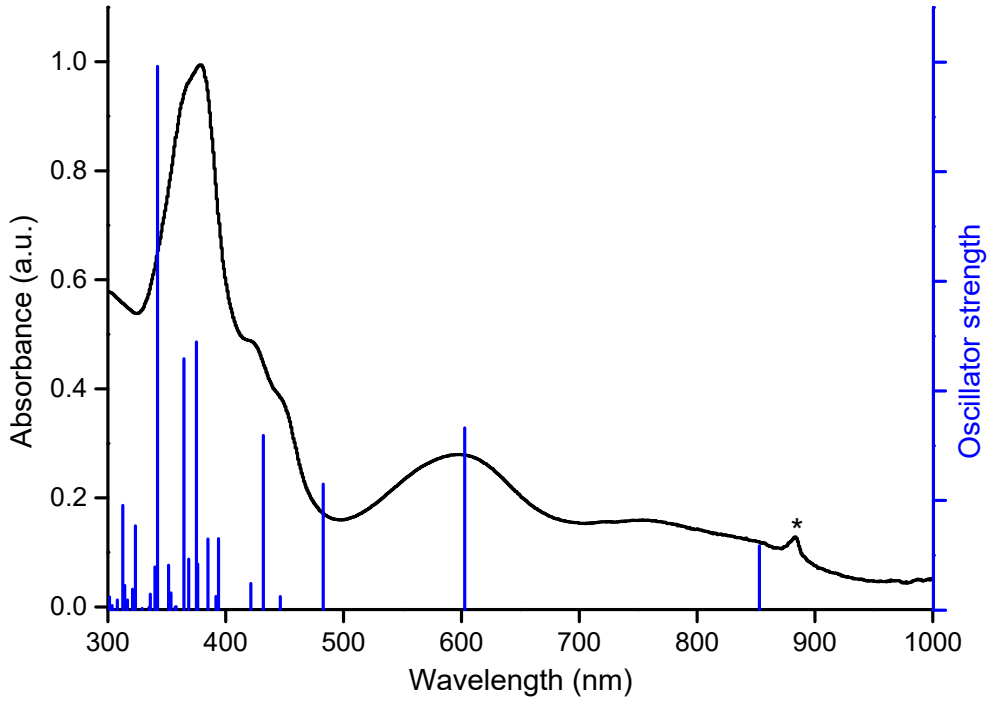


Figure S 52. UV-vis absorption spectrum of **4** (dichloromethane, 298 K) and calculated oscillator strength.

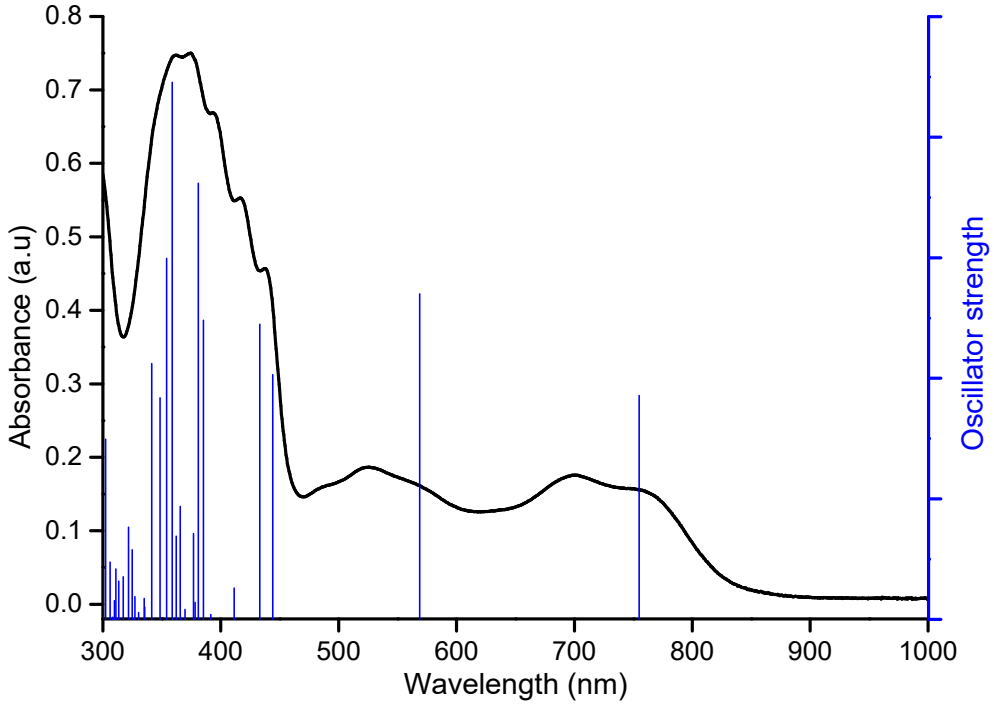


Figure S 53. UV-vis absorption spectrum of **5** (dichloromethane, 298 K) and calculated oscillator strength.

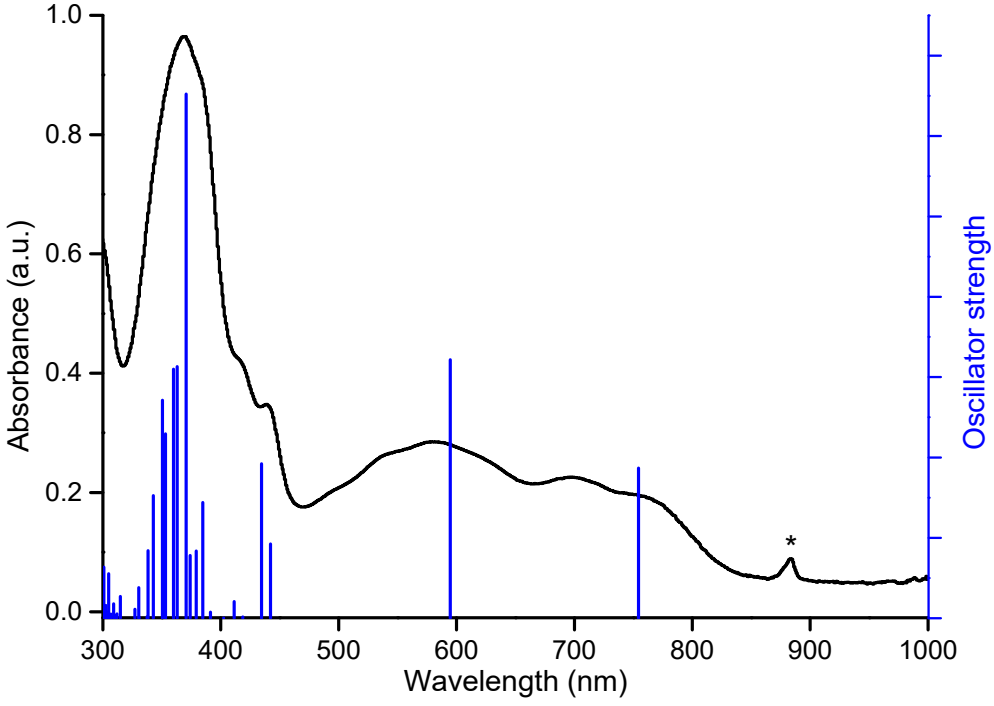


Figure S 54. UV-vis absorption spectrum of **6** (dichloromethane, 298 K) and calculated oscillator strength.

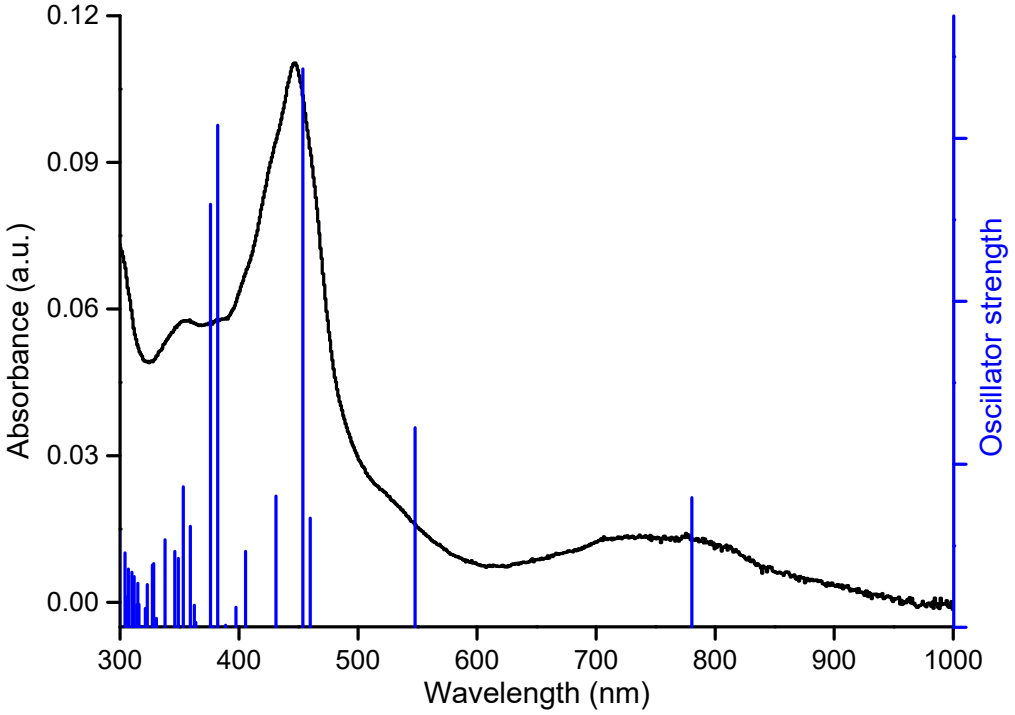


Figure S 55. UV-vis absorption spectrum of **7** (dichloromethane, 298 K) and calculated oscillator strength.

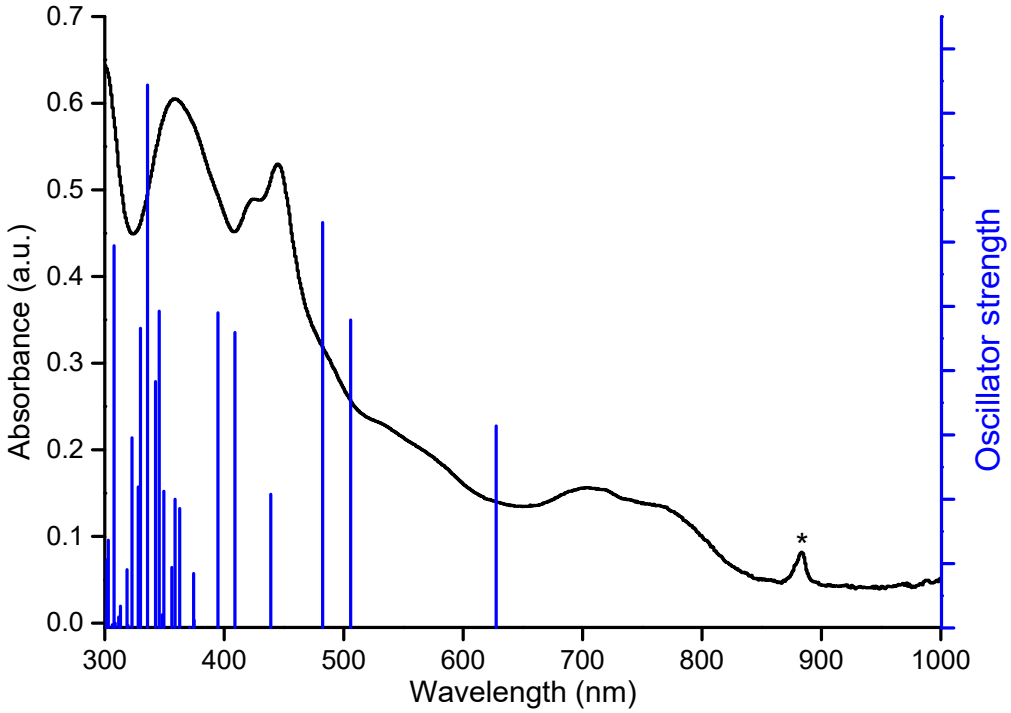


Figure S 56. UV-vis absorption spectrum of **8** (dichloromethane, 298 K) and calculated oscillator strength.

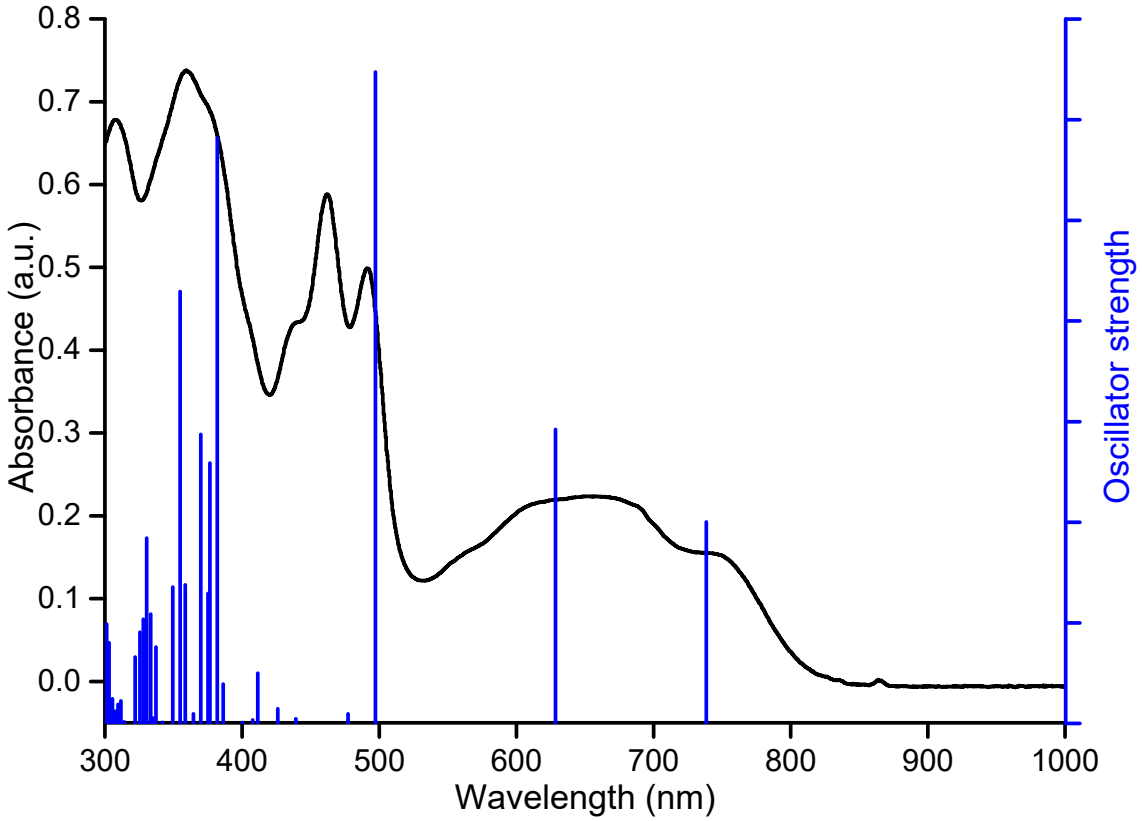


Figure S 57. UV-vis absorption spectrum of **9** (dichloromethane, 298 K) and calculated oscillator strength.

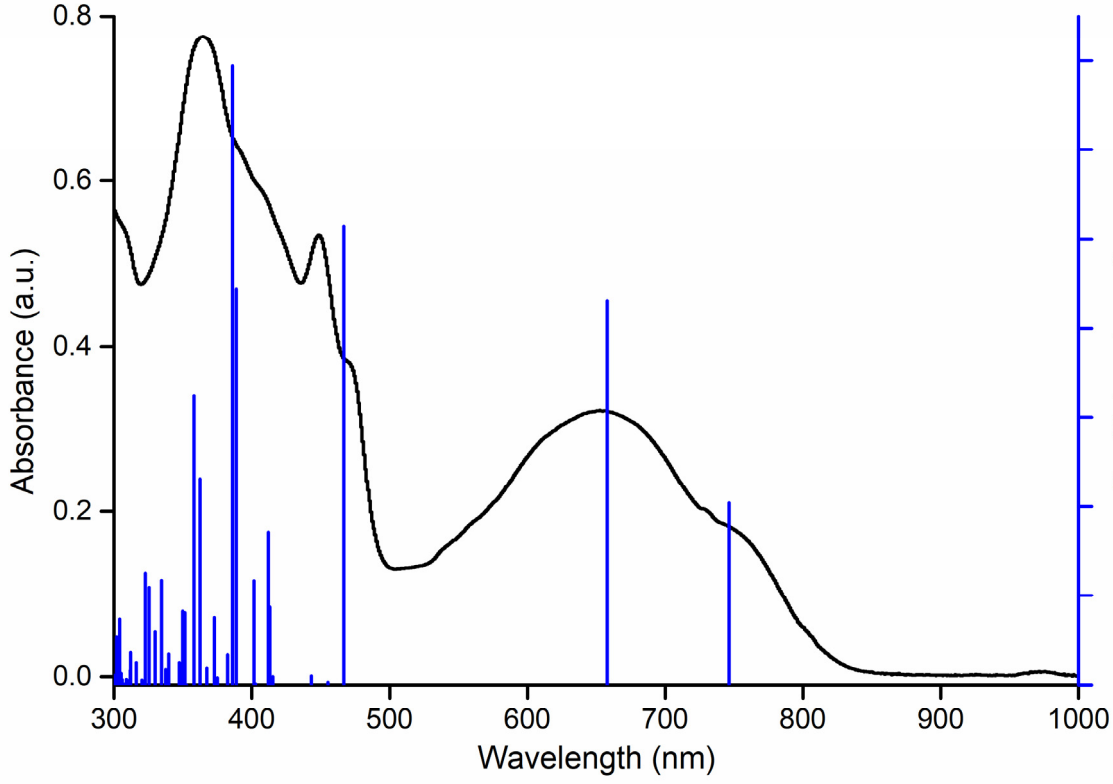


Figure S 58. UV-vis absorption spectrum of **10** (dichloromethane, 298 K) and calculated oscillator strength.

Absorption spectra in toluene

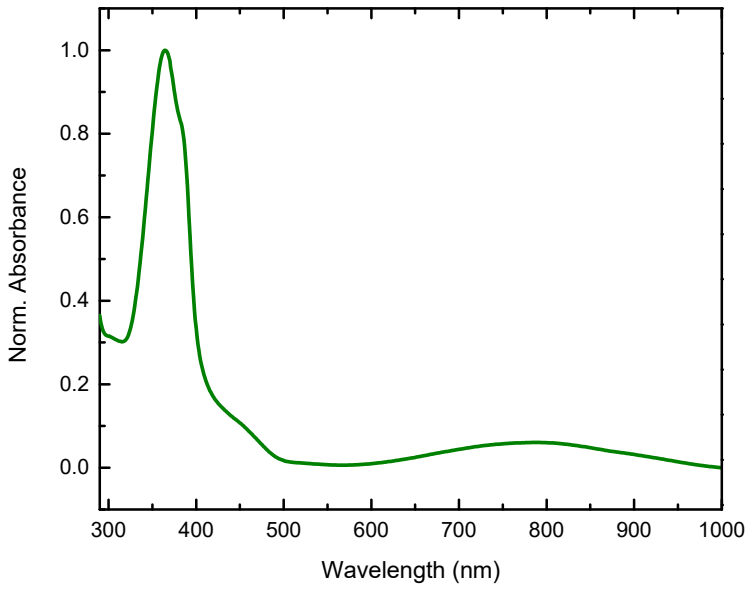


Figure S 59. The absorption spectrum of **1** (toluene, 298 K).

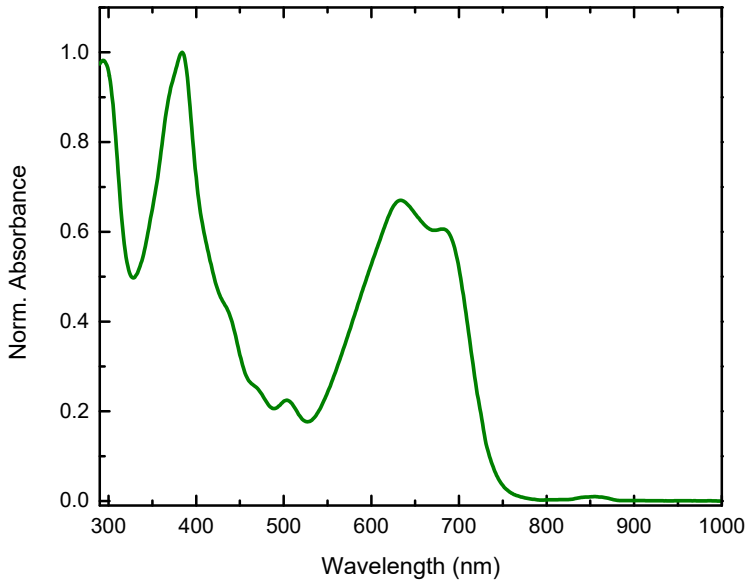


Figure S 60. The absorption spectrum of **2** (toluene, 298 K).

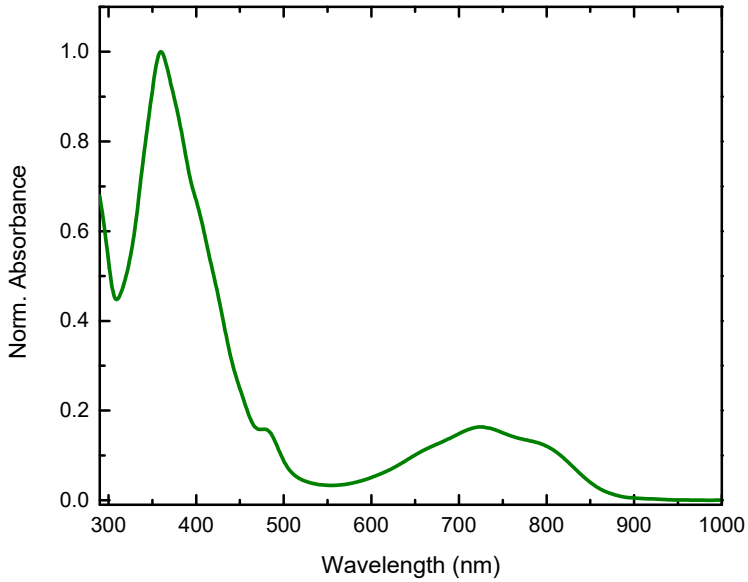


Figure S 61. The absorption spectrum of **3** (toluene, 298 K).

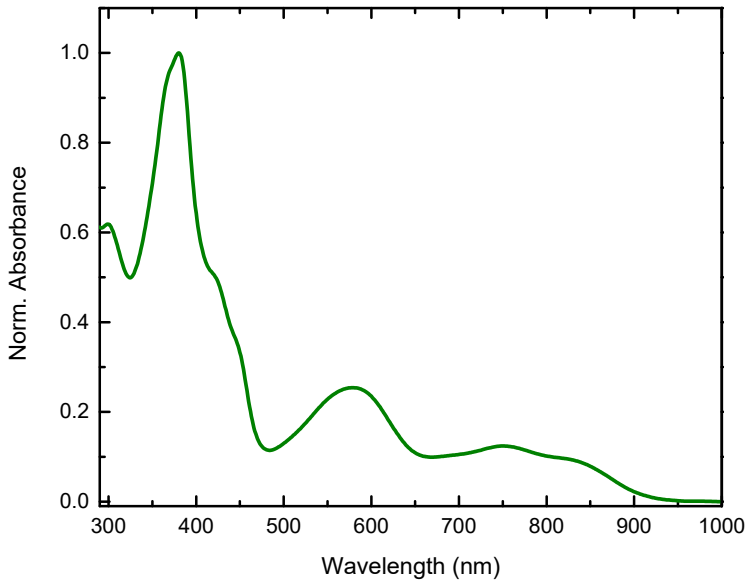


Figure S 62. The absorption spectrum of **4** (toluene, 298 K).

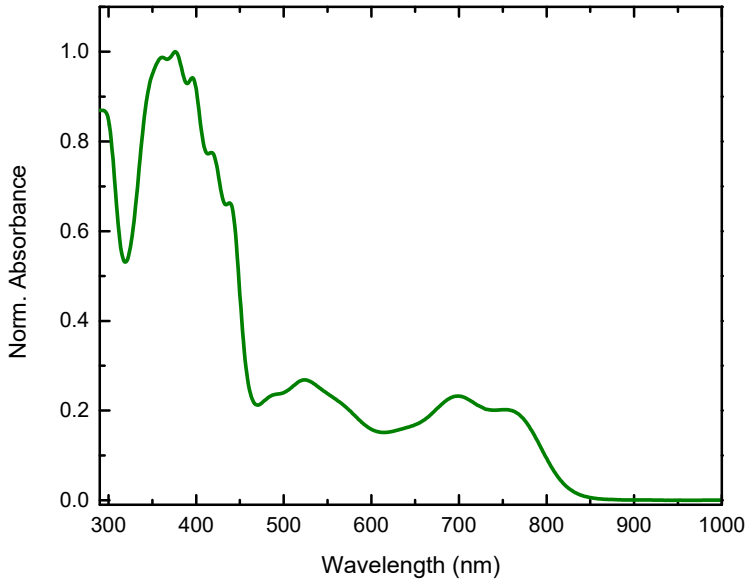


Figure S 63. The absorption spectrum of **5** (toluene, 298 K).

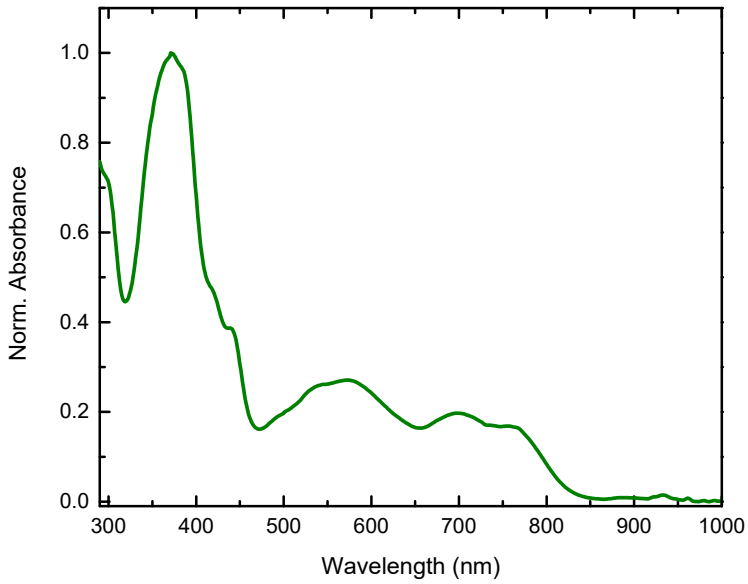


Figure S 64. The absorption spectrum of **6** (toluene, 298 K).

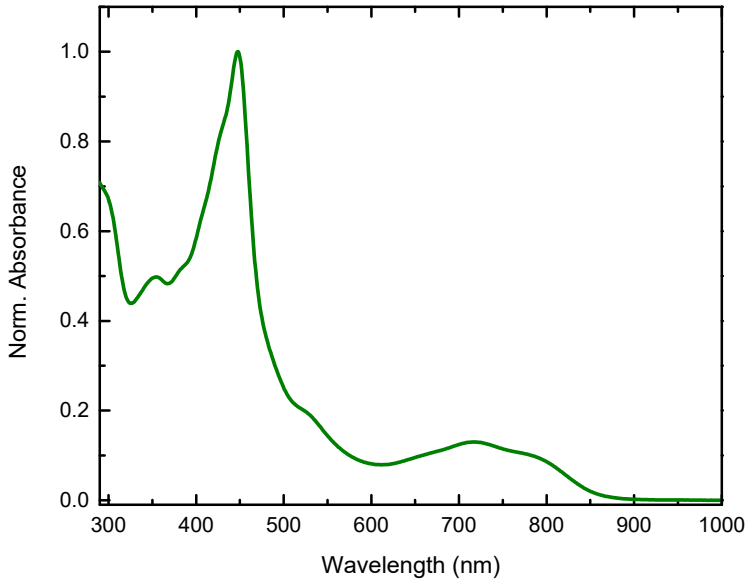


Figure S 65. The absorption spectrum of **7** (toluene, 298 K).

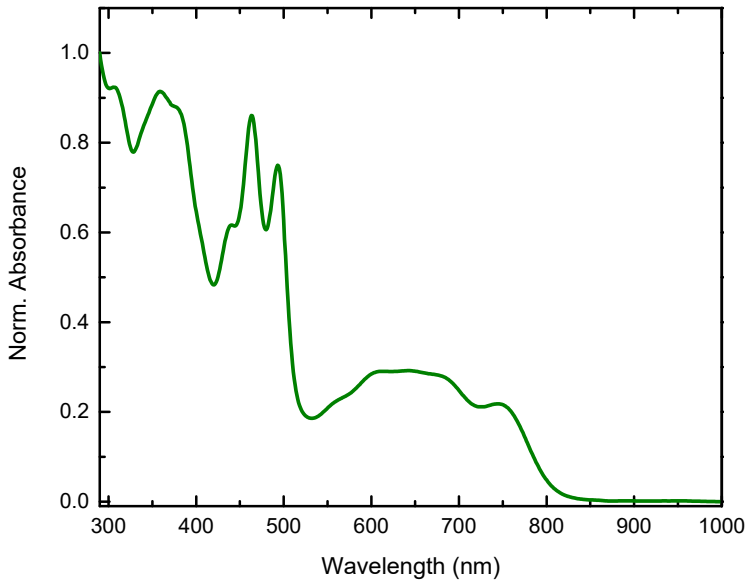


Figure S 66. The absorption spectrum of **9** (toluene, 298 K).

Electrochemistry

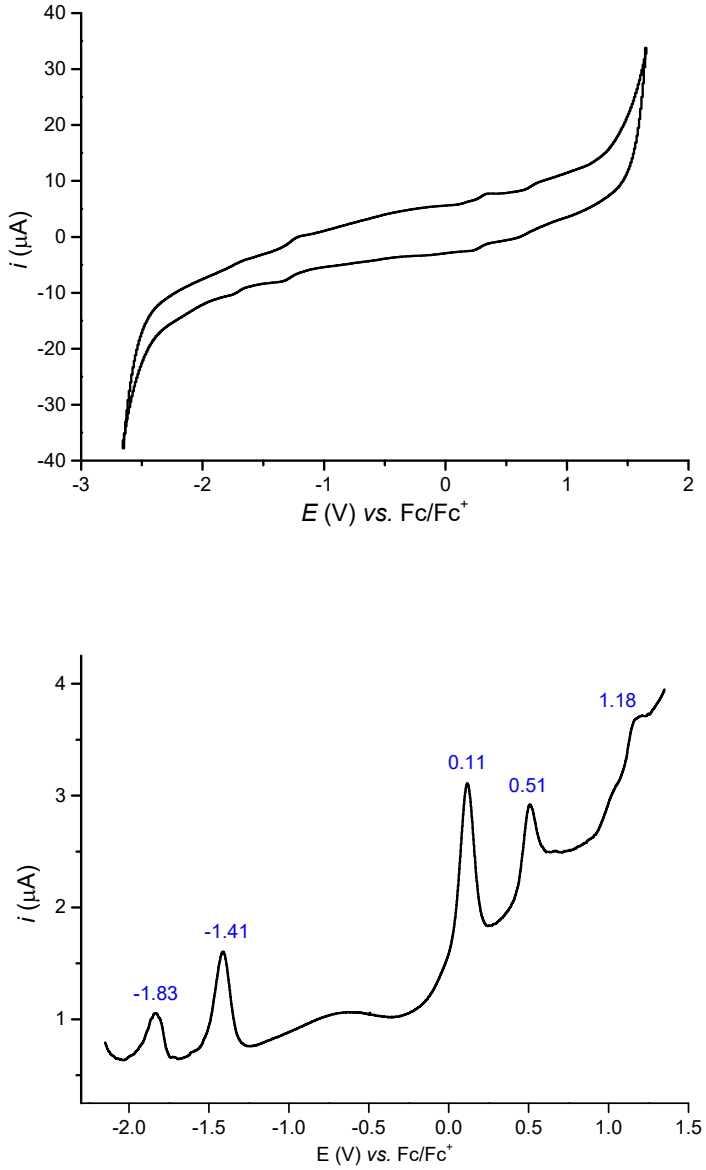


Figure S 67. Cyclic (top) and differential pulse voltammograms (bottom) of **1** in DCM.

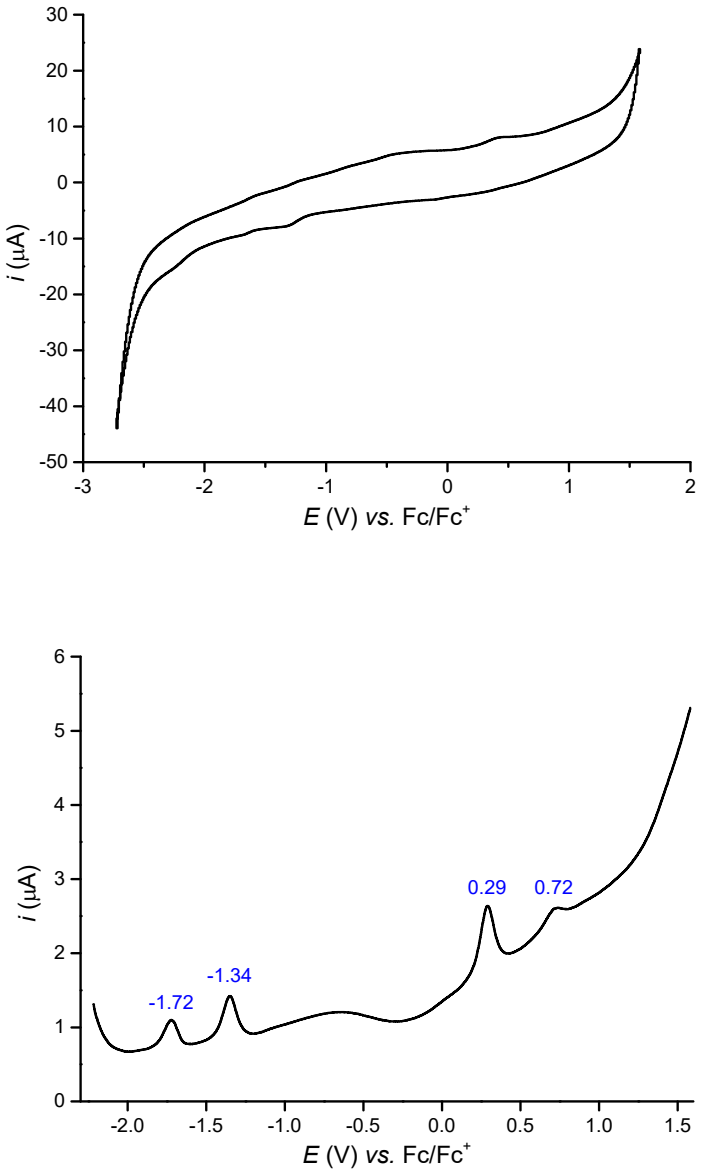


Figure S 68. Cyclic (top) and differential pulse voltammograms (bottom) of **3** in DCM.

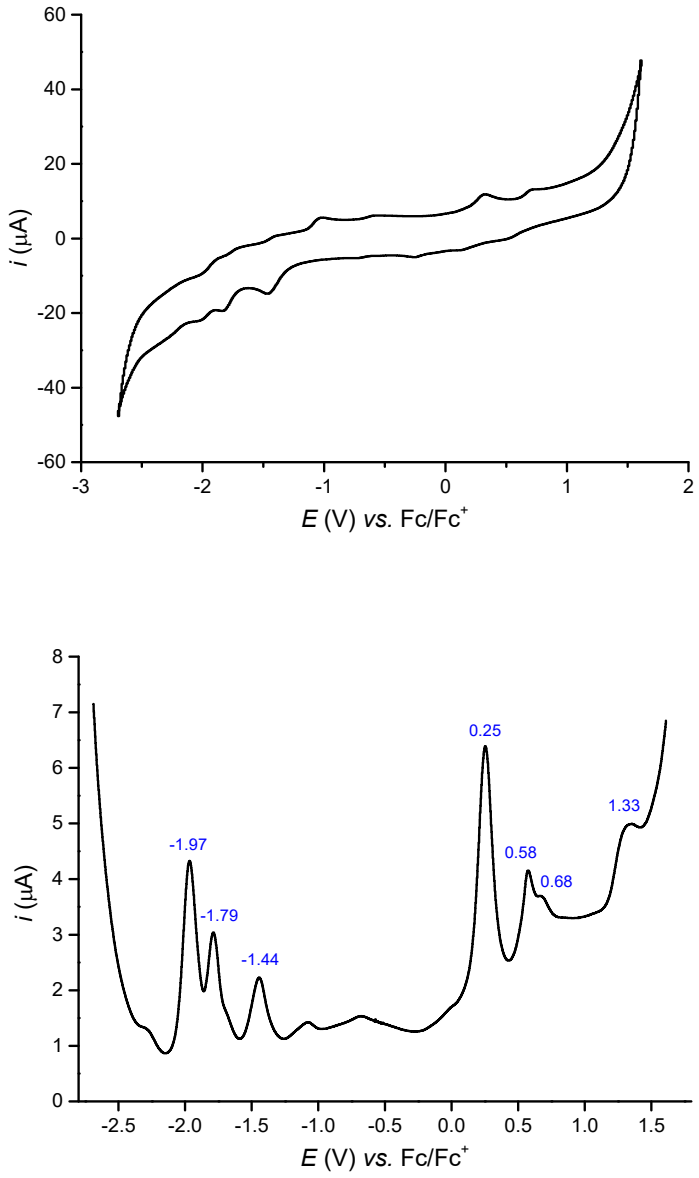


Figure S 69. Cyclic (top) and differential pulse voltammograms (bottom) of **5** in DCM.

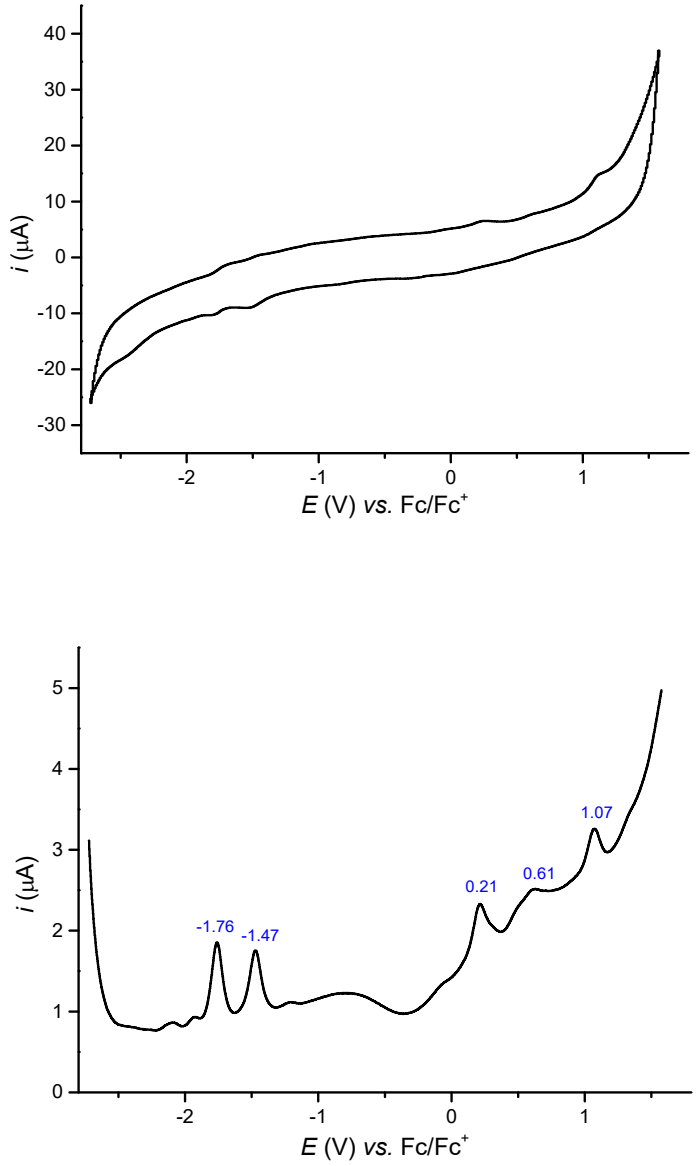
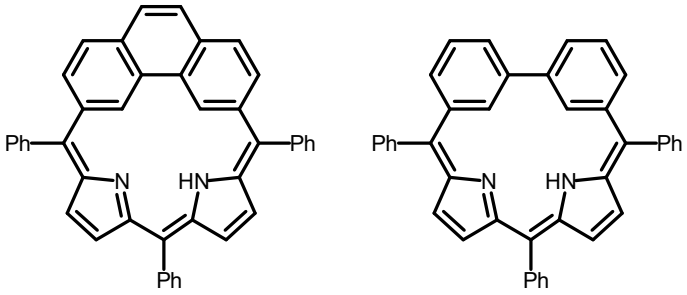


Figure S 70. Cyclic (top) and differential pulse voltammograms (bottom) of **9** in DCM.

DFT-optimized models



S1 **S2**

Scheme S 1. Computationally-studied phenanthriporphyrinoids.

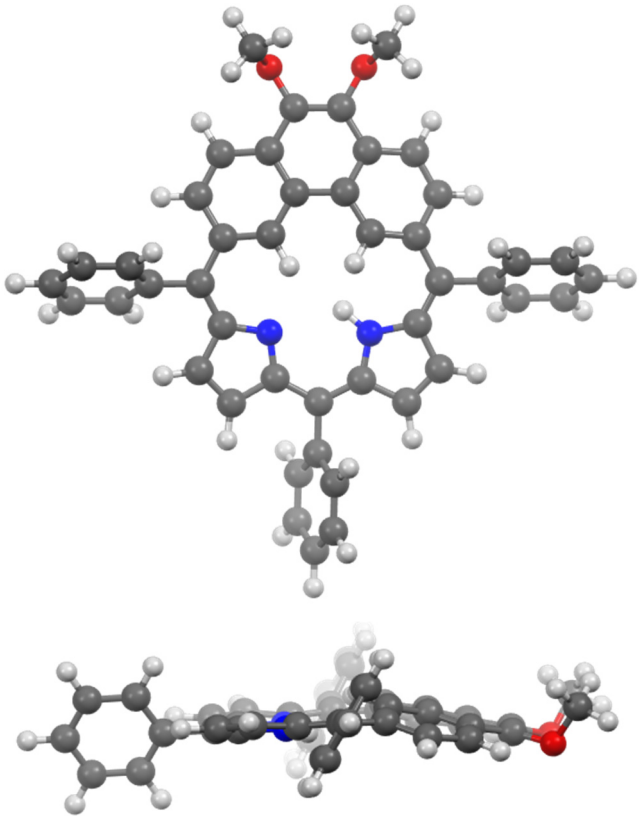


Figure S 71. DFT-optimized molecular geometry of **1**.

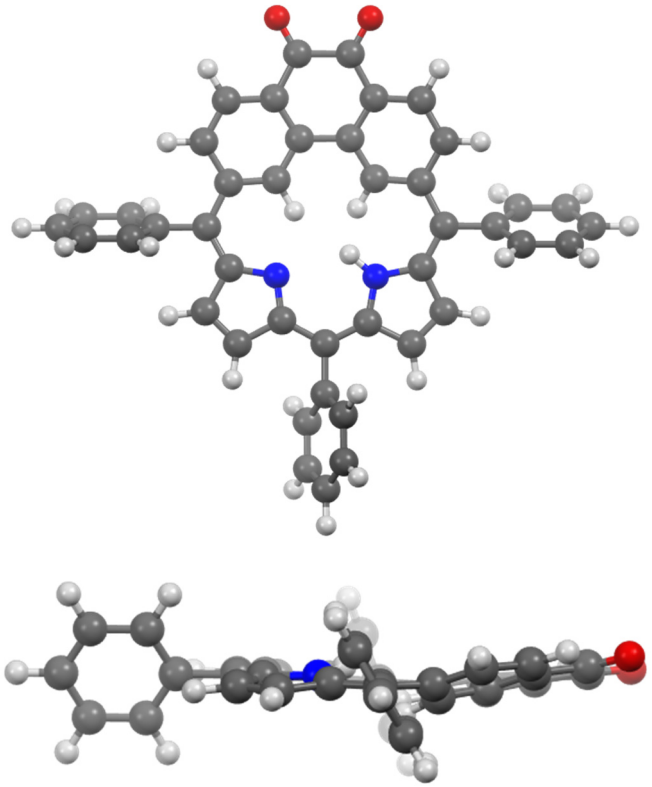


Figure S 72. DFT-optimized molecular geometry of **2**.

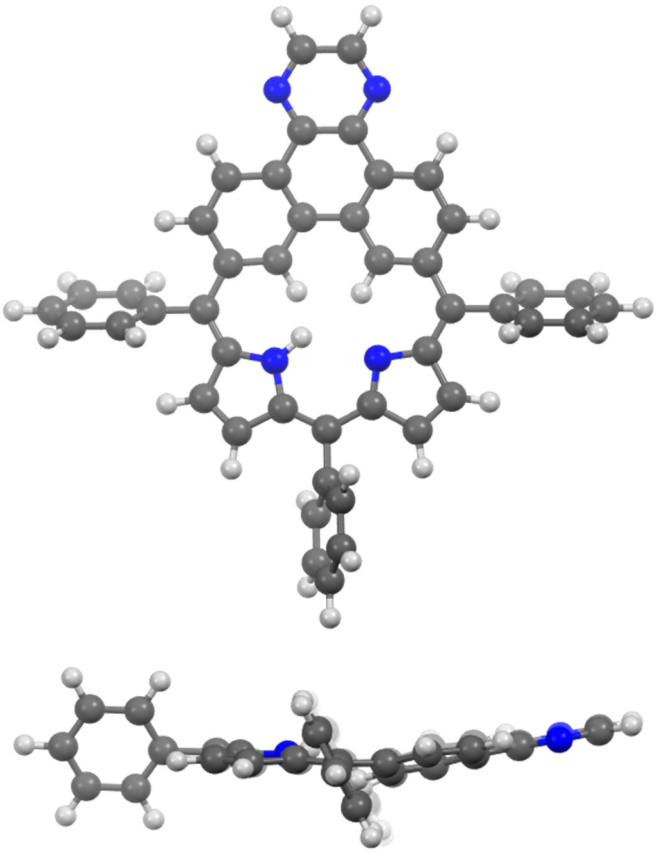


Figure S 73. DFT-optimized molecular geometry of **3**.

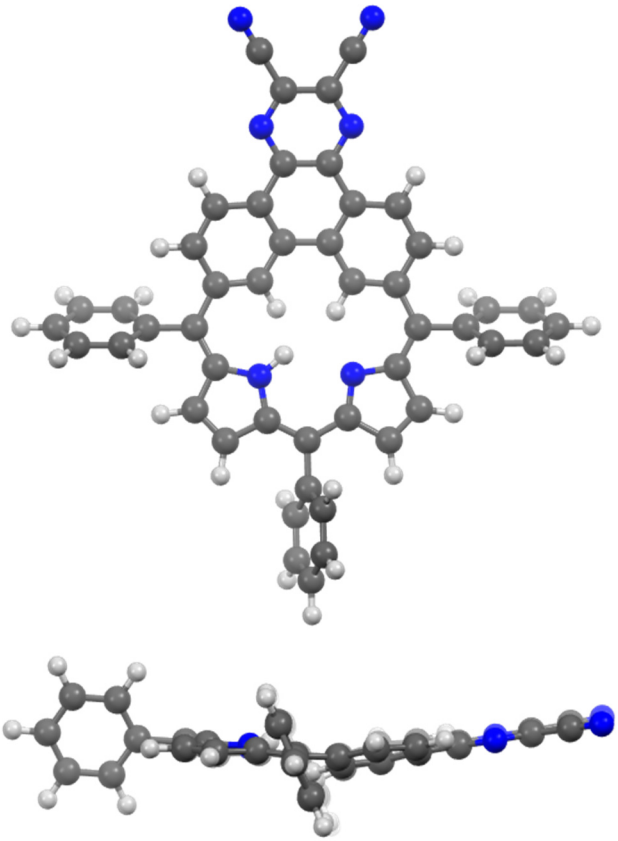


Figure S 74. DFT-optimized molecular geometry of **4**.

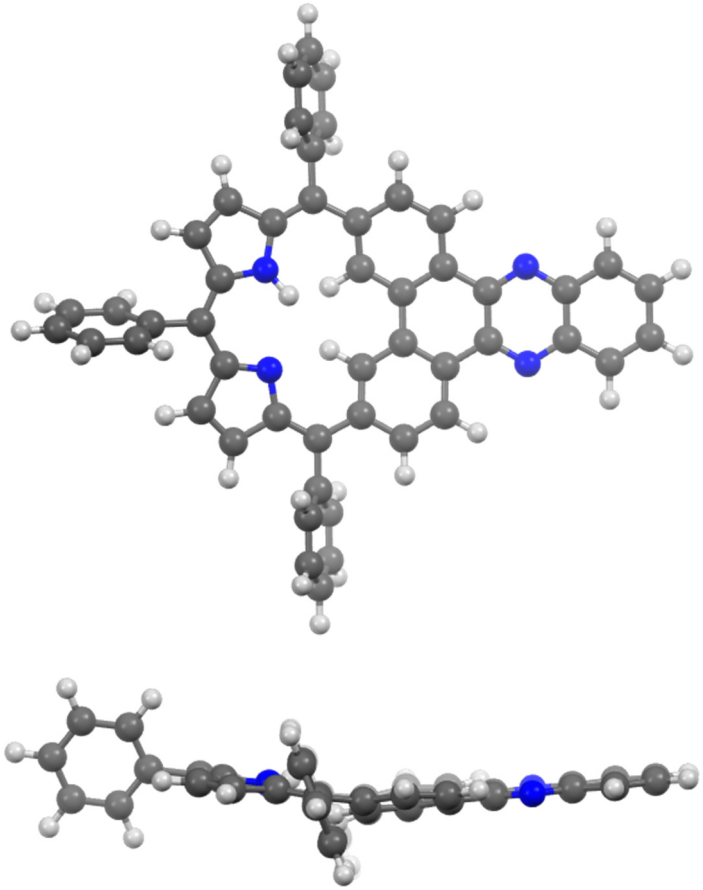


Figure S 75. DFT-optimized molecular geometry of **5**.

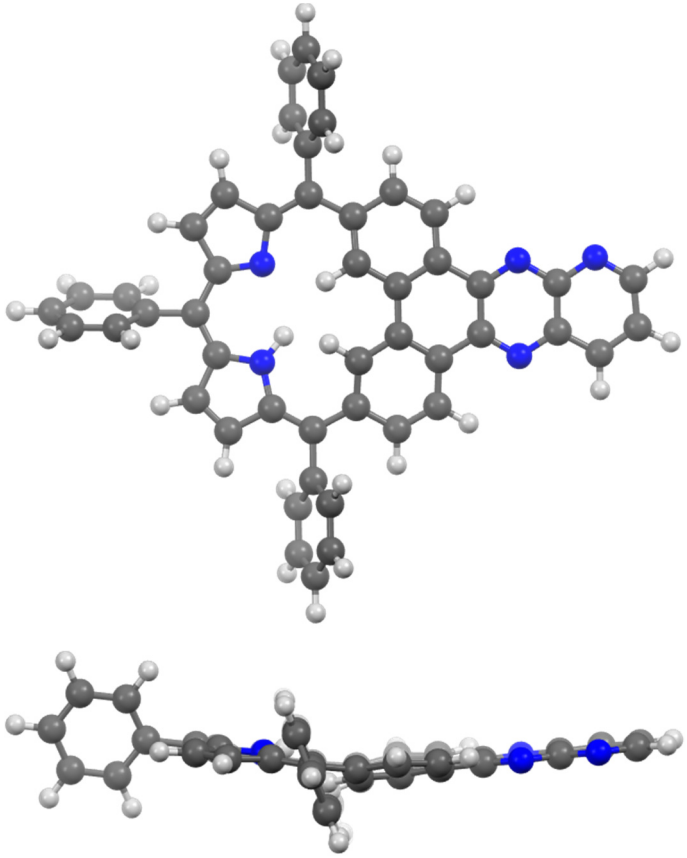


Figure S 76. DFT-optimized molecular geometry of **6**.

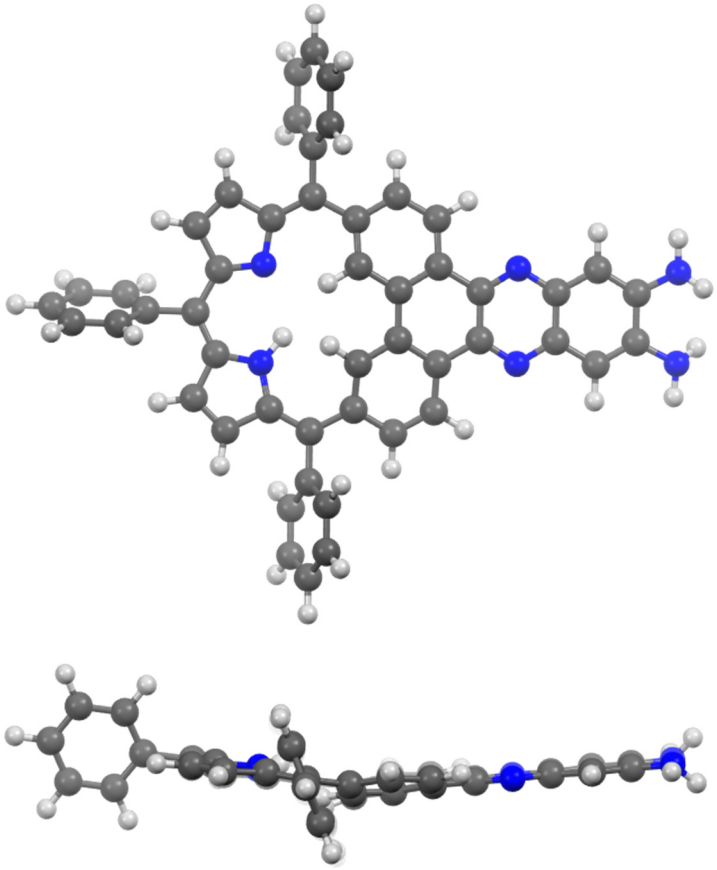


Figure S 77. DFT-optimized molecular geometry of **7**.

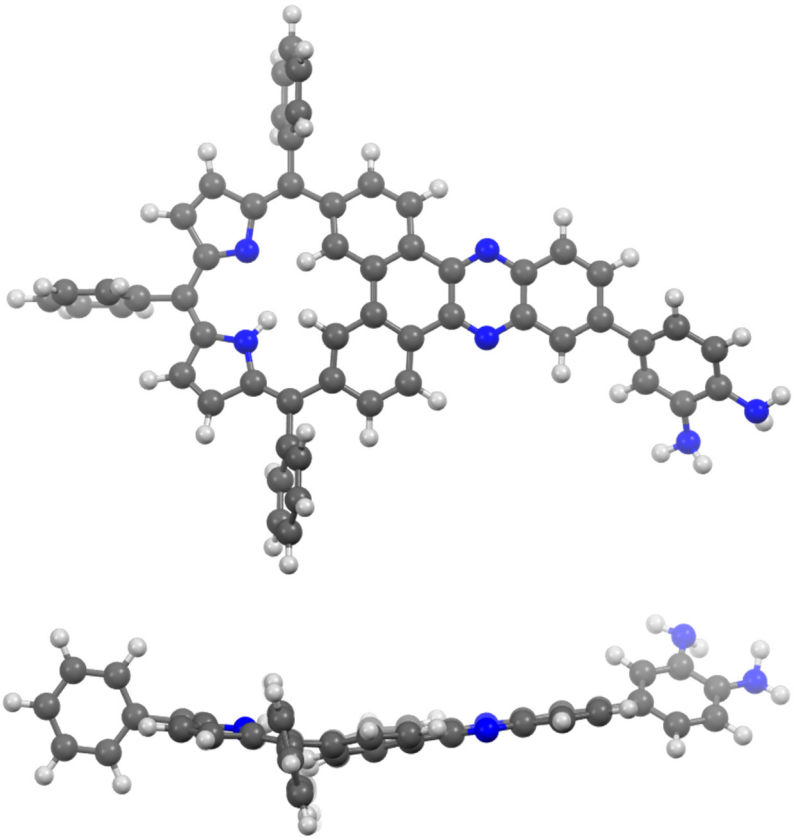


Figure S 78. DFT-optimized molecular geometry of **8**.

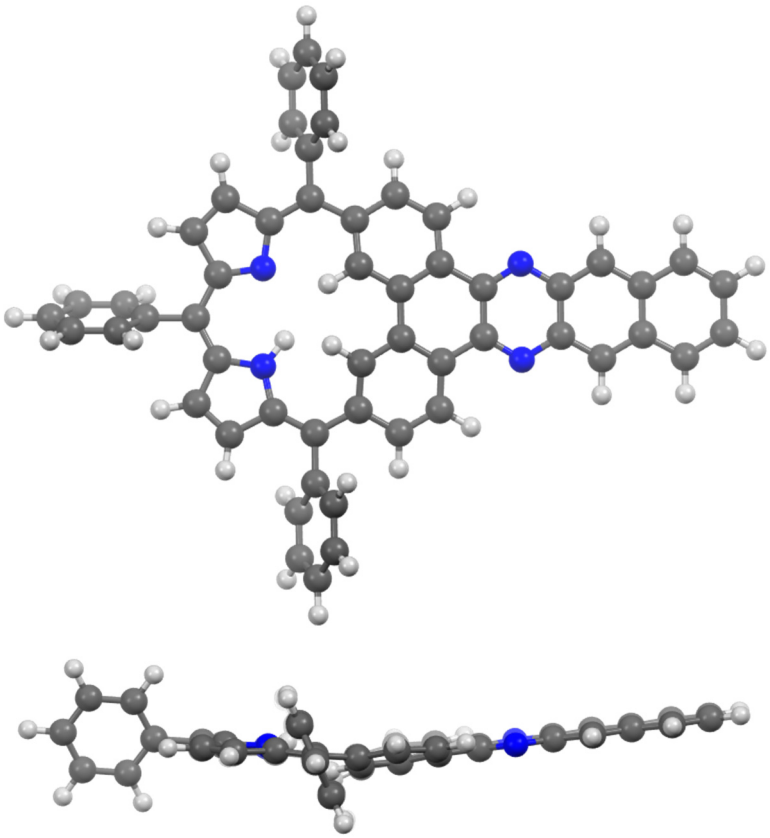


Figure S 79. DFT-optimized molecular geometry of **9**.

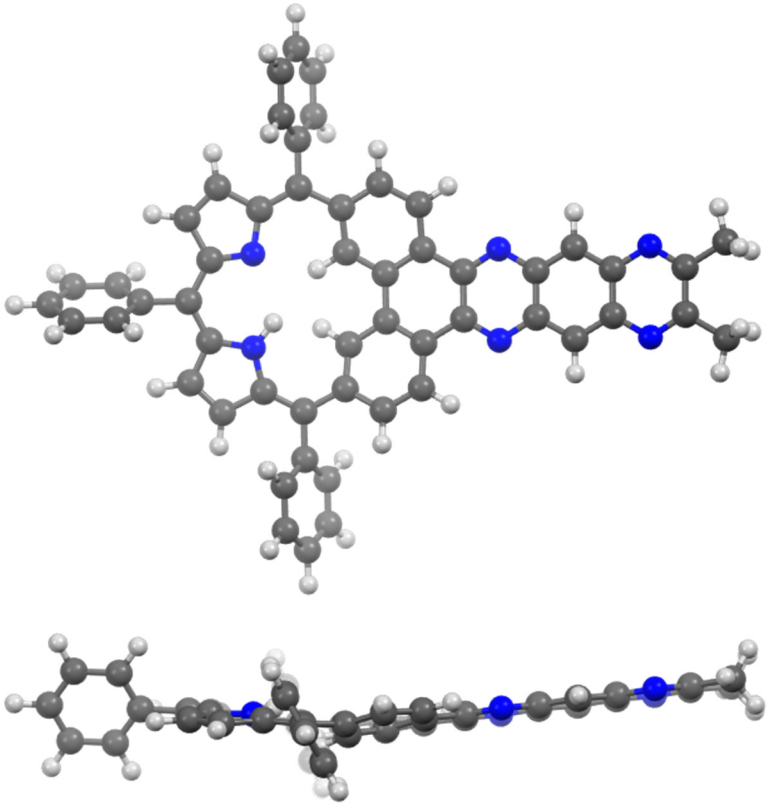


Figure S 80. DFT-optimized molecular geometry of **10**.

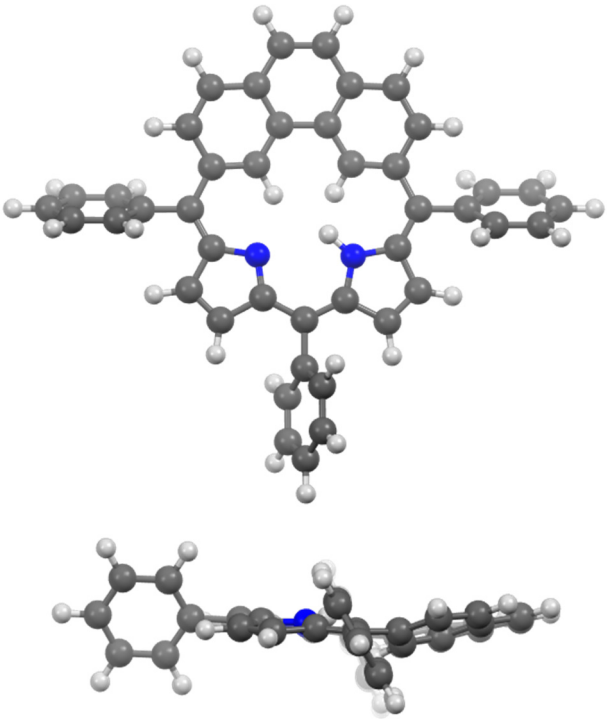


Figure S 81. DFT-optimized molecular geometry of **S1**.

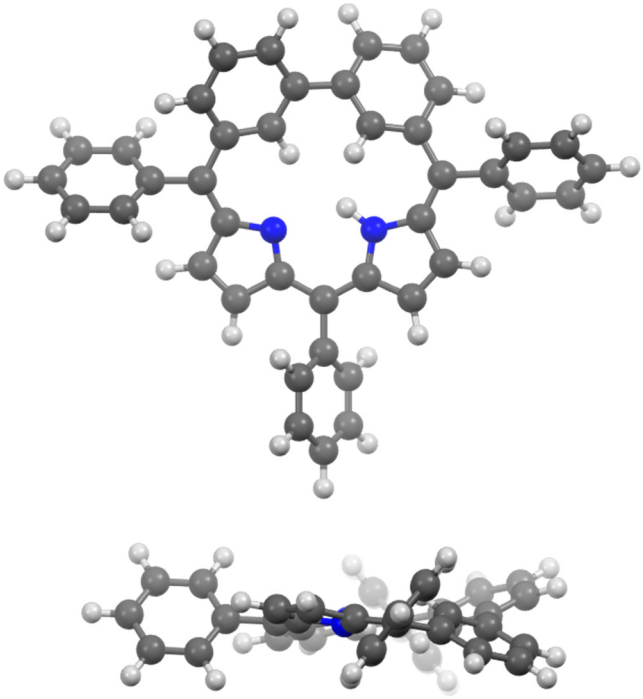


Figure S 82. DFT-optimized molecular geometry of **S2.**

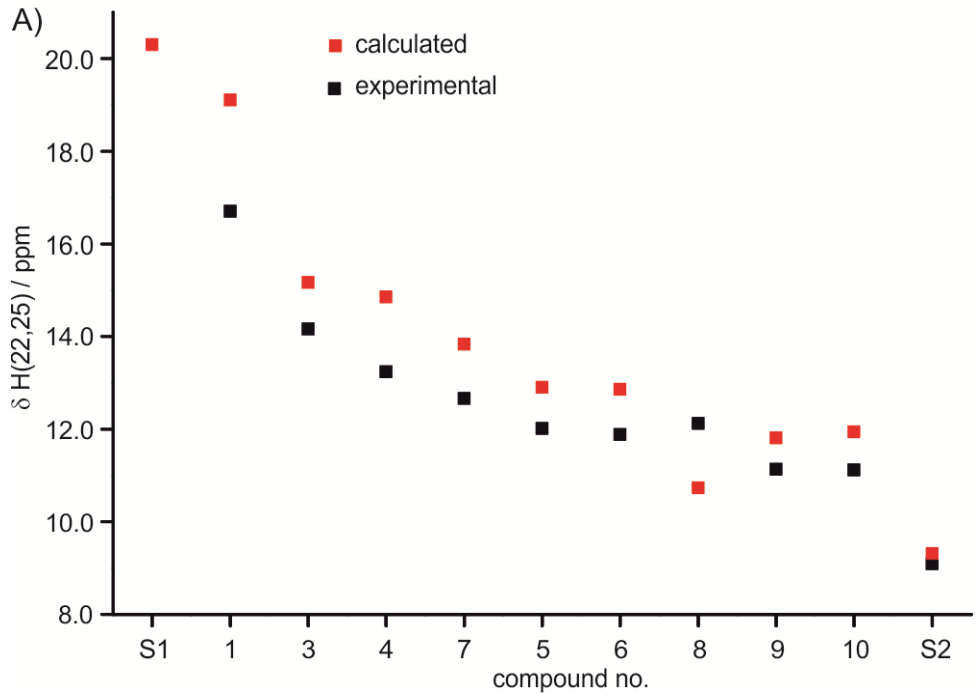


Figure S 83. The comparison of the DFT-calculated and experimental values of the ^{1}H NMR chemical shifts of H(22,25).

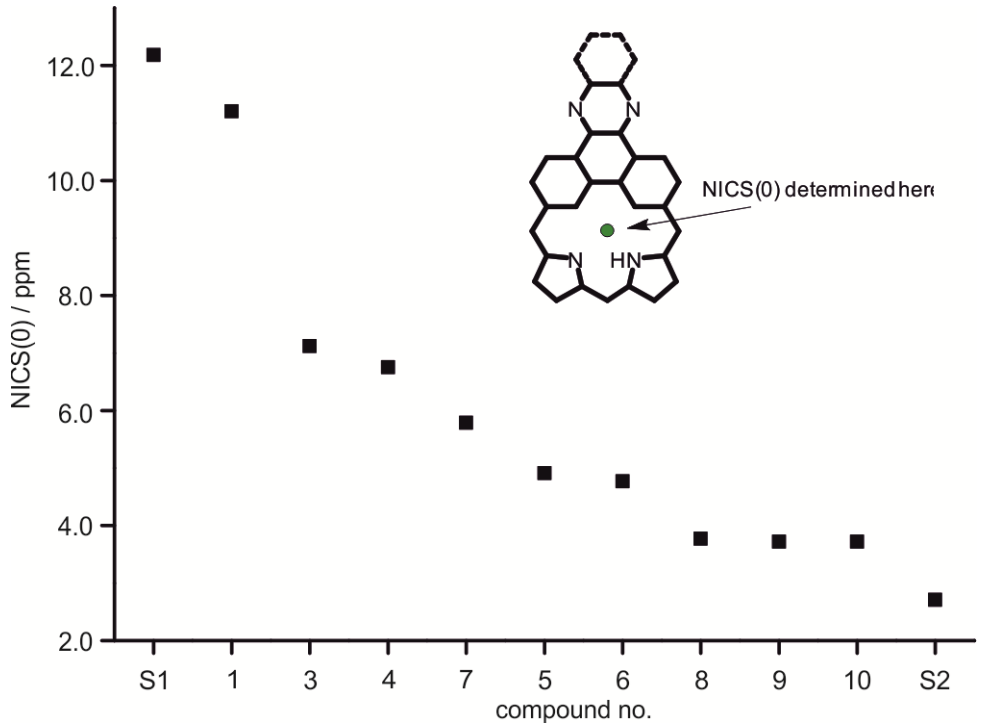


Figure S 84. The calculated NICS(0) values for **1** – **10**, **S1** and **S2**.

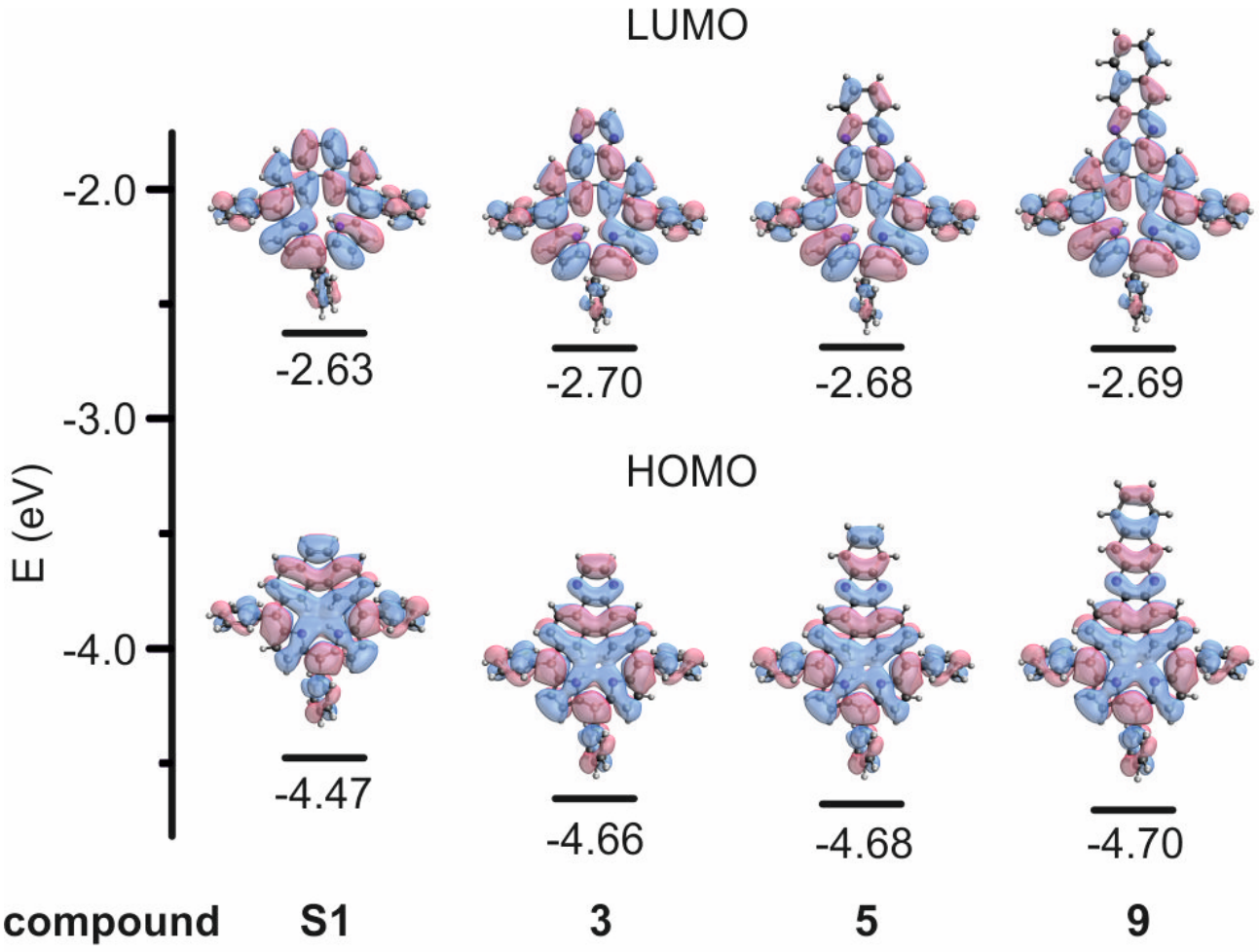


Figure S 85. Energy diagram for $HOMO_{\alpha}$ and $LUMO_{\alpha}$ molecular orbitals of **S1**, **3**, **5** and **9** (positive maxima marked in blue, isovalue = 0.02 $(e/a.u.^3)^{1/2}$).

DFT-calculated Cartesian coordinates

Table S 4. DFT-calculated Cartesian coordinates of **1**.

C	3.909000	-2.989400	0.495000
C	2.940100	-3.959000	0.441800
C	1.558300	-3.605300	0.196400
C	1.237800	-2.276200	-0.181000
C	2.273700	-1.258500	-0.165900
C	3.576400	-1.598400	0.274000
O	5.198500	-3.312200	0.849700
C	6.115300	-3.429400	-0.238700
O	3.254300	-5.266500	0.734000
C	3.332300	-6.137200	-0.395500
C	4.492800	-0.552400	0.536600
C	4.123200	0.770900	0.405000
C	2.829300	1.131200	-0.068600
C	1.968200	0.092700	-0.411200
C	0.499900	-4.521200	0.402700
C	-0.818200	-4.128100	0.281900
C	-1.156100	-2.798700	-0.098500
C	-0.108800	-1.925300	-0.373600
C	2.396300	2.540700	-0.112400
C	3.464500	3.580600	-0.184800
C	4.382800	3.576400	-1.250400
C	5.387800	4.537800	-1.333700
C	5.505500	5.520100	-0.347300
C	4.612200	5.528900	0.724200
C	3.604600	4.566800	0.806700
C	-2.555300	-2.331400	-0.116000
C	-3.608400	-3.386100	-0.200700
C	-4.583500	-3.529300	0.800600
C	-5.559900	-4.522200	0.711200
C	-5.580600	-5.390400	-0.380500
C	-4.612100	-5.265300	-1.379600
C	-3.631200	-4.280300	-1.285900
C	1.080000	2.959400	-0.048000
N	-0.092200	2.201600	0.091600
C	-1.217800	3.000700	0.085100
C	-0.735700	4.365000	-0.039900
C	0.615200	4.337000	-0.144000
C	-2.536700	2.570100	0.130400
C	-2.948500	1.186700	0.090100

N	-2.134000	0.125400	0.125400
C	-2.954100	-1.005000	-0.034400
C	-4.348600	-0.567200	-0.165300
C	-4.348700	0.781200	-0.085300
C	-3.611300	3.614000	0.154200
C	-3.850000	4.442800	-0.953800
C	-4.853800	5.412100	-0.921900
C	-5.645700	5.564600	0.216900
C	-5.426100	4.741900	1.323400
C	-4.418200	3.778100	1.292000
H	5.845200	-4.262100	-0.899900
H	6.162600	-2.507500	-0.831400
H	7.094400	-3.625900	0.202700
H	4.144400	-5.841200	-1.071500
H	3.538700	-7.134300	-0.001700
H	2.392900	-6.157300	-0.961000
H	5.478000	-0.806200	0.912100
H	4.823500	1.549100	0.686000
H	1.021700	0.331000	-0.869700
H	0.737200	-5.526900	0.731400
H	-1.604900	-4.835200	0.518100
H	4.295100	2.816100	-2.020700
H	6.078400	4.522700	-2.172000
H	6.290800	6.267600	-0.411000
H	4.703500	6.279500	1.504100
H	2.924400	4.565100	1.652800
H	-4.562000	-2.862300	1.656600
H	-6.301400	-4.619000	1.499100
H	-6.341400	-6.162200	-0.450900
H	-4.621400	-5.935800	-2.234100
H	-2.879700	-4.187900	-2.064300
H	-0.183900	1.211800	0.281400
H	-1.375700	5.233200	-0.075900
H	1.270400	5.180900	-0.294500
H	-5.196000	-1.214000	-0.335600
H	-5.194500	1.448900	-0.159900
H	-3.247100	4.315400	-1.848200
H	-5.022000	6.041900	-1.791000
H	-6.429100	6.316500	0.241600
H	-6.036200	4.854300	2.215200
H	-4.245300	3.145100	2.157500
H	-0.375800	-0.923000	-0.662400

Table S 5. DFT-calculated Cartesian coordinates of **2**.

C	0.740500	-5.347600	-0.361000
C	-0.800100	-5.365300	-0.195900
C	-1.481300	-4.066400	0.005600
C	-0.743800	-2.886300	0.238600
C	0.733000	-2.892700	0.190100
C	1.435600	-4.051600	-0.199300
O	1.325500	-6.386500	-0.622200
O	-1.398800	-6.425300	-0.277900
C	2.818900	-3.966500	-0.439400
C	3.491500	-2.761400	-0.341600
C	2.809800	-1.585200	0.069600
C	1.448600	-1.713200	0.394400
C	-2.880600	-3.990700	-0.096800
C	-3.539600	-2.773400	-0.037500
C	-2.813800	-1.571000	0.167100
C	-1.426000	-1.678600	0.356700
C	3.479900	-0.284800	0.105200
C	4.972100	-0.278100	0.160700
C	5.644400	-0.915700	1.218700
C	7.036200	-0.915700	1.283300
C	7.786400	-0.287700	0.286100
C	7.134000	0.338200	-0.776400
C	5.740100	0.341700	-0.839500
C	-3.457200	-0.256200	0.098500
C	-4.953900	-0.242000	0.101100
C	-5.678300	0.181400	-1.024600
C	-7.073800	0.184300	-1.014900
C	-7.768400	-0.234200	0.120400
C	-7.059600	-0.662300	1.245000
C	-5.665700	-0.673200	1.233100
C	2.834200	0.946200	0.058600
N	1.478500	1.236800	-0.119200
C	1.240400	2.593300	-0.062200
C	2.528700	3.216900	0.150700
C	3.470200	2.241200	0.230400
C	-0.003600	3.221900	-0.112500
C	-1.264100	2.534200	-0.106500
N	-1.422800	1.200400	-0.067300
C	-2.798300	0.968900	-0.005200
C	-3.502800	2.257500	-0.029900
C	-2.560400	3.222000	-0.105600

C	-0.004500	4.718900	-0.115000
C	0.529300	5.431500	-1.200800
C	0.542400	6.827000	-1.204600
C	0.019200	7.536000	-0.122700
C	-0.514600	6.840600	0.964100
C	-0.524500	5.446000	0.968800
H	3.335900	-4.871100	-0.742400
H	4.543200	-2.710800	-0.596700
H	0.940300	-0.867400	0.828200
H	-3.426700	-4.911900	-0.271900
H	-4.611800	-2.740300	-0.187400
H	5.066000	-1.404100	1.997200
H	7.535800	-1.404300	2.114600
H	8.871200	-0.291600	0.335200
H	7.708900	0.818100	-1.563000
H	5.236200	0.815000	-1.676600
H	-5.139400	0.501100	-1.911100
H	-7.616700	0.511000	-1.897000
H	-8.854300	-0.230600	0.128600
H	-7.592400	-0.987900	2.133700
H	-5.118500	-1.008000	2.109500
H	0.716300	0.602800	-0.321400
H	2.675900	4.279500	0.268000
H	4.522300	2.369900	0.431000
H	-4.573000	2.388300	0.020300
H	-2.710100	4.290400	-0.150600
H	0.926100	4.882600	-2.049700
H	0.956200	7.359000	-2.056400
H	0.027300	8.621900	-0.125500
H	-0.917500	7.384100	1.813800
H	-0.929300	4.909400	1.821700
H	-0.897300	-0.756900	0.523500

Table S 6. DFT-calculated Cartesian coordinates of **3**.

C	3.942400	1.777900	0.133400
C	3.215400	2.910300	0.019300
C	1.816200	2.491400	-0.129300
N	1.703100	1.156600	-0.117600
C	3.002200	0.653200	0.050100
C	2.469600	-1.828200	0.201000
C	3.387300	-0.675700	0.175500
C	-3.018800	-0.674800	0.164100

C	-1.761200	3.970200	-0.013200
C	-2.880800	3.217800	0.123600
C	-2.525300	1.806600	0.066900
N	-1.132300	1.800600	-0.086400
C	-0.619700	3.081400	-0.122400
C	-3.408100	0.744600	0.169700
C	1.106300	-1.648000	0.432700
C	0.173100	-2.682400	0.281500
C	0.634400	-3.983600	-0.018900
C	2.020200	-4.197700	-0.164000
C	2.916400	-3.148200	-0.079800
C	-3.531400	-3.010200	-0.326100
C	-2.187100	-3.380400	-0.111300
C	-1.259800	-2.385200	0.264700
C	-1.719400	-1.076400	0.477000
C	-1.724800	-4.752100	-0.301900
C	-0.335700	-5.052900	-0.240200
C	-3.932600	-1.691700	-0.229200
N	0.109200	-6.311100	-0.421700
N	-2.631700	-5.717000	-0.550200
C	0.723700	3.430100	-0.189800
C	-0.803500	-7.250000	-0.652900
C	-2.171300	-6.952800	-0.719500
C	4.846700	-0.982000	0.264300
C	5.730600	-0.630300	-0.769200
C	7.091400	-0.925300	-0.677200
C	7.593900	-1.576300	0.449800
C	6.725200	-1.938300	1.482100
C	5.364800	-1.652200	1.386600
C	-4.867600	1.053400	0.243300
C	-5.524100	1.759700	-0.778600
C	-6.889500	2.036100	-0.695800
C	-7.627000	1.605800	0.407500
C	-6.990600	0.891800	1.425700
C	-5.627800	0.614300	1.342000
C	1.062400	4.888000	-0.261500
C	0.826400	5.746700	0.824000
C	1.146300	7.103200	0.747600
C	1.717000	7.624900	-0.414000
C	1.965000	6.781400	-1.498500
C	1.639400	5.427100	-1.422800
H	5.006200	1.695100	0.297100
H	3.568100	3.930600	0.055900

H	-1.693500	5.047200	-0.009300
H	-3.887600	3.576100	0.272000
H	-0.519100	1.014200	-0.258200
H	0.784900	-0.646600	0.659000
H	2.363200	-5.200400	-0.392500
H	3.968000	-3.333500	-0.263900
H	-4.235500	-3.782100	-0.615700
H	-1.039900	-0.353000	0.896800
H	-4.955300	-1.427000	-0.470800
H	-0.446600	-8.268300	-0.793200
H	-2.902600	-7.734300	-0.915500
H	5.339900	-0.132900	-1.651300
H	7.757200	-0.649300	-1.489800
H	8.653100	-1.804600	0.522300
H	7.107800	-2.443800	2.364000
H	4.693400	-1.936900	2.191100
H	-4.957500	2.080300	-1.647500
H	-7.377400	2.580500	-1.499200
H	-8.689900	1.819200	0.471700
H	-7.556500	0.552800	2.288600
H	-5.137900	0.059600	2.136700
H	0.398200	5.340700	1.735800
H	0.957100	7.749700	1.599800
H	1.968900	8.679700	-0.473200
H	2.407400	7.178800	-2.407600
H	1.827000	4.775300	-2.271000

Table S 7. DFT-calculated Cartesian coordinates of **4**.

C	3.214500	-3.456800	0.087100
C	4.158200	-2.502000	-0.054300
C	3.441900	-1.225100	-0.169900
N	2.114800	-1.402900	-0.112600
C	1.910800	-2.780300	0.054100
C	-0.619100	-2.800100	0.288400
C	0.702200	-3.446700	0.216600
C	-0.682600	2.808900	0.257700
C	4.114700	2.586000	-0.068600
C	3.141600	3.515700	0.097000
C	1.840700	2.860900	0.081400
N	2.131400	1.501100	-0.079600
C	3.491400	1.279500	-0.158900
C	0.615900	3.495200	0.219300

C	-0.729600	-1.428900	0.523600
C	-1.945200	-0.743000	0.415700
C	-3.125200	-1.478000	0.159200
C	-3.041400	-2.878300	0.012800
C	-1.820200	-3.524100	0.053500
C	-3.090100	2.808600	-0.145100
C	-3.150800	1.414000	0.067200
C	-1.965900	0.720900	0.400300
C	-0.782400	1.451300	0.572400
C	-4.390000	0.667400	-0.078500
C	-4.381200	-0.763300	-0.016100
C	-1.887400	3.483900	-0.088100
N	-5.515800	-1.462500	-0.154900
N	-5.533500	1.336800	-0.285300
C	4.120300	0.043500	-0.247900
C	-6.650000	-0.784600	-0.347100
C	-6.657800	0.629400	-0.416000
C	0.721900	-4.938400	0.294300
C	1.211700	-5.716800	-0.767500
C	1.220500	-7.109700	-0.686400
C	0.741600	-7.749200	0.457300
C	0.245900	-6.987500	1.518100
C	0.228100	-5.596700	1.434300
C	0.605100	4.987800	0.282100
C	0.060600	5.643600	1.400500
C	0.040000	7.035100	1.472600
C	0.554300	7.801100	0.423800
C	1.086300	7.164800	-0.698000
C	1.109000	5.771300	-0.769500
C	5.614100	0.029100	-0.366300
C	6.433300	0.432000	0.700200
C	7.823700	0.413800	0.580700
C	8.420100	-0.015300	-0.605800
C	7.617500	-0.425700	-1.671900
C	6.227800	-0.402600	-1.553200
C	-7.862100	-1.546500	-0.484700
N	-8.844000	-2.158400	-0.596400
C	-7.878000	1.360300	-0.631800
N	-8.865900	1.947200	-0.806400
H	3.367600	-4.514500	0.238200
H	5.231200	-2.625300	-0.056400
H	5.180500	2.753000	-0.096800
H	3.275900	4.576500	0.240100

H	1.493600	0.731200	-0.236100
H	0.186500	-0.898800	0.715600
H	-3.952000	-3.433500	-0.181200
H	-1.779200	-4.591000	-0.128800
H	-4.004300	3.332500	-0.400200
H	0.084700	0.944200	0.961700
H	-1.858500	4.540700	-0.324900
H	1.575200	-5.221300	-1.662200
H	1.598000	-7.694100	-1.520400
H	0.749500	-8.833200	0.520900
H	-0.126900	-7.477200	2.412900
H	-0.158500	-5.009300	2.261900
H	-0.338900	5.053000	2.219600
H	-0.375500	7.522000	2.349900
H	0.534900	8.885400	0.479200
H	1.477100	7.751900	-1.524000
H	1.507500	5.279800	-1.651900
H	5.972700	0.750800	1.630700
H	8.440200	0.727500	1.418200
H	9.501900	-0.032100	-0.698400
H	8.073100	-0.759400	-2.599700
H	5.606300	-0.715700	-2.387100

Table S 8. DFT-calculated Cartesian coordinates of **5**.

C	-3.269400	-3.461100	-0.085400
C	-4.216900	-2.508600	0.053200
C	-3.505100	-1.230500	0.170300
N	-2.176900	-1.405600	0.116000
C	-1.968300	-2.781700	-0.049600
C	0.563600	-2.799300	-0.286300
C	-0.756300	-3.444500	-0.210600
C	0.618400	2.811200	-0.246900
C	-4.181600	2.580200	0.069700
C	-3.208800	3.511800	-0.091300
C	-1.907600	2.859700	-0.072600
N	-2.197700	1.498600	0.085800
C	-3.557300	1.274800	0.159800
C	-0.682400	3.493900	-0.207600
C	0.674500	-1.425800	-0.514800
C	1.890100	-0.740700	-0.414800
C	3.071700	-1.472500	-0.166800
C	2.986500	-2.871200	-0.022000

C	1.765900	-3.521200	-0.059000
C	3.024700	2.809700	0.155500
C	3.091900	1.418800	-0.064300
C	1.908800	0.726500	-0.396100
C	0.722800	1.453600	-0.562700
C	4.349600	0.681300	0.069700
C	4.342900	-0.763500	-0.000600
C	1.820200	3.485600	0.102600
N	5.460400	-1.465200	0.119300
N	5.473300	1.356800	0.263500
C	-4.184800	0.037000	0.246300
C	6.617800	-0.782500	0.304900
C	6.623800	0.648000	0.381000
C	7.853500	1.328100	0.581800
C	9.024200	0.613900	0.699700
C	9.018300	-0.803600	0.623000
C	7.841600	-1.490800	0.429900
C	-0.776400	-4.936800	-0.286600
C	-1.265700	-5.714700	0.775700
C	-1.276400	-7.107700	0.695600
C	-0.799400	-7.748700	-0.448100
C	-0.303800	-6.987800	-1.509500
C	-0.284400	-5.596900	-1.426300
C	-0.674600	4.986400	-0.270600
C	-0.122300	5.643700	-1.384400
C	-0.105800	7.035000	-1.458200
C	-0.631900	7.801000	-0.415200
C	-1.171000	7.163900	0.702700
C	-1.189400	5.770300	0.775500
C	-5.678700	0.020900	0.360500
C	-6.496300	0.433500	-0.703700
C	-7.887100	0.414100	-0.588100
C	-8.486700	-0.026600	0.592400
C	-7.686500	-0.447300	1.656200
C	-6.296500	-0.422300	1.541200
H	-3.420200	-4.519300	-0.236600
H	-5.289500	-2.635800	0.052400
H	-5.247600	2.746500	0.095400
H	-3.345200	4.572600	-0.233300
H	-1.558400	0.729000	0.237900
H	-0.242800	-0.894900	-0.698700
H	3.900600	-3.422400	0.167400
H	1.728400	-4.588700	0.122800

H	3.939900	3.331000	0.412300
H	-0.143600	0.944400	-0.951500
H	1.790300	4.540900	0.346800
H	7.832000	2.411600	0.636400
H	9.964400	1.135100	0.853000
H	9.954100	-1.346200	0.718600
H	7.810400	-2.573800	0.368400
H	-1.628600	-5.217900	1.669900
H	-1.654300	-7.691100	1.530300
H	-0.809100	-8.832800	-0.511300
H	0.067800	-7.478300	-2.404600
H	0.102900	-5.009800	-2.253600
H	0.287300	5.052800	-2.198300
H	0.315800	7.522200	-2.332700
H	-0.616000	8.885400	-0.471900
H	-1.570900	7.750400	1.524800
H	-1.593800	5.278300	1.654900
H	-6.033200	0.761100	-1.629900
H	-8.501300	0.735800	-1.424400
H	-9.568900	-0.044600	0.682100
H	-8.144200	-0.790500	2.579600
H	-5.676900	-0.743400	2.373400

Table S 9. DFT-calculated Cartesian coordinates of **6**.

C	-3.249100	-3.471700	-0.088900
C	-4.200700	-2.523200	0.049500
C	-3.494200	-1.242300	0.167800
N	-2.165200	-1.411600	0.114400
C	-1.950900	-2.786800	-0.051700
C	0.581100	-2.793800	-0.286500
C	-0.736000	-3.444900	-0.211600
C	0.611900	2.817300	-0.248300
C	-4.186800	2.565500	0.069300
C	-3.217800	3.501100	-0.091400
C	-1.914000	2.854100	-0.073600
N	-2.198300	1.492100	0.083800
C	-3.557100	1.262600	0.158400
C	-0.691500	3.494100	-0.208200
C	0.685200	-1.419800	-0.516800
C	1.897500	-0.729600	-0.415500
C	3.081500	-1.456800	-0.166000
C	3.004200	-2.855900	-0.020400

C	1.786100	-3.510700	-0.057700
C	3.018200	2.826100	0.153300
C	3.090800	1.435000	-0.065400
C	1.910400	0.737700	-0.397200
C	0.721800	1.459800	-0.564000
C	4.349700	0.702200	0.069900
C	4.350200	-0.744400	0.001400
C	1.811100	3.497100	0.100000
N	5.466500	-1.446100	0.123200
N	5.472700	1.378500	0.264400
C	-4.179300	0.022400	0.244300
C	6.622100	-0.766100	0.310000
C	6.618100	0.664100	0.383300
C	7.854200	1.327600	0.585600
C	8.994500	0.569600	0.700200
C	8.888300	-0.843900	0.611400
N	7.761200	-1.502000	0.425100
C	-0.749800	-4.937100	-0.286700
C	-1.238300	-5.716000	0.775100
C	-1.242600	-7.109100	0.696100
C	-0.760200	-7.748800	-0.446000
C	-0.265500	-6.986700	-1.506900
C	-0.252300	-5.595800	-1.424900
C	-0.690500	4.986900	-0.268800
C	-0.143900	5.648300	-1.383000
C	-0.133600	7.039800	-1.454400
C	-0.660300	7.801700	-0.408600
C	-1.193900	7.160300	0.709500
C	-1.206100	5.766600	0.780000
C	-5.673100	-0.000200	0.358500
C	-6.492300	0.408900	-0.705800
C	-7.883000	0.383500	-0.590100
C	-8.480600	-0.059800	0.590500
C	-7.678600	-0.476900	1.654400
C	-6.288700	-0.446000	1.539300
H	-3.395100	-4.530400	-0.240900
H	-5.272700	-2.654800	0.047600
H	-5.253400	2.727300	0.095300
H	-3.358400	4.561400	-0.232400
H	-1.556000	0.724800	0.236200
H	-0.234300	-0.893600	-0.702800
H	3.921700	-3.401500	0.169000
H	1.753000	-4.578100	0.124700

H	3.930900	3.352000	0.410000
H	-0.142500	0.947000	-0.952300
H	1.776900	4.552500	0.343200
H	7.859000	2.411500	0.642700
H	9.966100	1.027700	0.855500
H	9.789000	-1.450400	0.700800
H	-1.605000	-5.220200	1.668400
H	-1.619500	-7.693500	1.530500
H	-0.764700	-8.833000	-0.508200
H	0.110600	-7.476300	-2.400500
H	0.134800	-5.007800	-2.251700
H	0.265800	5.060700	-2.199100
H	0.283400	7.530400	-2.329100
H	-0.649500	8.886200	-0.463500
H	-1.594400	7.743700	1.533600
H	-1.606400	5.271300	1.659400
H	-6.030800	0.738400	-1.632100
H	-8.498700	0.702400	-1.426300
H	-9.562700	-0.082400	0.680200
H	-8.134800	-0.822000	2.577800
H	-5.667700	-0.764500	2.371500

Table S 10. DFT-calculated Cartesian coordinates of **7**.

C	-3.705400	-3.474900	-0.057600
C	-4.655000	-2.526700	0.099100
C	-3.947500	-1.245700	0.205500
N	-2.619900	-1.414500	0.127400
C	-2.407400	-2.789800	-0.043800
C	0.120300	-2.794000	-0.328000
C	-1.194900	-3.445600	-0.228100
C	0.147800	2.816600	-0.293000
C	-4.644700	2.562500	0.116600
C	-3.680200	3.498900	-0.064600
C	-2.375200	2.854100	-0.070200
N	-2.655500	1.491200	0.095400
C	-4.012200	1.260000	0.195600
C	-1.156100	3.493400	-0.230600
C	0.220300	-1.420600	-0.558500
C	1.434100	-0.728400	-0.479700
C	2.624700	-1.452800	-0.250700
C	2.548100	-2.852500	-0.104500
C	1.330800	-3.509000	-0.120800

C	2.561000	2.826000	0.068200
C	2.632000	1.435000	-0.151500
C	1.445600	0.737800	-0.462300
C	0.253100	1.459900	-0.608900
C	3.893800	0.701900	-0.036600
C	3.892900	-0.735800	-0.104400
C	1.352500	3.496300	0.035900
N	5.019300	-1.434700	0.003900
N	5.021000	1.385700	0.139900
C	-4.631600	0.019300	0.294700
C	6.171100	-0.748800	0.172600
C	6.171900	0.685100	0.241500
C	7.399000	1.366300	0.442100
C	8.584000	0.671900	0.553800
C	8.589100	-0.767100	0.435100
C	7.402300	-1.446000	0.264600
N	9.829000	-1.405400	0.559800
N	9.826000	1.294300	0.725400
C	-1.209100	-4.937700	-0.306800
C	-1.678500	-5.720600	0.760800
C	-1.684300	-7.113600	0.677600
C	-1.222000	-7.749800	-0.474800
C	-0.745900	-6.984000	-1.541600
C	-0.731500	-5.593300	-1.455300
C	-1.156500	4.985500	-0.299600
C	-0.622900	5.640900	-1.423800
C	-0.614400	7.031900	-1.504100
C	-1.129700	7.800200	-0.457300
C	-1.649600	7.165300	0.670800
C	-1.660000	5.772000	0.750200
C	-6.122900	-0.004500	0.437500
C	-6.963400	0.409000	-0.608600
C	-8.351600	0.382500	-0.466300
C	-8.926500	-0.067000	0.723200
C	-8.103600	-0.489000	1.769100
C	-6.716300	-0.456400	1.627500
H	-3.854400	-4.533500	-0.207800
H	-5.726800	-2.659500	0.117000
H	-5.710800	2.723600	0.163200
H	-3.825400	4.558700	-0.205300
H	-2.008600	0.725400	0.234500
H	-0.702600	-0.894200	-0.726900
H	3.468400	-3.398300	0.070000

H	1.302300	-4.576600	0.062500
H	3.478200	3.351500	0.308900
H	-0.617600	0.946100	-0.982000
H	1.322100	4.551600	0.280600
H	7.373900	2.448900	0.524100
H	7.383100	-2.528400	0.177800
H	9.800400	-2.393700	0.342900
H	10.567500	-0.940900	0.040800
H	10.418300	0.818300	1.398400
H	9.760100	2.282400	0.934700
H	-2.029900	-5.227500	1.661600
H	-2.046900	-7.700500	1.516500
H	-1.228100	-8.833900	-0.540500
H	-0.385800	-7.470700	-2.443500
H	-0.359000	-5.002300	-2.286500
H	-0.221500	5.048200	-2.240300
H	-0.207500	7.517100	-2.386600
H	-1.120200	8.884400	-0.519100
H	-2.040800	7.753500	1.496100
H	-2.049000	5.282000	1.637500
H	-6.519900	0.743000	-1.542000
H	-8.983300	0.705200	-1.289100
H	-10.006700	-0.090700	0.833600
H	-8.541800	-0.839100	2.699600
H	-6.079100	-0.778500	2.445900

Table S 11. DFT-calculated Cartesian coordinates of **8**.

C	-5.485300	-2.914300	0.213900
C	-6.209100	-1.820800	0.427900
C	-5.258900	-0.690500	0.430500
N	-4.039900	-1.090900	0.258100
C	-4.080700	-2.488500	0.094700
C	-1.629100	-2.909100	-0.334200
C	-3.049100	-3.321200	-0.171200
C	-0.618600	2.562200	-0.497600
C	-5.306100	3.170900	0.238200
C	-4.245500	3.910500	-0.065700
C	-3.050300	3.055700	-0.133100
N	-3.535400	1.774100	0.140700
C	-4.888100	1.767600	0.348300
C	-1.798700	3.463000	-0.425400
C	-1.300900	-1.603000	-0.632900

C	0.013600	-1.140500	-0.618100
C	1.045700	-2.047600	-0.388600
C	0.731500	-3.393700	-0.175000
C	-0.574600	-3.816300	-0.128900
C	1.743500	2.166500	-0.191800
C	1.563900	0.790800	-0.385100
C	0.286500	0.309100	-0.652000
C	-0.760700	1.222200	-0.791500
C	2.688300	-0.150200	-0.285600
C	2.431900	-1.565000	-0.308300
C	0.677700	3.029700	-0.209900
N	3.404700	-2.420800	-0.226900
N	3.897800	0.308800	-0.175400
C	-5.698100	0.696500	0.541700
C	4.659500	-1.952700	-0.125500
C	4.911000	-0.571800	-0.093400
C	6.244800	-0.102200	0.016500
C	7.289500	-0.973800	0.096500
C	7.017500	-2.378200	0.064700
C	5.753600	-2.853000	-0.042800
C	8.694700	-0.495500	0.214700
C	9.712500	-1.070100	-0.528900
C	11.017000	-0.613000	-0.408200
C	11.335600	0.423500	0.448000
C	10.310600	1.030000	1.187400
C	9.017600	0.560200	1.069100
N	12.638600	0.929500	0.577300
N	10.658200	2.064500	2.073200
C	-3.323600	-4.793100	-0.288300
C	-3.685200	-5.549400	0.820500
C	-3.924600	-6.910200	0.700800
C	-3.805000	-7.531700	-0.529700
C	-3.438500	-6.787200	-1.640700
C	-3.193100	-5.431100	-1.519200
C	-1.547800	4.926100	-0.646500
C	-1.665000	5.848500	0.387700
C	-1.419100	7.196000	0.169200
C	-1.045500	7.639500	-1.087000
C	-0.915000	6.727800	-2.123900
C	-1.159900	5.384200	-1.904000
C	-7.160100	0.944600	0.795500
C	-8.061200	1.074600	-0.257900
C	-9.407800	1.297500	-0.019200

C	-9.877200	1.391600	1.281000
C	-8.992400	1.262100	2.338500
C	-7.645900	1.040500	2.095700
H	-5.837800	-3.920100	0.123400
H	-7.268400	-1.746900	0.557400
H	-6.316800	3.502600	0.348800
H	-4.231800	4.962800	-0.254400
H	-2.998000	0.957200	0.307400
H	-2.104600	-0.931400	-0.808300
H	1.530100	-4.089200	-0.003000
H	-0.781600	-4.845600	0.091900
H	2.730900	2.532100	0.015100
H	-1.711700	0.872100	-1.121300
H	0.838700	4.069200	0.003400
H	6.399500	0.960600	0.011000
H	7.839700	-3.065000	0.149500
H	5.545800	-3.907100	-0.057500
H	9.496900	-1.867200	-1.217300
H	11.797400	-1.074400	-0.989800
H	8.243600	1.014800	1.663200
H	12.893800	1.080800	1.532000
H	13.324700	0.367700	0.121800
H	11.249000	2.747300	1.643900
H	9.866700	2.508000	2.486500
H	-3.775300	-5.070700	1.779300
H	-4.202100	-7.480800	1.569600
H	-3.992000	-8.586800	-0.623700
H	-3.343400	-7.262600	-2.601000
H	-2.903400	-4.859600	-2.383300
H	-1.944400	5.507600	1.369000
H	-1.515200	7.894100	0.982200
H	-0.853400	8.684000	-1.257700
H	-0.623900	7.063900	-3.103500
H	-1.054300	4.681500	-2.711700
H	-7.701600	1.000100	-1.269300
H	-10.088000	1.397100	-0.846900
H	-10.922500	1.564200	1.467700
H	-9.348000	1.334700	3.351400
H	-6.962000	0.941500	2.920400

Table S 12. DFT-calculated Cartesian coordinates of **9**.

C	-4.007100	-3.478800	-0.041800

C	-4.958300	-2.532800	0.116200
C	-4.253400	-1.249600	0.213300
N	-2.925000	-1.415600	0.128200
C	-2.710800	-2.789600	-0.038400
C	-0.185000	-2.793700	-0.336100
C	-1.497600	-3.445500	-0.225700
C	-0.165300	2.819000	-0.298500
C	-4.955500	2.556200	0.125500
C	-3.991600	3.493900	-0.055600
C	-2.687100	2.849500	-0.066000
N	-2.965400	1.487000	0.097300
C	-4.321600	1.255200	0.201300
C	-1.468200	3.491700	-0.226700
C	-0.087800	-1.417600	-0.563500
C	1.125300	-0.726500	-0.498500
C	2.317800	-1.451500	-0.286000
C	2.244500	-2.850800	-0.141300
C	1.027400	-3.508600	-0.145400
C	2.250200	2.833600	0.040900
C	2.321800	1.443200	-0.180000
C	1.135100	0.742700	-0.479800
C	-0.059000	1.460400	-0.615100
C	3.590800	0.718000	-0.083100
C	3.591700	-0.738200	-0.157300
C	1.040400	3.501900	0.018400
N	4.709200	-1.431300	-0.074300
N	4.707200	1.399800	0.077700
C	-4.939200	0.012900	0.302400
C	5.878100	-0.741400	0.078800
C	5.876700	0.698800	0.159600
C	7.085900	1.382000	0.322500
C	8.301100	0.689600	0.407100
C	8.302600	-0.756300	0.324300
C	7.088500	-1.436700	0.162100
C	9.549500	1.365800	0.573200
C	10.724700	0.666300	0.653000
C	10.726200	-0.756900	0.571400
C	9.552200	-1.444800	0.412200
C	-1.511300	-4.938400	-0.294800
C	-1.966200	-5.713900	0.784300
C	-1.971300	-7.107300	0.710800
C	-1.523400	-7.751000	-0.443100
C	-1.062500	-6.992300	-1.521600

C	-1.048500	-5.601000	-1.445200
C	-1.472700	4.984700	-0.284200
C	-0.953600	5.650000	-1.409100
C	-0.949200	7.041700	-1.477900
C	-1.454100	7.799800	-0.418800
C	-1.960200	7.154600	0.709900
C	-1.966800	5.760700	0.777700
C	-6.430100	-0.012200	0.449400
C	-7.273100	0.395100	-0.596800
C	-8.660800	0.367300	-0.450800
C	-9.231900	-0.076500	0.742600
C	-8.406100	-0.491800	1.788900
C	-7.019100	-0.458600	1.643500
H	-4.153500	-4.538500	-0.186300
H	-6.029600	-2.667900	0.140400
H	-6.021600	2.716200	0.174400
H	-4.137300	4.554000	-0.193600
H	-2.318700	0.721000	0.236100
H	-1.013300	-0.891900	-0.718900
H	3.167100	-3.396400	0.021100
H	1.001900	-4.576700	0.035000
H	3.168600	3.361000	0.273300
H	-0.931500	0.944900	-0.981000
H	1.010100	4.557200	0.262600
H	7.060100	2.465900	0.381100
H	7.064200	-2.520400	0.098600
H	9.546000	2.450600	0.635000
H	11.665400	1.194000	0.779200
H	11.667900	-1.293700	0.636700
H	9.550700	-2.529600	0.349800
H	-2.306700	-5.215000	1.686200
H	-2.322200	-7.688900	1.558400
H	-1.528900	-8.835400	-0.501100
H	-0.713900	-7.484900	-2.424700
H	-0.688300	-5.015500	-2.285800
H	-0.560500	5.065200	-2.235400
H	-0.553500	7.535200	-2.360800
H	-1.447600	8.884500	-0.471600
H	-2.343400	7.735100	1.544100
H	-2.345600	5.262400	1.664800
H	-6.832400	0.725200	-1.533000
H	-9.295100	0.684900	-1.273600
H	-10.311700	-0.101000	0.855900

H	-8.841500	-0.837400	2.722200
H	-6.379500	-0.775700	2.462000

Table S 13. DFT-calculated Cartesian coordinates of **10**.

N	-9.005500	1.406600	-0.209100
C	-10.110900	0.719000	-0.356400
C	-10.100000	-0.733300	-0.469200
N	-8.984500	-1.419100	-0.428900
C	-7.809500	-0.722800	-0.275200
C	-7.820300	0.712300	-0.163500
C	-11.407600	1.482500	-0.406100
C	-11.385400	-1.499200	-0.637600
C	-6.620200	1.410000	-0.008300
C	-5.404100	0.716500	0.039600
C	-5.393400	-0.723300	-0.070600
C	-6.599300	-1.418600	-0.227300
N	-4.238000	1.411100	0.186100
C	-3.113500	0.725300	0.235900
C	-3.103300	-0.728600	0.133600
N	-4.217800	-1.415500	-0.022000
C	-1.843200	1.445900	0.352900
C	-0.641700	0.725800	0.527200
C	-0.642300	-0.742700	0.490200
C	-1.828700	-1.447100	0.198600
C	-1.781700	2.848000	0.230400
C	-0.568400	3.512700	0.212300
C	0.653200	2.801600	0.356200
C	0.569000	1.422000	0.569500
C	-1.752300	-2.834200	-0.041400
C	-0.538800	-3.496300	-0.037800
C	0.665600	-2.811000	0.278500
C	0.557000	-1.455000	0.605200
C	1.957700	3.458900	0.196700
C	3.172700	2.811000	-0.006600
N	3.404600	1.433400	-0.099800
C	4.730100	1.281300	-0.241700
C	5.412000	2.580500	-0.280000
C	4.453600	3.519000	-0.120800
C	5.422700	0.021900	-0.312600
C	4.808100	-1.224000	-0.214900
N	3.453200	-1.471800	-0.154300
C	3.186800	-2.830800	0.050700

C	4.498200	-3.457400	0.108600
C	5.456000	-2.510700	-0.058500
C	1.970900	-3.479900	0.211600
C	1.958400	4.954800	0.218000
C	1.578700	5.647400	1.380400
C	1.577500	7.040800	1.412100
C	1.940800	7.769900	0.277600
C	2.306100	7.095100	-0.887600
C	2.315300	5.699900	-0.917400
C	1.985200	-4.970500	0.290600
C	2.527100	-5.756000	-0.740900
C	2.532100	-7.148700	-0.653800
C	1.990700	-7.783800	0.464100
C	1.438700	-7.016700	1.492900
C	1.431200	-5.626300	1.404900
C	6.914500	0.032400	-0.438100
C	7.726600	0.546000	0.587000
C	9.116200	0.544600	0.468000
C	9.723100	0.024600	-0.677000
C	8.930000	-0.492600	-1.701900
C	7.539400	-0.486400	-1.583600
H	-11.937600	1.311300	-1.350500
H	-12.085400	1.174400	0.398600
H	-11.200200	2.548400	-0.305200
H	-11.919300	-1.191800	-1.544500
H	-11.162100	-2.564700	-0.702500
H	-12.066500	-1.329200	0.204600
H	-6.629100	2.490900	0.074600
H	-6.592600	-2.499500	-0.310400
H	-2.711000	3.391000	0.100800
H	-0.554500	4.583400	0.048100
H	1.501600	0.899400	0.689200
H	-2.670200	-3.363900	-0.270200
H	-0.505100	-4.548900	-0.292700
H	1.430800	-0.938300	0.967500
H	6.473400	2.734900	-0.405000
H	4.586400	4.589000	-0.067900
H	2.798200	-0.714300	-0.297600
H	4.651800	-4.508300	0.298500
H	6.525800	-2.651300	-0.036300
H	1.294100	5.084500	2.264400
H	1.293400	7.557800	2.324100
H	1.935100	8.855600	0.301400

H	2.581400	7.653500	-1.777700
H	2.592200	5.176600	-1.827200
H	2.932800	-5.266100	-1.620700
H	2.951800	-7.736400	-1.465100
H	1.993000	-8.867700	0.531800
H	1.015700	-7.502300	2.367500
H	1.002200	-5.035000	2.208300
H	7.259800	0.939800	1.484900
H	9.725600	0.942900	1.274300
H	10.805200	0.022500	-0.768900
H	9.392200	-0.896000	-2.598300
H	6.924400	-0.878400	-2.388400

Table S 14. DFT-calculated Cartesian coordinates of **S1**.

C	0.663800	-5.541600	-0.585200
C	-0.696700	-5.553800	-0.512700
C	-1.434600	-4.354200	-0.215200
C	-0.725300	-3.175500	0.133400
C	0.726000	-3.176500	0.098800
C	1.412600	-4.336800	-0.339300
C	2.806400	-4.241000	-0.569600
C	3.477700	-3.042700	-0.434700
C	2.804400	-1.873200	0.023300
C	1.458800	-2.002600	0.352500
C	-2.842400	-4.274800	-0.339000
C	-3.508500	-3.072400	-0.210100
C	-2.802500	-1.875700	0.106800
C	-1.434700	-1.980400	0.337700
C	3.487400	-0.566700	0.087500
C	4.975000	-0.574900	0.195600
C	5.604100	-1.256400	1.253700
C	6.992200	-1.273700	1.369700
C	7.785900	-0.619100	0.424500
C	7.178400	0.048700	-0.639100
C	5.787800	0.067200	-0.754500
C	-3.466400	-0.557900	0.095200
C	-4.960000	-0.565000	0.152300
C	-5.735600	-0.063000	-0.905500
C	-7.129600	-0.081900	-0.841400
C	-7.773700	-0.603100	0.281000
C	-7.014700	-1.113200	1.336900
C	-5.622800	-1.102400	1.269500

C	2.843400	0.655900	0.024100
C	3.468400	1.961300	0.193400
C	2.523000	2.927900	0.103900
C	1.232300	2.295300	-0.104200
N	1.481700	0.939800	-0.160200
C	-0.009400	2.918600	-0.138300
C	-1.276200	2.226200	-0.113500
N	-1.436100	0.897600	-0.101100
C	-2.819000	0.665600	-0.002000
C	-3.515300	1.957000	0.027500
C	-2.570500	2.918700	-0.056900
C	-0.015700	4.416100	-0.132300
C	0.481600	5.137600	-1.229600
C	0.493800	6.533300	-1.226300
C	0.002600	7.236000	-0.125600
C	-0.496600	6.533100	0.972900
C	-0.502600	5.138500	0.970300
H	1.207300	-6.440500	-0.864200
H	-1.250700	-6.462700	-0.731900
H	3.343800	-5.123300	-0.908100
H	4.529900	-2.987200	-0.689100
H	0.954200	-1.169000	0.814500
H	-3.397900	-5.172800	-0.596900
H	-4.577200	-3.035800	-0.385600
H	-0.916500	-1.072400	0.594000
H	4.992400	-1.765100	1.992800
H	7.455700	-1.796000	2.201800
H	8.868100	-0.635400	0.513800
H	7.786400	0.548900	-1.387500
H	5.320200	0.570400	-1.595100
H	-5.236200	0.334100	-1.783600
H	-7.711000	0.307700	-1.672000
H	-8.858500	-0.616300	0.331800
H	-7.507600	-1.519600	2.215400
H	-5.036900	-1.501700	2.092000
H	4.518800	2.099600	0.397700
H	2.663500	3.992400	0.214000
H	0.725600	0.296600	-0.353400
H	-4.582200	2.093500	0.118800
H	-2.717400	3.988400	-0.073000
H	0.853500	4.593300	-2.092800
H	0.881400	7.070400	-2.087400
H	0.008700	8.322100	-0.122700

H	-0.874500	7.071200	1.837700
H	-0.879800	4.596600	1.832600

Table S 15. DFT-calculated Cartesian coordinates of **S2**.

C	-3.404900	-3.215900	-0.820800
C	-2.724100	-4.406200	-1.070400
C	-1.368100	-4.536100	-0.763600
C	-0.683300	-3.458000	-0.184900
C	-1.392800	-2.290700	0.110500
C	-2.742800	-2.120500	-0.223600
C	0.771300	-3.447900	0.104600
C	1.459400	-4.509300	0.706200
C	2.806400	-4.353100	1.041900
C	3.468700	-3.149900	0.812200
C	2.804600	-2.065500	0.195100
C	1.470100	-2.269600	-0.186500
C	-3.427100	-0.838900	0.022600
C	-4.917200	-0.880500	0.091600
C	-5.561500	-1.709500	1.028000
C	-6.951600	-1.752200	1.107700
C	-7.729800	-0.982200	0.239700
C	-7.105800	-0.169100	-0.706700
C	-5.713300	-0.118100	-0.780000
C	-2.789500	0.386000	0.165300
N	-1.423100	0.651000	0.003400
C	-1.275900	1.972900	0.162400
C	-2.554900	2.617100	0.485600
C	-3.484700	1.636600	0.492900
C	-0.033400	2.695300	0.037000
C	1.212400	2.083500	-0.059300
C	-0.083800	4.186900	-0.006500
C	-0.834000	4.853500	-0.991500
C	-0.882000	6.246100	-1.037600
C	-0.177500	7.005700	-0.101200
C	0.571300	6.360100	0.883500
C	0.613700	4.966400	0.932300
N	1.467200	0.734900	0.065300
C	2.827300	0.448000	-0.087700
C	3.445400	1.738400	-0.356900
C	2.494200	2.705500	-0.330800
C	3.478300	-0.770500	-0.004300
C	4.968100	-0.779900	-0.082200

C	5.759300	-0.031100	0.806100
C	7.152000	-0.053100	0.720200
C	7.783300	-0.829800	-0.251500
C	7.011400	-1.590000	-1.133600
C	5.621200	-1.569800	-1.046300
H	-4.448200	-3.128900	-1.101700
H	-3.251800	-5.234600	-1.534200
H	-0.837600	-5.453400	-1.002900
H	-0.890400	-1.479900	0.613400
H	0.937700	-5.431600	0.944300
H	3.338800	-5.170100	1.520500
H	4.501600	-3.039900	1.122100
H	0.952400	-1.511500	-0.759100
H	-4.961400	-2.311100	1.703900
H	-7.428700	-2.386900	1.848900
H	-8.813600	-1.020600	0.298100
H	-7.702100	0.423900	-1.394200
H	-5.230400	0.505600	-1.525400
H	-2.698000	3.666800	0.696300
H	-4.535900	1.730100	0.720900
H	-1.373000	4.268300	-1.730400
H	-1.464100	6.738800	-1.811300
H	-0.214000	8.090500	-0.138000
H	1.115800	6.941100	1.622600
H	1.181000	4.469000	1.713300
H	0.700200	0.093800	0.217100
H	4.496200	1.868400	-0.564800
H	2.630600	3.761100	-0.509400
H	5.273300	0.558800	1.577100
H	7.742900	0.530600	1.420400
H	8.867100	-0.848300	-0.318000
H	7.493600	-2.197600	-1.894000
H	5.026500	-2.161600	-1.735500

References:

[1] *CrysAlisPro, Version* 1.171.36.28, Rigaku Oxford Diffraction (Poland): Wrocław, **2013**.

[2] Sheldrick, G. M. *Acta Cryst.* **2008**, A64, 112-122.

[3] J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ort, **2019**.

[4] J.-D. Chai, M. Head-Gordon, *J. Chem. Phys.* **2008**, *128*, 84106.

[5] Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. von Ragué Schleyer, *Chem. Rev.* **2005**, DOI 10.1021/cr030088+.

[6] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.