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Supporting Information

for

Synthesis of *meso*-pyrrole-substituted corroles by condensation of 1,9-diformyldipyrromethanes with pyrrole

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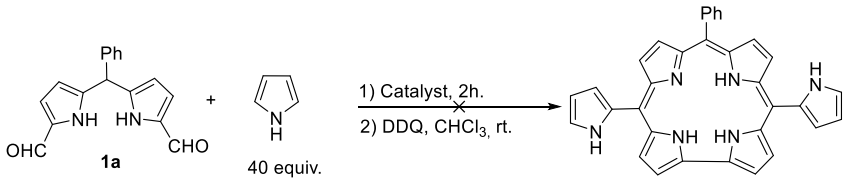
Table S1 and experimental part

Table S1: Unsuccessful acid catalysts for the synthesis of pyrrole-substituted corrole[a].



Entry	Catalyst	equiv of catalyst	Temperature (°C)
1	TFA[b]	0.1	−20
2	TFA[b]	0.1	0
4	I_2[c]	0.1	−20
5	I_2[b]	0.1	0
6	I_2[b]	0.1	rt
7	$InCl_3$[b]	0.1	−20
8	$InCl_3$[b]	0.1	0
9	$AlCl_3$[c]	1	−20
10	$AlCl_3$[b]	1	0
11	$AlCl_3$[b]	1	rt
12	$FeCl_3$[c]	1	−20
13	$FeCl_3$[b]	1	0
14	$FeCl_3$[b]	1	rt
15	H_2SO_4[b]	0.1	−20
16	H_2SO_4[b]	0.1	0
17	*p*-TsOH[b]	0.1	−20
18	*p*-TsOH[b]	0.1	0
19	Mont. K-10[b,d]		−20
20	Mont. K-10[b,d]		0
21	Mont. KSF[c,d]		−20
22	Mont. KSF[c,d]		0
23	Mont. KSF[c,d]		rt
24	Ag(OTf)[c]	0.1	−20
25	Ag(OTf)[b]	0.1	0

[a]Reaction conditions: **1a** (0.36 mmol, 0.10 g), pyrrole (14.4 mmol, 0.97, 1 mL), DDQ (0.72 mmol, 0.16 g), $CHCl_3$ (2 mL); [b]Unidentified oligomeric products were obtained. [c]No product was observed on TLC and the starting materials were recovered without the oxidation step; [d]0.36 g of clay catalyst was used.

[10-Phenyl-5,15-dipyrrolylcorrolato]copper(III) (2a): Green solid, mp> 250 ºC; 24 mg (0.043 mmol), 12% yield; UV/Vis ($CHCl_3$) λ_{max} (ε x 10^{-4} L mol^{-1} cm^{-1}): 412 (4.33), 542 (0.16), 611 (0.11) nm; FTIR (ATR): 702, 748, 842, 865, 980, 1005, 1058, 1168, 1276, 1460, 1590, 2843, 2960 cm^{-1}; ^{1}H NMR (400 MHz, THF-d_8): δ 6.51 (d, ^3J= 1.2 Hz, 2H), 7.05 (s, 2H), 7.27 (s, 2H), 7.41 (d, ^3J= 4.6 Hz, 2H), 7.45-7.60 (m, 4H), 7.61-7.65 (m, 1H), 7.66-7.76 (m, 2H), 7.94 (d, ^3J= 1.2 Hz, 2H), 8.07 (d, ^3J= 4.2 Hz, 2H), 8.90 (brs, 2H, NH); HRMS (ESI) m/z calcd for $C_{33}H_{21}CuN_6$ [M] 564.1124, found 564.1072.

[10-(4-Chlorophenyl)-5,15- dipyrrolylcorrolato]copper(III) (2b): Green solid, mp> 250 ºC; 28 mg (0.047 mmol), 13% yield; UV/Vis ($CHCl_3$) λ_{max} (ε x 10^{-4} L mol^{-1} cm^{-1}): 410 (4.58), 544 (0.30), 612 (0.20) nm; FTIR (ATR): 690, 850, 882, 1014, 1068, 1170, 1282, 1460, 2840, 2958 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.49 (d, ^3J= 3.0 Hz, 2H), 7.39 (d, ^3J= 4.3 Hz, 2H), 7.46 (d, ^3J= 7.6 Hz, 2H), 7.65-7.74 (m, 8H), 7.92-7.95 (m, 2H), 8.03-8.08 (m, 2H), 8.91 (brs, 2H, NH); HRMS (ESI) m/z calcd for $C_{33}H_{20}ClCuN_6$ [M] 598.0734, found 598.0752.

[10-(Pentafluorophenyl)-5,15- dipyrrolylcorrolato]copper(III) (2c): Green solid, mp> 250 ºC; 26 mg (0.047 mmol), 13% yield; UV/Vis ($CHCl_3$) λ_{max} (ε x 10^{-4} L mol^{-1} cm^{-1}): 410 (4.64), 534 (0.20) nm; FTIR (ATR): 712, 812, 898, 1021, 1068, 1170, 1198, 1455, 2988, 3012 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.49 (brs, 2H), 7.05 (brs, 2H), 7.41 (brs, 2H), 7.54 (brs, 2H), 7.73 (brs, 2H), 7.93 (brs, 2H), 8.05 (brs 2H), 8.89 (brs, 2H); HRMS (ESI) m/z calcd for $C_{33}H_{16}CuF_5N_6$ [M] 654.0653, found 654.0593.

[10-(4-Nitrophenyl)-5,15- dipyrrolylcorrolato]copper(III) (2d): Green solid, mp> 250 °C; 29 mg (0.047 mmol), 13% yield; UV/Vis ($CHCl_3$) λ_{max} (ε x 10^{-4} L mol^{-1} cm^{-1}): 420 (3.88), 551 (0.15) nm; FTIR (ATR): 734, 823, 941, 1013, 1070, 1187, 1381, 1545, 2988, 2990 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 6.49 (s, 2H), 6.96 (s, 2H), 7.65 (s, 2H), 7.76 (s, 2H), 8.02 (s, 2H), 8.14 (s, 2H), 8.19 (s, 2H), 8.43-8.50 (m, 4H), 8.84 (brs, 2H, NH); HRMS (ESI) m/z calcd for $C_{33}H_{20}CuN_7O_2$ [M] 609.0974, found 609.0923.

[10-(4-Metoxyphenyl)-5,15- dipyrrolylcorrolato]copper(III) (2e): Green solid, mp> 250 °C; 17 mg (0.029 mmol), 8% yield; UV/Vis ($CHCl_3$) λ_{max} (ε x 10^{-4} L mol^{-1} cm^{-1}): 414 (4.27), 536 (0.17), 608 (0.11) nm; FTIR (ATR): 760, 845, 935, 1025, 1077, 1214, 1490, 1575, 2820, 2992 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 4.09 (s, 3H, OCH_3), 6.49 (s, 2H), 7.41 (s, 2H), 7.43-7.55 (m, 10H), 7.93 (s, 2H), 8.04 (s, 2H), 8.90 (brs, 2H, NH); HRMS (ESI) m/z calcd for $C_{34}H_{23}CuN_6O$ [M] 594.1229, found 594.1276.

[10-(Tolyl)-5,15- dipyrrolylcorrolato]copper(III) (2f): Green solid, mp> 250 °C; 25 mg, 12% yield (0.043 mmol); UV/Vis ($CHCl_3$) λ_{max} (ε x 10^{-4} L mol^{-1} cm^{-1}): 412 (4.09), 534 (0.28), 614 (0.18) nm; FTIR (ATR): 712, 750, 815, 843, 981, 1005, 1060, 1163, 1276, 1454, 1583, 2855, 2981 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 2.94 (s, 3H, CH_3), 6.49 (d, ^3J= 2.5 Hz, 2H), 7.35-7.40 (m, 3H), 7.43-7.48 (m, 2H), 7.52 (s, 3H), 7.63-7.68 (m, 2H), 7.69-7.73 (m, 2H), 7.90-7.94 (m, 2H), 8.05 (d, ^3J= *4.2* Hz, 2H), 8.89 (brs, 2H, NH); HRMS (ESI) m/z calcd for $C_{34}H_{23}CuN_6$ [M] değeri 578.1280, found 578.1225.

5,15-Diphenylporphyrin (**3**): Purple solid, mp> 250 °C; 8 mg (0.017 mmol), 4% yield; ^{1}H NMR (400 MHz,$CDCl_3$): δ -3.18 (s, 2H, NH), 7.74-7.75 (m, 6H), 8.20-8.22 (m, 4H), 9.02 (d, *J*= 4.5 Hz, 4H, β-H), 9.34 (d, *J*= 4.5 Hz, 4H, β-H), 10.26 (s, 2H, meso-H). Analytical data were as described in the literature [1].

5-Phenylporphyrin (**4**): Purple solid, mp> 250 °C; 2 mg (0.005 mmol), 1% yield; ^{1}H NMR (400 MHz,$CDCl_3$): δ -3.48 (s, 2H, NH), 7.75-7.85 (m, 3H), 8.25-8.30 (m, 2H), 9.10-9.20 (m, 2H), 9.40-9.50 (m, 2H), 9.52-9.60 (m, 4H), 10.27 (s, 1H), 10.37 (s, 2H);); HRMS (ESI) m/z calcd for $C_{26}H_{18}N_4$ $[M+H]^+$ 387.1604, found 387.1632. Analytical data were as described in the literature. [2]

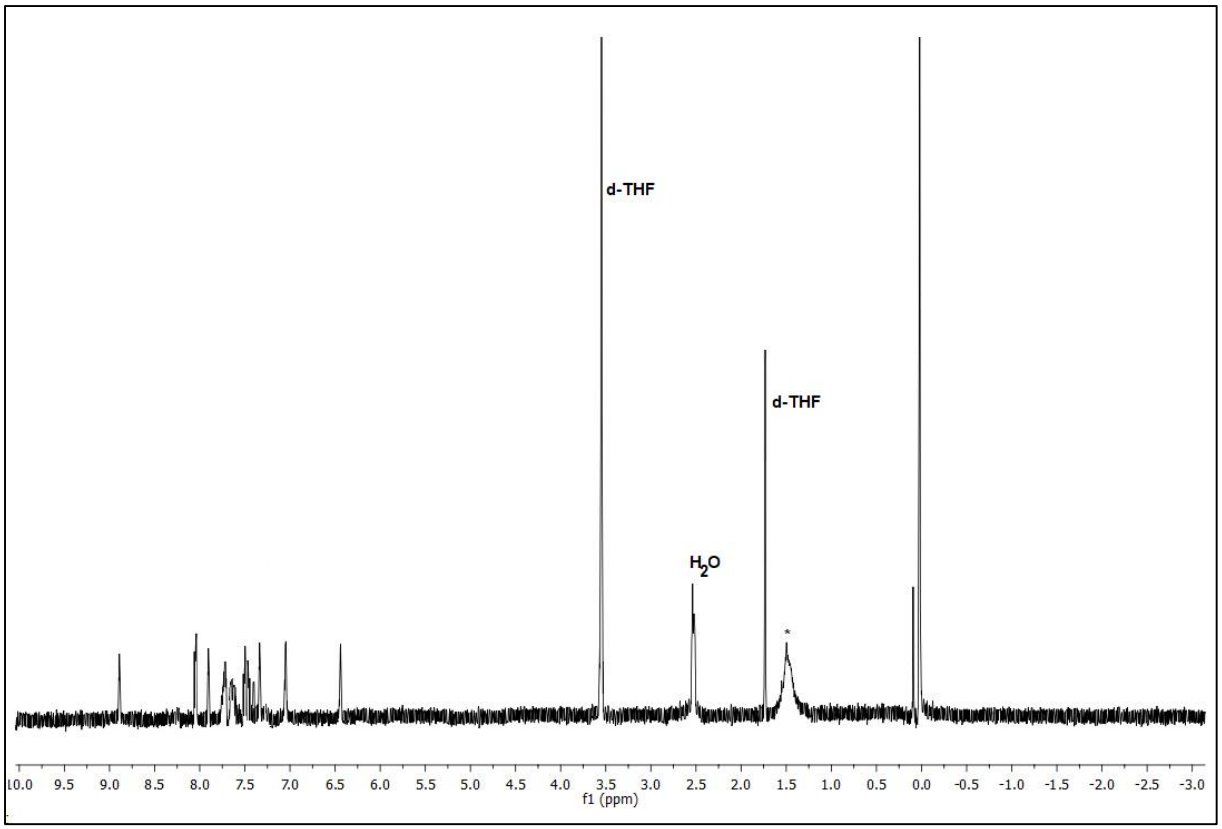


Figure S1: ^{1}H NMR spectrum of **2a** (−3–10 ppm, Solvent: THF-d_8).

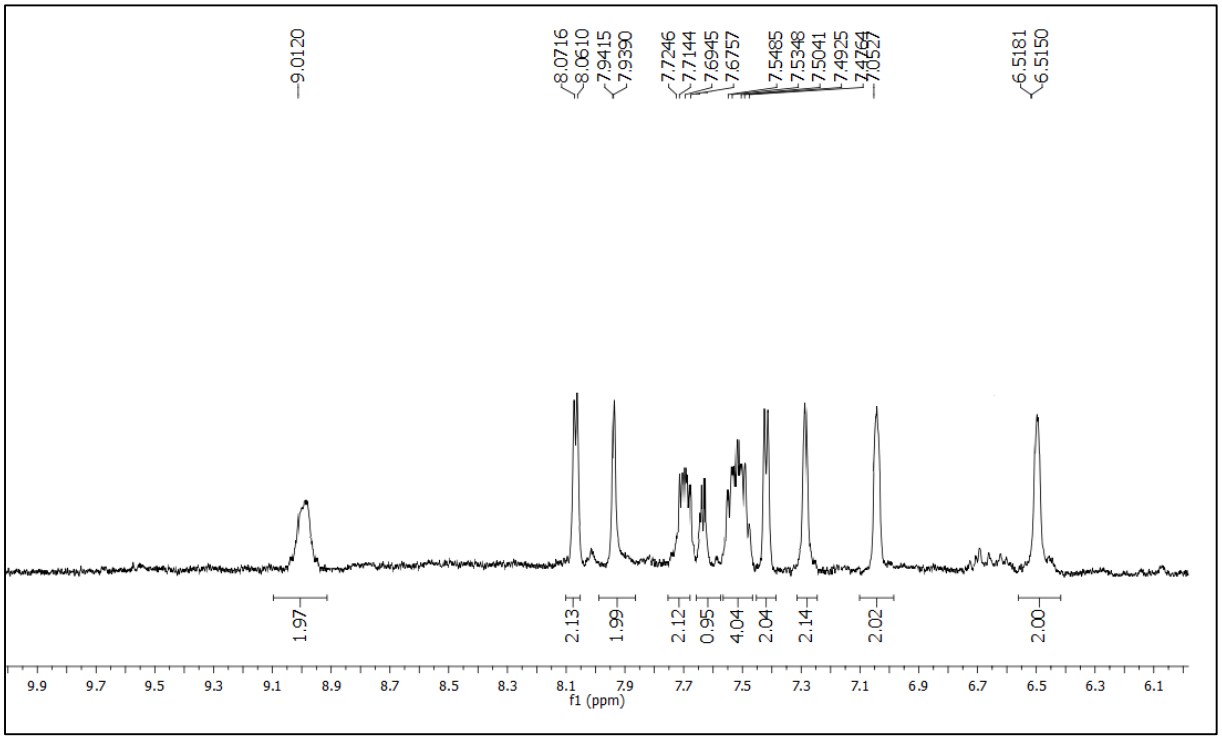


Figure S2: ^{1}H NMR spectrum of **2a** (6.0–10.0 ppm, Solvent: THF-d_8).

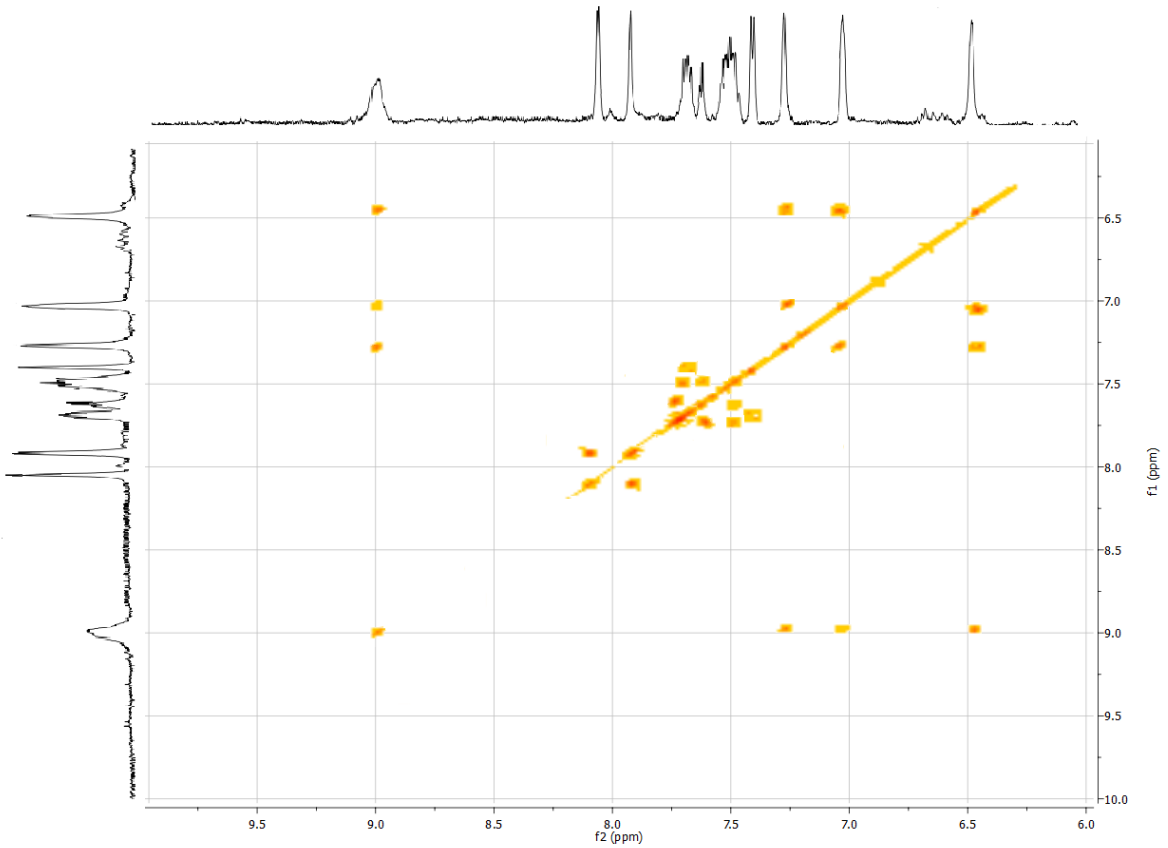


Figure S3: ^{1}H-^{1}H COSY NMR spectrum of **2a** (6.0–10.0 ppm, Solvent: THF-d_8).

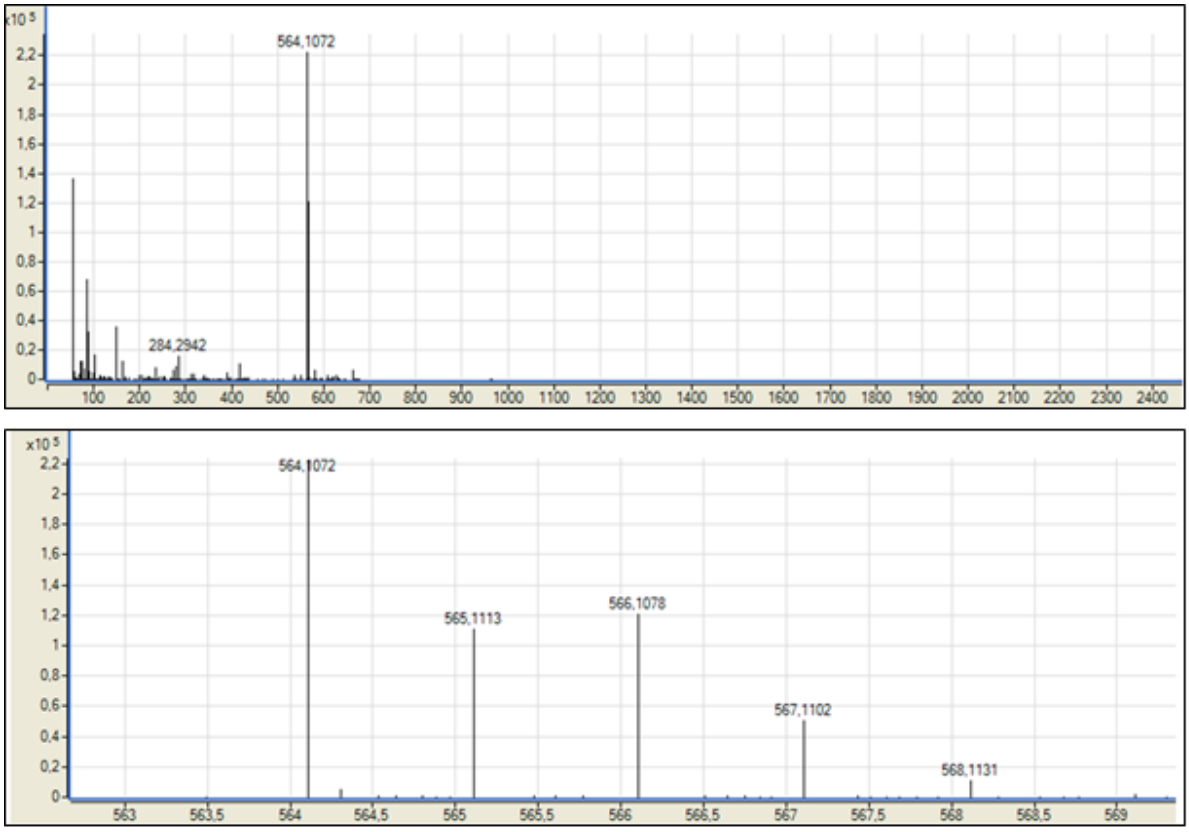


Figure S4: ESI HRMS (positive mode) of compound **2a**.

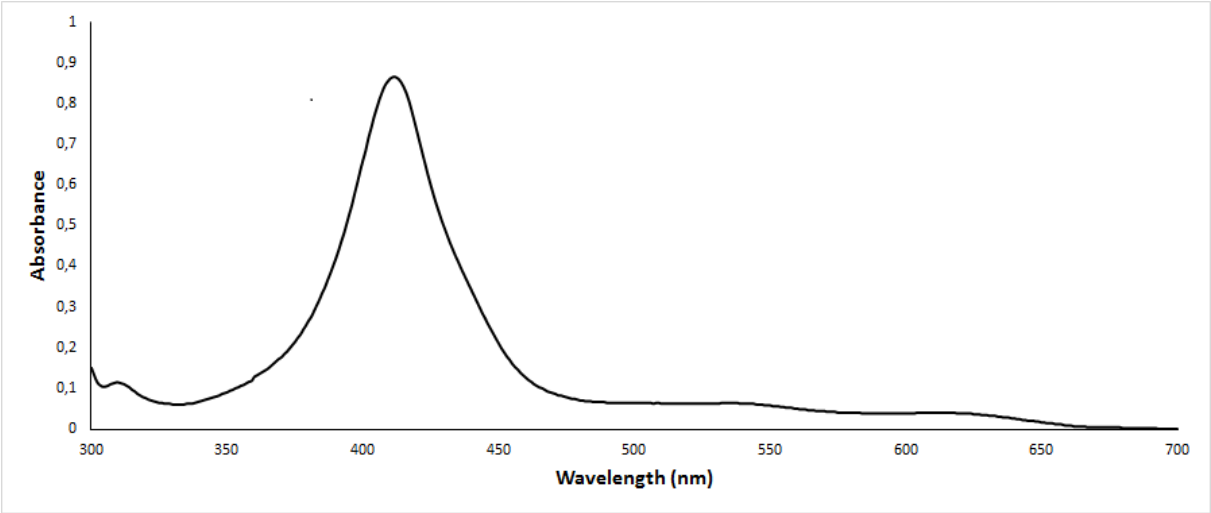


Figure S5: Electronic absorption spectra of **2a** in $CHCl_3$.

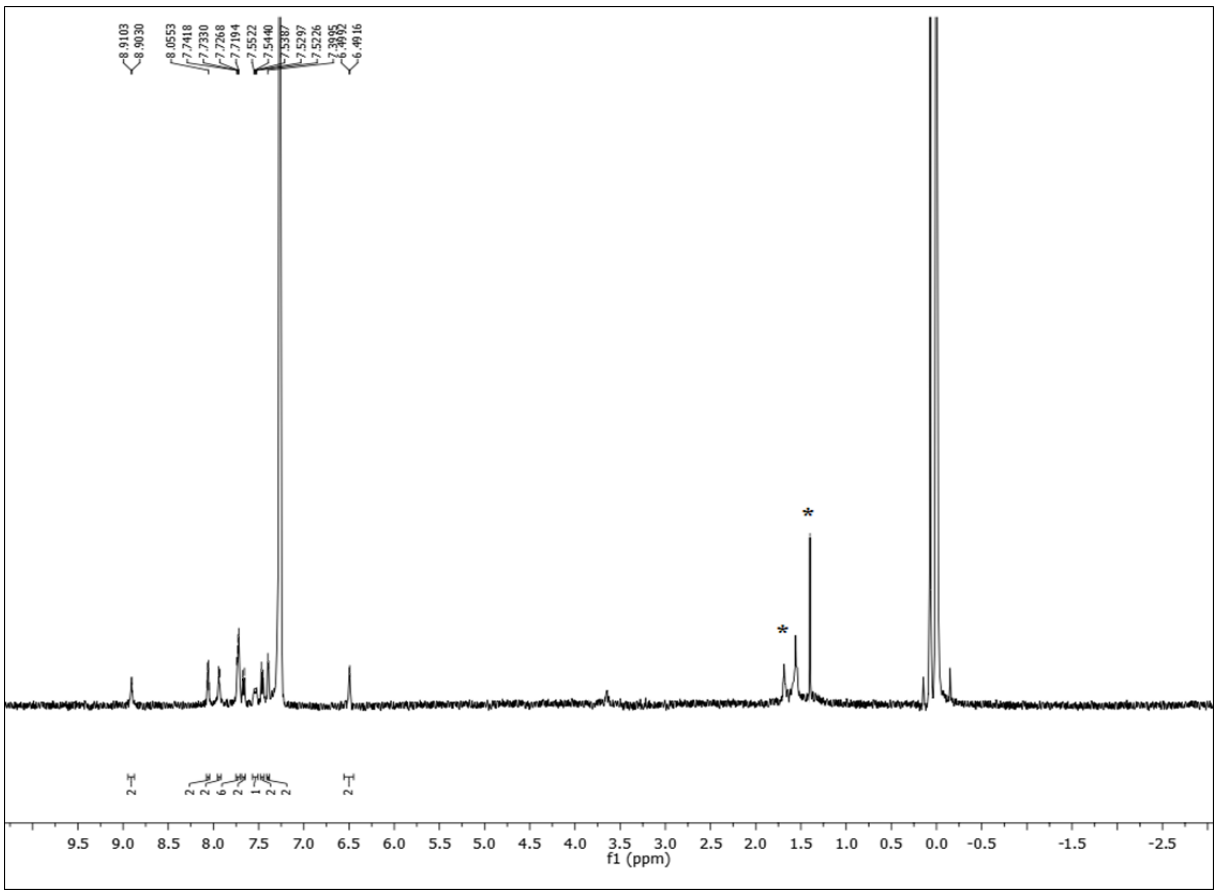


Figure S6: ^{1}H NMR spectrum of **2b** (−3–10 ppm, Solvent: $CDCl_3$).

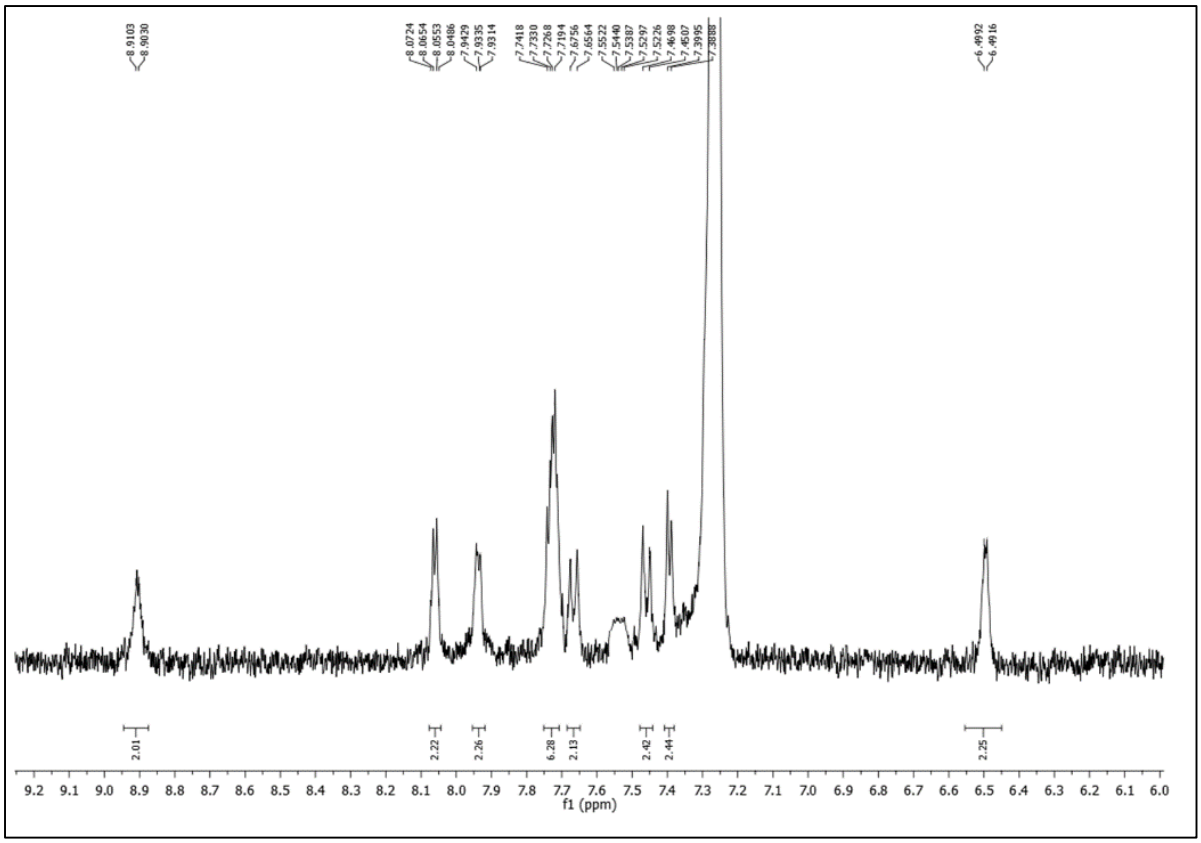


Figure S7: ^{1}H NMR spectrum of **2b** (6.0–9.3 ppm, Solvent: $CDCl_3$).

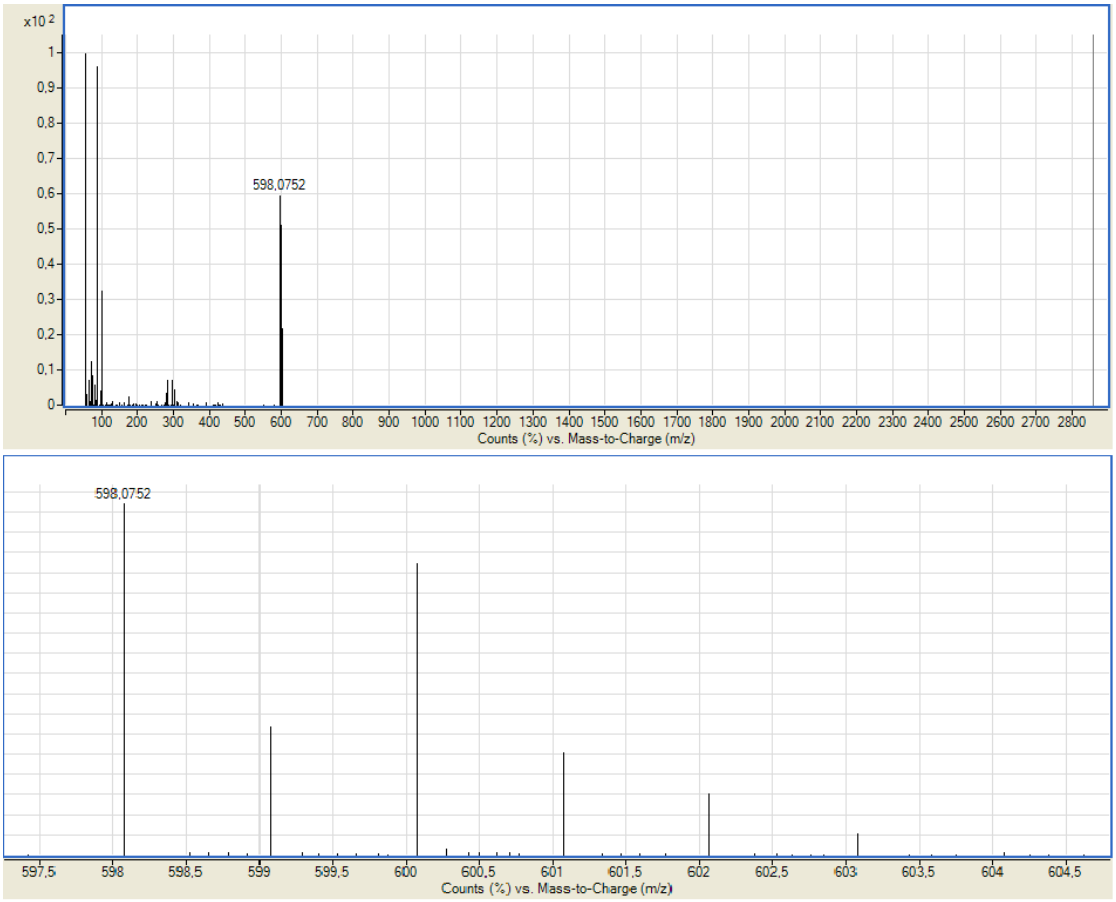


Figure S8: ESI HRMS (positive mode) of compound **2b**.

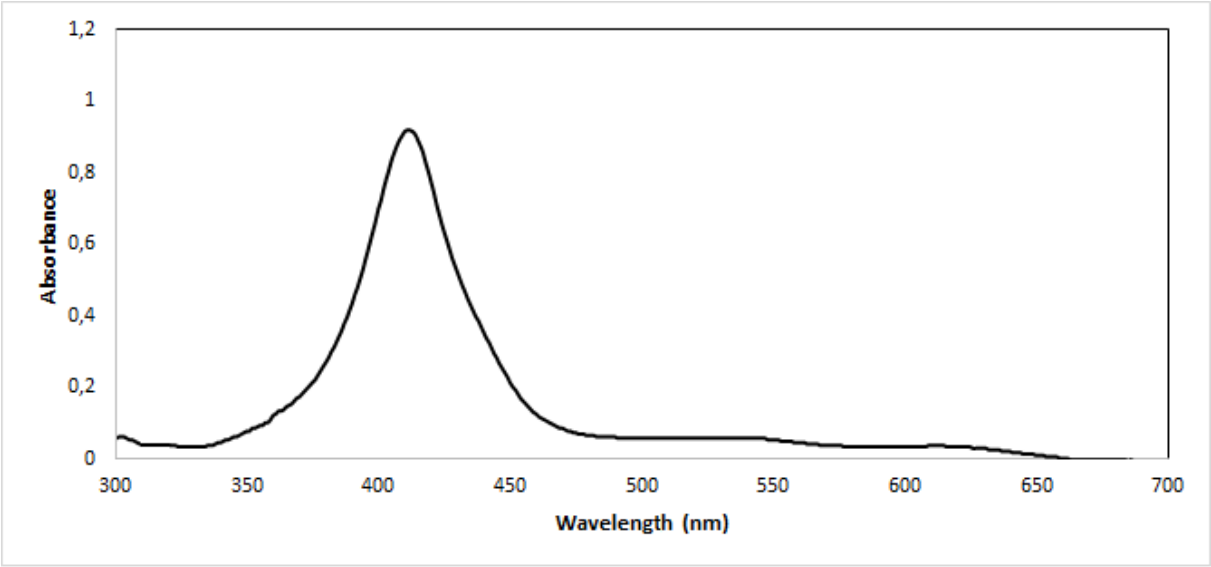


Figure S9: Electronic absorption spectra of **2b** in $CHCl_3$.

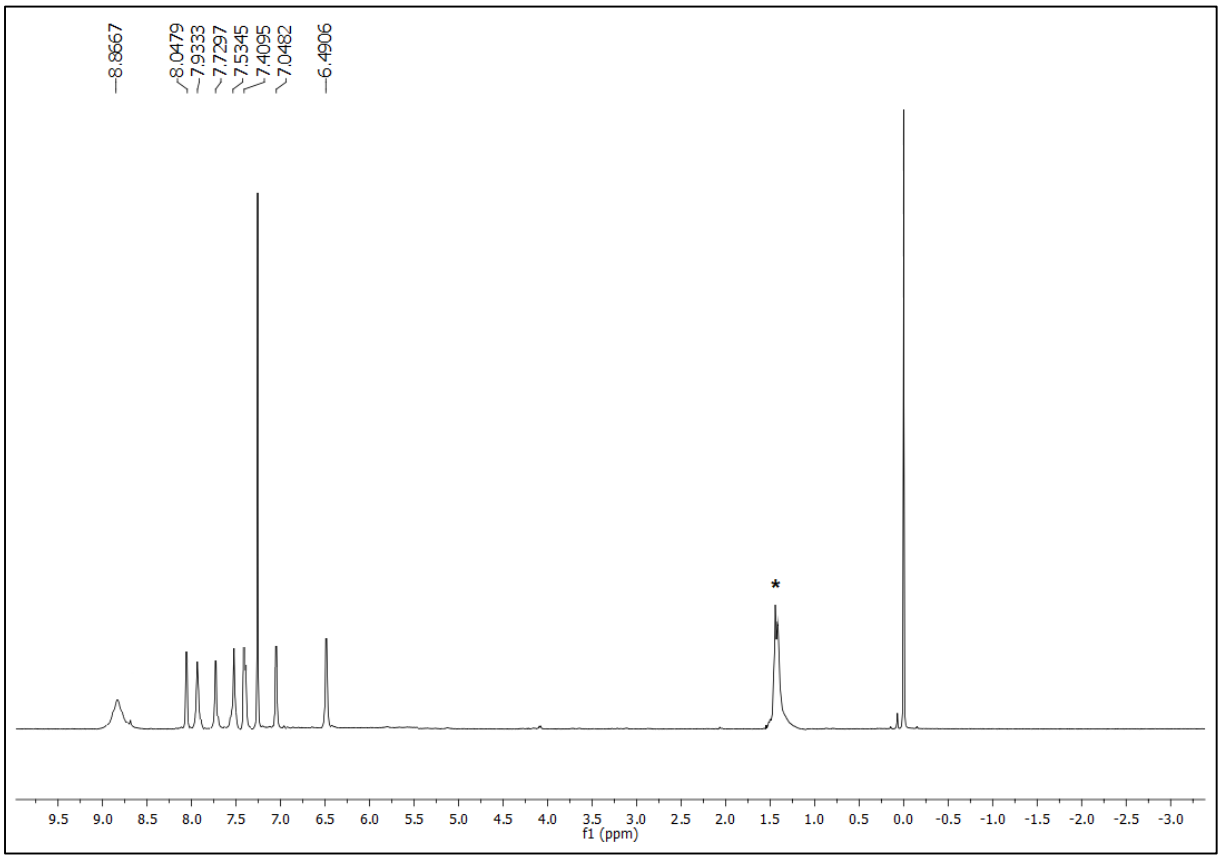


Figure S10: ^1H NMR spectrum of **2c** (−3–10 ppm, Solvent: $CDCl_3$).

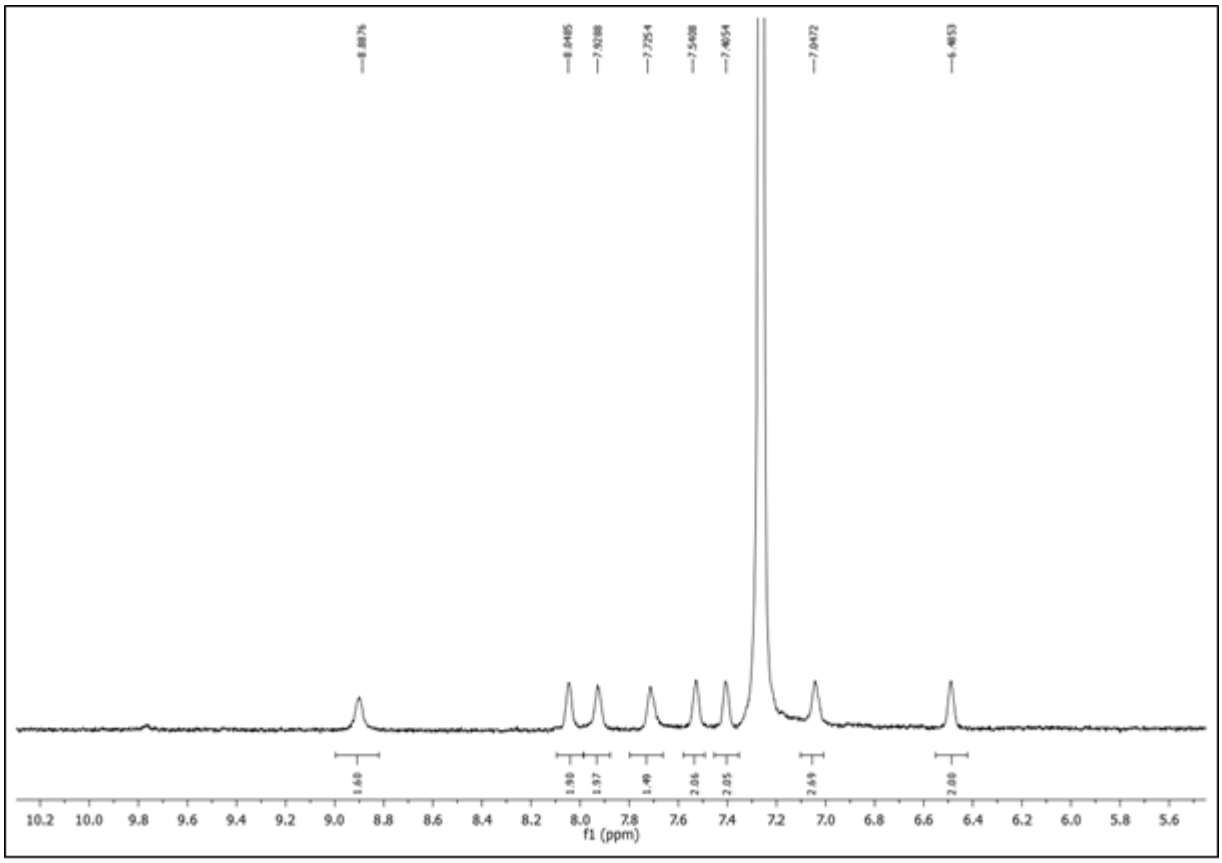


Figure S11: ^{1}H NMR spectrum of **2c** (5.5–10.2 ppm, Solvent: $CDCl_3$).

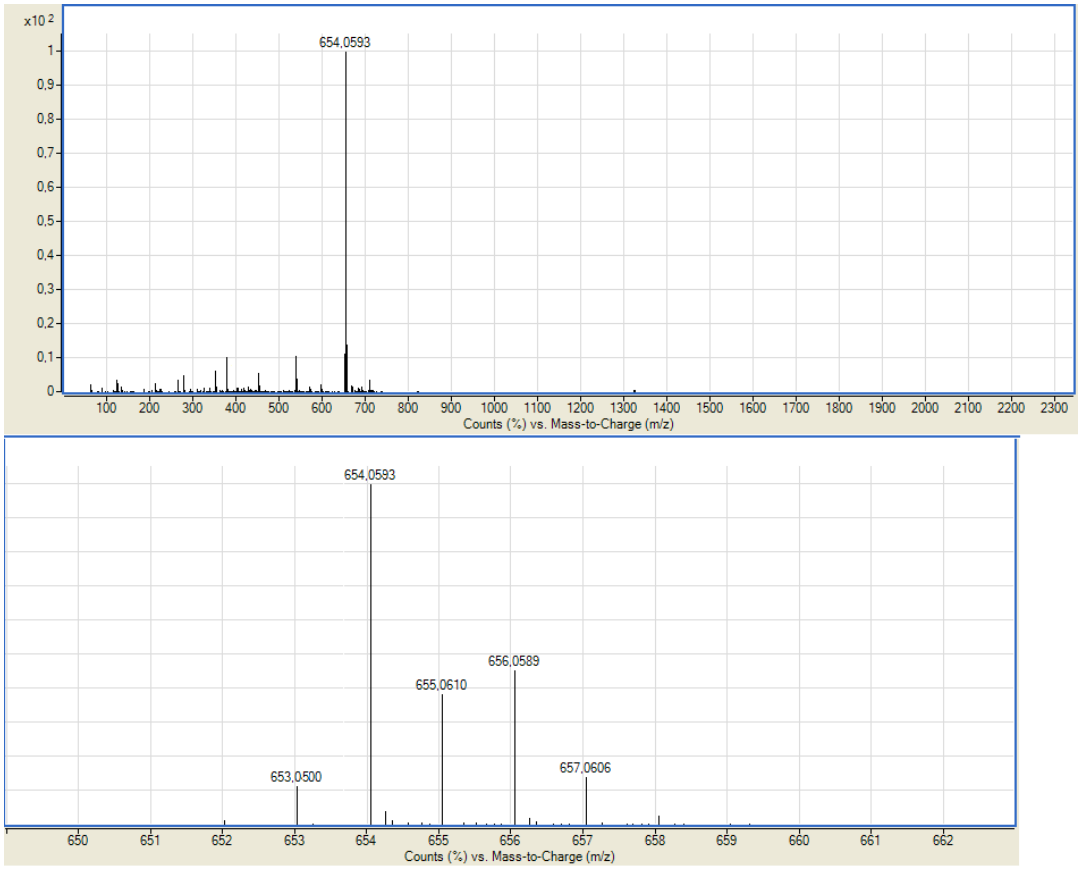


Figure S12: ESI HRMS (positive mode) of compound **2c**.

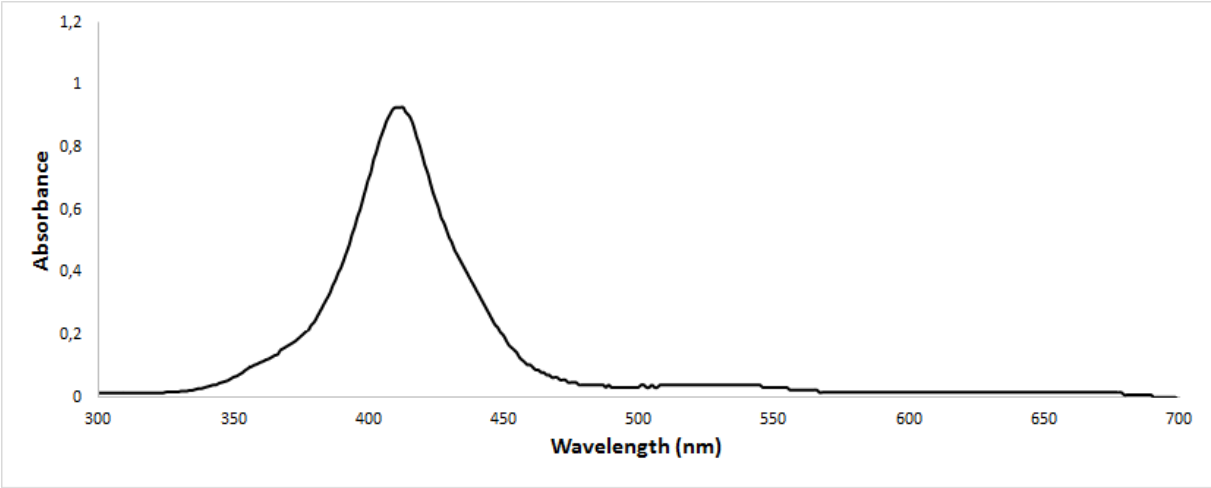


Figure S13: Electronic absorption spectra of **2c** in $CHCl_3$.

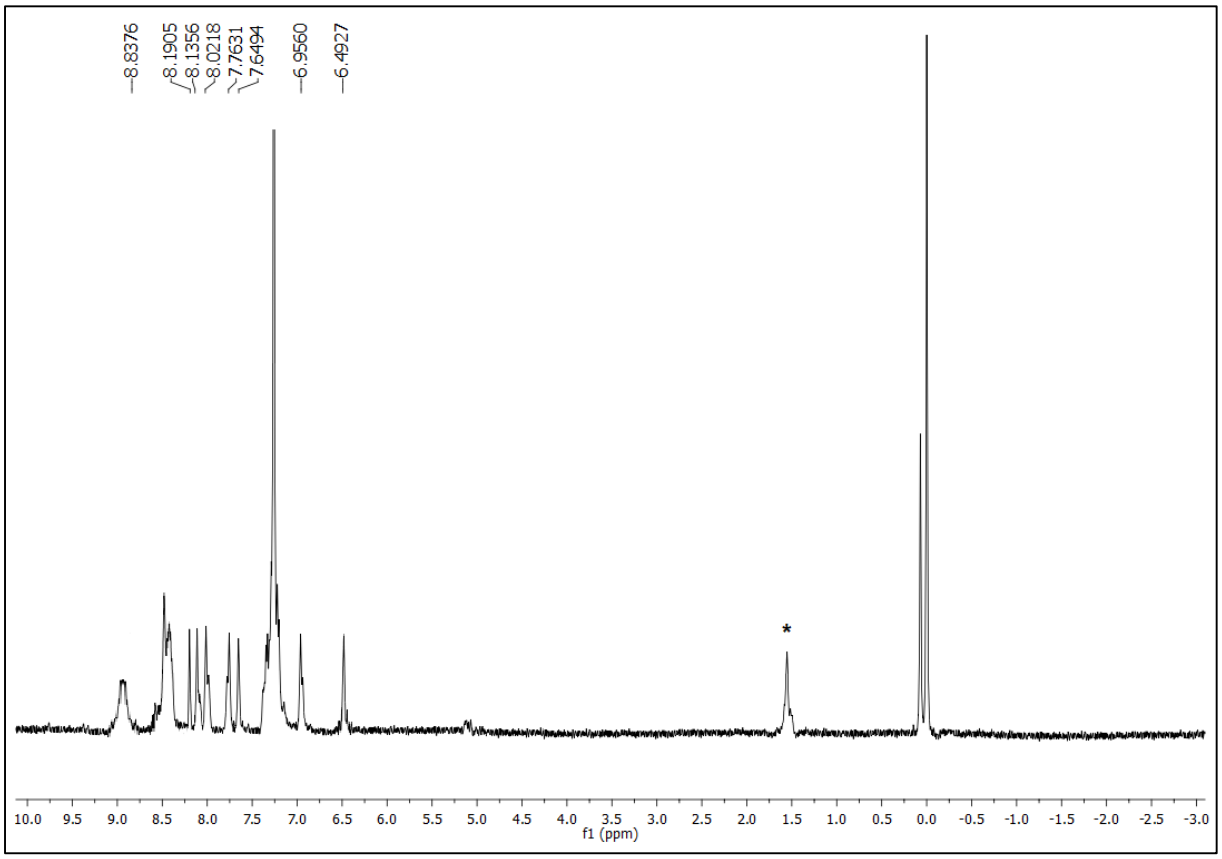


Figure S14: ^{1}H NMR spectrum of **2d** (−3–10 ppm, Solvent: $CDCl_3$).

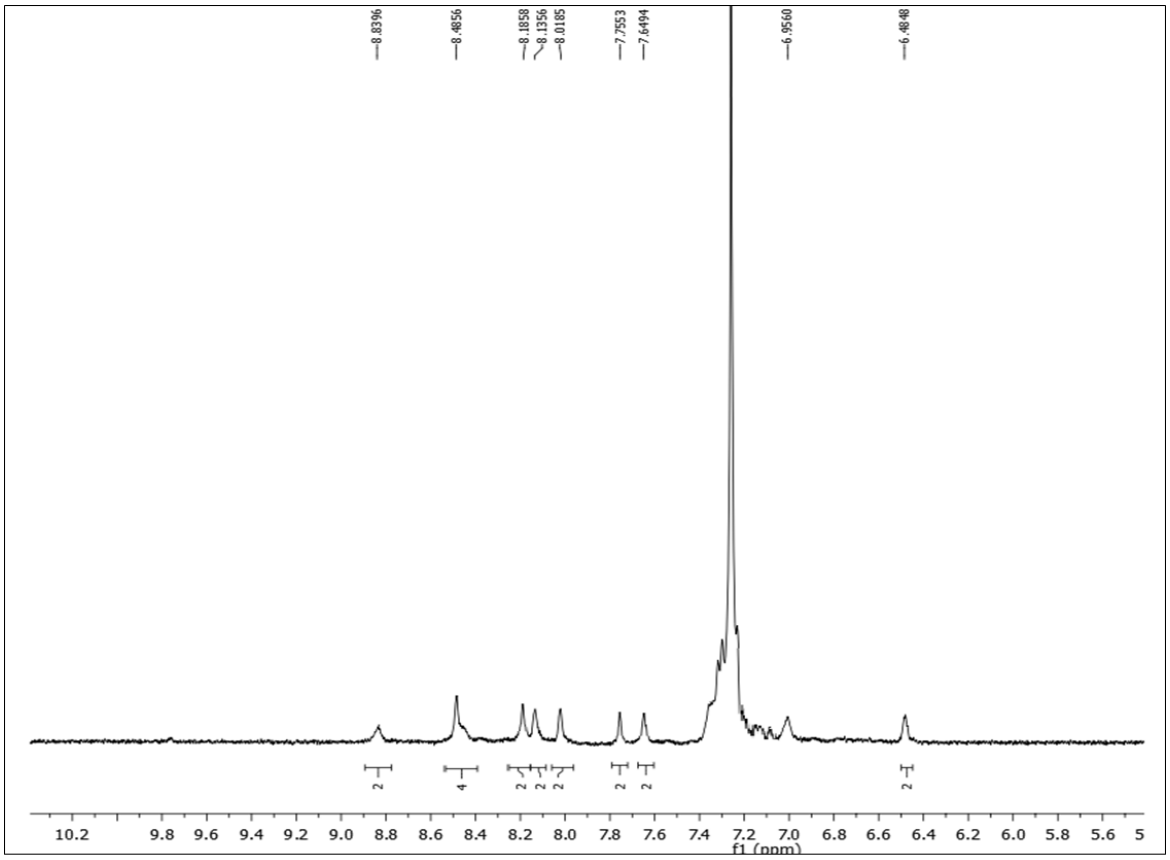


Figure S15: ^{1}H NMR spectrum of **2d** (6.0–9.3 ppm, Solvent: $CDCl_3$).

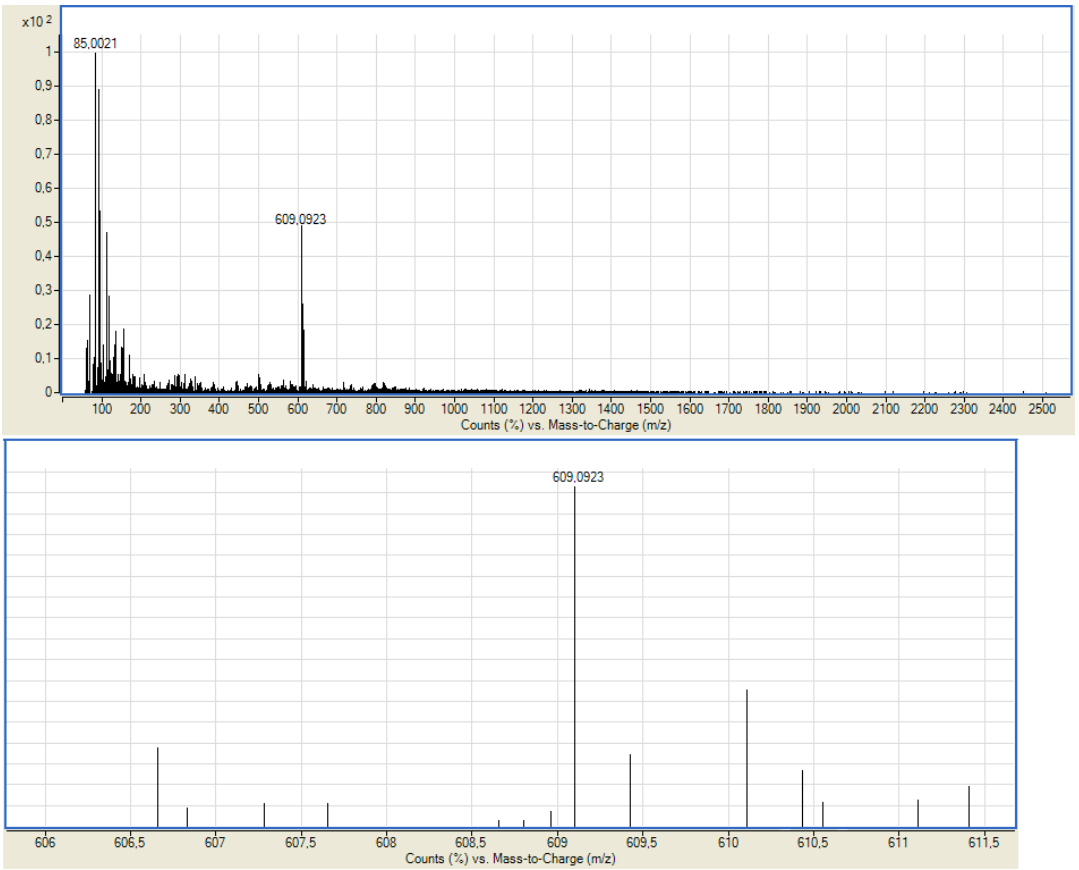


Figure S16: ESI HRMS (positive mode) of compound **2d**.

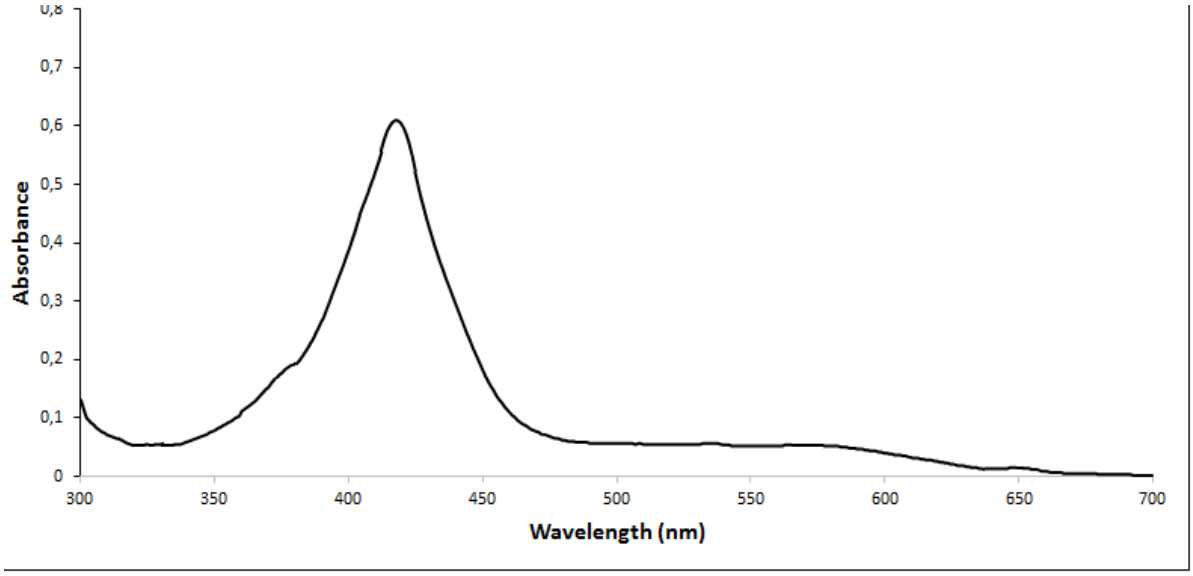


Figure S17: Electronic absorption spectra of **2d** in $CHCl_3$.

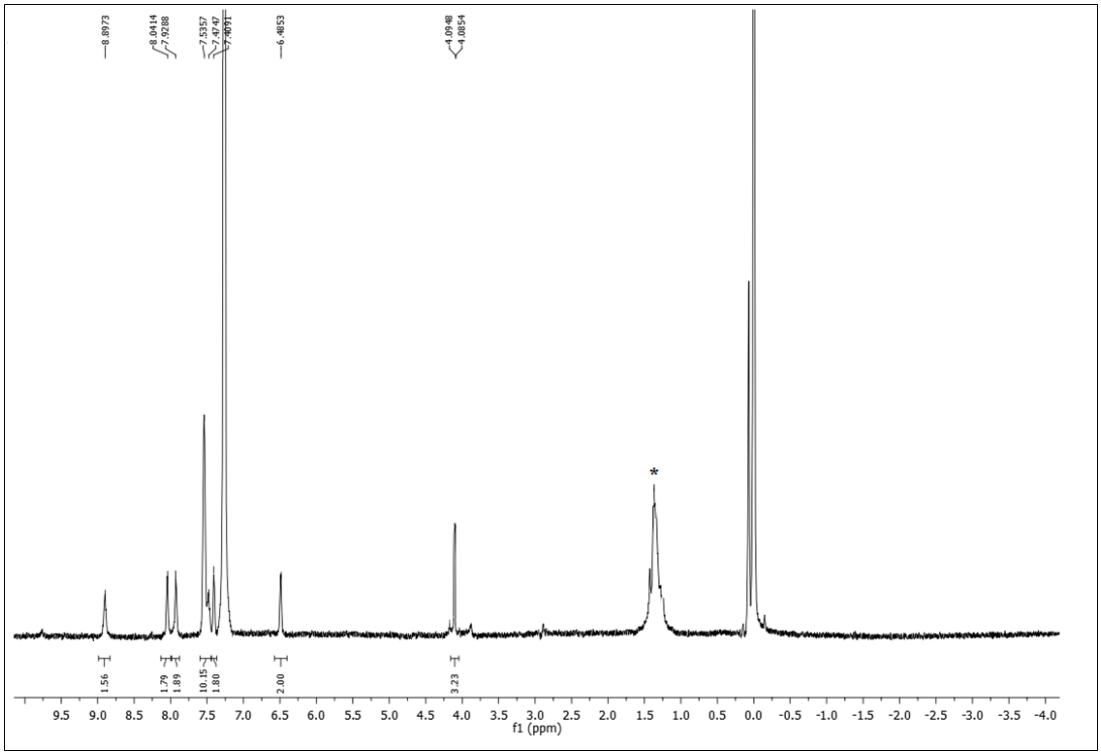


Figure S18: ^1H NMR spectrum of **2e** (−4–10 ppm, Solvent: $CDCl_3$).

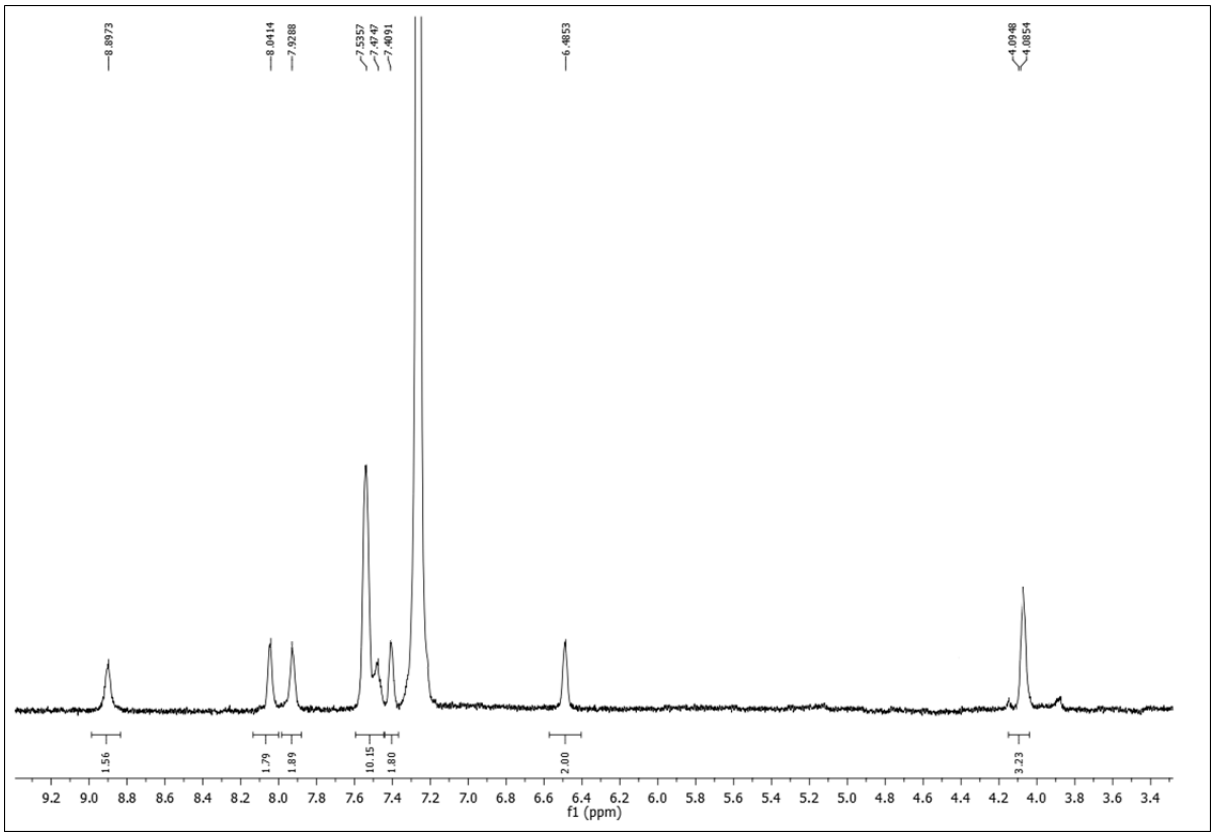


Figure S19: ^{1}H NMR spectrum of **2e** (3.3–9.3 ppm, Solvent: $CDCl_3$).

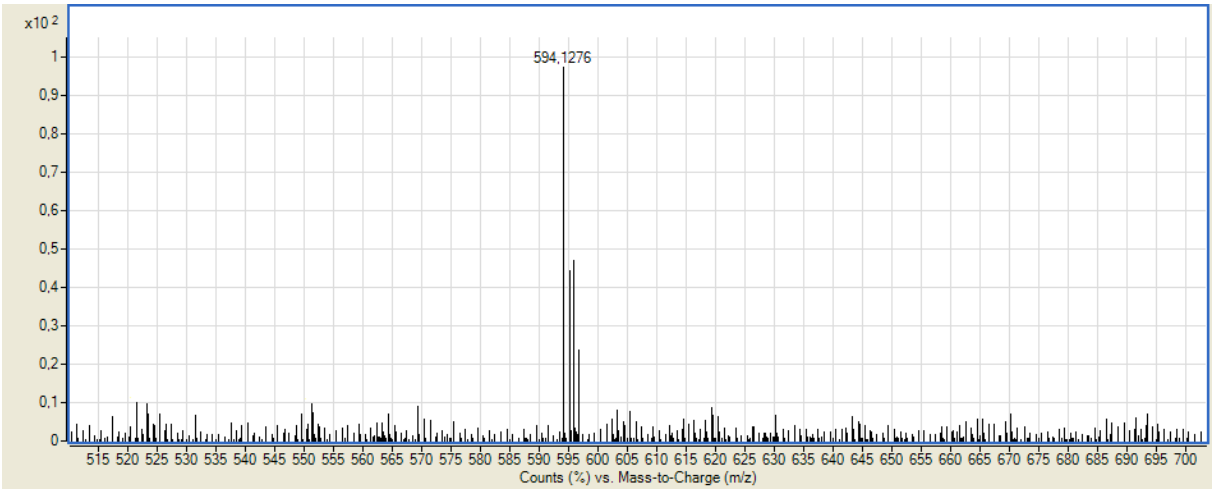


Figure S20: ESI HRMS (positive mode) of compound **2e**.

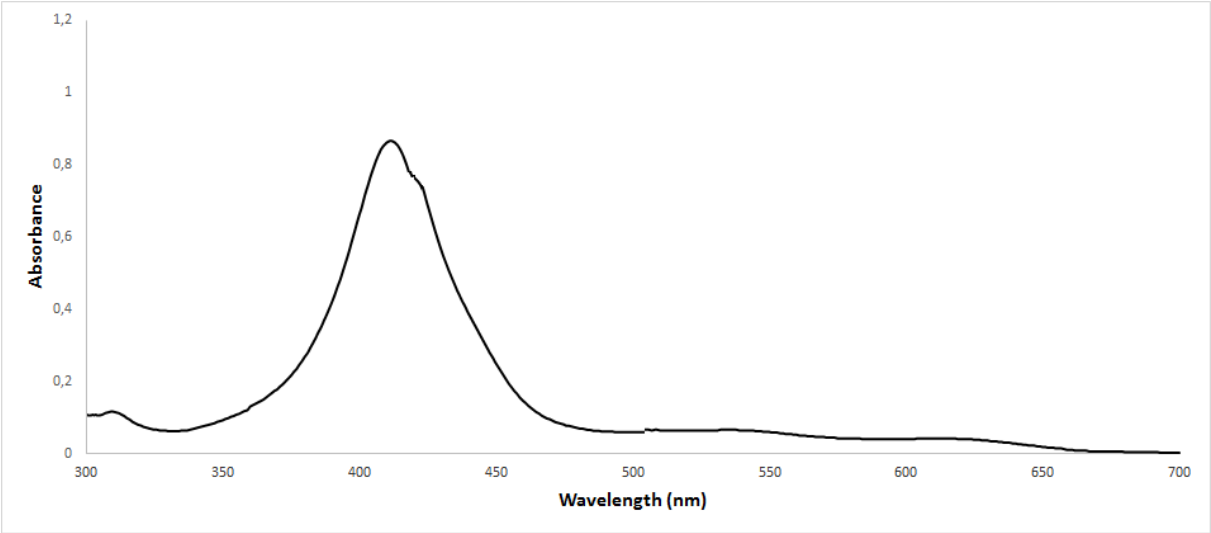


Figure S21: Electronic absorption spectra of **2e** in $CHCl_3$.

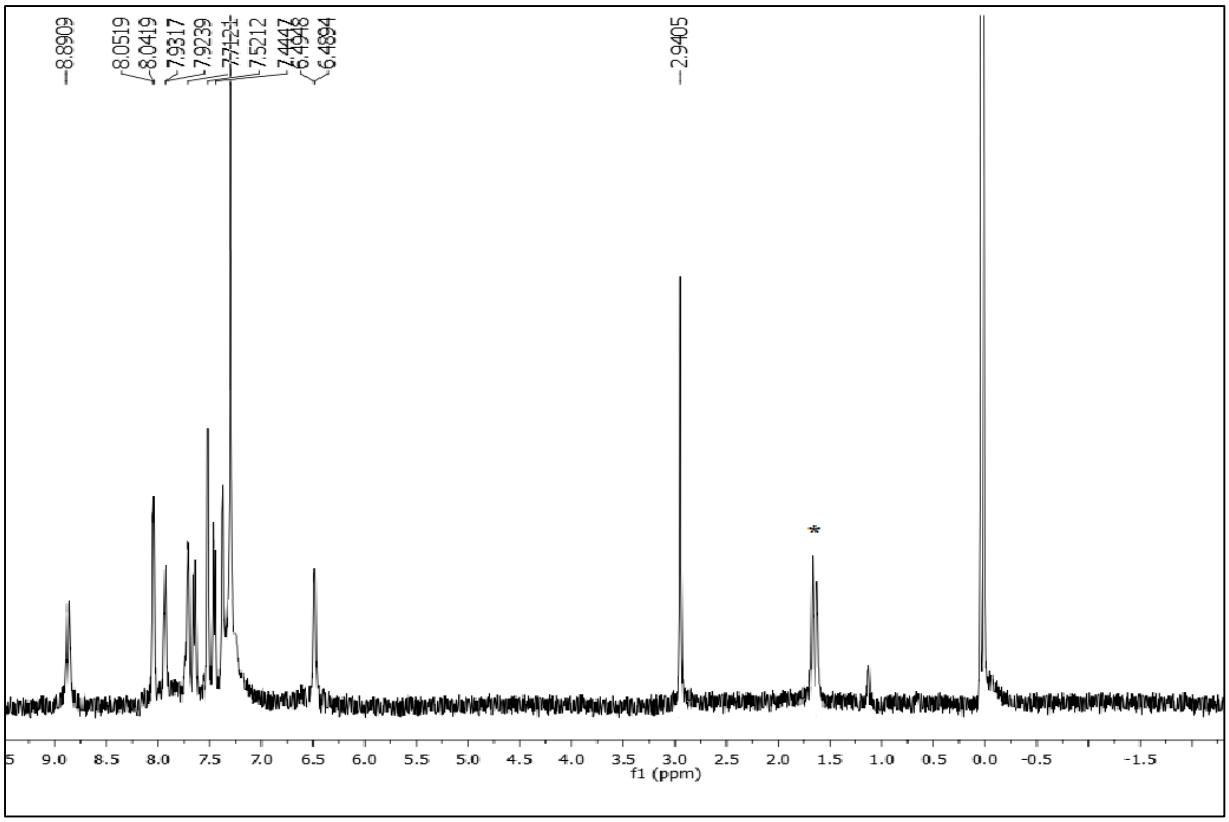


Figure S22: ^{1}H NMR spectrum of **2f** (−2–10 ppm, Solvent: $CDCl_3$).

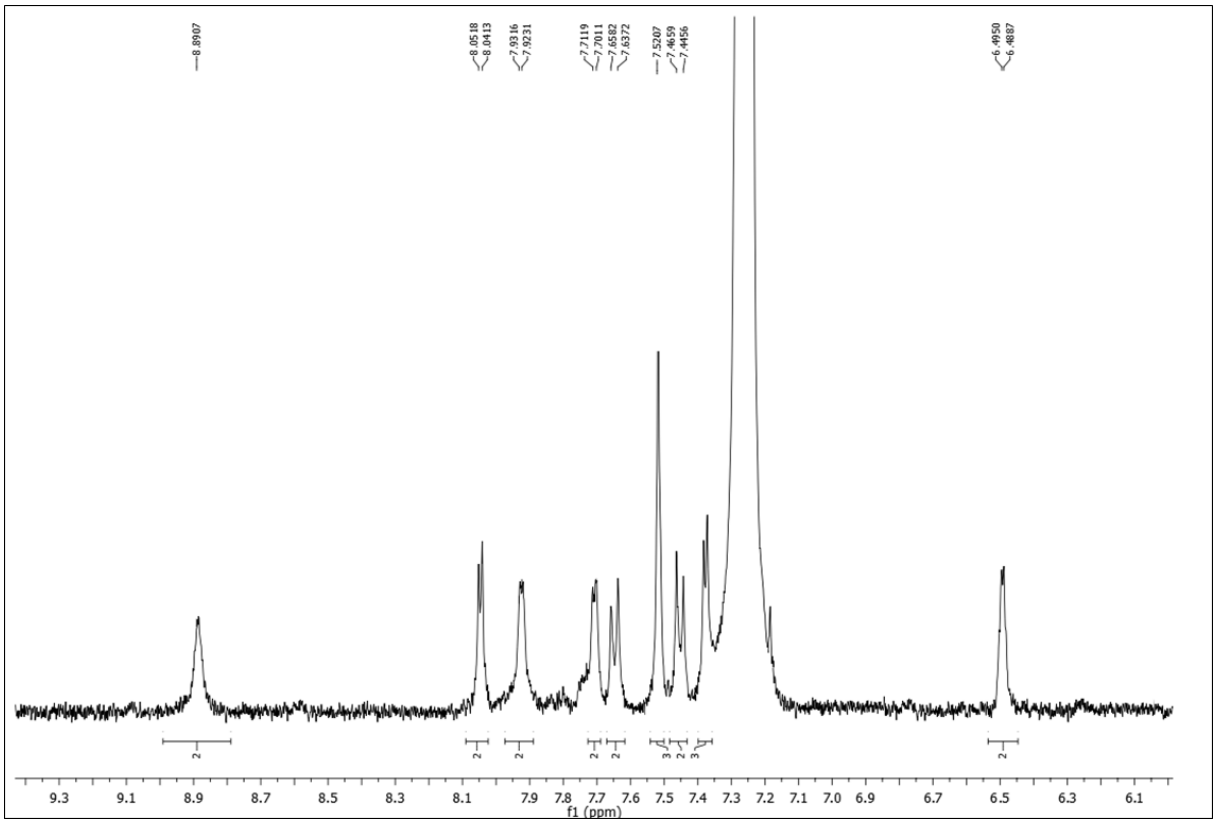


Figure S23: ^{1}H NMR spectrum of **2f** (6.0–9.3 ppm, Solvent: $CDCl_3$).

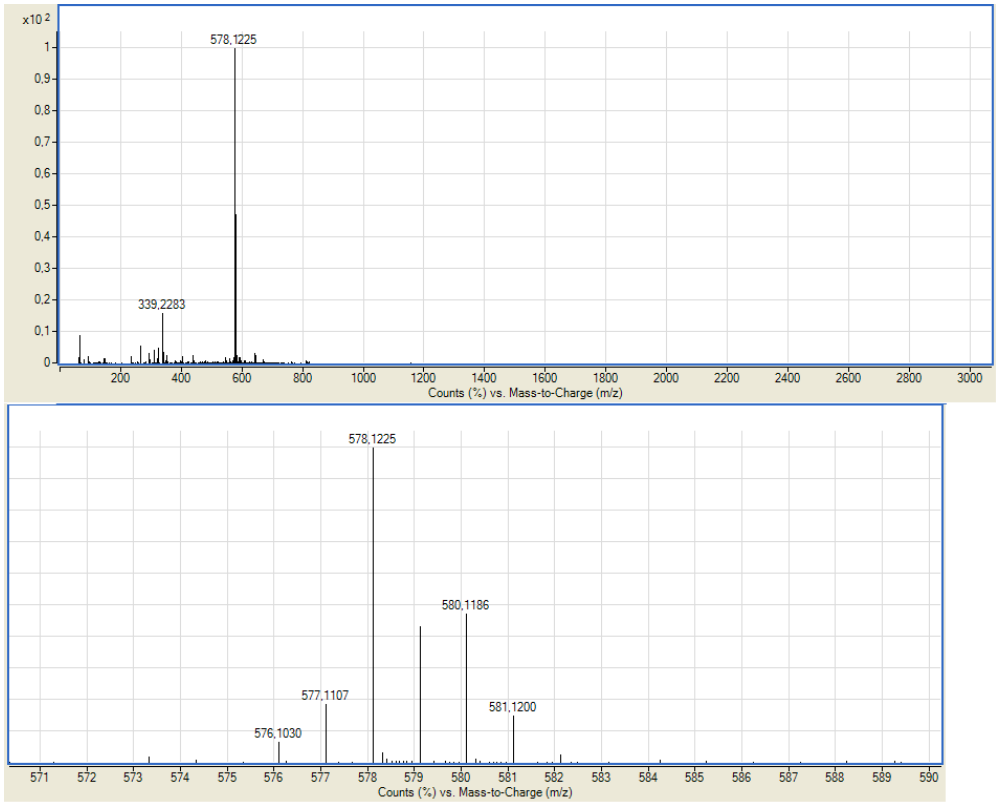


Figure S24: ESI HRMS (positive mode) of compound **2f**.

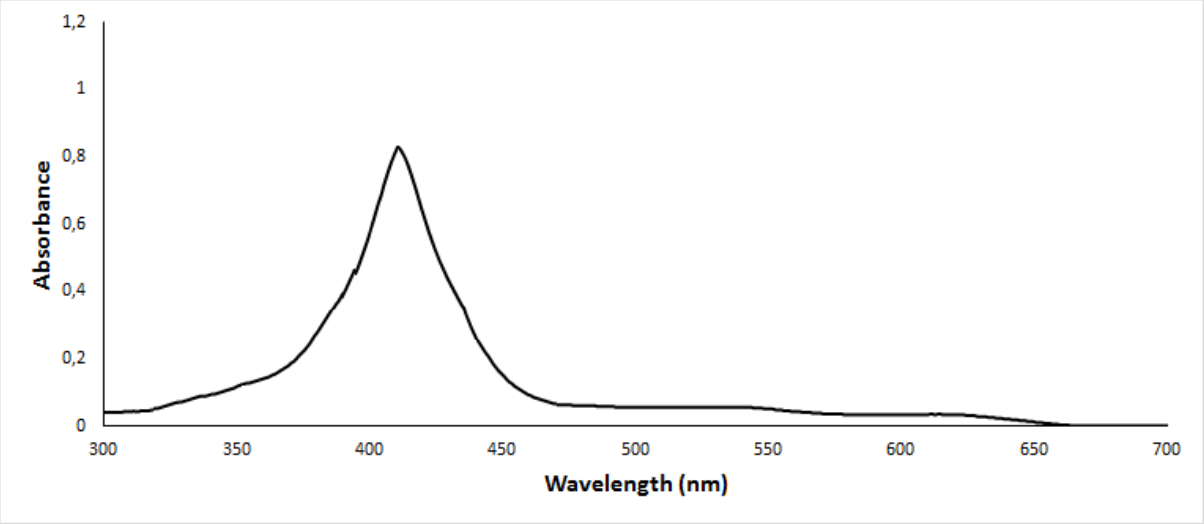


Figure S25: Electronic absorption spectra of **2f** in $CHCl_3$.

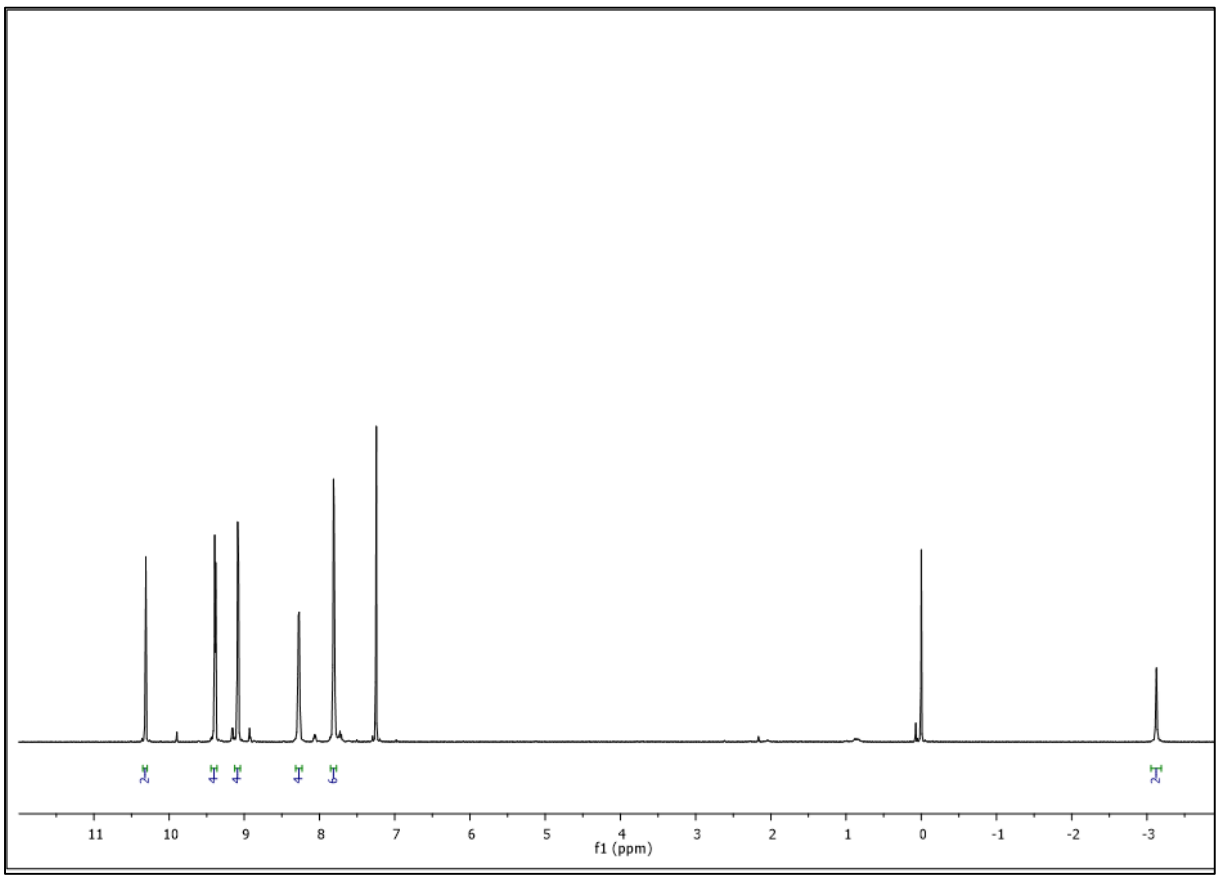


Figure S26: ^1H NMR spectrum of **3** (Solvent: $CDCl_3$).

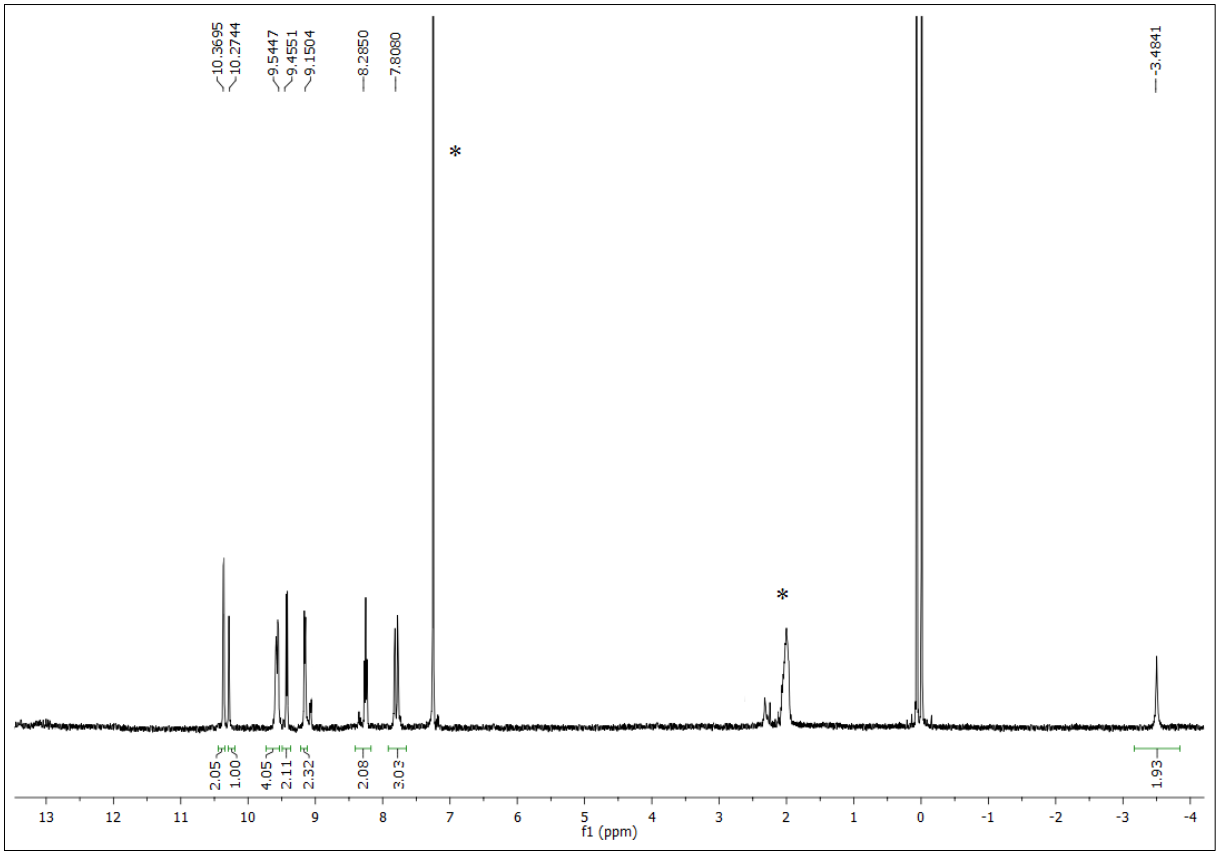


Figure S27: ^{1}H NMR spectrum of **4** (Solvent: $CDCl_3$).

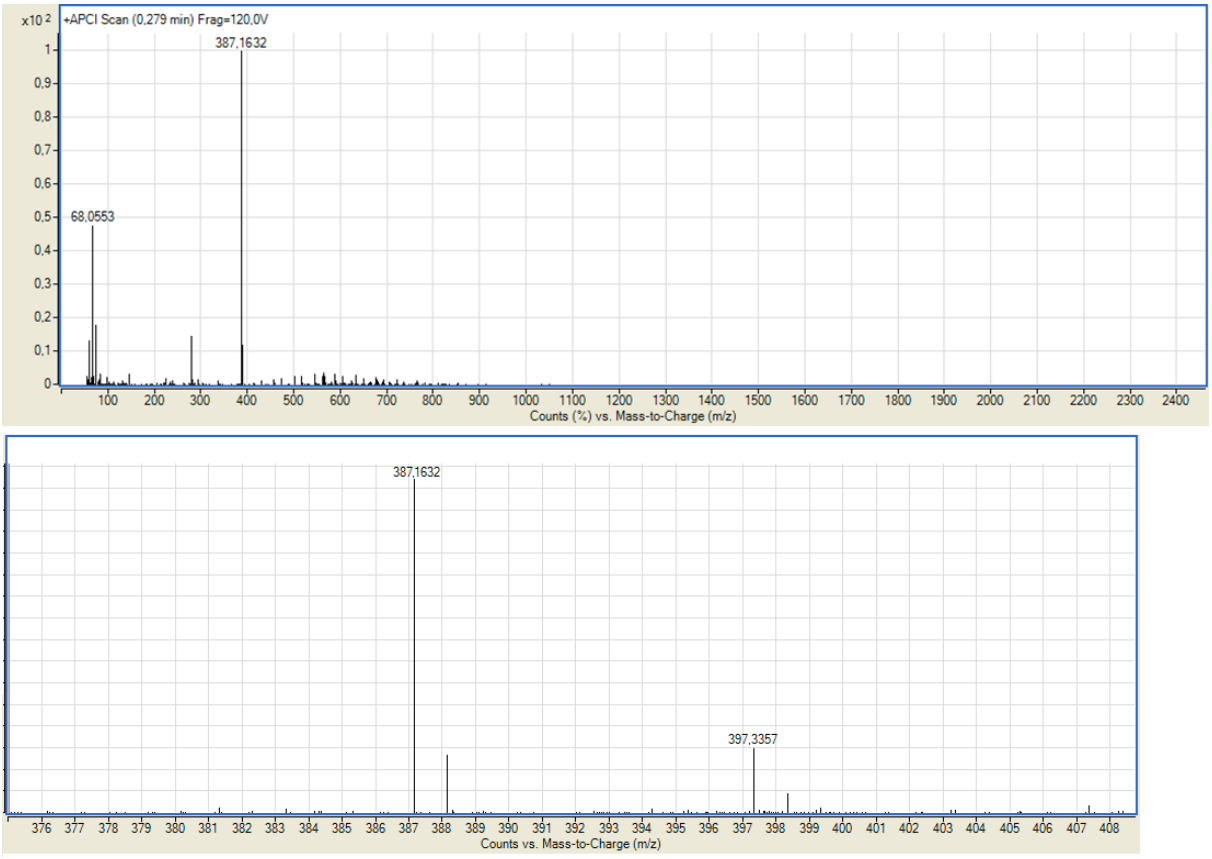


Figure S28: ESI HRMS (positive mode) of compound **4**.

References

1. Brückner, C.; Posakony, J. J.; Johnson, C. K.; Boyle, R. W.; James, B. R.; Dolphin, D. *J. Porphyrins Phthalocyanines* **1998**, *2*, 455-465.

2. Ryppa, C.; Senge, M. O.; Hatscher, S. S.; Kleinpeter, E.; Wacker, P.; Schilde, U.; Wiehe, A. *Chem. Eur. J.* **2005**, *11*, 3427-3442.