Supporting Information

For

"One-Pot" Synthesis of Oligopyrrolic Dialdehydes

Fei Wang,[a] Yi Zhang,[a] Wei Zhou,[a] Zhiqing Long,[a] Shenglun Xiong,[a] Qinpeng Zhang,[a] Jonathan L. Sessler,*[b] and Qing He*[a]

[a] *State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P. R. China.*

[b] *Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712-1224, United States.*

*Correspondence: Jonathan L. Sessler, sessler@mail.utexas.edu; Qing He, heqing85@hun.edu.cn

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I. Synthesis and Characterization

Chemicals and Consumables

All reagents and reactants (such as diamines **4**, **5** and **6**) were purchased from Aldrich, TCI, Acros, Energy Chemicals, Adamas-beta®, or other local suppliers. Unless specifically indicated, these chemicals were used as received, without further purification. Similarly, all solvents used in the reactions were obtained from local sources and were employed as is, without extra drying, except where explicitly mentioned. The primary reactions were carried out under a nitrogen (N_2) atmosphere unless stated otherwise. Silica gel (200–300 mesh) sourced from local suppliers was used for chromatographic separations. The progress of the reactions was monitored using preparative thin-layer chromatographic (TLC) analyses, conducted on Silica Gel60 F245 (1.0 mm) glass sheets measuring 20 cm × 20 cm, also obtained from local suppliers.

Investigation and Characterization

^{1}H and ^{13}C NMR data were acquired at room temperature using a Bruker AVANCE 400 MHz NMR spectrometer, typically at 298 K, unless otherwise specified. The spectroscopic solvents were purchased from Cambridge Isotope Laboratories or Sigma–Aldrich. Residue solvent or tetramethylsilane (TMS) was used as an internal reference. High-resolution mass spectra (HRMS) were recorded using a Bruker Apex–Q IV FTMS mass spectrometer equipped with electrospray ionization (ESI); a $CHCl_3/CH_3OH$ mixture (9:1, v/v) was used as the solvent. X-ray crystallographic studies were performed using various Bruker instruments: A D8 Venture diffractometer (for compound **3a**), Bruker P4 (for **3h**), or a Bruker APEX-II CCD (for **3i**, **3s**, **3u**, and the diformyl bipyrrole by-product).
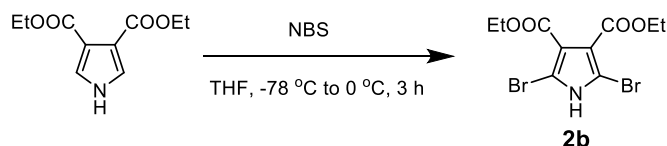
Synthesis

Compound **S1** was synthesized according to a literature procedure:[S1]
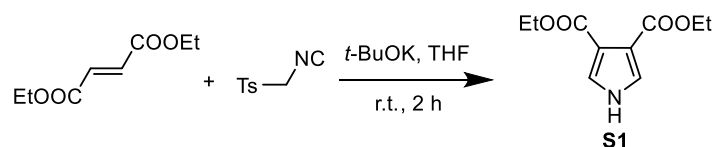
Scheme S1. Synthesis of **S1**.

Compound **S1**: White solid, yield: 80%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 10.16 (s, 1H, pyrrole NH), 7.37 (d, J = 2.8 Hz, 2H, pyrrole α-H), 4.27 (q, J = 7.1 Hz, 4H, ester CH$_2$), 1.32 (t, J = 7.1 Hz, 6H, ester CH$_3$). The characterization data proved consistent with those reported in the literature.[S1]
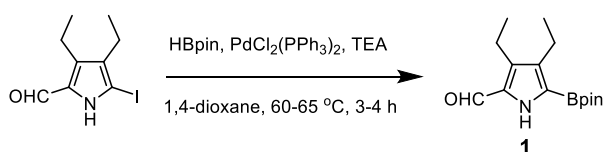
Synthesis of Compound **2b**:

Scheme S2. Synthesis of **2b**.

Compound **S1** (1 mmol) was dissolved in 10 mL of THF and cooled in an ethyl alcohol bath at -78 °C. *N*-Bromosuccinimide (NBS) (2.5 mmol) was dissolved in 10 mL of THF and added through a syringe. The reaction mixture was stirred for 20 min at -78 °C after removal from the ethyl alcohol bath. The mixture was allowed to stand for 3 h at 0 °C. The volatiles were then removed under vacuum. The residue was purified by chromatography over silica gel (petroleum ether/ethyl acetate, 20/1–10/1, v/v, eluent) to give **2b** as a white solid (312 mg, yield: 85%). ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.60 (s, 1H, pyrrole NH), 4.32 (q, J = 7.1 Hz, 4H, ester CH$_2$), 1.33 (t, J = 7.1 Hz, 6H, ester CH$_3$). The characterization data proved consistent with those reported in the literature.[S2]

Compound **1** was synthesized according to a reported literature procedure:[S3]

Scheme S3. Synthesis of **1**.

Compound **1**: Brown thick oil, yield: 65%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.66 (s, 1H, CHO), 9.33 (s, 1H, pyrrole NH), 2.73 (q, J = 7.6 Hz, 2H, ethyl CH$_2$), 2.63 (q, J = 7.5 Hz, 2H, ethyl CH$_2$), 1.30 (s, 12H, borate CH$_3$), 1.22 (t, J = 7.6 Hz, 3H, ethyl CH$_3$), 1.13 (t, J = 7.5 Hz, 3H, ethyl CH$_3$). The characterization data proved consistent with those reported in the literature.[S3]

Synthesis of **3**:
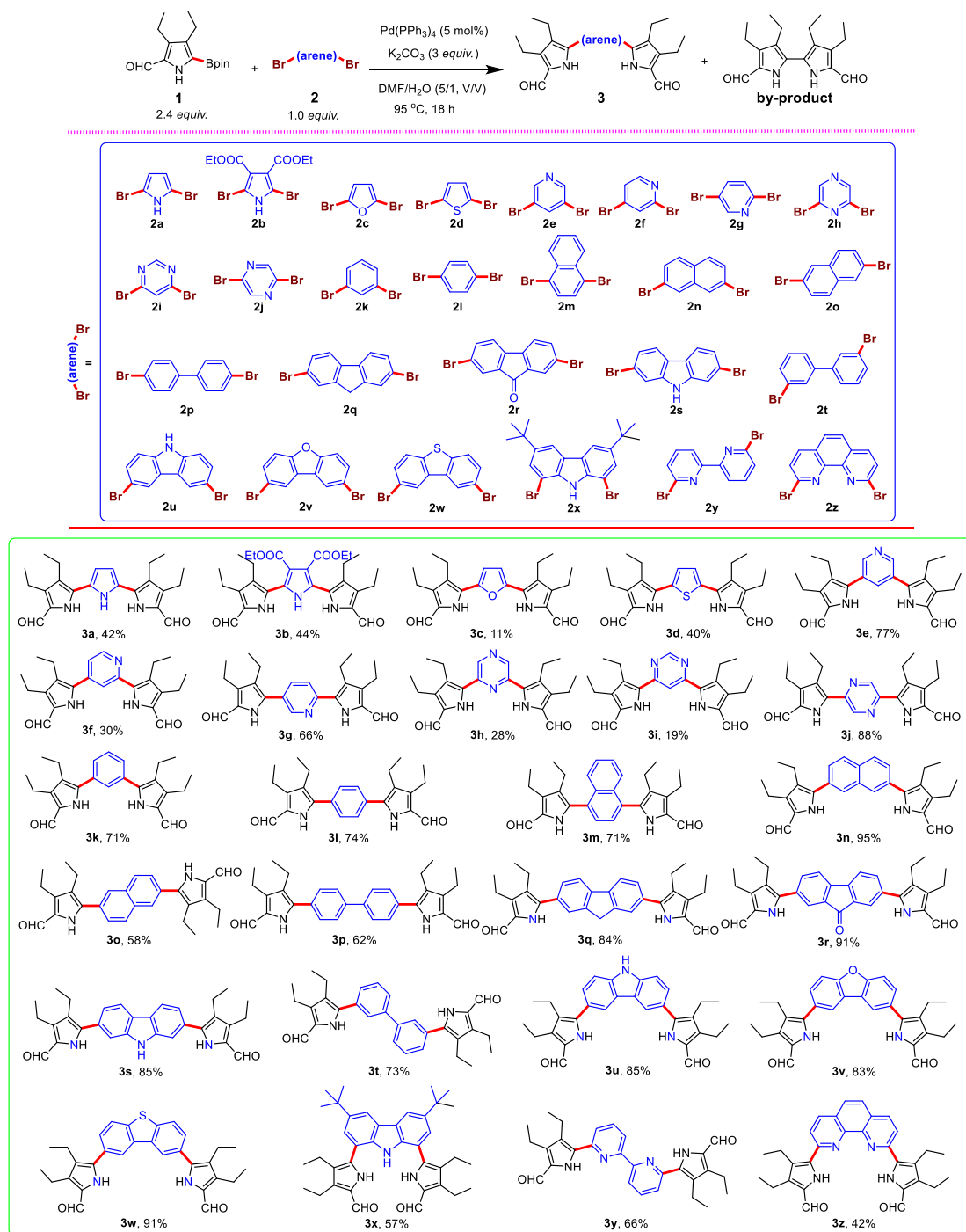
Scheme S4. Synthesis of **3**.

Compounds **3a-3z** were synthesized using the same basic synthetic procedure. The specific steps are as follows: An oven-dried two-necked round-bottom flask containing **2** (0.5 mmol), **1** (1.2 mmol), Pd(PPh$_3$)$_4$ (0.025 mmol) and K$_2$CO$_3$ (1.5 mmol) was degassed with a strong flow of N$_2$ for 20 min. Concurrently, a round-bottom flask containing DMF (50 mL) and H$_2$O (10 mL) was degassed with N$_2$ for 20 min. The DMF/H$_2$O (5/1, v/v) solution was added into the flask via a two-necked cannula. The reaction vessel was placed in an oil bath and heated to 95 °C for 18 h while maintaining the N$_2$ atmosphere. After the completeness of the reaction, the volatiles were removed under reduced pressure using a high vacuum pump. To the resultant crude solid was added CH$_2$Cl$_2$ and H$_2$O. The water layer was extracted with CH$_2$Cl$_2$ and washed with CH$_2$Cl$_2$ 3 times, and the CH$_2$Cl$_2$ extracts combined. After removal of the volatiles, the resultant crude solid was purified by flash column chromatography over silica gel to yield the target compounds **3a-3z**. A diformyl bipyrrole by-product was also generated the above tandem Suzuki cross-coupling reactions and obtained in yields ranging from 2% to 20%.

Compound **3a**: Eluent used for the silica gel column: PE/EA, 5/1–2/1, V/V. Light brown solid, 77 mg, yield: 42%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 12.19 (s, 1H, pyrrole NH), 10.40 (s, 2H, pyrrole NH), 9.69 (s, 2H, CHO), 6.74 (d, J = 2.3 Hz, 2H, pyrrole CH), 2.84 (q, J = 7.6 Hz, 4H, pyrrole CH$_2$), 2.72 (q, J = 7.5 Hz, 4H, pyrrole CH$_2$), 1.30 (t, J = 7.6 Hz, 6H, pyrrole CH$_3$), 1.24 (t, J = 6.0 Hz, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 176.1, 131.6, 127.6, 124.9, 111.6, 29.7, 17.7, 17.6, 16.9, 14.7, 14.1. HRMS (ESI) m/z: [M - H]$^-$ Calcd for C$_{22}$H$_{26}$N$_3$O$_2$, 364.2031; Found: 364.2025.

Compound **3b**: Eluent used for the silica gel column: PE/EA, 5/1–2/1, V/V. Off-white solid, 112 mg, yield: 44%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 11.17 (s, 2H, pyrrole NH), 9.71 (s, 2H, CHO), 8.97 (s, 1H, pyrrole NH), 4.33 (q, J = 7.1 Hz, 4H, ester CH$_2$), 2.78 (q, J = 7.6 Hz, 4H, pyrrole CH$_2$), 2.67 (q, J = 7.6 Hz, 4H, pyrrole CH$_2$), 1.33 (t, J = 7.1 Hz, 6H, ester CH$_3$), 1.27 (t, J = 7.6 Hz, 6H, pyrrole CH$_3$), 1.23 (t, J = 7.6 Hz, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.6, 165.8, 136.6, 128.8, 126.9, 124.8, 124.7, 115.3, 62.0, 17.9, 17.5, 16.9, 16.1, 14.0. HRMS (ESI) m/z: [M + H]$^+$

Calcd for $C_{28}H_{36}N_3O_6$, 510.2599; Found: 510.2596.

Compound **3c**: Eluent used for the silica gel column: PE/EA, 20/1–15/1, V/V. Brown solid, 20 mg, yield: 11%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 10.86 (s, 2H, pyrrole NH), 9.68 (s, 2H, CHO), 6.73 (s, 2H, furan CH), 2.77 (q, J = 7.5 Hz, 4H, pyrrole CH$_2$), 2.67 (q, J = 7.4 Hz, 4H, pyrrole CH$_2$), 1.26 (t, J = 7.7 Hz, 6H, pyrrole CH$_3$), 1.22 (t, J = 7.6 Hz, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.4, 145.4, 139.1, 128.3, 127.6, 124.4, 109.7, 17.6, 17.6, 16.9, 14.6. HRMS (ESI) m/z: [M - H]$^-$ Calcd for $C_{22}H_{25}N_2O_3$, 365.1871; Found: 365.2452.

Compound **3d**: Eluent used for the silica gel column: PE/EA, 5/1–2/1, V/V. Yellow solid, 76 mg, yield: 40%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.64 (s, 2H, CHO), 9.17 (s, 2H, pyrrole NH), 7.25 (d, J = 1.3 Hz, 2H, thiophene CH), 2.78 (q, J = 14.8, 7.3 Hz, 4H, pyrrole CH$_2$), 2.70 (q, J = 14.3, 7.0 Hz, 4H, pyrrole CH$_2$), 1.29 (t, J = 7.5 Hz, 6H, pyrrole CH$_3$), 1.22 (t, J = 7.2 Hz, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.0, 138.8, 133.5, 129.9, 128.6, 125.5(2), 17.7, 17.6, 17.0, 15.5. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{22}H_{27}N_2O_2S$, 383.1788; Found: 383.1790.

Compound **3e**: Eluent used for the silica gel column: PE/EA, 10/1–2/1, V/V. Off-white powder, 145 mg, yield: 77%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 10.51 (s, 2H, pyrrole NH), 9.70 (s, 2H, CHO), 8.79 (s, 2H, pyridine CH), 8.27 (s, 1H, pyridine CH), 2.81 (q, J = 7.4 Hz, 4H, pyrrole CH$_2$), 2.68 (q, J = 7.2 Hz, 4H, pyrrole CH$_2$), 1.29 (t, J = 7.5 Hz, 6H, pyrrole CH$_3$), 1.21 (t, J = 7.4 Hz, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 178.2, 147.2, 139.7, 133.7, 133.5, 129.5, 128.2, 125.4, 17.7, 17.3, 17.1, 16.0. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{23}H_{28}N_3O_2$, 378.2176; Found: 378.2176.

Compound **3f**: Eluent used for the silica gel column: PE/EA, 10/1–2/1, V/V. Yellow powder, 57 mg, yield: 30%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 10.27 (s, 1H, pyrrole NH), 9.73 (s, 1H, CHO), 9.73 (s, 1H, CHO), 9.65 (s, 1H, pyrrole NH), 8.65 (d, J = 5.1 Hz, 1H, pyridine CH), 7.82 (s, 1H, pyridine CH), 7.28 (d, J = 5.1 Hz, 1H, pyridine CH), 2.88–2.75 (m, 6H, pyrrole CH$_2$), 2.69 (q, J = 7.5 Hz, 2H, pyrrole CH$_2$), 1.30 (m, 6H,

pyrrole CH$_3$), 1.24 (m, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 178.1, 178.0, 150.3, 150.2, 140.1, 138.7, 138.3, 133.5, 133.2, 129.5, 128.5, 126.4, 126.0, 119.6, 118.2, 17.8, 17.7, 17.7, 17.4, 17.0, 16.9, 15.9, 15.6. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{23}$H$_{28}$N$_3$O$_2$, 378.2176; Found: 378.2176.

Compound **3g**: Eluent used for the silica gel column: PE/EA, 10/1–5/1, V/V. Light green powder, 124 mg, yield: 66%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 10.17 (s, 1H, pyrrole NH), 9.74 (s, 1H, CHO), 9.68 (s, 1H, CHO), 9.55 (s, 1H, pyrrole NH), 8.78 (d, J = 2.1 Hz, 1H, pyridine CH), 7.86 (d, J = 8.3 Hz, 1H, pyridine CH), 7.70 (d, J = 8.3 Hz, 1H, pyridine CH), 2.91–2.74 (m, 6H, pyrrole CH$_2$), 2.64 (q, J = 7.5 Hz, 2H, pyrrole CH$_2$), 1.29 (m, 9H, pyrrole CH$_3$), 1.21 (t, J = 7.5 Hz, 3H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.9, 177.5, 148.4, 148.2, 138.9, 138.3, 135.1, 133.2, 133.0, 129.3, 128.6, 126.2, 126.2, 125.7, 120.1, 17.8, 17.7, 17.3, 17.1, 16.9, 16.0, 15.3. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{23}$H$_{28}$N$_3$O$_2$, 378.2176; Found: 378.2175.

Compound **3h**: Eluent used for the silica gel column: PE/EA, 5/1–2/1, V/V. Yellow solid, 53 mg, yield: 28%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 11.18 (s, 2H, pyrrole NH), 9.69 (s, 2H, CHO), 8.82 (s, 2H, pyrazine CH), 2.81 (m, 8H, pyrrole CH$_2$), 1.51–1.14 (m, 12H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 178.7, 144.5, 139.2, 139.2, 131.5, 129.5, 127.1, 18.0, 17.8, 16.8, 15.4. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{22}$H$_{27}$N$_4$O$_2$, 379.2129; Found: 379.2128.

Compound **3i**: Eluent used for the silica gel column: PE/EA, 15/1–10/1, V/V. Off-white solid, 36 mg, yield: 19%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 10.25 (s, 2H, pyrrole NH), 9.80 (s, 2H, CHO), 9.05 (s, 1H, pyrimidine CH), 7.83 (s, 1H, pyrimidine CH), 3.08–2.59 (m, 8H, pyrrole CH$_2$), 1.30 (m, 12H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 178.5, 158.5, 156.1, 137.5, 130.8, 129.3, 128.4, 111.7, 18.1, 17.7, 16.7, 15.5. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{22}$H$_{27}$N$_4$O$_2$, 379.2129; Found: 379.2125.

Compound **3j**: Eluent used for the silica gel column: PE/EA, 10/1–5/1, V/V. Bright yellow powder, 166 mg, yield: 88%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 10.00 (s, 2H,

pyrrole NH), 9.76 (s, 2H, CHO), 8.90 (s, 2H, pyrazine CH), 2.82 (m, 8H, pyrrole CH$_2$), 1.29 (m, 12H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 178.0, 142.9, 140.9, 138.1, 130.9, 129.5, 127.0, 18.0, 17.7, 16.8, 15.4. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{22}$H$_{27}$N$_4$O$_2$, 379.2129; Found: 379.2127.

Compound **3k**: Eluent used for the silica gel column: DCM/EA, 100/1–100/5, V/V. Off-white solid, 134 mg, yield: 71%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.83 (s, 2H, pyrrole NH), 9.66 (s, 2H, CHO), 7.82 (s, 1H, benzene CH), 7.51 (d, J = 1.3 Hz, 3H, benzene CH), 2.80 (q, J = 7.6 Hz, 4H, pyrrole CH$_2$), 2.65 (q, J = 7.5 Hz, 4H, pyrrole CH$_2$), 1.30 (t, J = 7.6 Hz, 6H, pyrrole CH$_3$), 1.19 (t, J = 7.5 Hz, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.5, 139.2, 136.3, 132.6, 129.4, 128.5, 127.0, 126.6, 124.6, 17.8, 17.3, 17.1, 16.0. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{24}$H$_{29}$N$_2$O$_2$, 377.2224; Found: 377.2224. The characterization data proved consistent with that recorded in the literature.[S4]

Compound **3l**: Eluent used for the silica gel column: DCM/EA, 100/1–100/7, V/V. Light green solid, 139 mg, yield: 74%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.66 (s, 2H, CHO), 9.38 (s, 2H, pyrrole NH), 7.58 (s, 4H, benzene CH), 2.80 (q, J = 7.6 Hz, 4H, pyrrole CH$_2$), 2.64 (q, J = 7.5 Hz, 4H, pyrrole CH$_2$), 1.30 (t, J = 7.6 Hz, 6H, pyrrole CH$_3$), 1.20 (t, J = 7.5 Hz, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.2, 138.8, 135.9, 131.6, 128.7, 127.8, 124.9, 17.8, 17.3, 17.1, 15.9. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{24}$H$_{29}$N$_2$O$_2$, 377.2224; Found: 377.2222. The characterization data proved consistent with that recorded in the literature.[S5]

Compound **3m**: Eluent used for the silica gel column: PE/EA, 10/1–2/1, V/V. Off-white powder, 151 mg, yield: 71%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.61 (s, 2H, CHO), 9.50 (s, 2H, pyrrole NH), 7.71 (m, 2H, naphthalene CH), 7.50 (s, 2H, naphthalene CH), 7.44 (m, 2H, naphthalene CH), 2.85 (q, J = 7.6 Hz, 4H, pyrrole CH$_2$), 2.42 (q, J = 7.5 Hz, 4H, pyrrole CH$_2$), 1.35 (t, J = 7.6 Hz, 6H, pyrrole CH$_3$), 0.96 (t, J = 7.5 Hz, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.3, 137.9, 135.5, 132.4, 130.9, 128.7, 127.3, 126.9, 126.4, 126.1, 17.7, 17.4, 17.4, 15.9. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{28}$H$_{31}$N$_2$O$_2$, 427.2380; Found: 427.2375.

Compound **3n**: Eluent used for the silica gel column: PE/EA, 10/1–2/1, V/V. Off-white powder, 202 mg, yield: 95%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.68 (s, 2H, CHO), 9.32 (s, 2H, pyrrole NH), 7.98 (s, 2H, naphthalene CH), 7.93 (d, J = 8.5 Hz, 2H, naphthalene CH), 7.65 (d, J = 8.5 Hz, 2H, naphthalene CH), 2.82 (q, J = 7.6 Hz, 4H, pyrrole CH$_2$), 2.70 (q, J = 7.5 Hz, 4H, pyrrole CH$_2$), 1.32 (t, J = 7.6 Hz, 6H, pyrrole CH$_3$), 1.23 (t, J = 7.5 Hz, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.2, 138.9, 136.4, 133.3, 132.2, 130.2, 128.8, 128.5, 126.8, 125.8, 125.0, 17.8, 17.3, 17.1, 16.0. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{28}$H$_{31}$N$_2$O$_2$, 427.2380; Found: 427.2369.

Compound **3o**: Eluent used for the silica gel column: PE/EA, 10/1–2/1, V/V. Dark-green powder, 124 mg, yield: 58%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.68 (s, 2H, CHO), 9.36 (s, 2H, pyrrole NH), 7.97 (s, 2H, naphthalene CH), 7.93 (d, J = 8.6 Hz, 2H, naphthalene CH), 7.67 (d, J = 8.5 Hz, 2H, naphthalene CH), 2.82 (q, J = 7.6 Hz, 4H, pyrrole CH$_2$), 2.70 (q, J = 7.6 Hz, 4H, pyrrole CH$_2$), 1.32 (t, J = 7.6 Hz, 6H, pyrrole CH$_3$), 1.22 (t, J = 7.5 Hz, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.2, 138.8, 136.3, 132.8, 130.1, 129.0, 128.8, 126.3, 125.9, 125.1, 17.8, 17.4, 17.2, 16.0. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{28}$H$_{31}$N$_2$O$_2$, 427.2380; Found: 427.2374.

Compound **3p**: Eluent used for the silica gel column: DCM/EA, 100/1–100/4, V/V. Light green-white solid, 140 mg, yield: 62%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.66 (s, 2H, CHO), 9.07 (s, 2H, pyrrole NH), 7.73 (d, J = 8.2 Hz, 4H, benzene CH), 7.59 (d, J = 8.1 Hz, 4H, benzene CH), 2.81 (q, J = 7.6 Hz, 4H, pyrrole CH$_2$), 2.66 (q, J = 7.5 Hz, 4H, pyrrole CH$_2$), 1.32 (t, J = 7.6 Hz, 6H, pyrrole CH$_3$), 1.21 (t, J = 7.5 Hz, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.1, 139.9, 138.8, 136.0, 131.2, 128.6, 127.8, 127.5, 124.8, 17.8, 17.3, 17.1, 15.9. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{30}$H$_{33}$N$_2$O$_2$, 453.2537; Found: 453.2537. The characterization data proved consistent with that recorded in the literature.[S6]

Compound **3q**: Eluent used for the silica gel column: PE/EA, 10/1–2/1, V/V. Pale yellow powder, 195 mg, yield: 84%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 10.07 (s, 2H, pyrrole NH), 9.73 (s, 2H, CHO), 7.79 (d, J = 7.9 Hz, 2H, fluorene CH), 7.62 (s, 2H,

fluorene CH), 7.49 (d, J = 7.9 Hz, 2H, fluorene CH), 3.96 (s, 2H, fluorene CH_2), 2.63 (m, 8H, pyrrole CH_2), 1.25 (m, 12H, pyrrole CH_3). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.5, 144.1, 141.1, 139.5, 137.6, 130.5, 128.3, 126.7, 124.3, 124.2, 120.2, 37.1, 17.8, 17.3, 17.1, 15.9. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{31}H_{33}N_2O_2$, 465.2537; Found: 465.2531.

Compound **3r**: Eluent used for the silica gel column: PE/EA, 10/1–2/1, V/V. Orange solid, 218 mg, yield: 91%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.70 (s, 2H, CHO), 9.45 (s, 2H, pyrrole NH), 7.90 (s, 2H, fluorenone CH), 7.69–7.59 (m, 4H, fluorenone CH), 2.77 (t, J = 7.6 Hz, 4H, pyrrole CH_2), 2.64 (q, J = 7.3 Hz, 4H, pyrrole CH_2), 1.29 (t, J = 7.6 Hz, 6H, pyrrole CH_3), 1.20 (t, J = 7.5 Hz, 6H, pyrrole CH_3). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 180.1, 177.4, 146.5, 143.3, 138.0, 133.4, 133.1, 133.0, 125.2, 124.2, 123.2, 121.1, 17.7, 17.3, 17.1, 15.8. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{31}H_{31}N_2O_3$, 479.2329; Found: 479.2328.

Compound **3s**: Eluent used for the silica gel column: PE/EA, 5/1–2/1, V/V. Off-white solid, 186 mg, yield: 85%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.67 (s, 2H, CHO), 9.09 (s, 2H, pyrrole NH), 8.40 (s, 1H, carbazole NH), 8.14 (d, J = 8.1 Hz, 2H, carbazole CH), 7.57 (s, 2H, carbazole CH), 7.39 (d, J = 8.0 Hz, 2H, carbazole CH), 2.82 (q, J = 7.5 Hz, 4H, pyrrole CH_2), 2.69 (q, J = 7.5 Hz, 4H, pyrrole CH_2), 1.33 (t, J = 7.6 Hz, 6H, pyrrole CH_3), 1.21 (t, J = 7.5 Hz, 6H, pyrrole CH_3). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.0, 140.3, 137.3, 132.1, 129.9, 128.5, 124.6, 123.0, 121.0, 119.5, 109.5, 17.8, 17.4, 17.2, 15.9. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{30}H_{32}N_3O_2$, 466.2489; Found: 466.2487.

Compound **3t**: Eluent used for the silica gel column: DCM/EA, 100/1–100/1, V/V. Off-white solid, 165 mg, yield: 73%. ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.65 (s, 1H), 9.17 (s, 1H), 7.73 (s, 1H), 7.63 (d, J = 7.5 Hz, 1H), 7.55 (t, J = 7.6 Hz, 1H), 7.50 (d, J = 7.7 Hz, 1H), 2.80 (q, J = 7.6 Hz, 2H), 2.65 (q, J = 7.5 Hz, 2H), 1.31 (t, J = 7.6 Hz, 3H), 1.20 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.2, 141.3, 138.9, 136.5, 132.6, 129.5, 128.4, 126.6, 126.2, 124.7, 17.8, 17.3, 17.2, 16.0. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{30}H_{33}N_2O_2$, 453.2537; Found: 453.2534.

Compound **3u**: Eluent used for the silica gel column: PE/EA, 5/1–2/1, V/V. Off-white solid, 198 mg, yield: 85%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.64 (s, 2H, CHO), 9.04 (s, 2H, pyrrole NH), 8.35 (s, 1H, carbazole NH), 8.18 (s, 2H, carbazole CH), 7.60–7.50 (m, 4H, carbazole CH), 2.82 (q, J = 7.6 Hz, 4H, pyrrole CH$_2$), 2.68 (q, J = 7.5 Hz, 4H, pyrrole CH$_2$), 1.32 (t, J = 7.6 Hz, 6H, pyrrole CH$_3$), 1.21 (t, J = 7.5 Hz, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 176.8, 139.7, 139.1, 137.8, 128.3, 126.1, 124.2, 123.9, 123.6, 119.6, 111.5, 17.9, 17.4, 17.3, 16.1. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{30}$H$_{32}$N$_3$O$_2$, 466.2489; Found: 466.2486.

Compound **3v**: Eluent used for the silica gel column: PE/EA, 20/1–10/1, V/V. Light pink powder, 193 mg, yield: 83%. ^{1}H NMR (400 MHz, CDCl$_3$)) δ: 9.65 (s, 2H, CHO), 9.38 (s, 2H, pyrrole NH), 8.06 (s, 2H, dibenzofuran CH), 7.66 (d, J = 8.5 Hz, 2H, dibenzofuran, CH), 7.60 (d, J = 8.6 Hz, 2H, dibenzofuran, CH), 2.80 (q, J = 7.6 Hz, 4H, pyrrole CH$_2$), 2.65 (q, J = 7.5 Hz, 4H, pyrrole CH$_2$), 1.30 (t, J = 7.6 Hz, 6H, pyrrole CH$_3$), 1.19 (t, J = 7.5 Hz, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.1, 156.4, 138.9, 136.8, 128.5, 127.4, 127.2, 124.5, 124.4, 119.9, 112.4, 17.8, 17.3, 17.2, 16.0. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{30}$H$_{31}$N$_2$O$_3$, 467.2329; Found: 467.2327.

Compound **3w**: Eluent used for the silica gel column: PE/EA, 20/1–5/1, V/V. Pale green solid, 219 mg, yield: 91%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.68 (s, 2H, CHO), 9.12 (s, 2H, pyrrole NH), 8.27 (s, 2H, dibenzothiophene CH), 7.96 (d, J = 8.7 Hz, 2H, dibenzothiophene CH), 7.61 (d, J = 8.2 Hz, 2H, dibenzothiophene CH), 2.83 (q, J = 8.0, 7.6 Hz, 4H, pyrrole CH$_2$), 2.69 (q, J = 7.5 Hz, 4H, pyrrole CH$_2$), 1.33 (t, J = 7.6 Hz, 6H, pyrrole CH$_3$), 1.22 (t, J = 7.5 Hz, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.1, 139.9, 138.7, 136.3, 135.7, 128.7, 128.6, 126.4, 124.7, 123.5, 120.5, 17.8, 17.4, 17.2, 16.0. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{30}$H$_{31}$N$_2$O$_2$S, 483.2101; Found: 483.2102.

Compound **3x**: Eluent used for the silica gel column: PE/DCM, 1/1–1/4, V/V. Gray solid, 165 mg, yield: 57%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 10.05 (s, 2H, pyrrole NH), 9.36 (s, 2H, CHO), 9.30 (s, 1H, pyrrole NH), 8.16 (s, 2H, carbazole CH), 7.54 (s, 2H,

carbazole CH), 2.74 (q, $J = 7.5$ Hz, 4H, pyrrole CH$_2$), 2.60 (q, $J = 7.4$ Hz, 4H, pyrrole CH$_2$), 1.49 (s, 12H, carbazole CH$_3$), 1.24 (t, $J = 7.5$ Hz, 6H, pyrrole CH$_3$), 1.11 (t, $J = 7.5$ Hz, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.0, 142.6, 139.1, 136.2, 135.1, 128.7, 125.1, 124.8, 124.2, 116.7, 114.6, 34.8, 32.0, 17.7, 17.6, 17.4, 15.9. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{38}$H$_{48}$N$_3$O$_2$, 578.3741; Found: 578.3737.

Compound **3y**: Eluent used for the silica gel column: PE/EA, 10/1–5/1, V/V. White solid, 150 mg, yield: 66%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 10.10 (s, 2H, pyrrole NH), 9.75 (s, 2H, CHO), 8.45 (d, $J = 7.5$ Hz, 2H, pyridine CH), 7.95 (t, $J = 7.8$ Hz, 2H, pyridine CH), 7.71 (d, $J = 7.6$ Hz, 2H, pyridine CH), 2.84 (m, 8H, pyrrole CH$_2$), 1.31 (m, 12H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 177.8, 155.4, 148.7, 138.6, 138.0, 133.8, 128.2, 125.9, 120.9, 119.9, 17.9, 17.8, 16.9, 15.3. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{28}$H$_{31}$N$_4$O$_2$, 455.2442; Found: 455.2431.

Compound **3z**: Eluent used for the silica gel column: PE/EA, 10/1–5/1, V/V. White solid, 100 mg, yield: 42%. ^{1}H NMR (400 MHz, CDCl$_3$): δ 10.72 (s, 2H, pyrrole NH), 9.84 (s, 2H, CHO), 8.27 (d, $J = 8.4$ Hz, 2H, pyridine CH), 7.96 (d, $J = 8.4$ Hz, 2H, pyridine CH), 7.74 (s, 2H, benzene CH), 3.01 (q, $J = 7.0$ Hz, 4H, pyrrole CH$_2$), 2.86 (q, $J = 7.3$ Hz, 4H, pyrrole CH$_2$), 1.32 (m, 12H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 178.4, 149.7, 145.8, 137.0, 134.0, 129.2, 127.8, 127.2, 126.0, 120.5, 29.7, 18.0, 17.6, 17.1, 15.7. MALDI-TOF MS Calcd for C$_{30}$H$_{30}$N$_4$O$_2$, 478.237; Found: 478.937 [M]$^+$.HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{30}$H$_{31}$N$_4$O$_2$, 479.2442; Found: 479.2437.

diformyl bipyrrole: This by-product was obtained as a white solid, yield: 2-20%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 9.65 (s, 2H, CHO), 9.35 (s, 2H, pyrrole NH), 2.78 (q, $J = 7.6$ Hz, 4H, pyrrole CH$_2$), 2.53 (q, $J = 7.6$ Hz, 4H, pyrrole CH$_2$), 1.28 (t, $J = 7.6$ Hz, 6H, pyrrole CH$_3$), 1.08 (t, $J = 7.6$ Hz, 6H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, , CDCl$_3$) δ: 177.5, 137.9, 129.3, 127.6, 126.6, 17.7, 17.6, 17.2, 15.8. The characterization data proved consistent with that recorded in the literature.[S7]

Reaction scale up for the synthesis of **3v**:
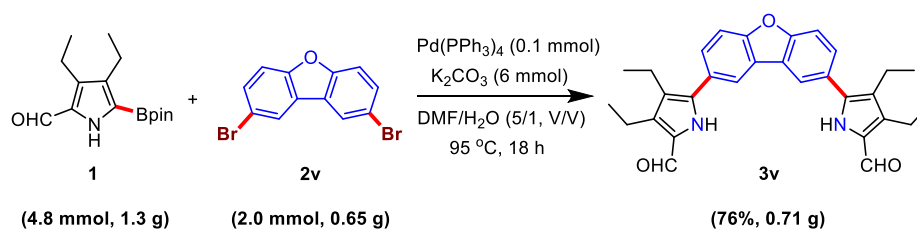
Scheme S5. Reaction scale up of the coupling between **1** and **2v**.

Scale up experiment for the synthesis of **3v**: An oven-dried two-necked round-bottom flask containing **2v** (2.0 mmol, 0.65 g), **1** (4.8 mmol, 1.3 g), Pd(PPh$_3$)$_4$ (0.1 mmol, 116 mg) and K$_2$CO$_3$ (6.0 mmol, 0.83 g) was degassed with a strong flow of N$_2$ for 20 min. Then the DMF/H$_2$O (100 mL/20 mL) solution which has been removed from the air was added into the flask via a two-necked cannula. The reaction vessel was placed in an oil bath and heated to 95 °C for 18 h while maintaining the N$_2$ atmosphere. After the completeness of the reaction, the volatiles were removed under a reduced pressure. To the resultant crude solid was added CH$_2$Cl$_2$ and H$_2$O. The water layer was extracted with CH$_2$Cl$_2$ and washed with CH$_2$Cl$_2$ 3 times, and the CH$_2$Cl$_2$ extracts combined. After removal of the volatiles, the resultant crude solid was purified by flash column chromatography over silica gel (Eluent: PE/EA, 10/1–5/1, V/V) to yield the target compound as a light pink powder, 0.71 g, yield: 76%.

Synthesis and characterization of **7** via the imine-forming condensation between **3h** and **4** (commercially available):
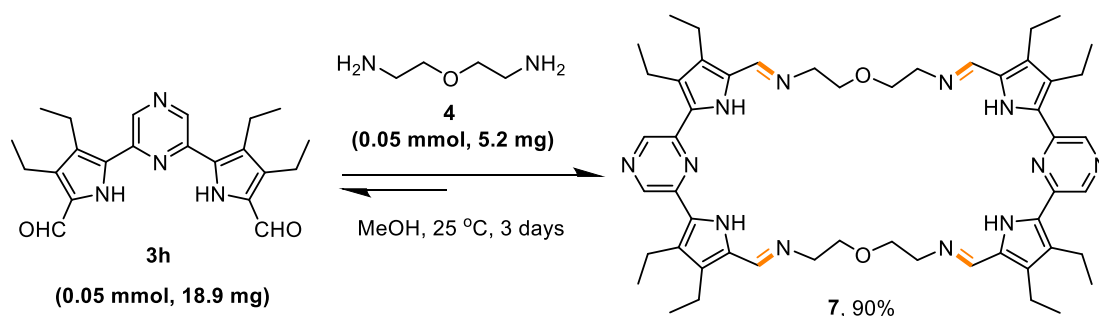
Scheme S6. Synthesis of **7**.

To a round-bottom flask containing compound **3h** (0.05 mmol) was added enough solvent MeOH (15 mL). Then diamine **4** (0.05 mmol) was added by syringe. After mixing, the solution became clear. It was then stirred at 25 °C until a white-to-light

yellow suspension was formed. Vigorous stirring of the reaction mixture was then continued at the same temperature for ≥3 days. Then the resulting precipitate was collected by vacuum filtration to give compound **7** as a light yellow powder 20 mg, yield: 90%. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 11.47 (s, 4H, pyrrole NH), 8.57 (s, 4H, pyrazine CH), 8.13 (s, 4H, imine CH), 3.89 (t, *J* = 6.0 Hz, 8H, diamine CH$_2$), 3.79 (t, *J* = 6.0 Hz, 8H, diamine CH$_2$), 2.75 (q, *J* = 7.5 Hz, 8H, pyrrole CH$_2$), 2.57 (q, *J* = 7.5 Hz, 8H, pyrrole CH$_2$), 1.24 (t, *J* = 7.5 Hz, 12H, pyrrole CH$_3$), 1.17 (t, *J* = 7.5 Hz, 12H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 152.1, 144.8, 136.8, 132.9, 128.4, 125.9, 71.2, 60.8, 18.3, 17.6, 16.8, 15.5. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{52}$H$_{69}$N$_{12}$O$_2$, 893.5661; Found: 893.5690.

Synthesis and characterization of **8** and **9** via the imine-forming condensation between **3aa** and **5** or **6** (both **5** and **6** are commercially available; **3aa** was prepared according to our previously reported method.[S3]):
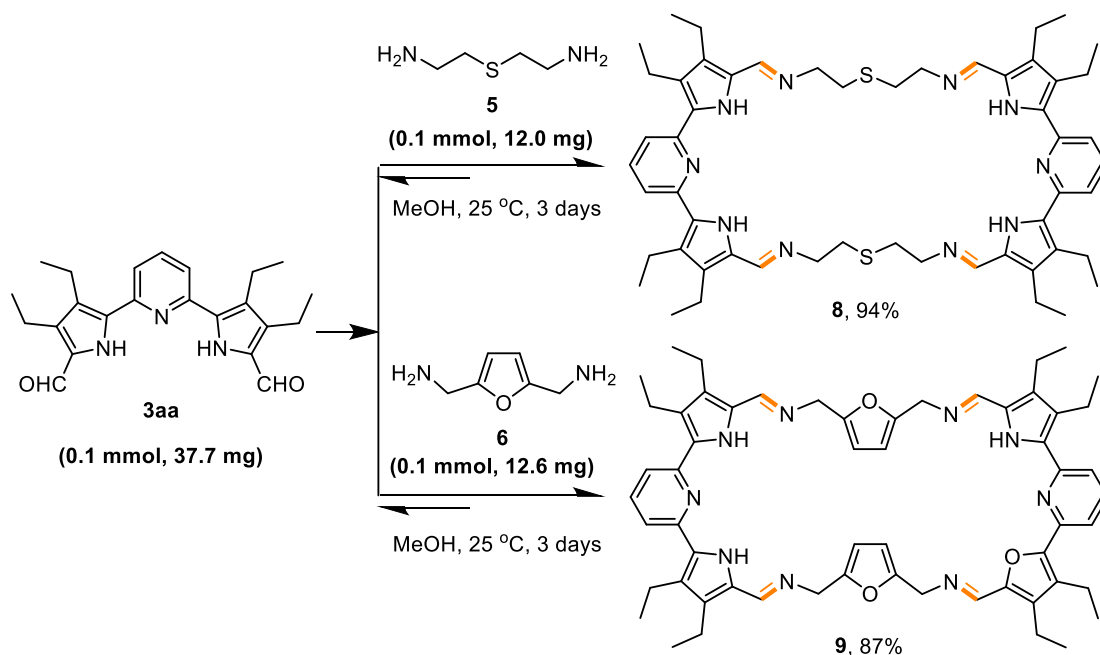
Scheme S7. Synthesis of **8** and **9**.

Macrocycles **8** and **9** were synthesized using a similar procedure as that used to prepare **7**. In this case the clear solution in MeOH (15 mL) produced upon the initial mixing of **3aa** (0.10 mmol) with **5** (0.10 mmol) or **6** (0.10 mmol) was stirred at 25 °C for more than 3 days to give **8** or **9** in the form of a light yellow precipitate (**8**: 43 mg, yield: 94%; **9**: 41 mg, yield: 87%).

Macrocycle **8**: ^{1}H NMR (400 MHz, CDCl$_3$) δ: 11.66 (s, 4H, pyrrole NH), 8.13 (s, 4H, imine CH), 7.67 (t, J = 7.9 Hz, 2H, pyridine CH), 7.39 (d, J = 7.9 Hz, 4H, pyridine CH), 3.84 (t, J = 7.1 Hz, 8H, diamine CH$_2$), 2.99 (t, J = 7.1 Hz, 8H, diamine CH$_2$), 2.76 (q, J = 7.5 Hz, 8H, pyrrole CH$_2$), 2.61 (q, J = 7.6 Hz, 8H, pyrrole CH$_2$), 1.23 (t, J = 7.5 Hz, 12H, pyrrole CH$_3$), 1.18 (t, J = 7.5 Hz, 12H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 151.6, 149.4, 137.1, 133.3, 131.2, 125.1, 124.7, 116.5, 61.4, 34.2, 18.2, 17.7, 16.9, 15.4. HRMS (ESI) m/z: [M - H]$^-$ Calcd for C$_{54}$H$_{69}$N$_{10}$S$_2$, 921.5154; Found: 921.5111.

Macrocycle **9**: ^{1}H NMR (400 MHz, CDCl$_3$) δ: 11.71 (s, 4H, pyrrole NH), 8.20 (s, 4H, imine CH), 7.68 (t, J = 7.8 Hz, 2H, pyridine CH), 7.41 (d, J = 8.0 Hz, 4H, pyridine CH), 6.13 (s, 4H, furan β-CH), 4.71 (s, 8H, diamine CH$_2$), 2.77 (q, J = 7.5 Hz, 8H, pyrrole CH$_2$), 2.63 (q, J = 7.5 Hz, 8H, pyrrole CH$_2$), 1.23 (t, J = 7.5 Hz, 12H, pyrrole CH$_3$), 1.19 (t, J = 7.6 Hz, 12H, pyrrole CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ: 152.8, 151.9, 149.4, 137.2, 133.6, 131.3, 125.1, 124.7, 116.6, 107.2, 58.2, 18.2, 17.7, 16.9, 15.3. HRMS (ESI) m/z: [M + H]$^+$ Calcd for C$_{59}$H$_{67}$N$_{10}$O$_2$, 935.5433; Found: 935.5441.

II. NMR & Mass Spectra
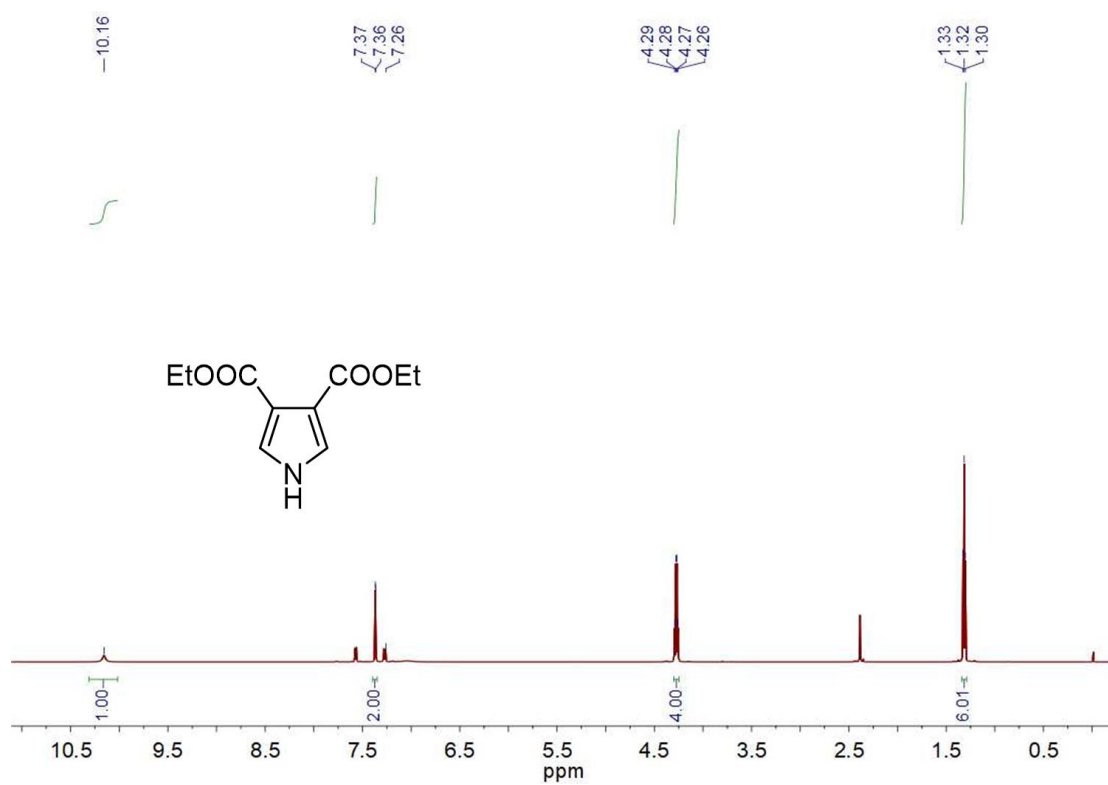
Figure S1. ^{1}H NMR (400 MHz) spectrum of **S1** as recorded in CDCl$_3$.
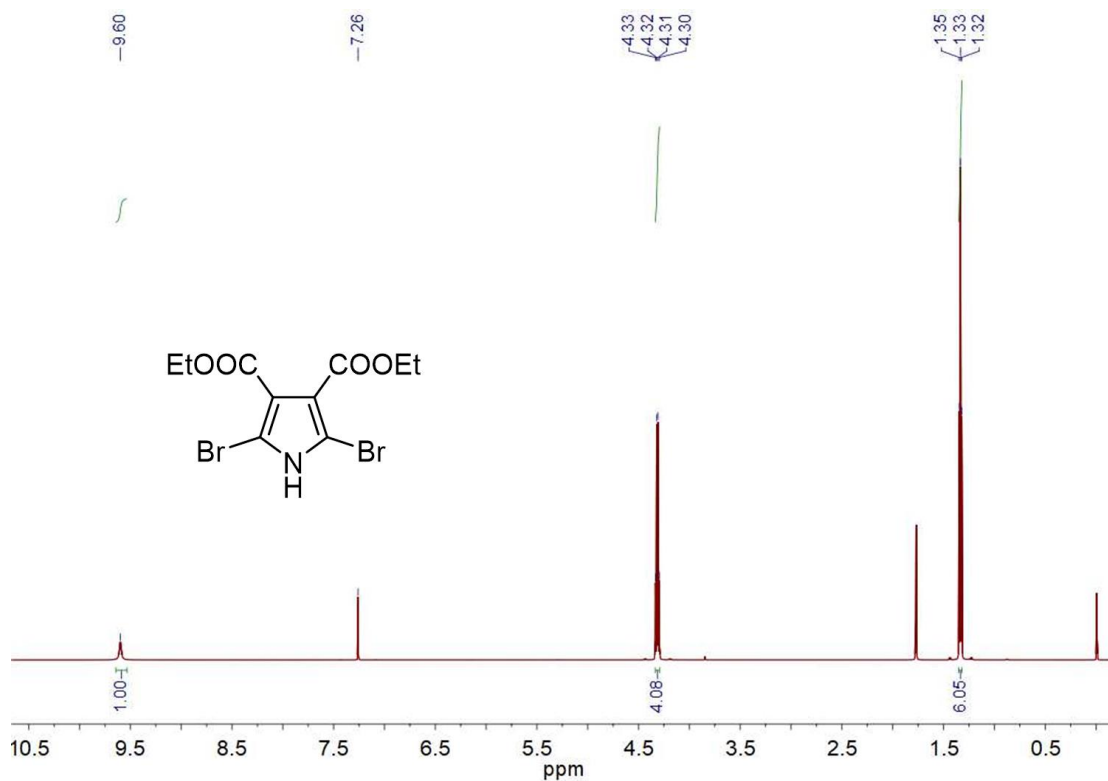
Figure S2. ^{1}H NMR (400 MHz) spectrum of **2b** as recorded in CDCl$_3$.
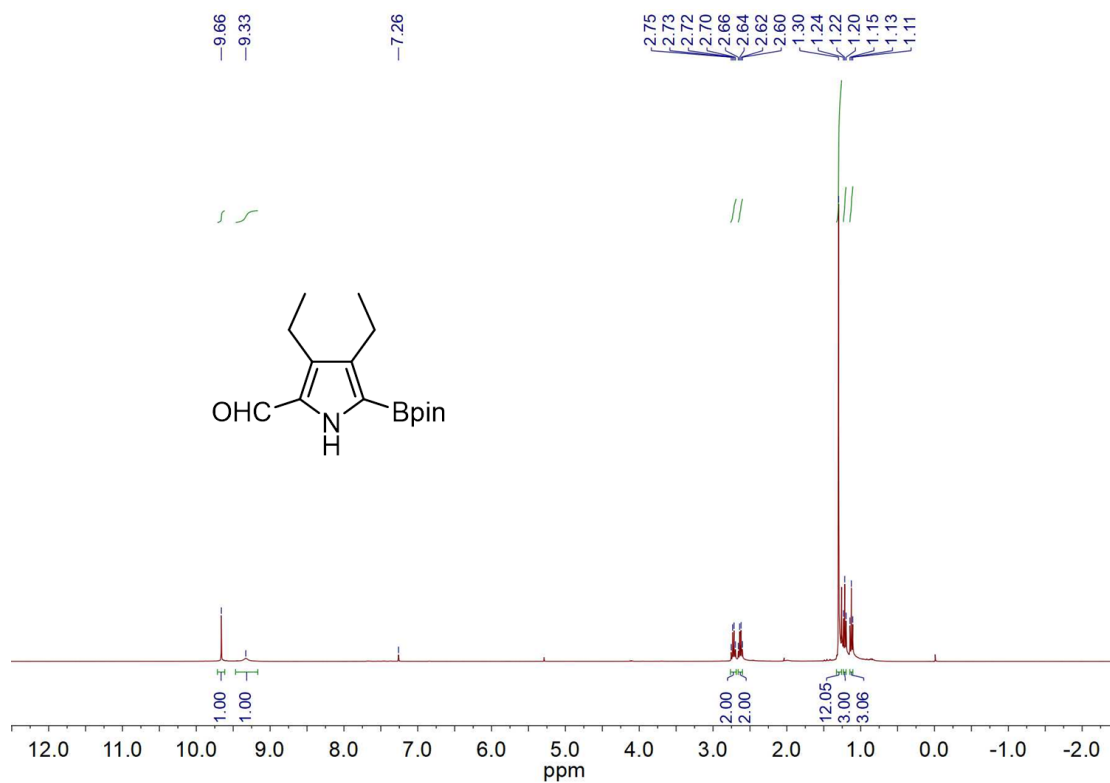
Figure S3. ^{1}H NMR (400 MHz) spectrum of **1** as recorded in CDCl$_3$.
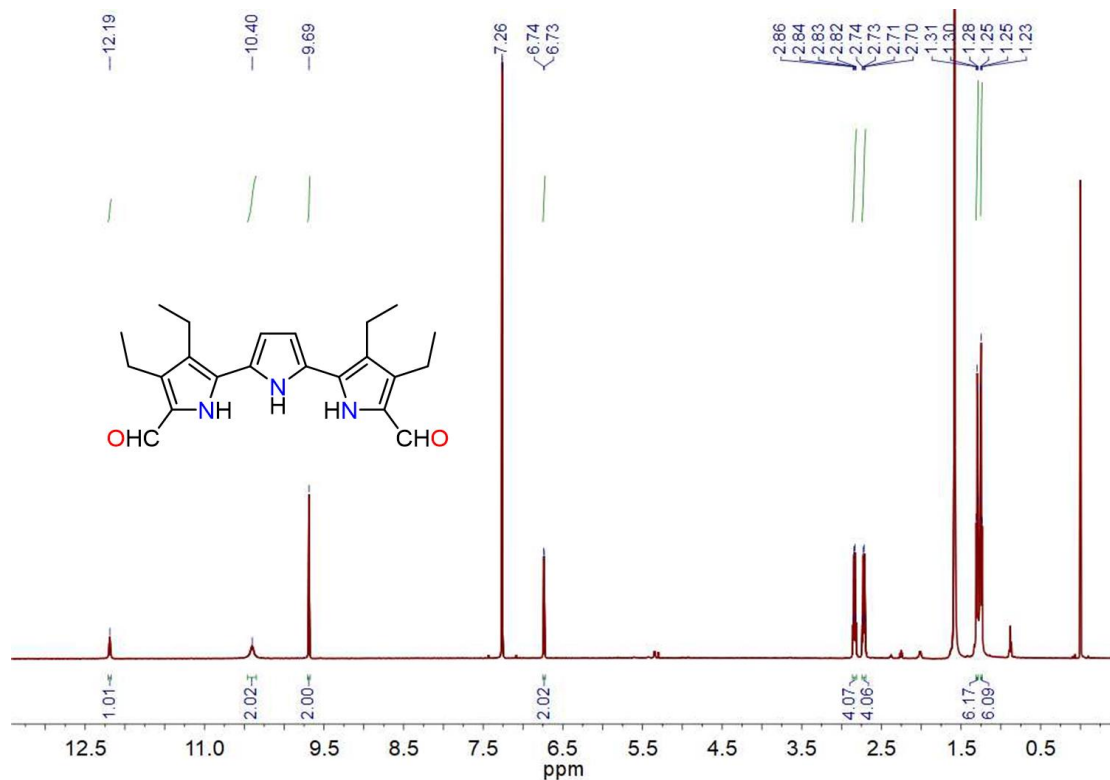
Figure S4. ^{1}H NMR (400 MHz) spectrum of **3a** as recorded in CDCl$_3$.
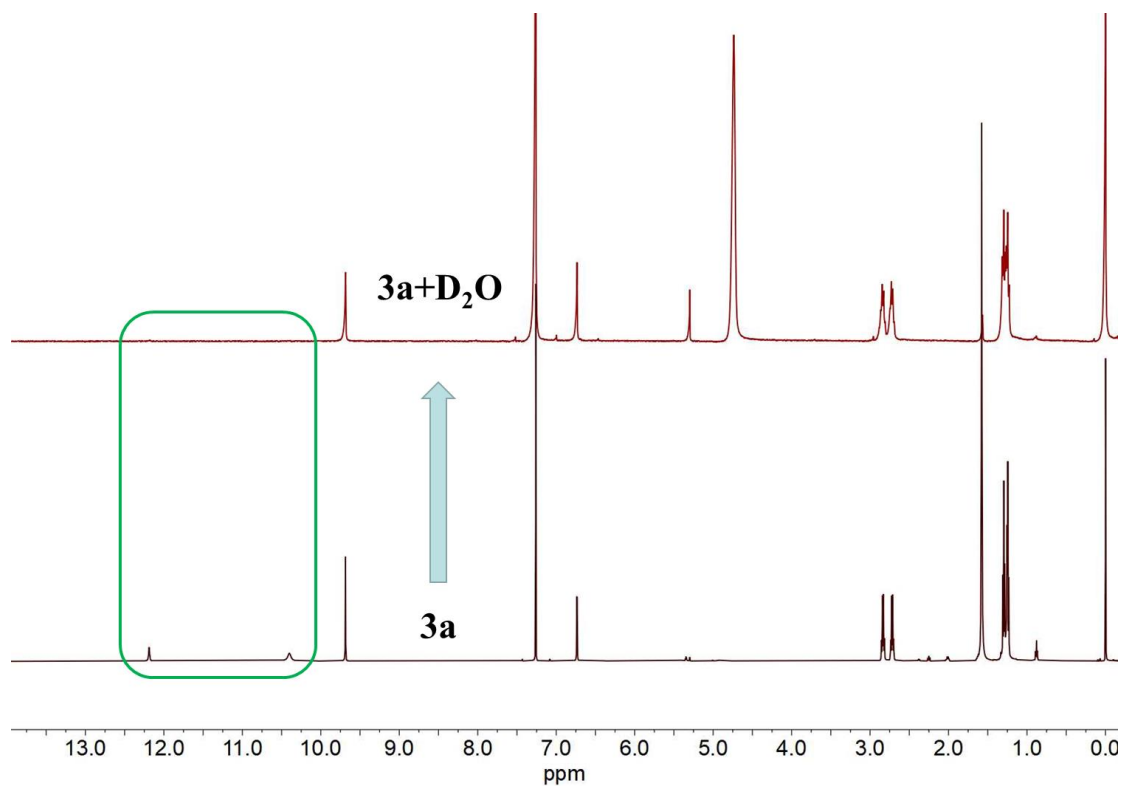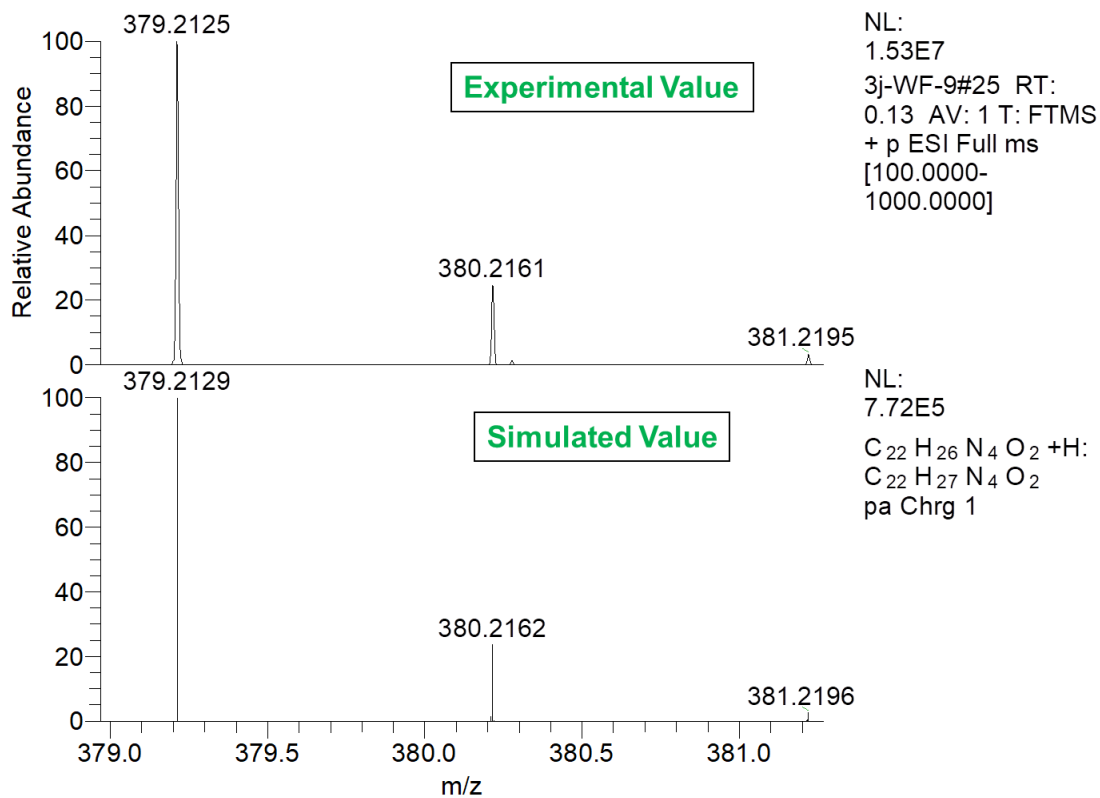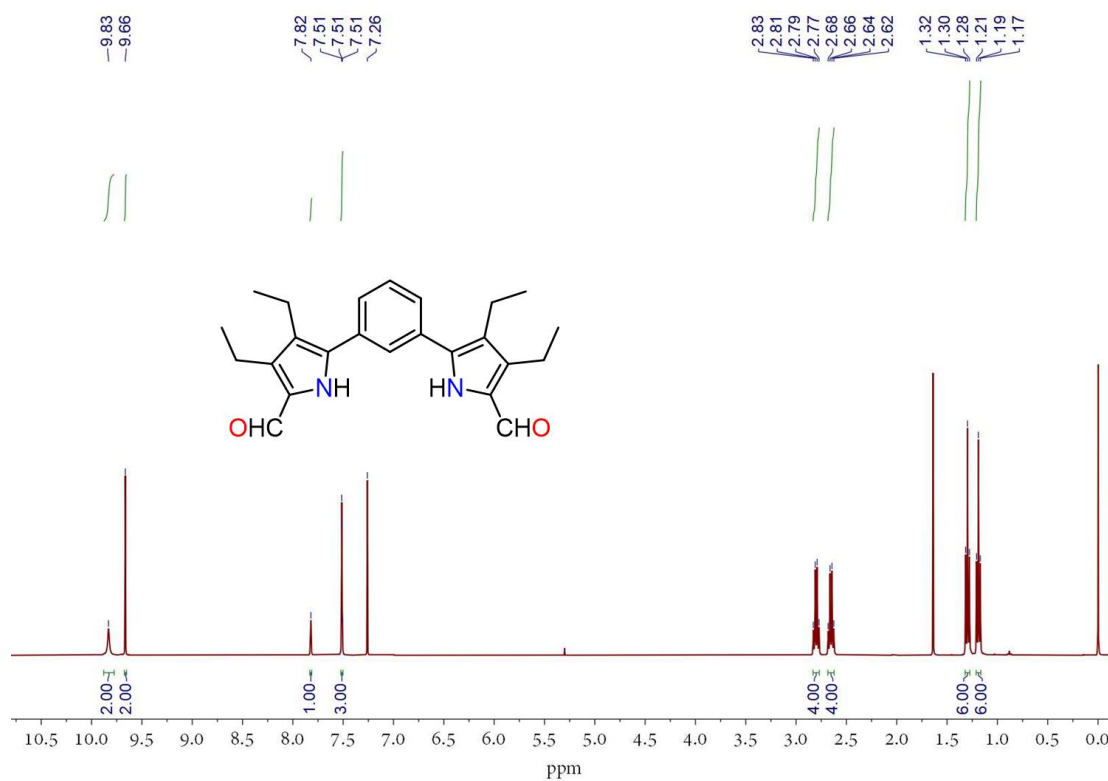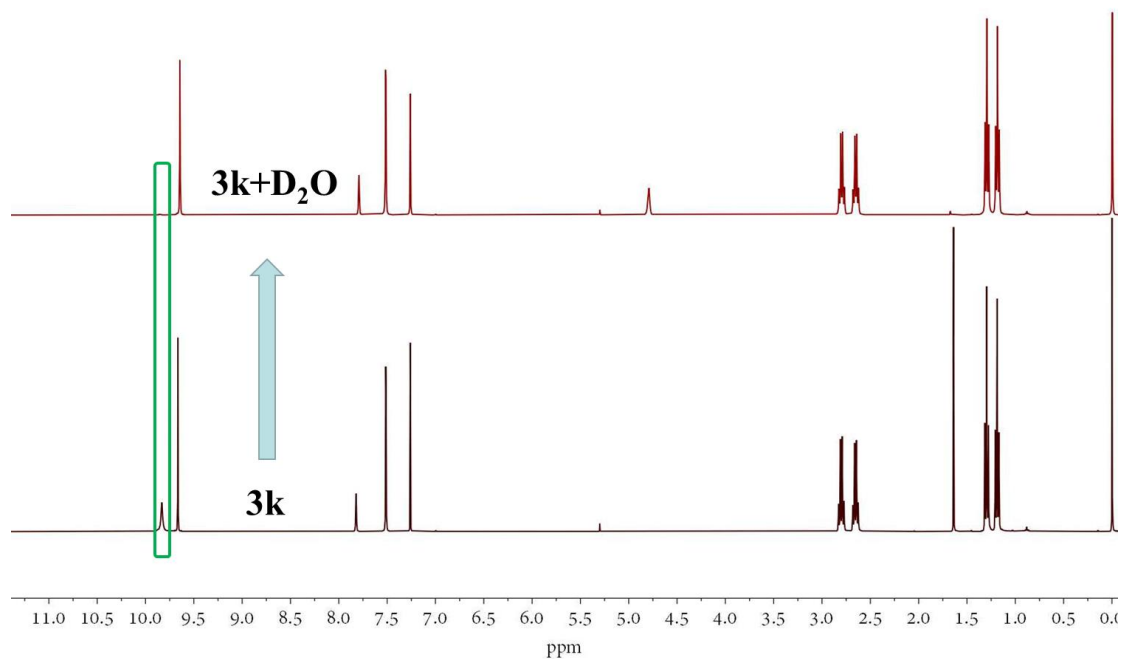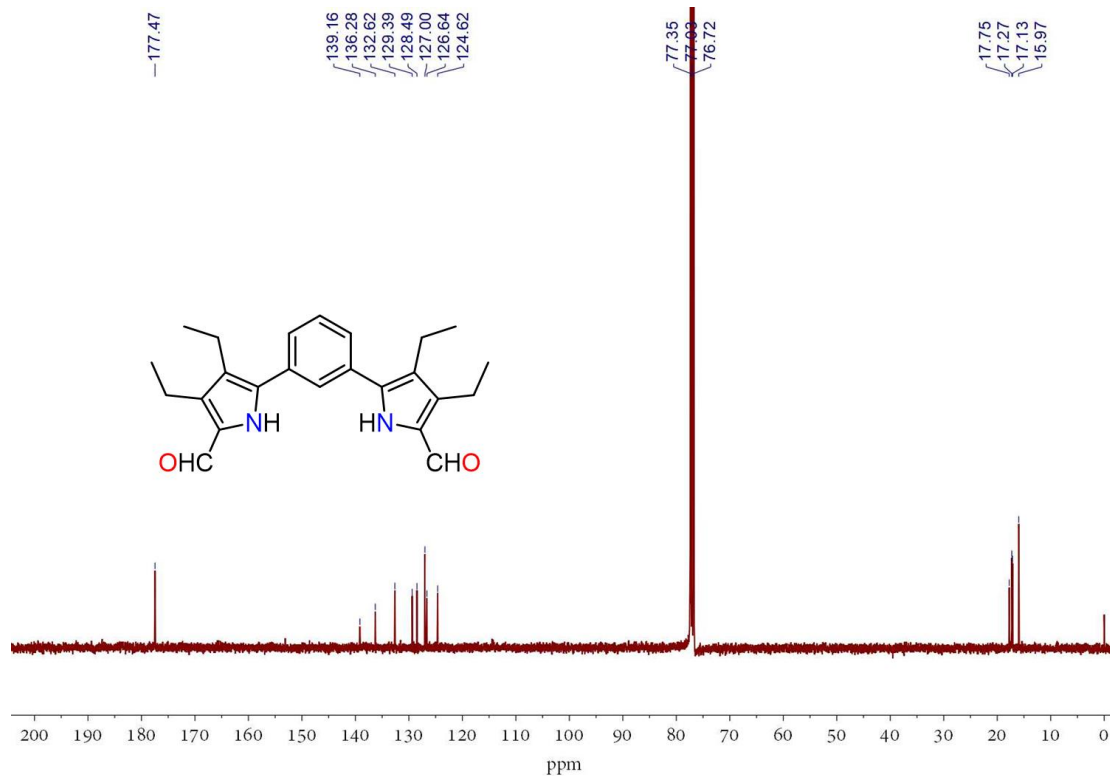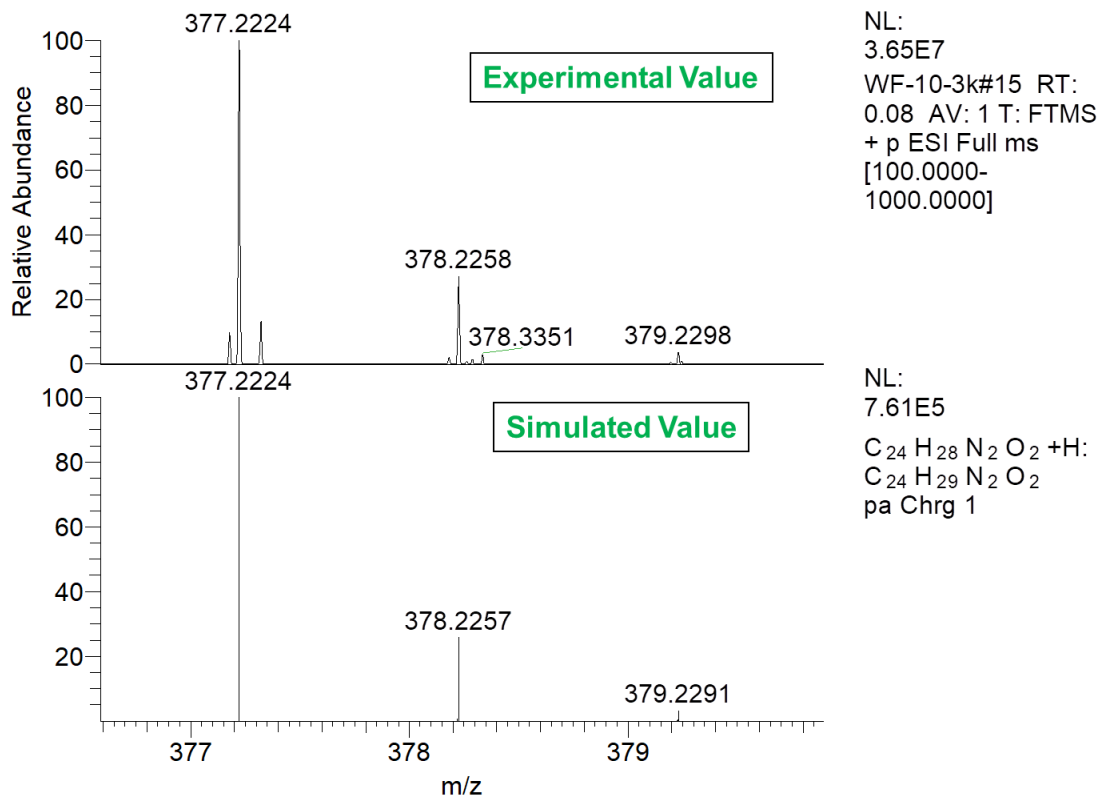
Figure S5. ^{1}H NMR (400 MHz) spectrum of **3a**+**D$_2$O** as recorded in CDCl$_3$.
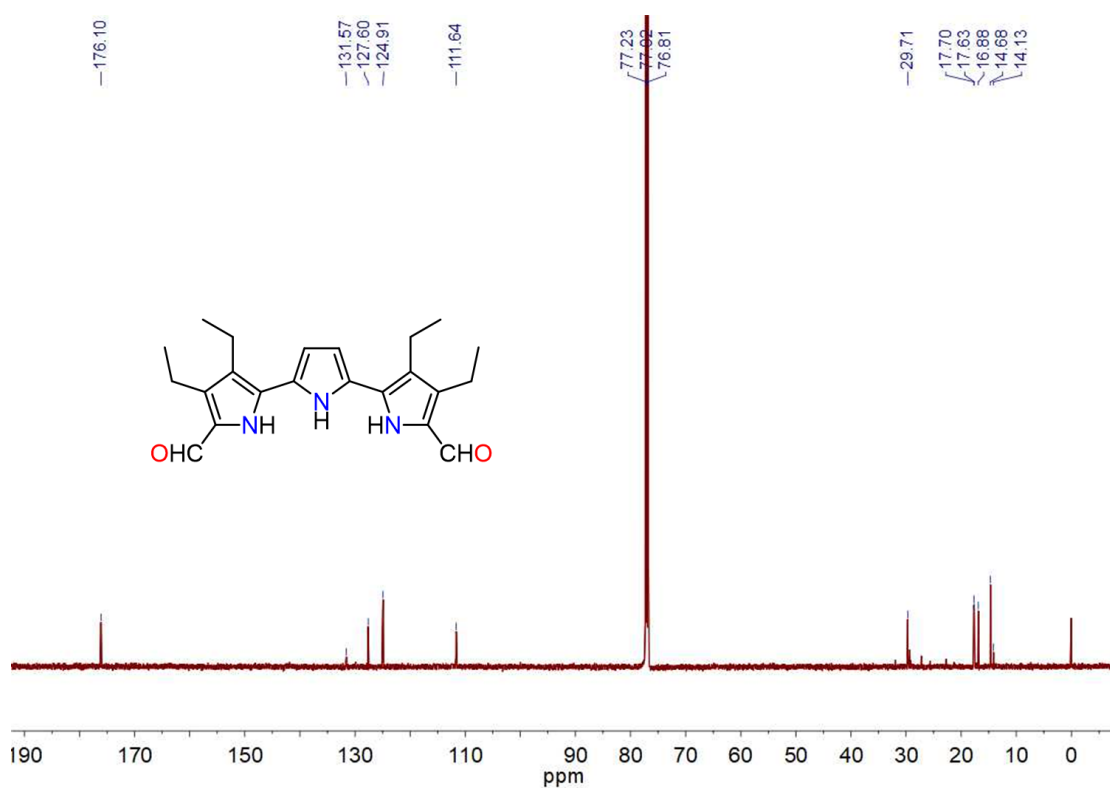
Figure S6. ^{13}C NMR (100 MHz) spectrum of **3a** as recorded in CDCl$_3$.
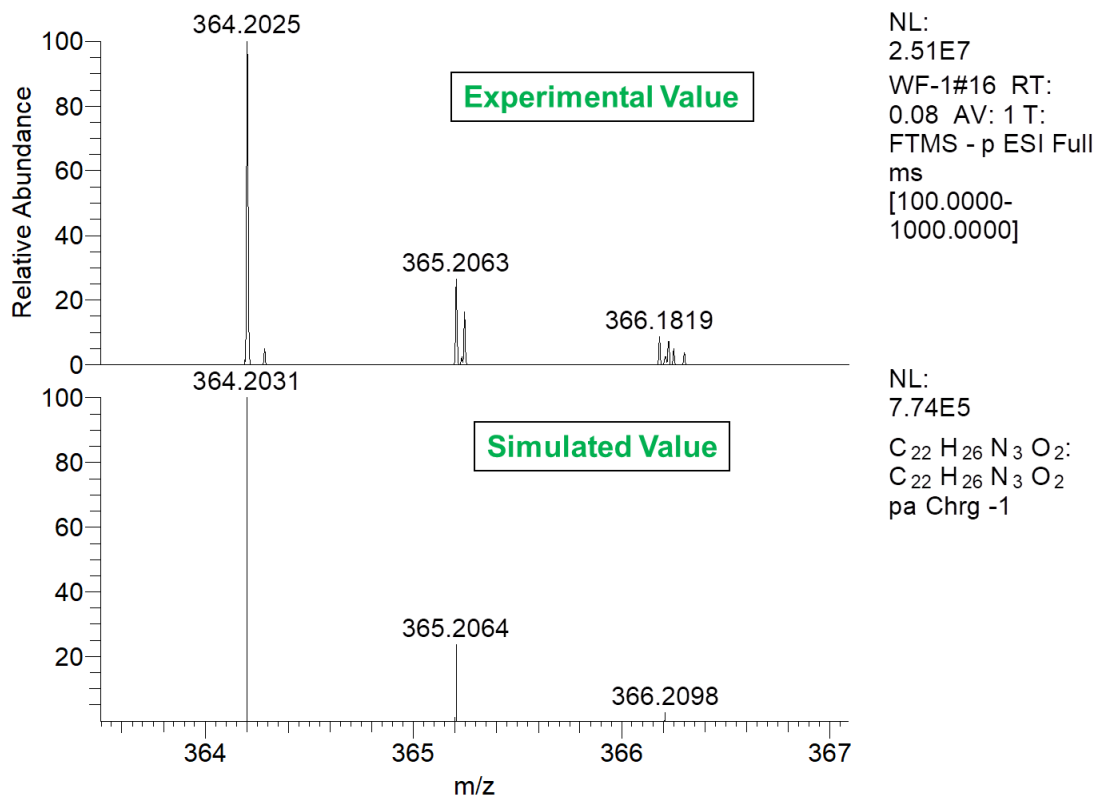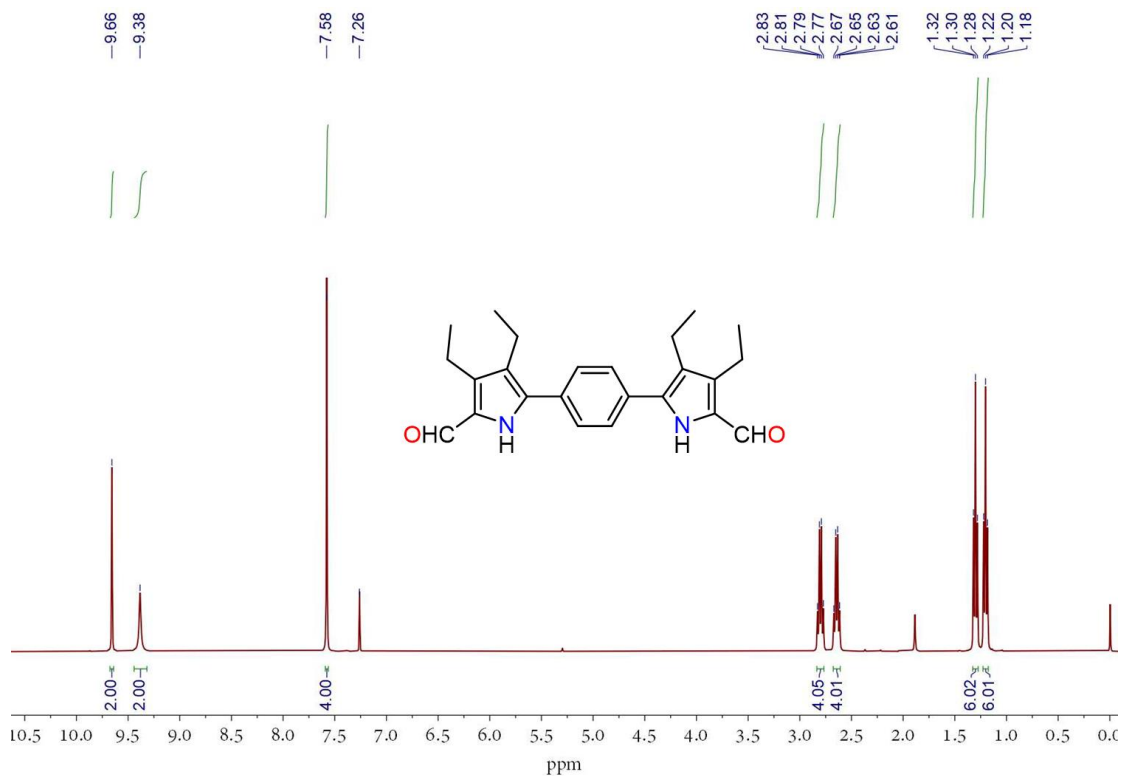
Figure S7. HRMS (ESI) spectrum of **3a**.
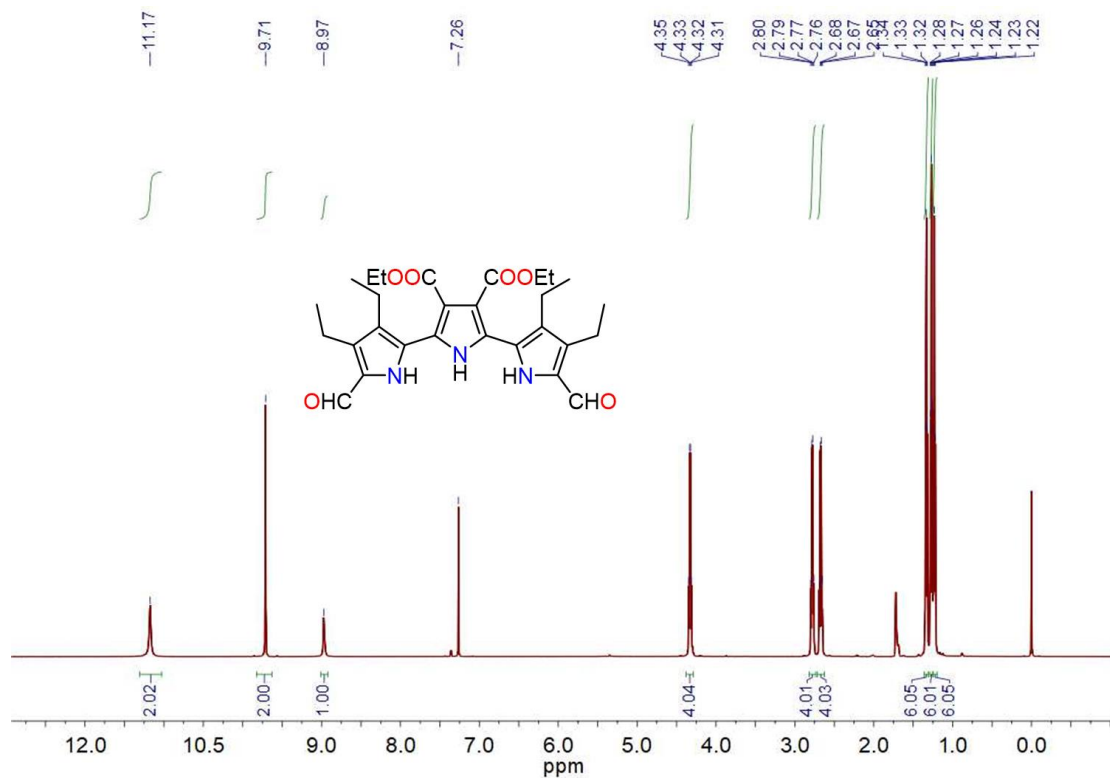
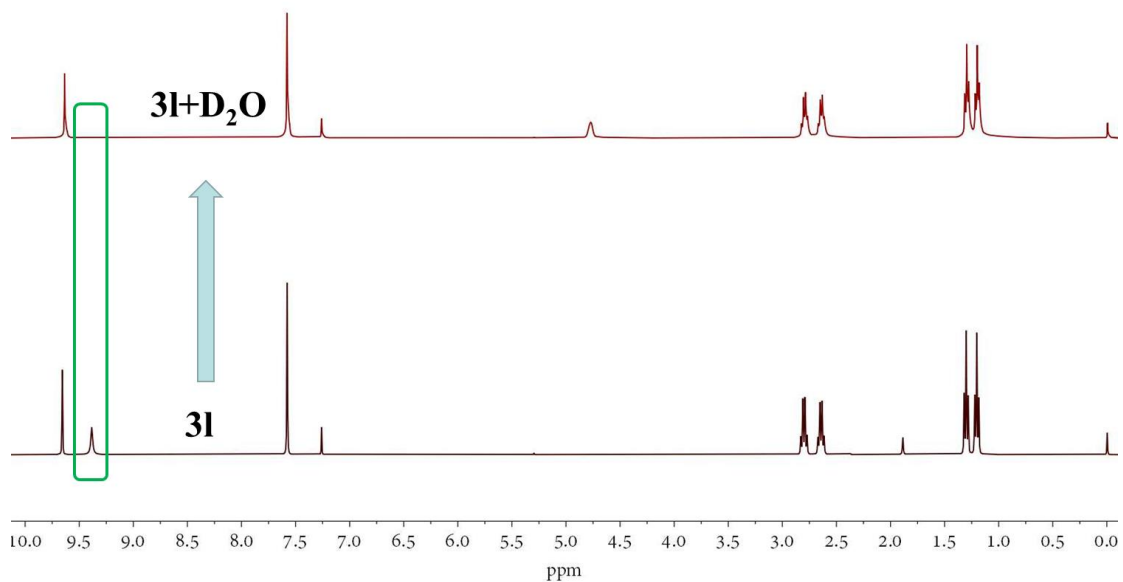**Figure S8.** ^{1}H NMR (400 MHz) spectrum of **3b** as recorded in CDCl$_3$.
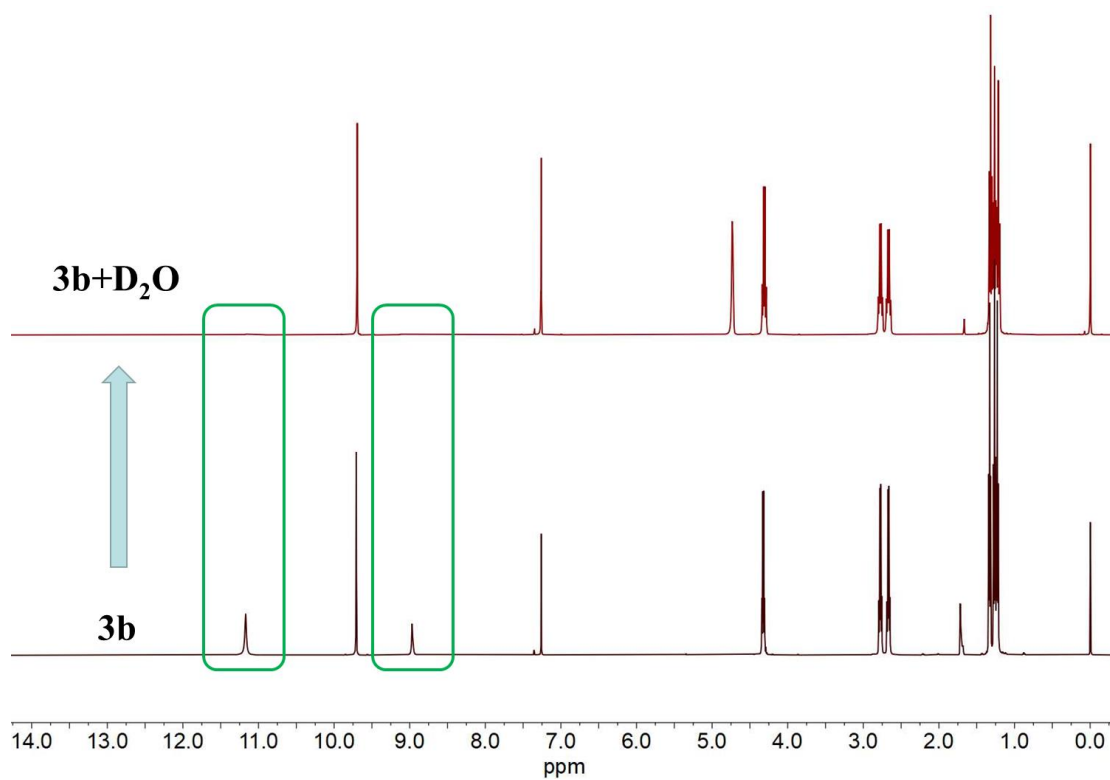
Figure S9. ^{1}H NMR (400 MHz) spectrum of **3b**+**D₂O** as recorded in CDCl₃.
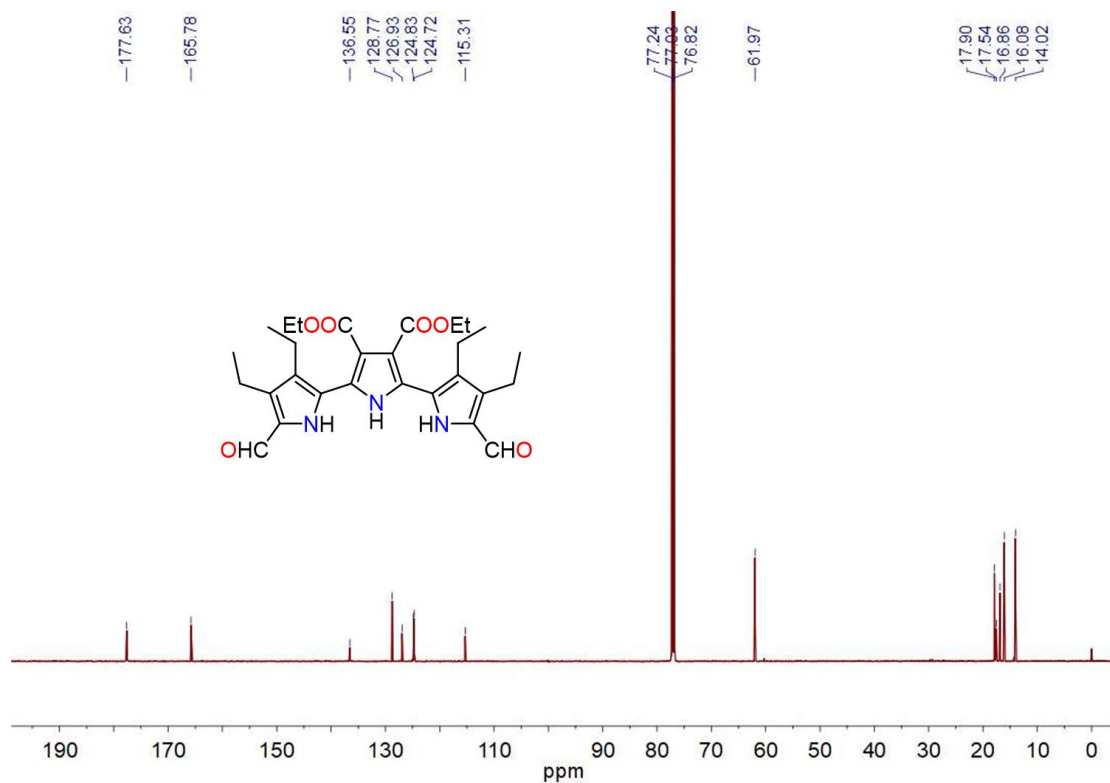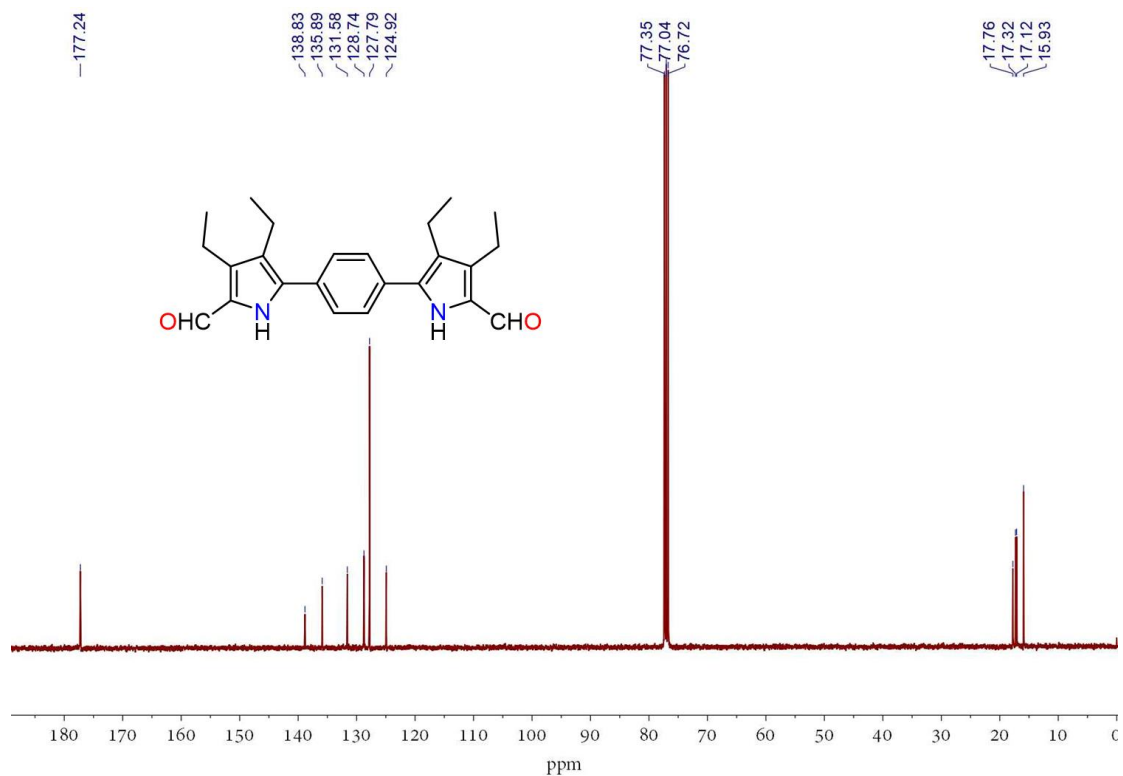

Figure S10. ^{13}C NMR (100 MHz) spectrum of **3b** as recorded in CDCl₃.
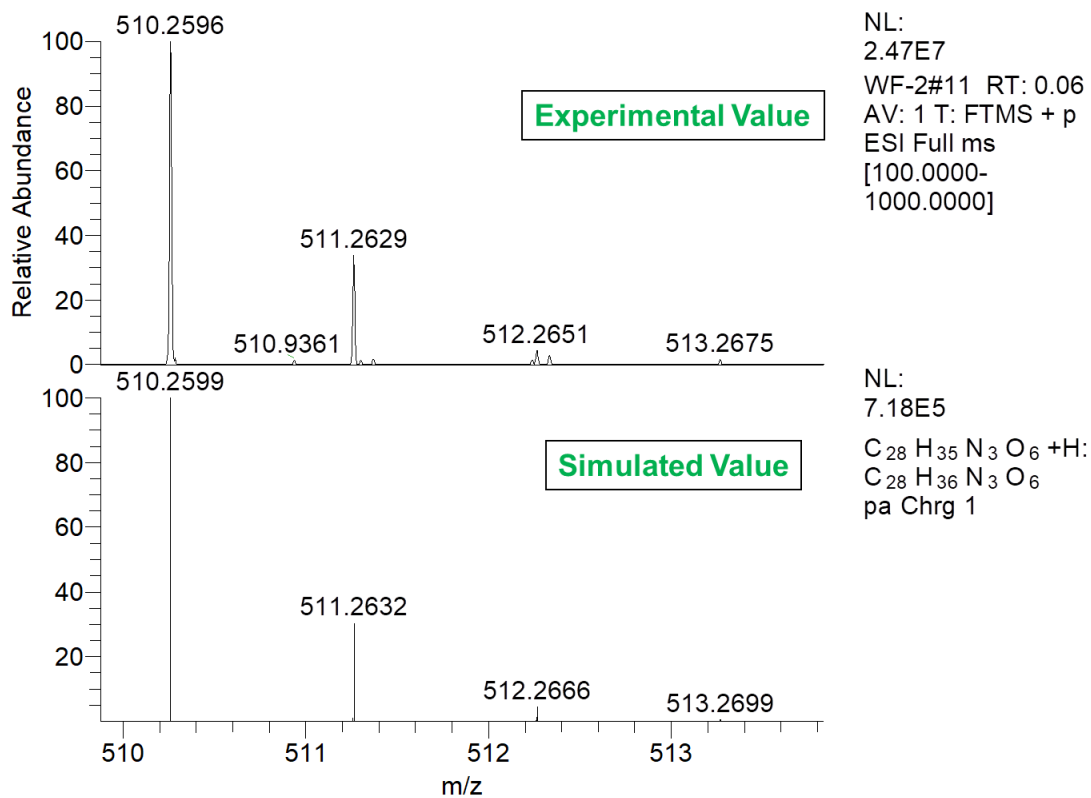
Figure S11. HRMS (ESI) spectrum of **3b**.
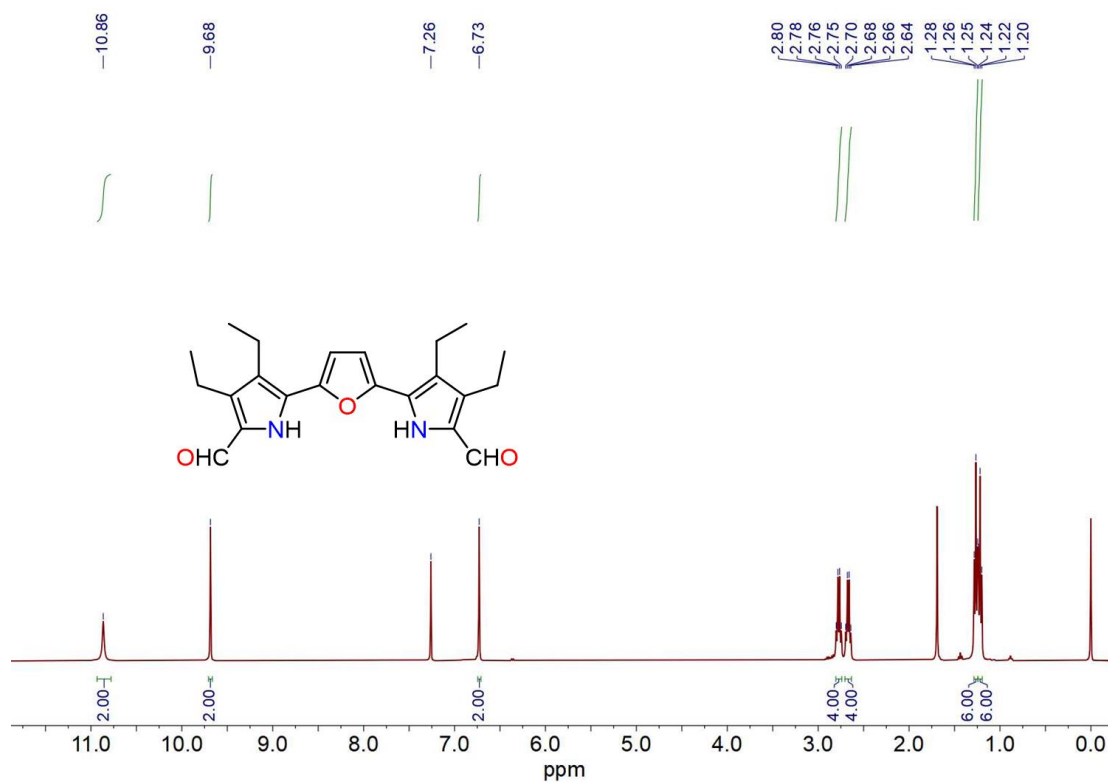
Figure S12. ^{1}H NMR (400 MHz) spectrum of **3c** as recorded in CDCl$_3$.
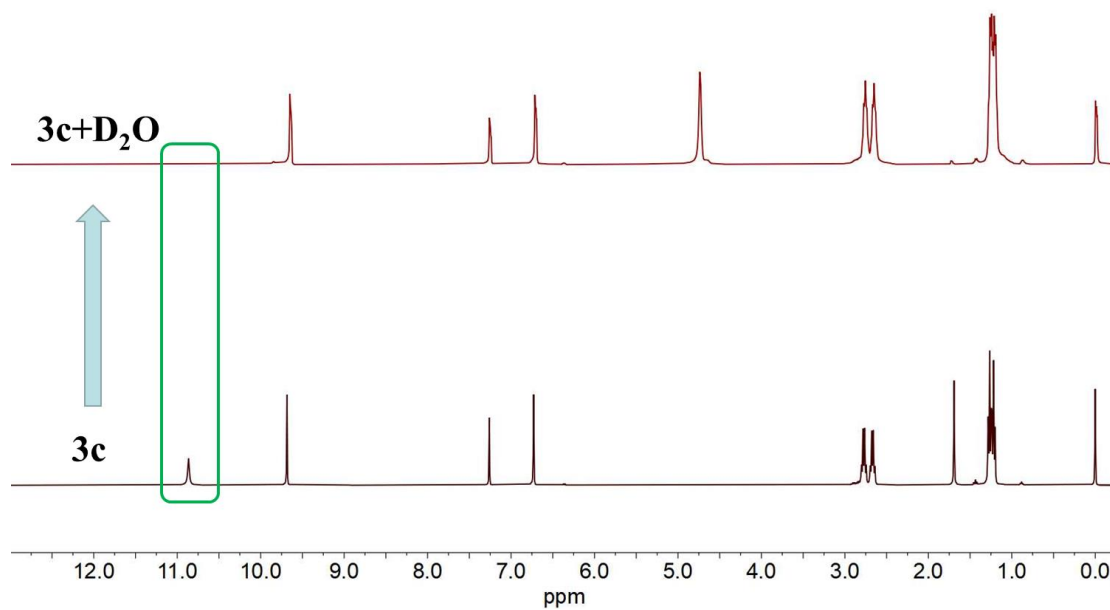
Figure S13. ^{1}H NMR (400 MHz) spectrum of **3c**+**D$_2$O** as recorded in CDCl$_3$.
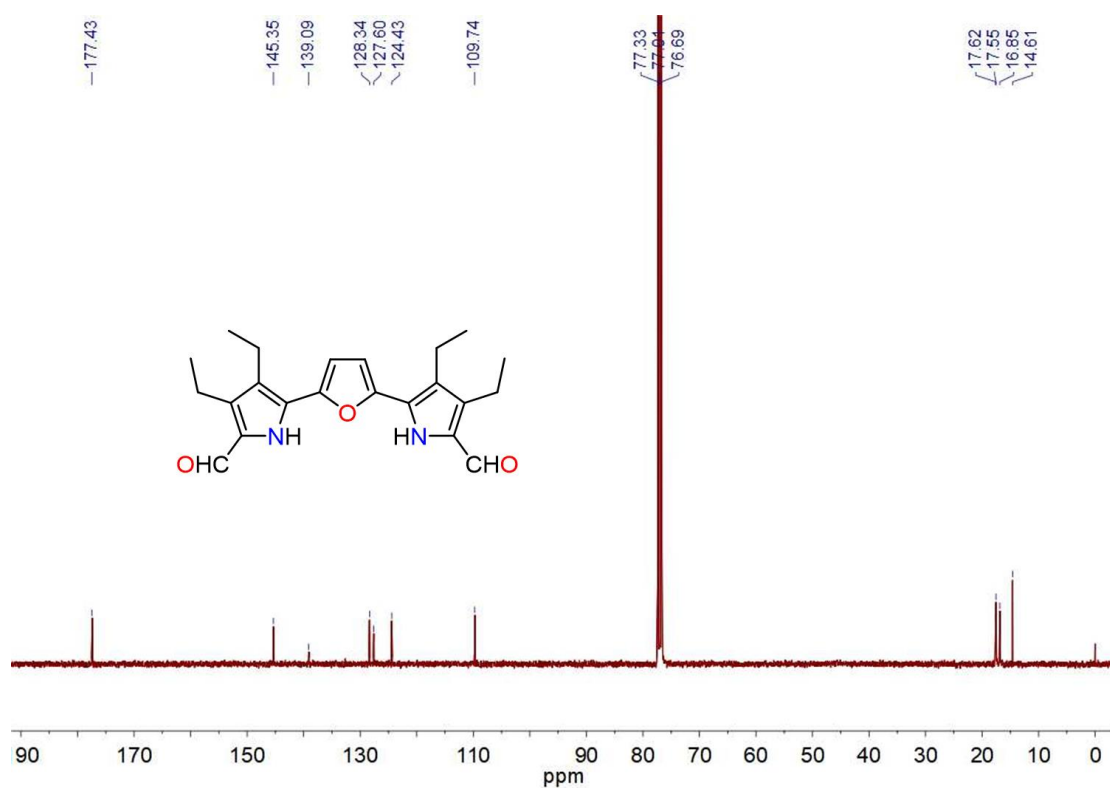
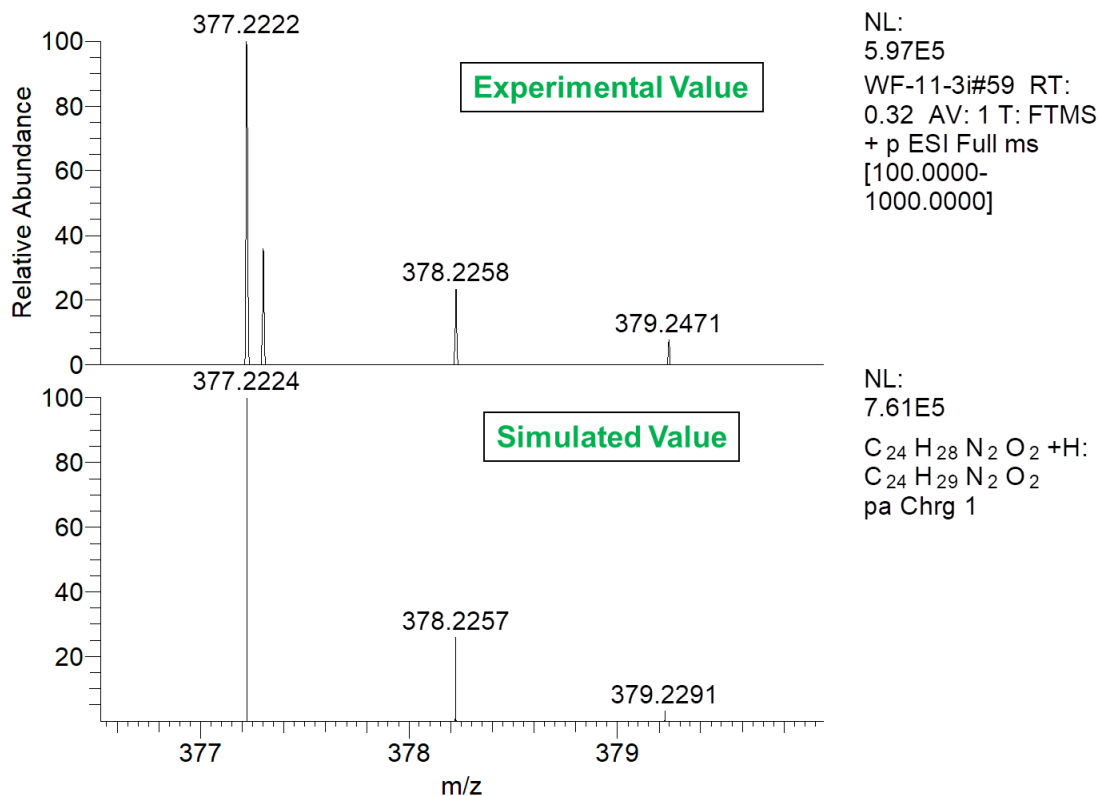**Figure S14.** ^{13}C NMR (100 MHz) spectrum of **3c** as recorded in CDCl$_3$.
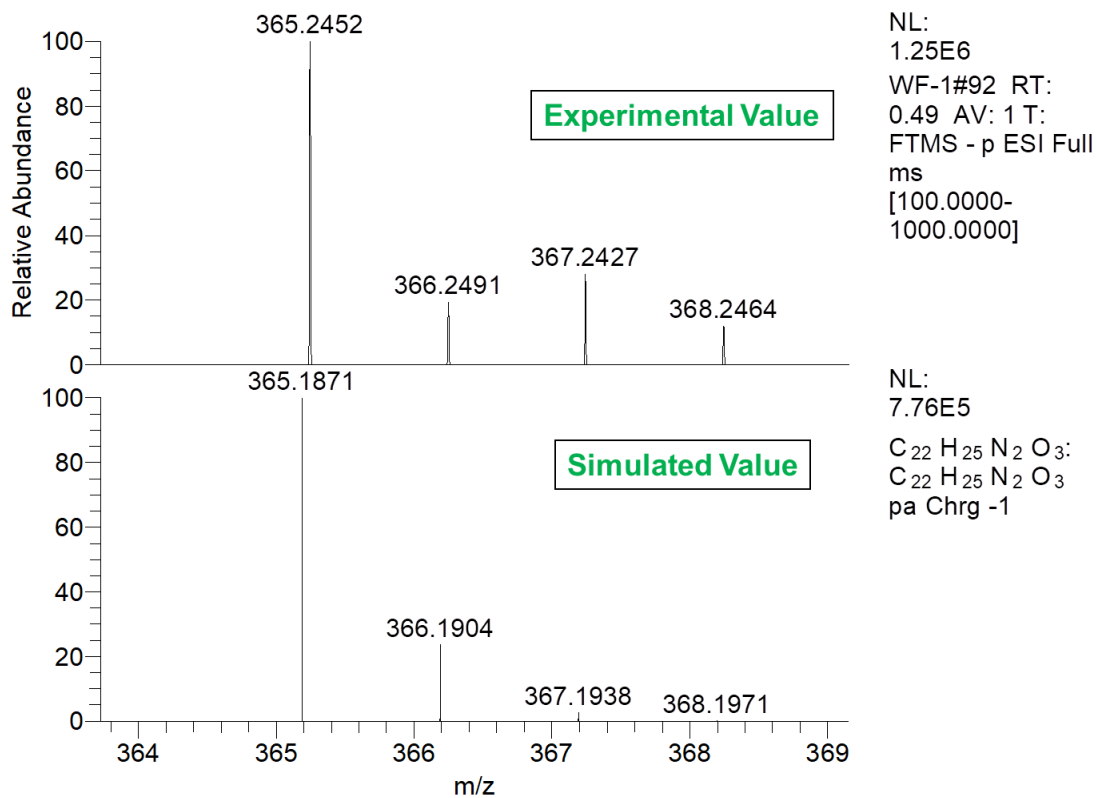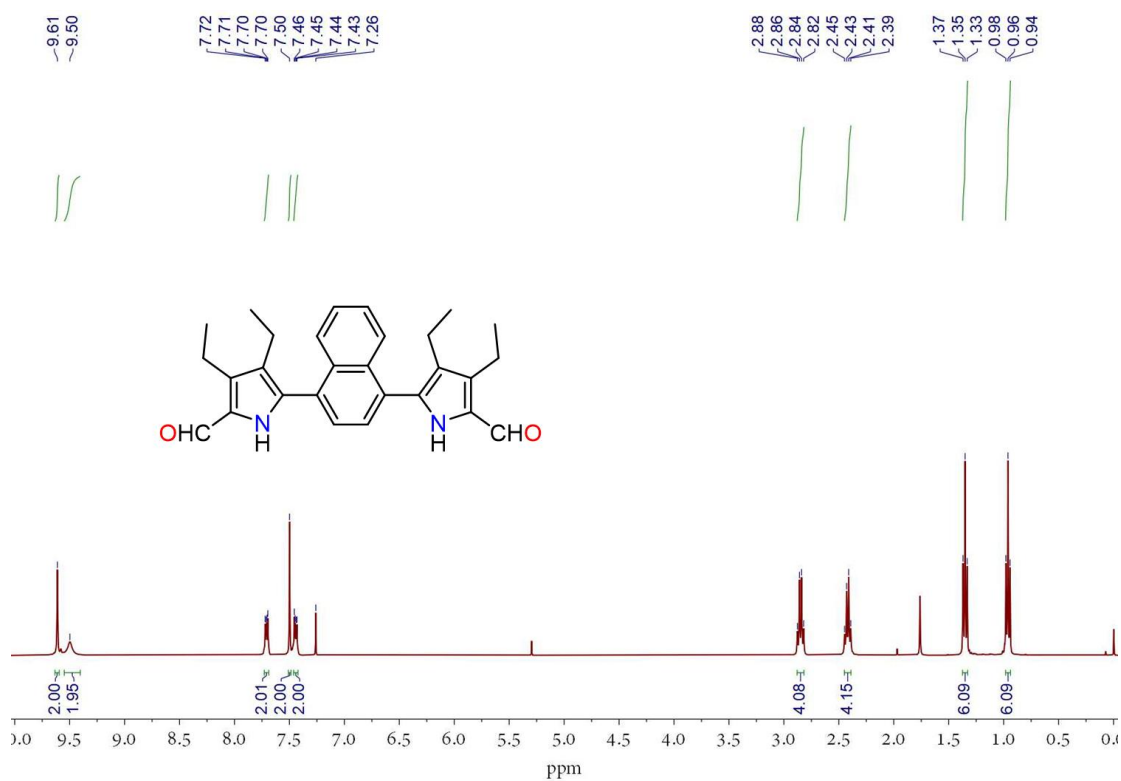
Figure S15. HRMS (ESI) spectrum of **3c**.
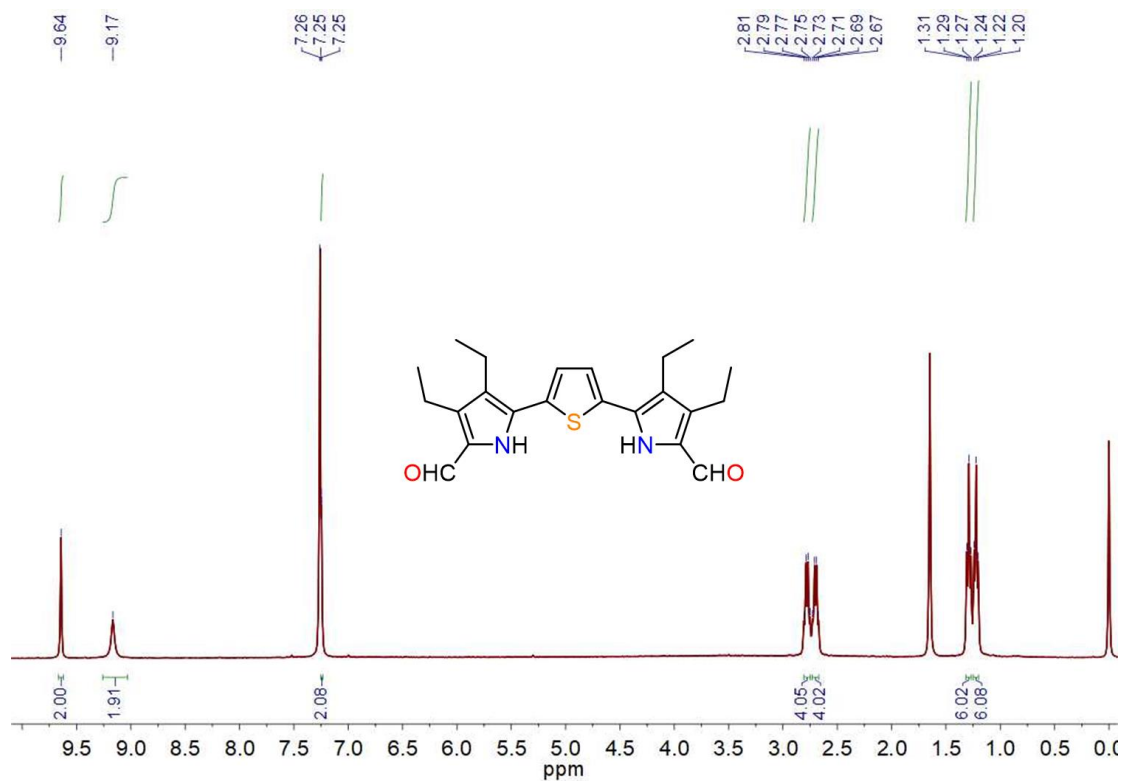
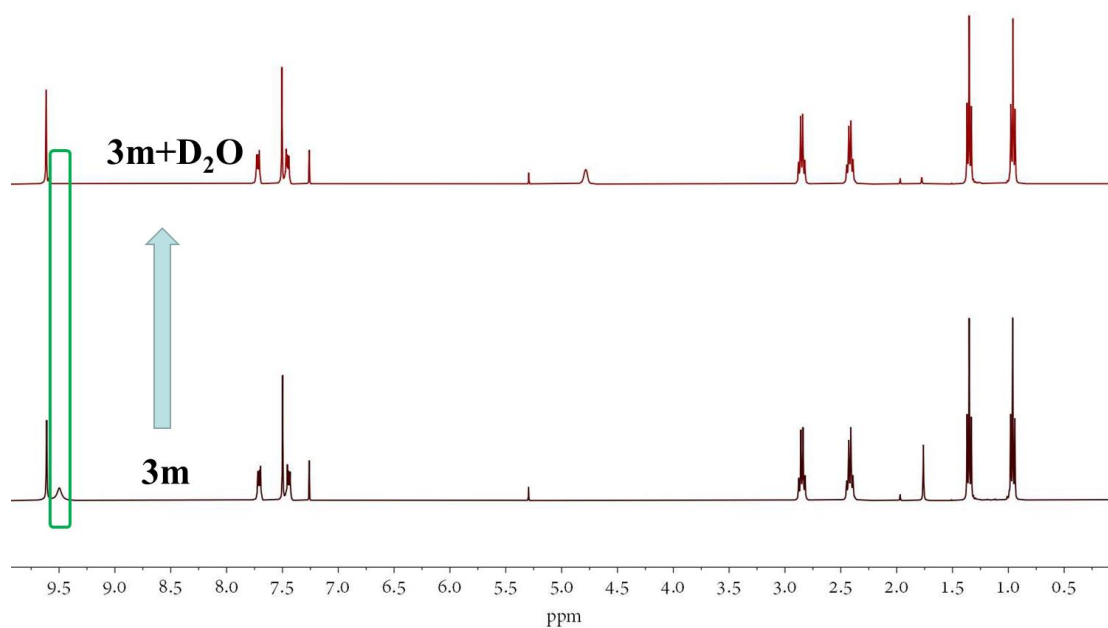**Figure S16.** ^{1}H NMR (400 MHz) spectrum of **3d** as recorded in CDCl$_3$.
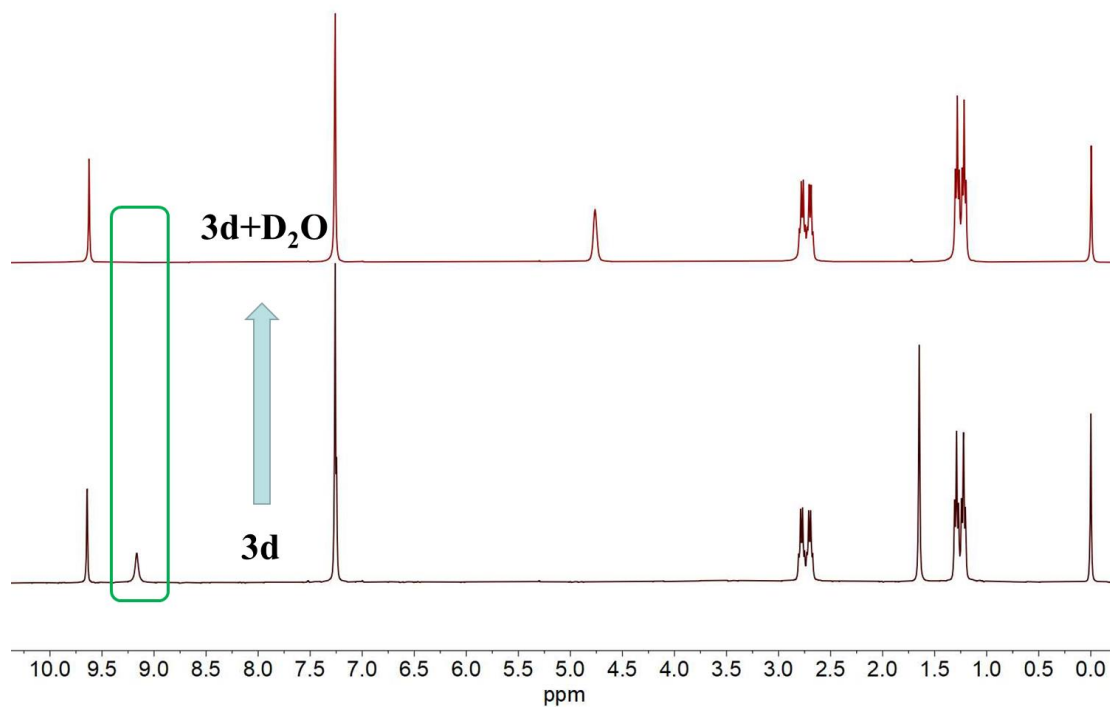
Figure S17. ^{1}H NMR (400 MHz) spectrum of **3d**+**D₂O** as recorded in CDCl₃.
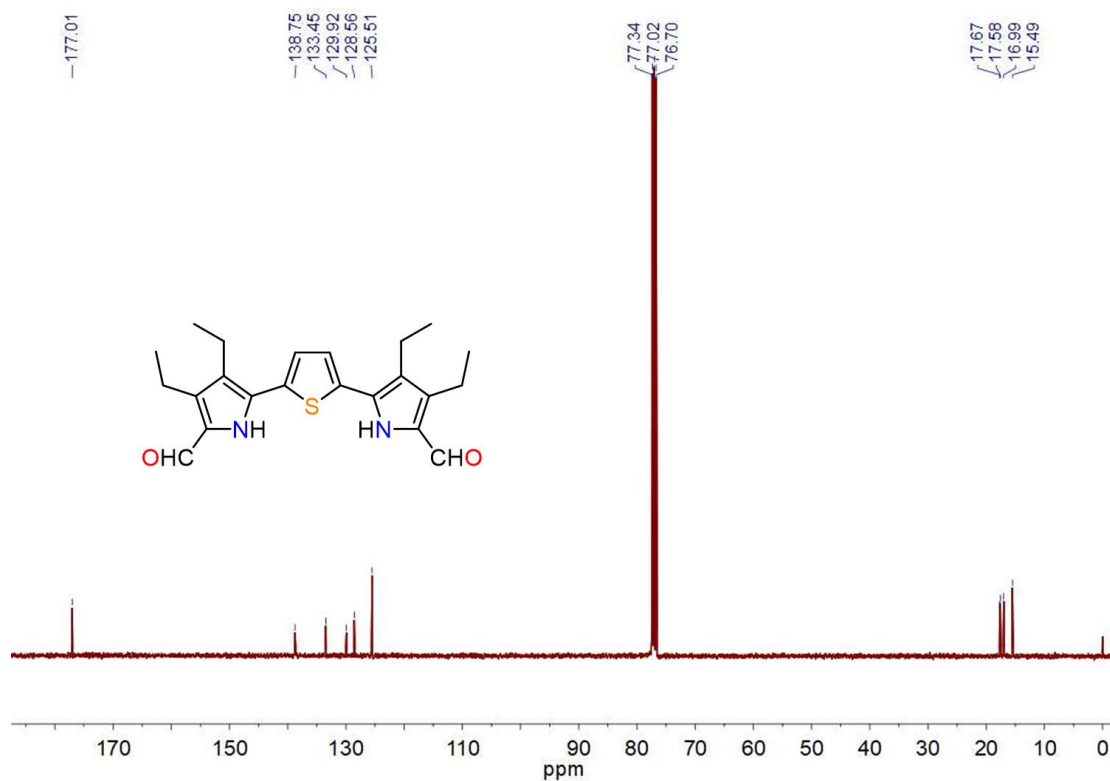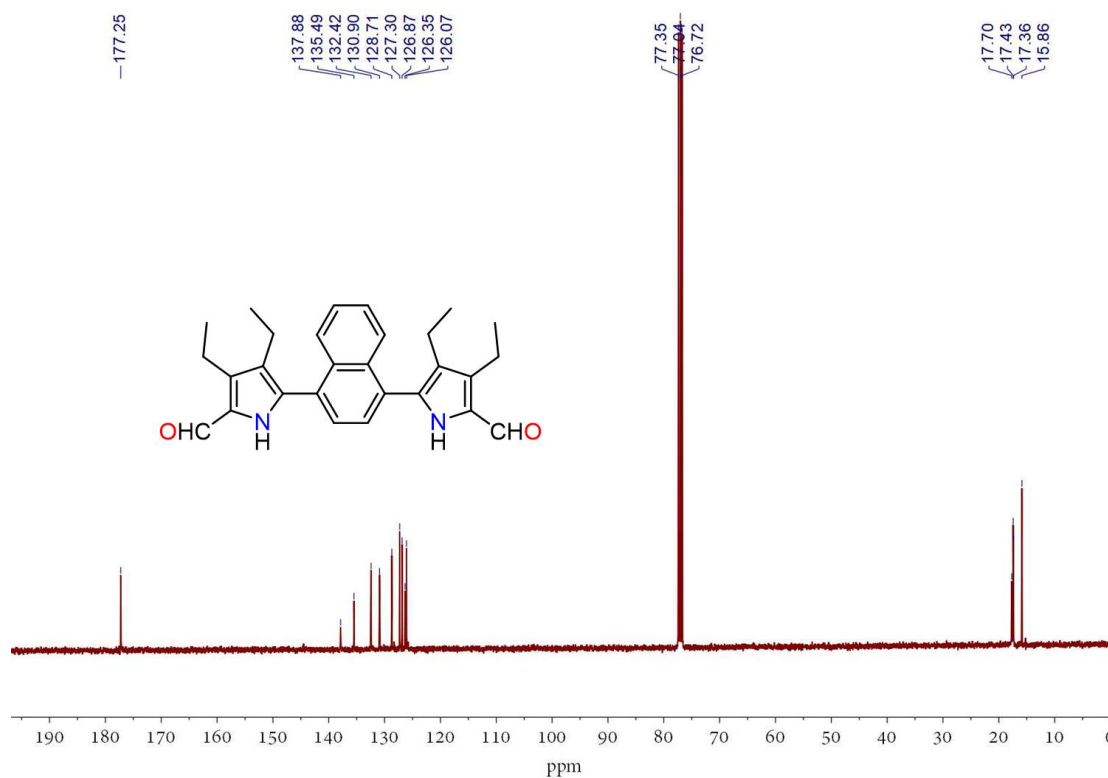

Figure S18. ^{13}C NMR (100 MHz) spectrum of **3d** as recorded in CDCl₃.
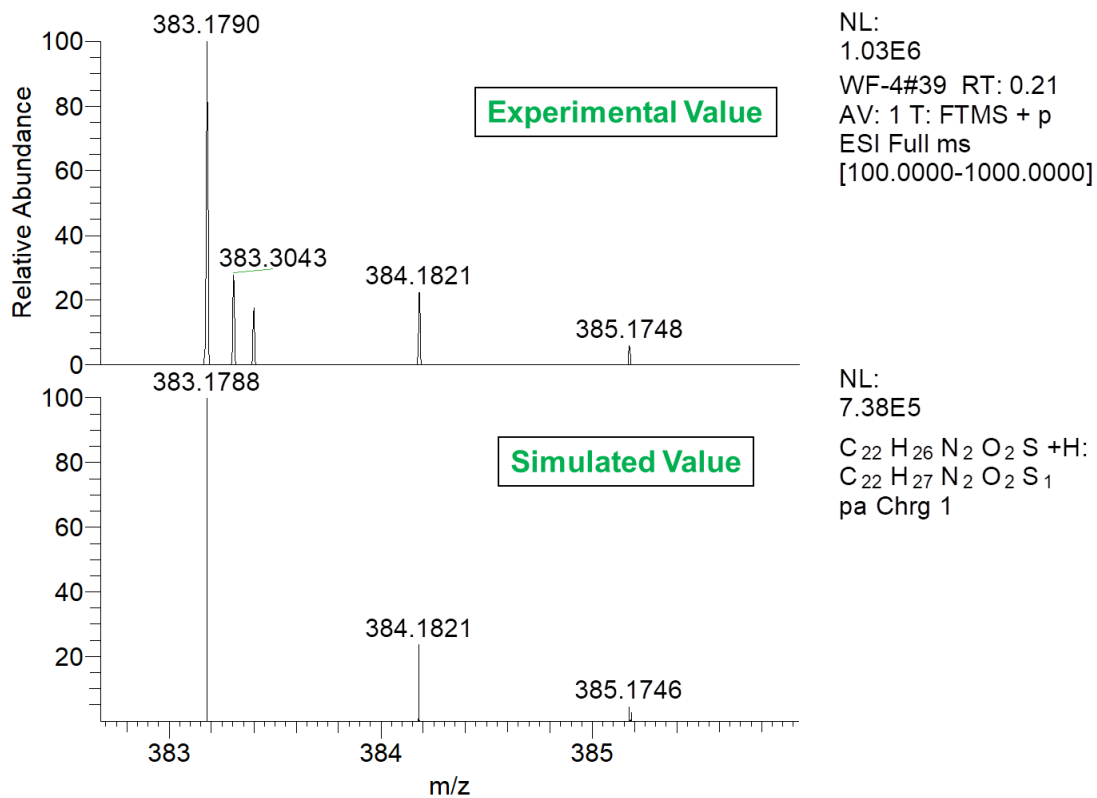
Figure S19. HRMS (ESI) spectrum of **3d**.
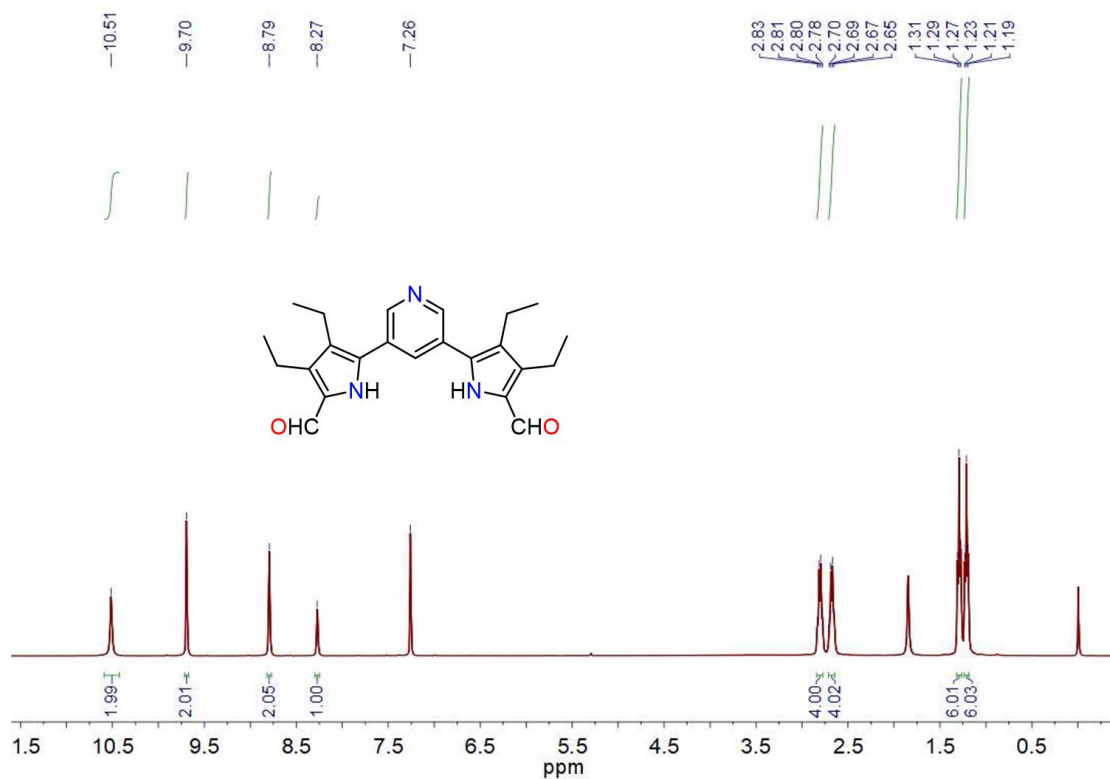
Figure S20. ^{1}H NMR (400 MHz) spectrum of **3e** as recorded in CDCl$_3$.
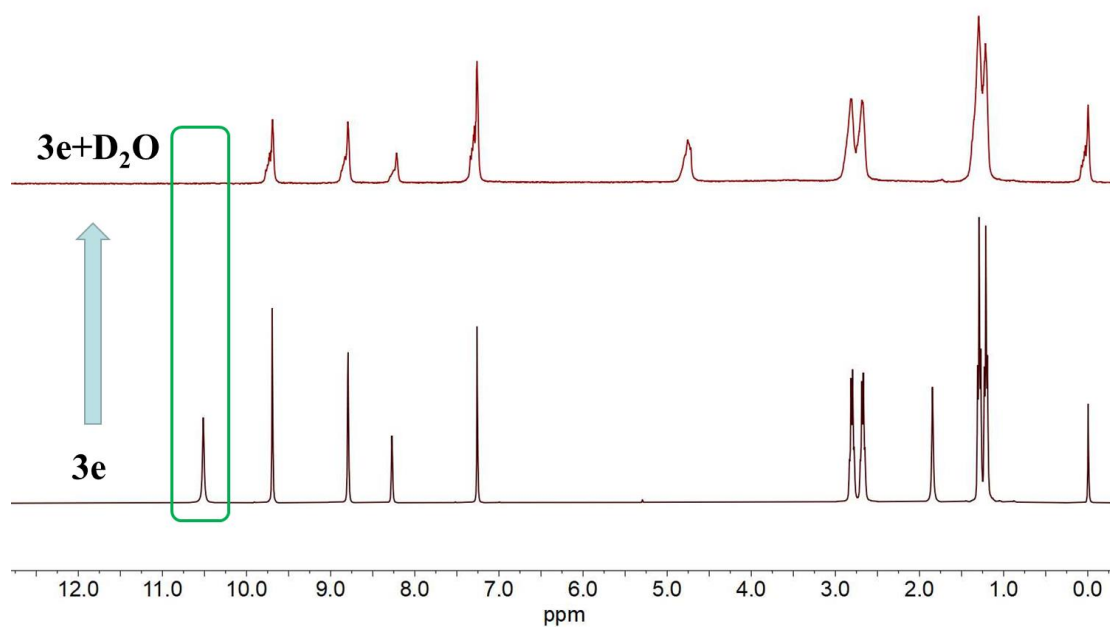
Figure S21. ^{1}H NMR (400 MHz) spectrum of **3e**+**D$_2$O** as recorded in CDCl$_3$.
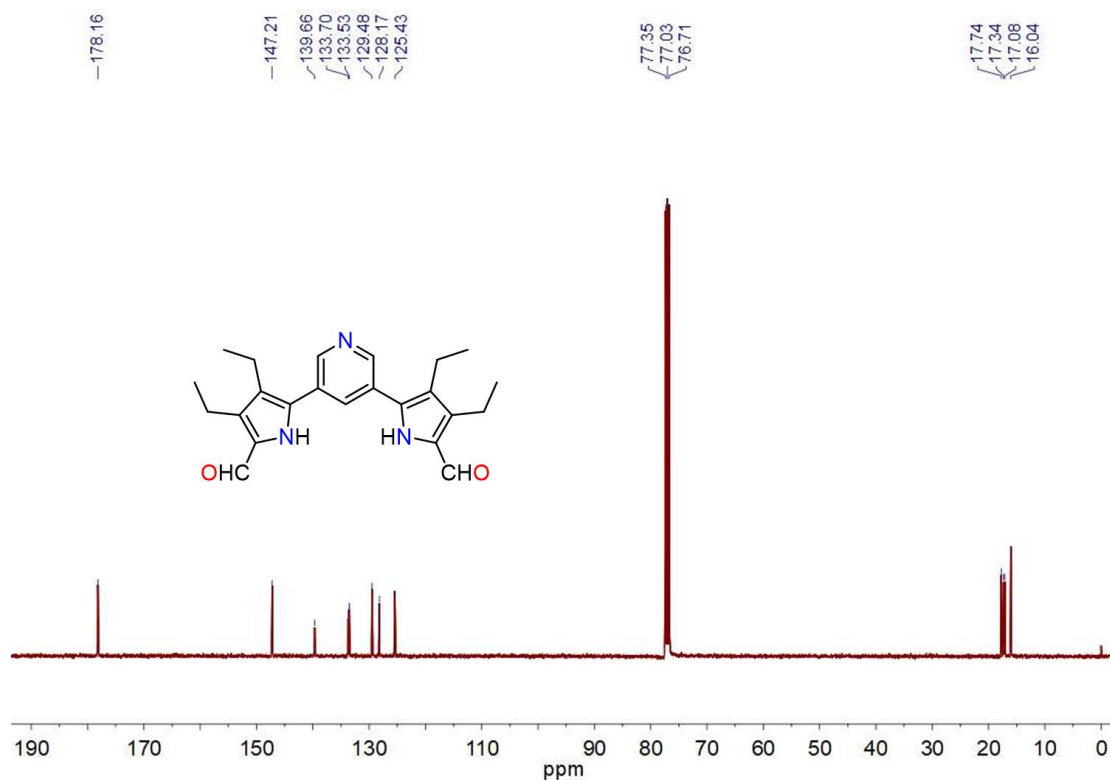
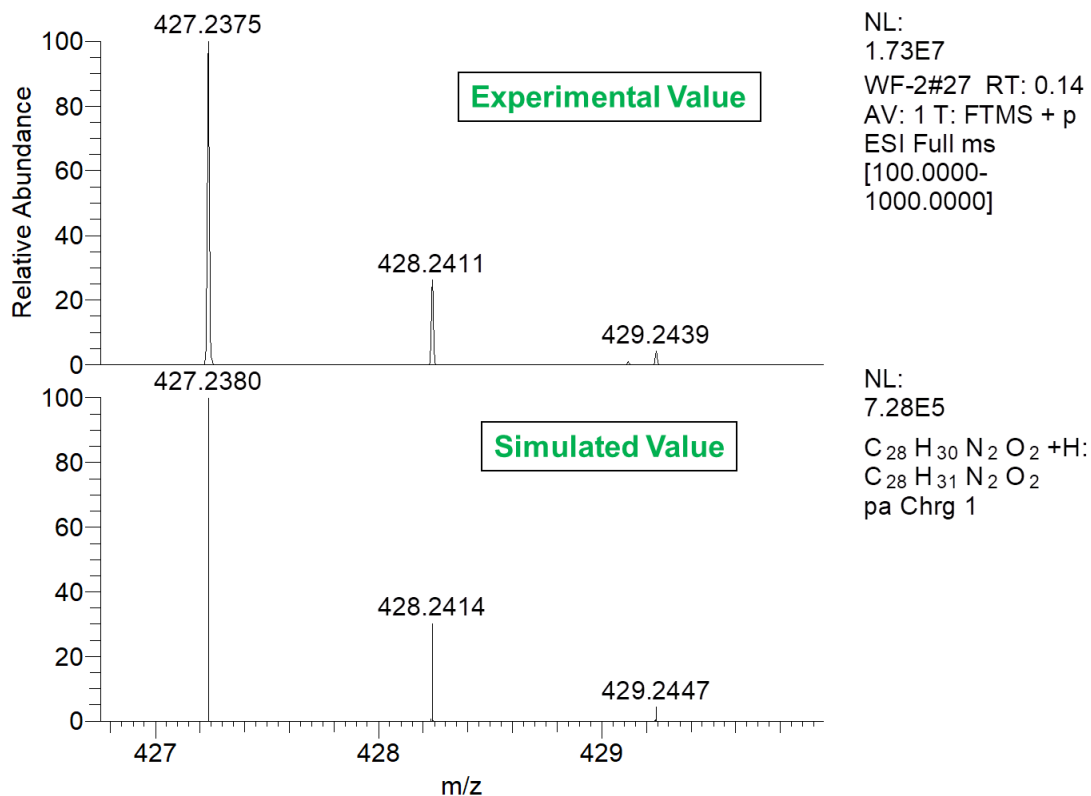**Figure S22.** ^{13}C NMR (100 MHz) spectrum of **3e** as recorded in CDCl$_3$.
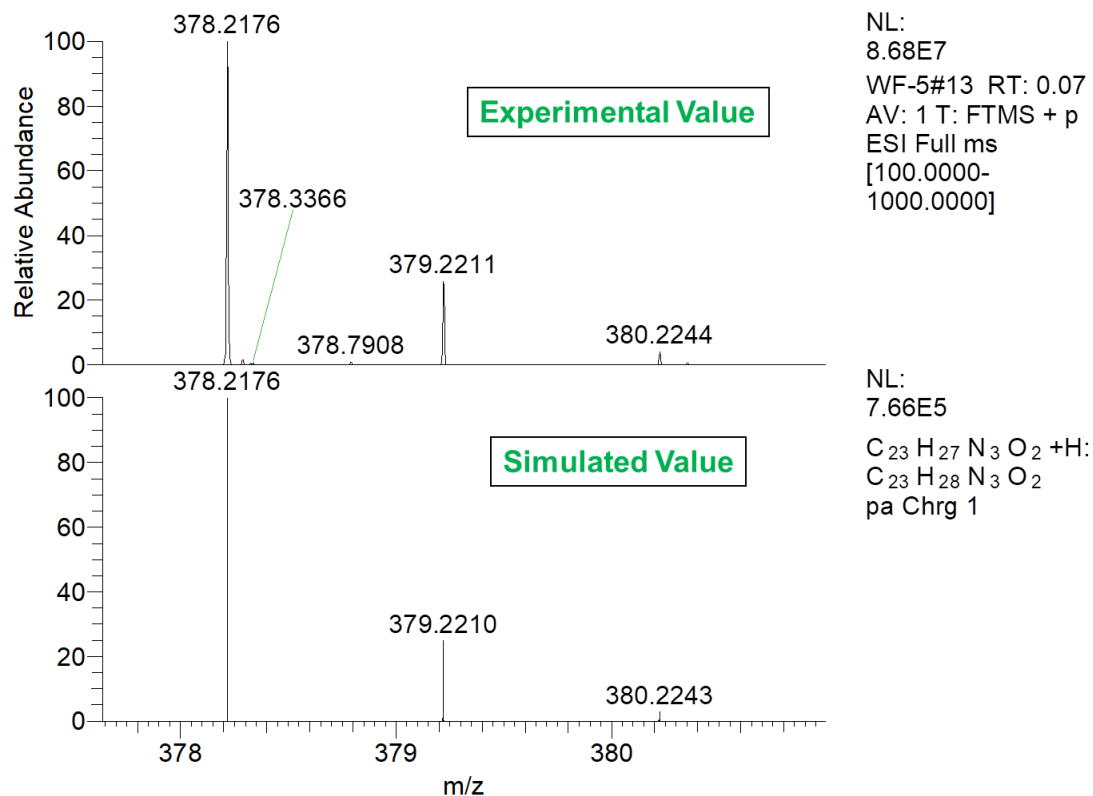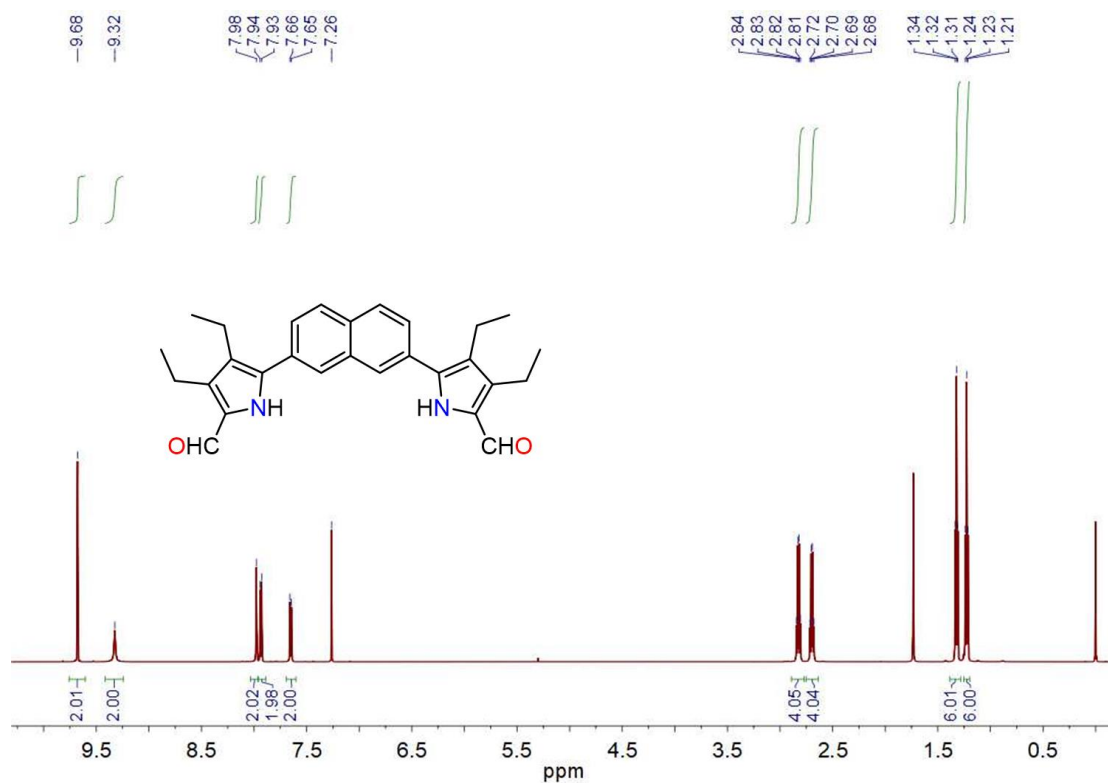
Figure S23. HRMS (ESI) spectrum of **3e**.
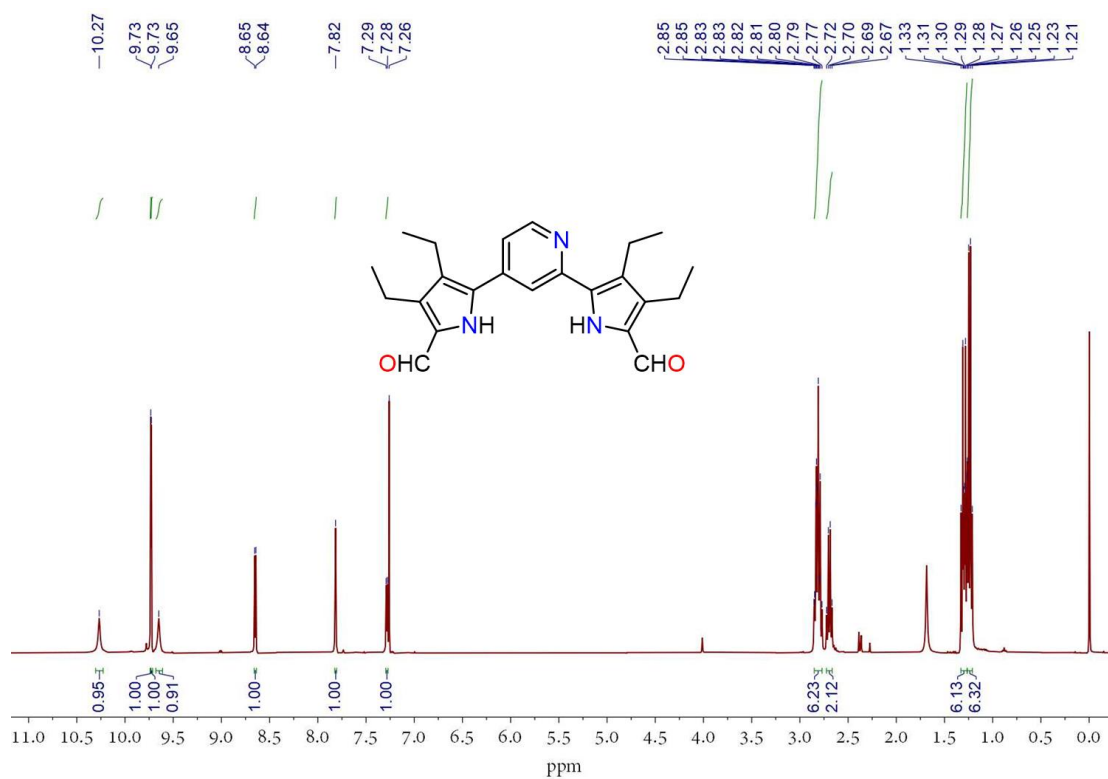
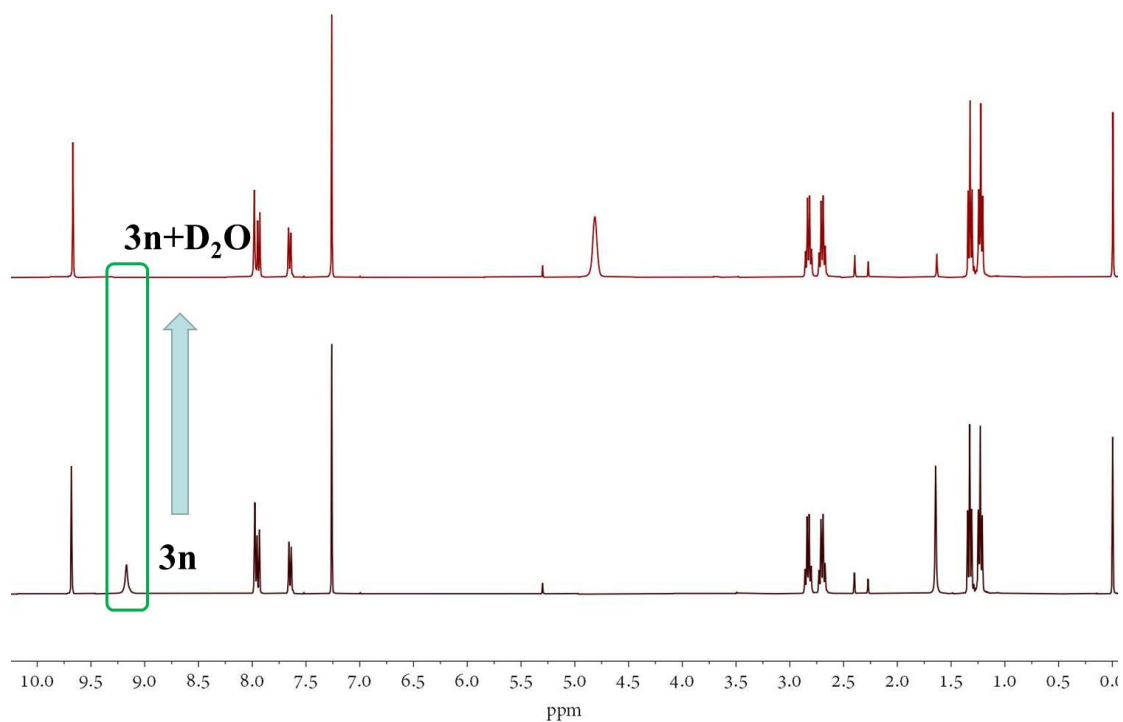**Figure S24.** ^{1}H NMR (400 MHz) spectrum of **3f** as recorded in CDCl$_3$.
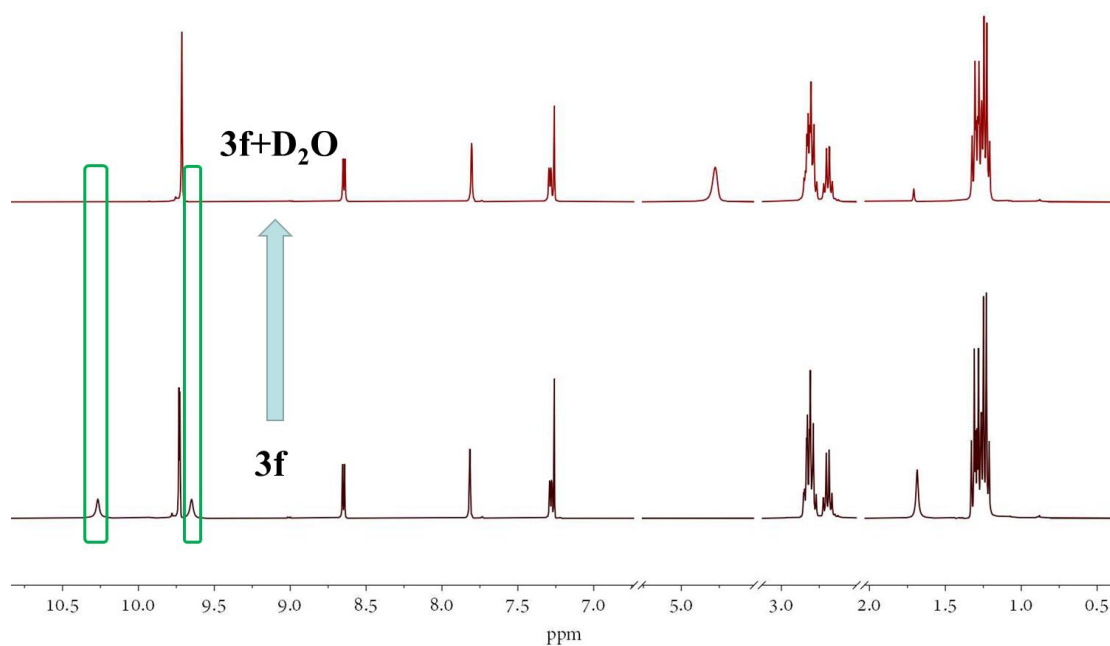
Figure S25. ^{1}H NMR (400 MHz) spectrum of **3f+D$_2$O** as recorded in CDCl$_3$.
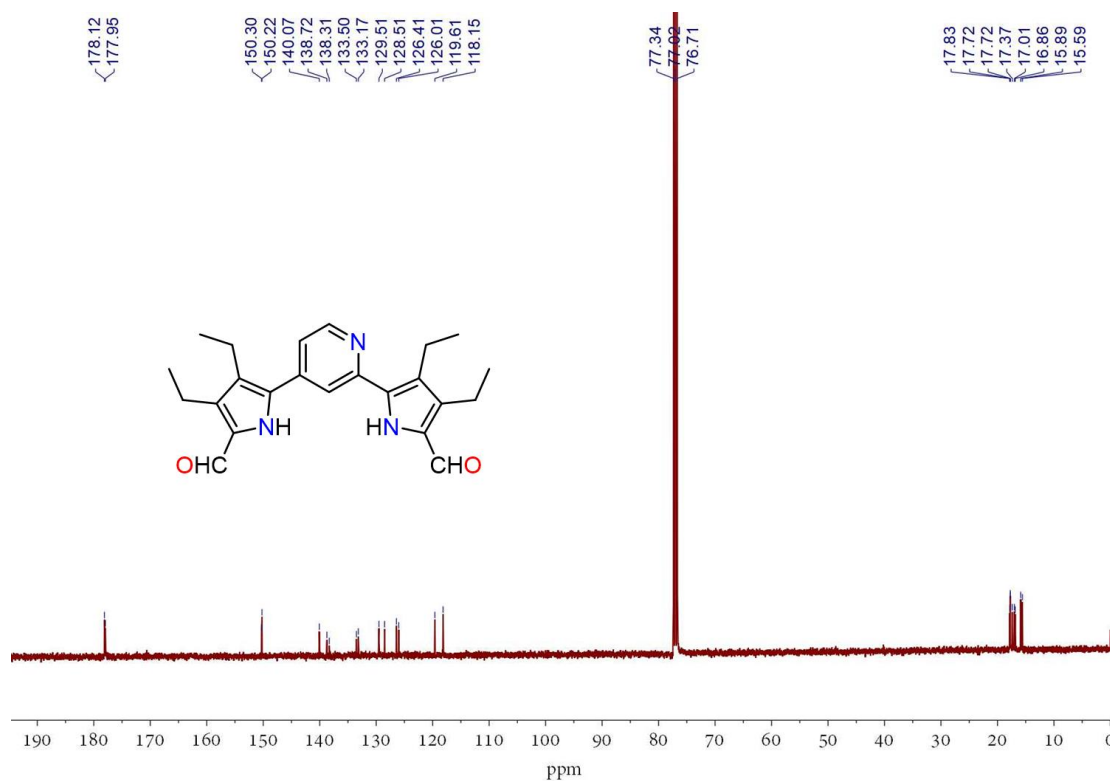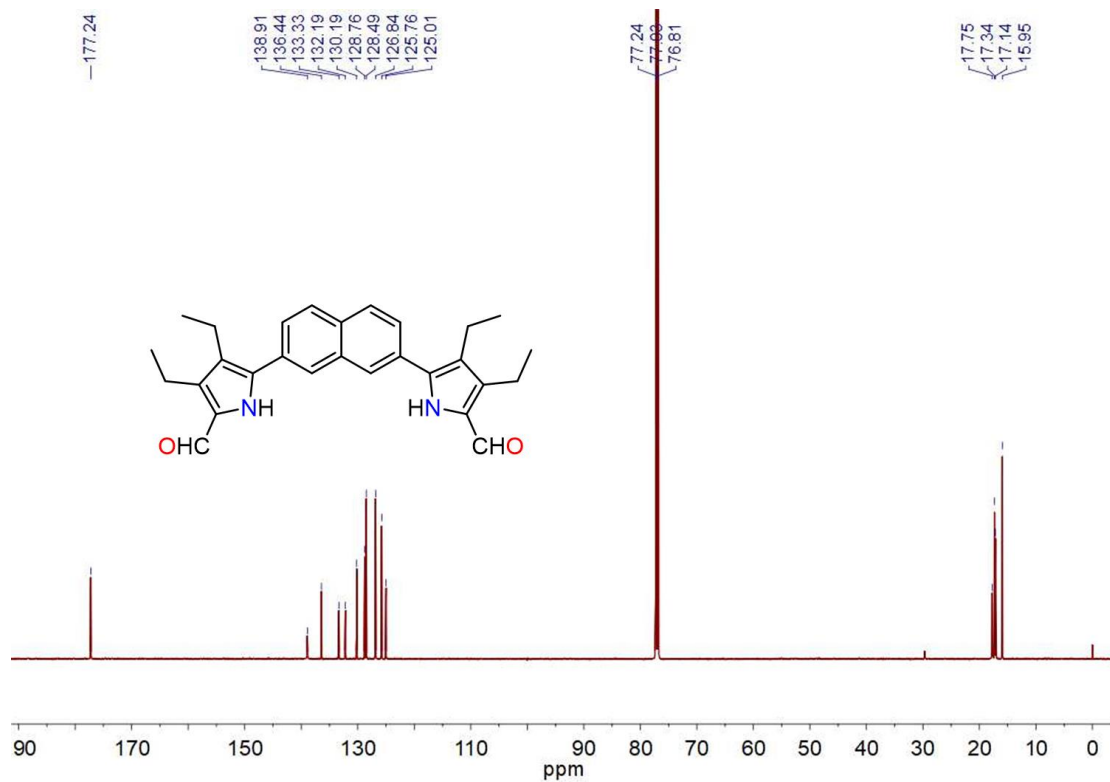

Figure S26. ^{13}C NMR (100 MHz) spectrum of **3f** as recorded in CDCl$_3$.
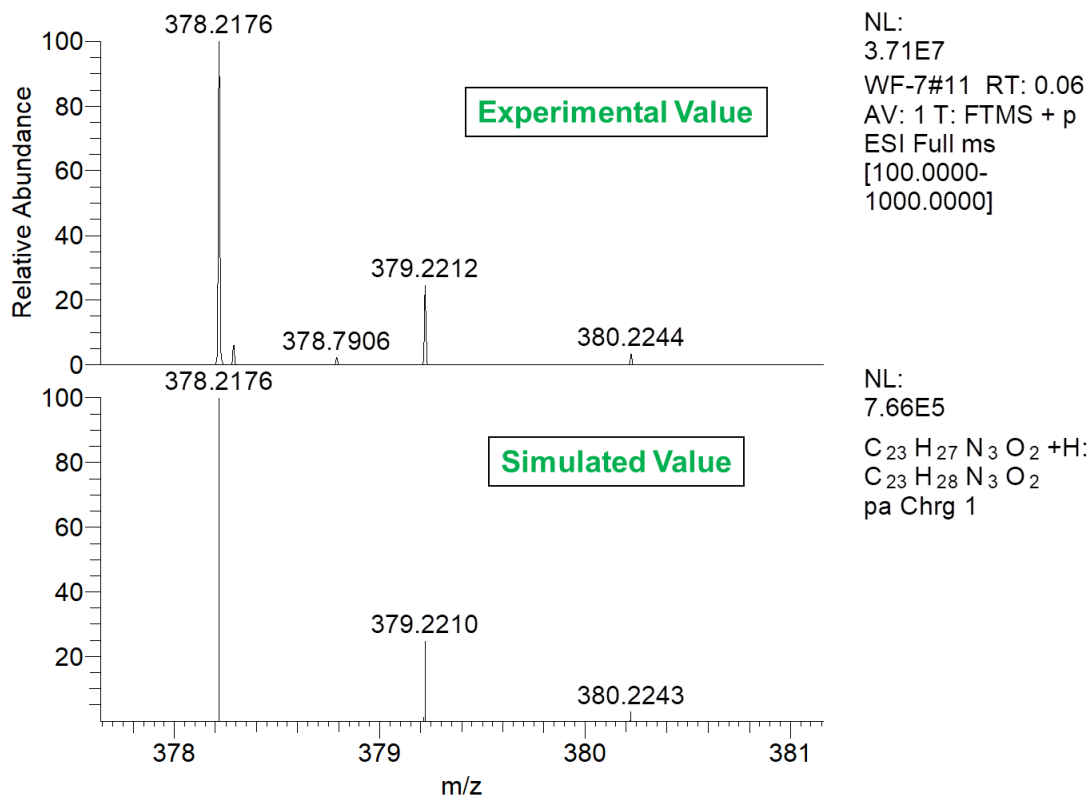
Figure S27. HRMS (ESI) spectrum of **3f**.
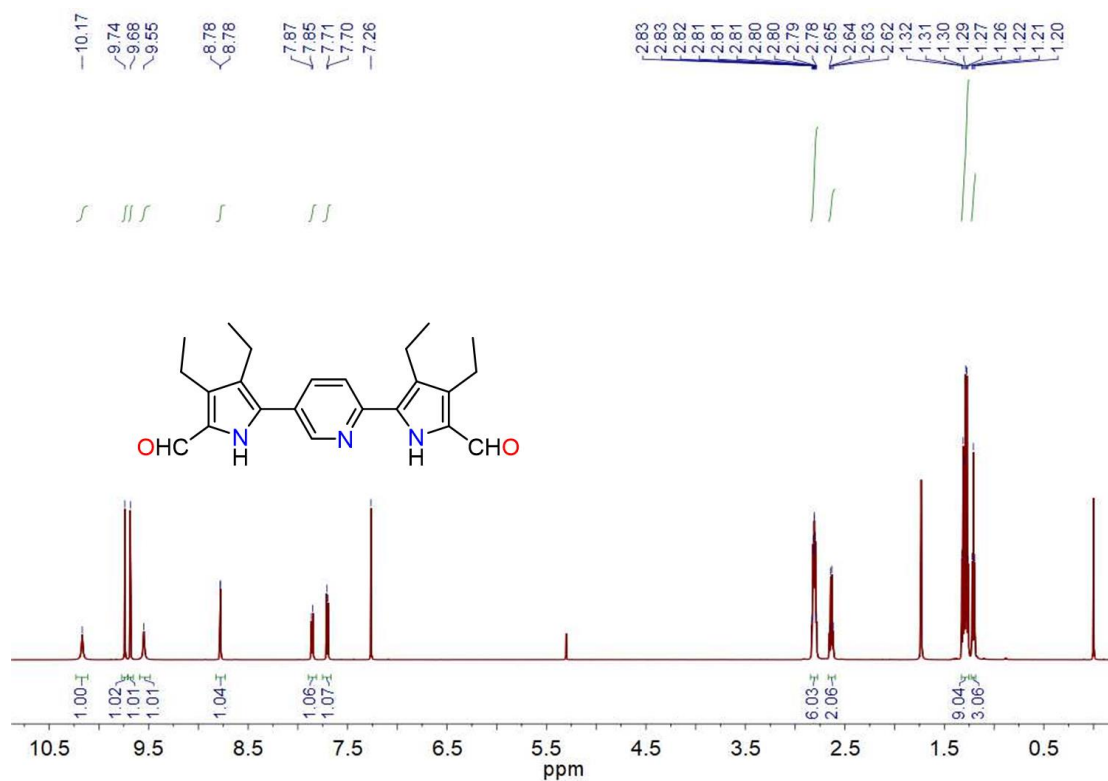
Figure S28. ^{1}H NMR (400 MHz) spectrum of **3g** as recorded in CDCl$_3$.
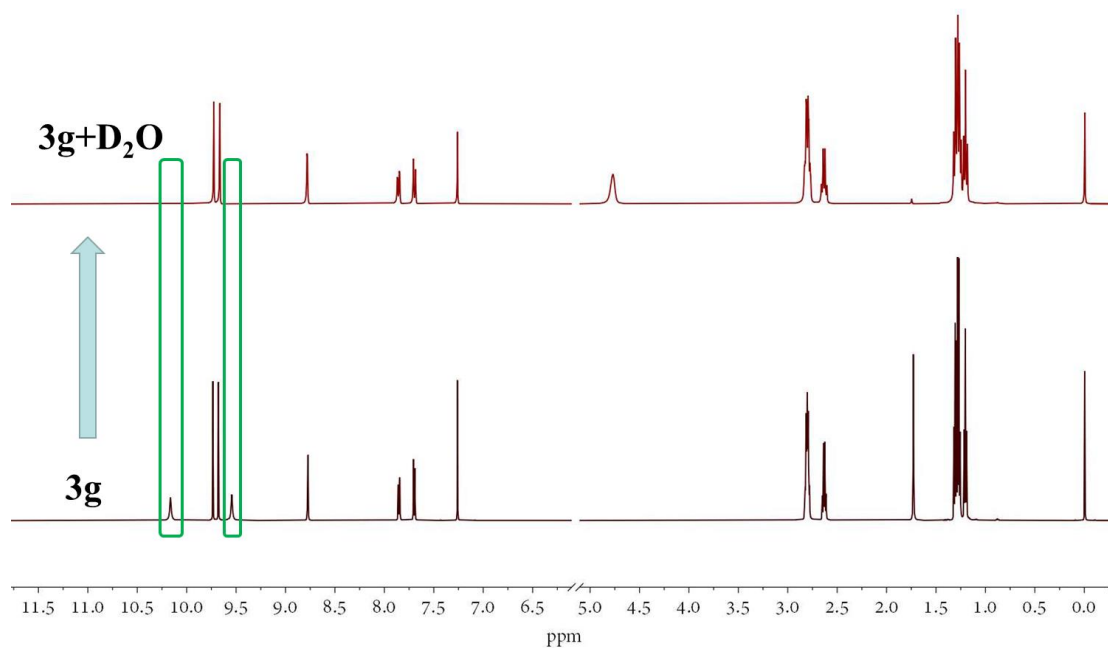
Figure S29. ^{1}H NMR (400 MHz) spectrum of **3g**+**D₂O** as recorded in CDCl₃.
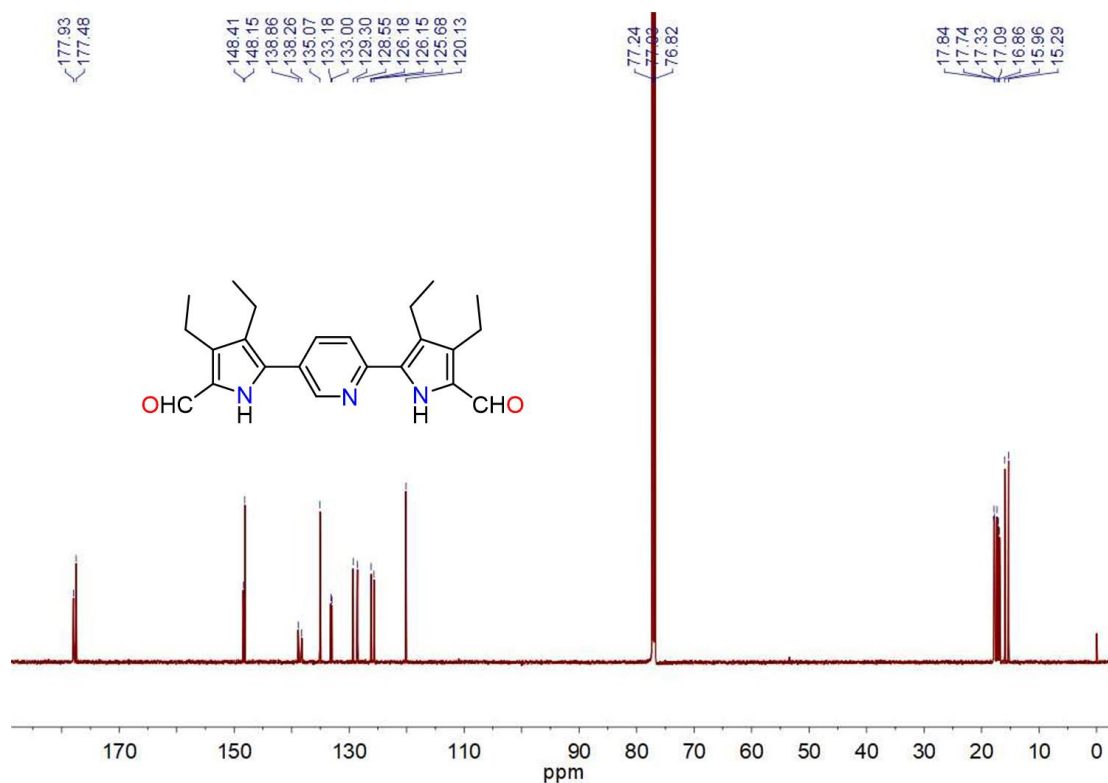
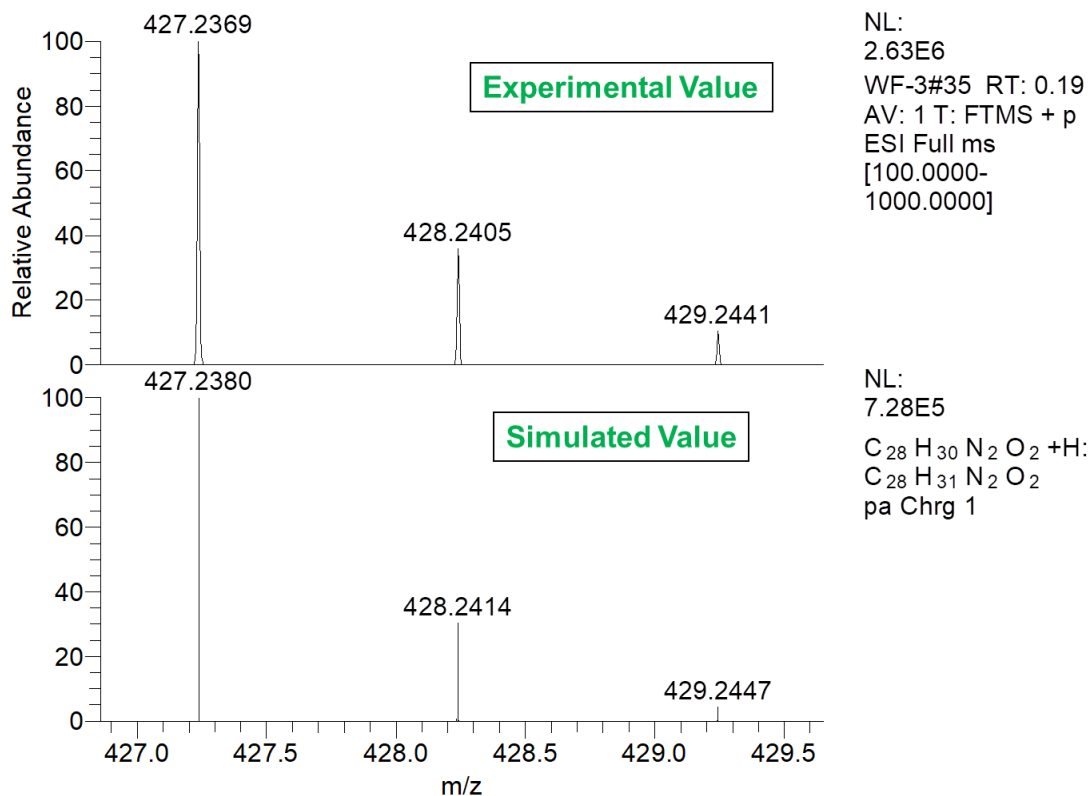**Figure S30.** ^{13}C NMR (100 MHz) spectrum of **3g** as recorded in CDCl₃.
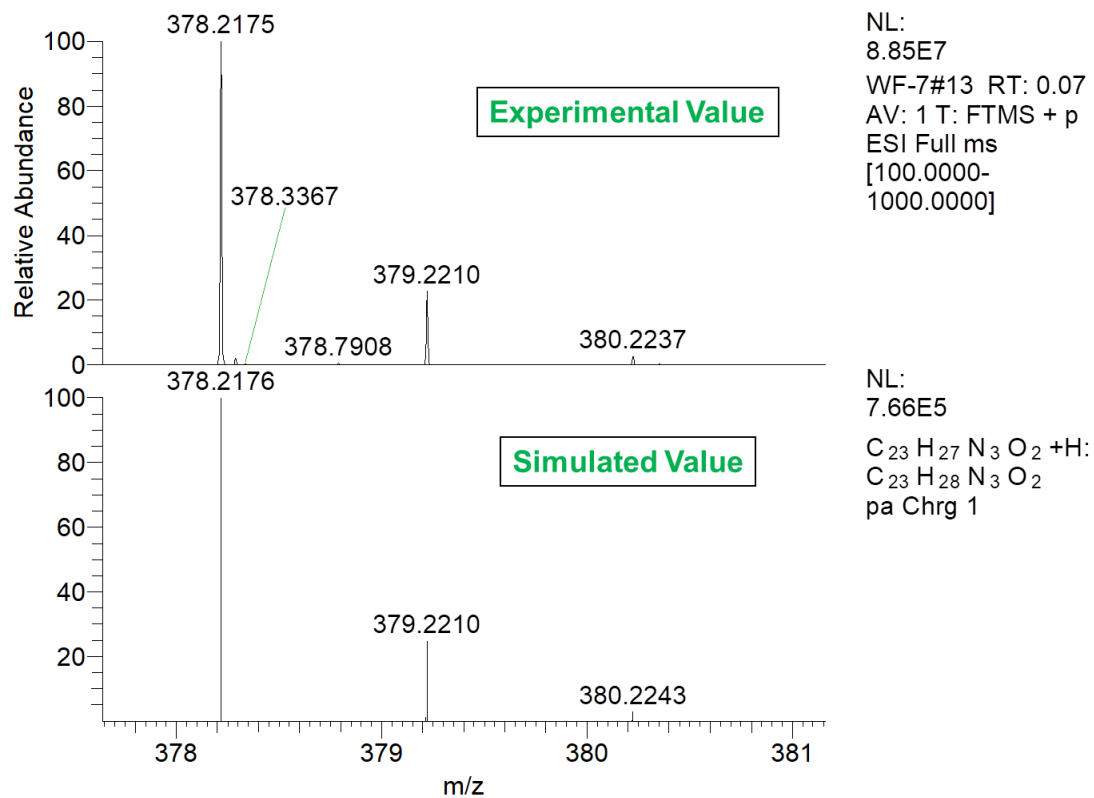
Figure S31. HRMS (ESI) spectrum of **3g**.
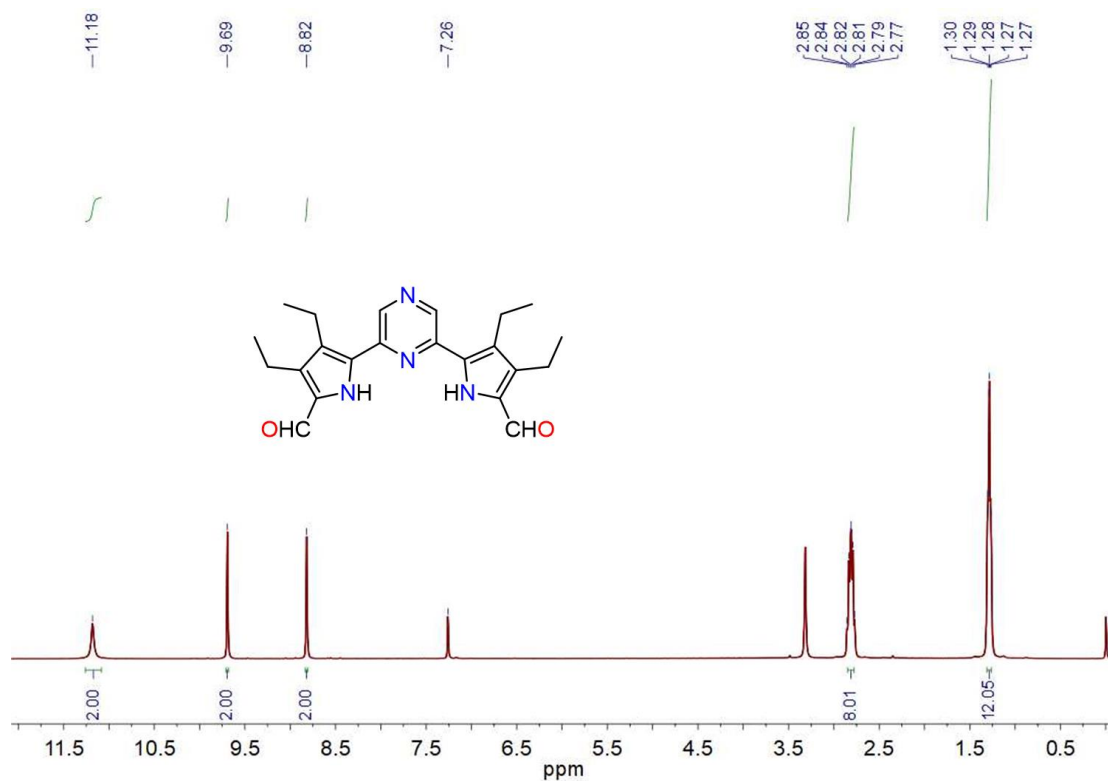
Figure S32. ^{1}H NMR (400 MHz) spectrum of **3h** as recorded in CDCl$_3$.
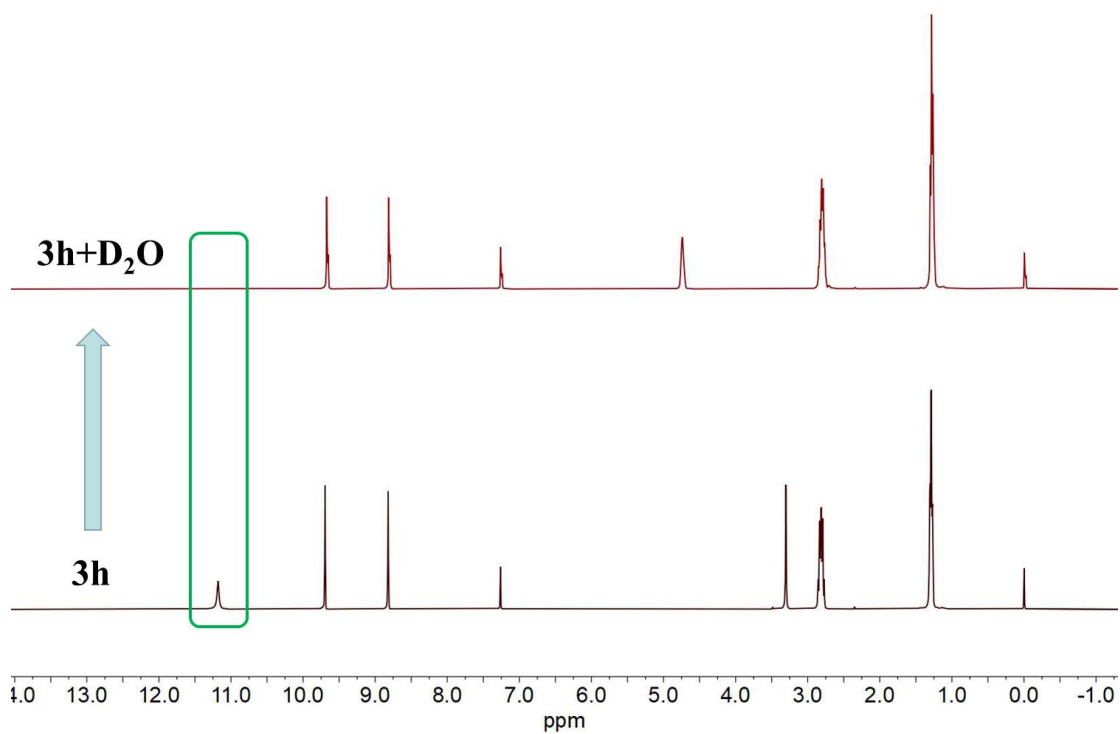
Figure S33. ^{1}H NMR (400 MHz) spectrum of **3h**+**D₂O** as recorded in CDCl₃.
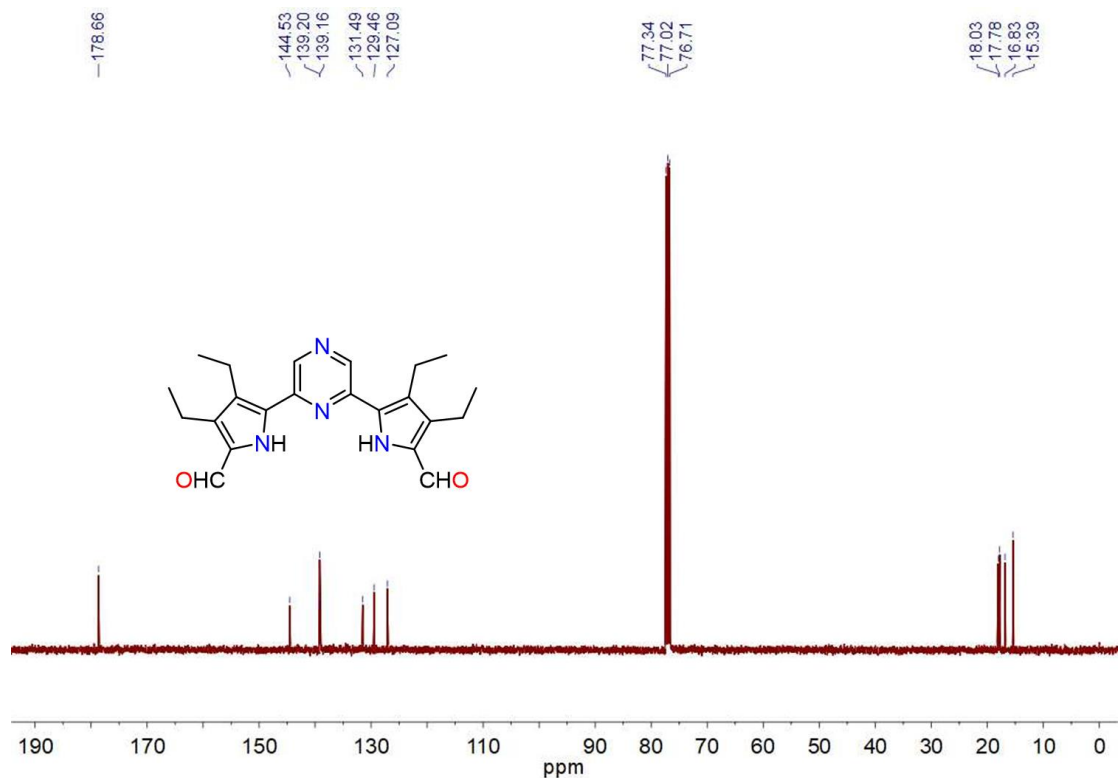
Figure S34. ^{13}C NMR (100 MHz) spectrum of **3h** as recorded in CDCl₃.
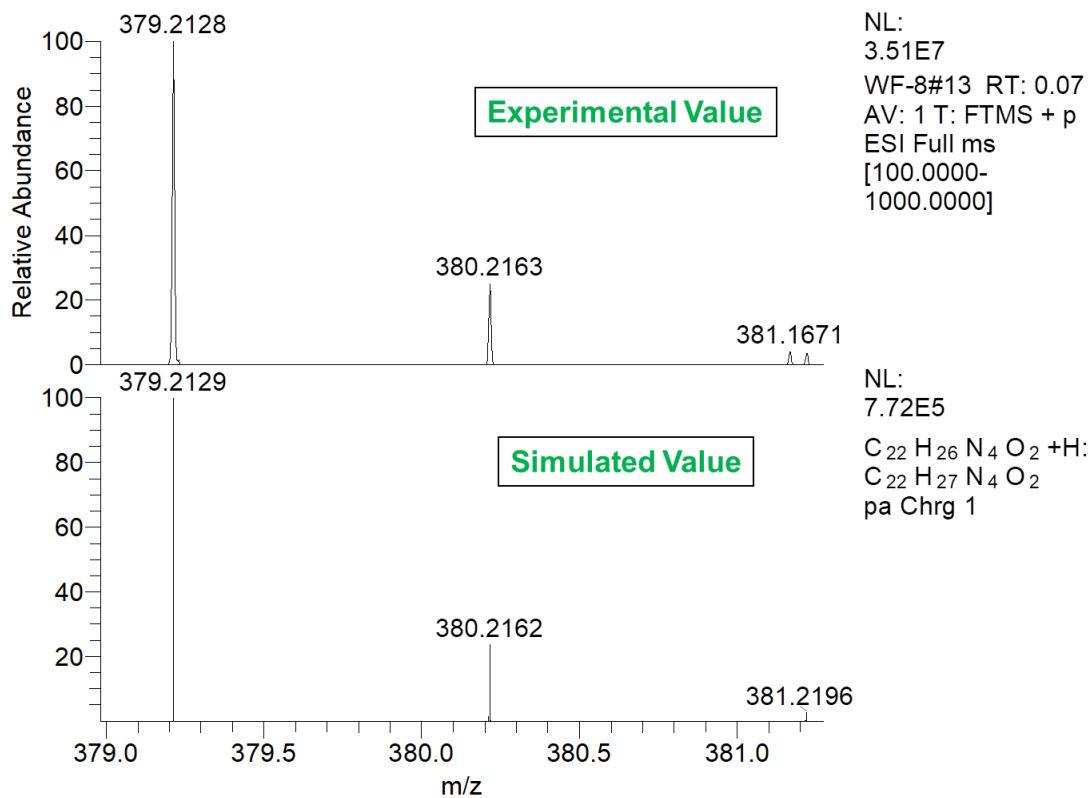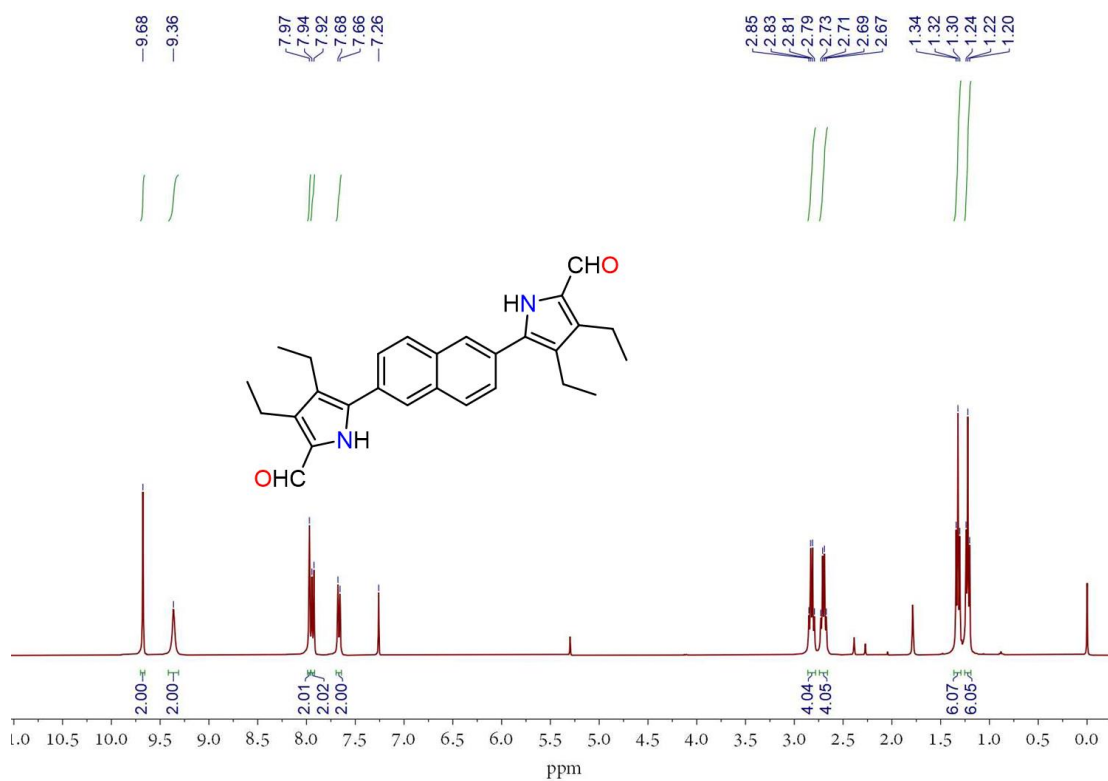
Figure S35. HRMS (ESI) spectrum of **3h**.
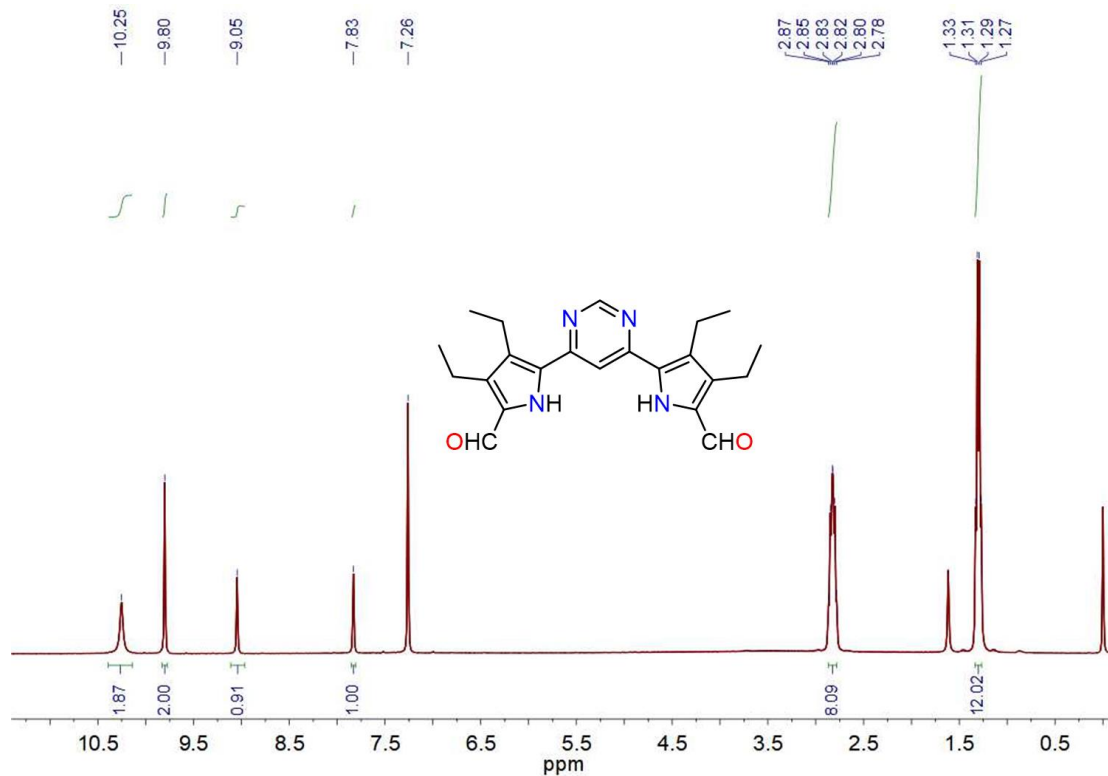
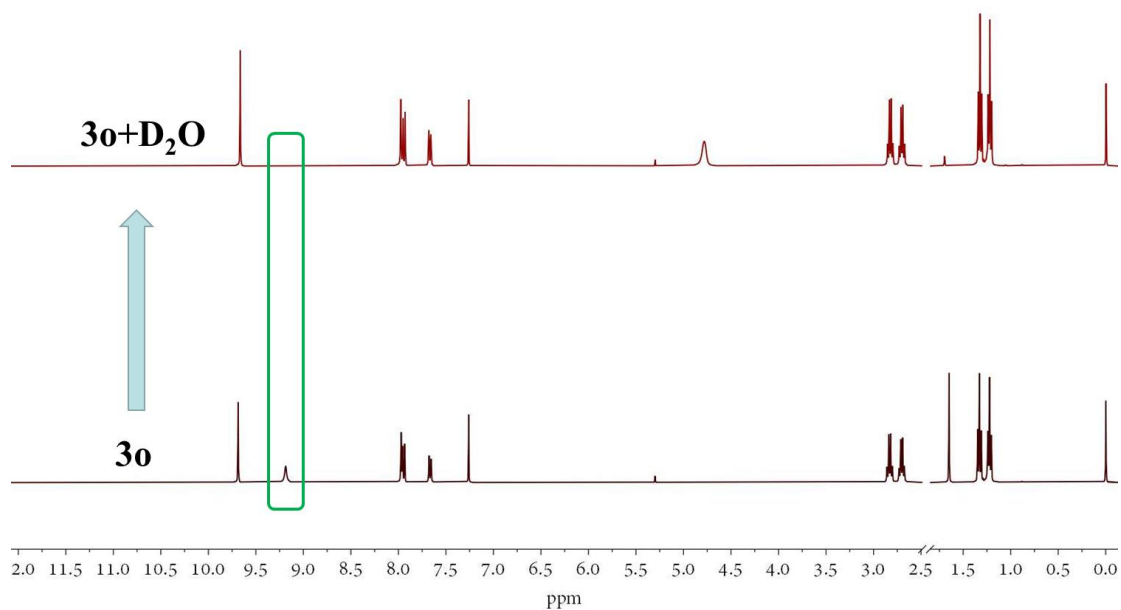**Figure S36.** ^{1}H NMR (400 MHz) spectrum of **3i** as recorded in CDCl$_3$.
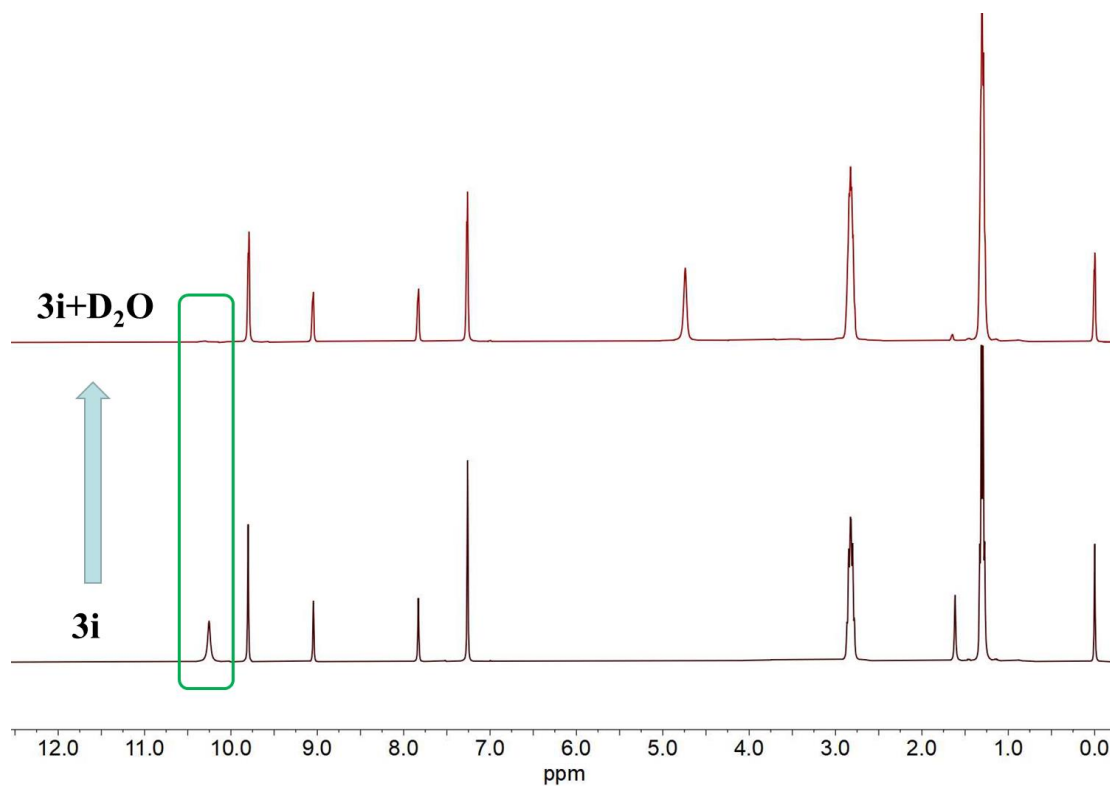
Figure S37. ^{1}H NMR (400 MHz) spectrum of **3i+D₂O** as recorded in CDCl₃.
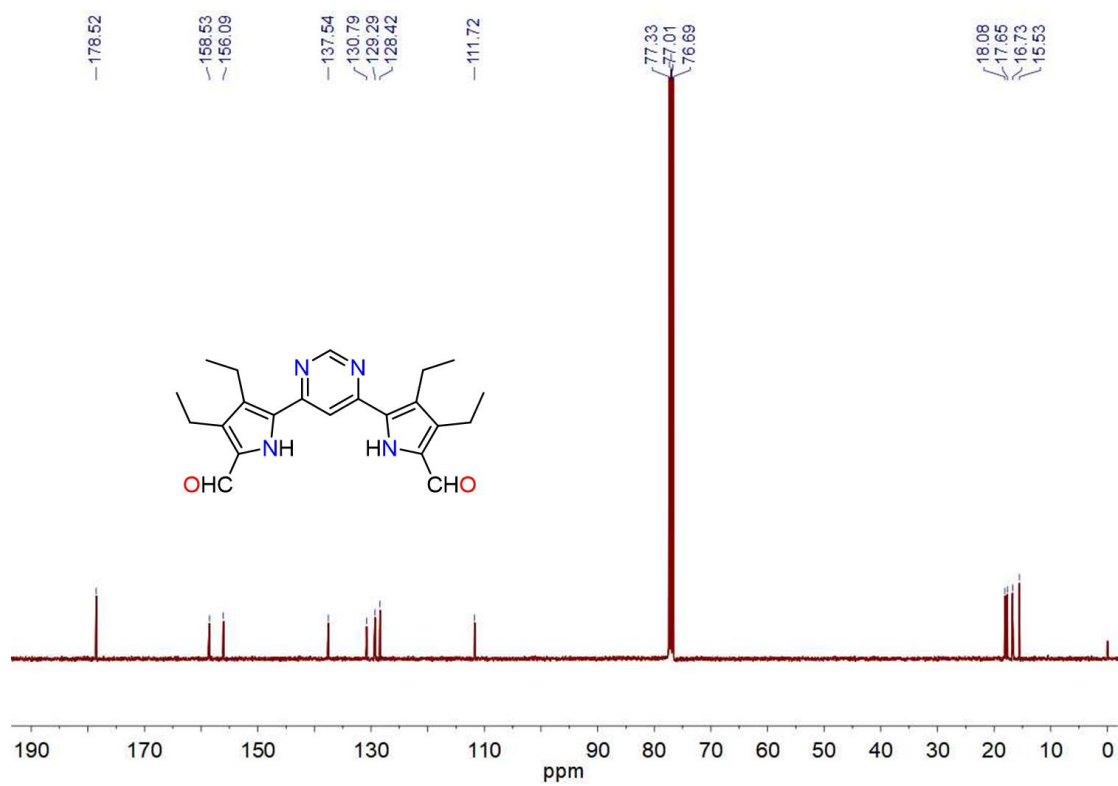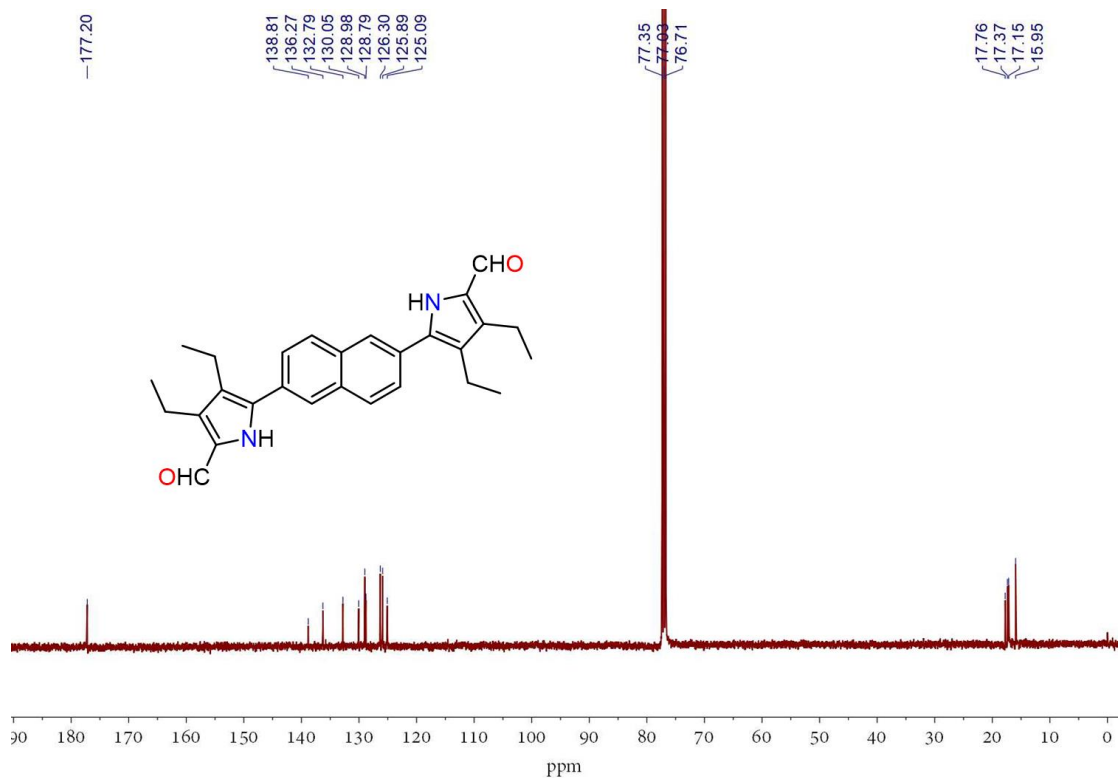

Figure S38. ^{13}C NMR (100 MHz) spectrum of **3i** as recorded in CDCl₃.

Figure S39. HRMS (ESI) spectrum of **3i**.
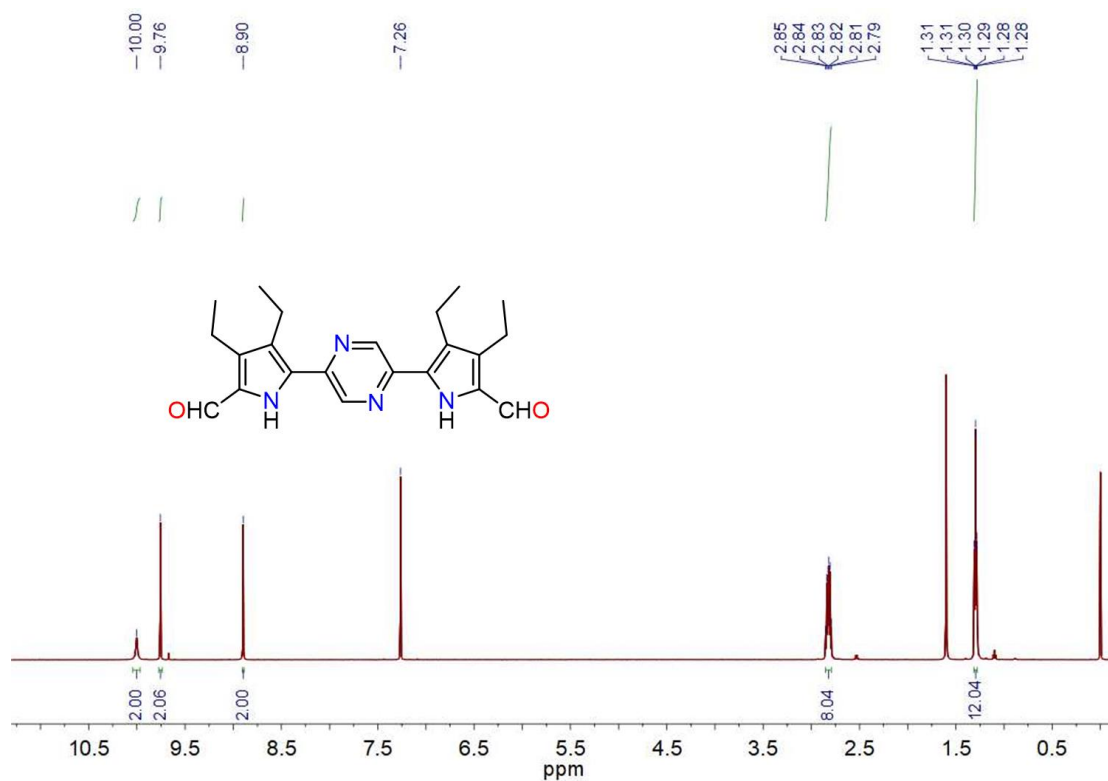
Figure S40. ^{1}H NMR (400 MHz) spectrum of **3j** as recorded in CDCl$_3$.
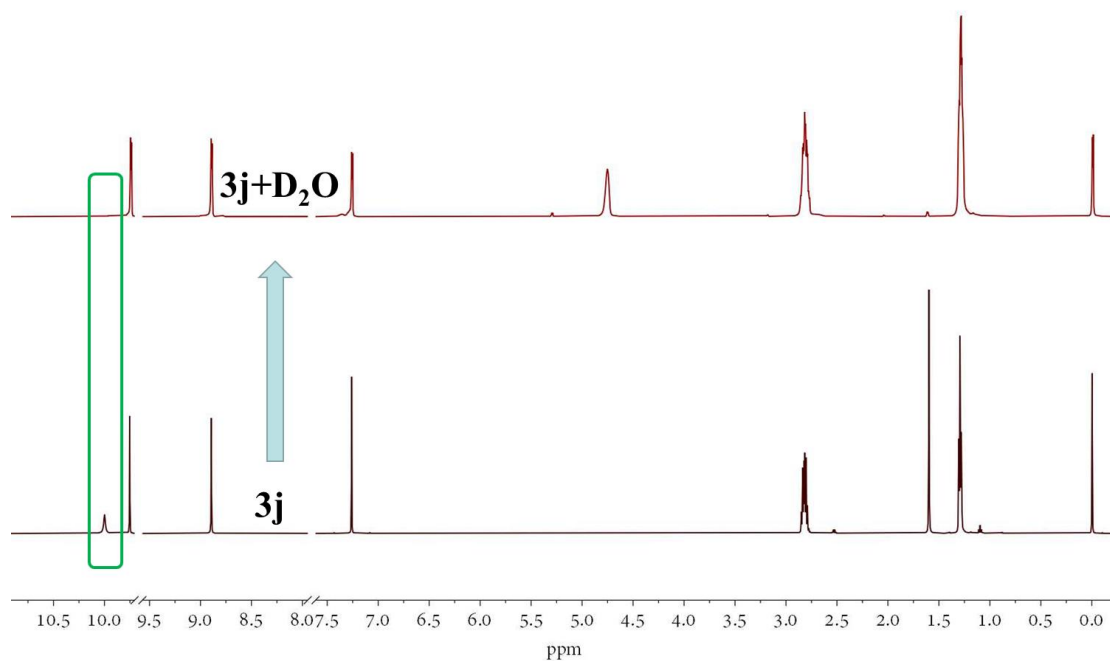
Figure S41. ^{1}H NMR (400 MHz) spectrum of **3j+D₂O** as recorded in CDCl₃.
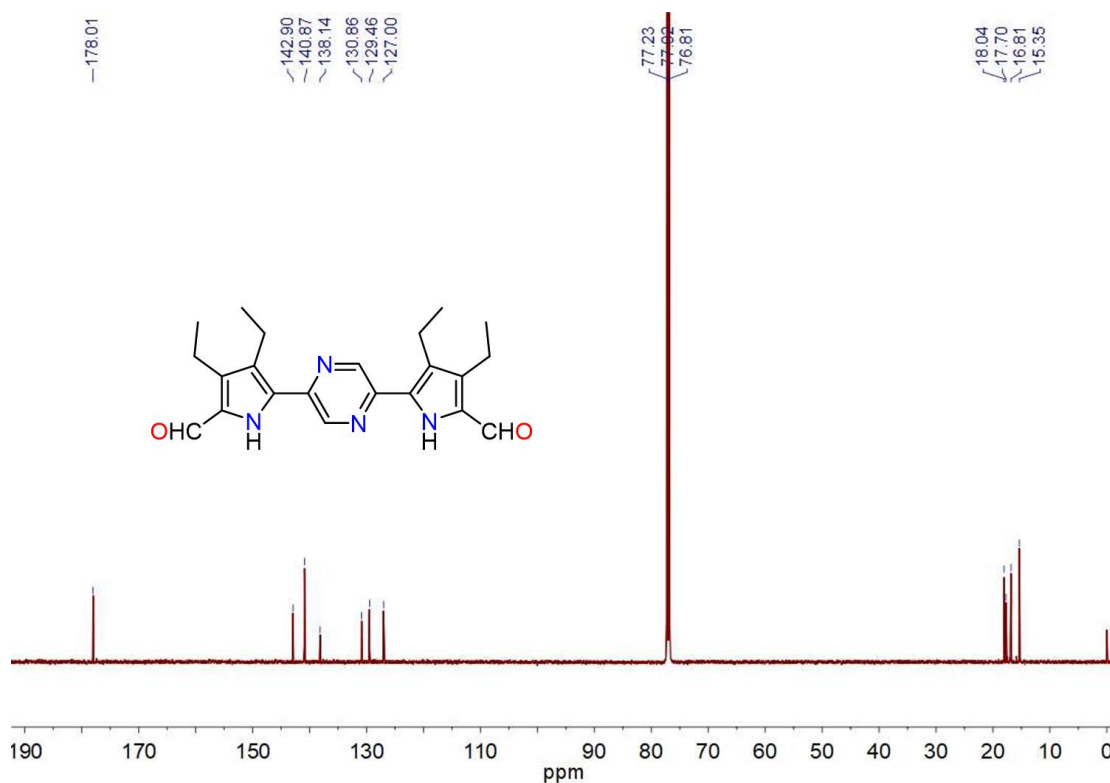
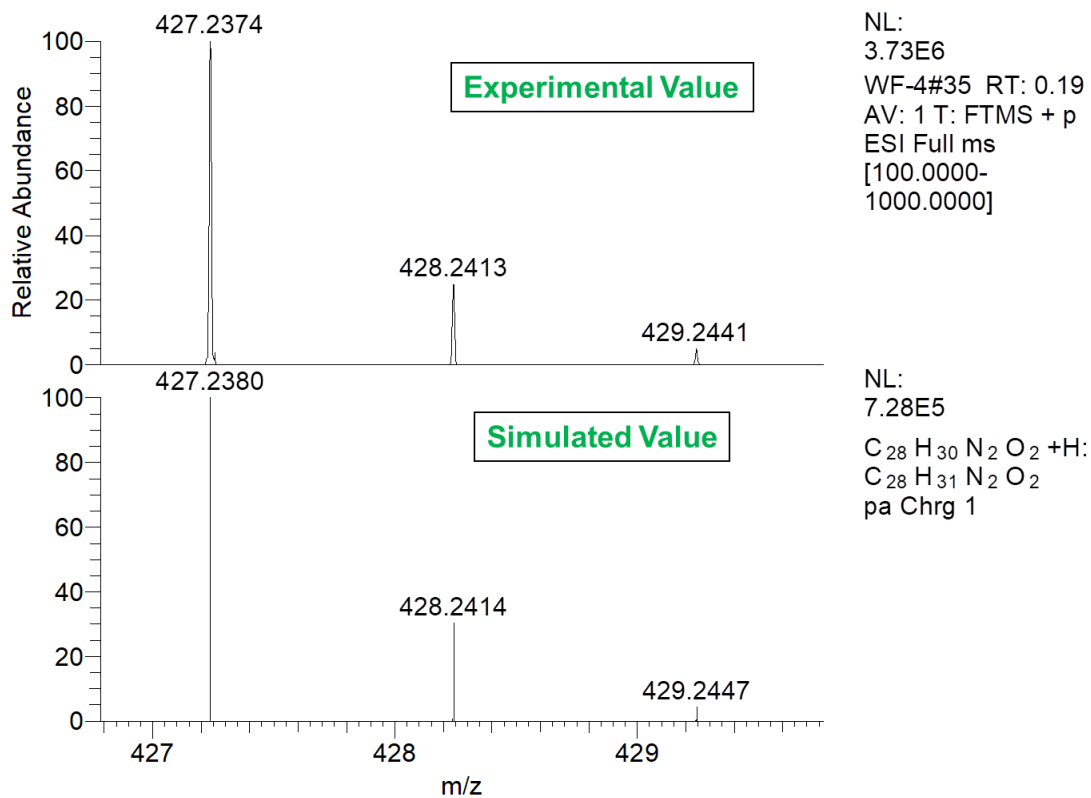**Figure S42.** ^{13}C NMR (100 MHz) spectrum of **3j** as recorded in CDCl₃.
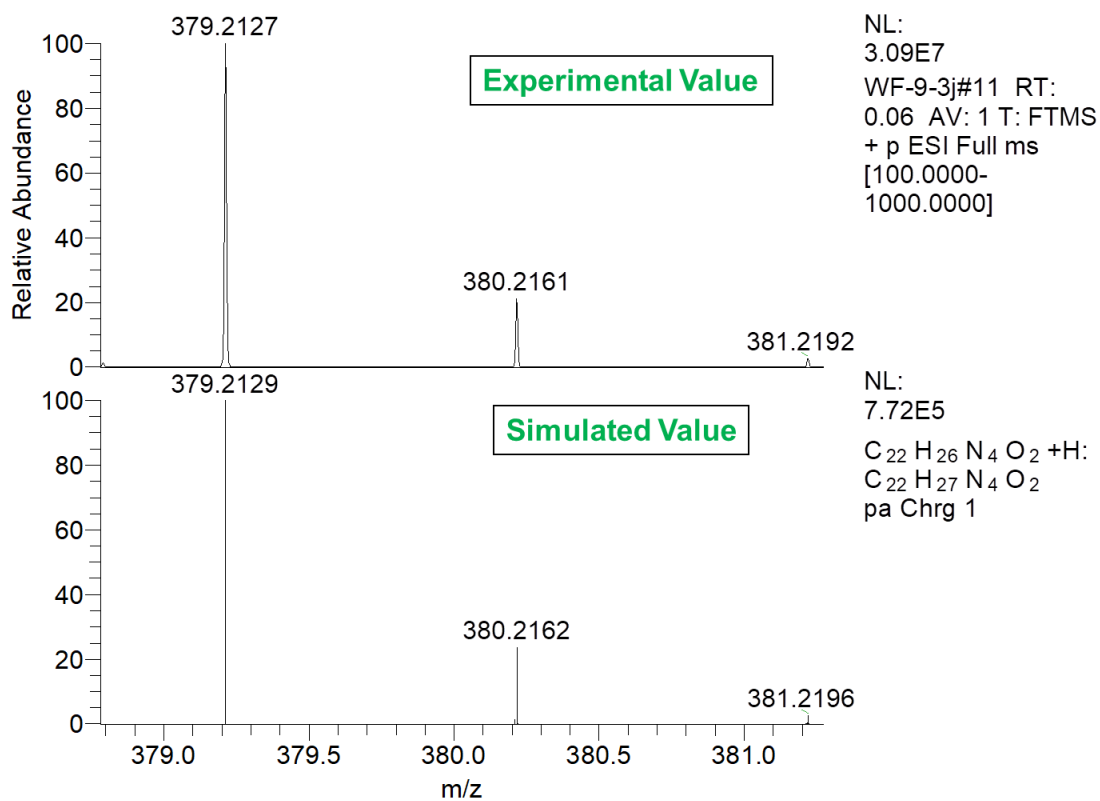
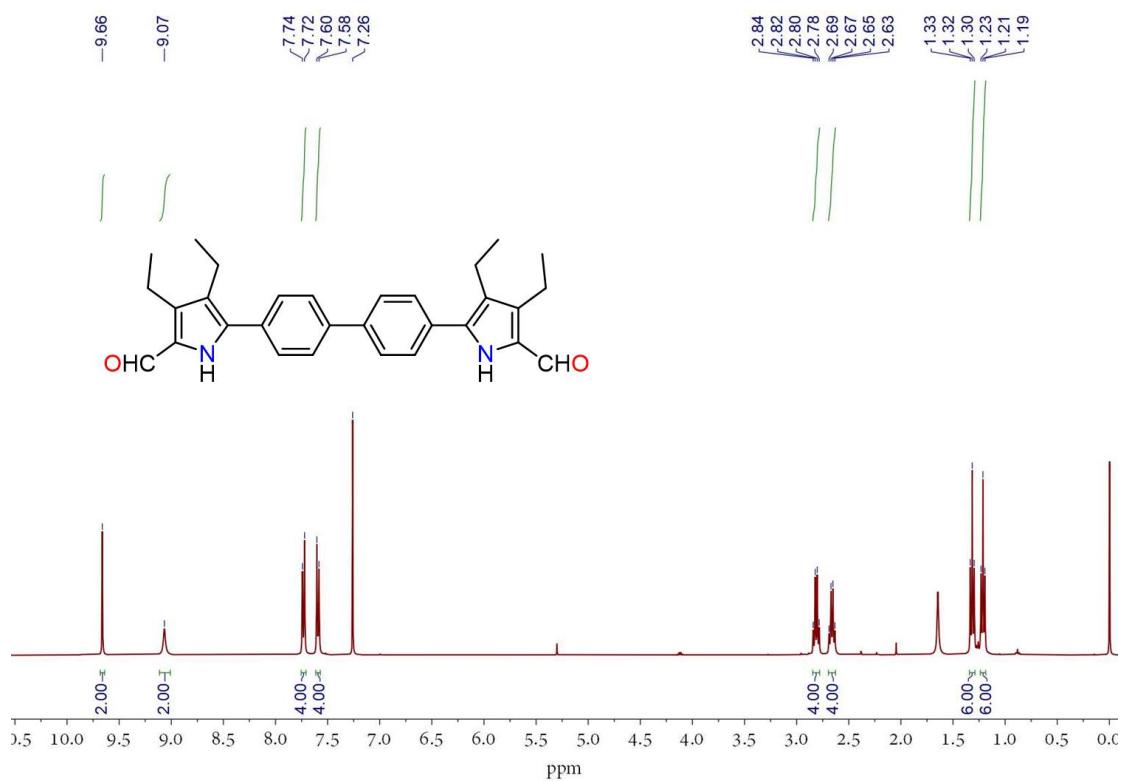**Figure S43.** HRMS (ESI) spectrum of **3j**.

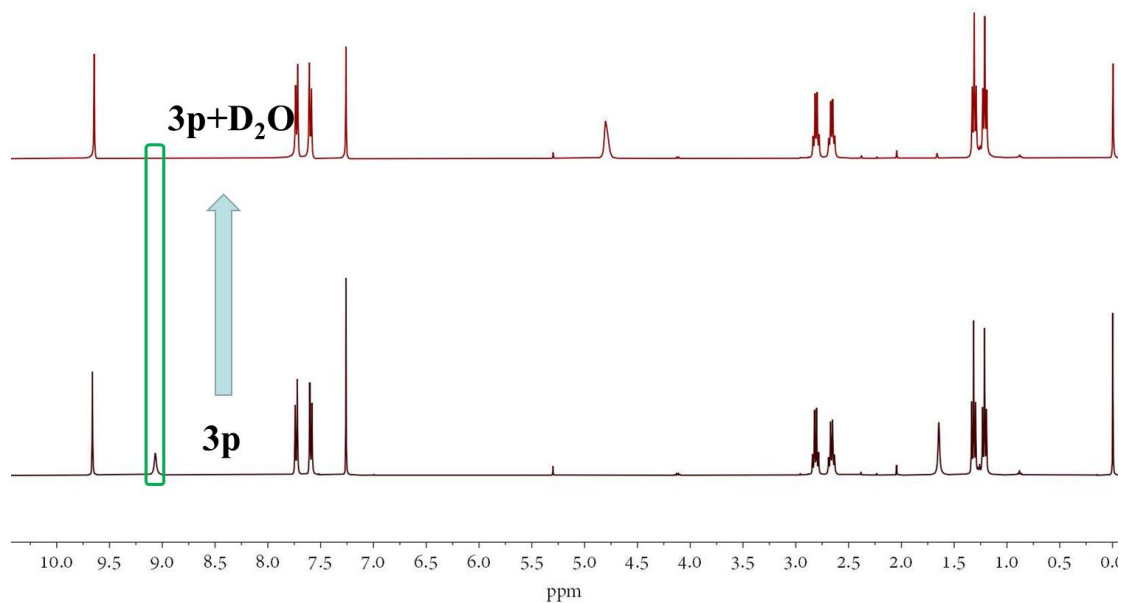**Figure S44.** ^{1}H NMR (400 MHz) spectrum of **3k** as recorded in CDCl$_3$.

Figure S45. ^{1}H NMR (400 MHz) spectrum of **3k+D$_2$O** as recorded in CDCl$_3$.
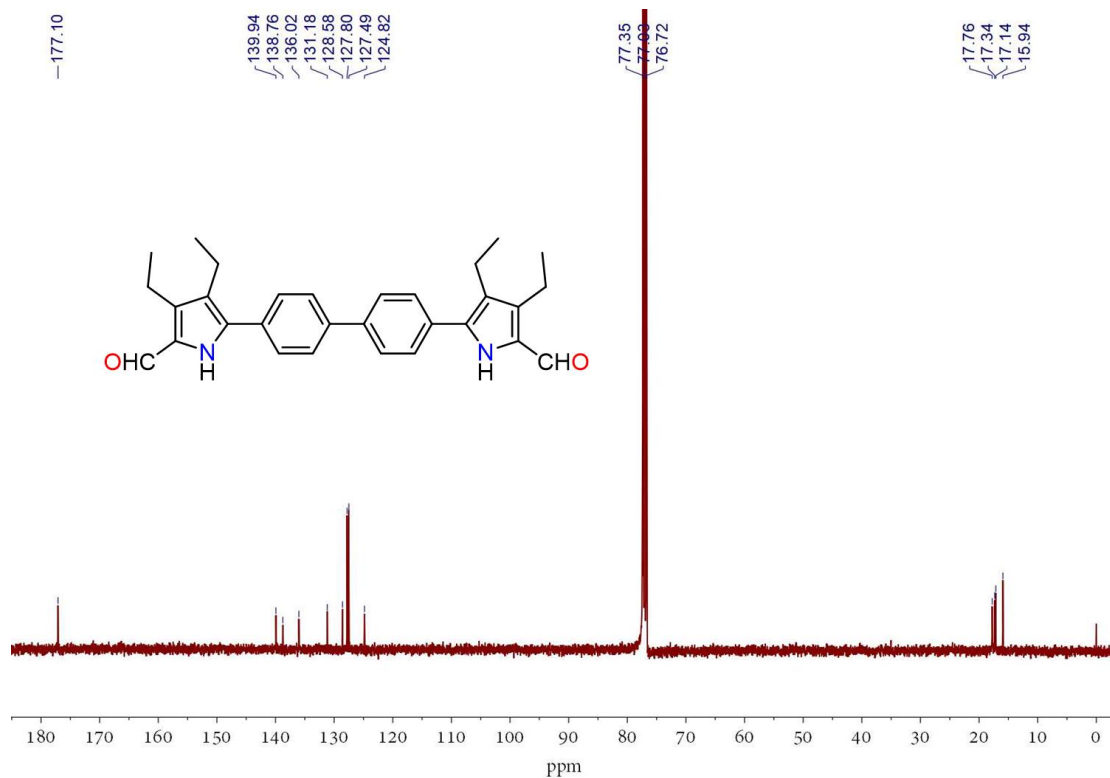

Figure S46. ^{13}C NMR (100 MHz) spectrum of **3k** as recorded in CDCl$_3$.

Figure S47. HRMS (ESI) spectrum of **3k**.

Figure S48. ^{1}H NMR (400 MHz) spectrum of **3l** as recorded in CDCl$_3$.

Figure S49. ^{1}H NMR (400 MHz) spectrum of **3l+D$_2$O** as recorded in CDCl$_3$.

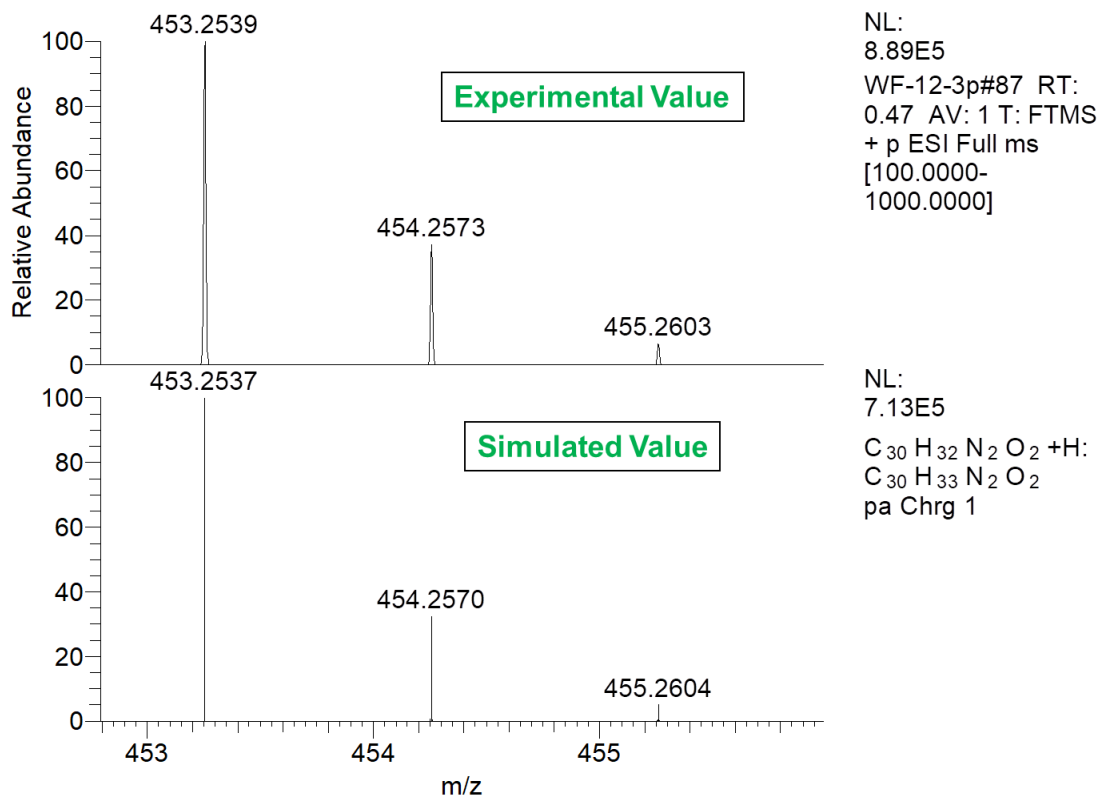**Figure S50.** ^{13}C NMR (100 MHz) spectrum of **3l** as recorded in CDCl$_3$.
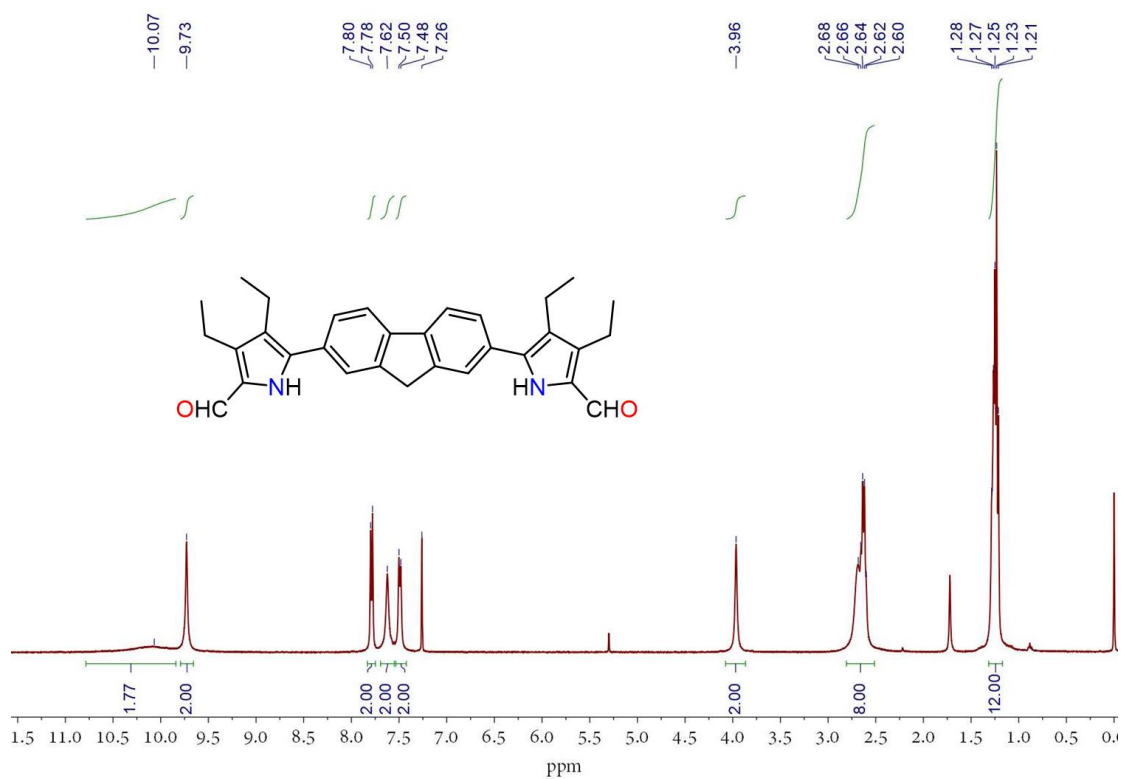
Figure S51. HRMS (ESI) spectrum of **3l**.

Figure S52. ^{1}H NMR (400 MHz) spectrum of **3m** as recorded in CDCl$_3$.

Figure S53. ^{1}H NMR (400 MHz) spectrum of **3m**+**D₂O** as recorded in CDCl₃.

Figure S54. ^{13}C NMR (100 MHz) spectrum of **3m** as recorded in CDCl₃.

Figure S55. HRMS (ESI) spectrum of **3m**.

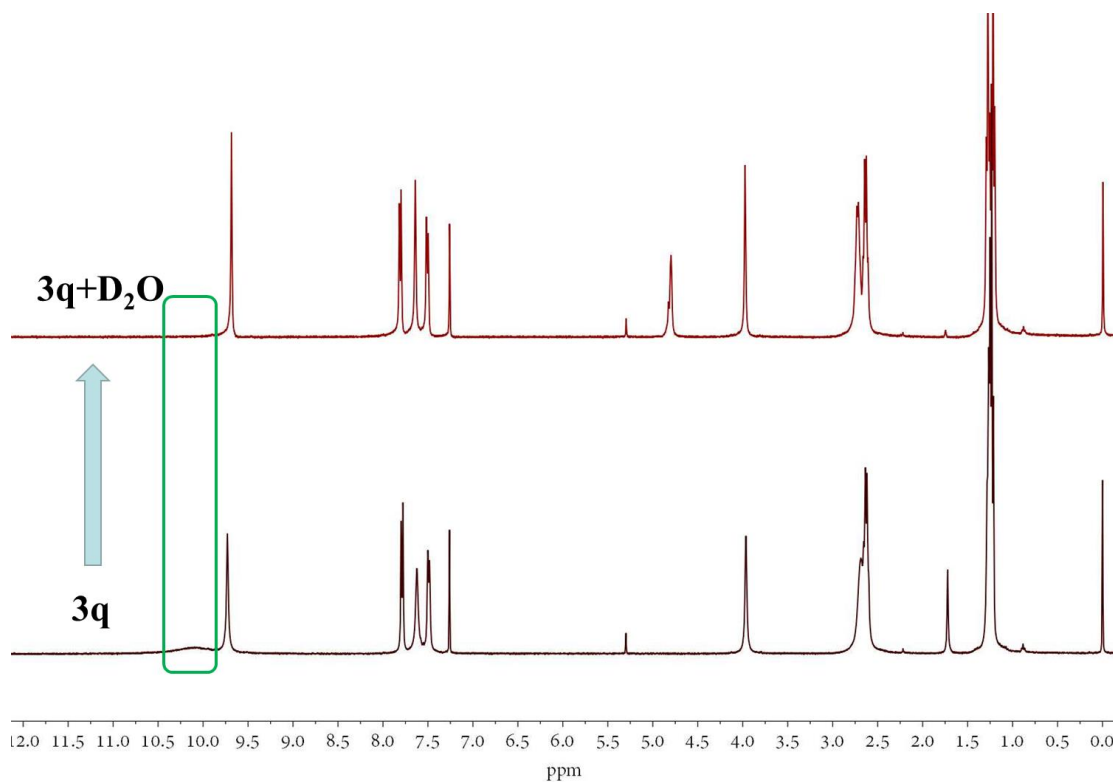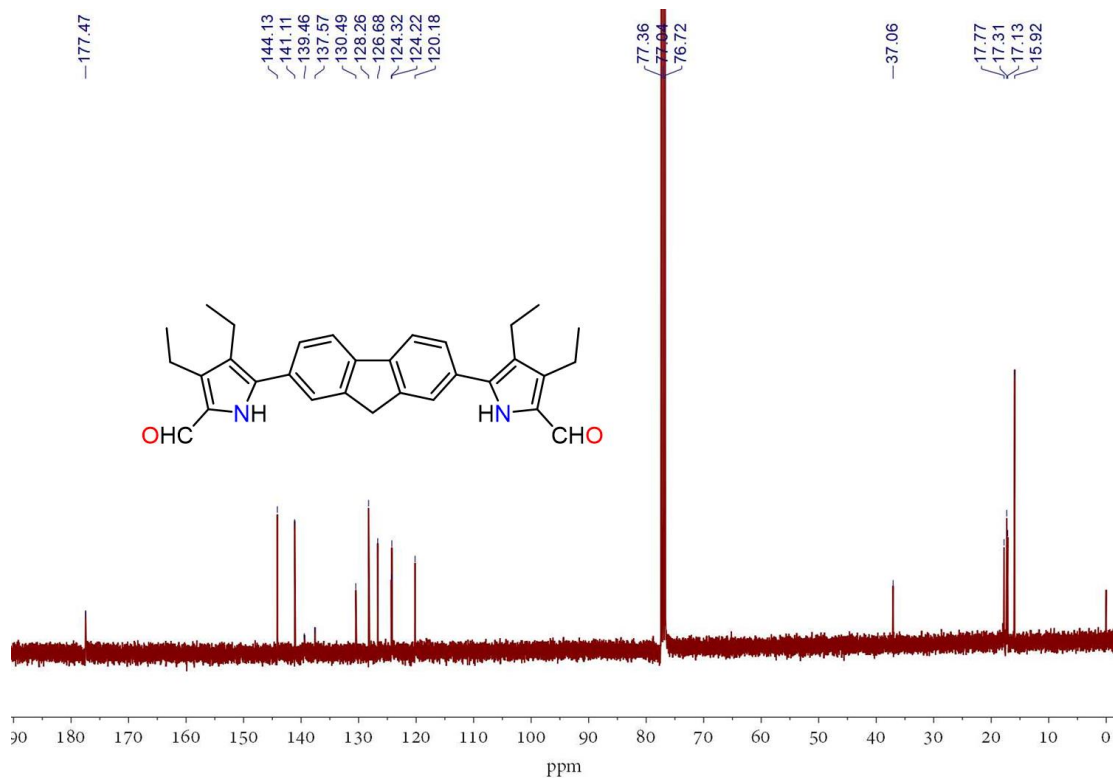**Figure S56.** ^{1}H NMR (400 MHz) spectrum of **3n** as recorded in CDCl$_3$.

Figure S57. ^{1}H NMR (400 MHz) spectrum of **3n**+**D$_2$O** as recorded in CDCl$_3$.

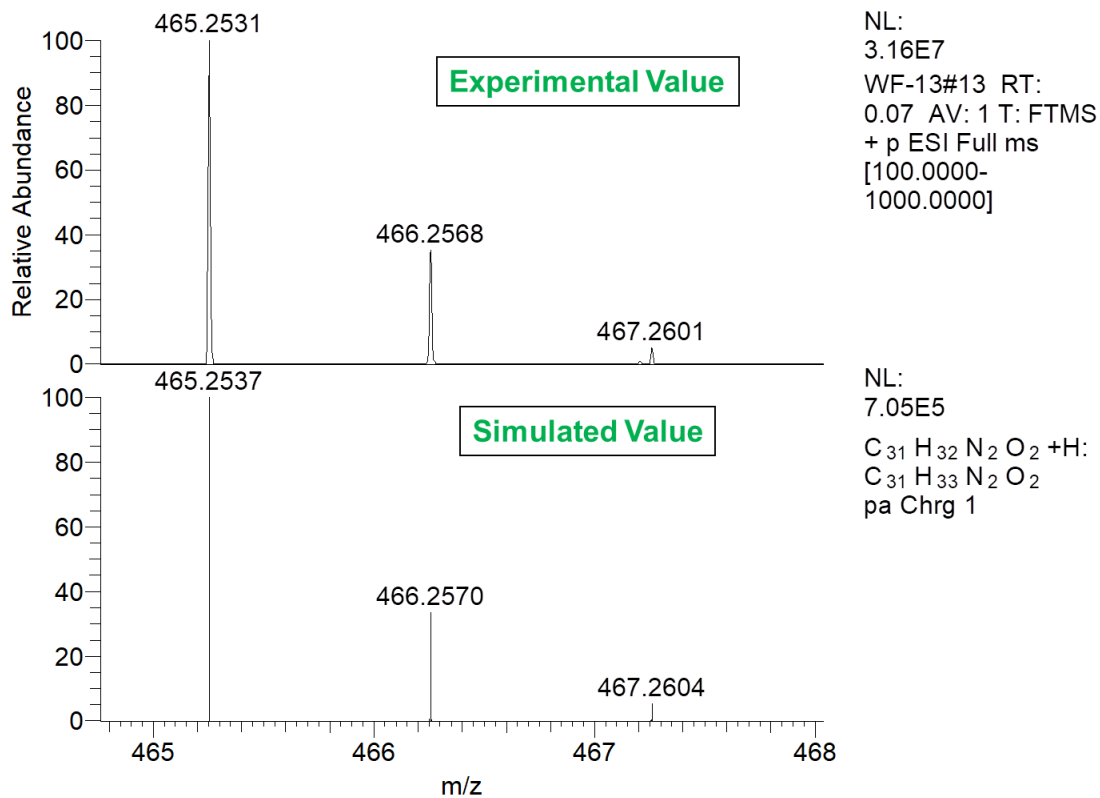**Figure S58.** ^{13}C NMR (100 MHz) spectrum of **3n** as recorded in CDCl$_3$.

Figure S59. HRMS (ESI) spectrum of **3n**.

Figure S60. ^{1}H NMR (400 MHz) spectrum of **3o** as recorded in CDCl$_3$.

Figure S61. ^{1}H NMR (400 MHz) spectrum of **3o+D$_2$O** as recorded in CDCl$_3$.

Figure S62. ^{13}C NMR (100 MHz) spectrum of **3o** as recorded in CDCl$_3$.

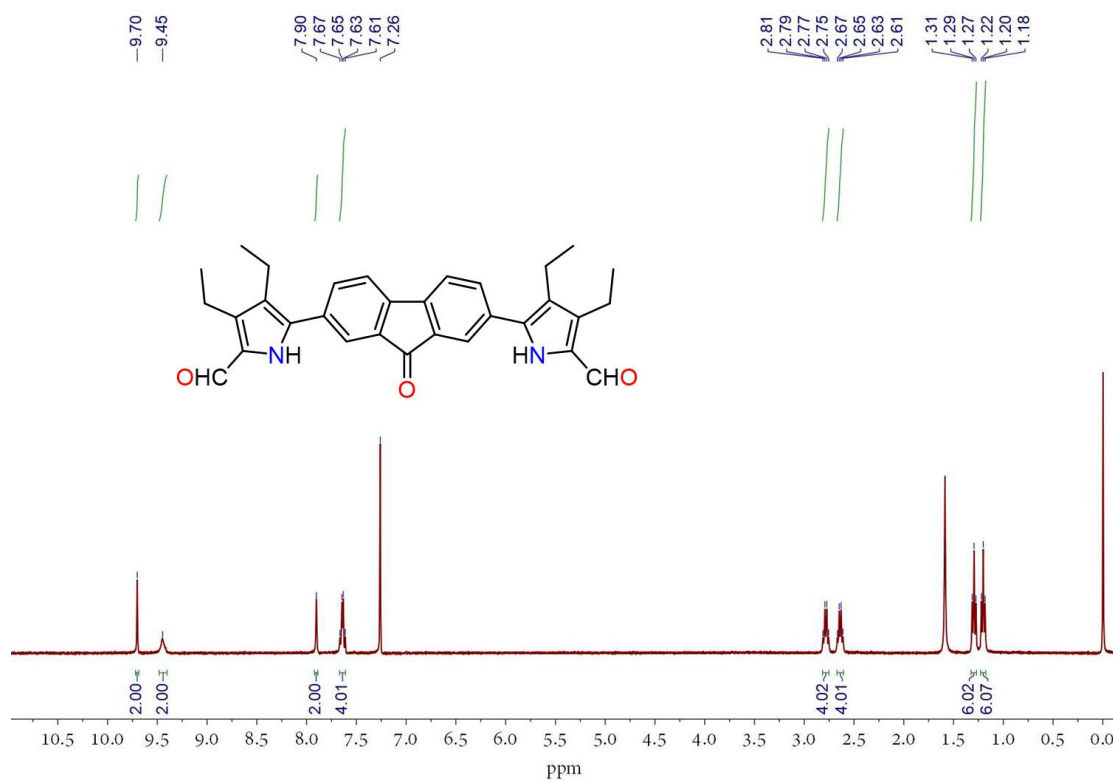**Figure S63.** HRMS (ESI) spectrum of **3o**.

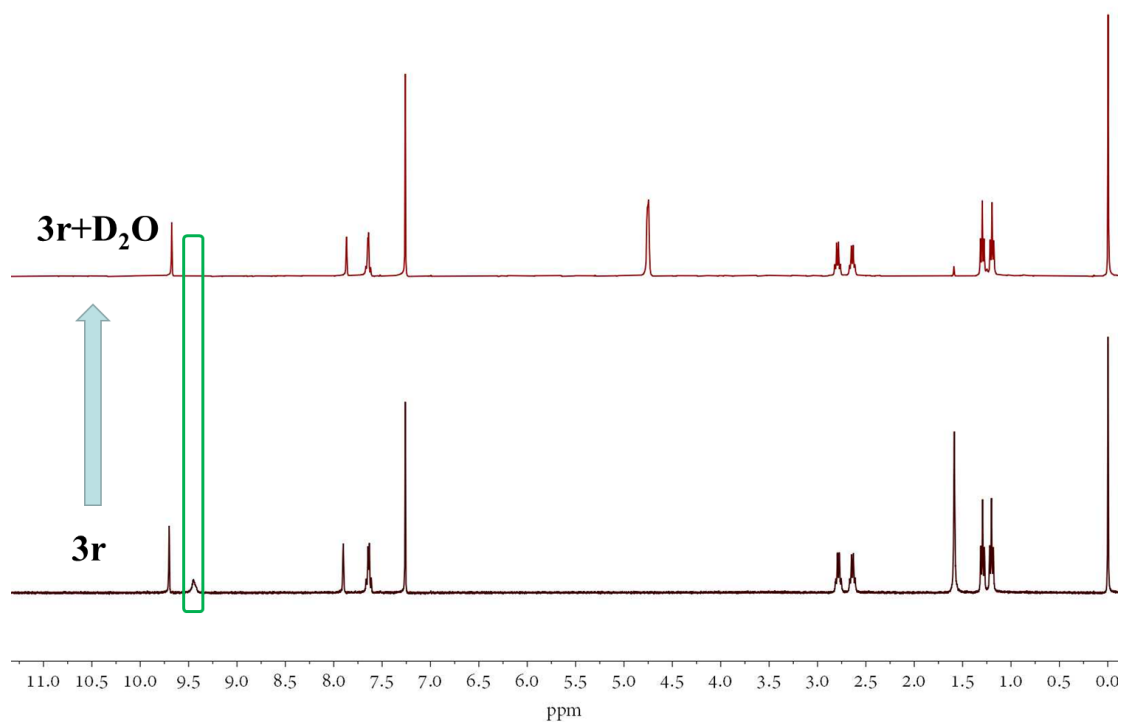**Figure S64.** ¹H NMR (400 MHz) spectrum of **3p** as recorded in CDCl₃.

Figure S65. ^{1}H NMR (400 MHz) spectrum of **3p**+**D₂O** as recorded in CDCl₃.
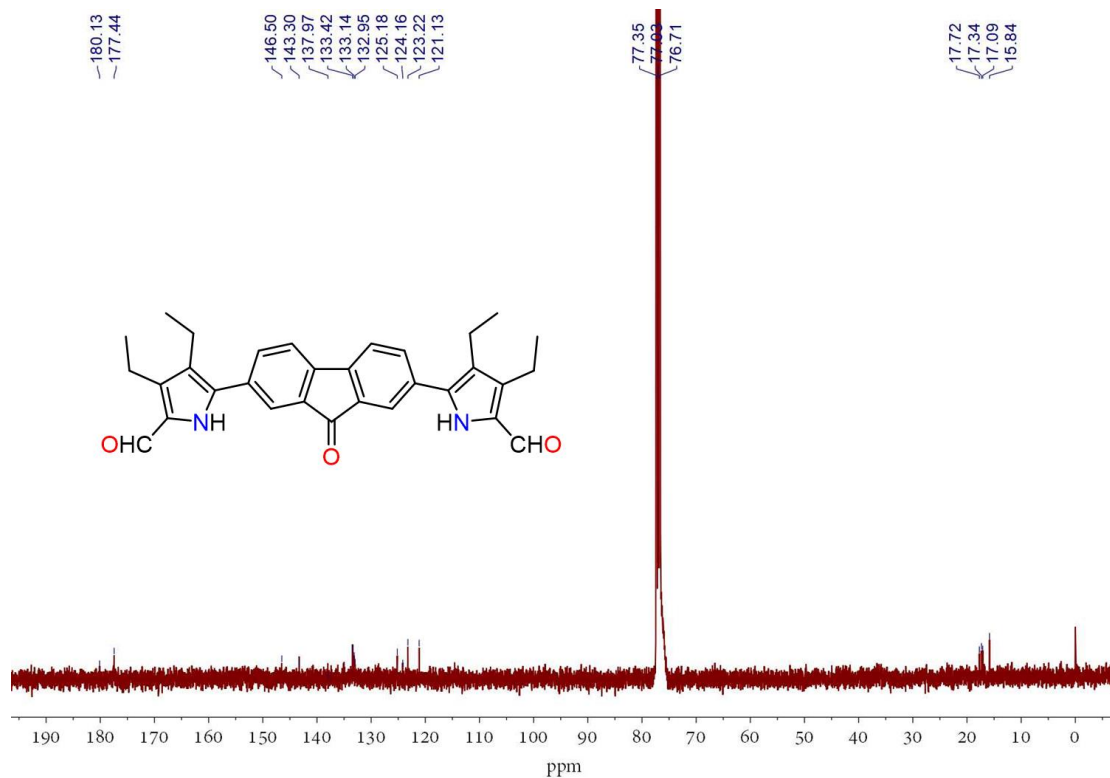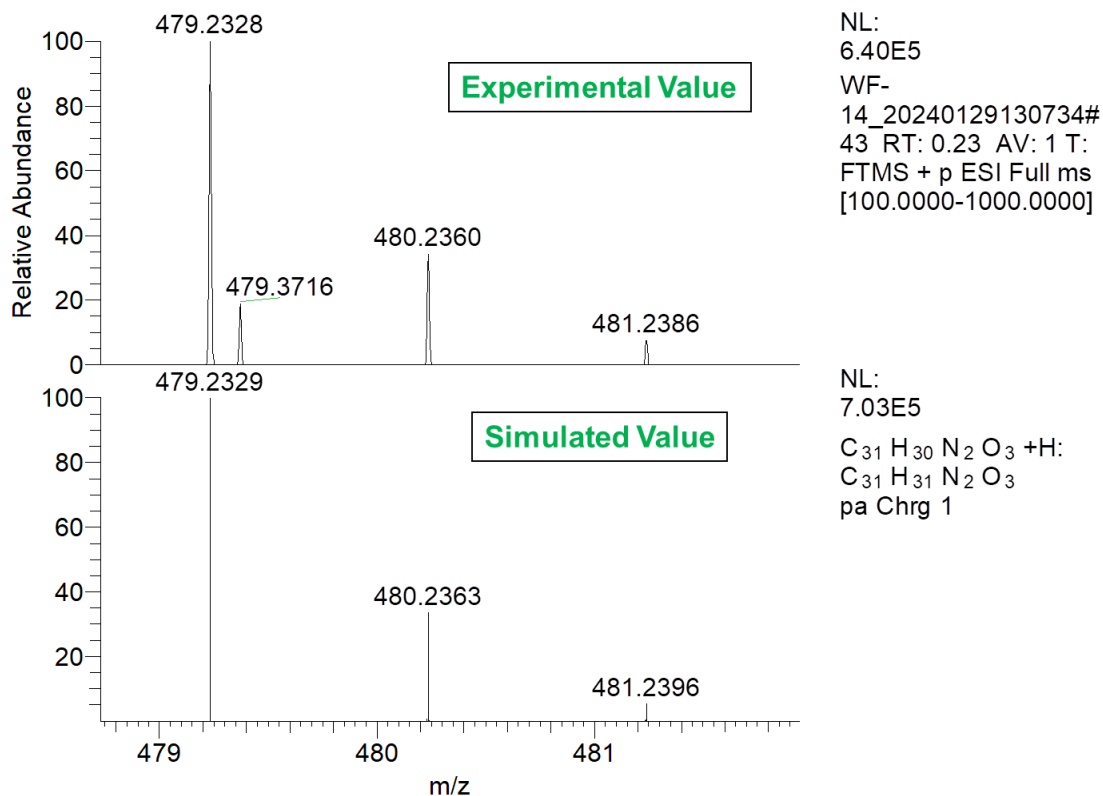

Figure S66. ^{13}C NMR (100 MHz) spectrum of **3p** as recorded in CDCl₃.

Figure S67. HRMS (ESI) spectrum of **3p**.

Figure S68. ^{1}H NMR (400 MHz) spectrum of **3q** as recorded in CDCl$_3$.

Figure S69. ^{1}H NMR (400 MHz) spectrum of **3q**+**D$_2$O** as recorded in CDCl$_3$.

Figure S70. ^{13}C NMR (100 MHz) spectrum of **3q** as recorded in CDCl$_3$.

Figure S71. HRMS (ESI) spectrum of **3q**.

Figure S72. ^{1}H NMR (400 MHz) spectrum of **3r** as recorded in CDCl$_3$.

Figure S73. ^{1}H NMR (400 MHz) spectrum of **3r**+**D₂O** as recorded in CDCl₃.

Figure S74. ^{13}C NMR (100 MHz) spectrum of **3r** as recorded in CDCl₃.
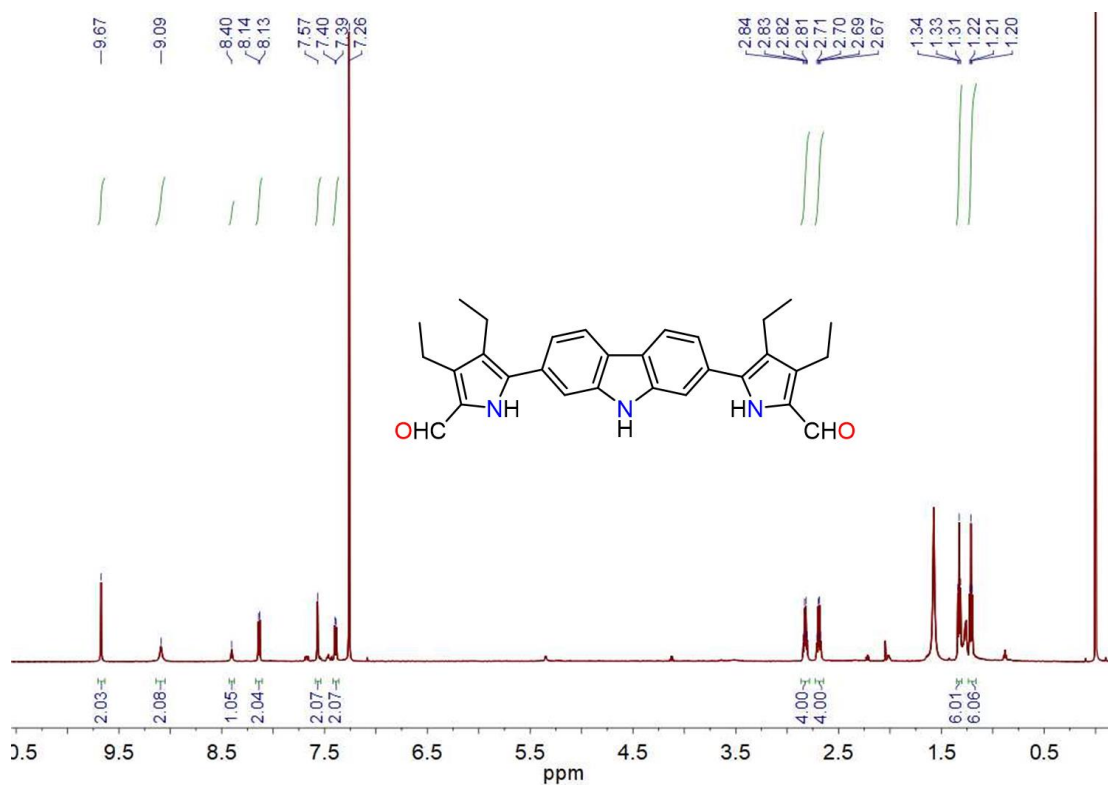
Figure S75. HRMS (ESI) spectrum of **3r**.

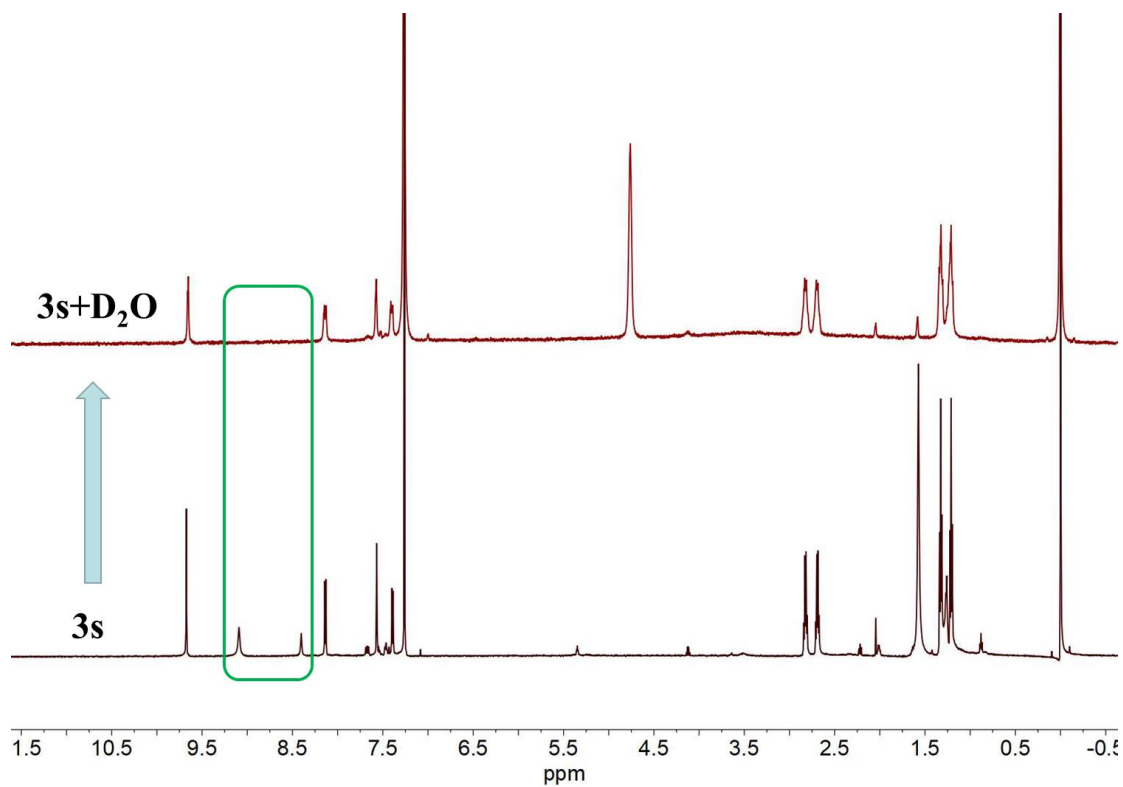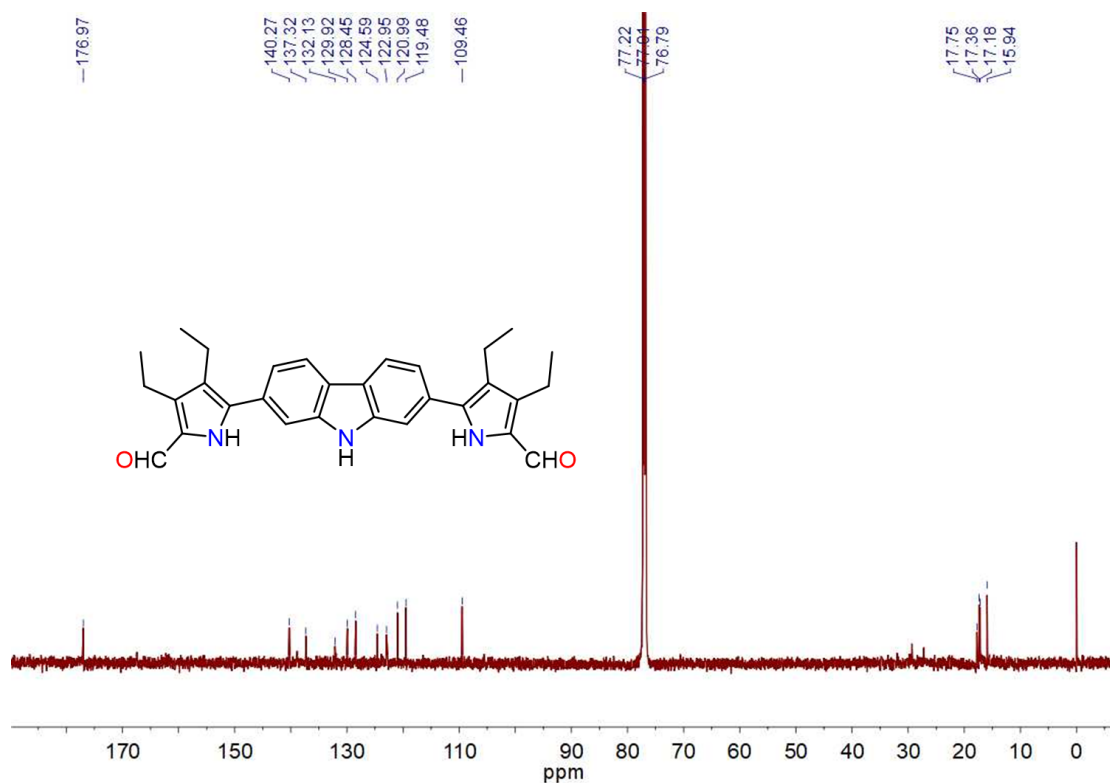**igure S76.** ^{1}H NMR (400 MHz) spectrum of **3s** as recorded in CDCl$_3$.

Figure S77. ^{1}H NMR (400 MHz) spectrum of **3s**+**D$_2$O** as recorded in CDCl$_3$.

Figure S78. ^{13}C NMR (100 MHz) spectrum of **3s** as recorded in CDCl$_3$.
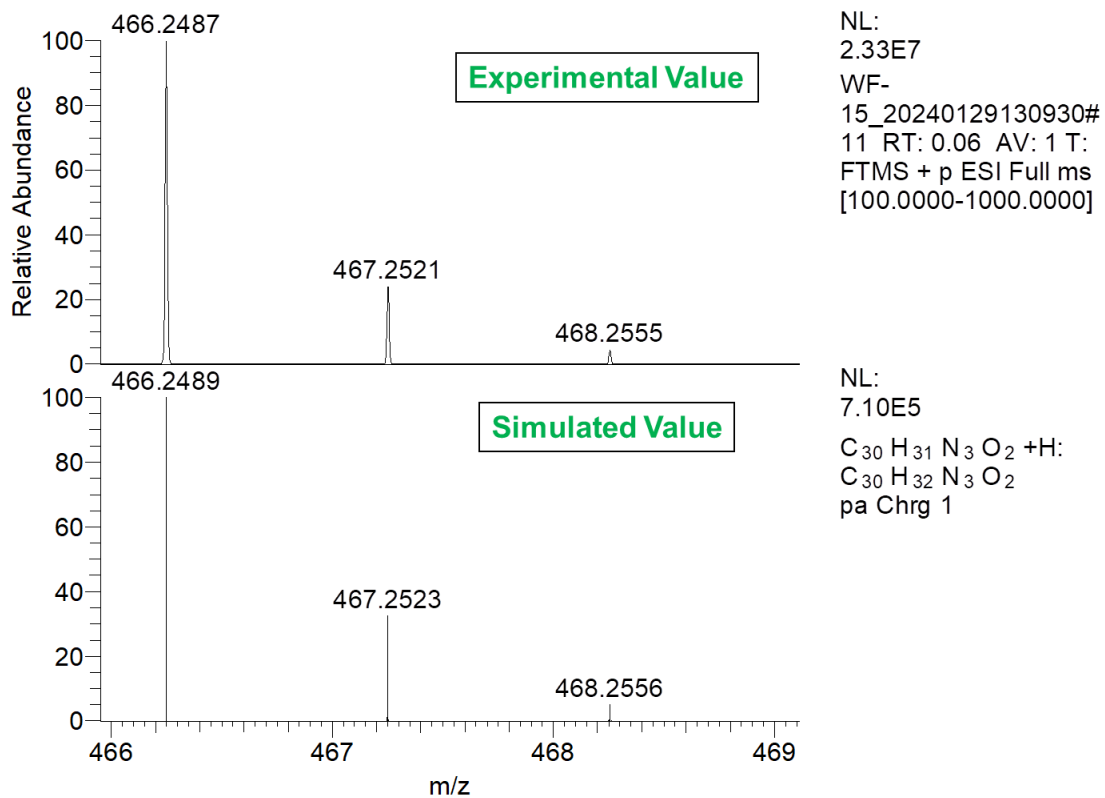
Figure S79. HRMS (ESI) spectrum of **3s**.
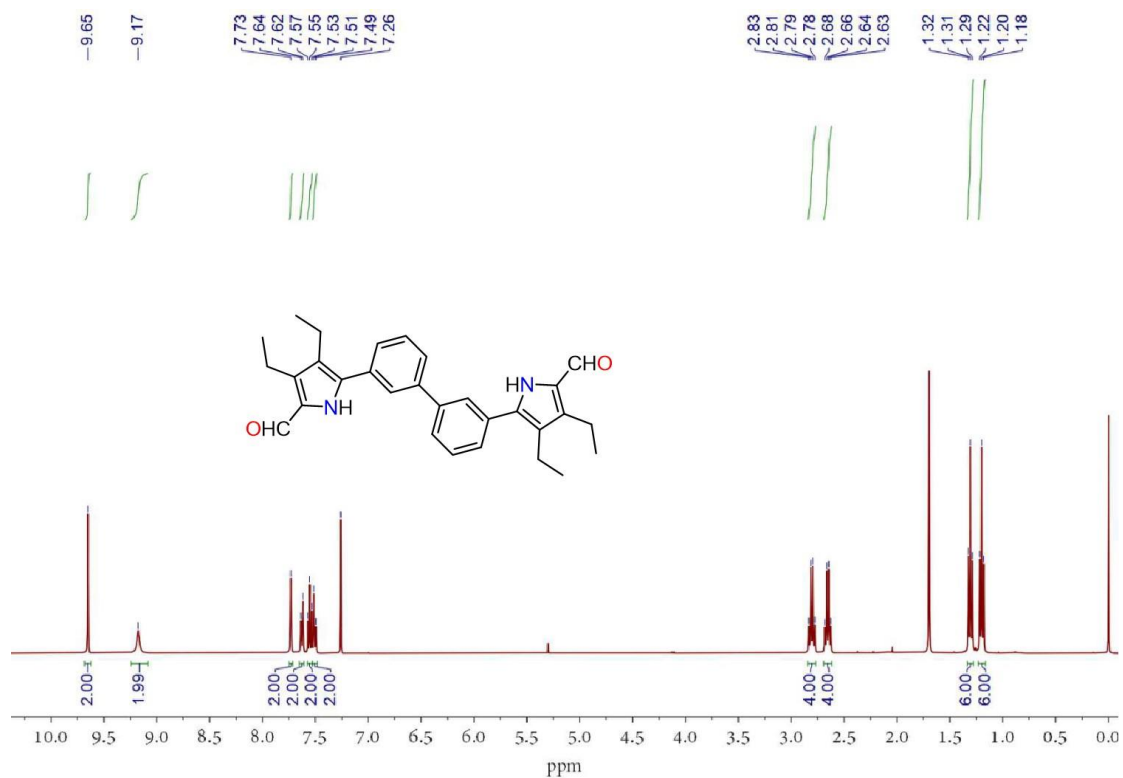
Figure S80. ^{1}H NMR (400 MHz) spectrum of **3t** as recorded in CDCl$_3$.

Figure S81. ^{1}H NMR (400 MHz) spectrum of **3t**+**D₂O** as recorded in CDCl₃.

Figure S82. ^{13}C NMR (100 MHz) spectrum of **3t** as recorded in CDCl₃.

Figure S83. HRMS (ESI) spectrum of **3t**.

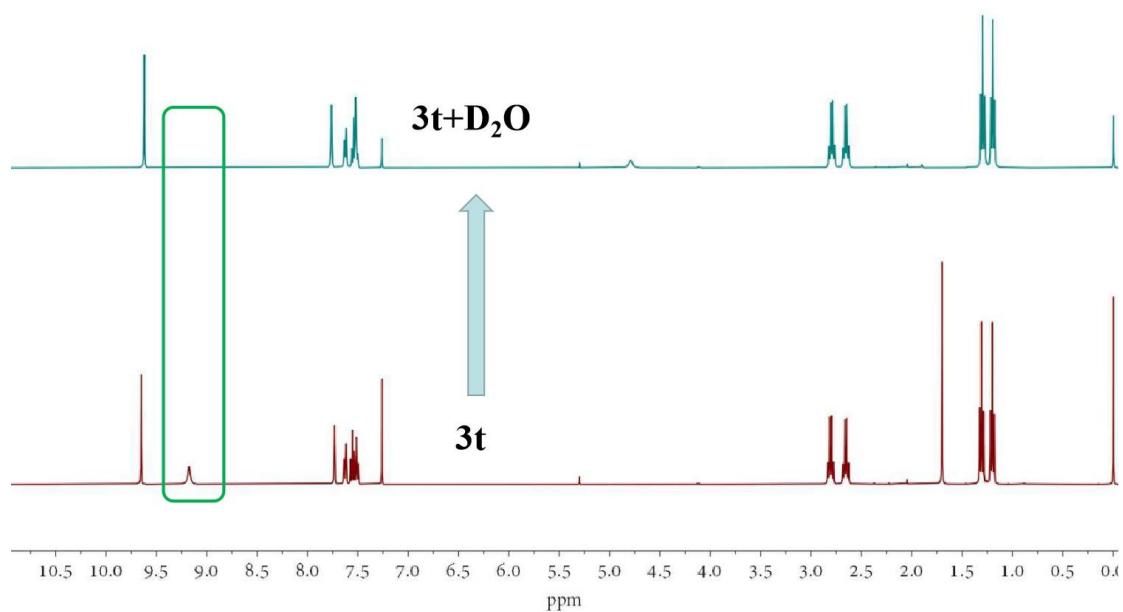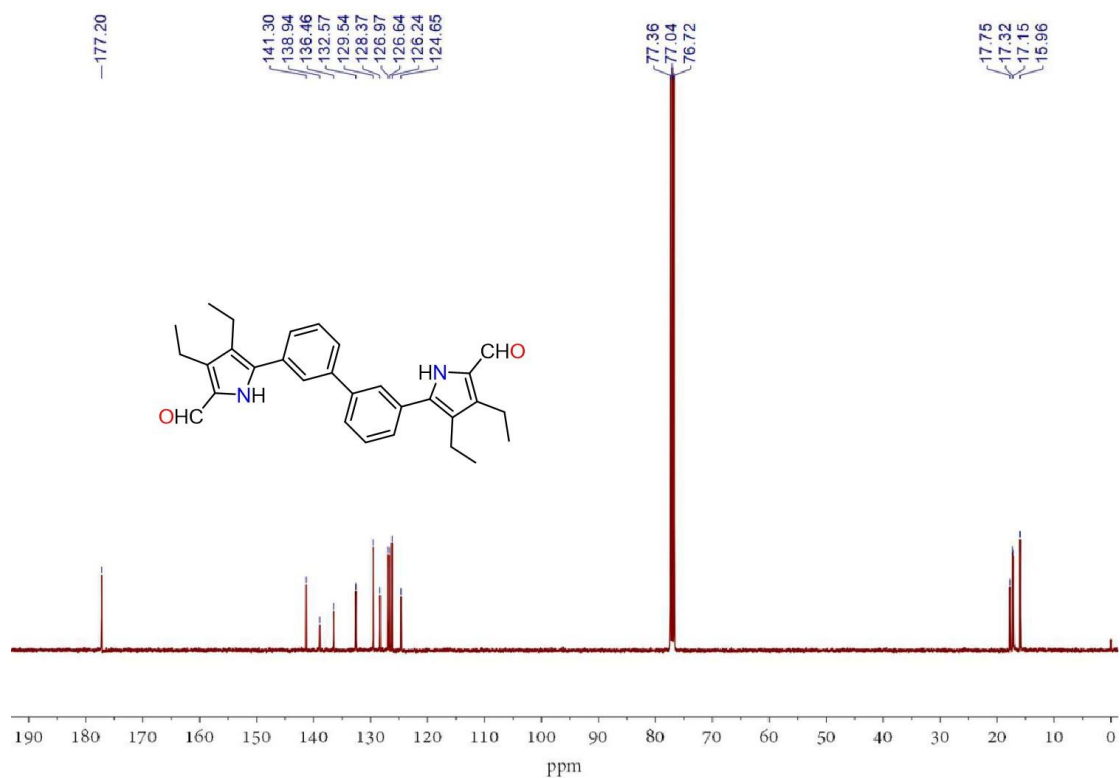**Figure S84.** ^{1}H NMR (400 MHz) spectrum of **3u** as recorded in CDCl$_3$.

Figure S85. ^{1}H NMR (400 MHz) spectrum of **3u**+**D$_2$O** as recorded in CDCl$_3$.

Figure S86. ^{13}C NMR (100 MHz) spectrum of **3u** as recorded in CDCl$_3$.
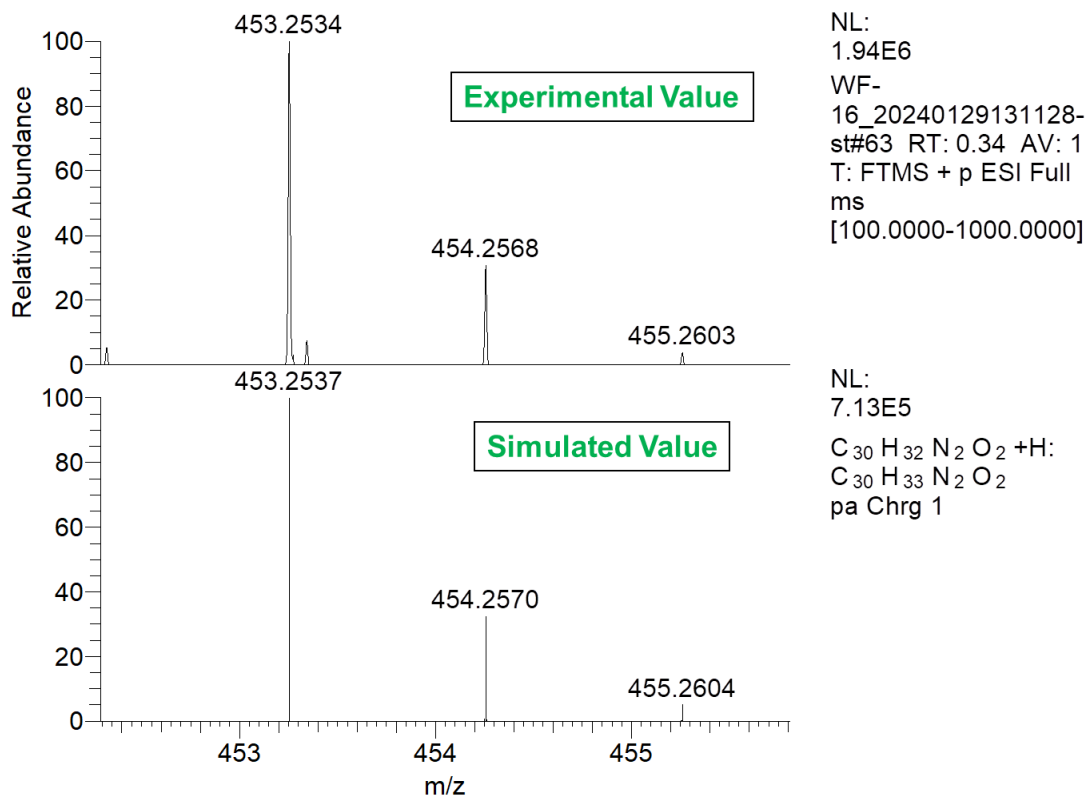
Figure S87. HRMS (ESI) spectrum of **3u**.

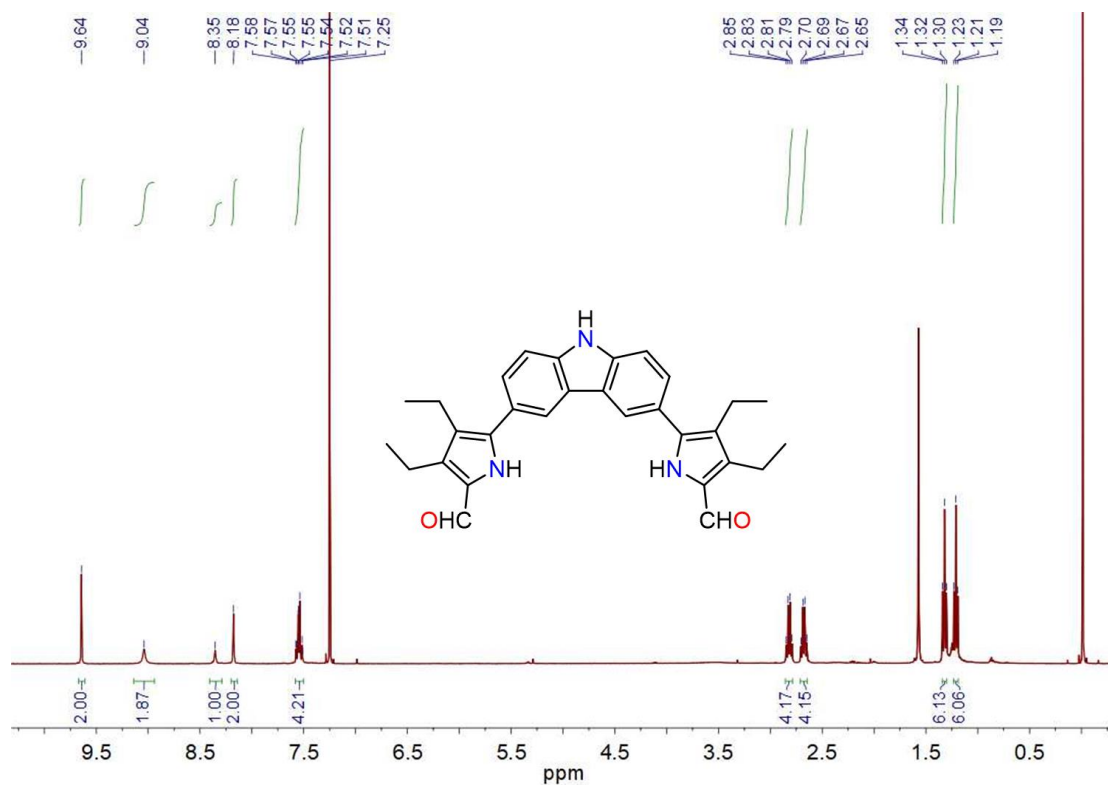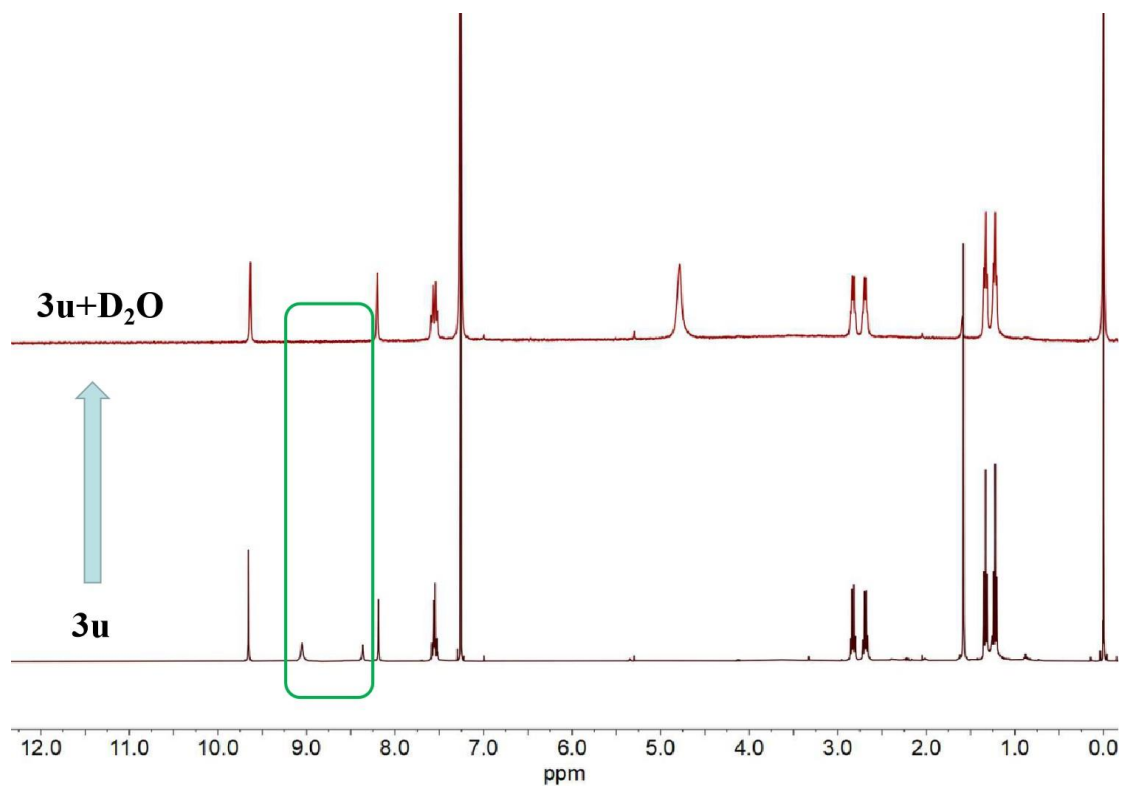**Figure S88.** ^{1}H NMR (400 MHz) spectrum of **3v** as recorded in CDCl$_3$.

Figure S89. ¹H NMR (400 MHz) spectrum of **3v+D₂O** as recorded in CDCl₃.

Figure S90. ¹³C NMR (100 MHz) spectrum of **3v** as recorded in CDCl₃.

Figure S91. HRMS (ESI) spectrum of **3v**.

Figure S92. ^{1}H NMR (400 MHz) spectrum of **3w** as recorded in CDCl$_3$.

Figure S93. ^{1}H NMR (400 MHz) spectrum of **3w+D₂O** as recorded in CDCl₃.
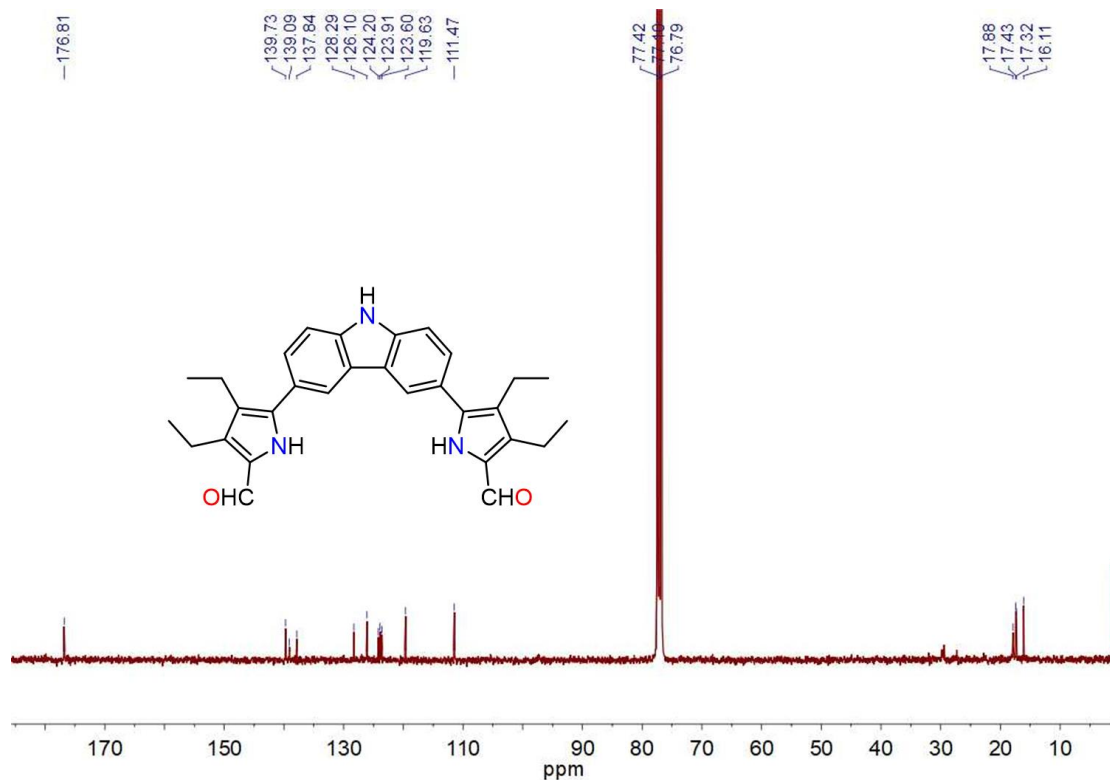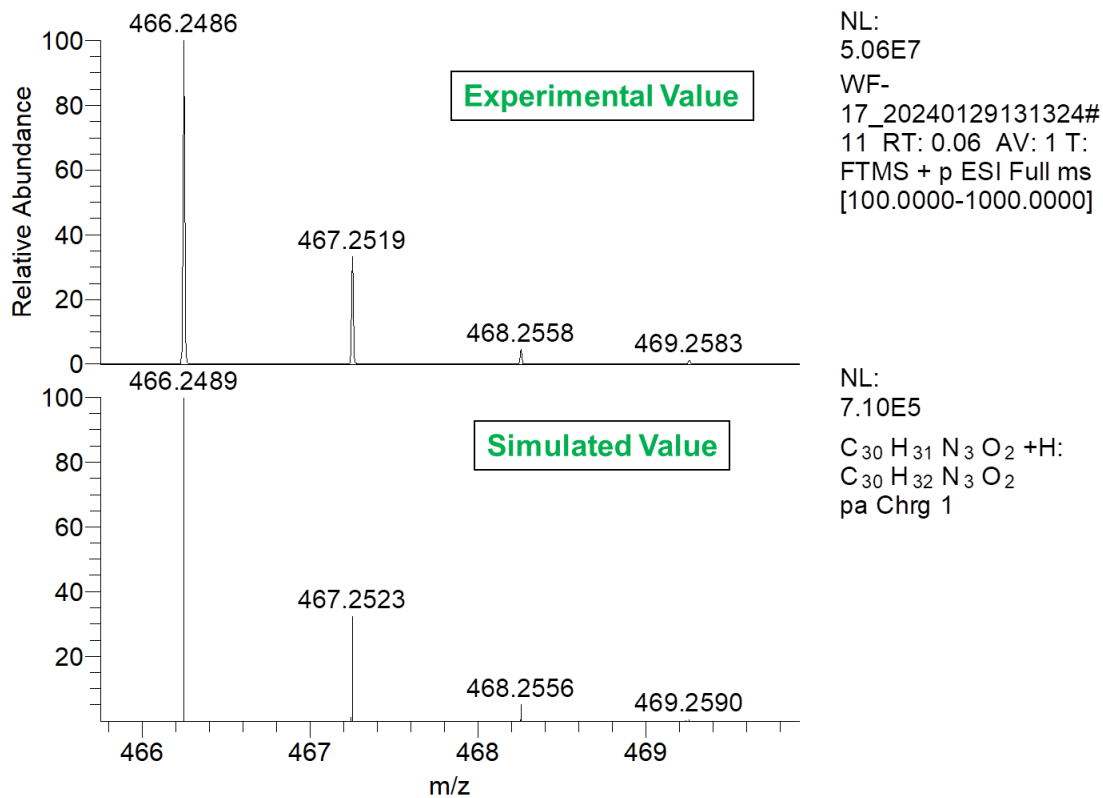

Figure S94. ^{13}C NMR (100 MHz) spectrum of **3w** as recorded in CDCl₃.
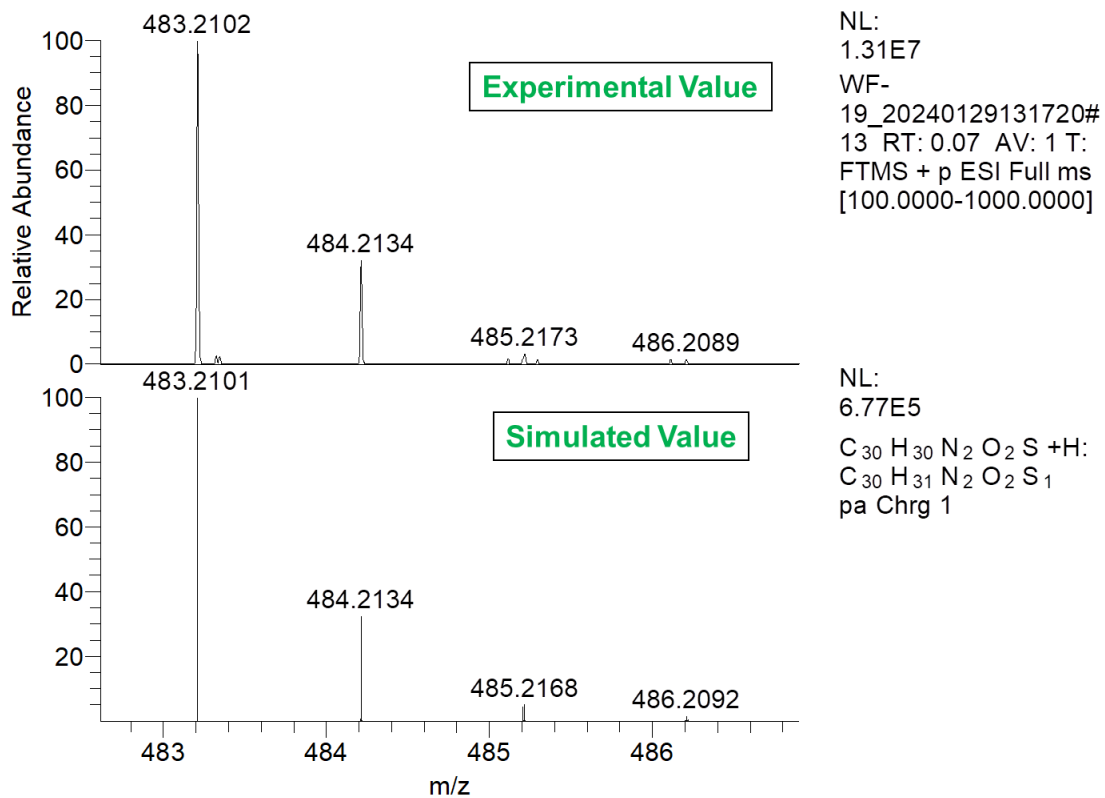
Figure S95. HRMS (ESI) spectrum of **3w**.
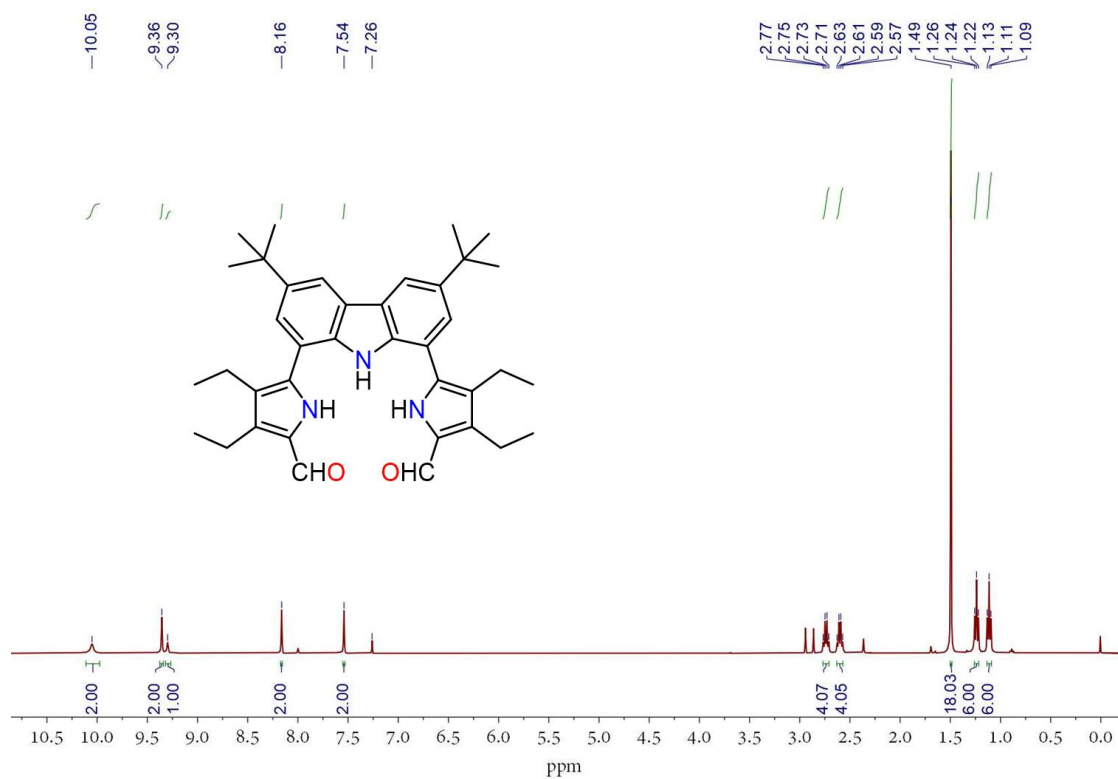
Figure S96. ^{1}H NMR (400 MHz) spectrum of **3x** as recorded in CDCl$_3$.

Figure S97. ^{1}H NMR (400 MHz) spectrum of **3x+D₂O** as recorded in CDCl₃.

Figure S98. ^{13}C NMR (100 MHz) spectrum of **3x** as recorded in CDCl₃.

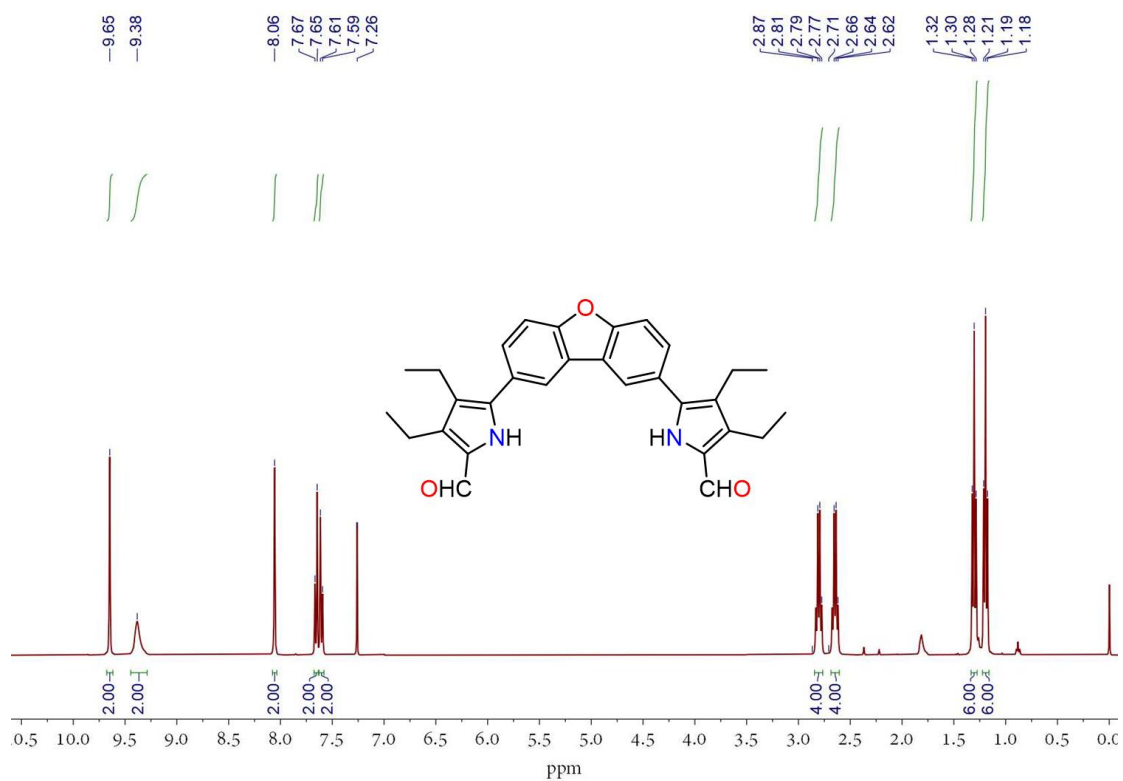**Figure S99.** HRMS (ESI) spectrum of **3x**.

Figure S100. ^{1}H NMR (400 MHz) spectrum of **3y** as recorded in CDCl$_3$.
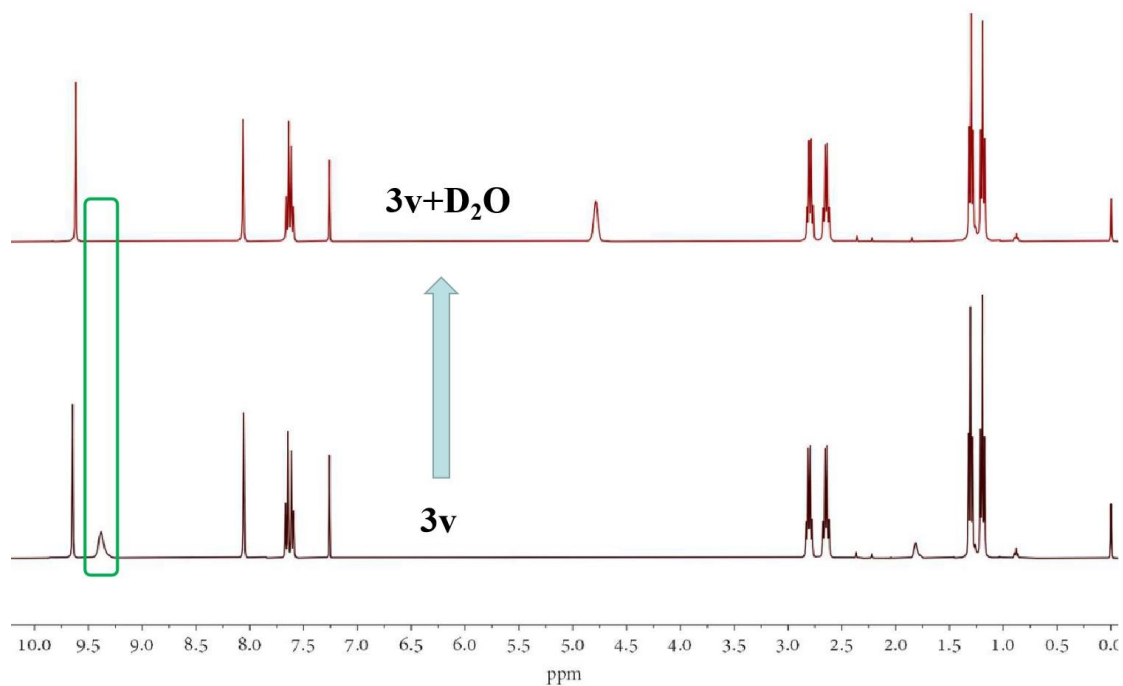
Figure S101. ^{1}H NMR (400 MHz) spectrum of **3y+D₂O** as recorded in CDCl₃.
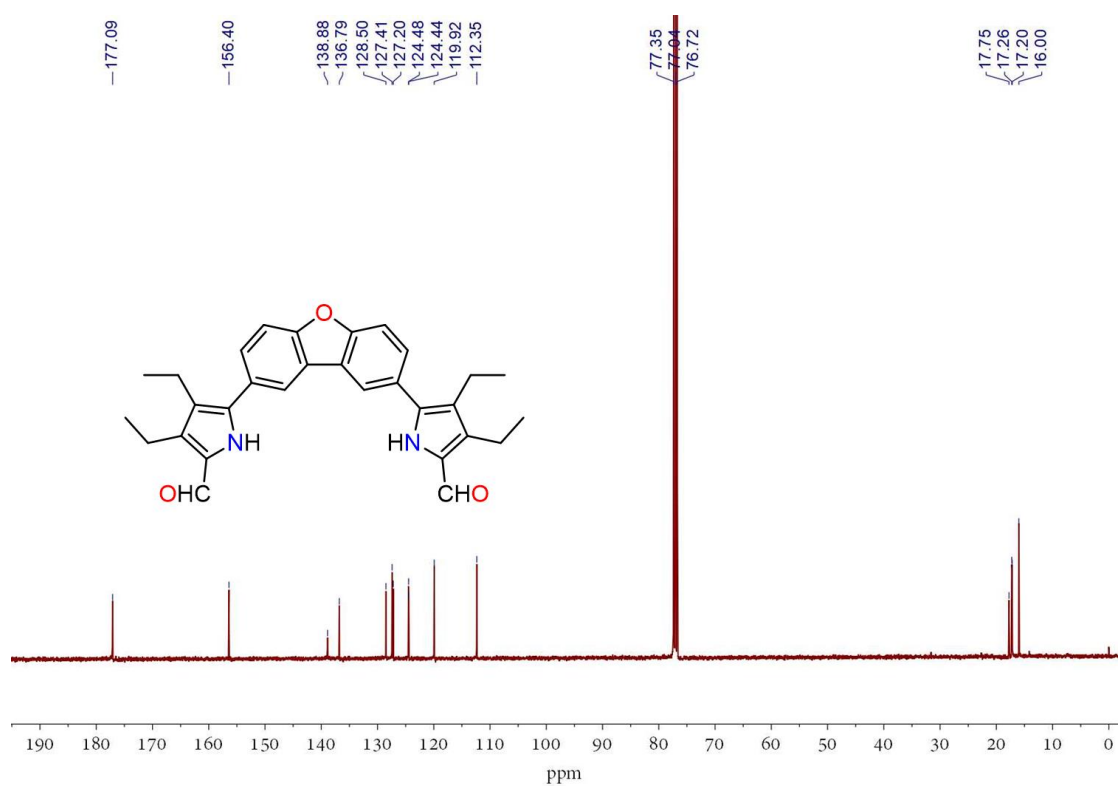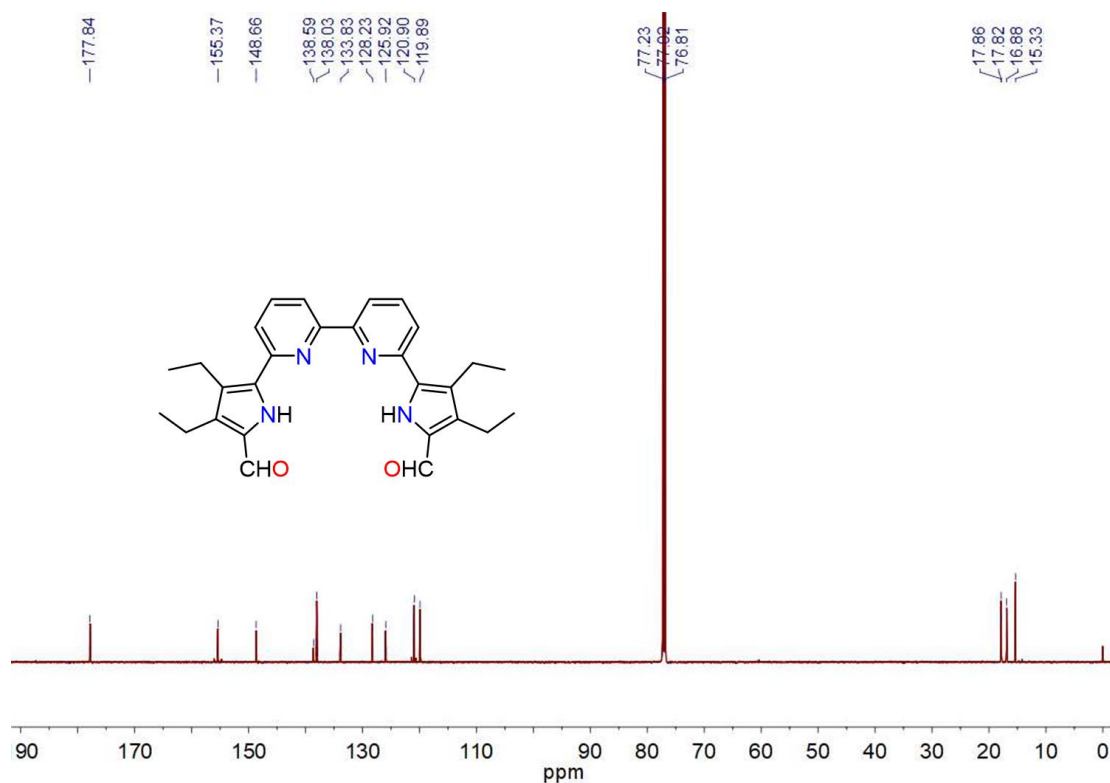

Figure S102. ^{13}C NMR (100 MHz) spectrum of **3y** as recorded in CDCl₃.

Figure S103. HRMS (ESI) spectrum of **3y**.

Figure S104. ^{1}H NMR (400 MHz) spectrum of **3z** as recorded in CDCl$_3$.

Figure S105. ^{1}H NMR (400 MHz) spectrum of **3z**+**D₂O** as recorded in CDCl₃.

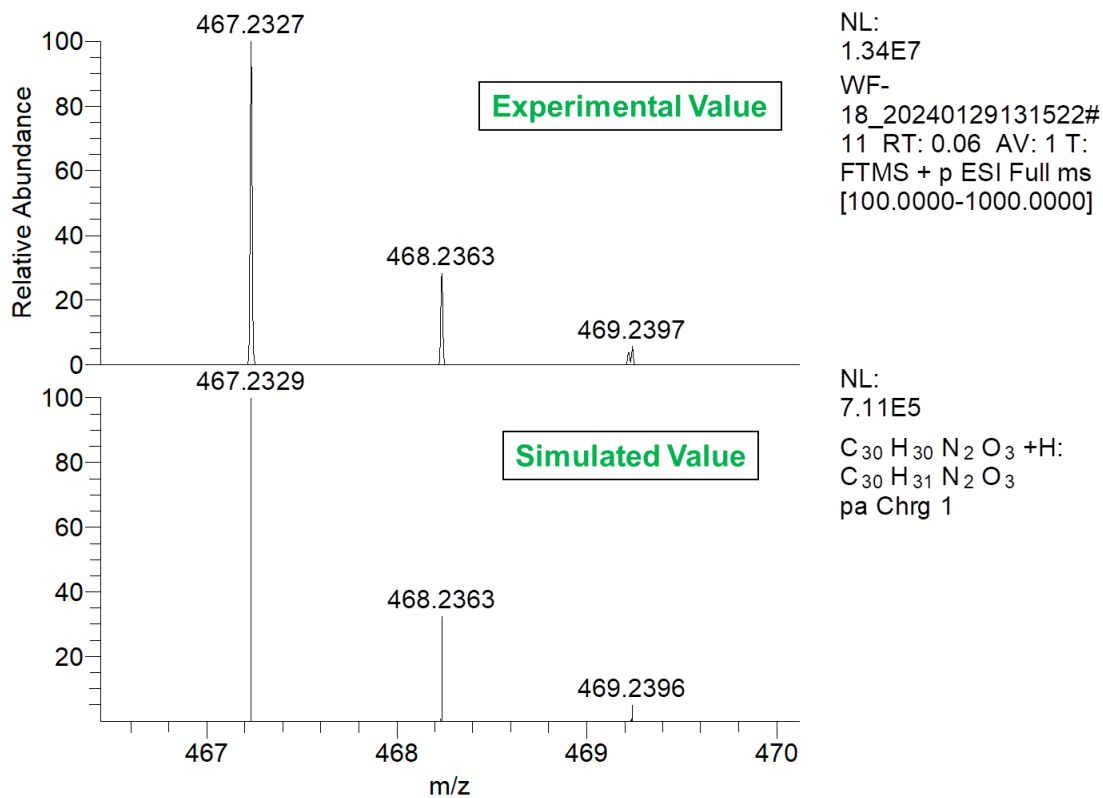**Figure S106.** ^{13}C NMR (100 MHz) spectrum of **3z** as recorded in CDCl₃.

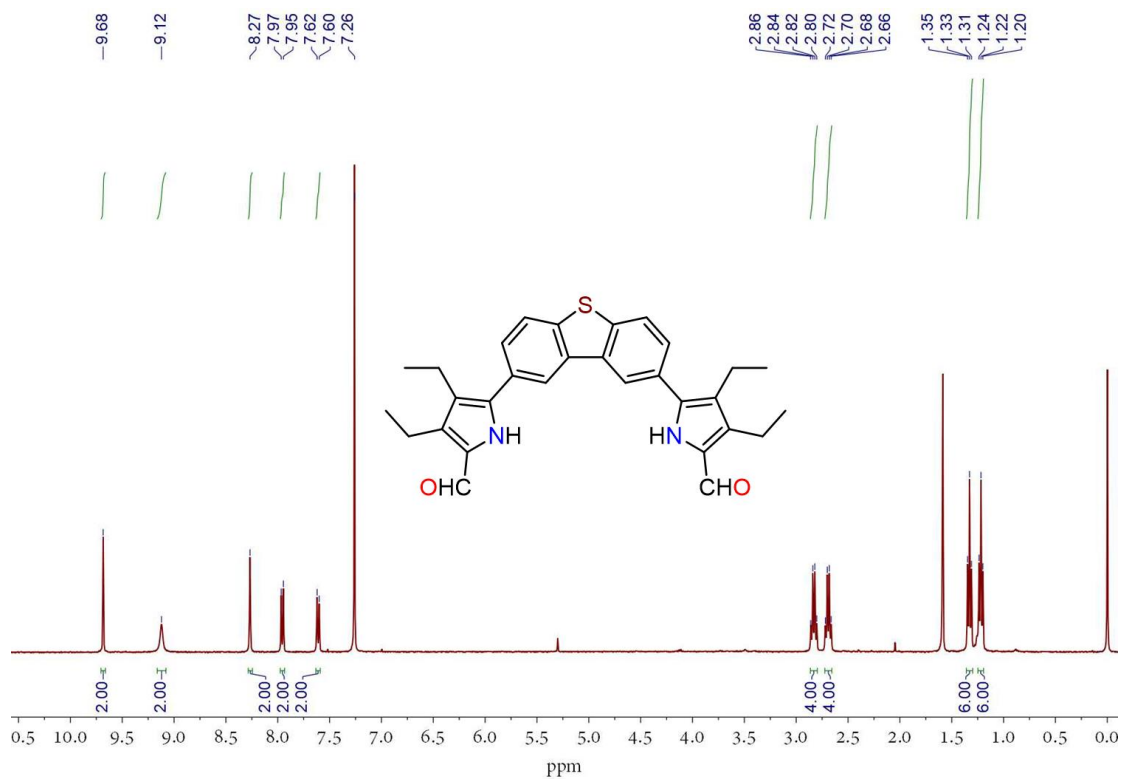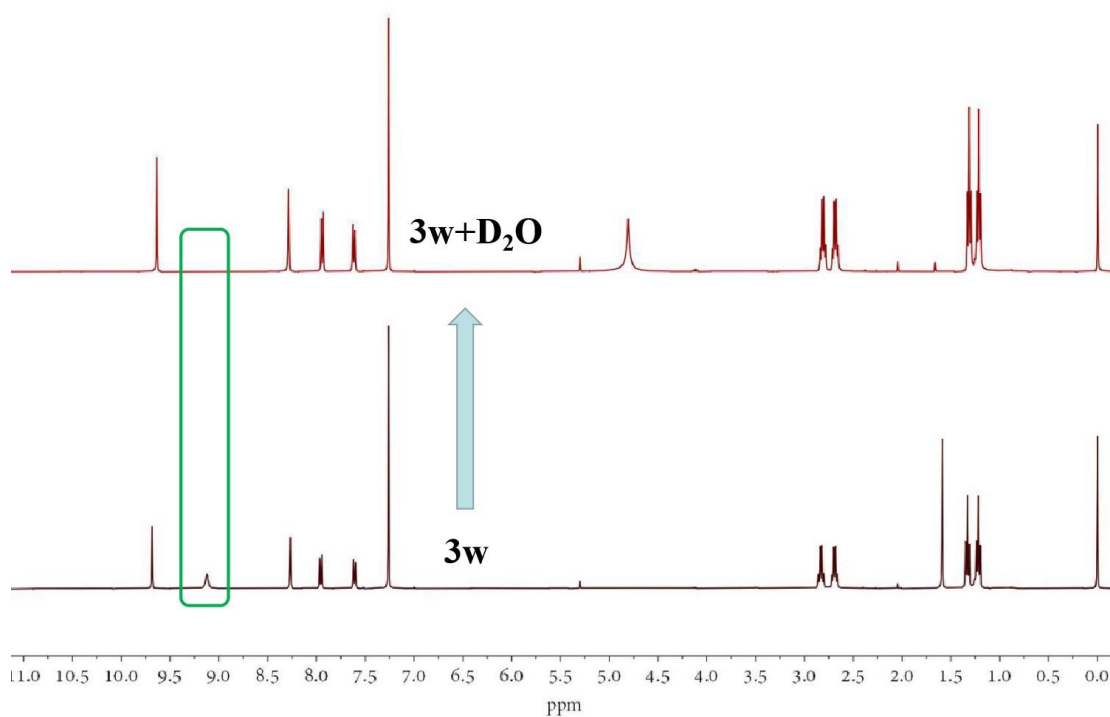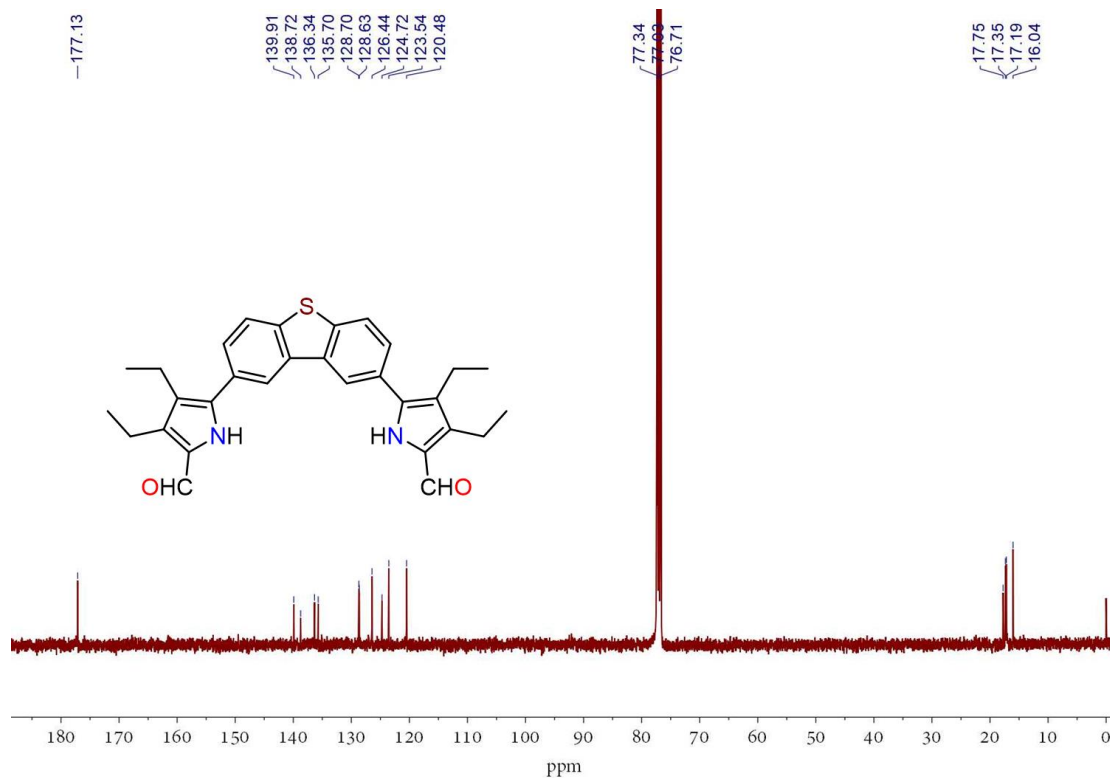**Figure S107.** HRMS (ESI) spectrum of **3z**.
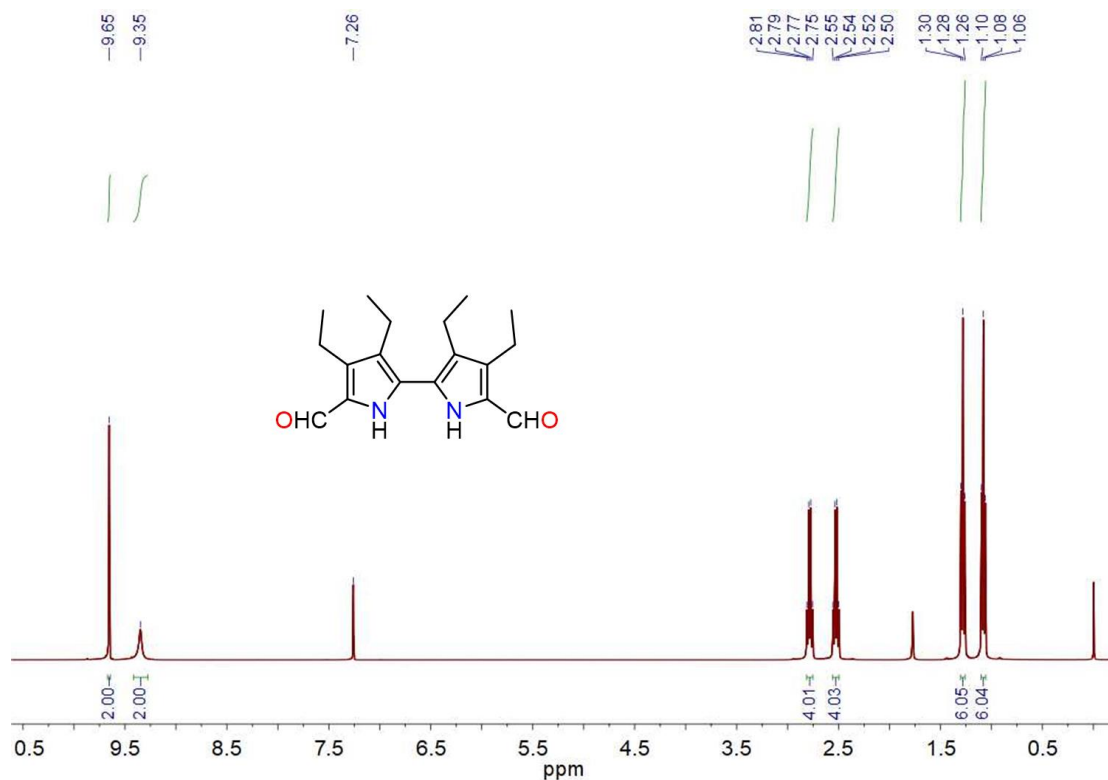
Figure S108. ¹H NMR (400 MHz) spectrum of **diformyl bipyrrole** as recorded in CDCl₃.
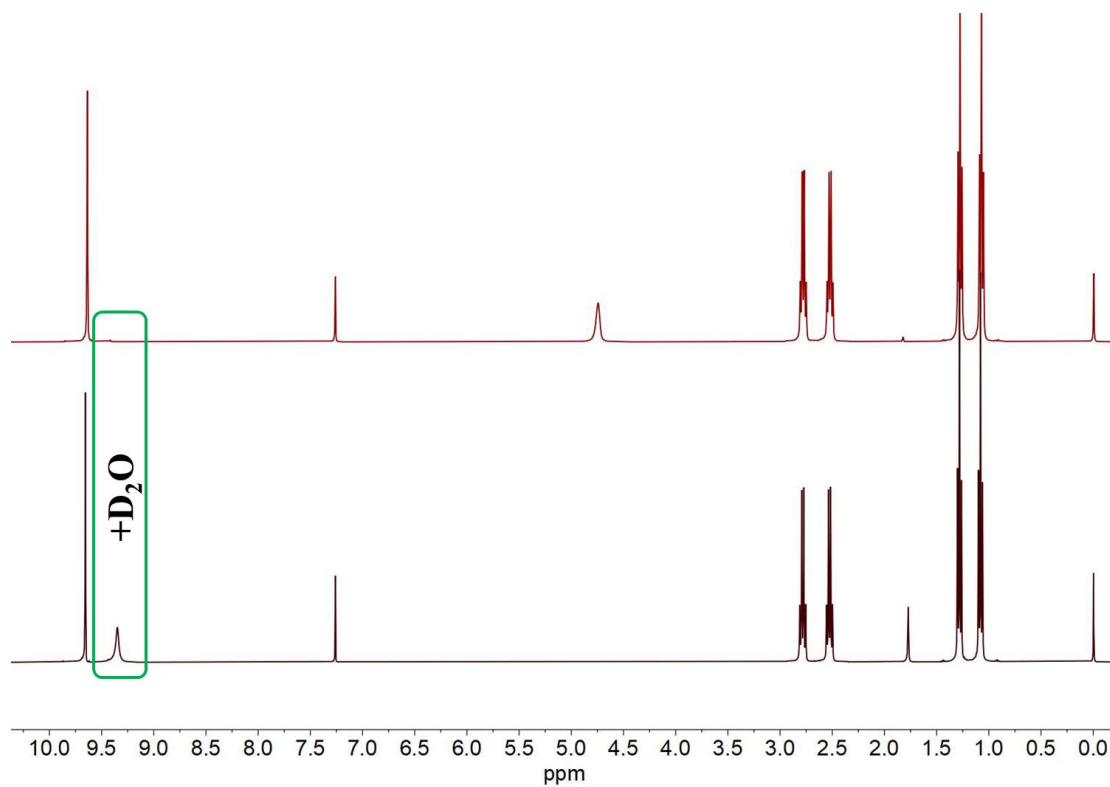
Figure S109. ^{1}H NMR (400 MHz) spectrum of **diformyl bipyrrole**+**D$_2$O** as recorded in CDCl$_3$.
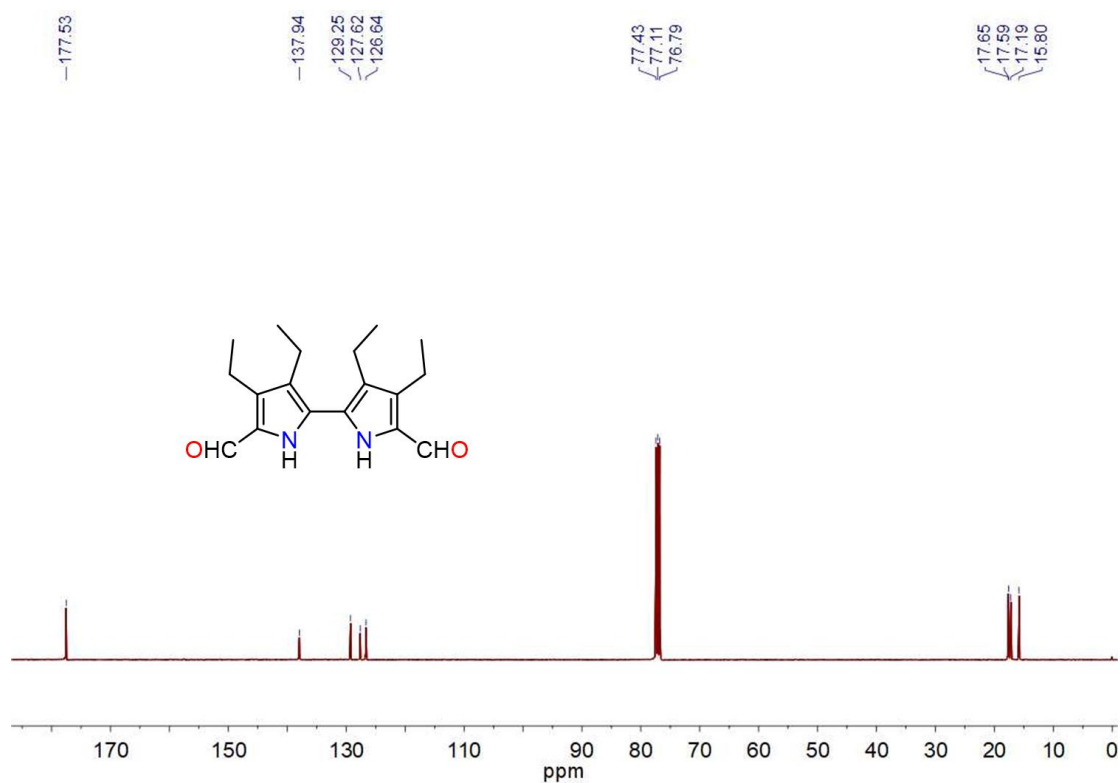
Figure S110. ^{13}C NMR (100 MHz) spectrum of **diformyl bipyrrole** as recorded in CDCl$_3$.

Figure S111. ^{1}H NMR (400 MHz) spectrum of **7** as recorded in CDCl$_3$.
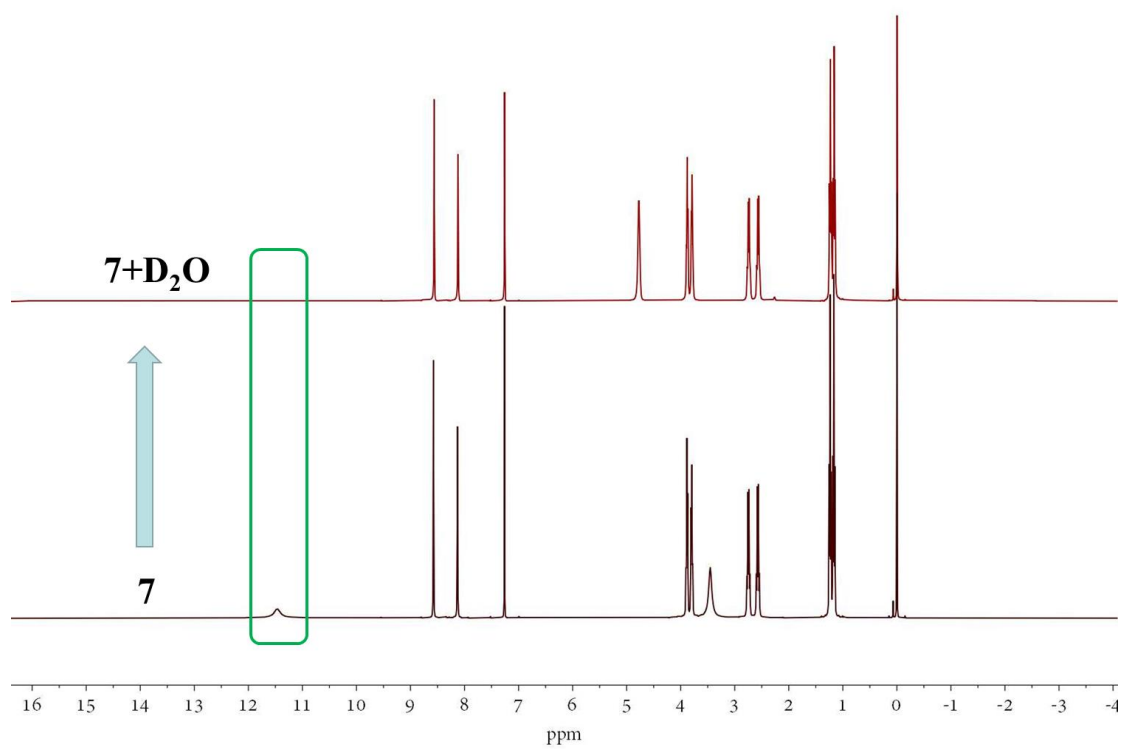
Figure S112. ^{1}H NMR (400 MHz) spectrum of **7**+**D$_2$O** as recorded in CDCl$_3$.
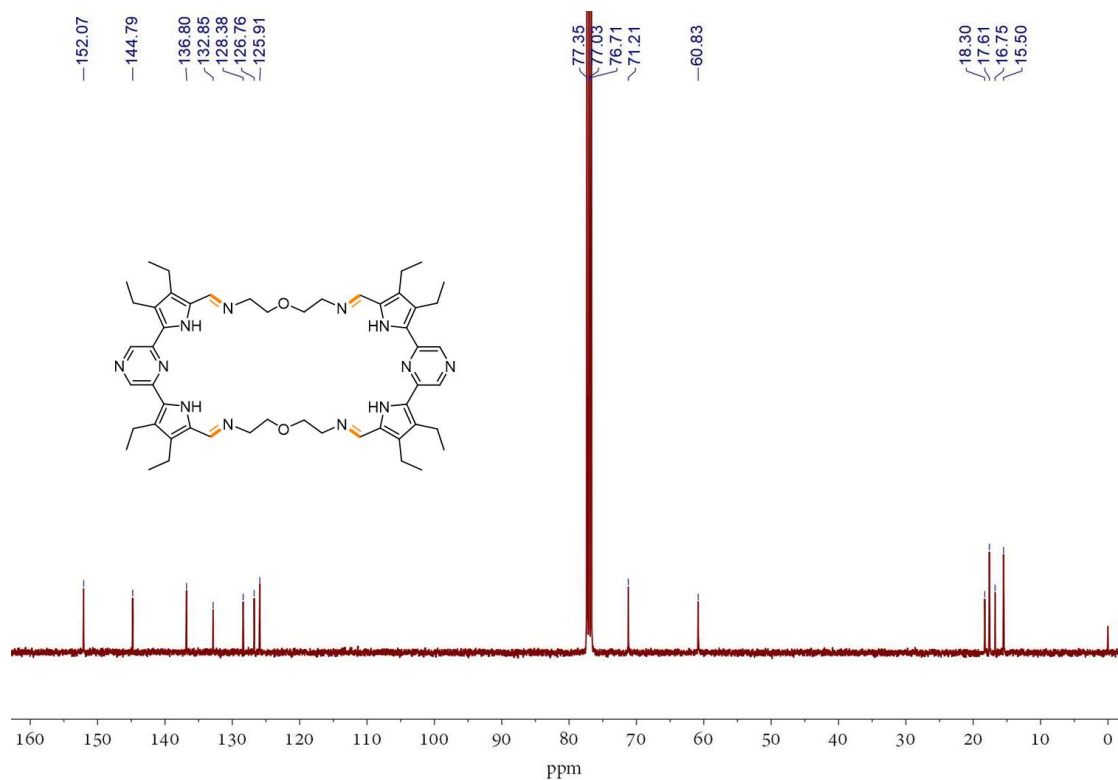
Figure S113. ^{13}C NMR (100 MHz) spectrum of **7** as recorded in CDCl$_3$.

NL:
5.72E6
wf-20#13 RT: 0.07
AV: 1 T: FTMS + p
ESI Full ms
[300.0000-
3000.0000]

Experimental Value

NL:
5.40E5

C$_{52}$H$_{68}$N$_{12}$O$_2$ +H:
C$_{52}$H$_{69}$N$_{12}$O$_2$
pa Chrg 1

Simulated Value
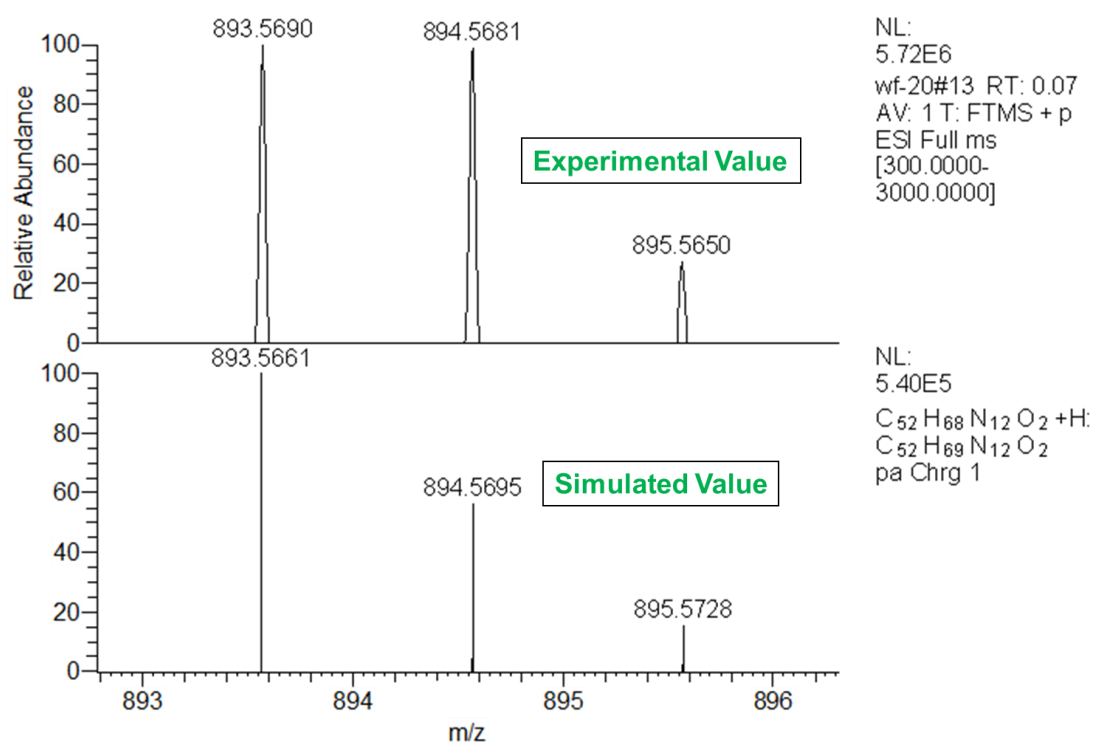
Figure S114. HRMS (ESI) spectrum of **7**.
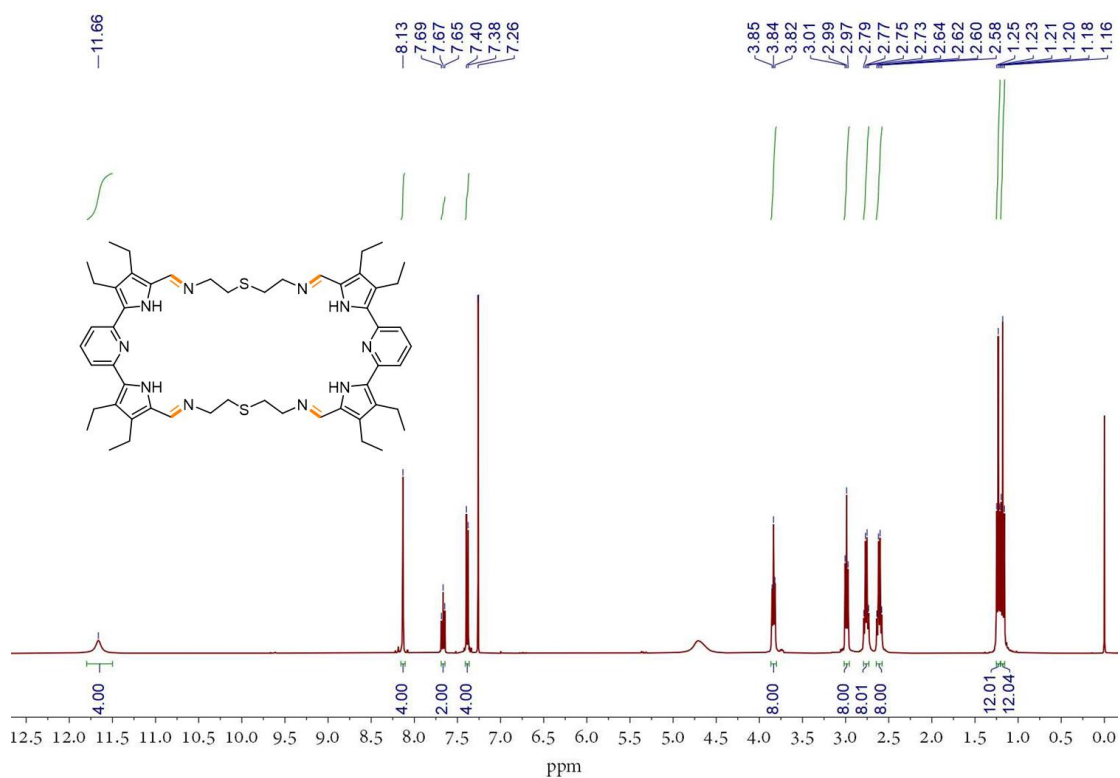
Figure S115. ^{1}H NMR (400 MHz) spectrum of **8** as recorded in CDCl$_3$.
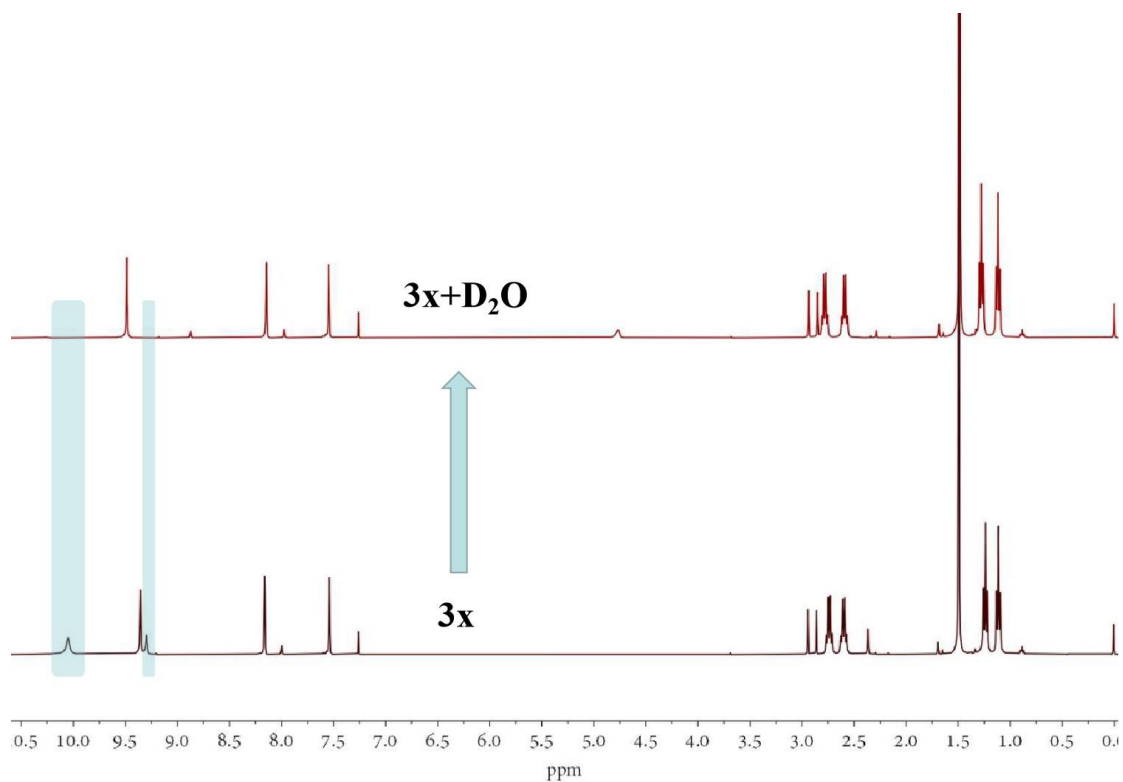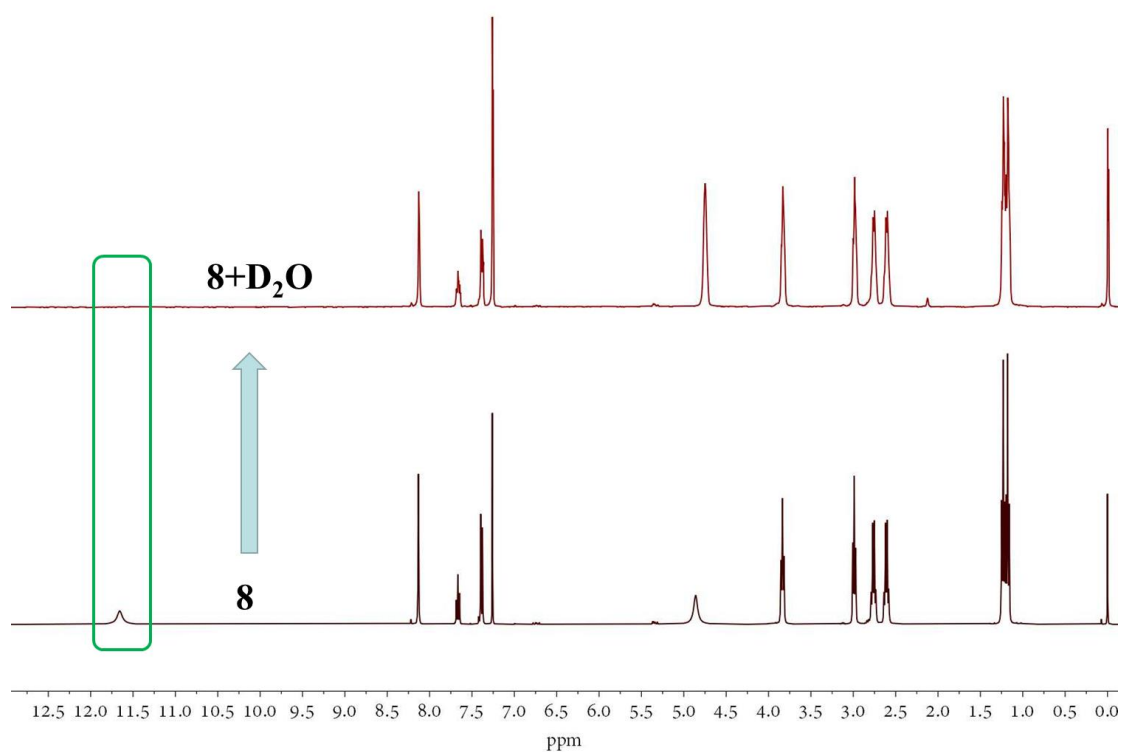

Figure S116. ^{1}H NMR (400 MHz) spectrum of **8**+**D$_2$O** as recorded in CDCl$_3$.
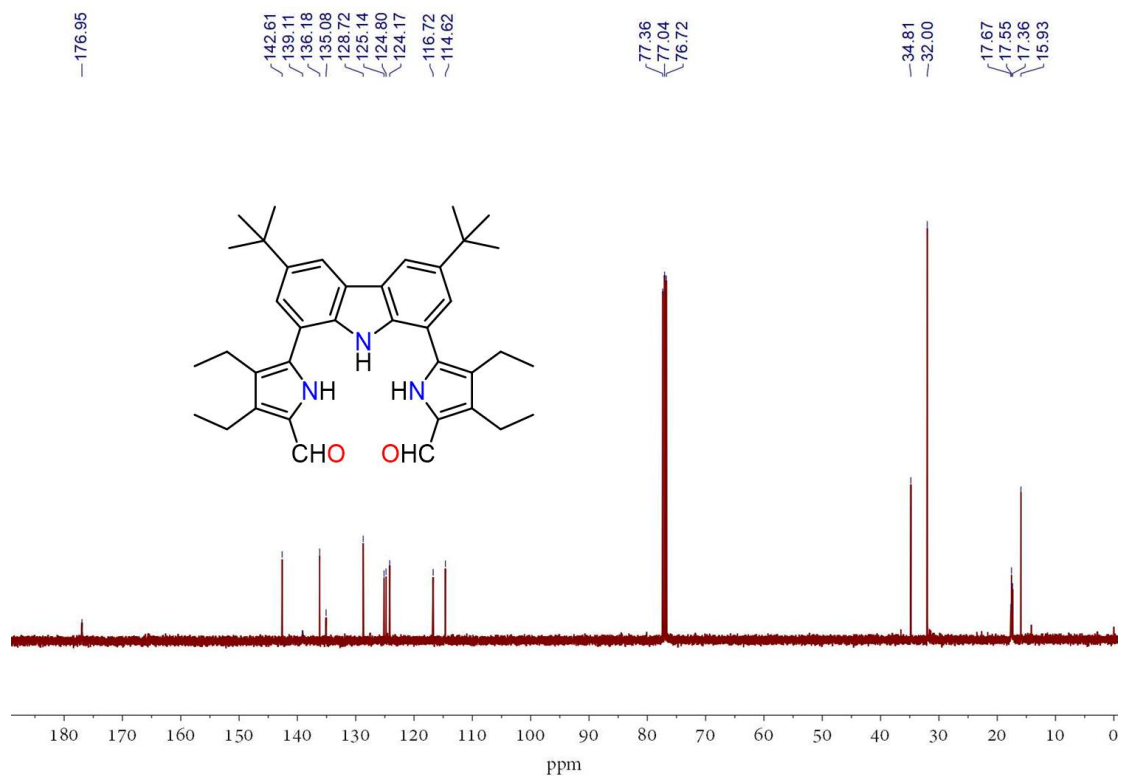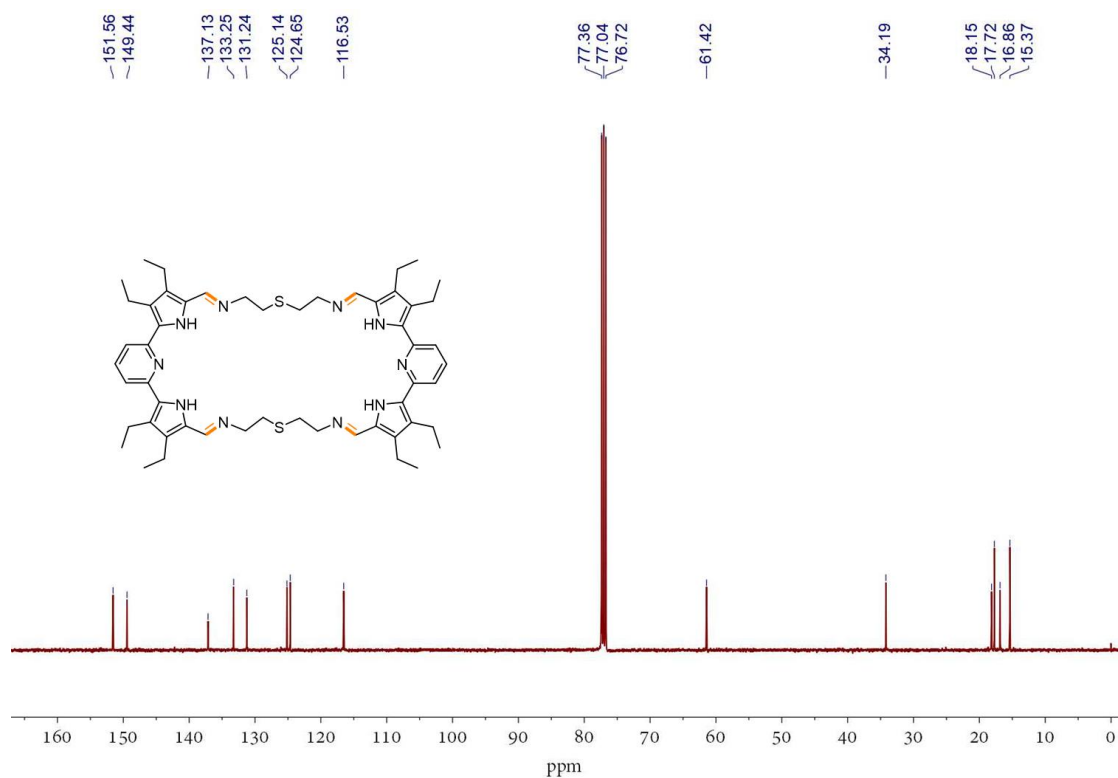
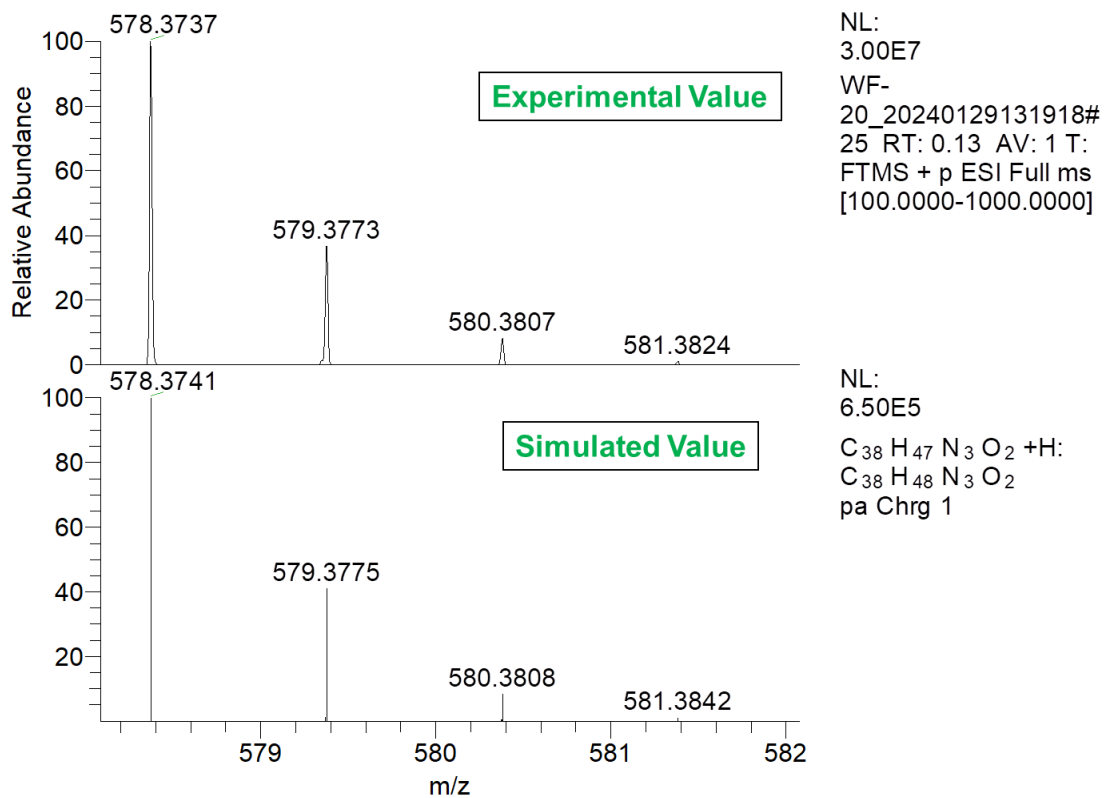**Figure S117.** ^{13}C NMR (100 MHz) spectrum of **8** as recorded in CDCl$_3$.
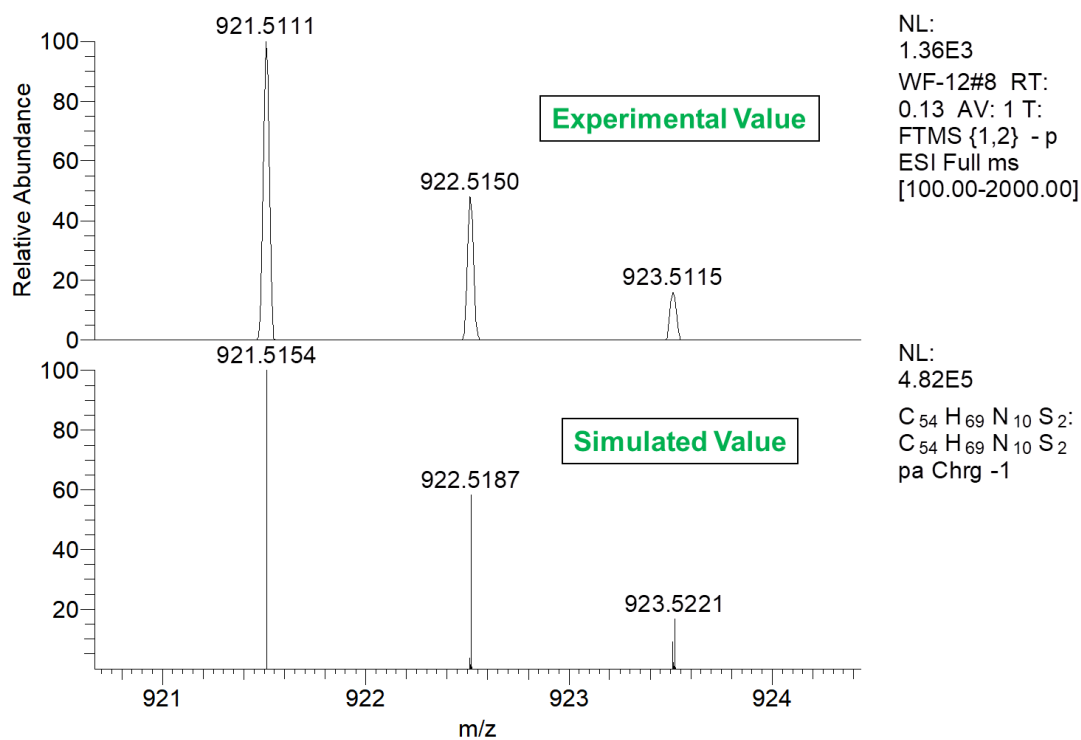
Figure S118. HRMS (ESI) spectrum of **8**.
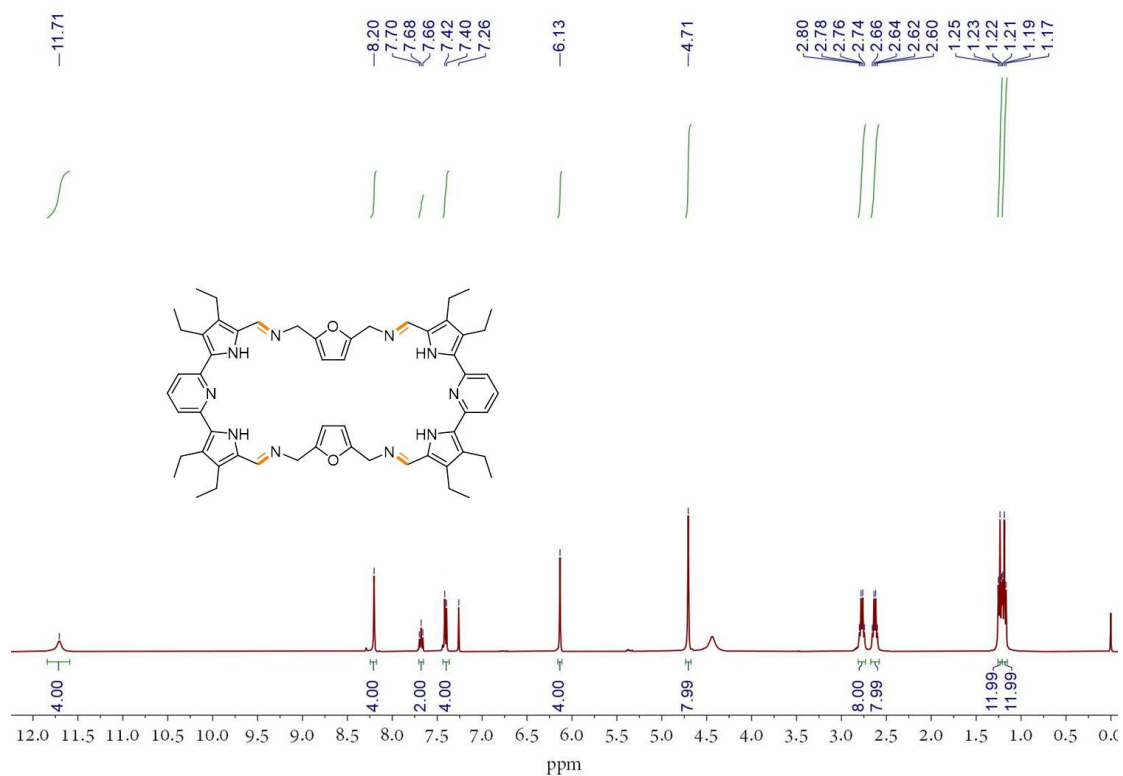
Figure S119. ¹H NMR (400 MHz) spectrum of **9** as recorded in CDCl₃.
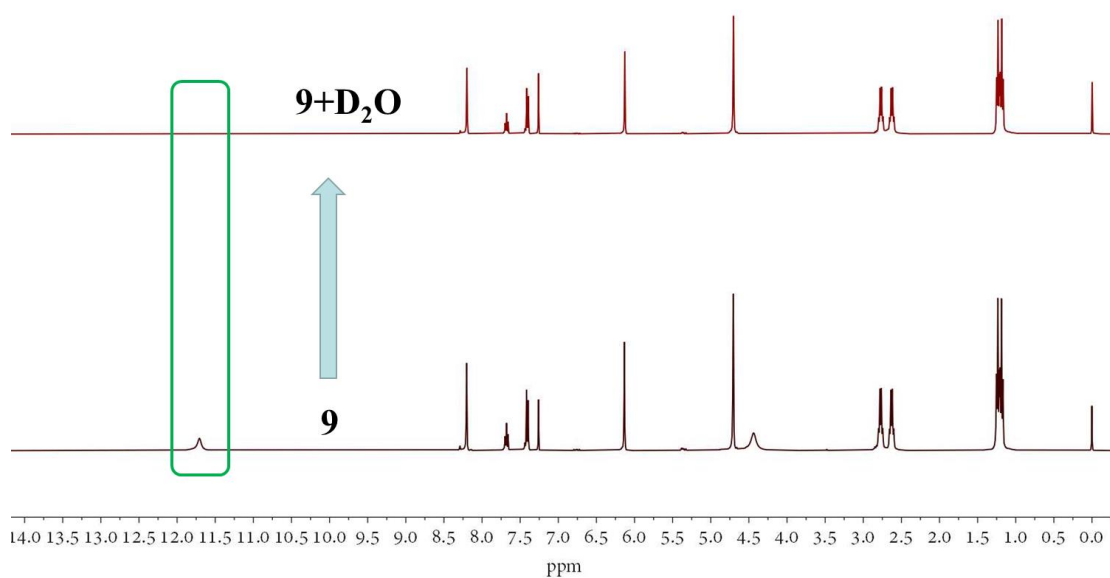
Figure S120. ¹H NMR (400 MHz) spectrum of **9**+**D₂O** as recorded in CDCl₃.
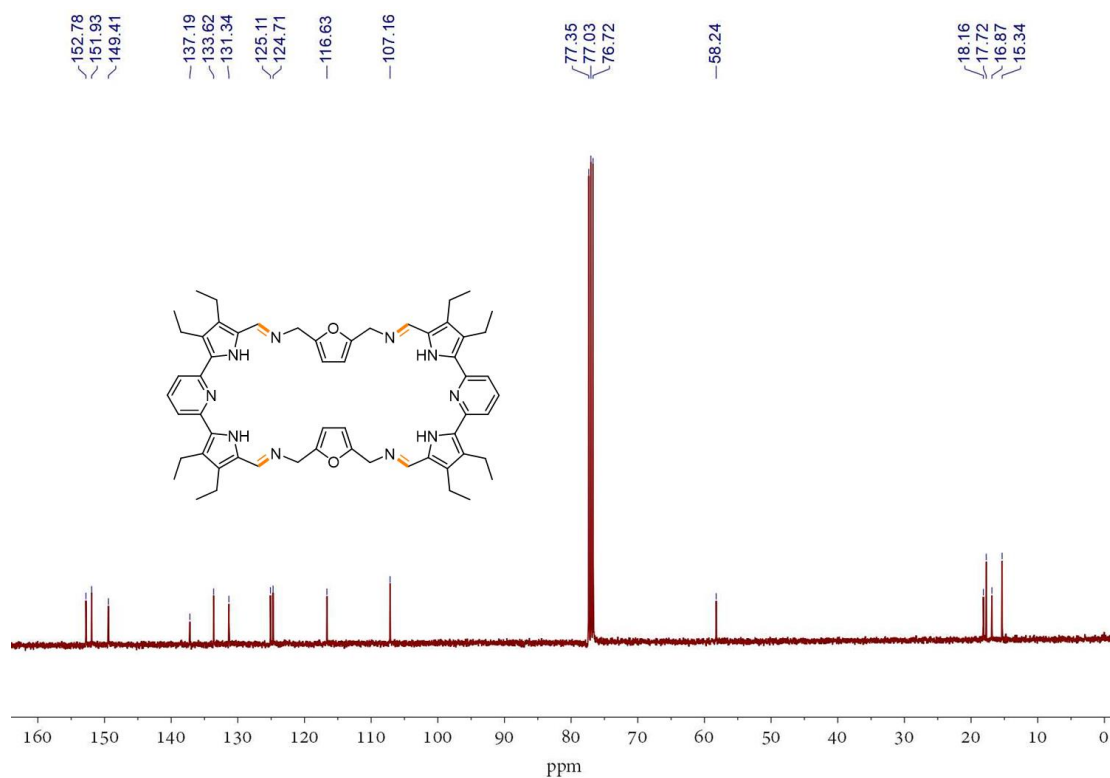
Figure S121. ^{13}C NMR (100 MHz) spectrum of **9** as recorded in CDCl$_3$.
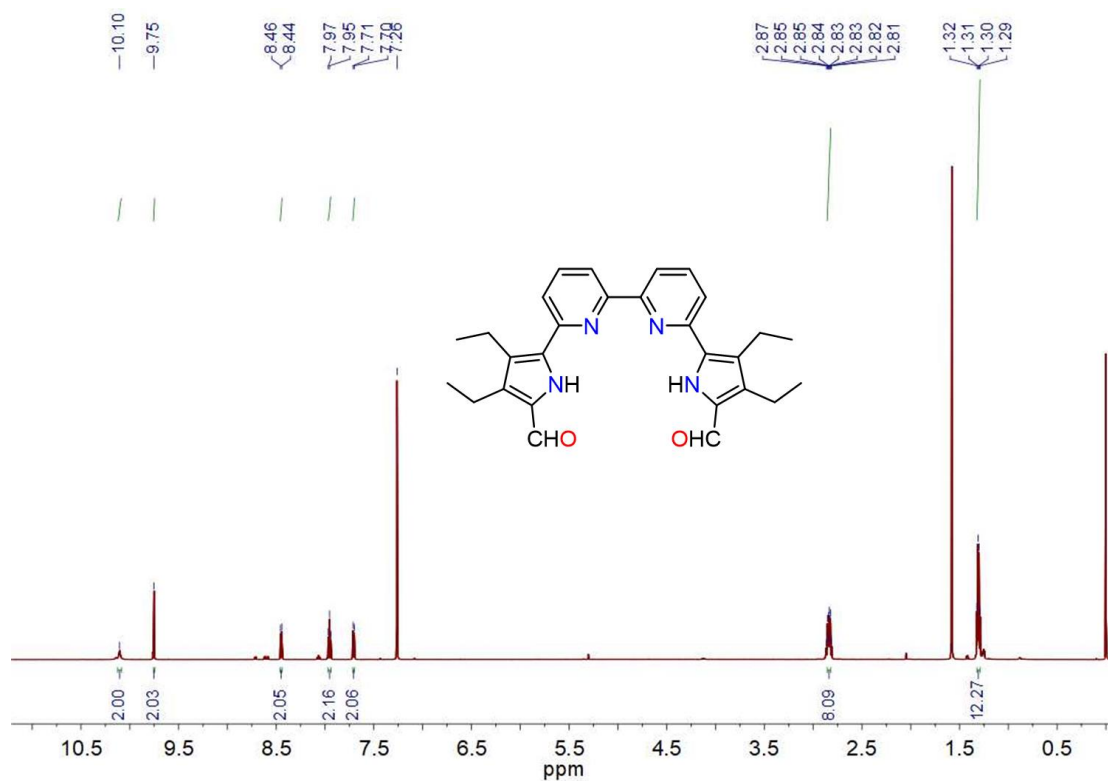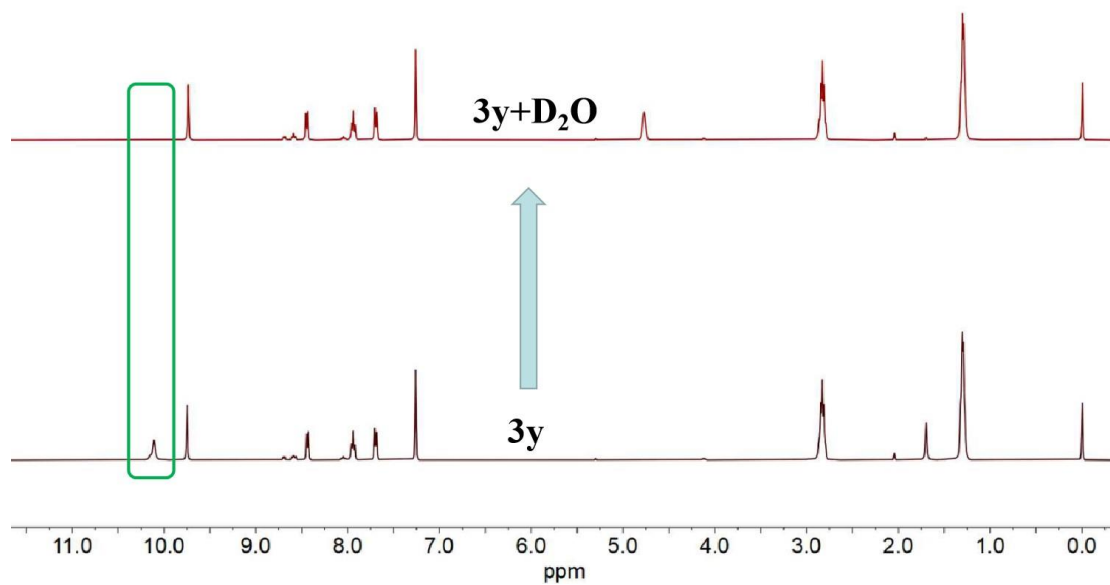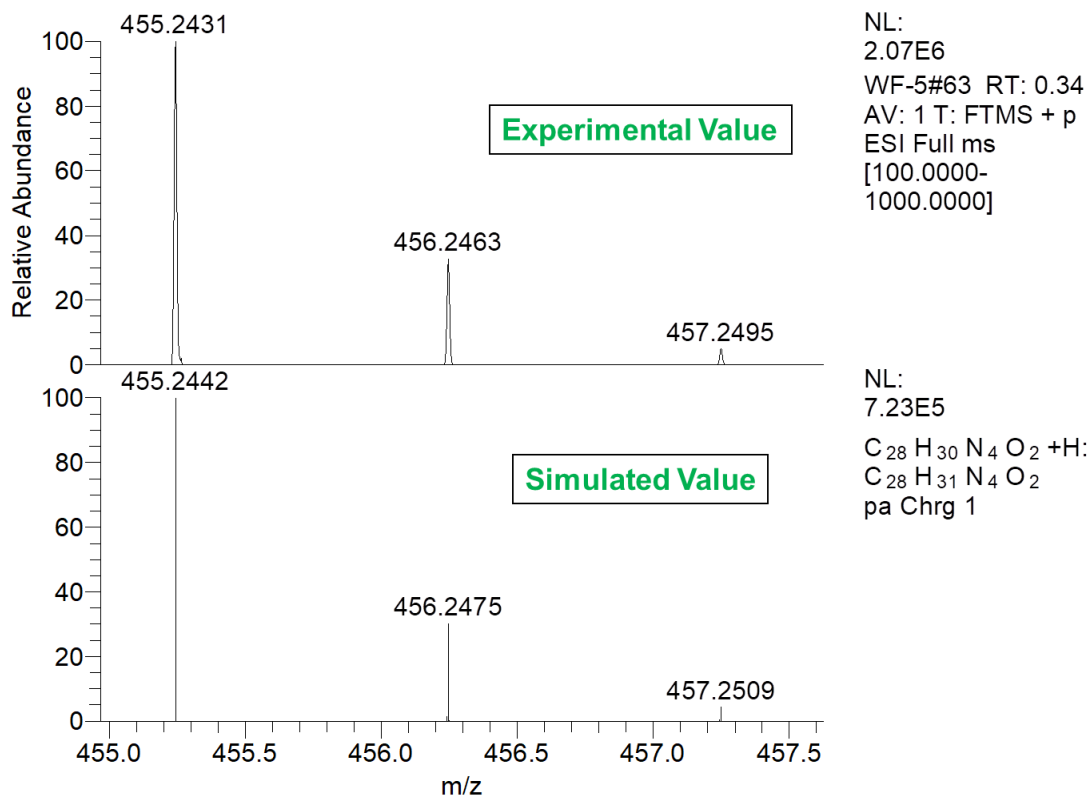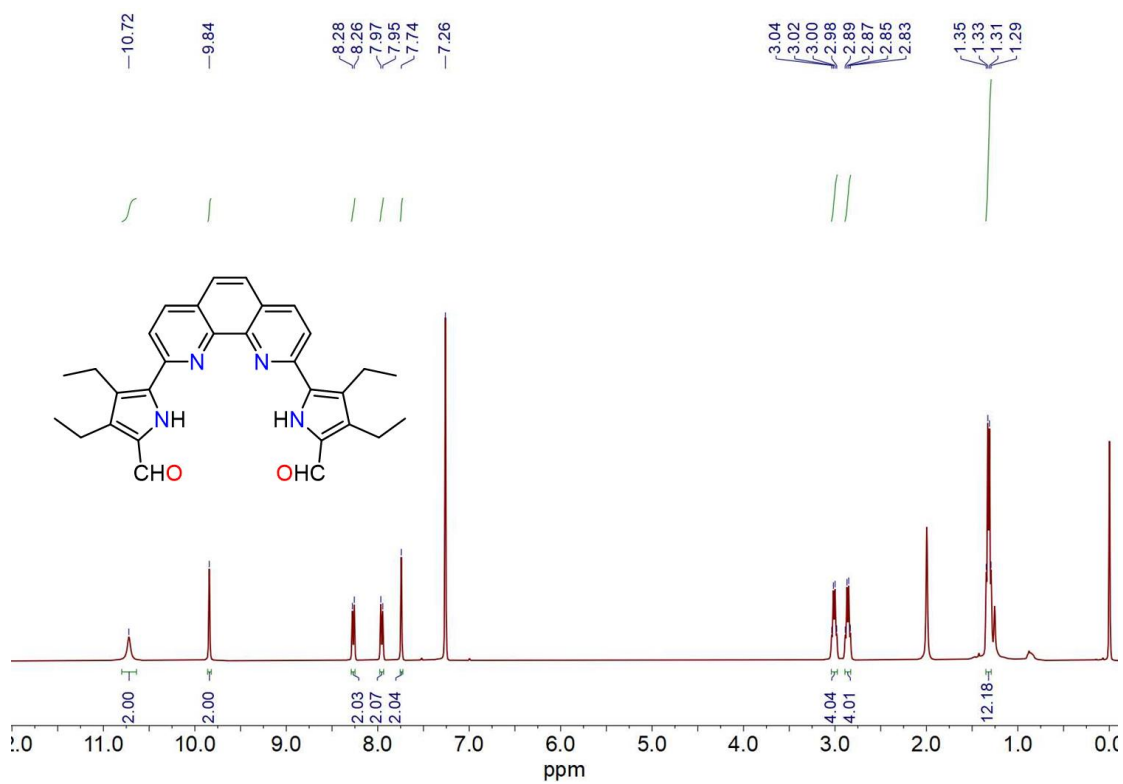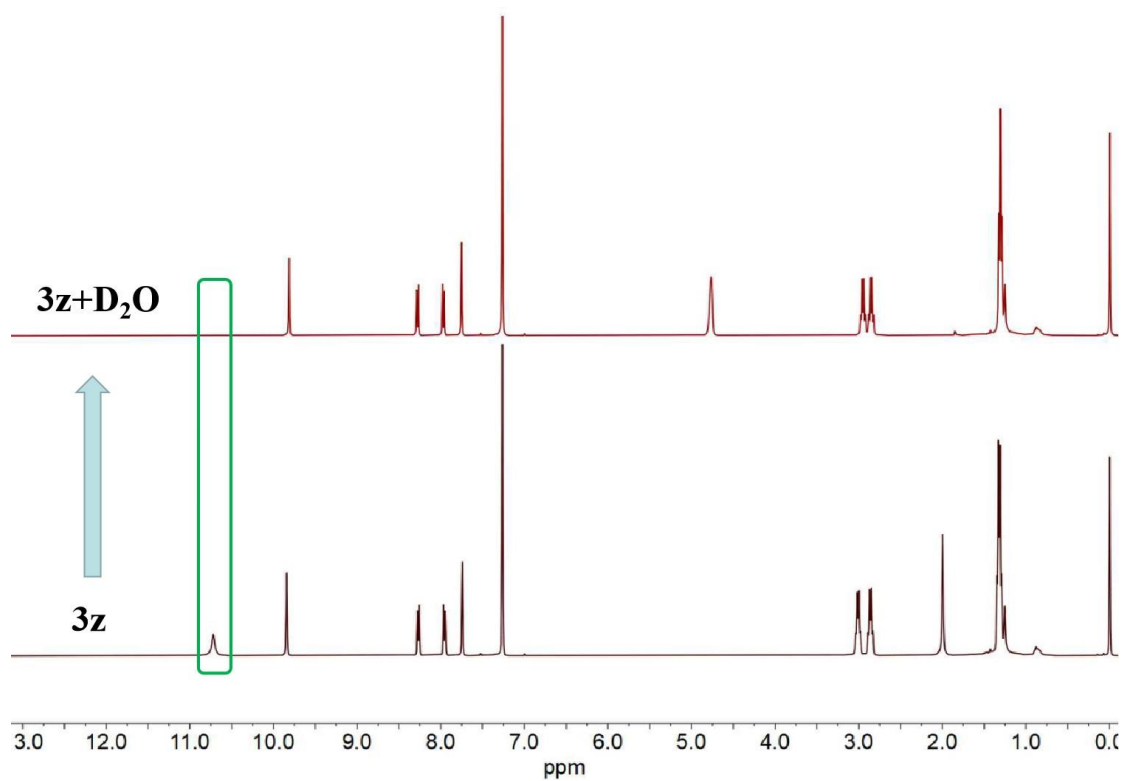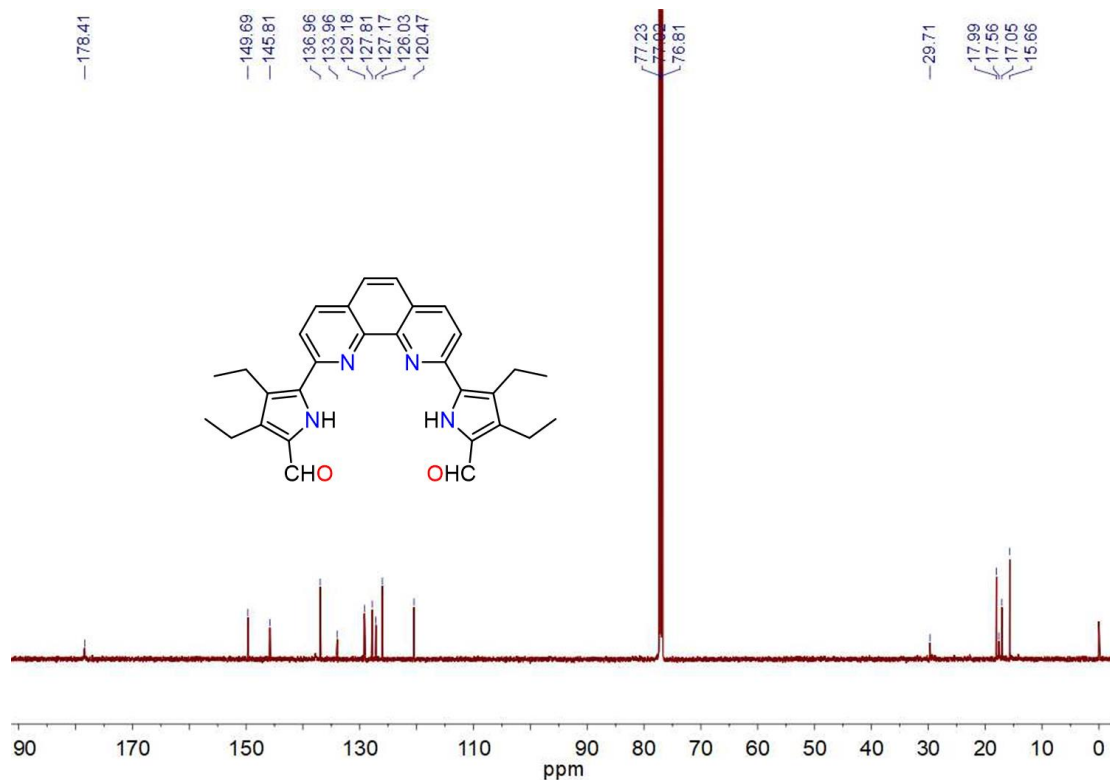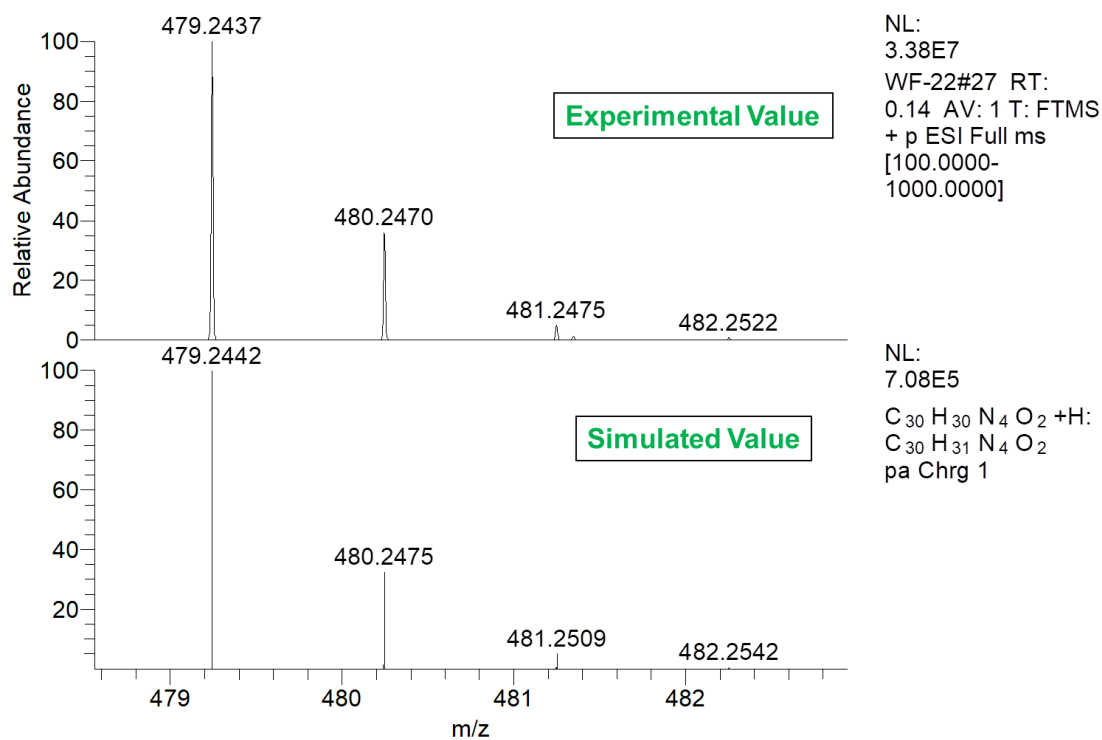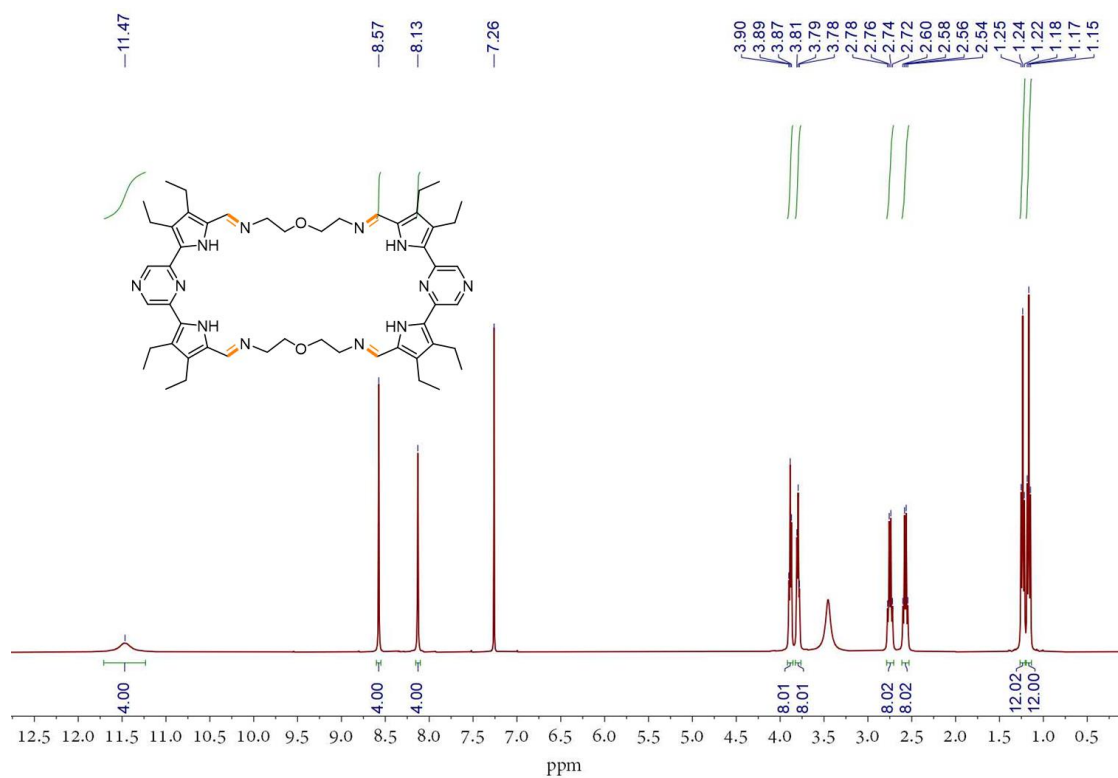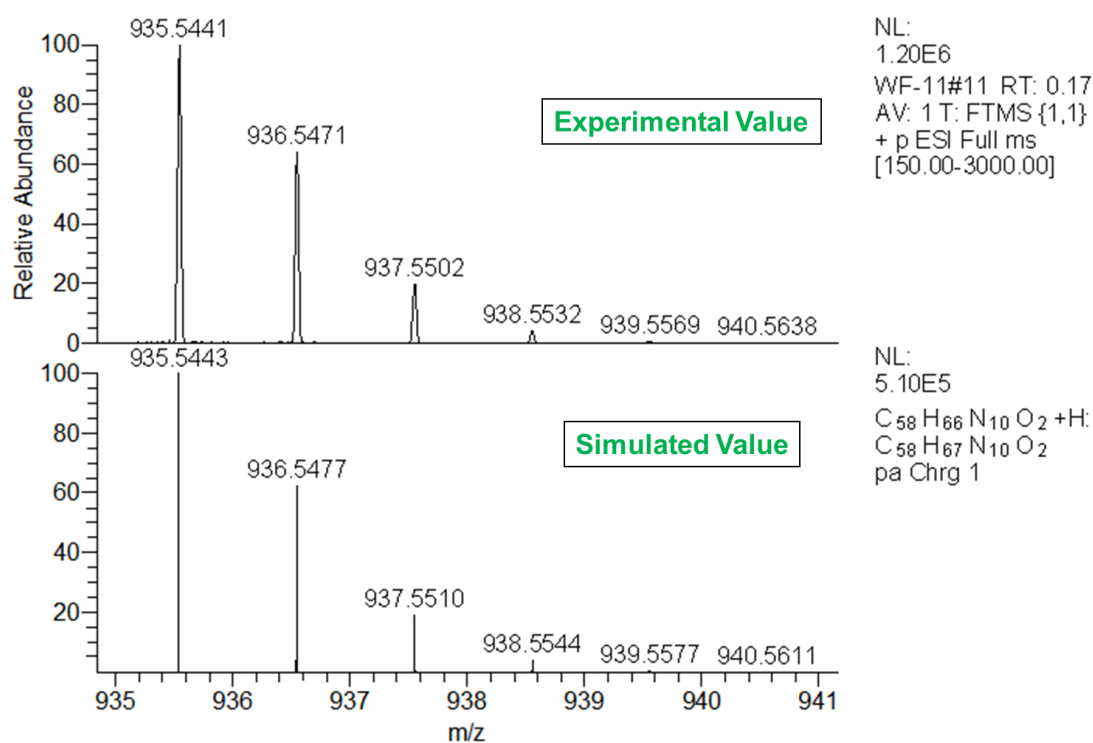

Figure S122. HRMS (ESI) spectrum of **9**.

III. X-ray Crystallography

(a) X-ray diffraction analysis of single crystals of 3a:

Yellowish block shaped crystals were obtained by vapor diffusion of hexanes into a THF solution of **3a**. The data were collected on a Bruker D8 Venture diffractometer equipped with a PHOTON 100 detector using a μ-focus Cu$K\alpha$ microfocus source (λ = 1.5418 Å) with collimating mirror monochromators. The data were collected at 173 K. Crystallographic data are listed in the **Table S1**. Data were collected using the Bruker APEXIII Bruker-AXS software. Unit cell refinement and data reduction were performed using the SAINT V8.37A Bruker-AXS software.[S8] The structure was solved by direct methods using SHELXT[S9] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3. The hydrogen atoms were calculated in ideal positions with a riding mode. SQUEEZE routine was applied by using PLATON[S10] for some electron densities which could not reasonably modeled.

Crystallographic data has been deposited in the Cambridge Crystallographic Data Center with CCDC number: 2298879. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement for **3a**.

Identification code	**3a**
Empirical formula	$C_{22} H_{27} N_3 O_2$
Formula weight	365.46
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 8.9704 (2) Å α = 90 °
	b = 14.6873 (4) Å β = 97.7410 (10) °
	c = 14.7777 (4) Å γ = 90 °
Volume	1929.23 (9) Å^3
Z, Calculated density	4, 1.258 Mg/m^3
Absorption coefficient	0.647 mm^-1
F(000)	784
Crystal size	$0.200 \times 0.050 \times 0.050$ mm^3
Theta range for data collection	4.263 to 68.211°

Limiting indices	-10<=h<=10, -17<=k<=17, -17<=l<=17
Reflections collected / unique	28890 / 3520 [R(int) = 0.0370]
Data completeness	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7531 and 0.6929
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3520 / 0 / 248
Goodness-of-fit on F^2	1.020
Final R indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.0904
R indices (all data)	R1 = 0.0427, wR2 = 0.0956
Largest diff. peak and hole	0.232 and -0.246 e.Å^-3
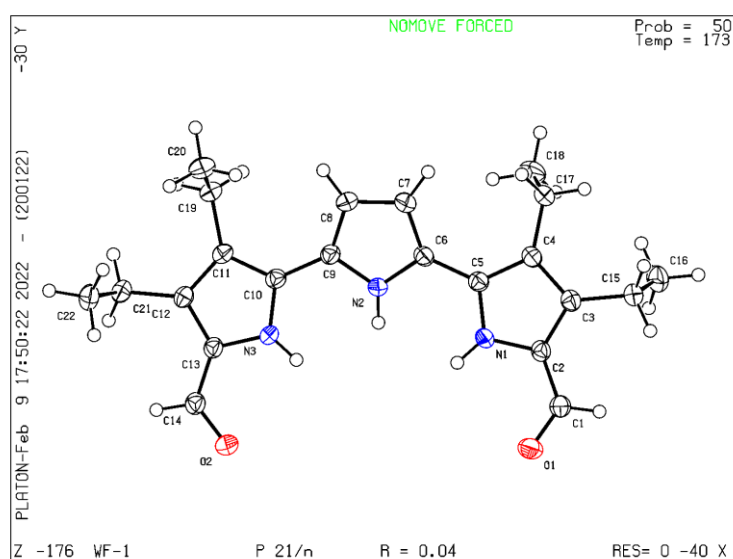
Figure S123. Asymmetric unit of **3a**, obtained from a single crystal X-ray diffraction analysis. The thermal ellipsoids are scaled at the 50% probability level.

Figure S124. Hydrogen bond interactions in **3a** inferred from the X-diffraction analysis. Hydrogen atoms have been removed for clarity.

Figure S125. Packing diagram of **3a** along the crystallographic "*a*" axis from a single crystal X-ray diffraction analysis. Hydrogen atoms have been removed for clarity.

(b) X-ray diffraction analysis of single crystals of 3h:

Brown needle-like crystals were obtained by vapor diffusion of hexanes into a $CHCl_3$ solution of **3h**. The data were collected on a Bruker P4 diffractometer with a Cu$K\alpha$ radiation source (λ = 1.54178 Å). The data were collected at 150 K. The data were collected using ϕ- and ω-scans with a scan range of 5.023-72.292°. Crystallographic data are listed in the **Table S2**. The unit cell refinement and data reduction were performed using SAINT V8.40B software. The structure was solved by direct methods using SHELXT[S9] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3.

Crystallographic data have been deposited in the Cambridge Crystallographic Data Center with CCDC number: 2298880. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

Table S2. Crystal data and structure refinement for **3h**.

Identification code	(3h•H₂O)•(3h•H₂O)
Empirical formula	$C_{44} H_{56} N_8 O_6$
Formula weight	792.96
Temperature	150 K

|	
Wavelength	1.54178 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.6855 (7) Å α = 105.506 (6)°
	b = 9.1540 (9) Å β = 102.442 (6)°
	c = 13.8725 (13) Å γ = 90.015 (6)°
Volume	1035.89 (17) Å^3
Z, Calculated density	1, 1.271 Mg/m^3
Absorption coefficient	0.695 mm^-1
F(000)	424
Crystal size	0.1 × 0.04 × 0.04 mm^3
Theta range for data collection	5.023 to 72.292°
Limiting indices	-10<=h<=10, -11<=k<=10, 0<=l<=17
Reflections collected / unique	5671 / 3985 [R(int) = 0.0814]
Data completeness	97.1 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3985 / 3 / 269
Goodness-of-fit on F^2	1.056
Final R indices [I>2sigma(I)]	R1 = 0.1186, wR2 = 0.2936
R indices (all data)	R1 = 0.1331, wR2 = 0.3078
Largest diff. peak and hole	1.09 and -0.53 e.Å^-3
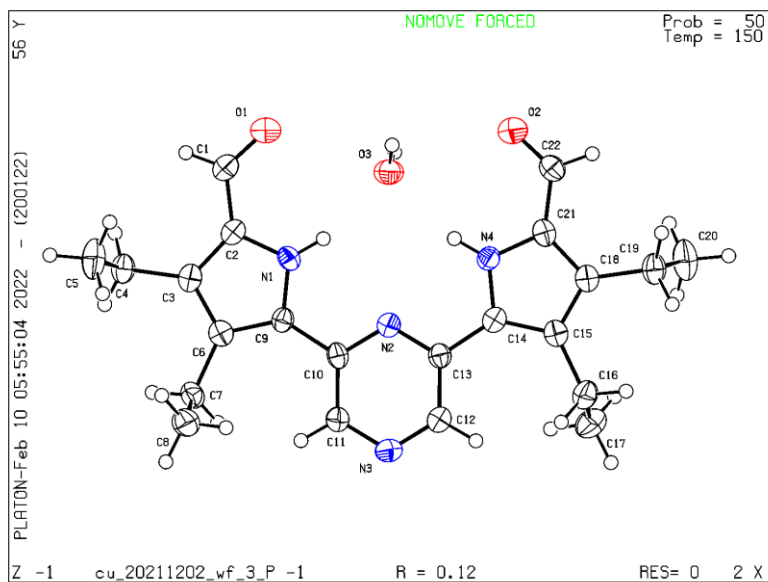
Figure S126. Asymmetric unit of **3h**, obtained from a single crystal X-ray diffraction analysis. The thermal ellipsoids are scaled at the 50% probability level.
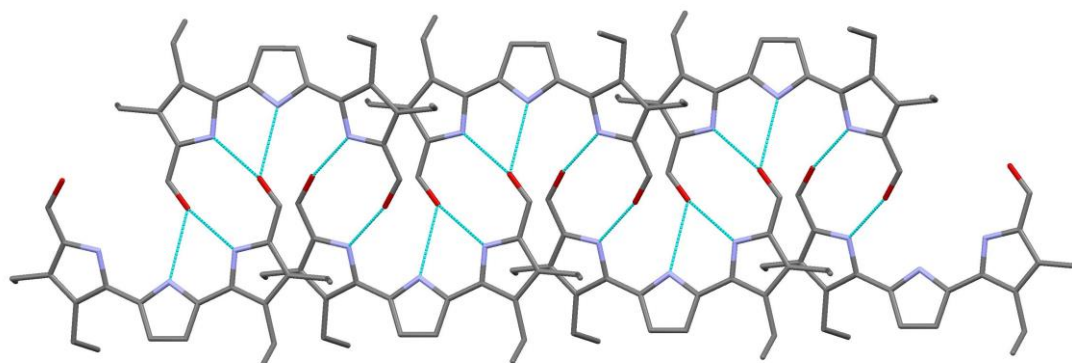
Figure S127. Hydrogen bond interactions in **3h** inferred from the X-ray diffraction analysis.
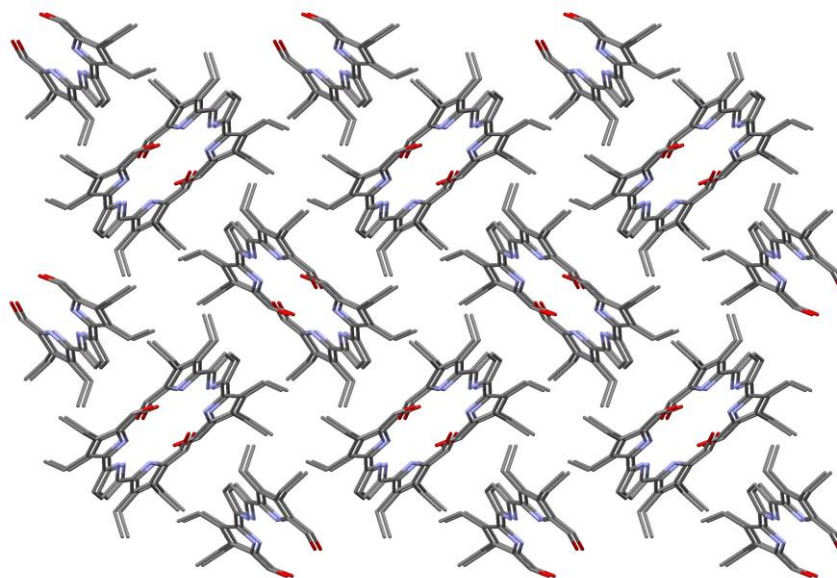

Figure S128. Packing diagram of **3h** along the crystallographic *"a"* axis from a single crystal X-ray diffraction analysis. Hydrogen atoms have been removed for clarity.

(c) X-ray diffraction analysis of single crystals of 3i:

Yellowish needle-like crystals were obtained by vapor diffusion of hexanes into a THF solution of **3i**. The data were collected on a Bruker APEX-II CCD diffractometer with a Cu$K\alpha$ radiation source (λ = 1.54178 Å). The data were collected at 150 K. The data were collected using ϕ- and ω-scans with a scan range of 3.094-63.870°. Crystallographic data are listed in the **Table S3**. The unit cell refinement and data reduction were performed using SAINT V8.40C software. The structure was solved by direct methods using SHELXT[S9] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3.

Crystallographic data has been deposited in the Cambridge Crystallographic Data Center with CCDC number: 2298881. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

Table S3. Crystal data and structure refinement for **3i**.

| Identification code	**3i**
Empirical formula	$C_{22} H_{26} N_4 O_2$
Formula weight	378.47
Temperature	150 K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 29.852 (15) Å $\alpha = 90°$
	b = 8.3792 (16) Å $\beta = 106.99$ (3)°
	c = 16.947 (4) Å $\gamma = 90°$
Volume	4054 (2) Å^3
Z, Calculated density	8, 1.240 Mg/m^3
Absorption coefficient	0.650 mm^-1
F(000)	1616
Crystal size	$0.1 \times 0.02 \times 0.01$ mm^3
Theta range for data collection	3.096 to 63.87°
Limiting indices	-34<=h<=31, -9<=k<=9, -15<=l<=19
Reflections collected / unique	11024 / 3265 [R(int) = 0.1291]
Data completeness	97.3 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3265 / 1 / 258
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.1445, wR2 = 0.3864
R indices (all data)	R1 = 0.2199, wR2 = 0.4465
Largest diff. peak and hole	0.56 and -0.40 e.Å^-3

Figure S129. Asymmetric unit of **3i**, obtained from a single crystal X-ray diffraction analysis. The thermal ellipsoids are scaled at the 50% probability level.
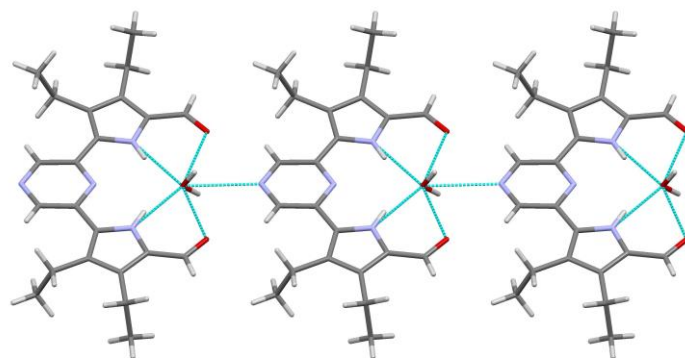
Figure S130. Hydrogen bond interactions in **3i** inferred from the single crystal X-ray diffraction analysis Hydrogen atoms have been removed for clarity.
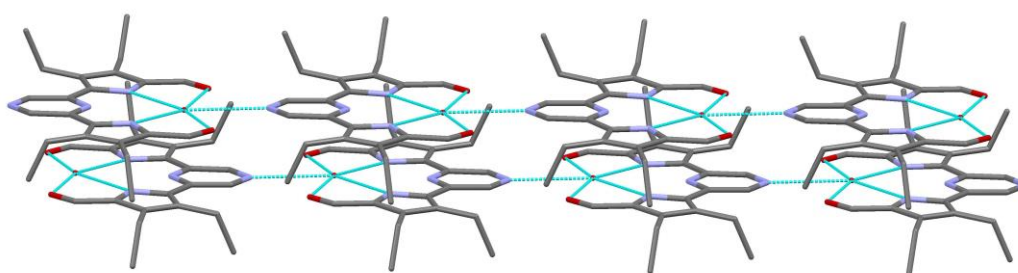

Figure S131. Packing diagram of **3i** along the crystallographic "*a*" axis from a single crystal X-ray diffraction analysis. Hydrogen atoms have been removed for clarity.
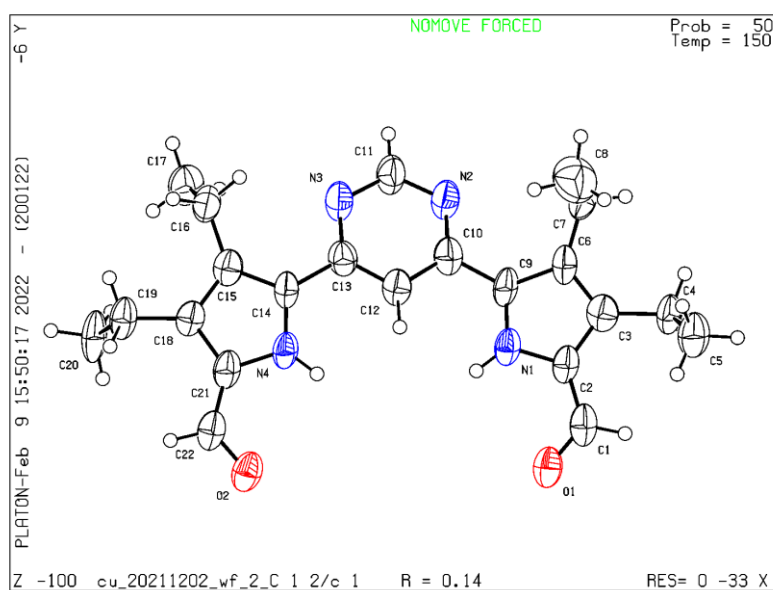
(d) X-ray diffraction analysis of single crystals of 3s:

Colorless block shaped crystals were obtained by vapor diffusion of hexanes into a THF solution of **3s**. The data were collected on a CCD area detector with a Cu$K\alpha$ radiation source (λ = 1.54178 Å). The data were collected at 173 K. The data were collected using ϕ- and ω-scans with a scan range of 4.019-66.732°. Crystallographic data are listed in the **Table S4**. Using Olex2[S11], the structure was solved with the SHELXT[S9] structure solution program using Intrinsic Phasing and refined with the SHELXL[S12] refinement package using Least Squares minimization.

Crystallographic data has been deposited in the Cambridge Crystallographic Data Center with CCDC number: 2298882. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

Table S4. Crystal data and structure refinement for **3s**.

Identification code	**3s**
Empirical formula	$C_{30} H_{31} N_3 O_2$
Formula weight	465.58
Temperature	173 K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, P2$_1$/n
Unit cell dimensions	a = 14.386 (6) Å α = 90º
	b = 7.518 (5) Å β = 101.20 (12)º
	c = 22.733 (12) Å γ = 90º
Volume	2412 (2) Å^3
Z, Calculated density	4, 1.282 Mg/m^3
Absorption coefficient	0.638 mm^-1
F(000)	992
Crystal size	0.500 x 0.400 x 0.400 mmm^3
Theta range for data collection	4.019 to 66.732º
Limiting indices	-17<=h<=16, -8<=k<=8, -26<=l<=27
Reflections collected / unique	15781 / 4207 [R(int) = 0.0758]
Data completeness	98.5 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4207 / 0 / 321
Goodness-of-fit on F^2	1.064
Final R indices [I>2sigma(I)]	R1 = 0.0465, wR2 = 0.1120
R indices (all data)	R1 = 0.0664, wR2 = 0.1235
Largest diff. peak and hole	0.22 and -0.23 e.Å^-3

Figure S132. Asymmetric unit of **3s**, obtained from a single crystal X-ray diffraction analysis. The thermal ellipsoids are scaled at the 50% probability level.
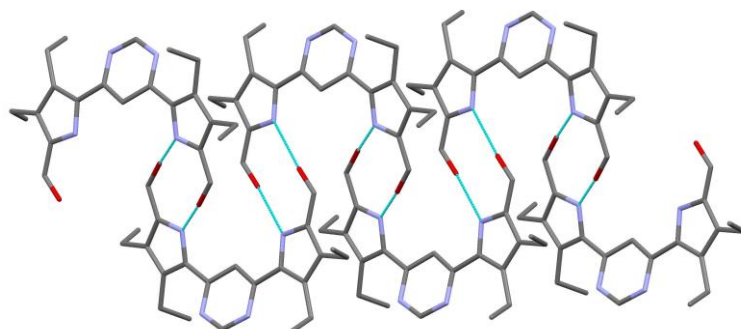
Figure S133. Hydrogen bond interactions in **3s** inferred from the single crystal X-ray diffraction analysis. Hydrogen atoms have been removed for clarity.
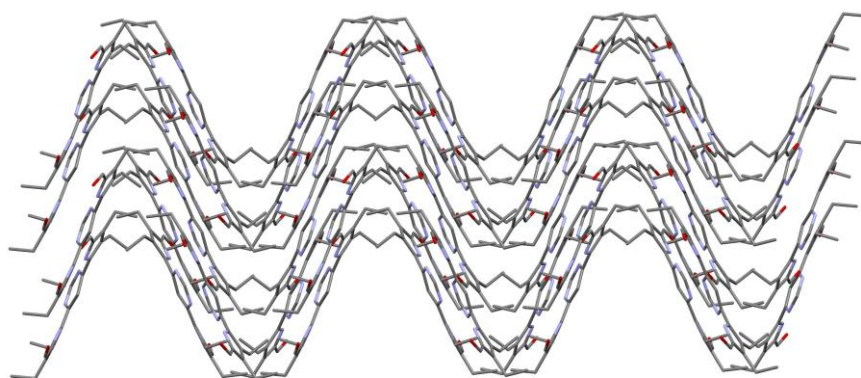

Figure S134. Packing diagram of **3s** along the crystallographic "*a*" axis from a single crystal X-ray diffraction analysis. Hydrogen atoms have been removed for clarity.
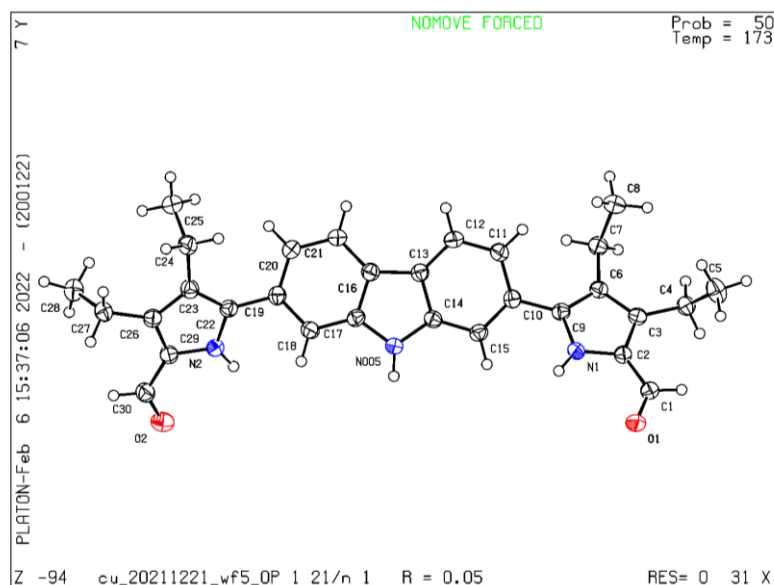
(e) X-ray diffraction analysis of single crystals of 3u:

Colorless block shaped crystals were obtained by vapor diffusion of hexanes into a THF solution of **3u**. The data were collected on a Bruker APEX-II CCD diffractometer with a Ga$K\alpha$ radiation source (λ = 1.34139 Å). The data were collected at 193 K. The data were collected using ϕ- and ω-scans with a scan range of 3.321-52.996°. Crystallographic data are listed in the **Table S5**. The structure was solved by direct methods using SHELXT[S9] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2018/3.

Crystallographic data has been deposited in the Cambridge Crystallographic Data Center with CCDC number: 2298883. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

Table S5. Crystal data and structure refinement for **3u**.

Identification code	3u•THF
Empirical formula	$C_{34} H_{39} N_3 O_3$
Formula weight	537.68
Temperature	193 (2) K
Wavelength	1.34139 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 11.1718 (7) Å α = 86.208 (3)º
	b = 11.1929 (7) Å β = 68.959 (3)º
	c = 12.4287 (8) Å γ = 88.712 (3)º
Volume	11447.34 (16) Å^3
Z, Calculated density	2, 1.234 Mg/m^3
Absorption coefficient	0.397 mm^-1
F(000)	576
Crystal size	$0.200 \times 0.050 \times 0.050$ mm^3
Theta range for data collection	3.321 to 52.996º
Limiting indices	-13<=h<=13, -13<=k<=13, -14<=l<=14
Reflections collected / unique	23837 / 5103 [R(int) = 0.0568]
Data completeness	99.6 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5103 / 0 / 353
Goodness-of-fit on F^2	1.111
Final R indices [I>2sigma(I)]	R1 = 0.0700, wR2 = 0.1408
R indices (all data)	R1 = 0.0903, wR2 = 0.1515
Largest diff. peak and hole	1.120 and -0.443 e.Å^-3

Figure S135. Asymmetric unit of **3u**, obtained from a single crystal X-ray diffraction analysis. The thermal ellipsoids are scaled at the 50% probability level.
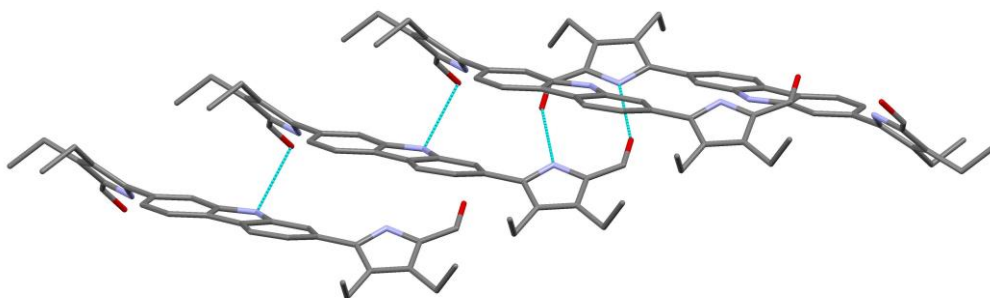
Figure S136. Hydrogen bond interaction in **3u** inferred from the single crystal X-ray diffraction analysis. Hydrogen atoms have been removed for clarity.
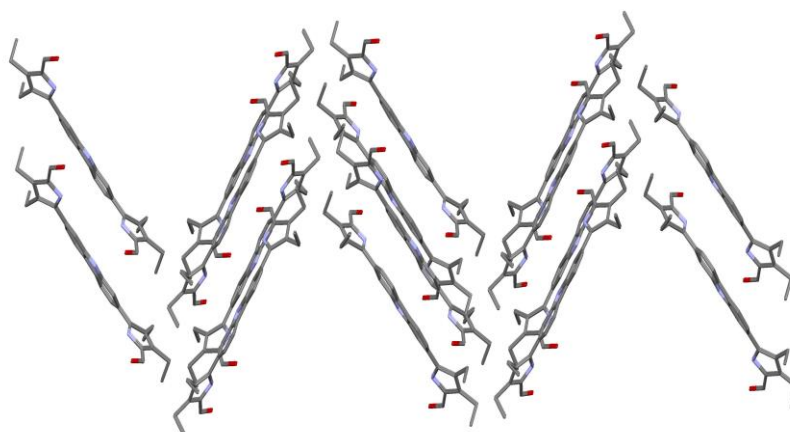

Figure S137. Packing diagram of **3u** along the crystallographic "*a"* axis from a single crystal X-ray diffraction analysis. Hydrogen atoms have been removed for clarity.
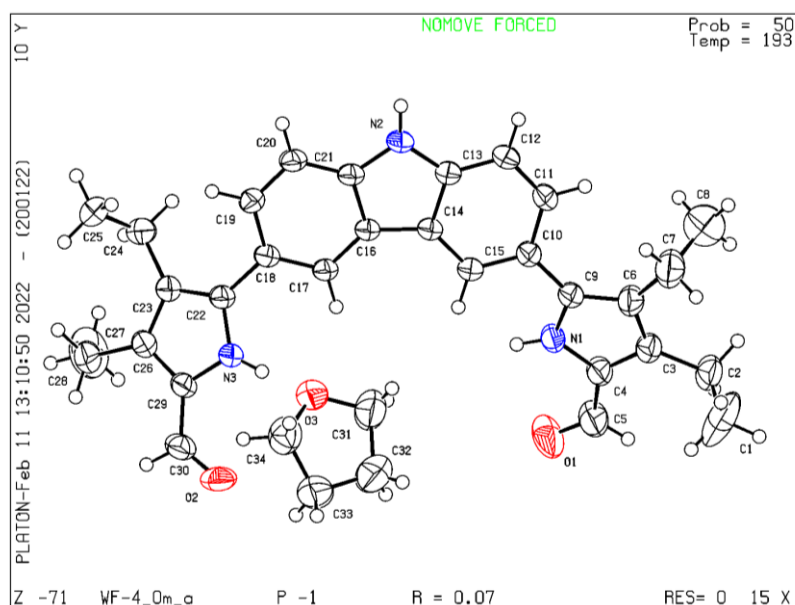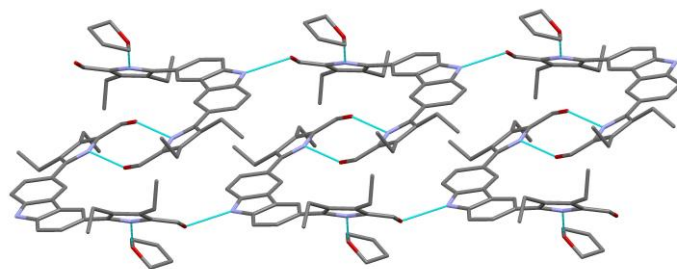
(f) X-ray diffraction analysis of single crystals of dipyrrole dialdehyde:

Colorless block shaped crystals were obtained by vapor diffusion of isopropyl ether into a CHCl$_3$ solution of **dipyrrole dialdehyde**. The data were collected on a Bruker APEX-II CCD diffractometer with a Cu$K\alpha$ radiation source (λ = 1.54178 Å). The data were collected at 173 K. The data were collected using ϕ- and ω-scans with a scan range of 3.566-63.813°. Crystallographic data are listed in the **Table S6**. Using Olex2[S11], the structure was solved with the SHELXT[S9] structure solution program using Intrinsic Phasing and refined with the SHELXL[S12] refinement package using Least Squares minimization.

Crystallographic data has been deposited in the Cambridge Crystallographic Data Center with CCDC number: 2298888. This data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

Table S6. Crystal data and structure refinement for **diformyl bipyrrole**.

Identification code	[diformyl bipyrrole]^2
Empirical formula	$C_{36} H_{46} N_4 O_4$
Formula weight	598.80
Temperature	173 K
Wavelength	1.54178 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 12.2720 (2) Å α = 72.2350 (10)º
	b = 12.5331 (2) Å β = 66.4510 (10)º
	c = 13.7088 (2) Å γ = 65.2320 (10)º
Volume	1730.90 (5) Å^3
Z, Calculated density	2, 1.1507 Mg/m^3
Absorption coefficient	0.598 mm^-1
F(000)	648
Crystal size	0.500 × 0.400 × 0.400 mm^3
Theta range for data collection	3.57 to 63.81º
Limiting indices	-14<=h<=14, -14<=k<=14, -15<=l<=15
Reflections collected / unique	27340 / 5708 [R(int) = 0.0577]
Data completeness	99.8 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5708 / 6 / 437
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0677, wR2 = 0.1690
R indices (all data)	R1 = 0.0982, wR2 = 0.1945
Largest diff. peak and hole	0.42 and -0.53 e.Å^-3

Figure S138. Asymmetric unit of **diformyl bipyrrole**, obtained from a single crystal X-ray diffraction analysis. The thermal ellipsoids are scaled at 50% probability level.

Figure S139. Hydrogen bond interactions seen in the solid-state structure of the **diformyl bipyrrole**. Hydrogen atoms have been removed for clarity.
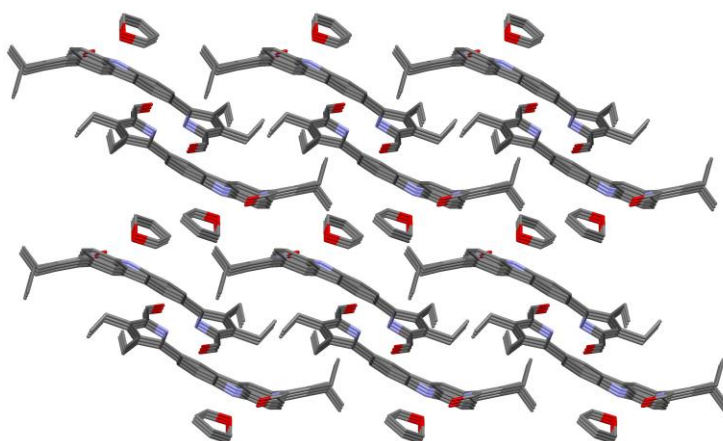

Figure S140. Packing diagram of **diformyl bipyrrole** along the crystallographic "*a*" axis from a single crystal X-ray diffraction analysis. Hydrogen atoms have been removed for clarity.

IV. References
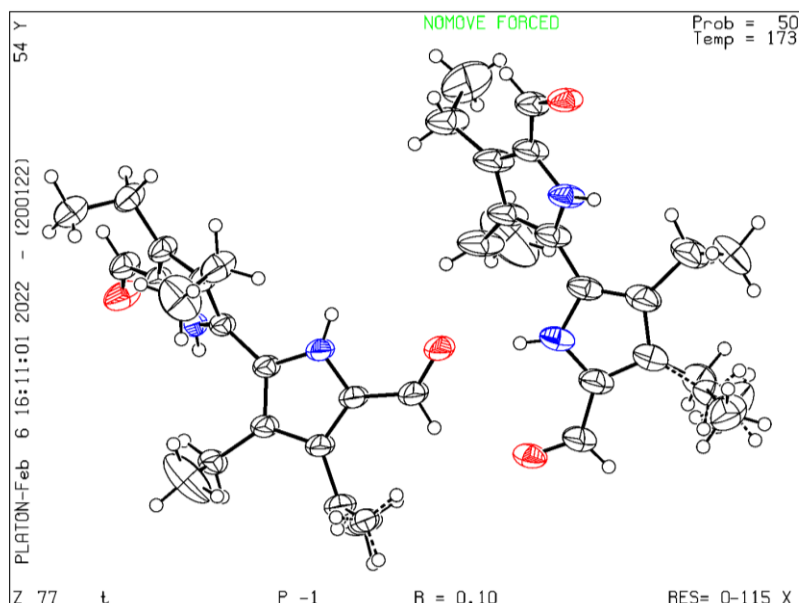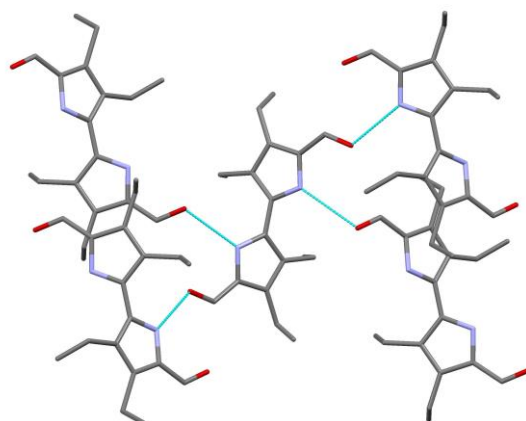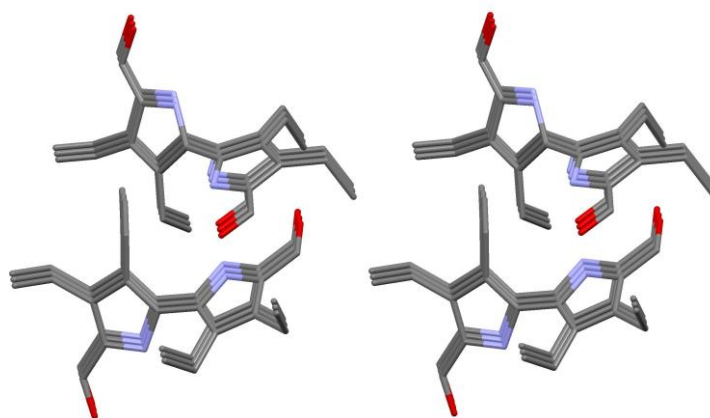
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