Supporting information

Insights into Extended Coupled Polymethines through the Investigation of Dual UV-to-NIR Acidochromic Switches Based on Heptamethine-Oxonol Dyes

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I. GENERAL REMARKS AND ANALYSIS CONDITIONS

Reagents and solvents. All reagents and solvents were purchased from Merck and were used as received. When heating was required, oil bathes were used. Column chromatography were performed on silica gel 60 (230–400 mesh). Optical properties were recorded in spectroscopic grade solvents.

Analytical methods and apparatus. Melting points (M.P.) were measured in open capillary tubes with a STUART SMP30 melting points apparatus and are uncorrected. NMR spectra were recorded with a Jeol 400 MHz NMR Spectrometer and a Bruker Avance III 600 MHz NMR Spectrometer equipped with a BBFO+ probe. NMR chemical shifts are given in ppm (δ) relative to Me_4Si with solvent resonances used as internal standards ($CDCl_3$: 7.26 ppm for ^1H and 77.2 for ^{13}C; CD_3OD: 3.31 ppm for ^1H and 49.0 for ^{13}C; DMSO-d_6: 2.50 ppm for ^1H and 39.5 for ^{13}C; TFA-*d*: 11.50 ppm for ^1H and 164.2 for ^{13}C). NMR peak assignments were confirmed using COSY, DEPT-135, HMQC and HMBC methods. The following abbreviations are used for multiplicity of NMR signals: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad signal and app = apparent multiplicity. FTIR spectra were recorded on an Agilent Cary 630 FTIR equipped with an attenuated total reflectance (ATR) sampling. UV-Vis-NIR absorption spectra were recorded on a Cary 50 Scan UV-Visible-NIR spectrophotometer at room temperature with a 300 nm/min scan rate. UV-Vis-NIR thin layer absorption spectra were recorded on a Cary 5000 UV-Vis-NIR Spectrophotometer, with 0% and 100% transmittance correction. HRMS analyses were performed on a QStar Elite (Applied Biosystems SCIEX) or a SYNAPT G2 HDMS (Waters) spectrometers by the “Spectropole” of the Aix-Marseille University. These two instruments are equipped with an ESI or MALDI source and a TOF mass analyzer.

Fluorescence. Emission spectra were measured using a Horiba-Jobin Yvon Fluorolog-3 spectrofluorometer equipped with a three-slit double-grating excitation and a spectrograph emission monochromator with dispersions of 2.1 nm mm^{-1} (1200 grooves per mm). A 450 W xenon continuous wave lamp provided excitation. The luminescence of diluted solutions was detected at right angle using 10 mm quartz cuvettes. Fluorescence quantum yields Φ were measured in diluted dichloromethane solution with an optical density lower than 0.1 using the following equation (eq. 1):

$$\frac{\Phi_x}{\Phi_r} = \left(\frac{A_r(\lambda)}{A_x(\lambda)}\right)\left(\frac{n_x^2}{n_r^2}\right)\left(\frac{D_x}{D_r}\right) \quad (eq.1)$$

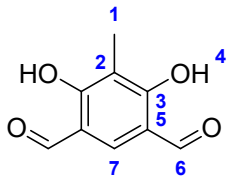
where A is the absorbance at the excitation wavelength (λ), n the refractive index and D the integrated intensity. The letters “r” and “x” stand for reference and sample. The fluorescence quantum yields of dicationic and cationic derivatives were measured relative Coumarin 153 (Φ = 38% in EtOH)[2] or Oxazine 725 (Φ = 14% in EtOH),[3] respectively.

Short luminescence decay was monitored using a Horiba DeltaFlex modular fluorescence lifetime system equipped with a TC-SPC. Excitation was performed using a DeltaDiode (Model: DD-440L; peak wavelength: 438 nm) and Ludox in distilled water was used to determine the instrumental response function used for deconvolution, which was performed using the EzTime software.

Thin film preparation and acidochromic switching. The thin films of **dsp-1** were prepared *via* spin coating technique by depositing 300 µL of a solution of **dsp-1** in CH_2Cl_2 (5 mg/mL + 10 wt.% polyvinylpyrrolidone (~55 kmol/g) on a glass substrate (25 mm x 25 mm x 1 mm), which was then subjected to an intense rotation (1000 rpm) for 60 seconds. The thin layers thus prepared were dried under vacuum for 1 hour before recording absorption spectra. The vapochromic properties were investigated by subjecting the thin layer of **dsp-1** to the vapours of a concentrated aqueous solution of hydrochloric acid (37%) or vapours of aqueous ammonia (28%) until the colour change was visible (within few seconds). The fatigue was evaluated by alternating HCl vapours or NH_3 vapours and recording the absorption spectra between each exposure to monitor the absorbance variation at 660 nm.

II. SYNTHETICS PROTOCOLS AND CHARACTERIZATION

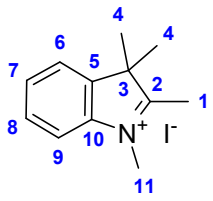
4,6-Dihydroxy-5-methylisophthalaldehyde (6)



This synthetic procedure was adapted from the literature.[4] Formamidine acetate (10.06 g, 96.7 mmol, 4.00 equiv.) and 2-methylresorcinol (3.00 g, 24.2 mmol, 1.00 equiv.) were dissolved in 300 mL of THF. Once the solution was heated up to 55 °C, acetic anhydride (19.74 g, 193.0 mmol, 8.00 equiv.) was added to the mixture. The reaction was then allowed to proceed under stirring for 24 hours, then it was cooled to room temperature and the solvents were removed under reduced pressure. The residue was dissolved in 250 mL of distilled water and was stirred for 2 hours. Then, 150 mL of an aqueous solution of HCl (1 M) were added and the solution was further stirred for 4 hours at room temperature. The mixture was then extracted with CH_2Cl_2, the organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. If necessary, the crude can be further purified by column chromatography (SiO_2, pure CH_2Cl_2 as eluent) to afford **6** as a white fibre-like solid (2.84 g, 15.76 mmol, 64% yield).

R*f* = 0.60 (SiO_2, pure CH_2Cl_2). **M. P.:** 185 – 187 °C. **^{1}H NMR (400 MHz, DMSO-d_6):** δ (ppm) = 11.92 (s, 2H, *H*-4). 9.92 (s, 2H, *H*-6), 8.18 (s, 1H, *H*-7), 2.03 (s, 3H, *H*-1).**^{13}C{^{1}H} NMR (101 MHz. DMSO-d_6):** δ (ppm) = 195.1 (*C*-6), 164.8 (*C*-3), 139.2 (*C*-7), 115.3 (*C*-5), 111.7 (*C*-2), 6.9 (*C*-1). **IR (neat):** ν (cm^{-1}) = 3740, 3676, 3652, 1633, 1603, 1512, 1453, 1393, 1374, 1337, 1298, 1157, 1004, 771, 722.

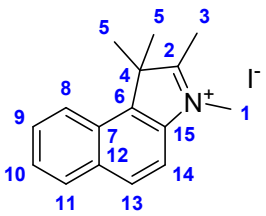
1,1,2,3-tetramethyl-1*H*-indolium iodide (7)



This synthetic procedure was adapted from the literature.[5] Methyl iodide (2.77 g, 19.5 mmol, 1.50 equiv.) was added to a solution of 1,1,2-trimethylindolenine (2.07 g, 13.0 mmol, 1.00 equiv.) in 15 mL of anhydrous MeCN. The mixture was refluxed for 16 hours. The solution was then cooled to room temperature, diluted with Et_2O and filtered to recover the precipitate, which was further washed with Et_2O to afford **7** as a pale pink powder (3.64 g, 12.1 mmol, 93% yield).

R*f* = 0.29 (SiO_2, CH_2Cl_2:MeOH, 95:5). **M. P.:** 256 – 258 °C. **^{1}H NMR (400 MHz, DMSO-d_6):** δ (ppm) = 7.92 – 7.87 (m, 1H, *H*-15), 7.85 – 7.80 (m, 1H, *H*-10), 7.67 – 7.58 (m, 2H, *H*-11), 3.97 (s, 3H, *H*-11), 2.77 (s, 3H, *H*-1), 1.53 (s, 6H, *H*-4).**^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6):** δ (ppm) = 196.0 (*C*-2), 142.1 (*C*-10), 141.6 (*C*-5), 129.3 (*C*-8), 128.8 (*C*-7), 123.3 (*C*-6), 115.1 (*C*-9), 53.9 (*C*-3), 34.7 (*C*-11), 21.7 (*C*-4), 14.1 (*C*-1). **IR (neat):** ν (cm^{-1}) = 3025, 2965, 2929, 2002, 1630, 1480, 1455, 1393, 1356, 1296, 1171, 1124, 1091, 989, 938, 816, 776, 679, 629, 571, 540.

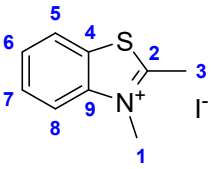
1,1,2,3-tetramethyl-1*H*-benzo[e]indolium iodide (8)



This synthetic procedure was adapted from the literature.[5] Methyl iodide (2.16 g, 15.21 mmol, 1.5 equiv.) was added to a solution of 1,1,2-trimethyl-3*H*-benzo[*e*]indole (2.12 g, 10.14 mmol, 1.0 equiv.) in 10 mL of anhydrous MeCN. The mixture was refluxed for 16 hours, then it was cooled to room temperature. The formed precipitate was recovered by filtration and washed with Et_2O to afford **8** as a pale green powder (3.23 g, 9.20 mmol, 91% yield).

R*f* = 0.29 (SiO_2, CH_2Cl_2:MeOH, 95:5). **M. P.:** 233 – 235 °C. **^{1}H NMR (400 MHz, DMSO-d_6):** δ (ppm) = 8.37 (d, $^3J_{8.9}$ = 8.4 Hz, 1H, *H*-8), 8.29 (d, $^3J_{13.14}$ = 9.2 Hz, 1H, *H*-13), 8.22 (d, $^3J_{11.10}$ = 7.5 Hz, 1H, *H*-11), 8.11 (d, $^3J_{14.13}$ = 9.0 Hz, 1H, *H*-14), 7.78 (t, $^3J_{9.10}$ = 7.3 Hz, $^3J_{9.8}$ = 8.1 Hz, 1H, *H*-9), 7.72 (t, $^3J_{10.9}$ = 7.3 Hz, $^3J_{10.11}$ = 7.5 Hz, 1H, *H*-10), 4.45 (s, 3H, *H*-1), 2.88 (s, 3H, *H*-3), 1.75 (s, 6H, *H*-5). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6):** δ (ppm) = 196.0 (*C*-2), 139.5 (*C*-6), 136.5 (*C*-15), 133.0 (*C*-9), 130.5 (*C*-8), 129.8 (*C*-10), 128.4 (*C*-12), 127.1 (*C*-11), 123.4 (*C*-13), 113.2 (*C*-7), 55.3 (*C*-4), 35.1 (*C*-3), 21.3 (*C*-5), 14.0 (*C*-1). **IR (neat):** ν (cm^{-1}) = 3068, 2971, 2015, 1963, 1909, 1634, 1578, 1522, 1466, 1392, 1329, 1266, 1220, 1175, 1134, 1102, 1025, 994, 941, 893, 862, 808, 740, 701.

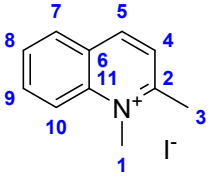
2,3-dimethylbenzothiazolium iodide (9)



This synthetic procedure was adapted from the literature.[6] Methyl iodide (2.25 g, 15.84 mmol, 1.5 equiv.) was added to a solution of 2-methylbenzothiazole (1.576 g, 10.56 mmol, 1.0 equiv.) in 8 mL of anhydrous MeCN. The mixture was refluxed for 16 hours, then it was cooled to room temperature and diluted with Et_2O. The formed precipitate was recovered by filtration and was washed with Et_2O to afford **9** as a white powder (2.897 g, 9.95 mmol, 94% yield).

R*f* = 0.23 (SiO_2, CH_2Cl_2:MeOH, 95:5). **M. P.:** 223 – 225 °C. **^{1}H NMR (400 MHz, DMSO-d_6):** δ (ppm) = 8.45 (d, $^3J_{5.6}$ = 8.2 Hz, 1H, *H*-5). 8.29 (d, $^3J_{8.7}$ = 8.6 Hz, 1H, *H*-8), 7.89 (dd, $^3J_{7.6}$ = 8.0 Hz, $^3J_{7.8}$ = 7.6 Hz, 1H, *H*-7), 7.80 (dd, $^3J_{6.5}$ = 7.3 Hz, $^3J_{6.7}$ = 8.0 Hz, 1H, *H*-6), 4.20 (s, 3H, *H*-1), 3.18 (s, 3H, *H*-3). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6):** δ (ppm) = 177.3 (*C*-2), 141.6 (*C*-9), 129.3 (*C*-7), 128.7 (*C*-4), 128.1 (*C*-6), 124.5 (*C*-5), 116.8 (*C*-8), 36.3 (*C*-1), 17.2 (*C*-3). **IR (neat):** ν (cm^{-1}) = 2962, 2063, 1994, 1942, 1581, 1524, 1442, 1361, 1333, 1272, 1207, 1161, 1129, 1094, 1054, 1010, 950, 810, 763, 717, 671.

1,2-dimethylquinolinium iodide (10)

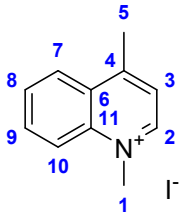


This synthetic procedure was adapted from the literature.[6] Methyl iodide (9.73 g, 68.53 mmol, 2.0 equiv.) was added to a solution of 2-methylquinoline (4.91 g, 34.27 mmol, 1.0 equiv.) in 10 mL of anhydrous MeCN. The mixture was refluxed for 16 hours, then it was cooled to room temperature. The solution was diluted with Et_2O

and the formed precipitate was recovered by filtration and was washed with Et_2O to afford **10** as a pale orange powder (9.33 g, 32.71 mmol, 95% yield).

R*f* = 0.14 (SiO_2, CH_2Cl_2:MeOH, 95:5). **M. P.:** 190 – 192 °C. **^{1}H NMR (400 MHz, CD_3OD):** δ (ppm) = 9.01 (d, $^3J_{5.4}$ = 8.6 Hz, 1H, *H*-5), 8.55 (d, $^3J_{10.9}$ = 8.6 Hz, 1H, *H*-10), 8.36 (d, $^3J_{7.8}$ = 8.2 Hz, 1H, *H*-7), 8.25 (dd, $^3J_{9.8}$ = 7.2 Hz, $^3J_{9.10}$ = 8.6 Hz, 1H,*H*-9), 8.03 (d, $^3J_{4.5}$ = 8.6 Hz, 1H. *H*-4), 7.99 (app t, $^3J_{8.9}$ = 7.5 Hz, $^3J_{8.7}$ = 7.5 Hz, 1H, *H*-8), 4.54 (s, 3H, *H*-1), 3.15 (s, 3H, *H*-3). **^{13}C{^{1}H} NMR (101 MHz, CD_3OD):** δ (ppm) = 162.4 (*C*-2), 147.2 (*C*-5), 141.3 (*C*-11), 136.7 (*C*-9), 131.7 (*C*-7), 130.5 (*C*-8), 129.9 (*C*-6), 126.2 (*C*-4), 119.7 (*C*-10), 40.4 (*C*-1), 23.6 (*C*-3). **IR (neat):** ν (cm^{-1}) = 3031, 2987, 2893, 2413, 1845, 1602, 1521, 1429, 1356, 1334, 1291, 1225, 1151, 1120, 1070, 1038, 973, 879, 855, 835, 777, 749, 687, 570.

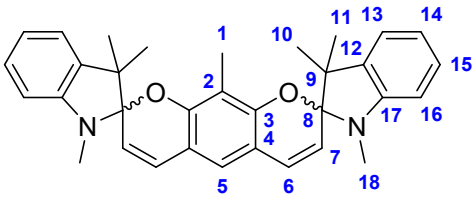
1,4-dimethylquinolinium iodide (11)



This synthetic procedure was adapted from the literature.[6] Methyl iodide (4.60 g, 32.37 mmol, 2.0 equiv.) was added to a solution of 4-methylquinoline (2.32 g, 16.19 mmol, 1.0 equiv.) in 5 mL of anhydrous MeCN. The mixture was refluxed for 16 hours, then it was cooled to room temperature. The solution was diluted with Et_2O and the formed precipitate was recovered by filtration and was washed with Et_2O to afford **11** as a pale orange powder (4.58 g, 16.05 mmol, 99% yield).

R*f* = 0.20 (SiO_2, CH_2Cl_2:MeOH, 95:5). **M. P.:** 168 – 170 °C. **^{1}H NMR (400 MHz, CD_3OD):** δ (ppm) = 9.20 (d, $^3J_{2.3}$ = 5.9 Hz, 1H, *H*-2), 8.57 (d, $^3J_{10.9}$ = 8.6 Hz, 1H, *H*-10), 8.49 (d, $^3J_{7.8}$ = 8.6 Hz, 1H, *H*-7), 8.28 (dd, $^3J_{9.8}$ = 7.5 Hz, $^3J_{9.10}$ = 7.9 Hz, 1H, *H*-9), 8.08 (d, $^3J_{8.7}$ = 8.1 Hz, $^3J_{8.9}$ = 7.4 Hz, 1H, *H*-8), 7.96 (d, $^3J_{3.2}$ = 5.7 Hz, 1H, *H*-3), 4.65 (s, 3H, *H*-1), 3.07 (s, 3H, *H*-3). **^{13}C{^{1}H} NMR (101 MHz, CD_3OD):** δ (ppm) = 160.7 (*C*-4), 149.9 (*C*-11), 139.7 (*C*-2), 136.6 (*C*-8), 131.1 (*C*-9), 130.6 (*C*-6), 128.0 (*C*-3), 123.7 (*C*-7), 120.2 (*C*-10), 56.0 (*C*-1), 20.2 (*C*-5). **IR (neat):** ν (cm^{-1}) = 3416, 3056, 3009, 2328, 2178, 1604, 1586, 1526, 1485, 1437, 1395, 1366, 1345, 1262, 1230, 1162, 1108, 1076, 1031, 951, 876, 833, 779, 700, 619, 543.

1,1",3,3,3",3",10'-Heptamethyldispiro[indoline-2,2'(2*H*,8*H*)-pyrano[3,2-g]chromene-8',2"-indoline] (dsp-1)

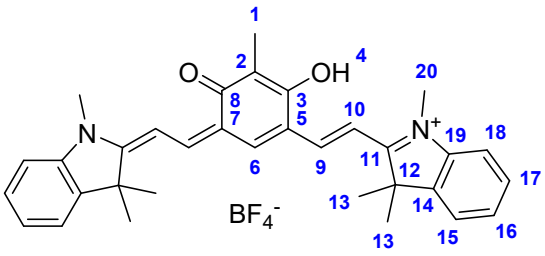


To a solution of 4,6-dihydroxy-5-methylisophthalaldehyde **6** (112.4 mg, 0.62 mmol, 1 equiv.) and 1,1,2,3-tetramethyl-1*H*-indolium iodide **7** (394.6 mg, 1.31 mmol, 2.1 equiv.) in 10 mL of absolute EtOH was added two drops of piperidine. The mixture was heated up to 95 °C for 16 hours, then the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2, washed two times with a saturated aqueous solution of $NaHCO_3$. The organic layer was dried over anhydrous $MgSO_4$, filtered and the solvent was removed under reduced pressure. The residue was further purified by column chromatography (SiO_2), first packed with pure CH_2Cl_2 and basified with a solution of triethylamine in

CH_2Cl_2, then eluted with CH_2Cl_2/MeOH (98:2) to afford **dsp-1** as a pink powder (289.7 mg, 0.59 mmol, 95% yield).

R*f* = 0.92 (SiO_2, CH_2Cl_2:MeOH, 98:2). **M. P.:** 65 – 67 °C. **^{1}H NMR (400 MHz, $CDCl_3$ filtered over basic Al_2O_3):** δ (ppm) = 7.14 (dd, $^3J_{14.15}$ = 7.5 Hz, $^3J_{14.13}$ = 7.6 Hz, 2H, *H*-14). 7.03 (d, $^3J_{16.15}$ = 7.2 Hz, 2H, *H*-16), 6.80 (dd, $^3J_{15.14}$ = 7.3 Hz, $^3J_{15.16}$ = 7.2 Hz, 2H, *H*-15), 6.75 (d, $^3J_{6.7}$ = 10.2 Hz, 2H, *H*-6), 6.62 (s, 1H, *H*-5), 6.48 (d, $^3J_{13.14}$ = 7.9 Hz, 2H, *H*-13), 5.51 (d, $^3J_{7.6}$ = 10.2 Hz, 2H, *H*-7), 2.67 (s, 6H, *H*-18), 1.58 (s, 3H, *H*-1), 1.25 (s, 6H, *H*-11), 1.15 (s, 6H, *H*-10). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ filtered over basic Al_2O_3):** δ (ppm) = 153.5 (*C*-3), 148.4 (*C*-17), 137.1 (*C*-12), 129.2 (*C*-6), 127.5 (*C*-14), 121.7 (*C*-16), 121.5 (*C*-5), 119.0 (*C*-15), 116.3 (*C*-7), 111.5 (*C*-4), 110.5 (*C*-2), 106.8 (*C*-13), 104.5 (*C*-8), 51.4 (*C*-9), 29.0 (*C*-18), 26.1 (*C*-10), 20.4 (*C*-11), 7.1 (*C*-1). **HRMS (ESI-TOF):** calculated for $[M+H]^+$ ($C_{33}H_{35}N_2O_2^+$) 491.2693, found 491.2694. **IR (neat):** ν (cm^{-1}) = 3048, 2959, 2865, 2068, 1634, 1607, 1484, 1456, 1419, 1390, 1358, 1329, 1300, 1277, 1240, 1183, 1132, 1097, 1066, 935, 882, 789, 741, 719, 659.

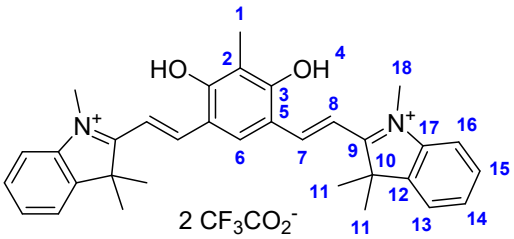
mono(2-((*E*)-2-((*Z*)-6-hydroxy-5-methyl-4-oxo-3-(2-((*E*)-1,3,3-trimethylindolin-2-ylidene)ethylidene)cyclohexa-1,5-dien-1-yl)vinyl)-1,1,3-trimethyl-3*H*-indol-1-ium) tetrafluoroborate (1•H$^+$)



To a solution of 4,6-dihydroxy-5-methylisophthalaldehyde **6** (100 mg, 0.55 mmol, 1 equiv.) and 1,1,2,3-tetramethyl-1*H*-indolium iodide **7** (351.1 mg, 1.17 mmol, 2.1 equiv.) in 10 mL of absolute EtOH was added two drops of piperidine. The mixture was heated up to 95 °C for 16 hours, then the solution was cooled down to room temperature. 100 µL of HBF_4 (48%, aqueous) were added and the mixture was allowed to stir at room temperature for 6 hours. The solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2, and further purified by column chromatography (SiO_2) using CH_2Cl_2:MeOH as eluent (98:2 to 9:1) to afford **1•H$^+$** as a bright blue powder (42.3 mg, 0.073 mmol, 13% yield).

R*f* = 0.66 (SiO_2, CH_2Cl_2/MeOH, 9:1). **M. P.:** 215 – 217 °C. **^{1}H NMR (400 MHz, DMSO-d_6):** δ (ppm) = 8.84 (s, 1H, *H*-6), 8.08 (d, $^3J_{9.10}$ = 15.4 Hz, 2H, *H*-9), 7.74 (d, $^3J_{18.17}$ = 7.3 Hz, 2H, *H*-18), 7.65 (d, $^3J_{15.14}$ = 8.0 Hz, 2H, *H*-15), 7.60 – 7.50 (m, 4H, *H*-10 and *H*-16), 7.43 (app t, $^3J_{17.16}$ = 7.4 Hz, $^3J_{17.18}$ = 7.5 Hz, 2H, *H*-17), 5.47 (br s, 1H, *H*-4), 3.82 (s, 6H, *H*-20), 1.74 (s, 12H, *H*-13), 1.40 (s, 3H, *H*-1).**^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6):** δ (ppm) = 198.3 (*C*-8), 179.6 (*C*-11), 142.7 (*C*-9), 129.5 (*CH*), 127.8 (*CH*), 123.2 (*CH*), 117.2 (*CH*), 113.6 (C_{quat}), 104.8 (*C*-10), 83.5 (*C*-2), 50.9 (*C*-12), 33.0 (*C*-20), 28.8 (*C*-1), 27.6 & 27.5 (*C*-13).**^{19}F NMR (DMSO-d_6, 377 MHz):** δ (ppm) = -148.0 (BF_4^-). **IR (neat):** ν (cm^{-1}) = 2954, 2927, 2121, 2084, 1997, 1944, 1927, 1734, 1679, 1631, 1564, 1538, 1520, 1474, 1442, 1398, 1347, 1262, 1223, 1199, 1170, 1100, 1012, 990, 923, 893, 857, 800, 745, 695, 662.

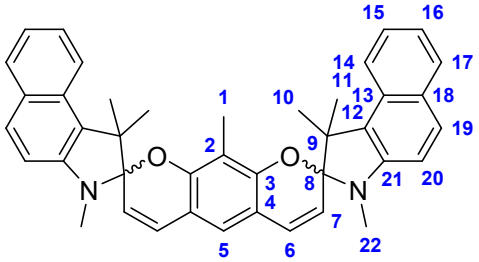
2,2'-((1*E*,1'*E*)-(4,6-dihydroxy-5-methyl-1,3-phenylene)bis(ethene-2,1-diyl))bis(1,3,3-trimethyl-3*H*-indol-1-ium) bis(trifluoroacetate) (1•2H^{2+})



1•H$^+$ was generated *in situ* by dissolution of compound **dsp-1** in deuterated trifluoroacetic acid.

^{1}H NMR (400 MHz, TFA-*d*): δ (ppm) = 8.46 – 8.55 (m, 8H, *H*-13, *H*-14, *H*-15, *H*-16), 8.45 (br s, 2H, *H*-4), 8.39 (d, $^3J_{7.8}$ = 13.0 Hz, 2H, *H*-7), 8.23 (s, 1H, *H*-6), 7.45 (d, $^3J_{8.7}$ = 12.7 Hz, 2H, *H*-8), 4.40 (s, 6H, *H*-18), 2.89 (s, 3H, *H*-1), 2.56 (s, 12H, *H*-11). **^{13}C{^{1}H} NMR (101 MHz, TFA-*d*):** δ (ppm) = 192.7 (*C*-9), 158.4 (*C*-3), 146.0 (*C*-7), 143.8 (*C*-12), 143.4 (*C*-17), 138.1 (*C*-6), 132.6 (*C*-13 or *C*-14 or *C*-15 or *C*-16), 131.5 (*C*-13 or *C*-14 or *C*-15 or *C*-16), 124.9 (*C*-13 or *C*-14 or *C*-15 or *C*-16), 119.1 (*C*-5), 116.2 (*C*-13 or *C*-14 or *C*-15 or *C*-16), 112.4 (*C*-8), 56.2 (*C*-10), 37.0 (*C*-18), 24.8 (*C*-11), 9.0 (*C*-1). **^{19}F NMR (TFA-*d*. 377 MHz):** δ (ppm) = -76.6 ($CF_3CO_2^-$).

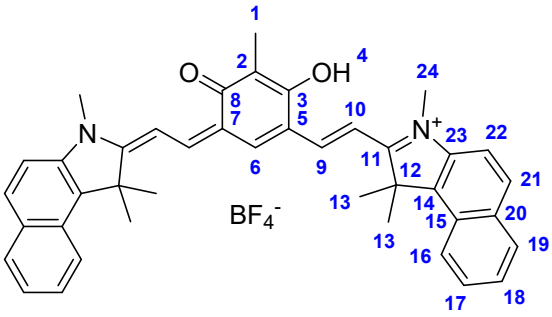
1,1",3,3,3",3",10'-Heptamethyldispiro[benzo[e]indoline-2,2'(2*H*,8*H*)-pyrano[3,2-g]chromene-8',2"-benzo[e]indoline] (dsp-2)



To a solution of 4,6-dihydroxy-5-methylisophthalaldehyde **6** (89.3 mg, 0.496 mmol, 1.0 equiv.) and 1,1,2,3-tetramethyl-1*H*-benzo[*e*]indolium iodide **8** (365.6 mg, 1.04 mmol, 2.1 equiv.) in 10 mL of absolute EtOH was added two drops of piperidine. The mixture was heated up to 95 °C for 16 hours, then it was cooled down to room temperature and the solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2. washed with a saturated aqueous solution of $NaHCO_3$. The organic layer was then dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was further purified by column chromatography (SiO_2), first packed with pure CH_2Cl_2 and basified with a solution of triethylamine in CH_2Cl_2, then eluted with CH_2Cl_2/MeOH (95:5) to afford **dsp-2** as a blue powder (237.0 mg, 0.401 mmol, 81% yield).

R*f* = 0.90 (SiO_2, CH_2Cl_2:MeOH, 98:2). **M. P.:** 130 – 132 °C. **^{1}H NMR (400 MHz, $CDCl_3$ filtered over basic Al_2O_3):** δ (ppm) = 7.92 (d, $^3J_{14.15}$ = 8.6 Hz, 2H, *H*-14), 7.78 (d, $^3J_{17.16}$ = 8.3 Hz, 2H, *H*-17), 7.70 (d, $^3J_{20.19}$ = 8.8 Hz, 2H, *H*-20), 7.38 (dd, $^3J_{15.14}$ = 7.2 Hz, $^3J_{15.16}$ = 7.6 Hz, 2H, *H*-15), 7.19 (dd, $^3J_{16.17}$ = 7.2 Hz, $^3J_{16.15}$ = 7.6 Hz, 2H, *H*-16), 6.93 (d, $^3J_{19.20}$ = 8.1 Hz, 2H, *H*-19), 6.82 (d, $^3J_{6.7}$ = 10.2 Hz, 2H, *H*-6), 5.59 (d, $^3J_{7.6}$ = 10.2 Hz, 2H, *H*-7), 6.66 (s, 1H, *H*-5), 2.77 (s, 6H, *H*-22), 1.60 (s, 6H, *H*-11), 1.49 (s, 3H, *H*-1), 1.33 (s, 6H, *H*-10). **RMN ^{13}C{^{1}H} (101 MHz, $CDCl_3$ filtered over basic Al_2O_3):** δ (ppm) = 153.7 (*C*-3), 146.0 (*C*-21), 130.2 (*C*-18), 129.6 (*C*-17), 129.4 (*C*-13), 128.8 (*C*-20), 126.1 (*C*-15), 126.0 (*C*-12), 121.9 (*C*-5), 121.6 (*C*-14), 121.4 (*C*-16), 115.7 (*C*-7), 111.3 (*C*-4), 110.4 (*C*-19), 110.2 (*C*-2), 105.4 (*C*-8), 53.0 (*C*-9), 29.3 (*C*-22), 24.2 (*C*-10), 21.9 (*C*-11), 7.1 (*C*-1). **HRMS (ESI-TOF):** calculated for $[M+H]^+$ ($C_{41}H_{39}N_2O_2^+$) 591.3006, found 591.3003. **IR (neat):** ν (cm^{-1}) = 3740, 3674, 2984, 2905, 2393, 2238, 2005, 1623, 1515, 1454, 1388, 1330, 1274, 1237, 1126, 1072, 1062, 1014, 926, 897, 802, 737.

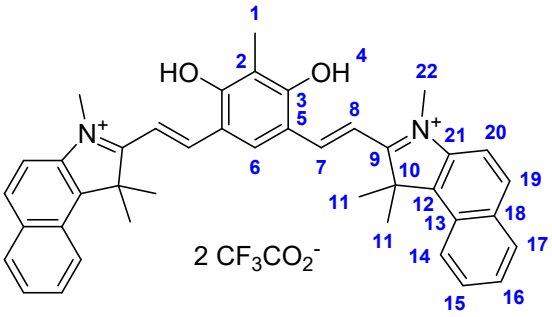
mono(2-((*E*)-2-((*Z*)-6-hydroxy-5-methyl-4-oxo-3-(2-((*E*)-1,3,3-trimethylindolin-2-ylidene)ethylidene)cyclohexa-1,5-dien-1-yl)vinyl)-1,1,3-trimethyl-3*H*-indol-1-ium) tetrafluoroborate (2•H$^+$)



To a solution of 4,6-dihydroxy-5-methylisophthalaldehyde **6** (113.1 mg, 0.63 mmol, 1.0 equiv.) and 1,1,2,3-tetramethyl-1*H*-benzo[*e*]indolium iodide **8** (463.0 mg, 1.32 mmol, 2.1 equiv.) in 20 mL of absolute EtOH was added two drops of piperidine. The mixture was heated up to 95 °C for 16 hours, then the solution was cooled down to room temperature. 300 µL of HBF_4 (48%, aqueous) were added and the mixture was allowed to stir at room temperature for 2 hours. The solvent was removed under reduced pressure and the residue was dissolved in CH_2Cl_2, and further purified by column chromatography (SiO_2, 98:2 to 9:1, CH_2Cl_2:MeOH as eluent) to afford **2•H$^+$** as a bright blue powder (41.3 mg, 0.061 mmol, 10% yield).

R*f* = 0.32 (SiO_2, CH_2Cl_2:MeOH, 9:1). **M. P.:** 231 – 233 °C. **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ (ppm) = 8.89 (s, 1H, *H*-6), 8.37 (d, $^3J_{16.17}$ = 8.5 Hz, 2H, *H*-16), 8.25 – 8.17 (m, 4H, *H*-10 and *H*-21), 8.15 (d, $^3J_{19.18}$ = 8.3 Hz, 2H, *H*-19), 7.95 (d, $^3J_{22\cdot21}$ = 8.8 Hz, 2H, *H*-22), 7.74 (t, $^3J_{17.16}$ = 7.4 Hz, $^3J_{17.18}$ = 7.6 Hz, 2H, *H*-17), 7.65 – 7.55 (m, 4H, *H*-9 and *H*-18), 5.49 (br s, 1H, *H*-4), 3.96 (s, 6H, *H*-24), 2.00 (s, 12H, *H*-13), 1.44 (s, 3H, *H*-1). **^{13}C{^{1}H} NMR (101 MHz, DMSO-*d*$_6$):** δ (ppm) = 197.6 (*C*-8), 179.7 (*C*-11), 148.6 (*C*-9), 139.9 (*C*-23), 135.4 (*C*-15), 132.2 (*C*-14), 130.5 (*C*-21), 130.0 (*C*-19), 128.1 (*C*-17), 127.1 (*C*-20), 125.9 (*C*-18), 122.7 (*C*-16), 116.7 (*C*-5), 112.5 (*C*-22), 103.8 (*C*-10), 51.9 (*C*-12), 33.0 (*C*-24), 28.1 (*C*-1), 26.7 & 26.6 (*C*-13). The signals corresponding to *C*-3 and *C*-6 are missing despite long accumulation in a concentrated NMR sample. **^{19}F NMR (DMSO-*d*$_6$, 377 MHz):** δ (ppm) = -148.1 (*BF_4^-*). **IR (neat):** ν (cm^{-1}) = 3637, 2971, 2925, 2861, 2129, 1920, 1680, 1629, 1565, 1540, 1521, 1473, 1441, 1397, 1346, 1262, 1223, 1196, 1170, 1013, 988, 920, 894, 745, 695, 661.

2,2'-((1*E*,1'*E*)-(4,6-dihydroxy-5-methyl-1,3-phenylene)bis(ethene-2,1-diyl))bis(1,3,3-trimethyl-3*H*-benzo[e]indol-3-ium) bis(trifluoroacetate) (2•2H^{2+})

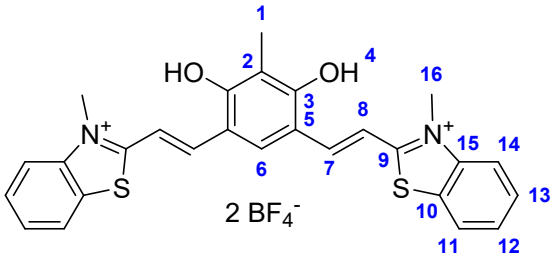


2•2H$^+$ was generated *in situ* by dissolution of compound **dsp-2** in deuterated trifluoroacetic acid.

^{1}H NMR (400 MHz. TFA-*d*): δ (ppm) = 9.68 (d, $^3J_{7.8}$ = 16.1 Hz, 2H, *H*-7), 9.32 (d, $^3J_{14.15}$ = 8.3 Hz, *H*-14). 9.20 (d, $^3J_{16\cdot17}$ = 8.8 Hz, 2H, *H*-17), 9.16 (s, 1H, *H*-6), 9.12 (d, $^3J_{19\cdot20}$ = 8.3 Hz, 2H, *H*-19), 8.89 – 8.78 (m, 4H, *H*-8 and *H*-15), 8.77 – 8.69 (m, 4H, *H*-16 and *H*-20), 5.24 (s, 6H, *H*-22), 3.40 (s, 3H, *H*-1), 3.16 (s, 12H, *H*-11). **^{13}C{^{1}H} NMR (101 MHz, TFA-*d*):** δ (ppm) = 185.8 (*C*-9), 163.4 (*C*-6), 151.1 (*C*-7), 140.3 (C_{quat}),

136.3 (C_{quat}), 133.9 (*C*-17), 132.1 (*C*-19), 130.7 (*C*-15), 129.7 (*C*-20), 129.3 (*C*-5), 124.2 (*C*-14), 112.5 (*C*-16), 56.2 (*C*-10), 35.5 (*C*-22), 27.5 & 27.4 (*C*-11), 8.5 (*C*-1). The signals corresponding to *C*-8 and two C_{quat} are missing despite long accumulation in a concentrated NMR sample. **^{19}F NMR (TFA-*d*, 377 MHz):** δ (ppm) = -76.6 ($CF_3CO_2^-$).

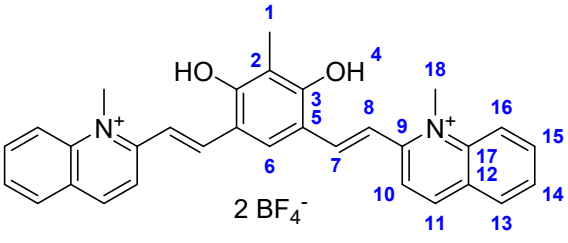
2,2-((1*E*,1'*E*)-(4,6-dihydroxy-5-methyl-1,3-phenylene)bis(ethene-2,1-diyl))bis(3-methylbenzo[*d*]thiazol-3-ium) bis(tetrafluoroborate) (3•2H^{2+})



To a solution of 4,6-dihydroxy-5-methylisophthalaldehyde **6** (100.0 mg, 0.56 mmol, 1.0 equiv.) and 2,3-dimethylbenzothiazolium iodide **9** (409.4 mg, 1.17 mmol, 2.1 equiv.) in 10 mL of absolute EtOH was added two drops of piperidine. The mixture was heated up to 95 °C for 16 hours. The mixture was cooled to room temperature. then an excess of HBF_4 (48%, aqueous) was added and the solution was stirred for 5 hours at room temperature. The solvent was removed under reduced pressure, then the residue was washed with a warm mixture of CH_2Cl_2:petroleum ether to give **3•2H$^+$** as a red powder (246.7 mg, 0.38 mmol, 69% yield).

R*f* = 0.15 (SiO_2, CH_2Cl_2:MeOH, 98:2). **M. P.:** the colour of the powder changes *ca*. 180 °C. then darkens *ca*. 260 °C. **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ (ppm) = 8.54 (s, 1 H, *H*-6), 8.38 (d, $^3J_{11.12}$ = 7.7 Hz, 2H, *H*-11), 8.31 (d, $^3J_{7.8}$ = 15.7 Hz, 2H, *H*-7), 8.22 (d, $^3J_{14.13}$ = 8.1 Hz, 2H, *H*-14), 7.96 (d, $^3J_{8.7}$ = 15.6 Hz, 2H, *H*-8), 7.87 (dd, $^3J_{13.12}$ = 7.5 Hz, $^3J_{13.14}$ = 8.1 Hz, 2H, *H*-13), 7.78 (dd, $^3J_{12.11}$ = 7.7 Hz, $^3J_{12.13}$ = 7.5 Hz, 2H, *H*-12), 4.32 (s, 6 H, *H*-16), 2.18 (s, 3 H, *H*-1). **^{13}C{^{1}H} NMR (101 MHz, DMSO-*d*$_6$):** δ (ppm) = 172.0 (*C*-9), 161.7 (*C*-3), 143.6 (*C*-7), 142.1 (*C*-15), 129.3 (*C*-12), 129.2 (*C*-6), 128.2 (*C*-13), 127.4 (*C*-10), 124.2 (*C*-11), 116.6 (*C*-14), 116.2 (*C*-5), 113.3 (*C*-2), 110.9 (*C*-8), 36.1 (*C*-16), 9.8 (*C*-1). **^{19}F NMR (DMSO-*d*$_6$, 377 MHz):** δ (ppm) = -148.1 (BF_4^-). **HRMS (ESI-TOF):** calculated for $[M]^{2+}$ ($C_{27}H_{24}N_2O_2S_2^{2+}$) 236.0634, found 236.0635. **IR (neat):** ν (cm^{-1}) = 3740, 3672, 3205, 3099, 2976, 2905, 2262, 2196, 2127, 1996, 1797, 1650, 1571, 1502, 1454, 1412, 1325, 1262, 1238, 1198, 1153, 1078, 962, 896, 838, 756.

2,2-((1*E*,1'*E*)-(4,6-dihydroxy-5-methyl-1,3-phenylene)bis(ethene-2,1-diyl))bis(3-methylbenzo[*d*]thiazol-3-ium) bis(tetrafluoroborate) (4•2H^{2+})

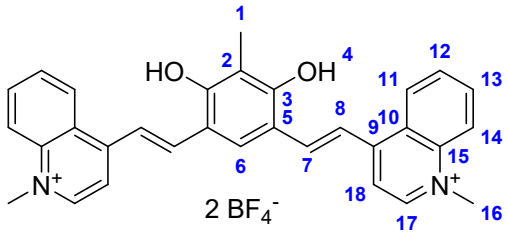


To a solution of 4,6-dihydroxy-5-methylisophthalaldehyde **6** (26.5 mg, 0.147 mmol, 1.0 equiv.) and 1,2-dimethylquinolinium iodide **10** (79.7 mg, 0.280 mmol, 1.9 equiv.) in 4 mL of absolute EtOH was added two drops of piperidine. The mixture was heated up to 95 °C for 16 hours. The mixture was cooled to room temperature. then an excess of HBF_4 (48%, aqueous) was added and

the solution was stirred for 2 hours at room temperature. The precipitate was then filtered and washed with MeOH, EtOH and Et_2O to afford **4•2H⁺** as a brown powder (78.7 mg, 0.124 mmol, 87% yield).

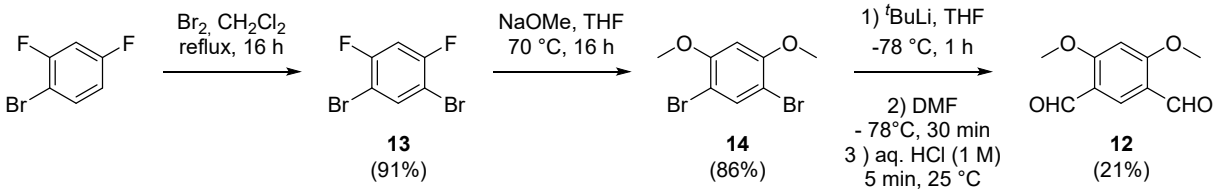
M. P.: 255 – 257 °C. **^{1}H NMR (400 MHz, DMSO-d_6):** δ (ppm) = 9.03 (d, $^3J_{11.10}$ = 9.3 Hz, 2 H, *H*-11), 8.55 (d, $^3J_{13.12}$ = 9.1 Hz, 4H, *H*-13 and *H*-10), 8.47 (s, 1H, *H*-6), 8.40 – 8.30 (m, 4H, *H*-15 and *H*-16), 8.19 (t, $^3J_{14.13}$ = 8.0 Hz, $^3J_{14.15}$ = 7.6 Hz, 2H, *H*-14), 7.97 – 7.90 (m, 4H, *H*-7 and *H*-8), 4.58 (s, 6 H, *H*-18), 2.22 (s, 3 H, *H*-1). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6):** δ (ppm) = 159.9 (*C*-3), 156.3 (*C*-9), 143.7 (*C*-11), 142.4 (*C*-15), 139.3 (*C*-17), 135.1 (*C*-12), 134.8 (*C*-14), 130.1 (*C*-16), 128.8 (*C*-7), 127.8 (*C*-6), 120.9 (*C*-10), 119.0 (*C*-13), 117.0 (*C*-8), 116.6 (*C*-5), 113.2 (*C*-2), 39.8 (*C*-18), 9.8 (*C*-1). **^{19}F NMR (DMSO-d_6, 377 MHz):** δ (ppm) = -148.12 (*BF_4^-*). **HRMS (ESI-TOF):** calculated for $[M\text{-}2BF_4^-]^{2+}$ ($C_{31}H_{28}N_2O_2^{2+}$) 230.1070, found 230.1071. **IR (neat):** ν (cm^{-1}) = 3123, 3100, 2123, 2084, 2002, 1563, 1519, 1474, 1438, 1344, 1324, 1294, 1236, 1218, 1154, 1027, 975, 853, 824, 756, 710.

2,2-((1*E*,1'*E*)-(4,6-dihydroxy-5-methyl-1,3-phenylene)bis(ethene-2,1-diyl))bis(3-methylbenzo[*d*]thiazol-3-ium) bis(tetrafluoroborate) (5•2H²⁺)



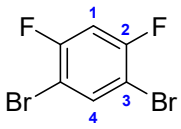
To a solution of 4,6-dihydroxy-5-methylisophthalaldehyde **6** (51.5 mg, 0.286 mmol, 1.0 equiv.) and 1,4-dimethylquinolinium iodide **11** (171.2 mg, 0.60 mmol, 2.1 equiv.) in 5 mL of absolute EtOH was added two drops of piperidine. The mixture was heated up to 95 °C for 16 hours. The mixture was cooled to room temperature, then an excess of HBF_4 (48%, aqueous) was added and the solution was stirred for 5 hours at room temperature. The precipitate was filtered and washed with EtOH and Et_2O to yield **5•2H⁺** as a red powder (135.0 mg, 0.213 mmol, 74% yield).

M. P.: 226 – 228 °C. **^{1}H NMR (600 MHz, DMSO-d_6):** δ (ppm) = 10.15 (br s, 2H, *H*-4), 9.28 (d, $^3J_{17.18}$ = 6.6 Hz, 2H, *H*-17), 9.03 (d, $^3J_{11.12}$ = 8.1 Hz, 2H, *H*-11), 8.60 (s, 1H, *H*-6), 8.45 (d, $^3J_{14.13}$ = 8.7 Hz, 2H, *H*-14), 8.43 (d, $^3J_{18.17}$ = 6.6 Hz, 2H, *H*-18), 8.38 (d, $^3J_{7.8}$ = 15.6 Hz, 2H, *H*-7), 8.32 (d, $^3J_{8,7}$ = 15.6 Hz, 2H, *H*-8), 8.29 (dt, $^3J_{13.12}$ = 7.2 Hz, $^3J_{13.14}$ = 7.5 Hz, $^4J_{13,11}$ = 1.1 Hz, 2H, *H*-13), 8.09 (t, $^3J_{12.11}$ = 7.4 Hz, $^3J_{12.13}$ = 7.7 Hz, 2H, *H*-12), 4.54 (s, 6 H, *H*-16), 2.21 (s, 3 H, *H*-1). **^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6):** δ (ppm) = 158.9 (*C*-3), 153.3 (*C*-15), 147.8 (*C*-17), 138.8 (*C*-10), 138.2 (*C*-8), 134.9 (*C*-13), 129.1 (*C*-12), 126.5 (*C*-11), 126.1 (*C*-9), 125.7 (*C*-6), 119.4 (*C*-14), 117.4 (*C*-7), 117.1 (*C*-5), 115.5 (*C*-18), 113.0 (*C*-2), 44.7 (*C*-16), 9.8 (*C*-1). **^{19}F NMR (DMSO-d_6, 377 MHz):** δ (ppm) = -148.2 (*BF_4^-*). **HRMS (ESI-TOF):** calculated for $[M\text{-}2BF_4^-]^{2+}$ ($C_{31}H_{28}N_2O_2^{2+}$) 230.1070, found 230.1073. **IR (neat):** ν (cm^{-1}) = 3090, 3036, 2174, 2104, 2083, 2001, 1584, 1553, 1440, 1395, 1366, 1339, 1310, 1293, 1259, 1225, 1169, 1029, 959, 854, 757.



Scheme S 1. Synthesis of precursor **12**.

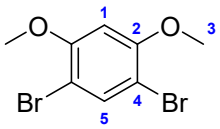
1,5-dibromo-2,4-difluorobenzene (13)



This synthetic procedure was adapted from the literature.[7] A solution of bromine (22.77 g, 142.48 mmol, 1.10 equiv.) in 20 mL CH_2Cl_2 was added dropwise to a mixture of 1-bromo-2,4-difluorobenzene (25.0 g, 129.54 mmol, 1.00 equiv.) and iron powder (2 g, 35.81 mmol, 0.27 equiv.) in 30 mL of CH_2Cl_2. The mixture was refluxed for 16 hours under an argon atmosphere and then cooled to room temperature. The mixture was quenched with 150 mL of a 10% w/w solution of $Na_2S_2O_5$ and extracted with CH_2Cl_2. The organic layer was washed with distilled water, dried over anhydrous Na_2SO_4, filtered, then the solvent was removed under reduced pressure. The crude was purified by column chromatography (SiO_2, petroleum ether as eluent) to give **13** as a pale-yellow fibre-like solid (32.148 g, 110.14 mmol, 91%).

R*f* = 0.84 (SiO_2, petroleum ether). **M. P.:** 29 – 31 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ (ppm) = 7.76 (t, $^3J_{H\text{-}4.F}$ = 7.34 Hz, 1H, *H*-4), 6.96 (t, $^3J_{H\text{-}1.F}$ = 8.44 Hz, 1H, *H*-1). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ (ppm) = 158.6 (dd, $^1J_{C\text{-}2.F}$ = 250 Hz, $^3J_{C\text{-}2.F}$ = 11 Hz, *C*-2), 136.5 (*C*-4), 106.0 (t, $^2J_{C\text{-}1.F}$ = 27 Hz, *C*-1), 104.7 (d, $^2J_{C\text{-}3.F}$ = 27 Hz, *C*-3). **^{19}F NMR (377 MHz, $CDCl_3$):** δ (ppm) = -103.3 (s). **IR (neat):** ν (cm^{-1}) = 3100, 3035, 2128, 1585, 1464, 1389, 1265, 1148, 1072, 880.

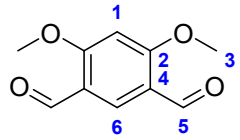
1,5-dibromo-2,4-dimethoxybenzene (14)



This synthetic procedure was adapted from the literature.[8] A solution of 1,5-dibromo-2,4-difluorobenzene **13** (1.0 g, 3.68 mmol, 1.00 equiv.) and sodium methoxide (95%) (2.09 g, 36.78 mmol, 10.0 equiv.) in 20 mL of anhydrous THF was heated up to 70 °C for 16 hours. The mixture was allowed to cool down to room temperature and the solvent was then removed under reduced pressure. The residue was dissolved in dichloromethane. the organic layer was washed with distilled water, dried over $MgSO_4$, filtered off and the solvent was removed under reduced pressure. The crude was further purified by column chromatography (SiO_2) using petroleum ether:CH_2Cl_2 (4:6) as eluent to afford the product **14** as a white powder (937.7 mg, 3.17 mmol, 86% yield).

R*f* = 0.72 (SiO_2, petroleum ether:CH_2Cl_2, 4:6). **M. P.:** 140 – 142 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ (ppm) = 7.66 (s, 1H, *H*-1), 6.49 (s, 1H, *H*-5), 3.90 (s, 6H, *H*-4). **^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ (ppm) = 156.3 (*C*-3), 136.1 (*C*-1), 102.6 (*C*-2), 97.5 (*C*-5), 56.7 (*C*-4). **IR (neat):** ν (cm^{-1}) = 2980, 2943, 1576, 1486, 1460, 1430, 1366, 1285, 1206, 1175, 1055, 1016, 874, 810, 683.

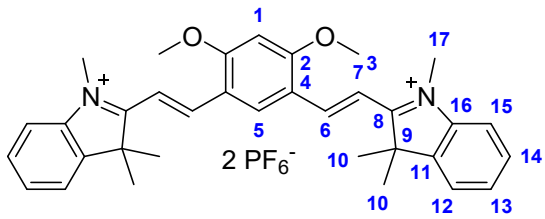
4,6-dimethoxyisophthalaldehyde (12)



This synthetic procedure was adapted from the literature.[9] Under an argon atmosphere, *tert*-butyllithium (^{t}BuLi) (5.96 mL, 1.7 M in pentane, 10.14 mmol, 6.0 equiv.) was added dropwise at -78 °C to a solution of 1,5-dibromo-4,6-dimethoxybenzene **14** (500.0 mg, 1.69 mmol, 1.0 equiv.) in 8 mL of THF, which was previously distilled over metallic sodium and benzophenone. The mixture was stirred for 1 hour at the same temperature. Distilled *N*,*N*-dimethylformamide (740.92 mg, 10.14 mmol, 6.00 equiv.) was added dropwise to the mixture, which was stirred for 30 minutes at -78 °C and was allowed to warm up to room temperature. Then, 4 mL of distilled water and 4 mL of aqueous HCl (1 M) were added to the solution, which was left to stir for 5 minutes at room temperature. The mixture was filtered to give a yellow precipitate, which was recovered with CH_2Cl_2. The solvent was removed under reduced pressure to afford **12** as a yellow solid (69.0 mg, 0.36 mmol, 21% yield). If necessary, this compound can be further purified by column chromatography (SiO_2) using CH_2Cl_2:acetone (98:2) as eluent.

R*f* = 0.71 (SiO_2, CH_2Cl_2:MeOH. 98:2). **M. P.:** 199 – 201 °C. **^{1}H NMR (400 MHz, $CDCl_3$):** δ (ppm) = 10.27 (s, 2H, *H*-5), 8.34 (s, 1H, *H*-6), 6.45 (s, 1H, *H*-1), 4.03 (s, 6H, *H*-3).**^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$):** δ (ppm) = 187.8 (*C*-5), 167.5 (*C*-2), 132.2 (*C*-1), 118.9 (*C*-4), 94.4 (*C*-6), 56.3 (*C*-3). **IR (neat):** ν (cm^{-1}) = 2997, 2949, 2889, 2864, 1670, 1582, 1463, 1435, 1398, 1296, 1277, 1243, 1210, 1101, 1013, 842, 708, 678.

2,2'-((1*E*,1'*E*)-(4,6-dimethoxy-1,3-phenylene)bis(ethene-2,1-diyl))bis(1,3,3-trimethyl-3*H*-indol-1-ium) bis(hexafluorophosphate) (1')



A solution of 4,6-dimethoxyisophthalaldehyde **12** (100.0 mg, 0.52 mmol, 1.00 equiv.), 1,1,2,3-tetramethyl-1*H*-indolium iodide **7** (325.7 mg, 1.08 mmol, 2.10 equiv.) and AcONa (84.5 mg, 1.03 mmol, 2.00 equiv.) in 10 mL of Ac_2O was heated up to 100 °C for 16 hours. The solvent was then removed under reduced pressure. then the residue was dissolved in CH_2Cl_2 and washed two times with an aqueous solution of KPF_6 (0.1 M). The organic layer was dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was further purified by column chromatography (SiO_2) using CH_2Cl_2:MeOH (95:5) as eluent to afford the product **1'** as a crystalline red solid (194.3 mg, 0.24 mmol, 47% yield).

R*f* = 0.38 (SiO_2, CH_2Cl_2:MeOH, 95:5). **M. P.:** 166 – 168 °C. **^{1}H NMR (Acetone-d_6, 400 MHz):** δ (ppm) = 8.86 (s, 1H, *H*-5), 8.61 (d, $^3J_{6,7}$ = 17.6, 2H, *H*-6), 7.87 – 7.92 (m, 6H, *H*-7, *H*-13 and *H*-15), 7.67 – 7.69 (m, 4H, *H*-12 and *H*-14), 7.13 (s, 1 H, *H*-1), 4.31 (s, 6 H, *H*-3), 4.28 (s, 6 H, *H*-17), 1.90 (s, 12 H, *H*-10). **^{13}C{^{1}H} NMR (Acetone-d_6, 101 MHz):** δ (ppm) = 183.3 (*C*-8), 167.2 (*C*-2), 148.5 (*C*-6), 144.3 (*C*-11), 143.0 (*C*-16), 135.1 (*C*-5), 130.3 (*C*-14), 130.1 (*C*-12), 123.6 (*C*-13), 118.1 (*C*-4), 115.7 (*C*-15), 112.9

(*C*-7), 97.4 (*C*-1), 57.9 (*C*-3), 53.2 (*C*-9), 34.7 (*C*-17), 26.5 (*C*-10). **^{19}F NMR (Acetone-d_6, 377 MHz):** δ (ppm) = -73.20 ($^2J_{P,F}$ = 709.8 Hz, PF_6^-). **HRMS (ESI-TOF):** calculated for $[M]^{2+}$ ($C_{34}H_{38}N_2O_2^{2+}$) 253.1461, found 253.1462. **IR (neat):** ν (cm^{-1}) = 3648, 2936, 1763, 1581, 1529, 1458, 1371, 1288, 1209, 1114, 1019, 974, 931, 877, 833, 750.

III. NMR SPECTRA

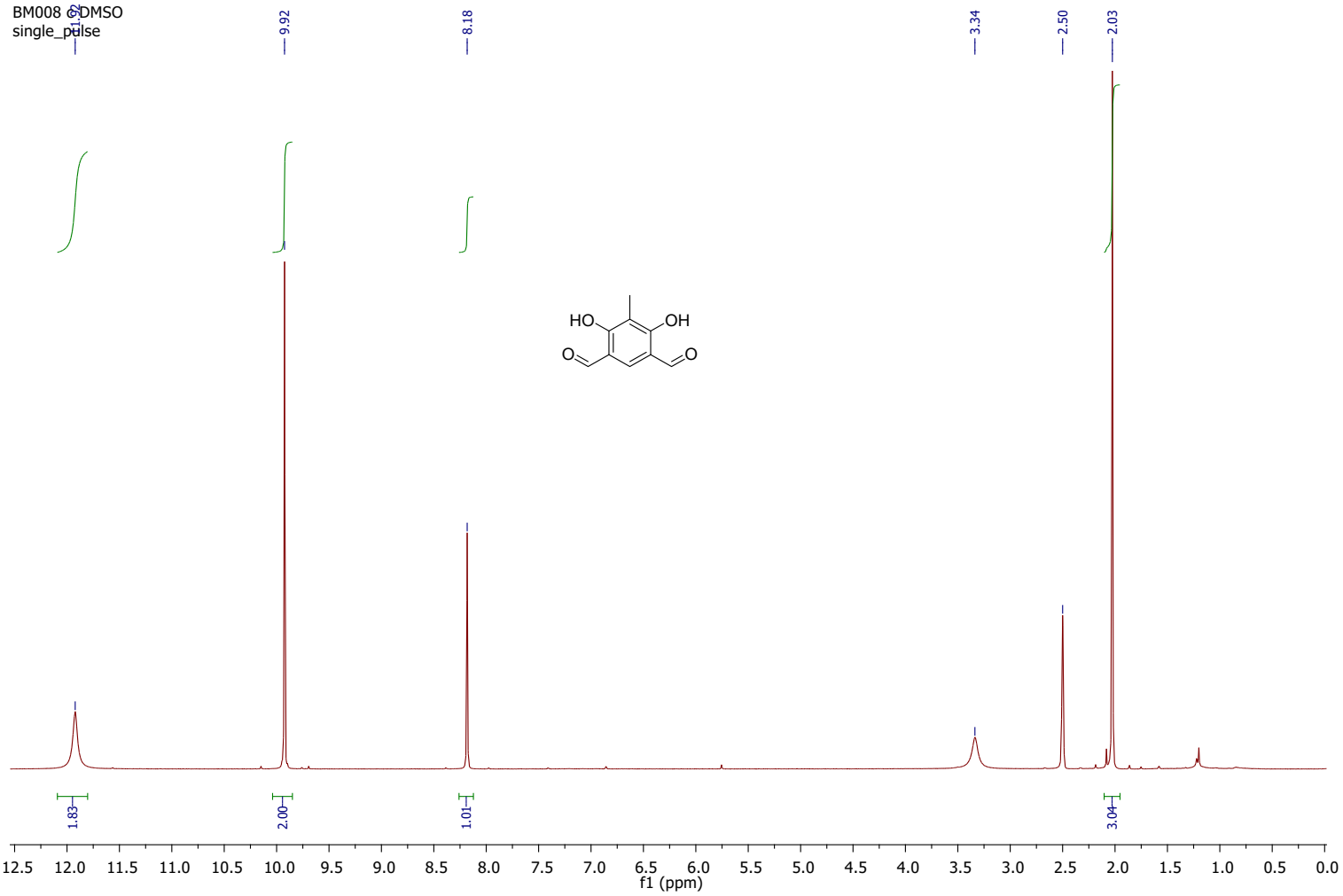


Figure S 1. ^{1}H NMR (400 MHz, DMSO-d_6) of compound **6**.

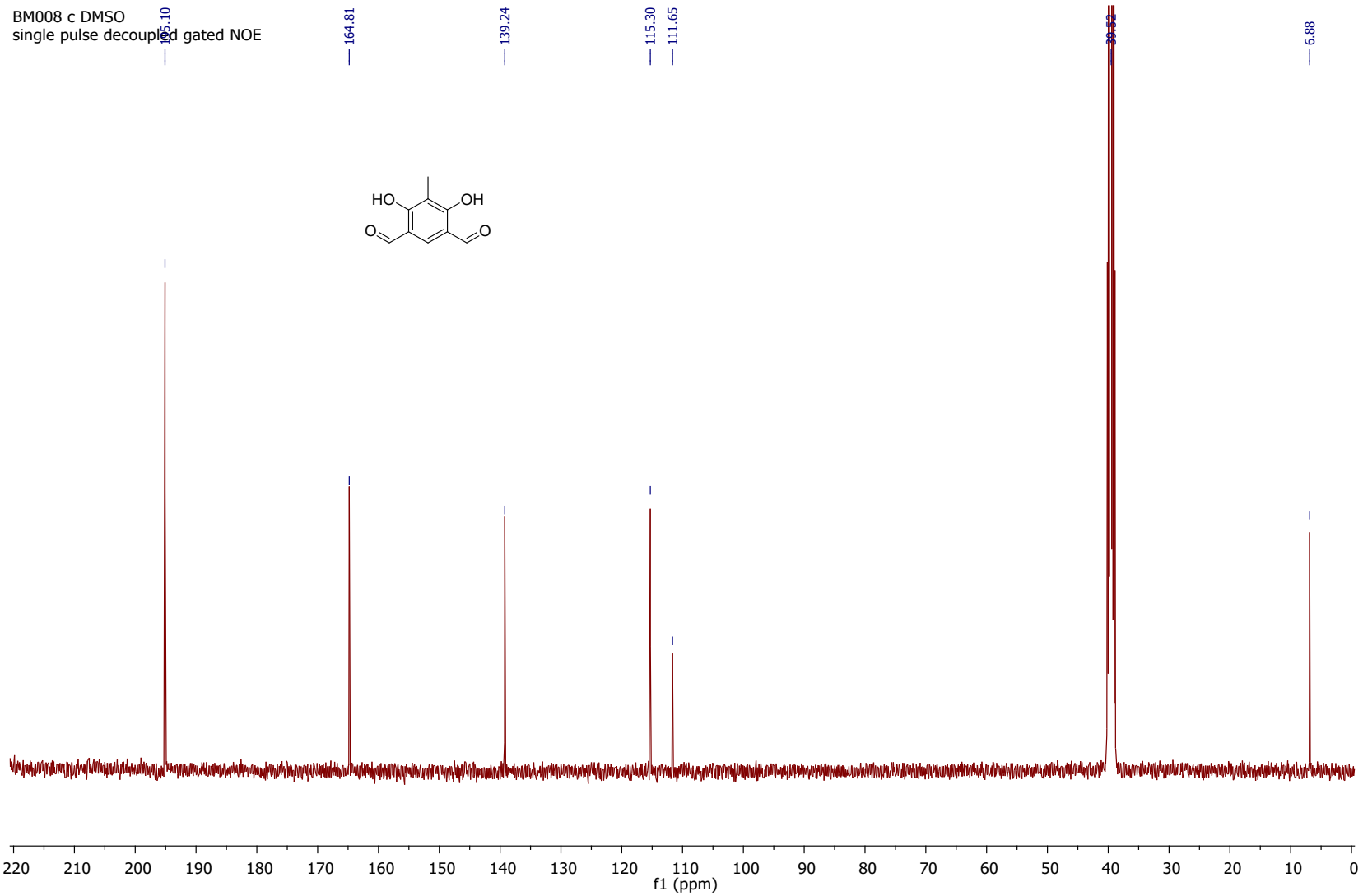


Figure S 2. ^{13}C NMR (101 MHz, DMSO-d_6) of compound **6**.

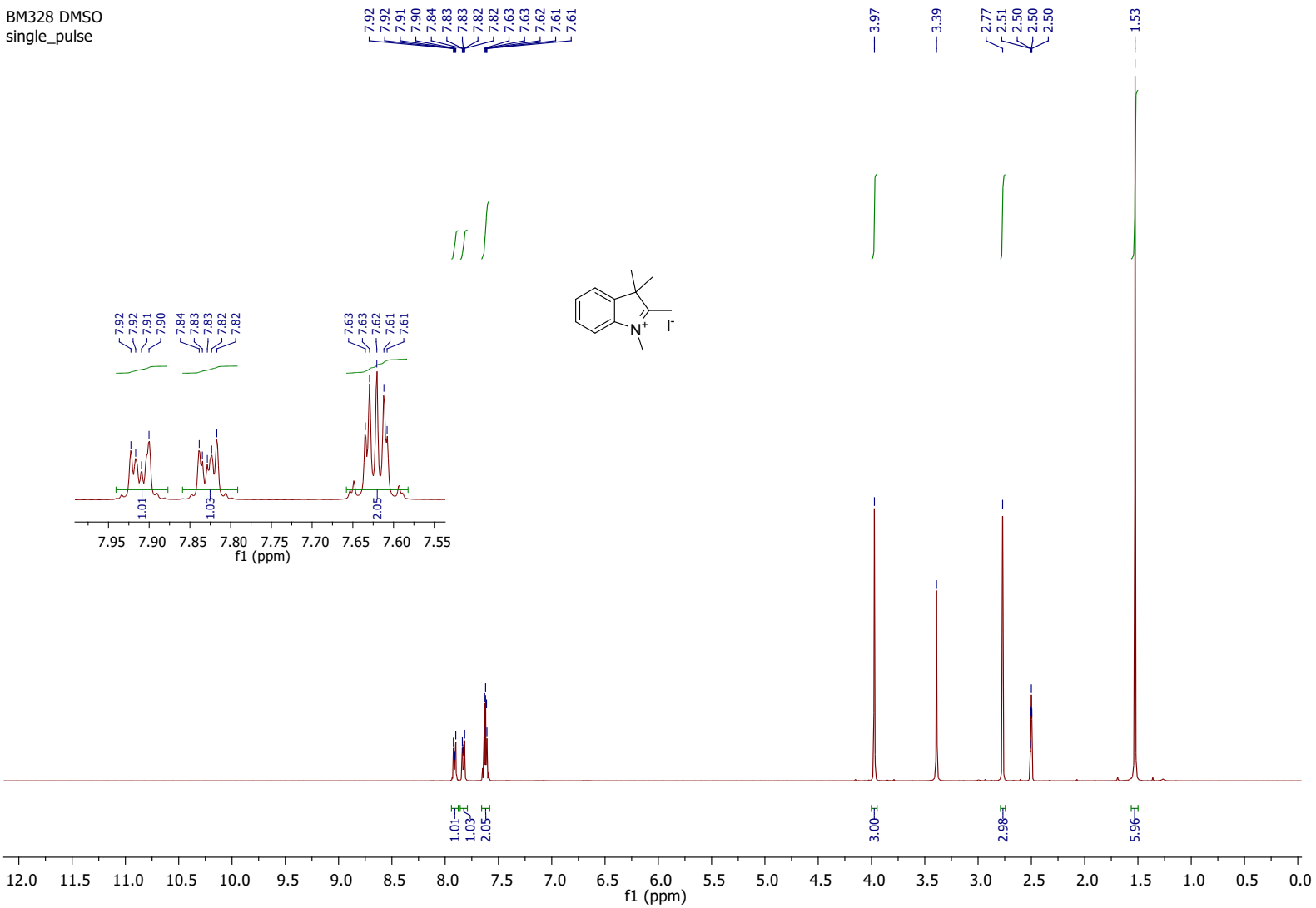


Figure S 3. ^{1}H NMR (400 MHz, DMSO-d_6) of compound **7**.

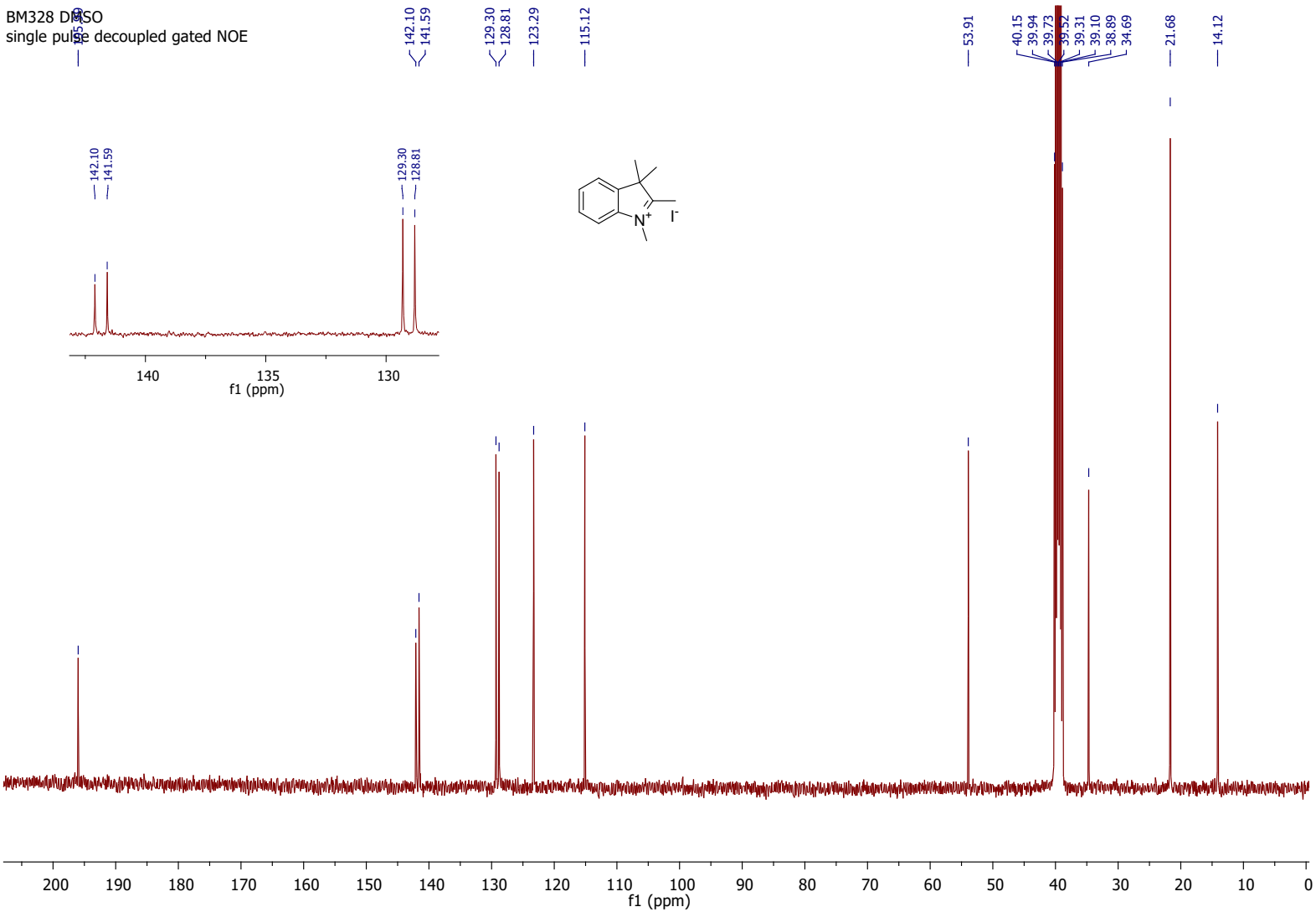


Figure S 4. ^{13}C NMR (101 MHz, DMSO-d_6) of compound **7**.

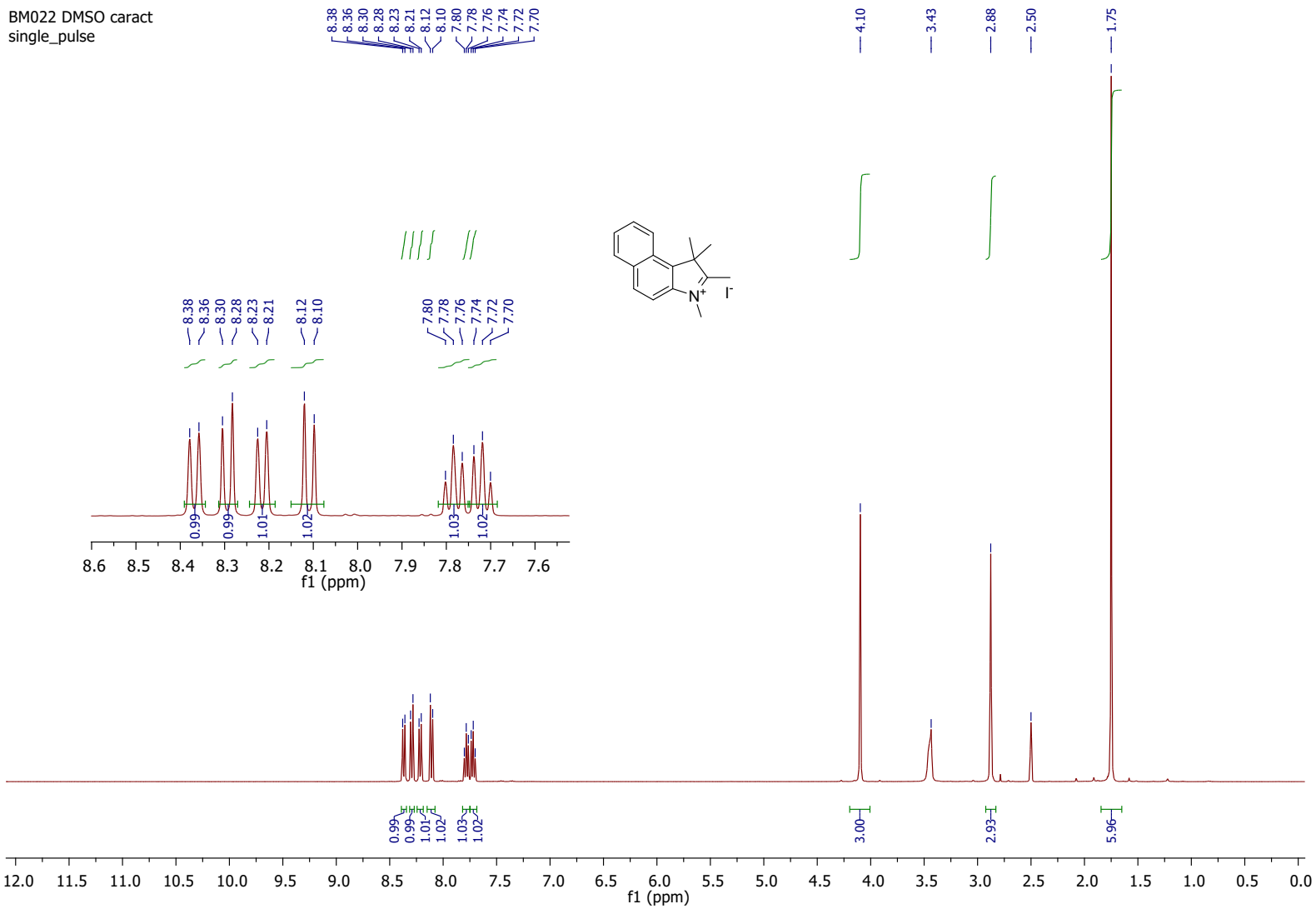


Figure S 5. ^{1}H NMR (400 MHz, DMSO-d_6) of compound **8**.

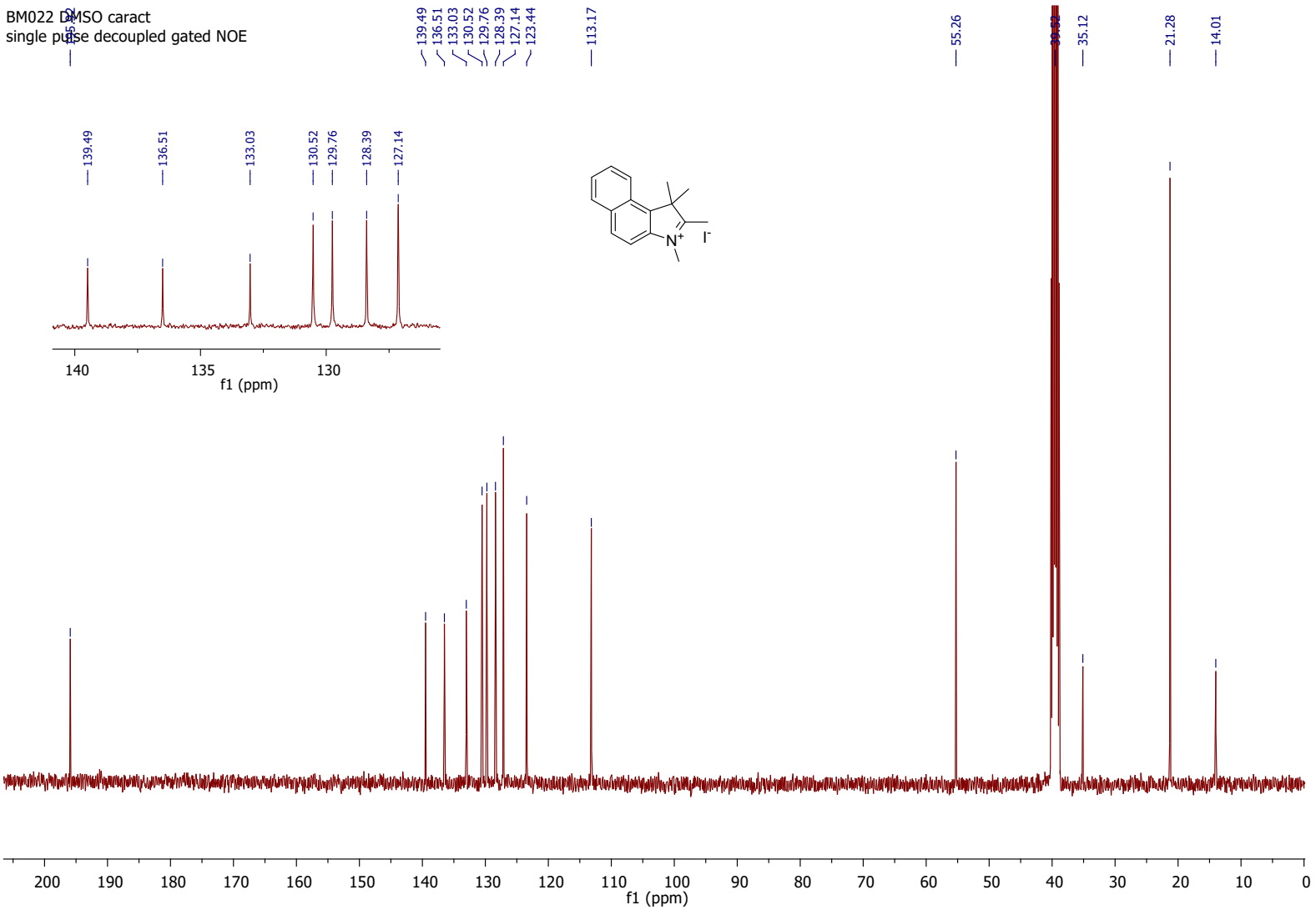


Figure S 6. ^{13}C NMR (101 MHz, DMSO-d_6) of compound **8**.

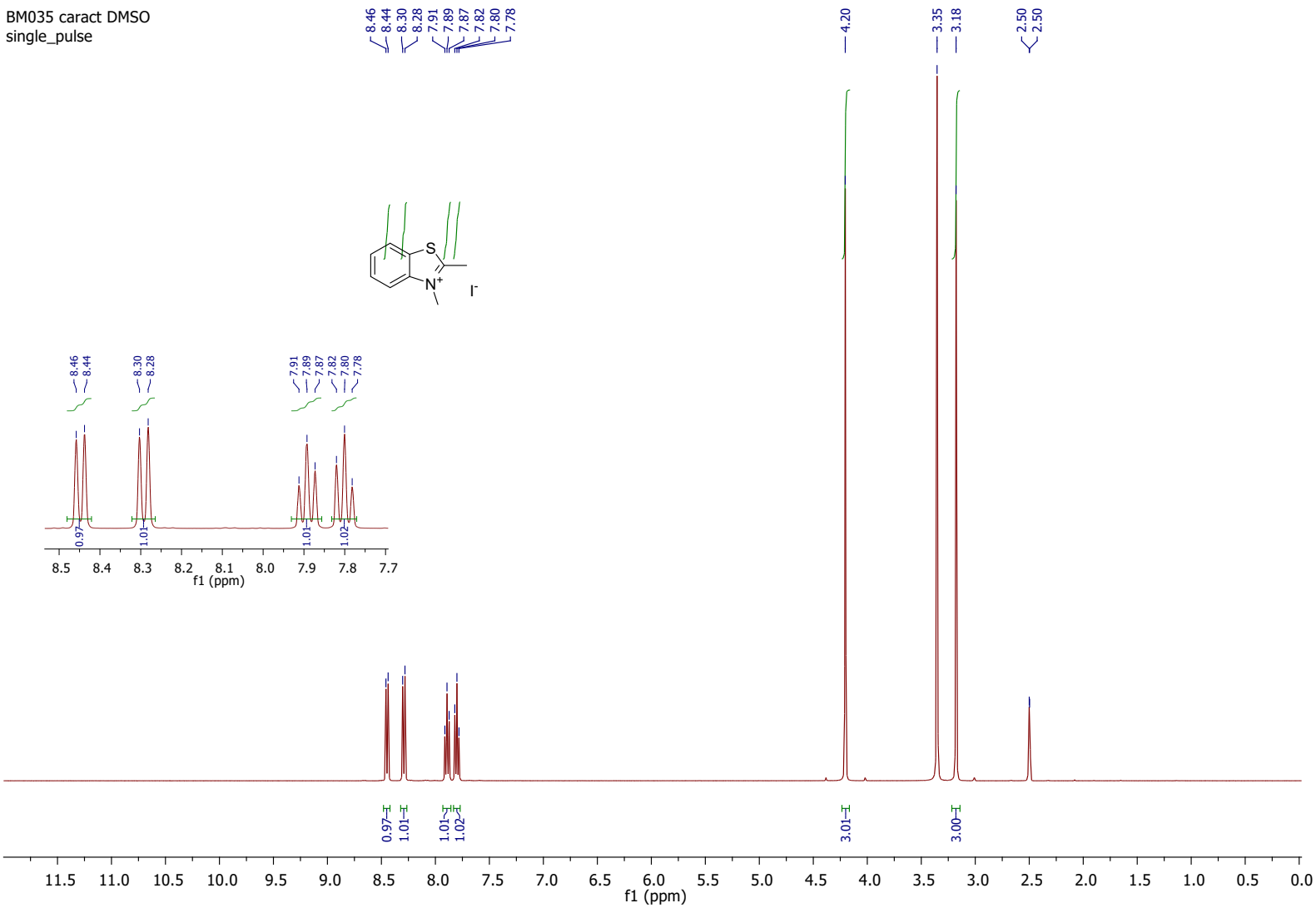


Figure S 7. ^{1}H NMR (400 MHz, DMSO-d_6) of compound **9**.

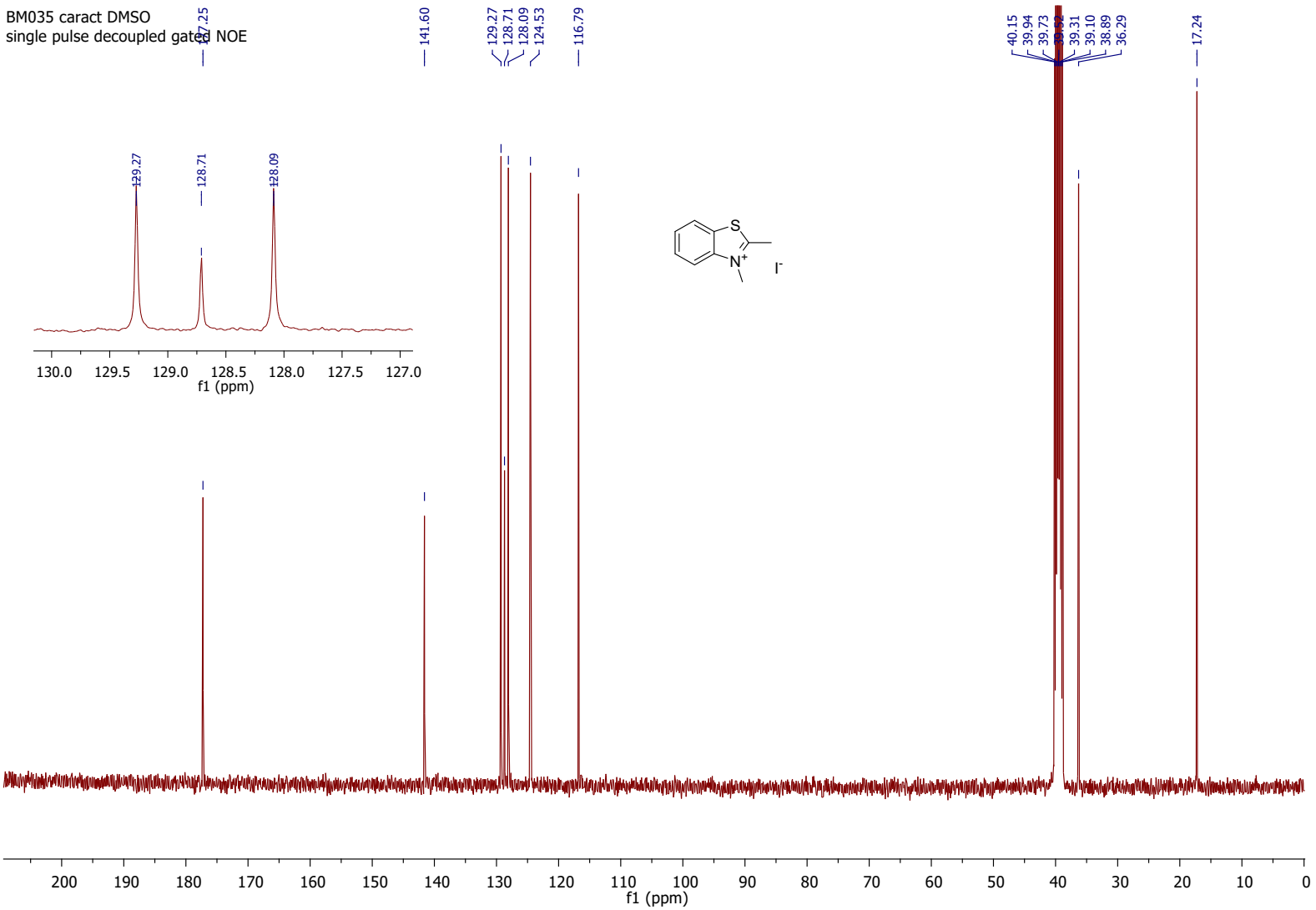


Figure S 8. ^{13}C NMR (101 MHz, DMSO-d_6) of compound **9**.

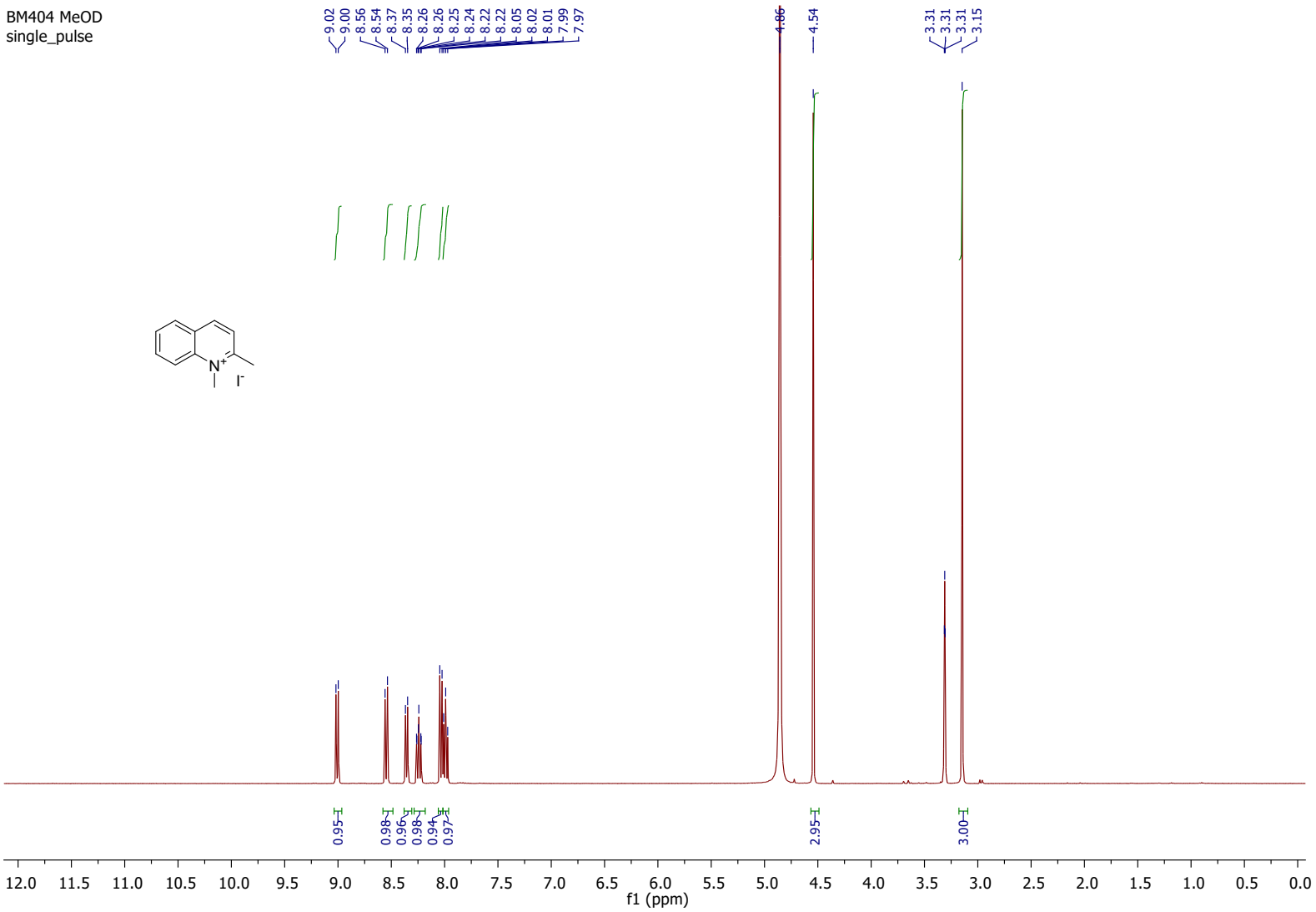


Figure S 9. ^{1}H NMR (400 MHz, CD_3OD) of compound **10**

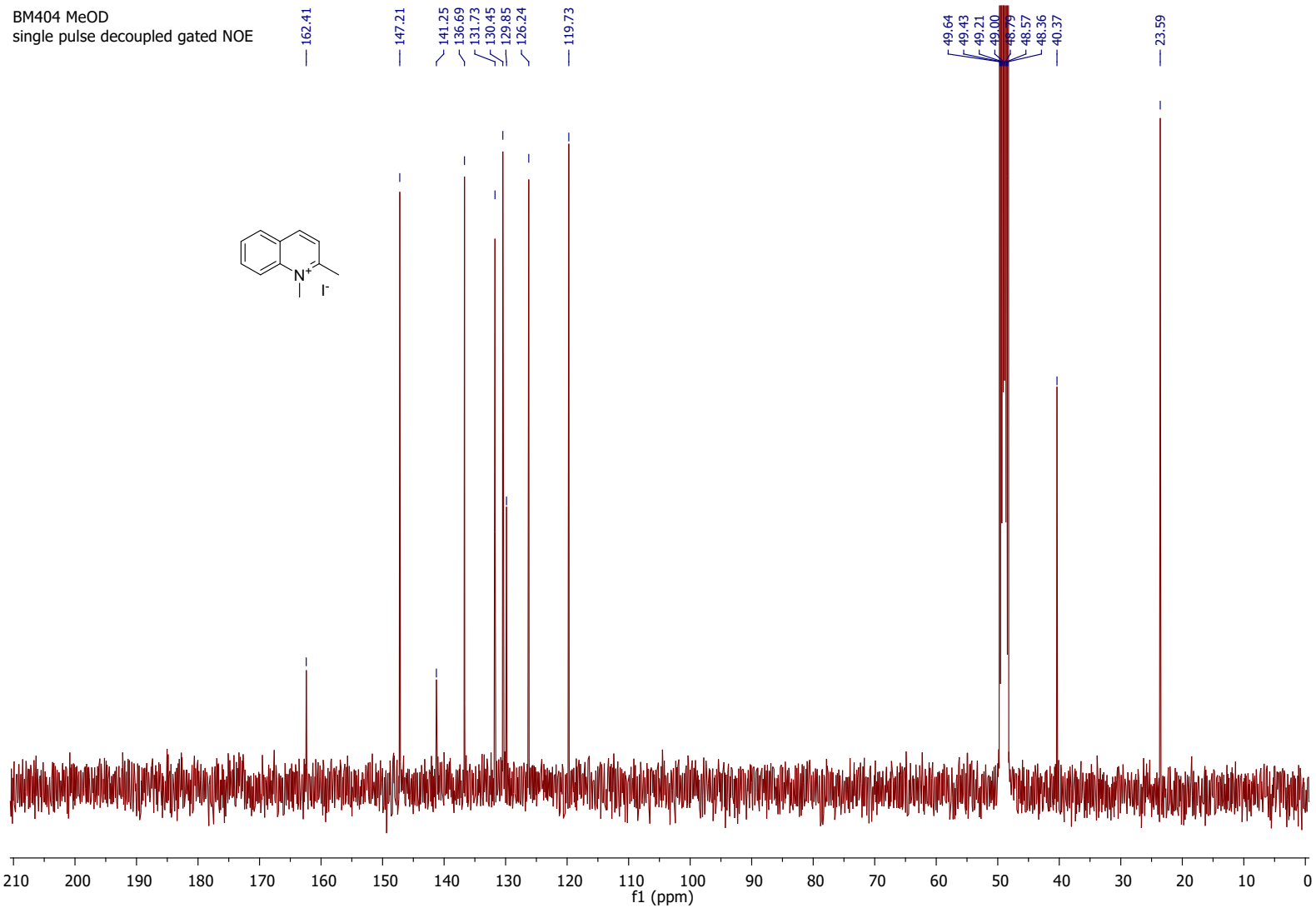


Figure S 10. ^{13}C NMR (101 MHz, CD_3OD) of compound **10**.

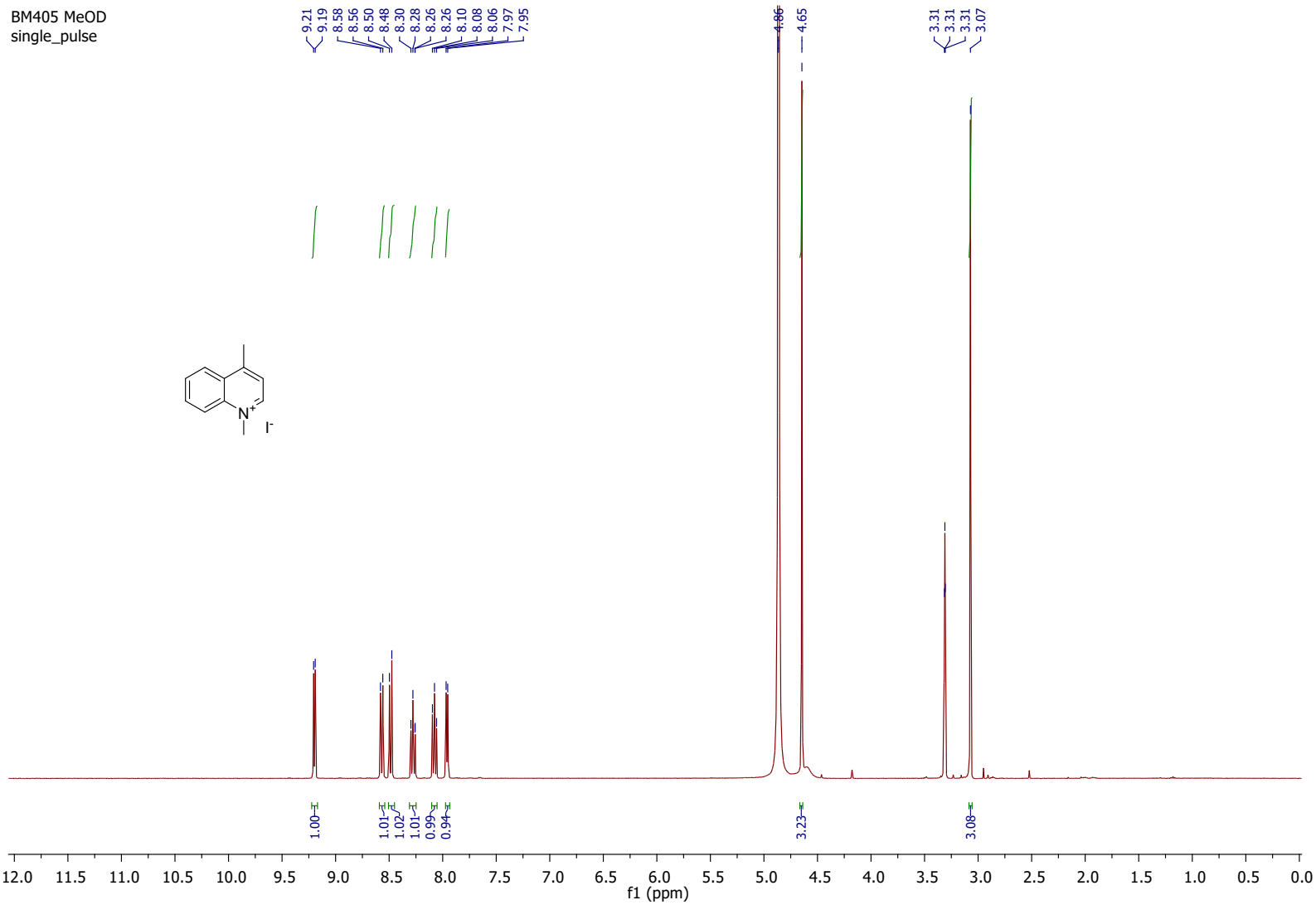


Figure S 11. ^{1}H NMR (400 MHz, CD_3OD) of compound **11**.

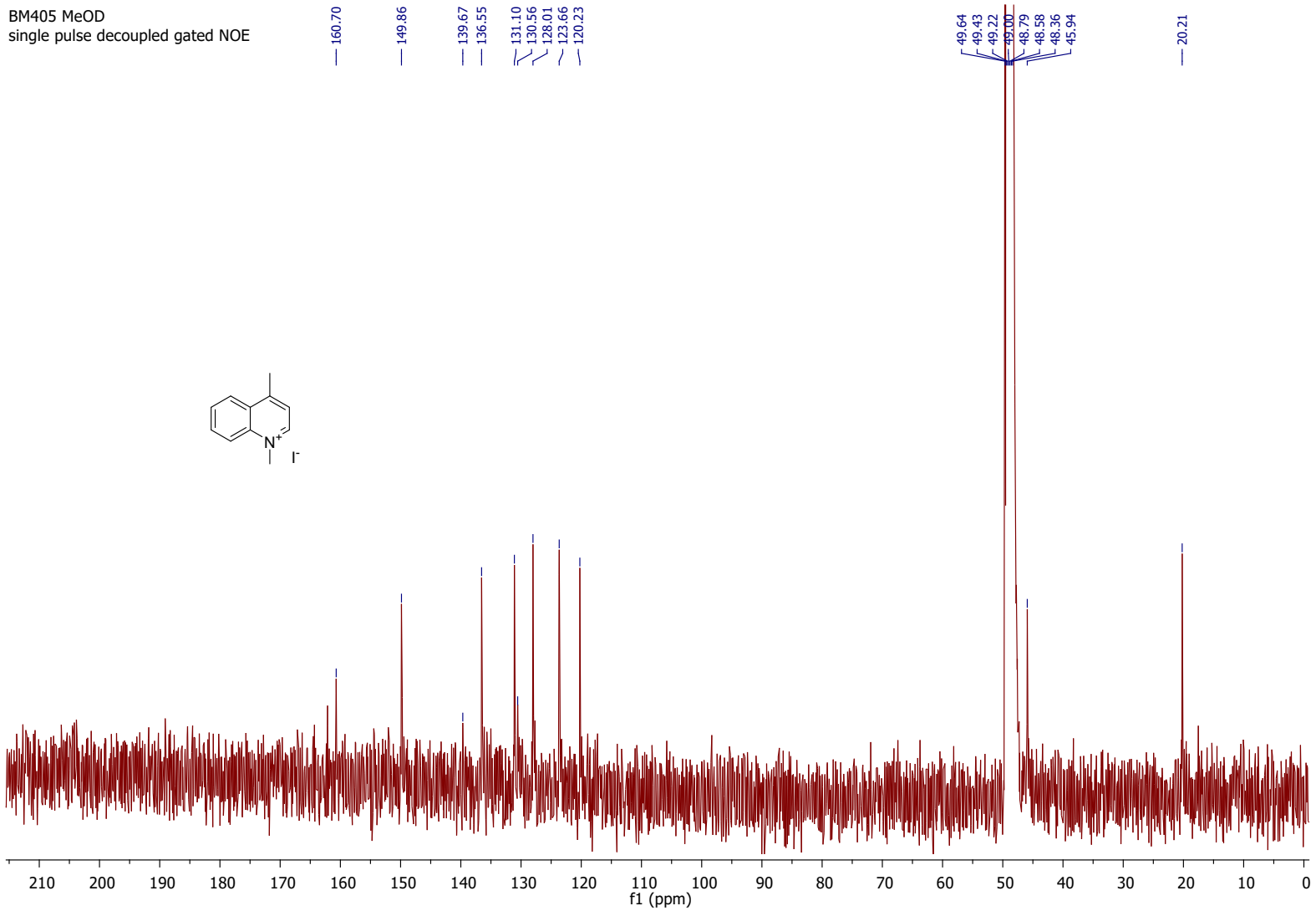


Figure S 12. ^{13}C NMR (101 MHz, CD_3OD) of compound **11**.

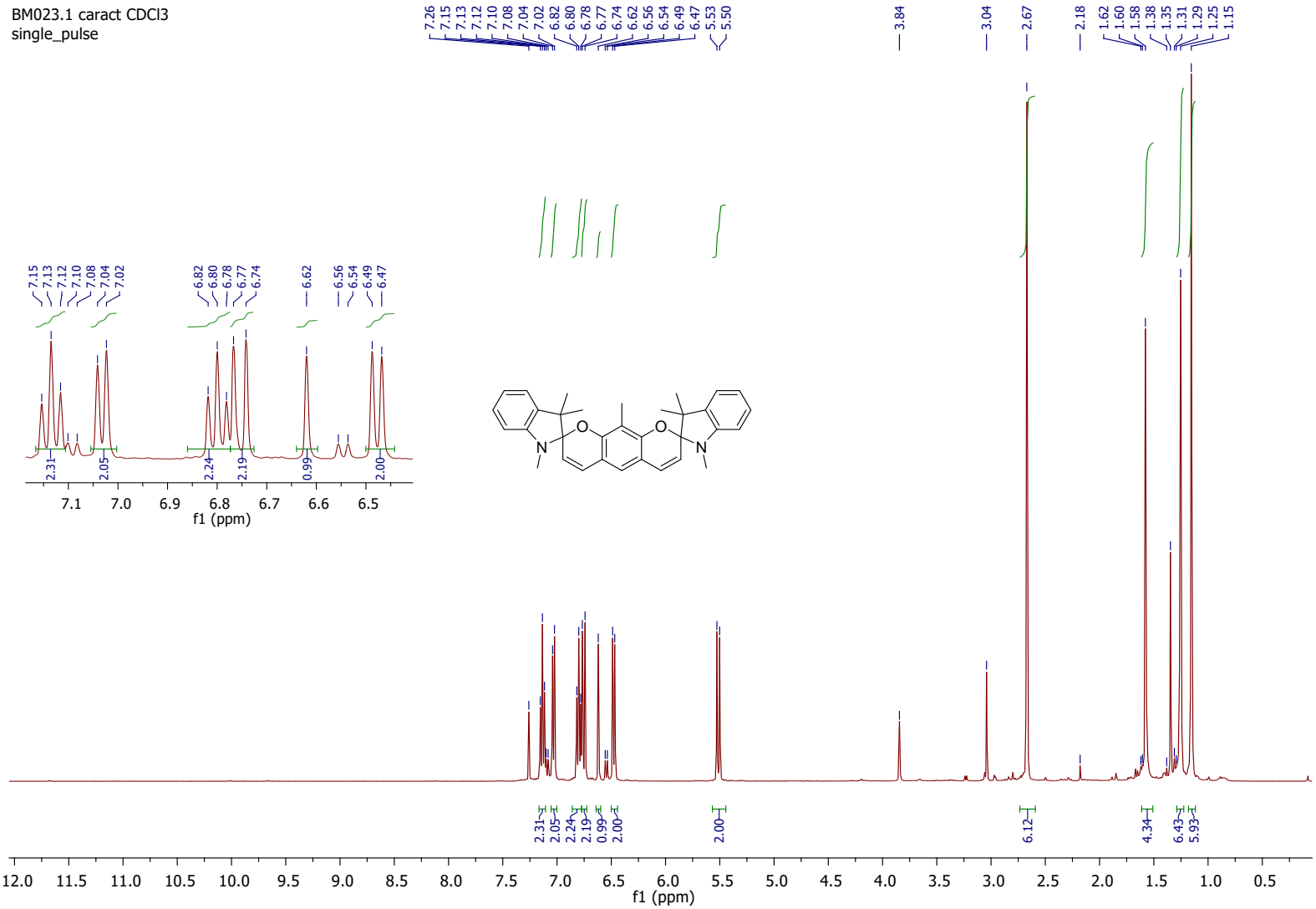


Figure S 13. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **dsp-1**.

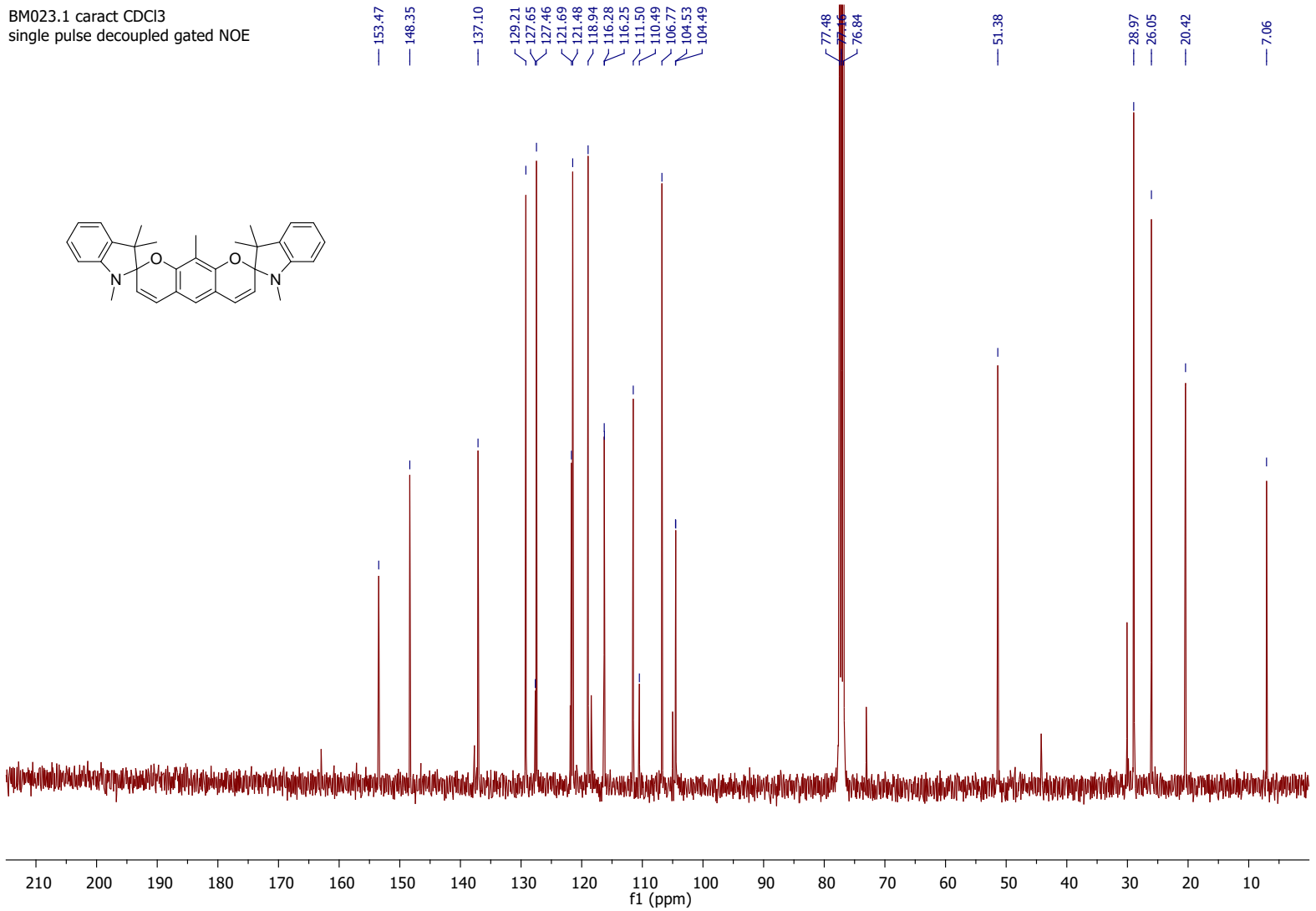


Figure S 14. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **dsp-1**.

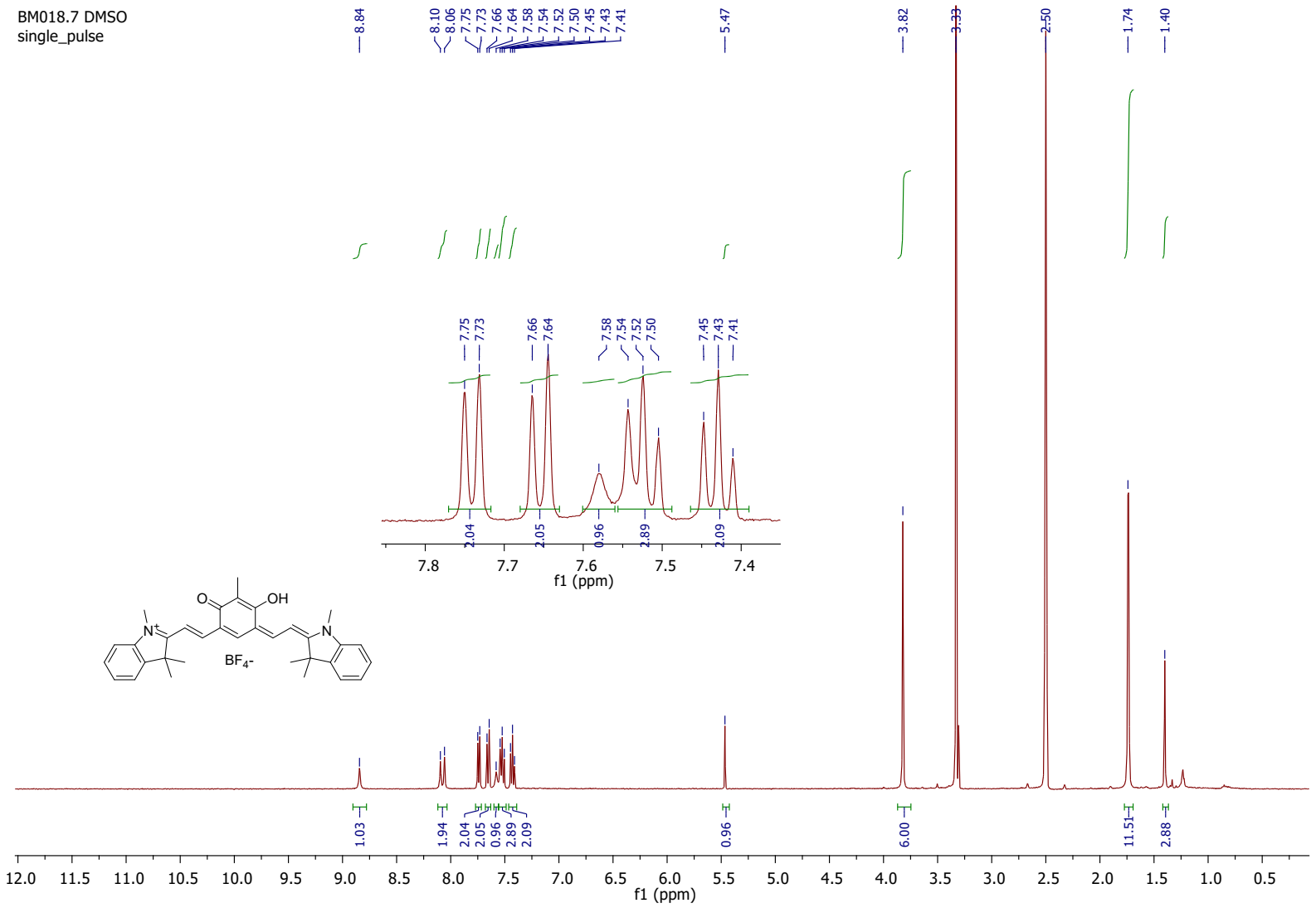


Figure S 15. ^{1}H NMR (400 MHz, DMSO-d_6) of compound **1•H^{+}**.

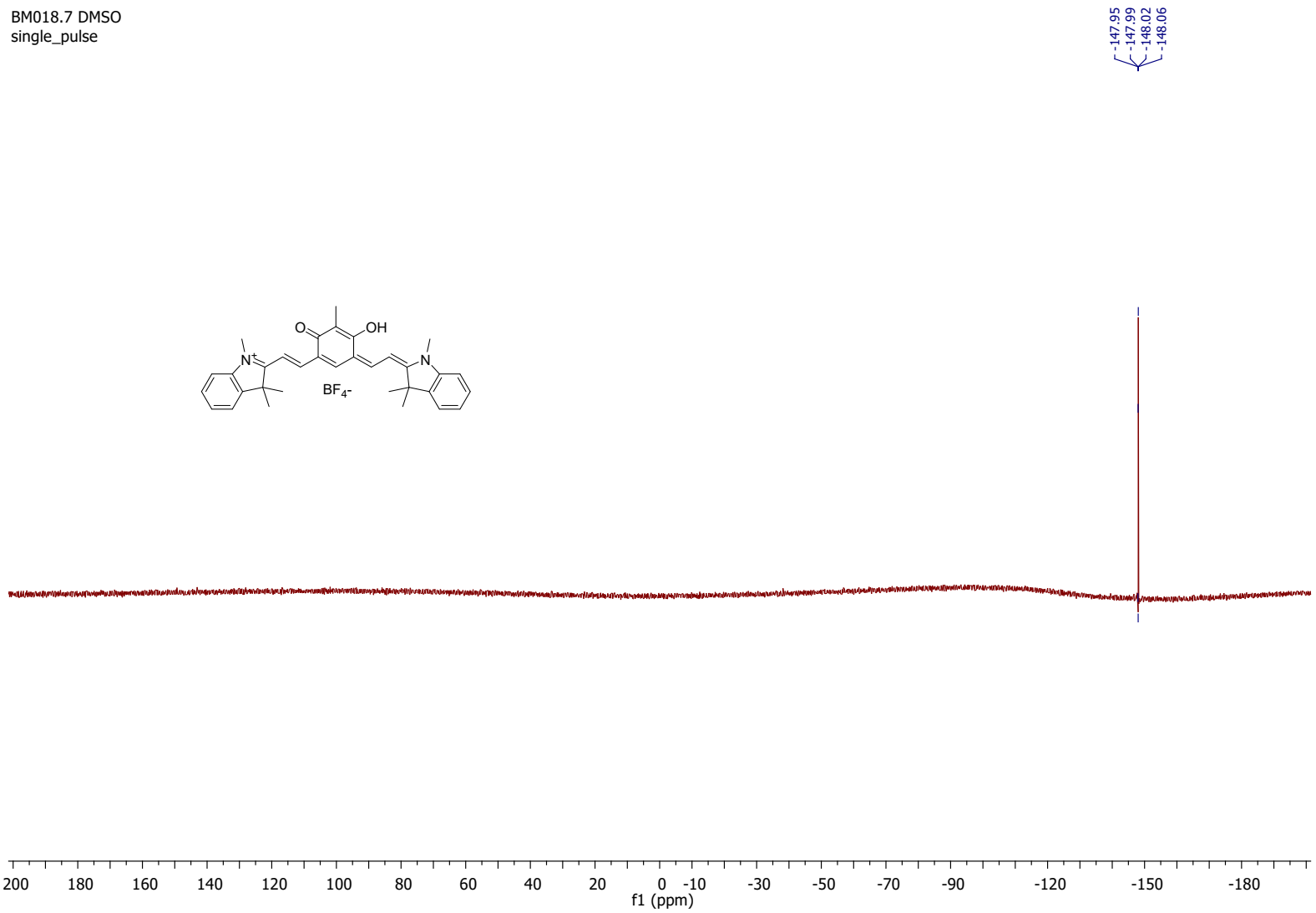


Figure S 16. ^{19}F NMR (377 MHz, DMSO-d_6) of compound **1•H⁺**.

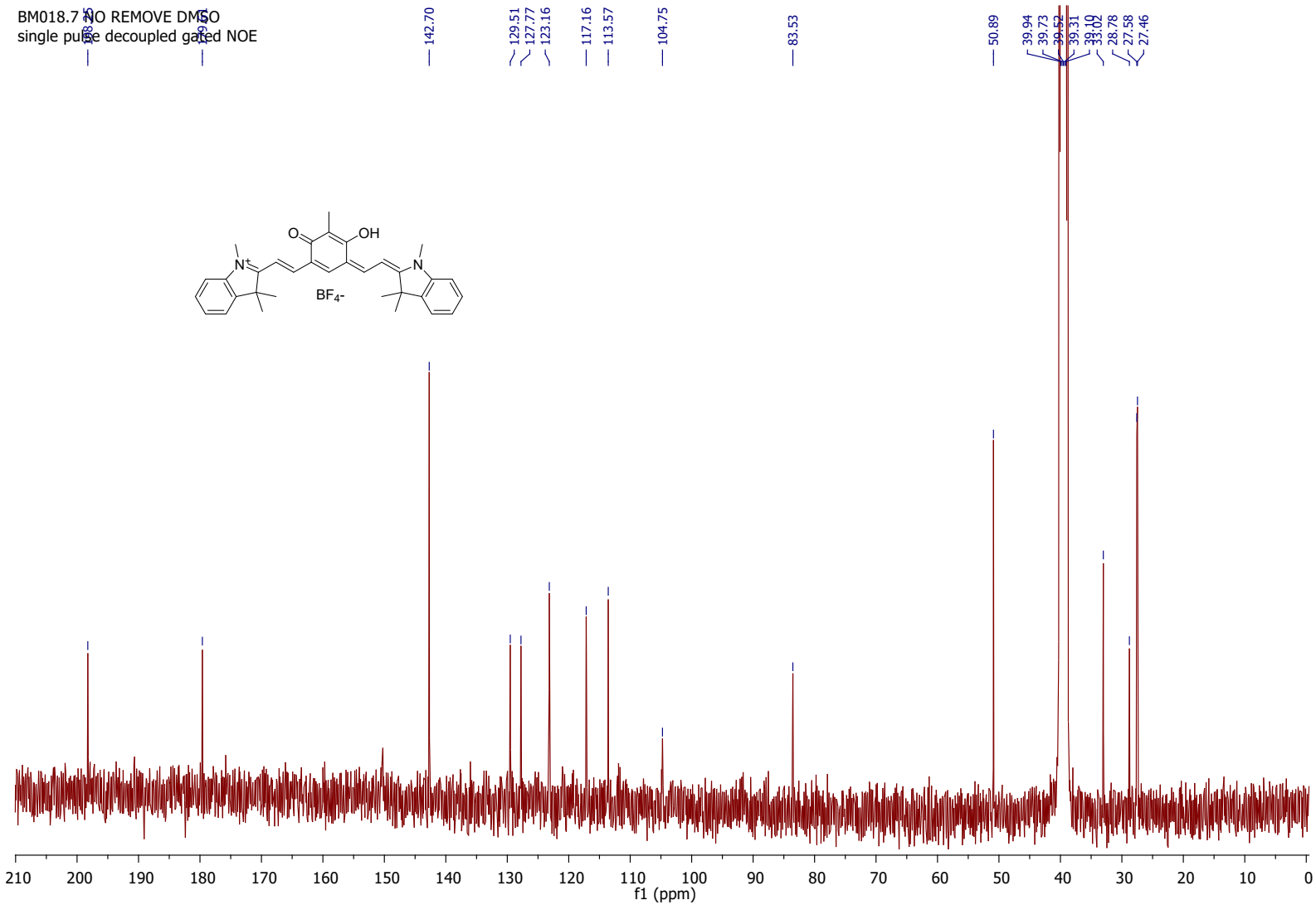


Figure S 17. ^{13}C NMR (101 MHz, DMSO-d_6) of compound **1•H⁺**.

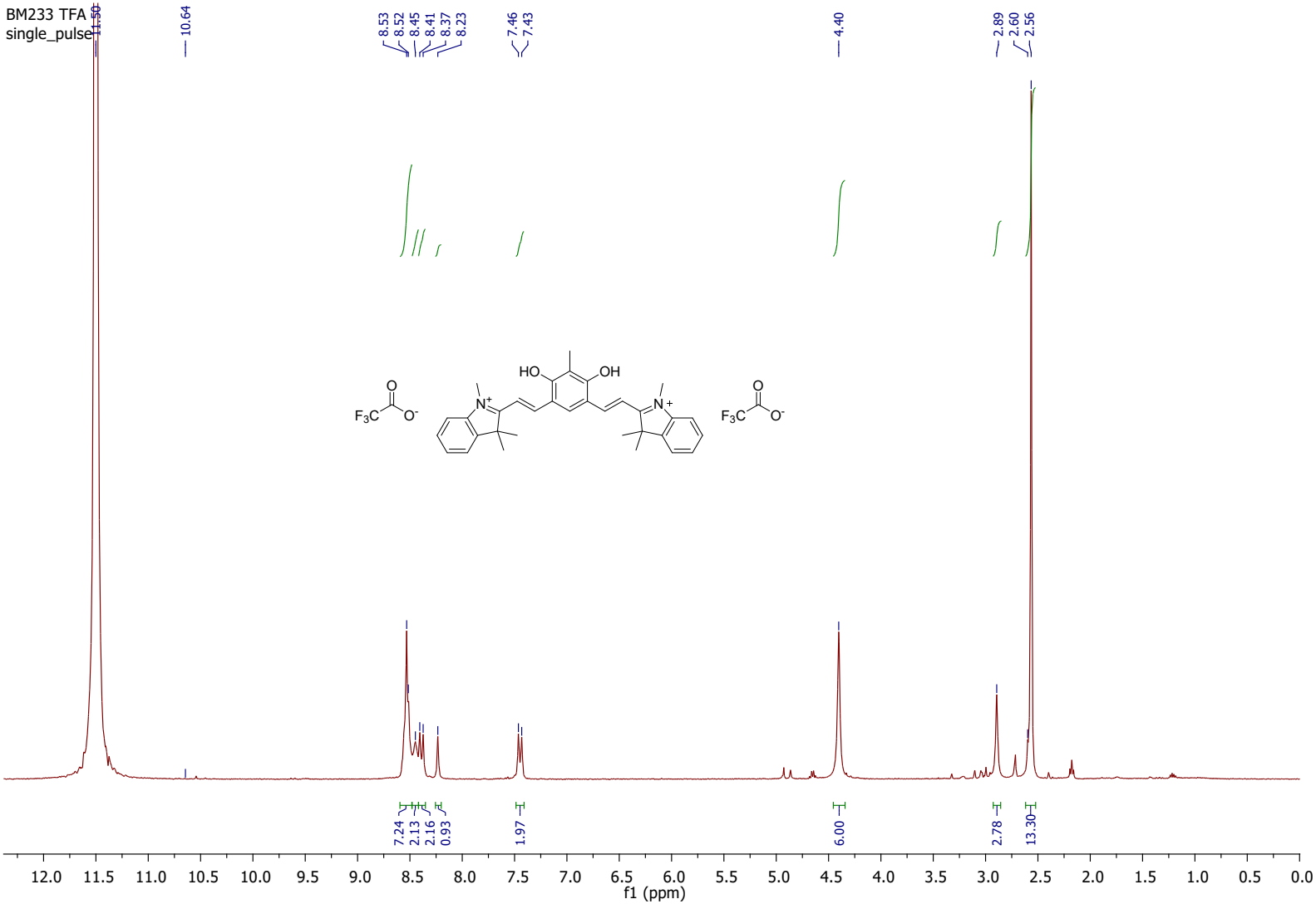


Figure S 18. ^{1}H NMR (400 MHz, TFA-*d*) of compound **1•2H^{2+}**.

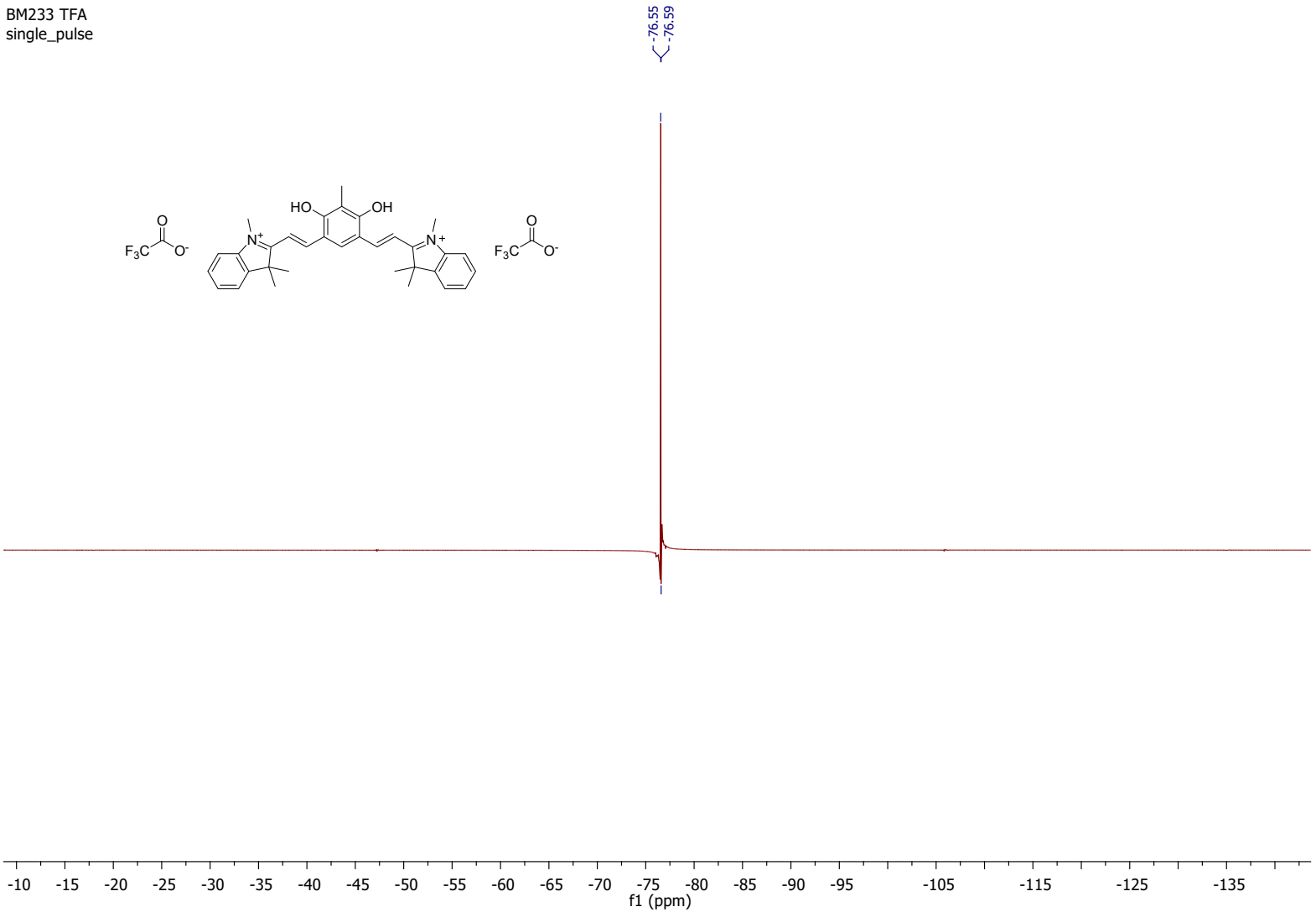


Figure S 19. ^{19}F NMR (377 MHz, TFA-*d*) of compound **1•2H^{2+}**.

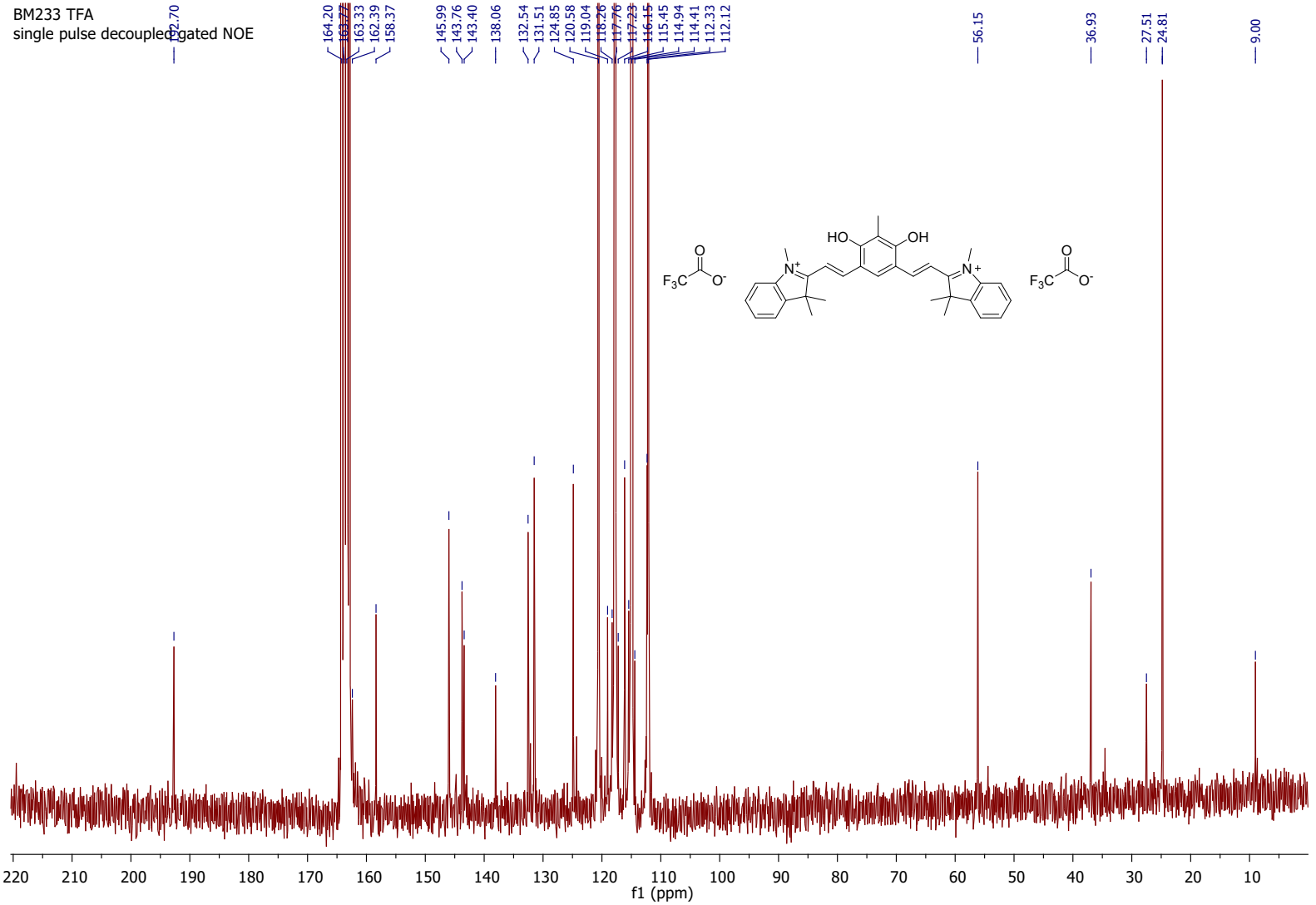


Figure S 20. ^{13}C NMR (101 MHz, TFA-*d*) of compound **1•2H^{2+}**.

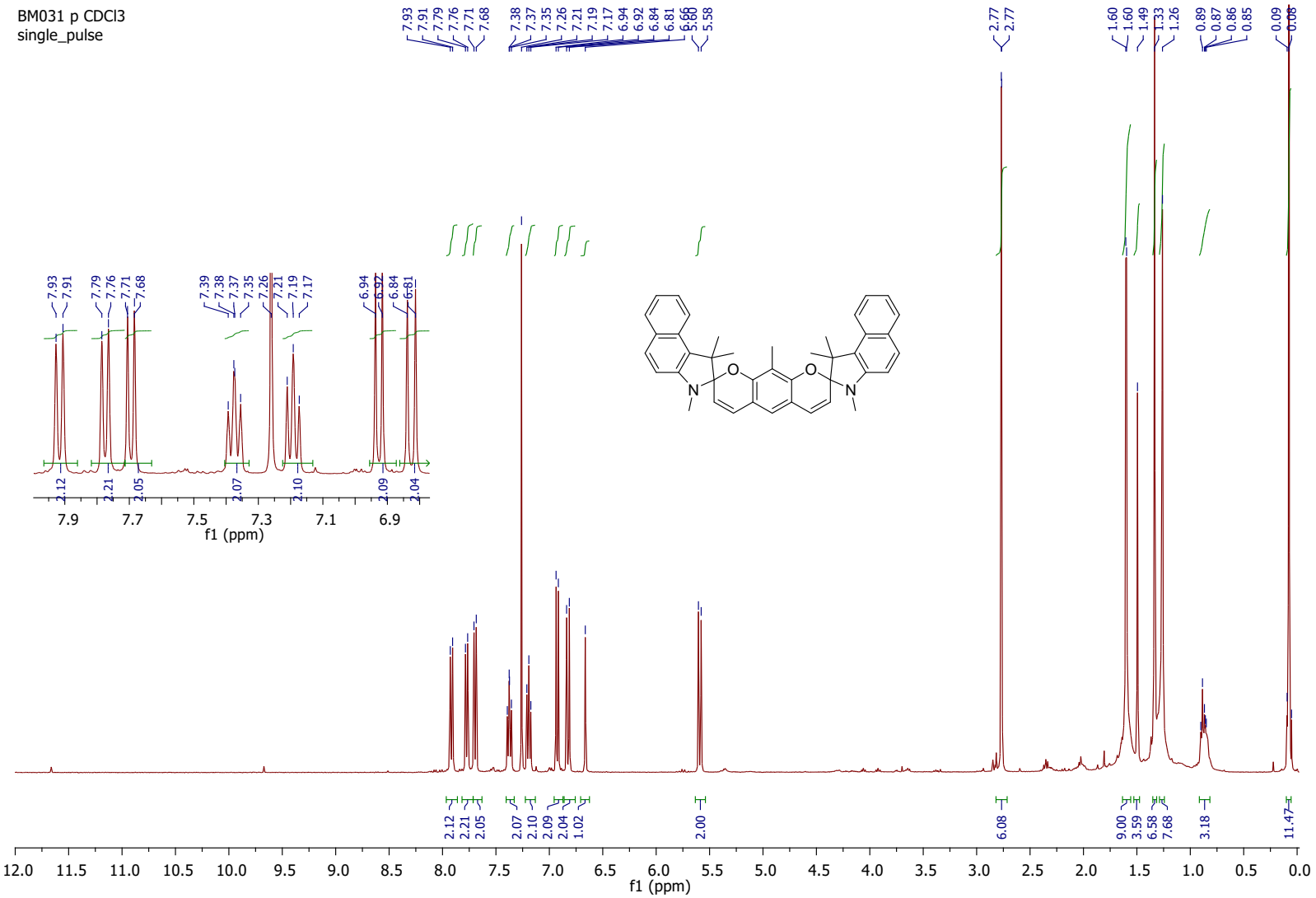


Figure S 21. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **dsp-2**.

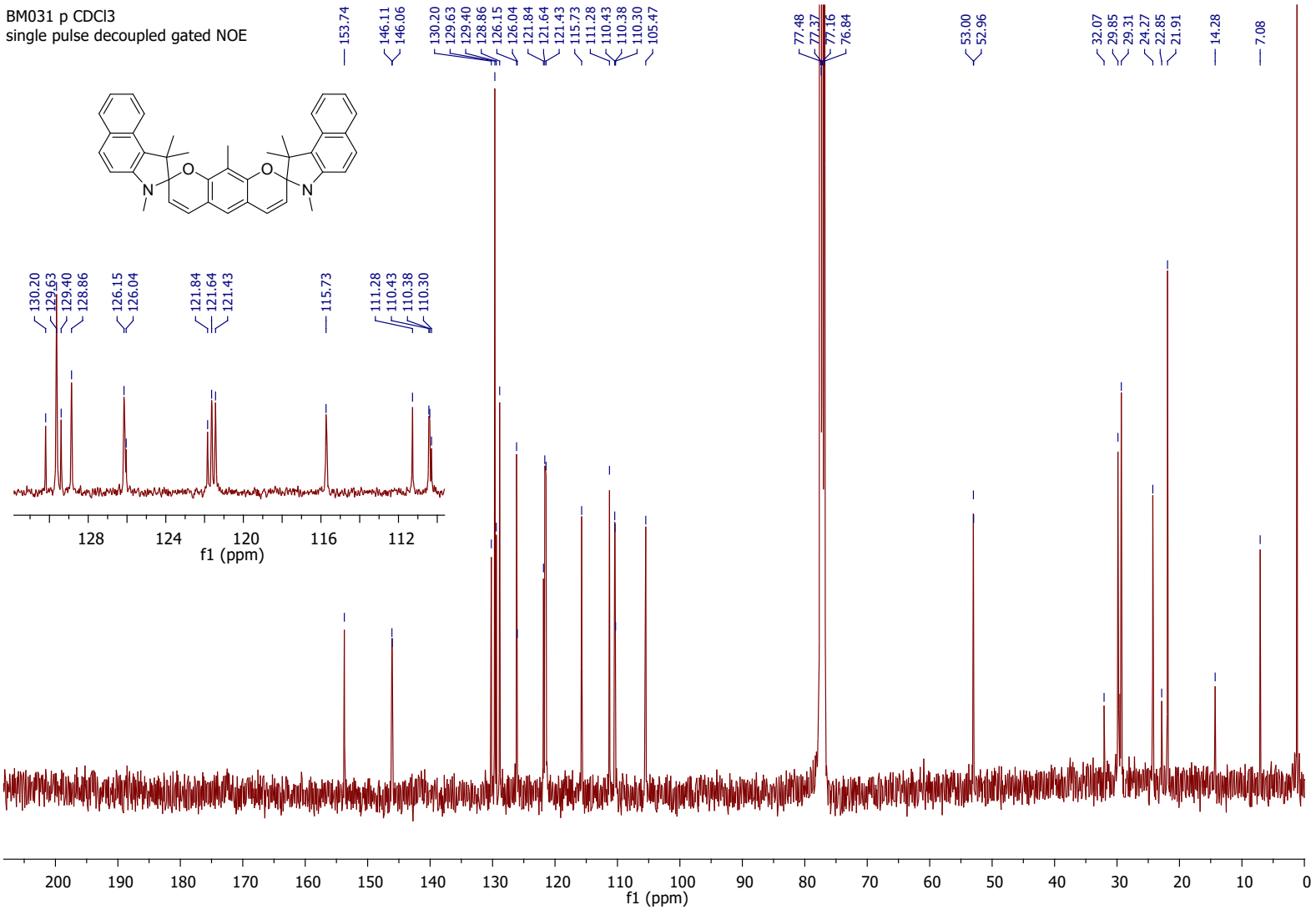


Figure S 22. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **dsp-2**.

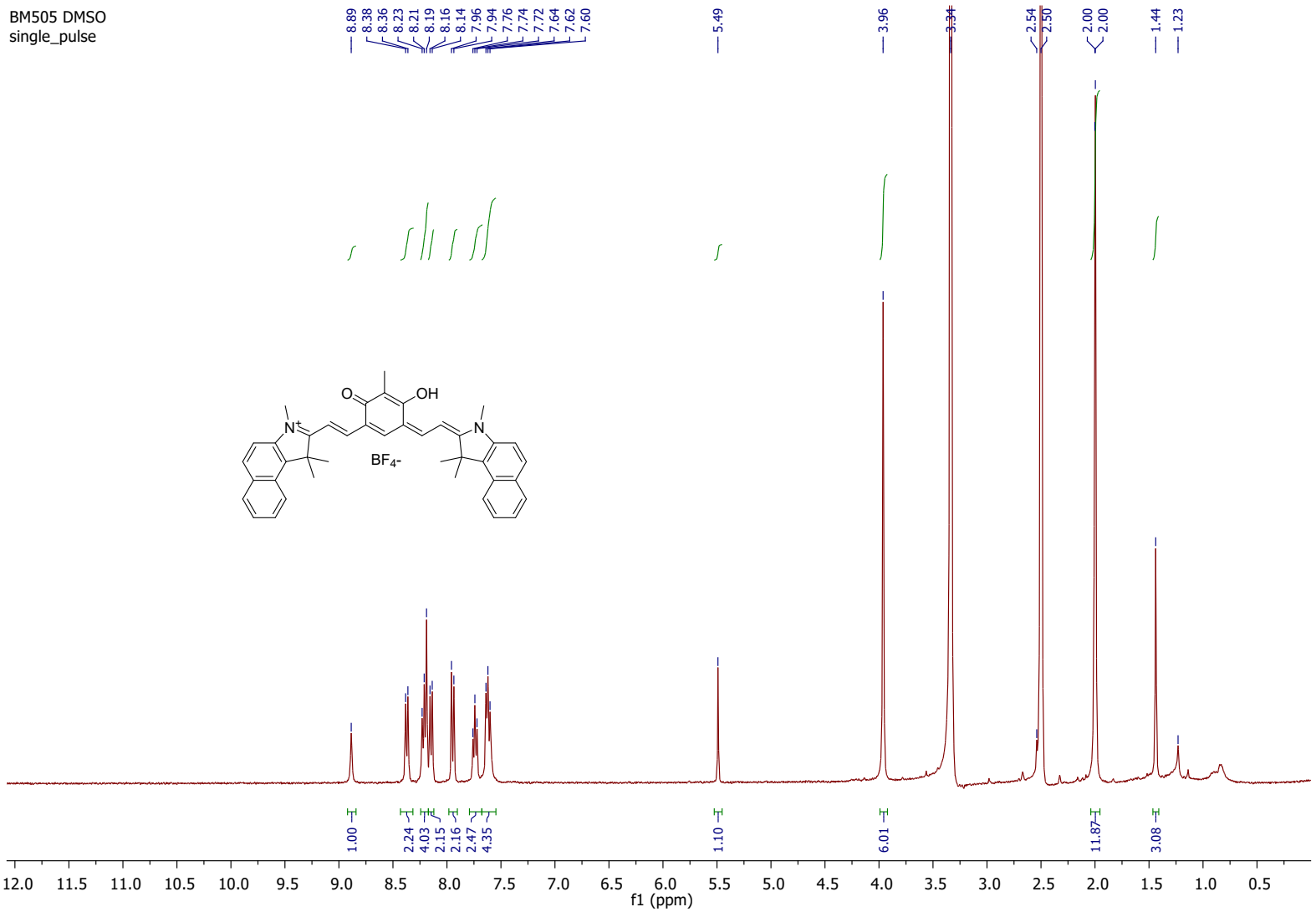


Figure S 23. ^{1}H NMR (400 MHz, DMSO-d_6) of compound **2•H^{+}**.

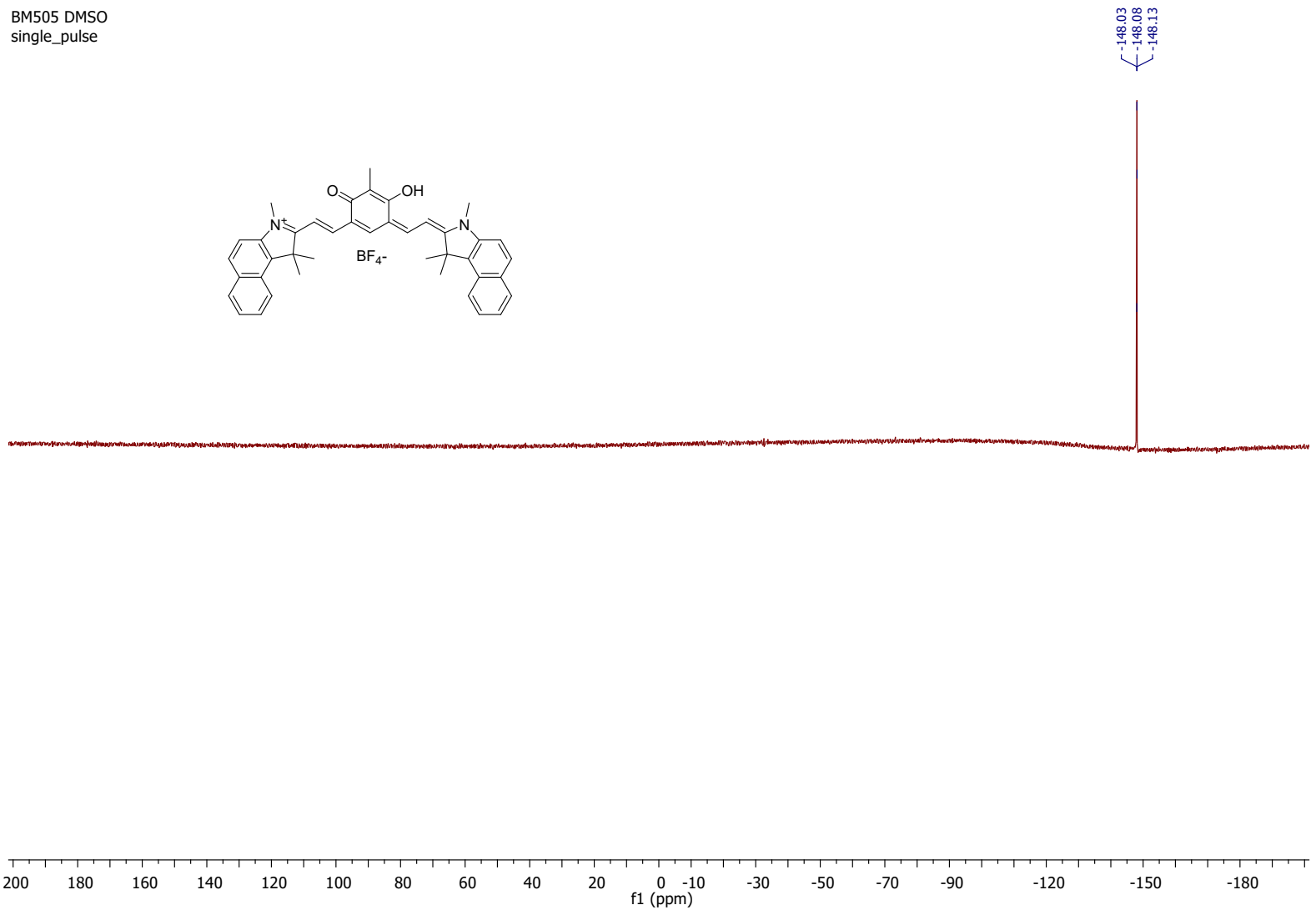


Figure S 24. ^{19}F NMR (377 MHz, DMSO-d_6) of compound **2•H$^+$**.

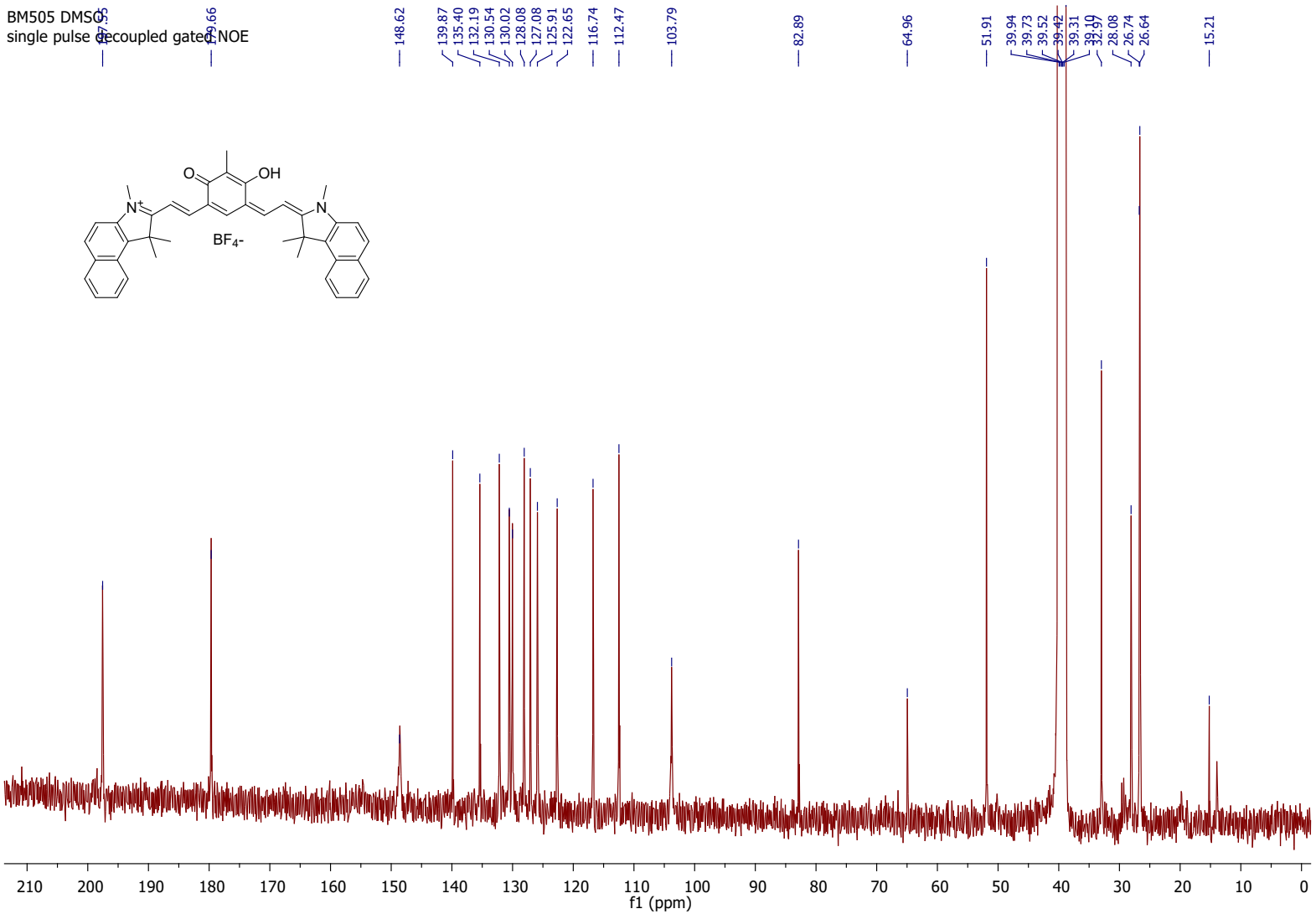


Figure S 25. ^{13}C NMR (101 MHz, DMSO-d_6) of compound **2•H⁺**.

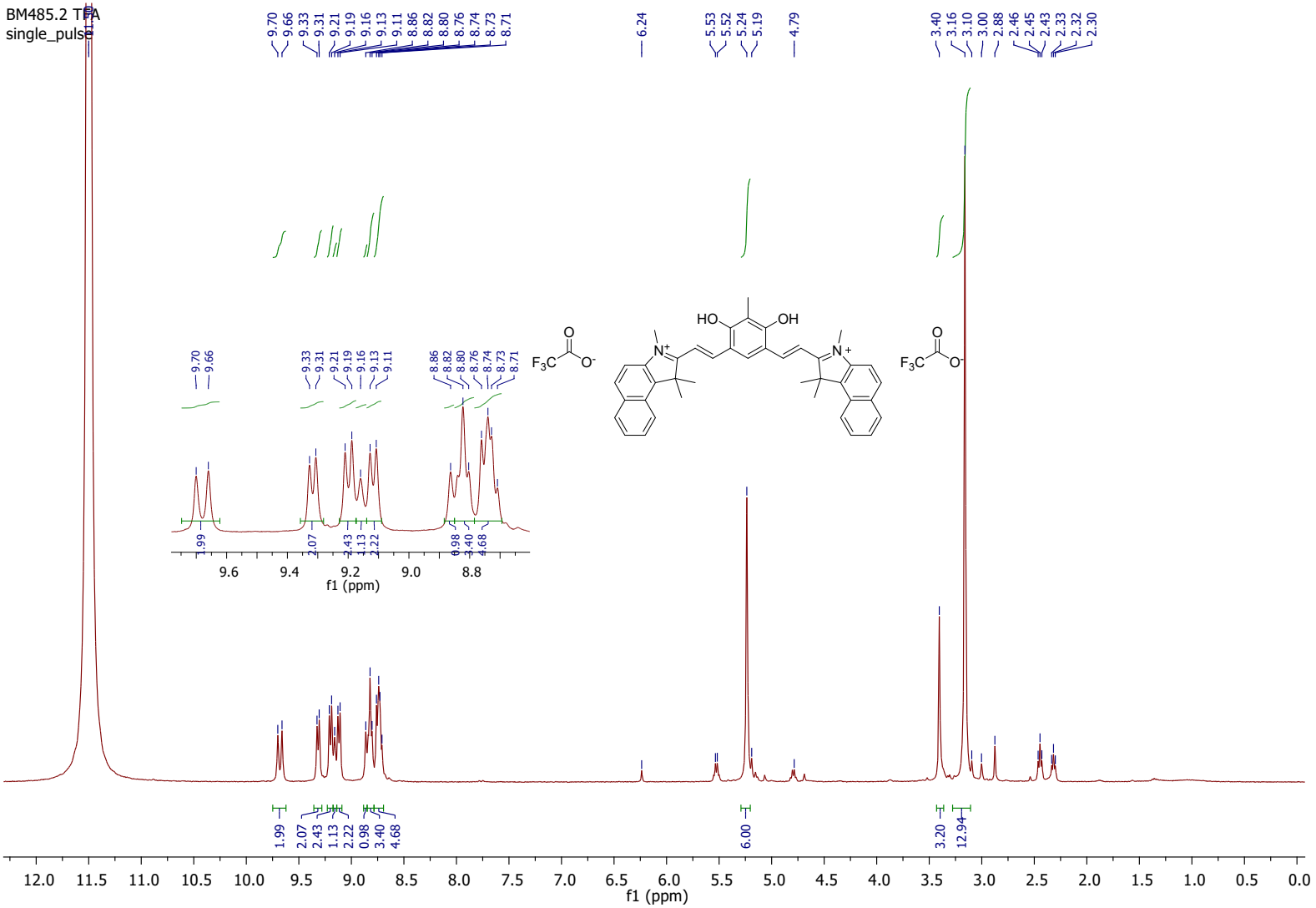


Figure S 26. ^{1}H NMR (400 MHz, TFA-*d*) of compound **2•2H^{2+}**.

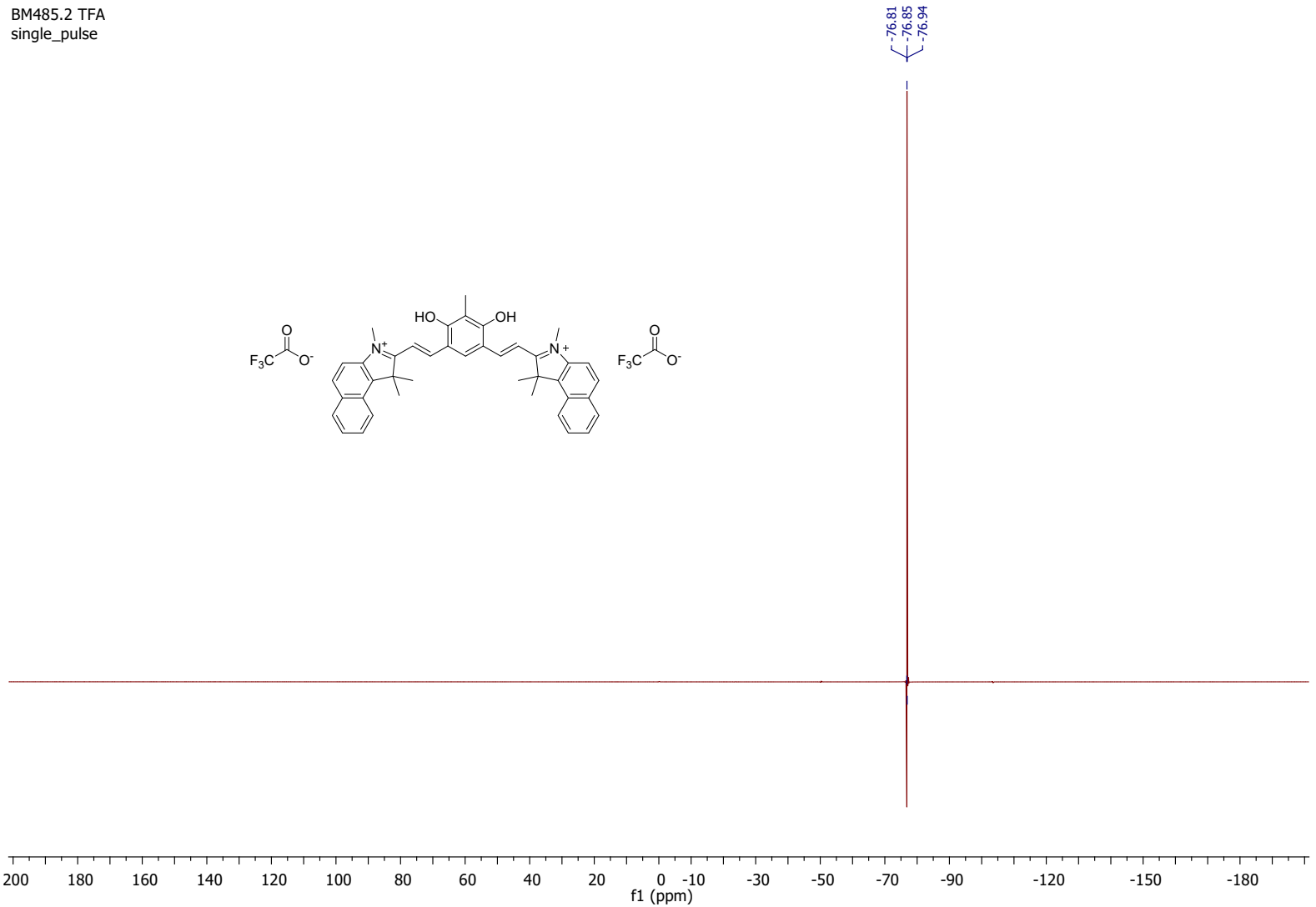


Figure S 27. ^{19}F NMR (377 MHz, TFA-*d*) of compound **2•2H^{2+}**.

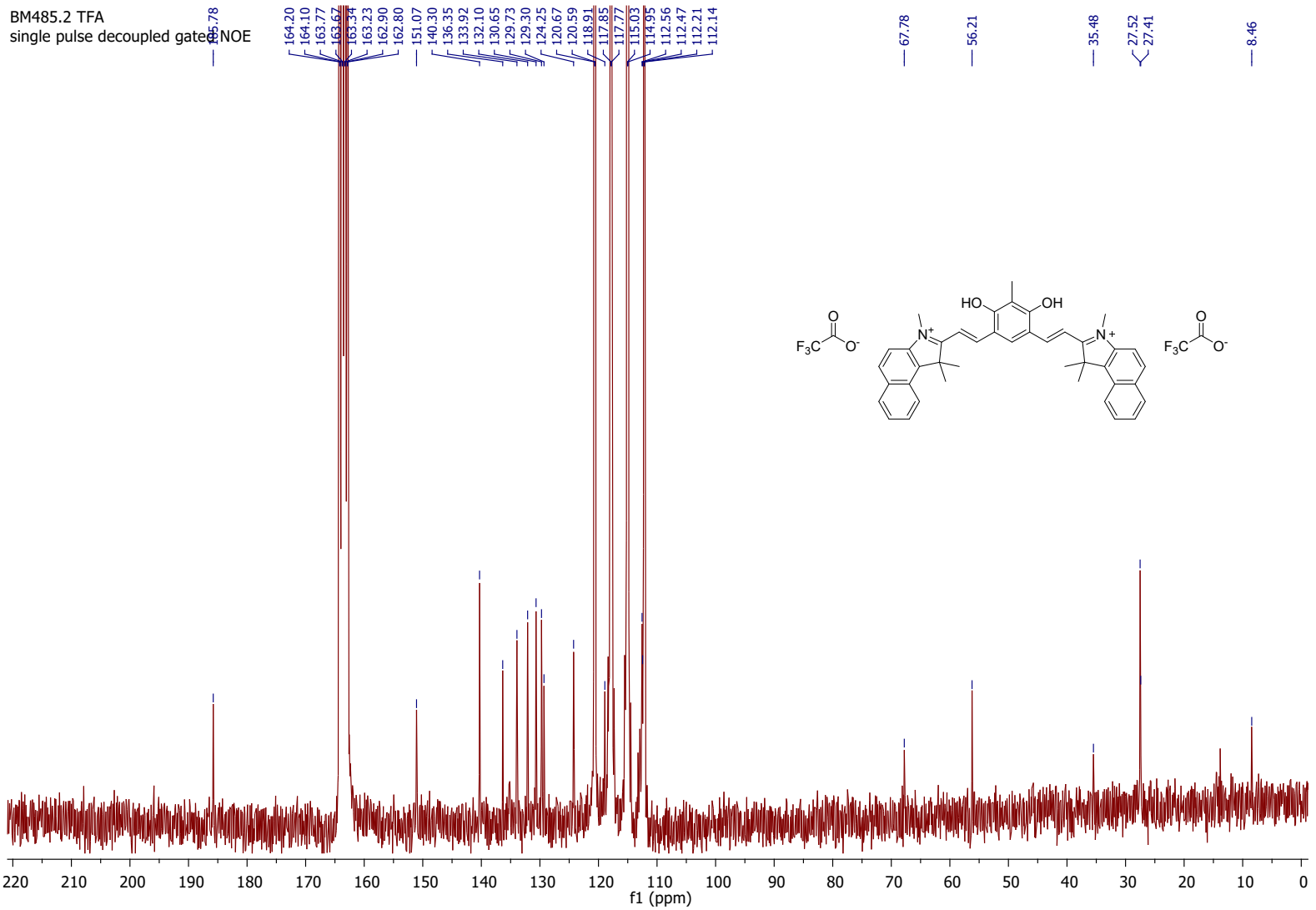


Figure S 28. ^{13}C NMR (101 MHz, TFA-*d*) of compound **2•2H^{2+}**.

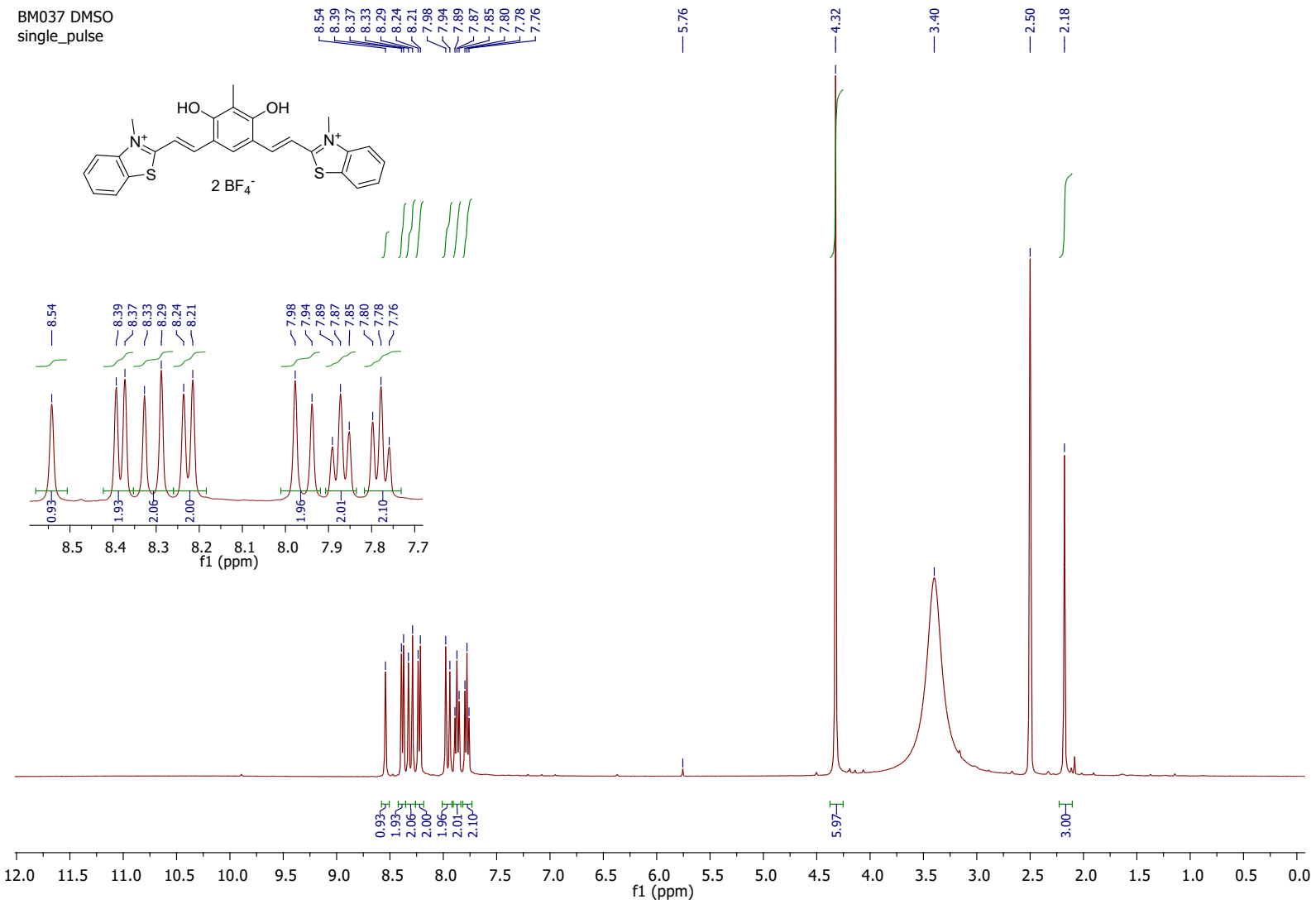


Figure S 29. ^{1}H NMR (400 MHz, DMSO-d_6) of compound **3•2H^{2+}**.

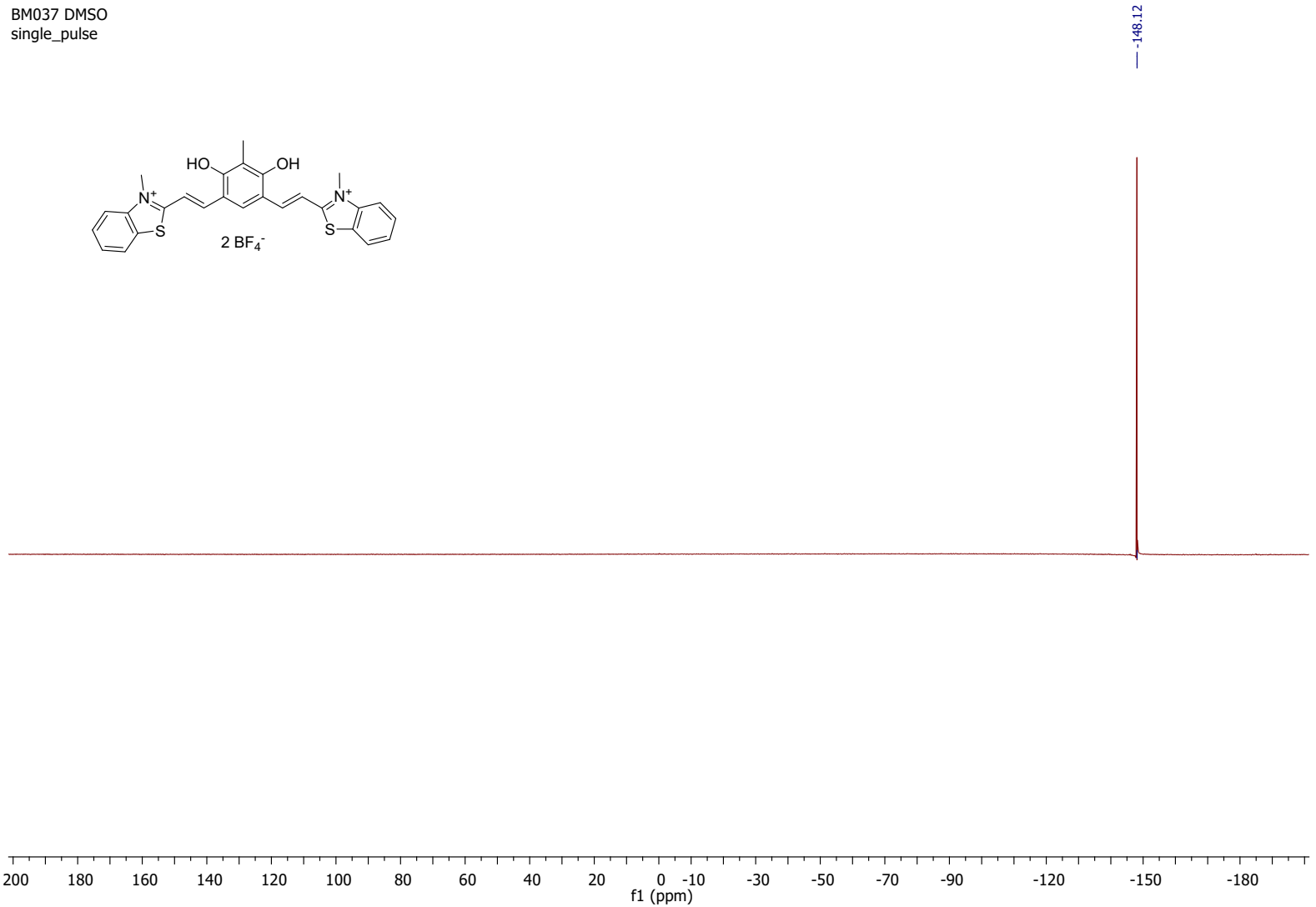


Figure S 30. ^{19}F NMR (377 MHz, DMSO-d_6) of compound **3•2H^{2+}**.

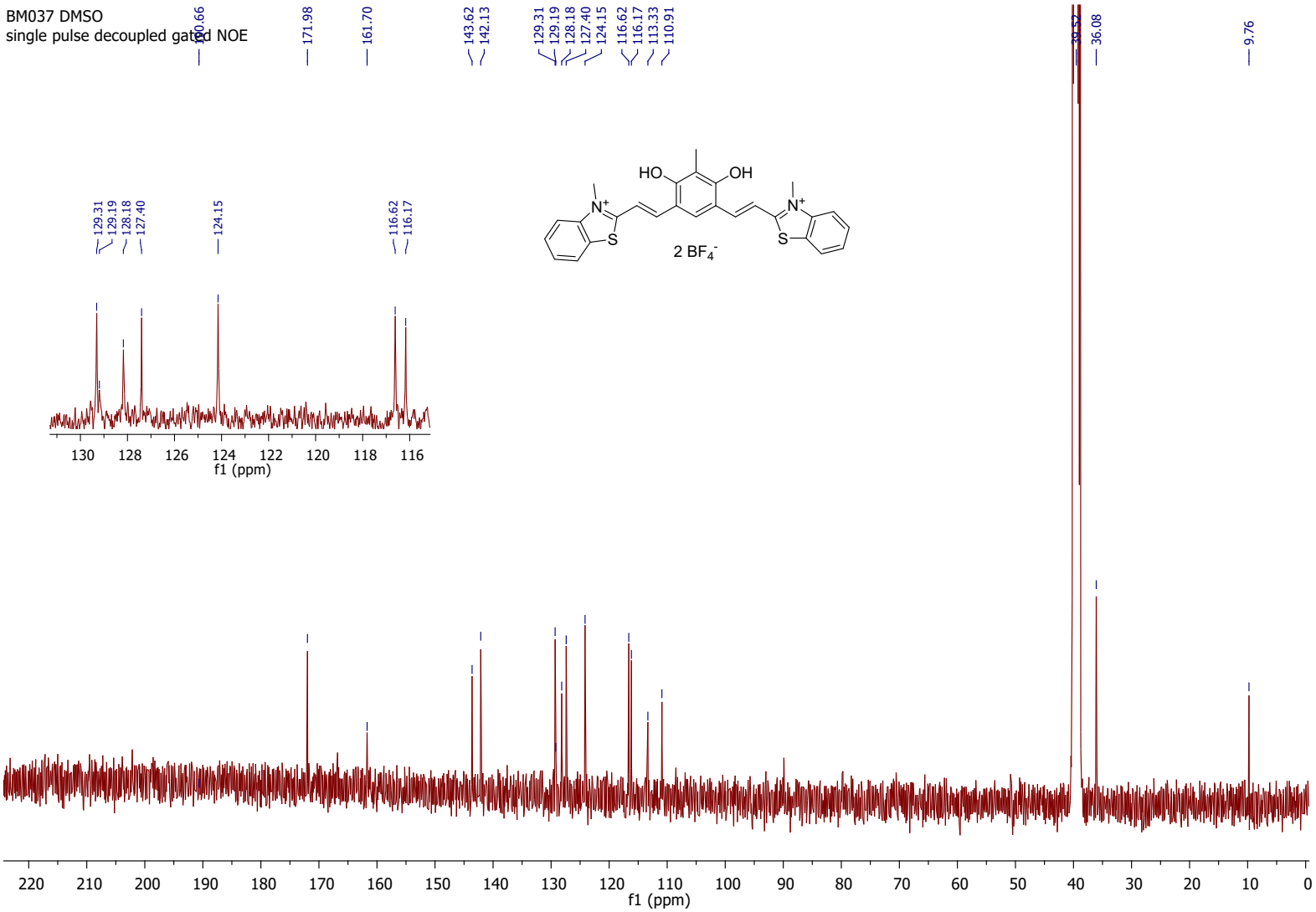


Figure S 31. ^{13}C NMR (101 MHz, DMSO-d_6) of compound **3•2H^{2+}**.

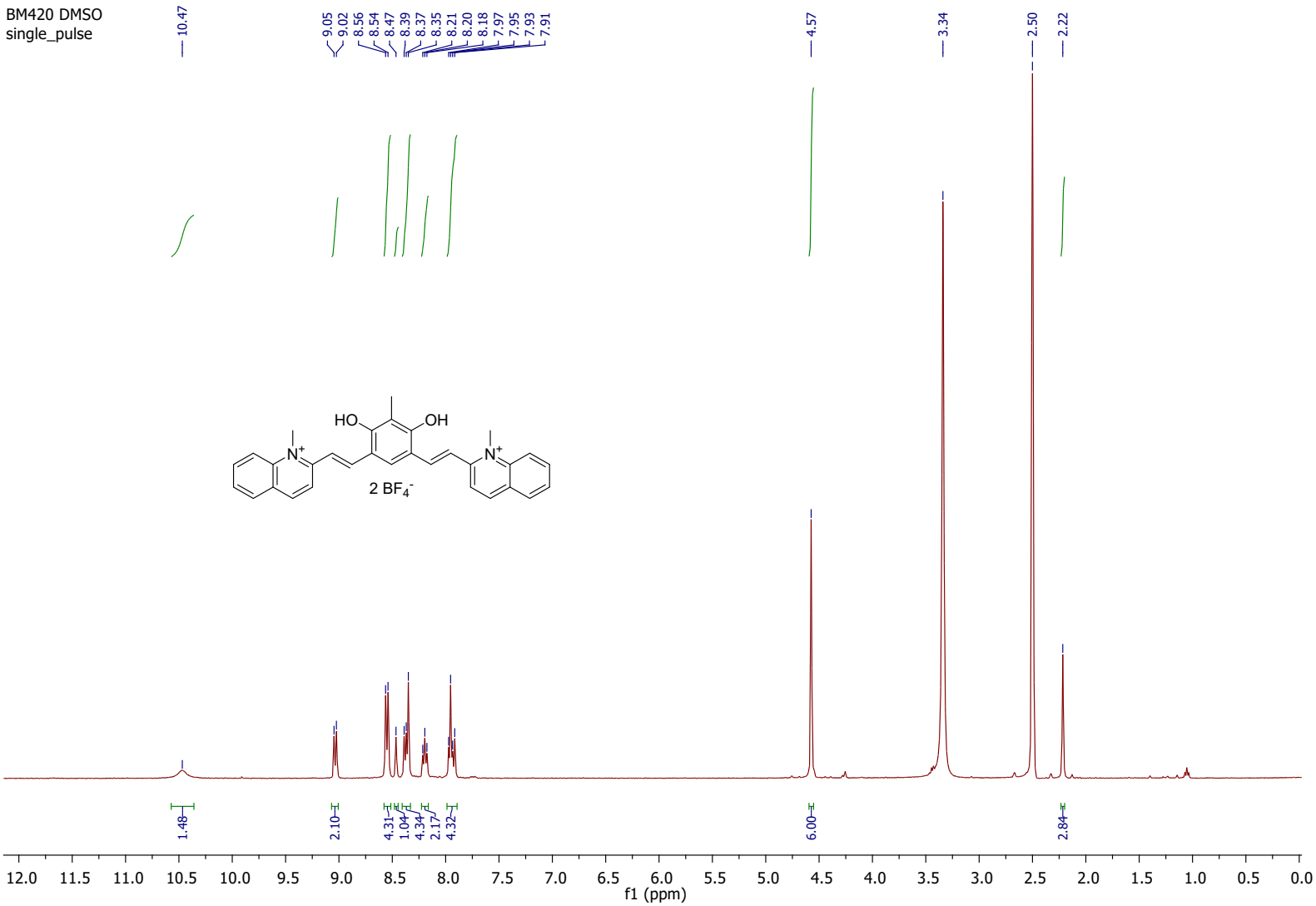


Figure S 32. ^{1}H NMR (400 MHz, DMSO-d_6) of compound **4•2H^{2+}**.

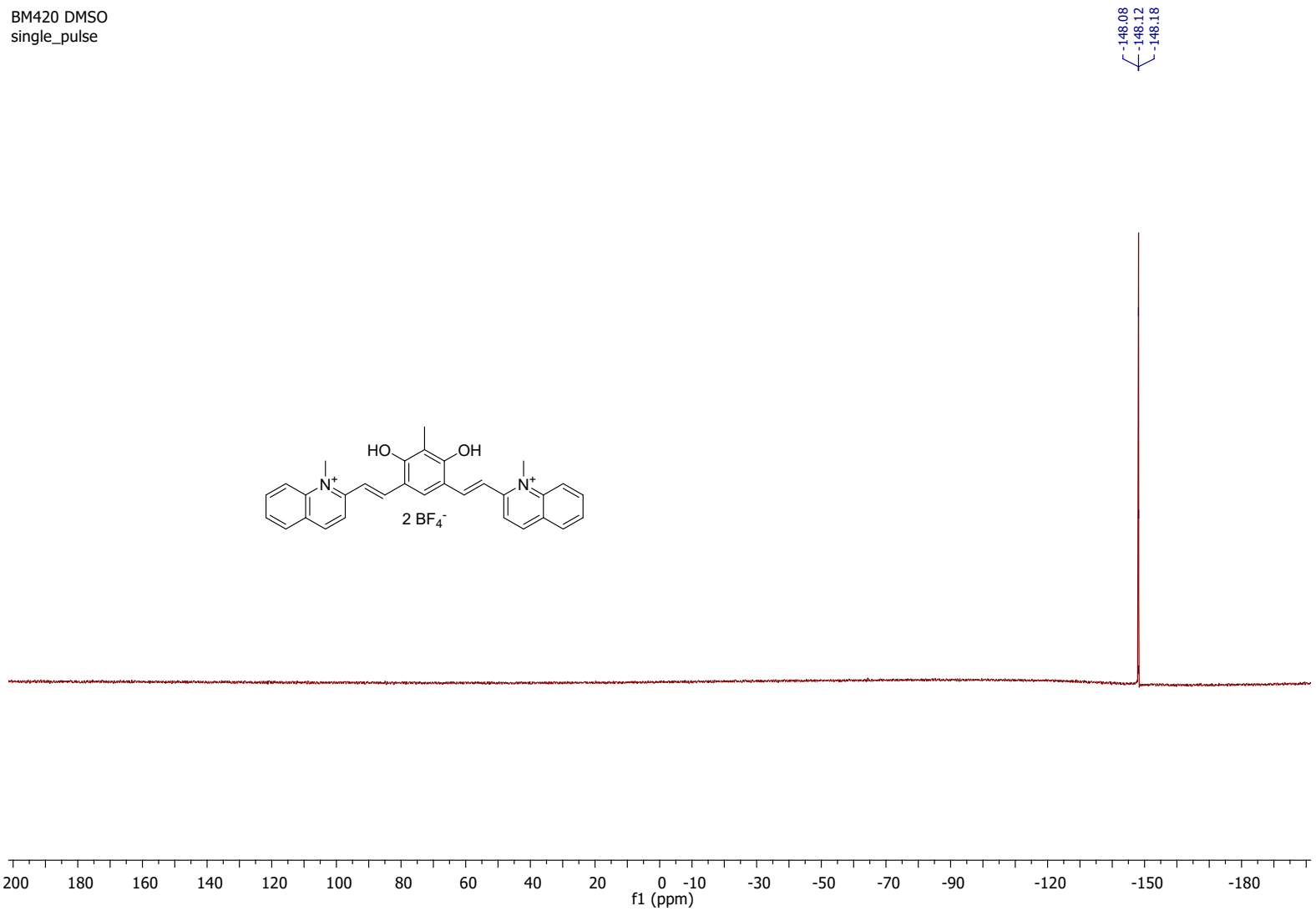


Figure S 33. ^{19}F NMR (377 MHz, DMSO-d_6) of compound **4•2H^{2+}**.

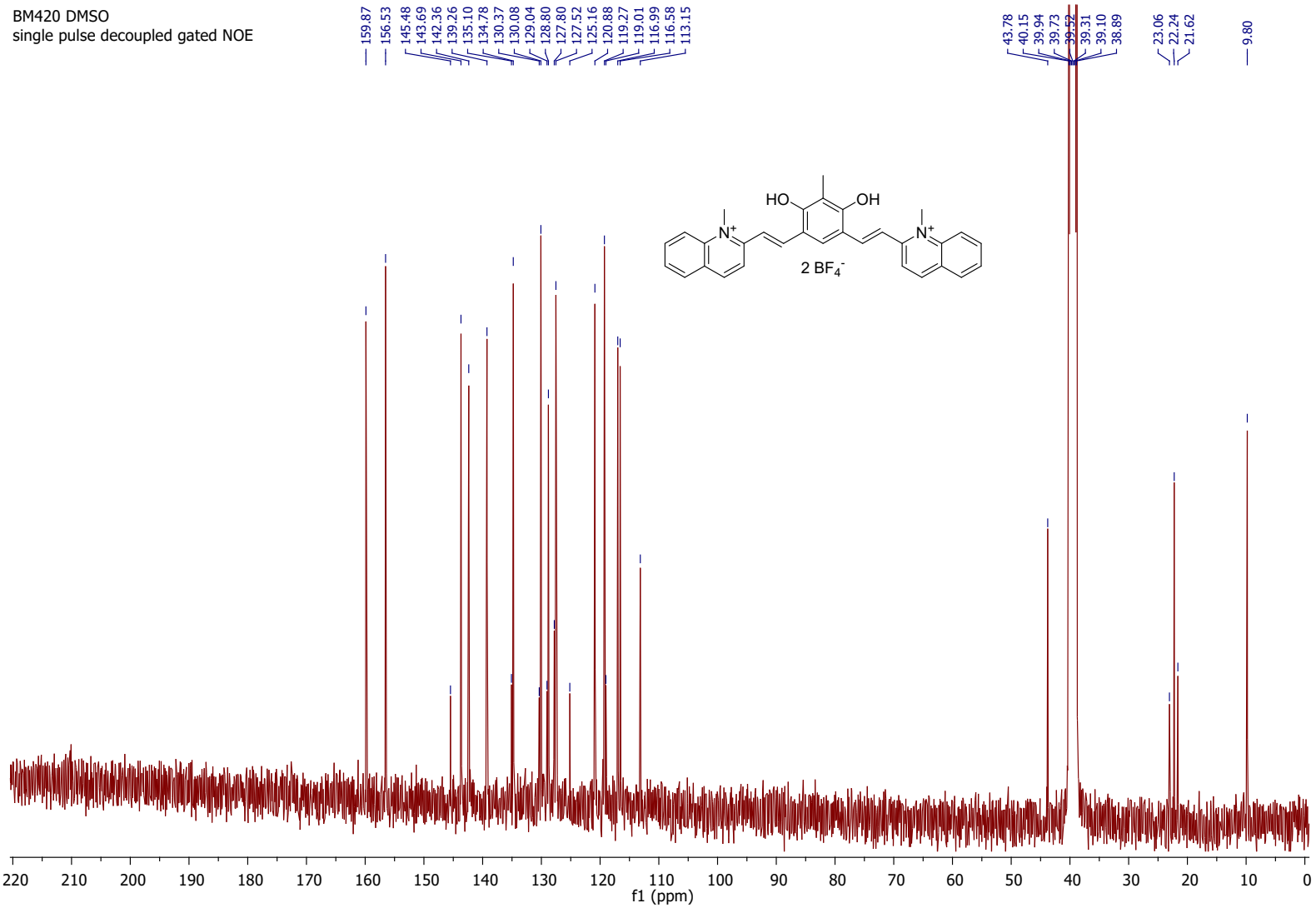


Figure S 34. ^{13}C NMR (101 MHz, DMSO-d_6) of compound **4•2H^{2+}**.

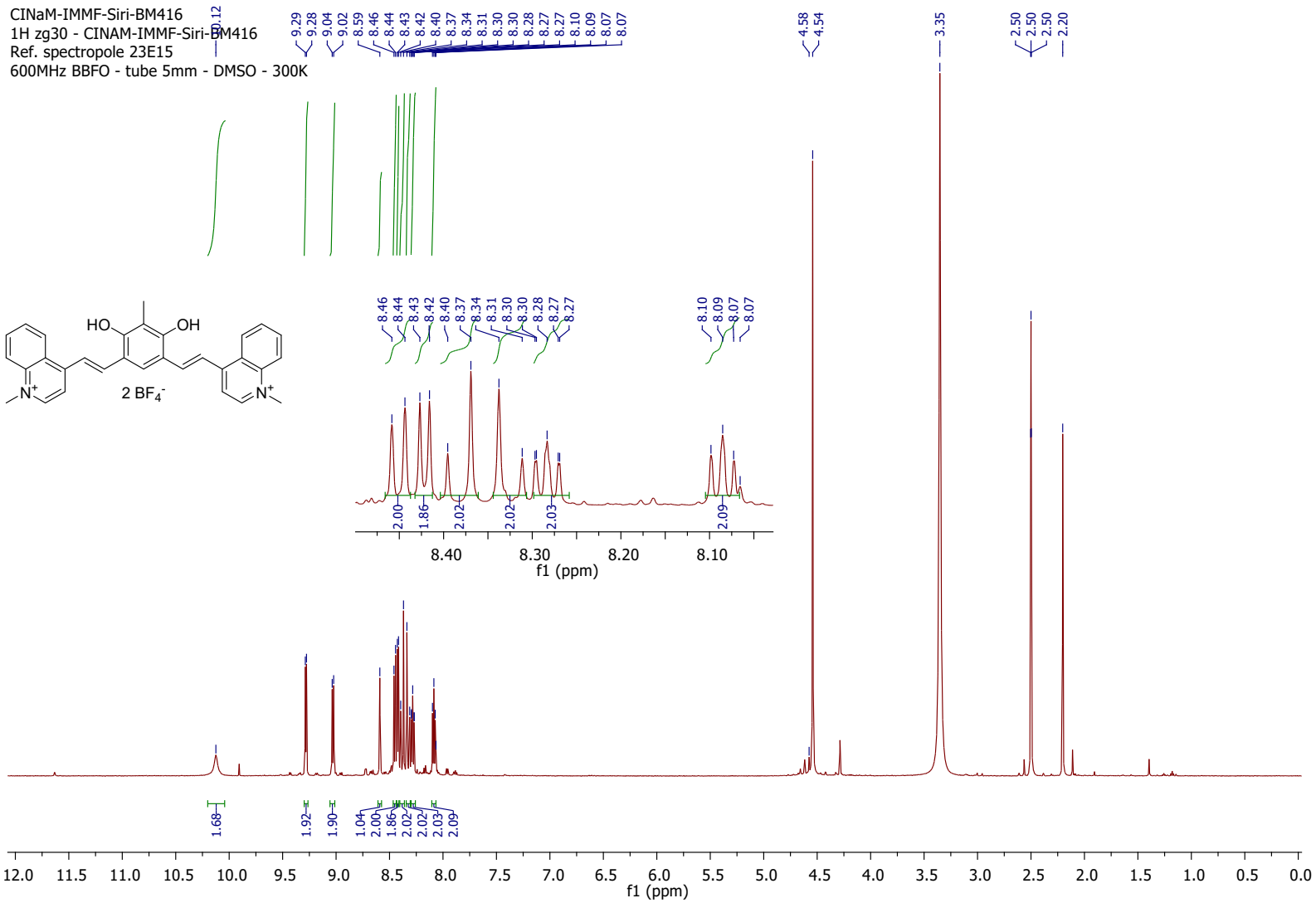


Figure S 35. ^{1}H NMR (600 MHz, DMSO-d_6) of compound **5•2H^{2+}**.

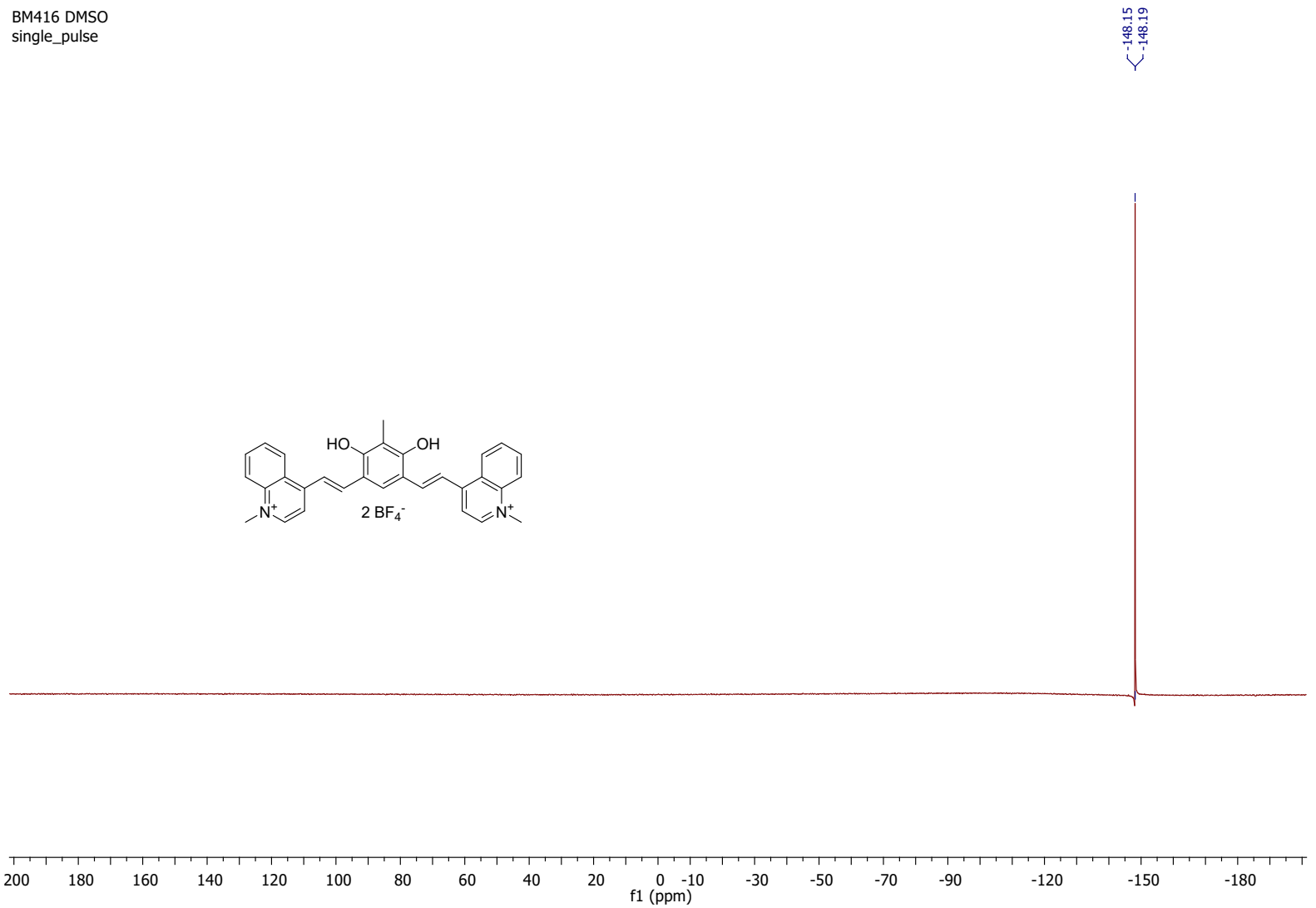


Figure S 36. ^{19}F NMR (377 MHz, DMSO-d_6) of compound **5•2H^{2+}**.

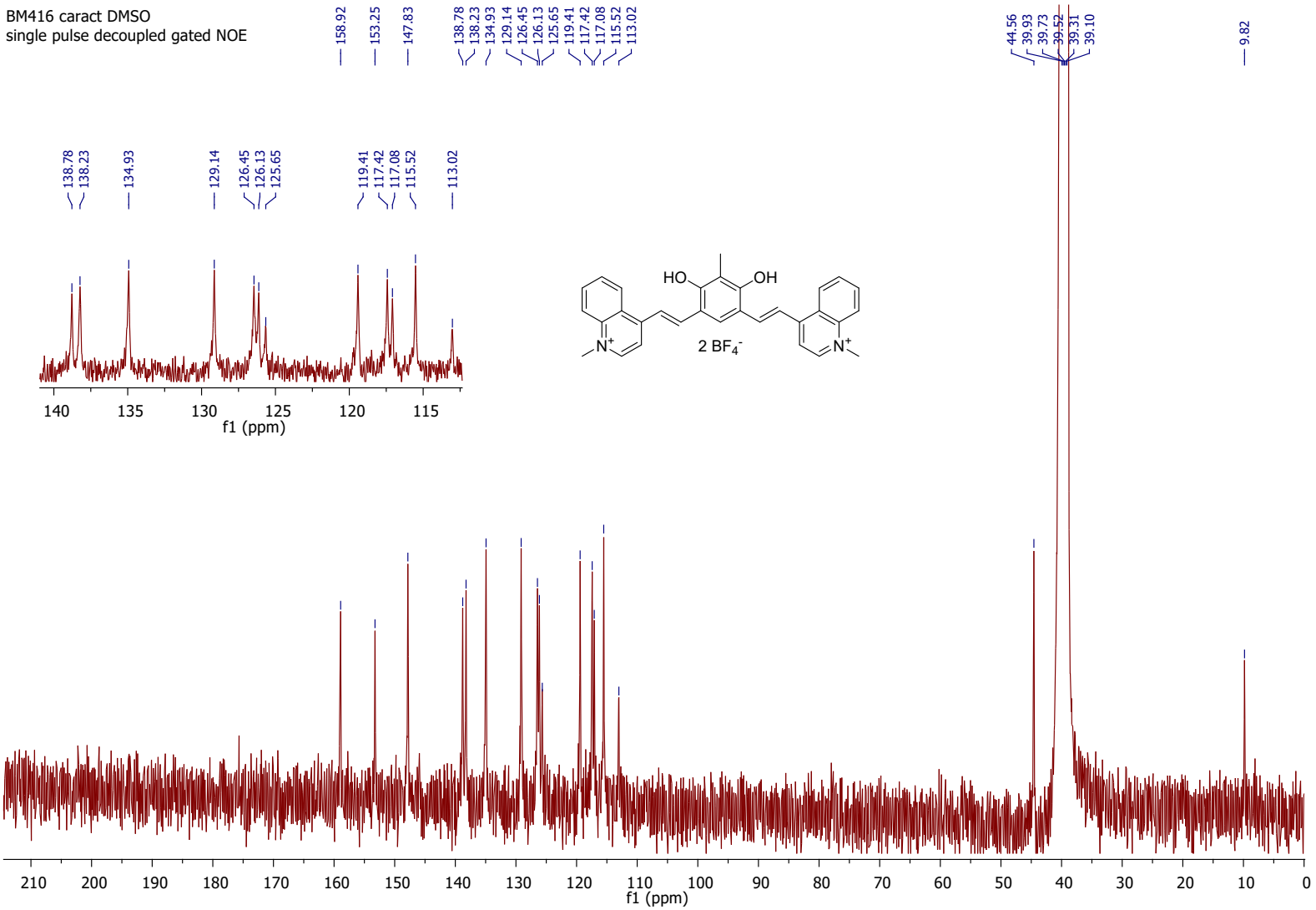


Figure S 37. ^{13}C NMR (101 MHz, DMSO-d_6) of compound **5•2H^{2+}**.

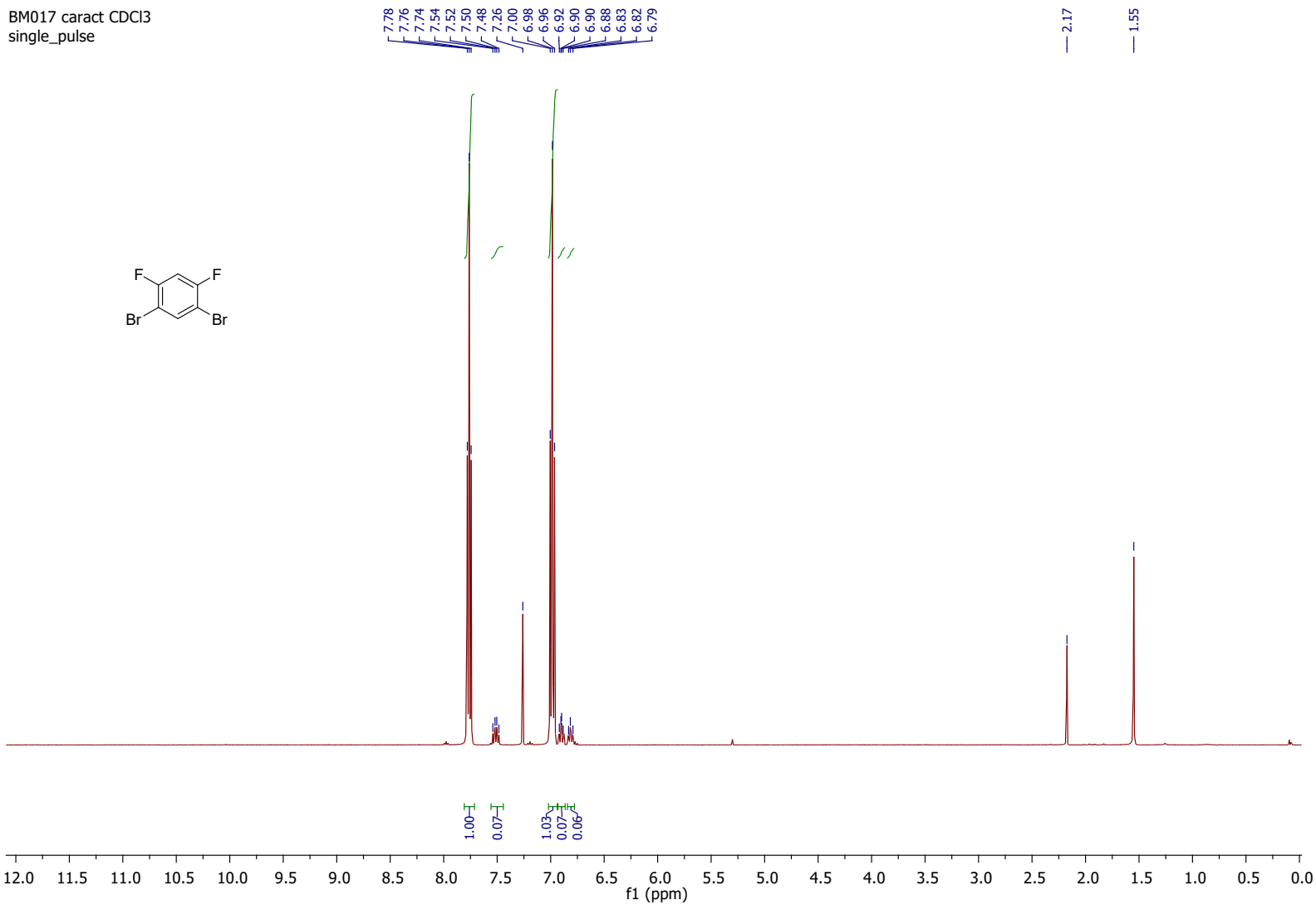


Figure S 38. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **13**.

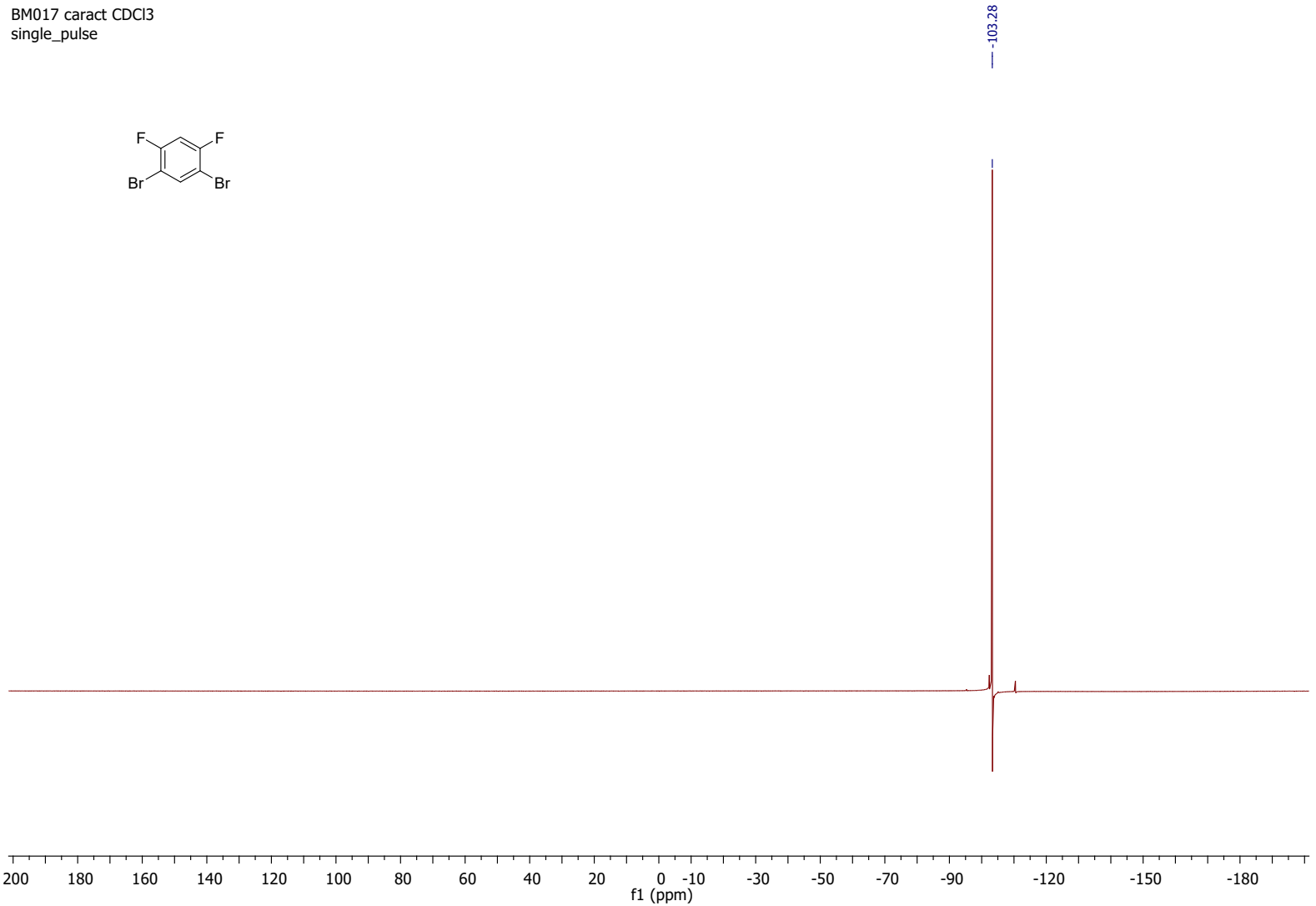


Figure S 39. ^{19}F NMR (377 MHz, $CDCl_3$) of compound **13**.

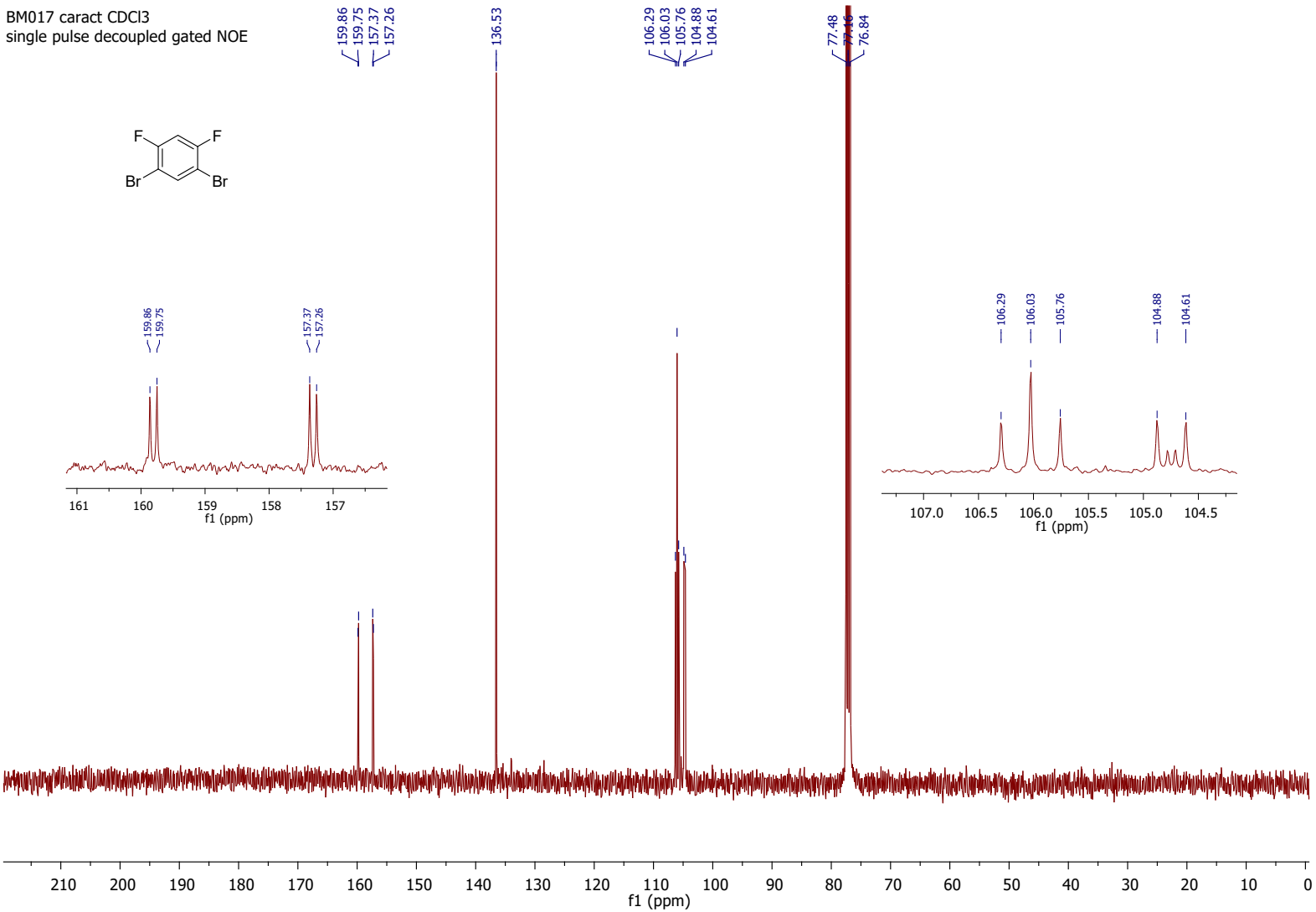


Figure S 40. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **13**.

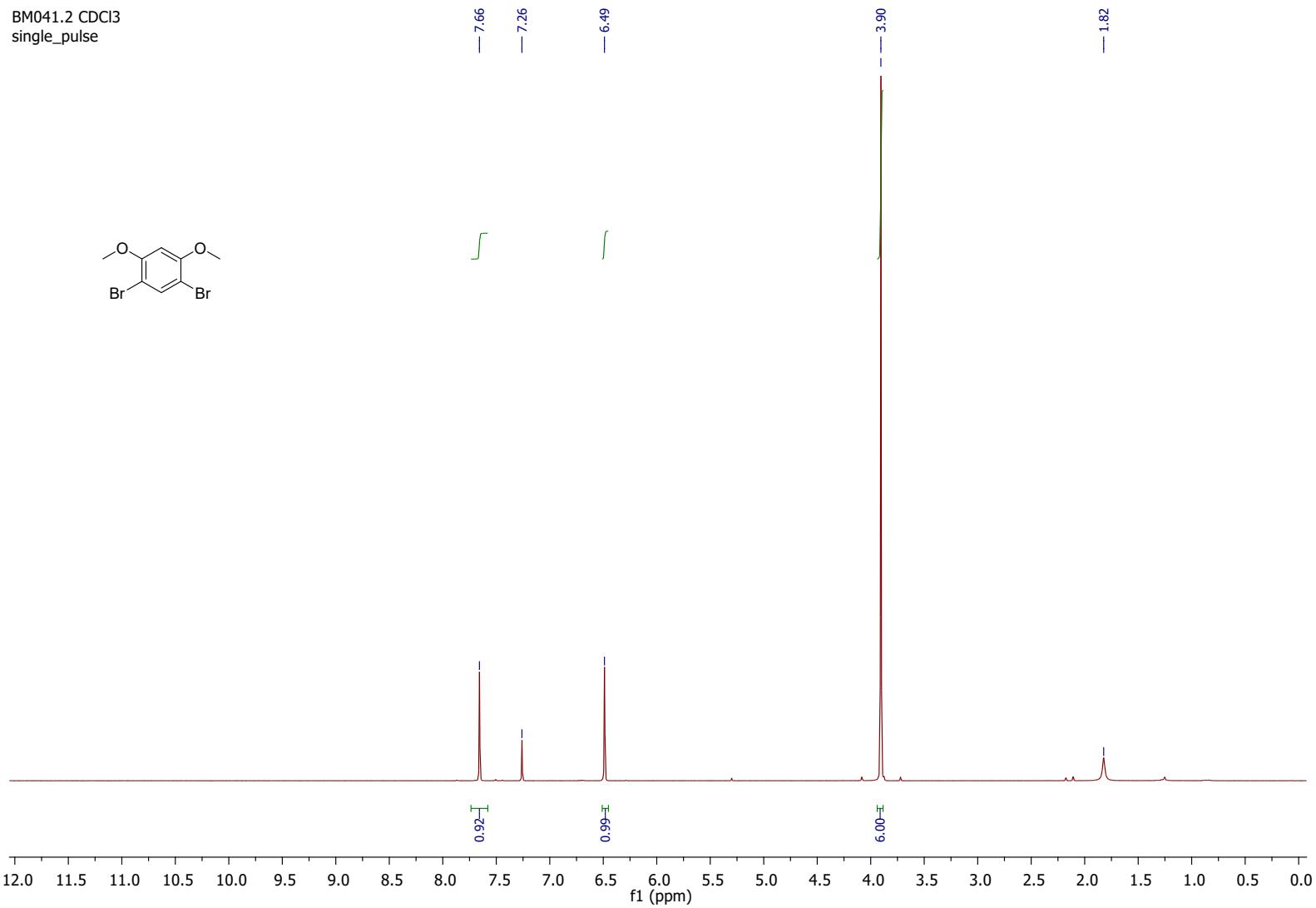


Figure S 41. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **14**.

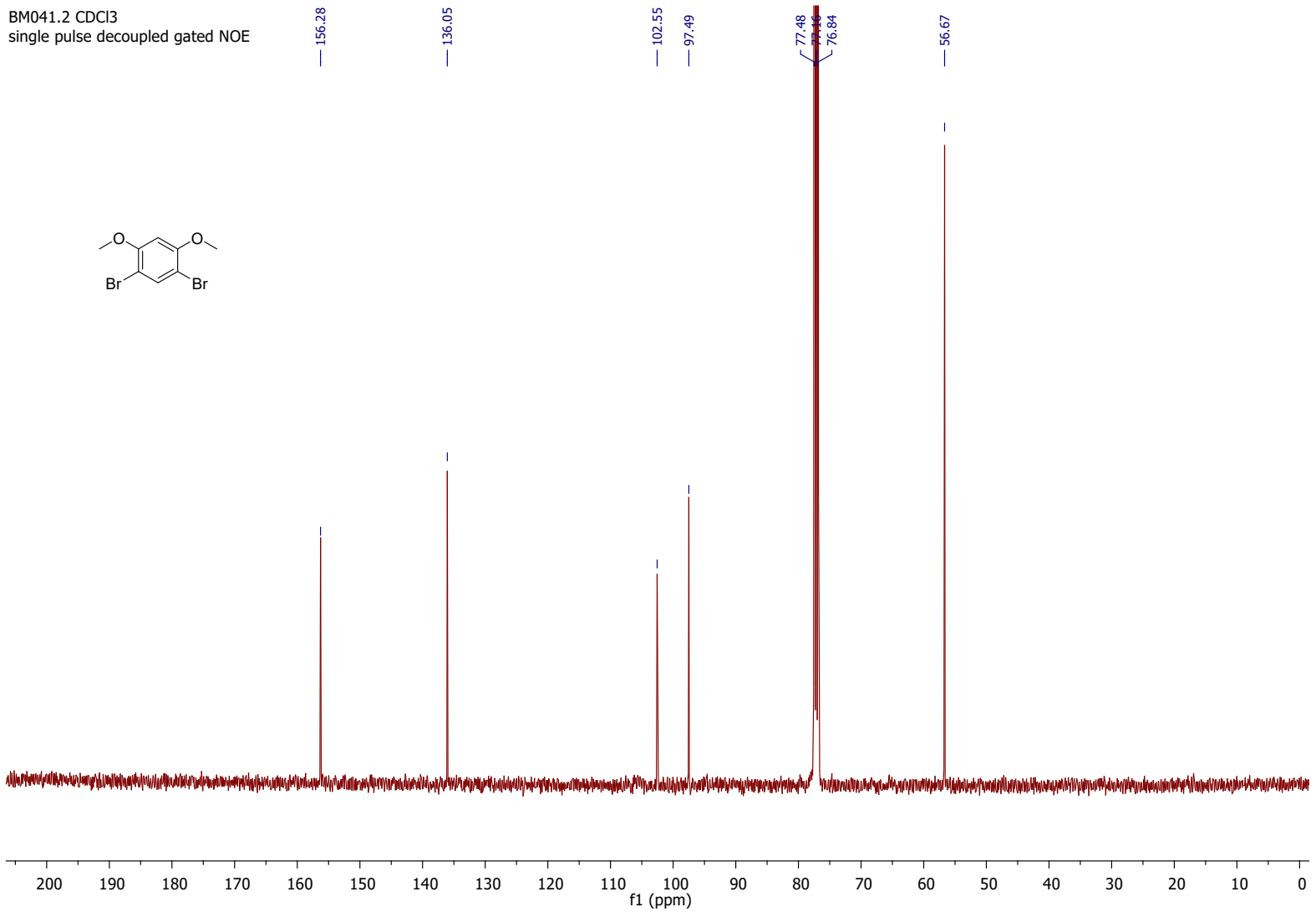


Figure S 42. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **14**.

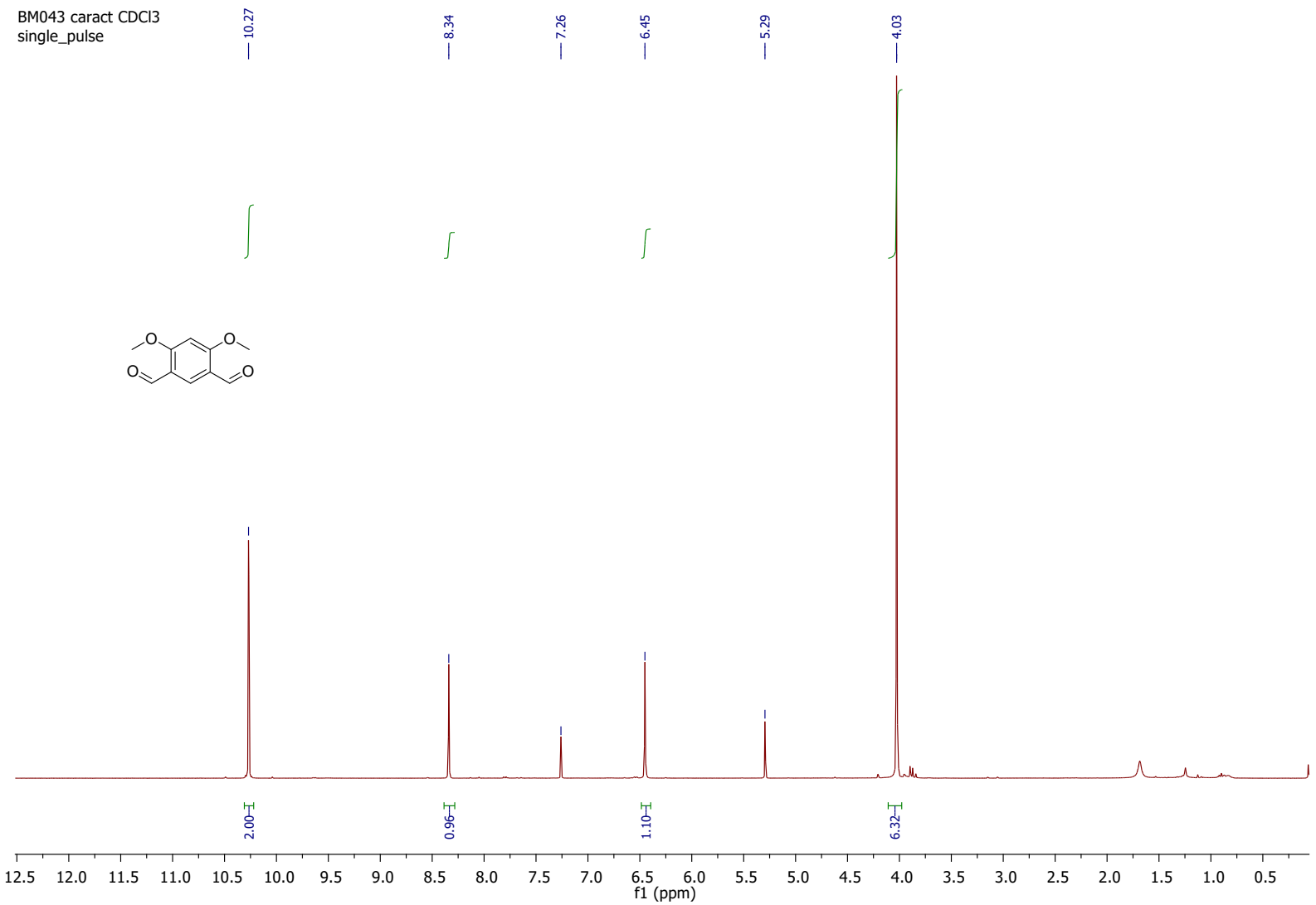


Figure S 43. ^{1}H NMR (400 MHz, $CDCl_3$) of compound **12**.

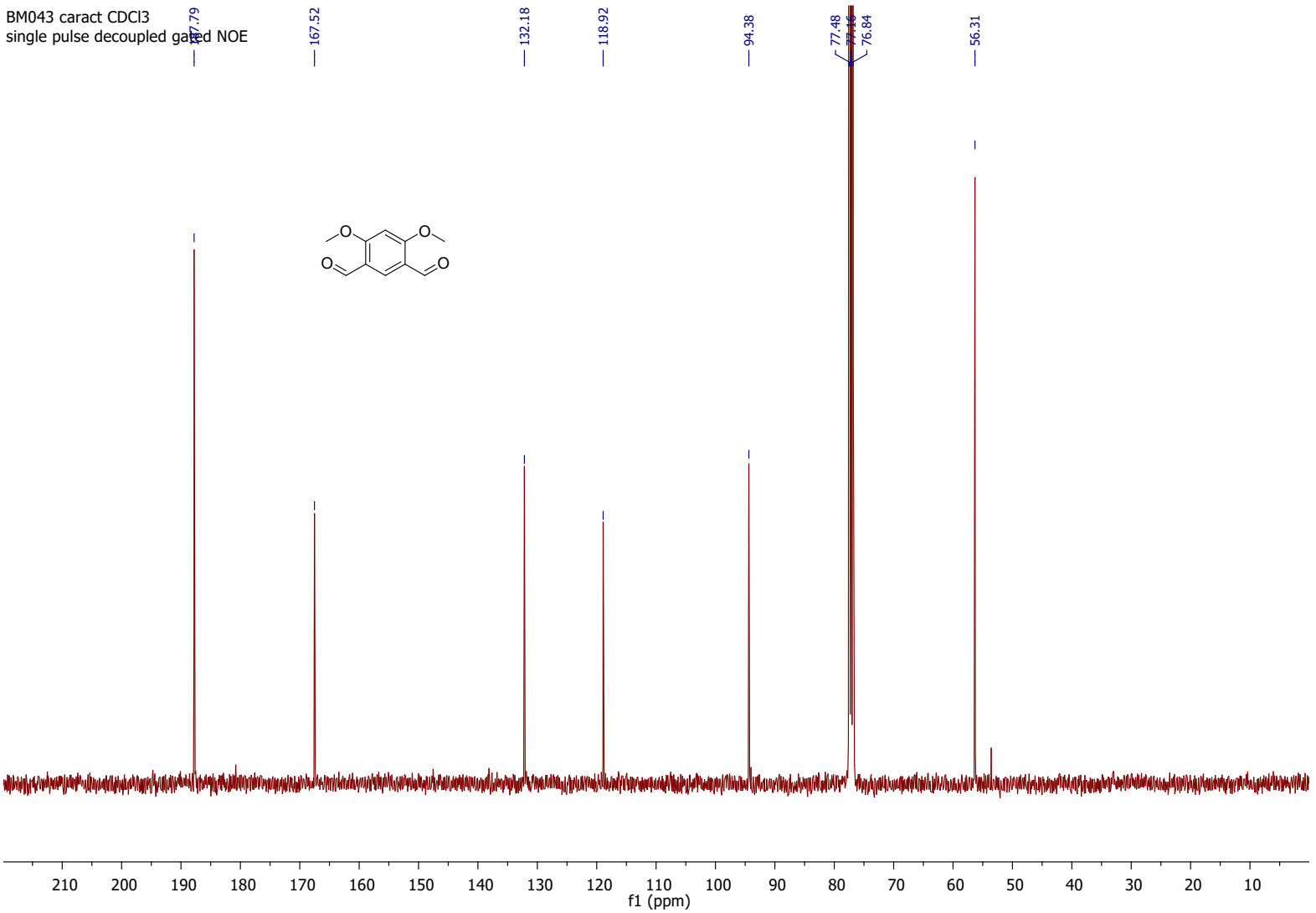


Figure S 44. ^{13}C NMR (101 MHz, $CDCl_3$) of compound **12**.

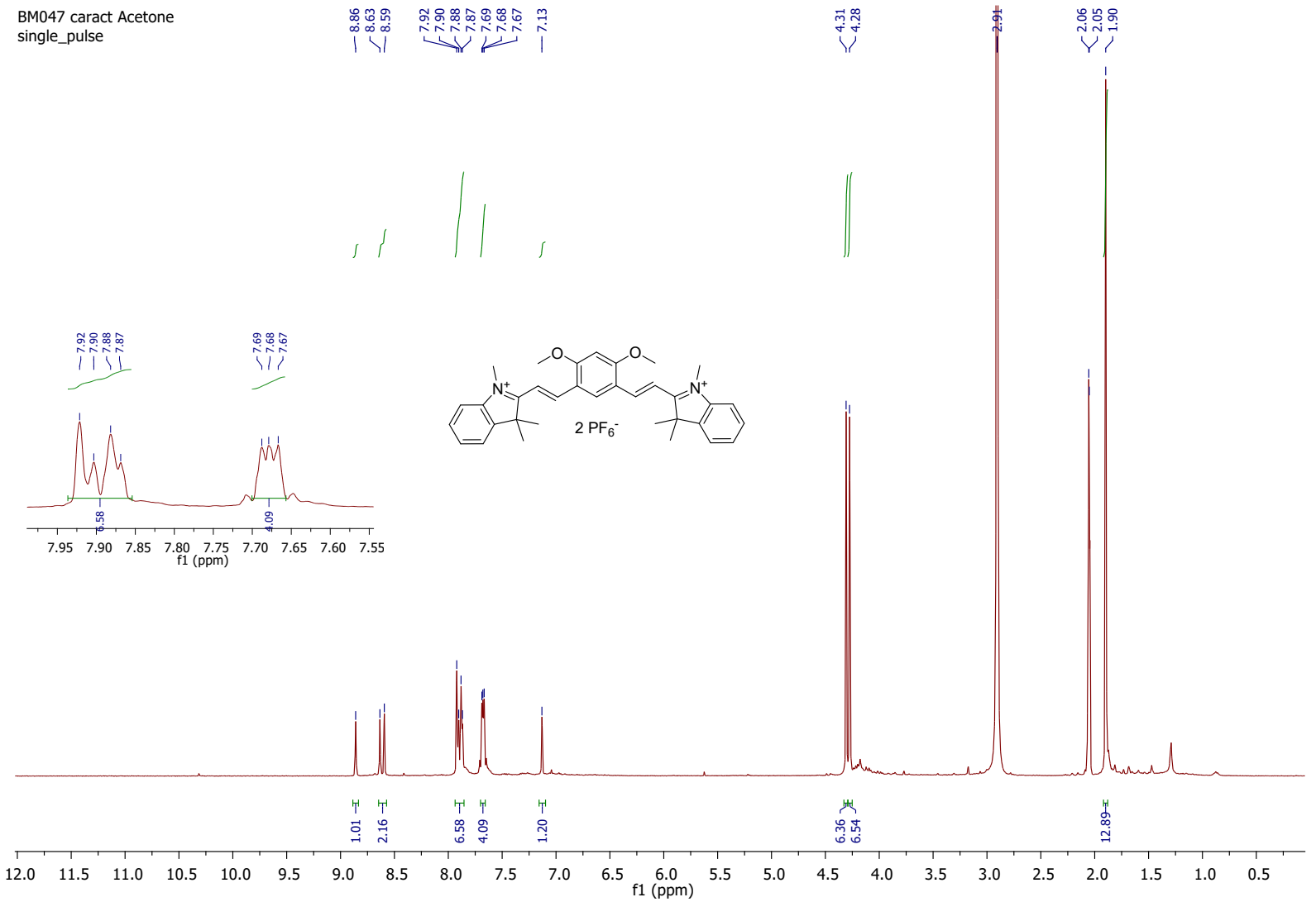


Figure S 45. ^{1}H NMR (400 MHz, Acetone-d_6) of compound **1'**.

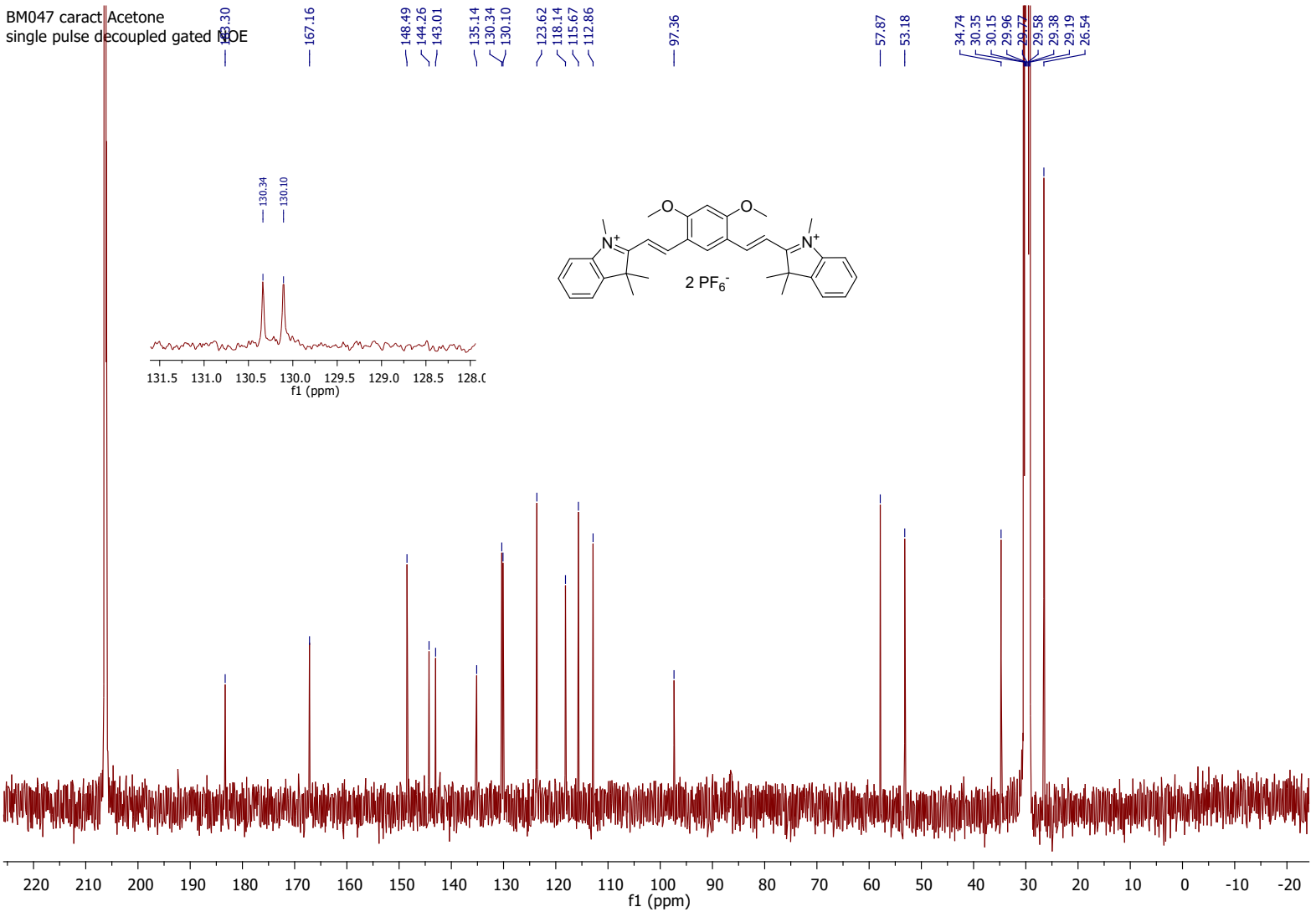


Figure S 46. ^{13}C NMR (101 MHz, Acetone-d_6) of compound **1'**.

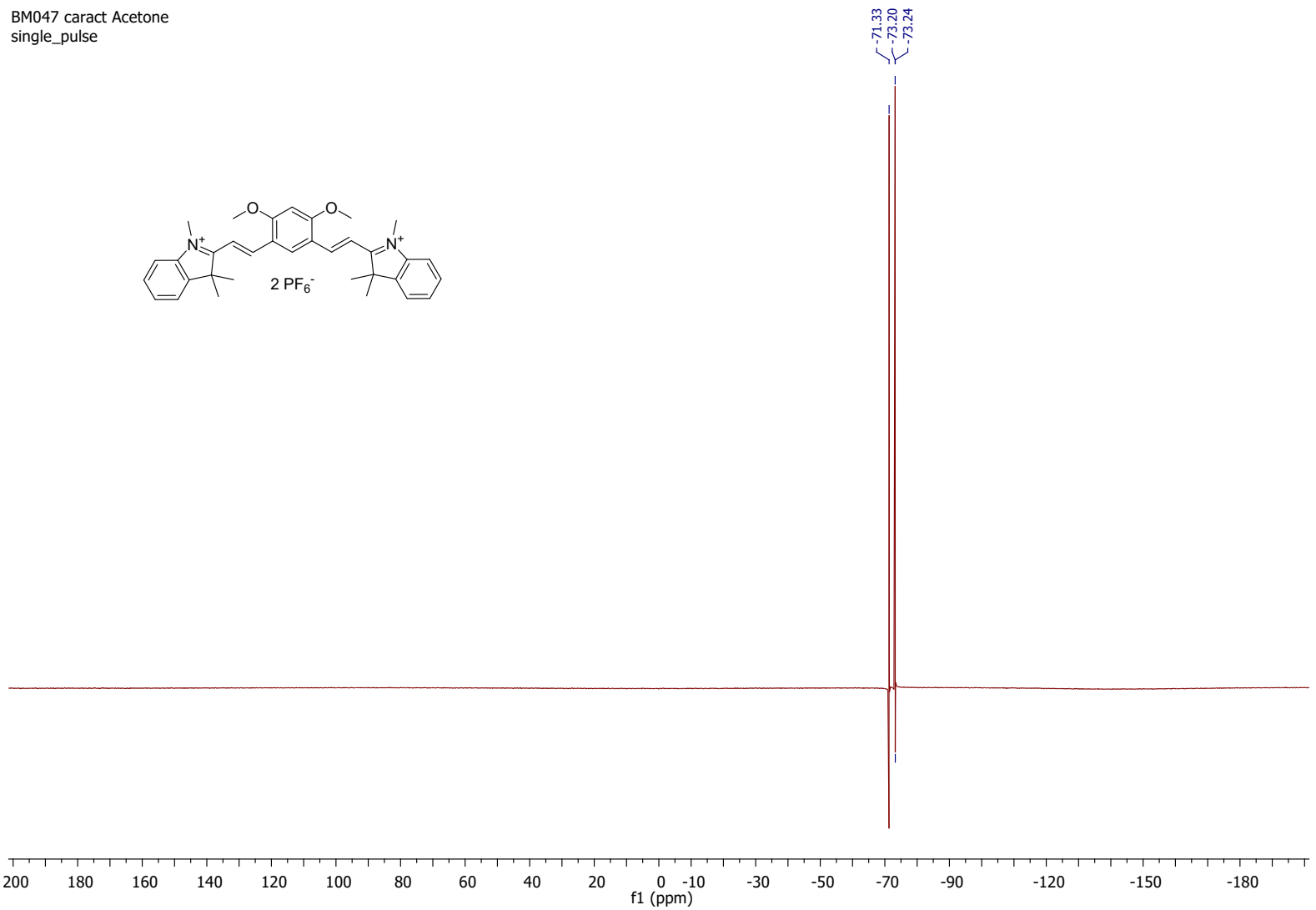


Figure S 47. ^{19}F NMR (101 MHz, Acetone-d_6) of compound **1'**.

IV. MASS SPECTROMETRY

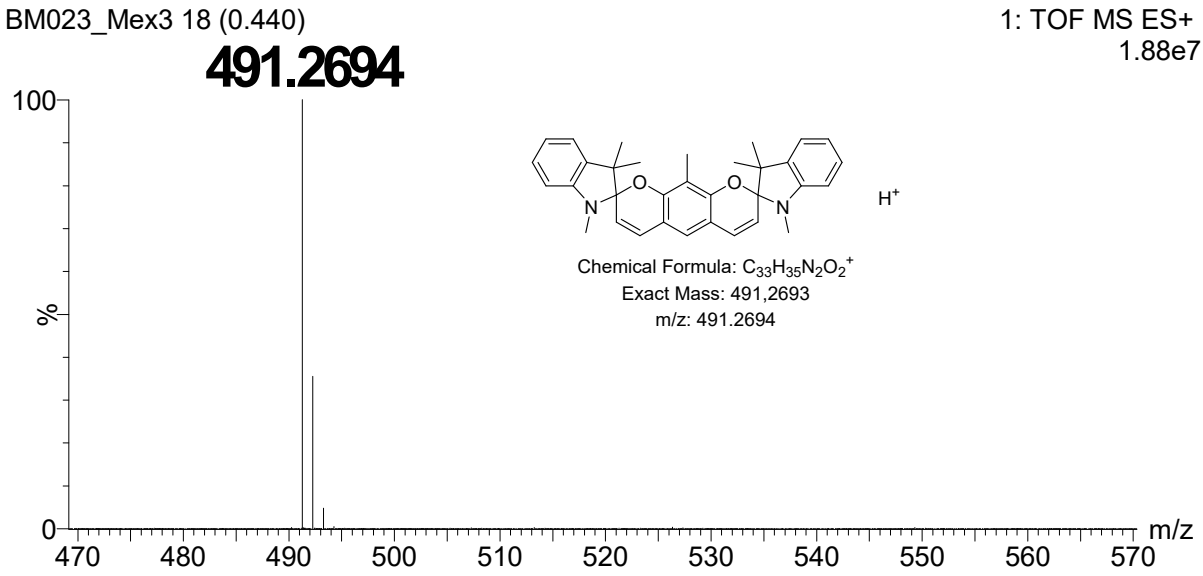


Figure S 48. HRMS spectrum of compound **dsp-1**.

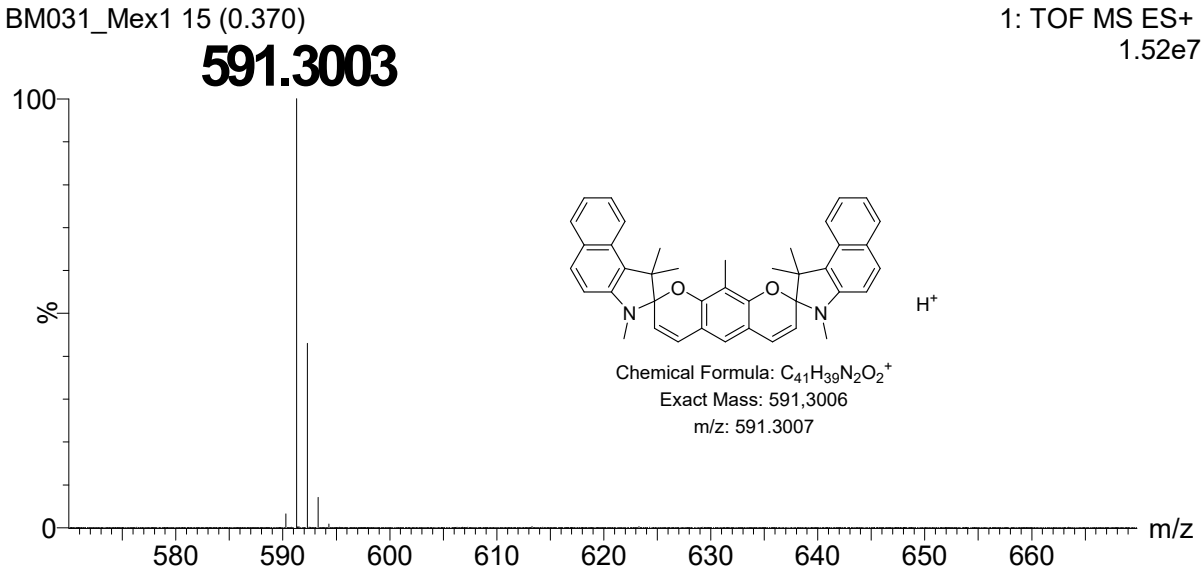
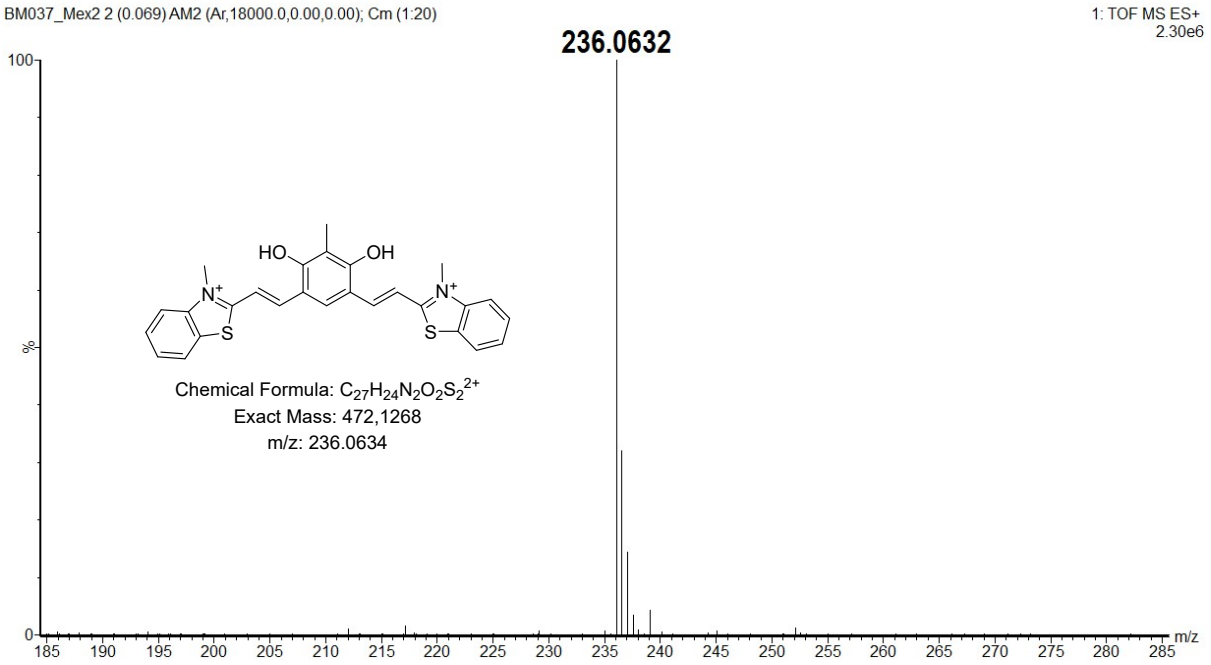


Figure S 49. HRMS spectrum of compound **dsp-2**.



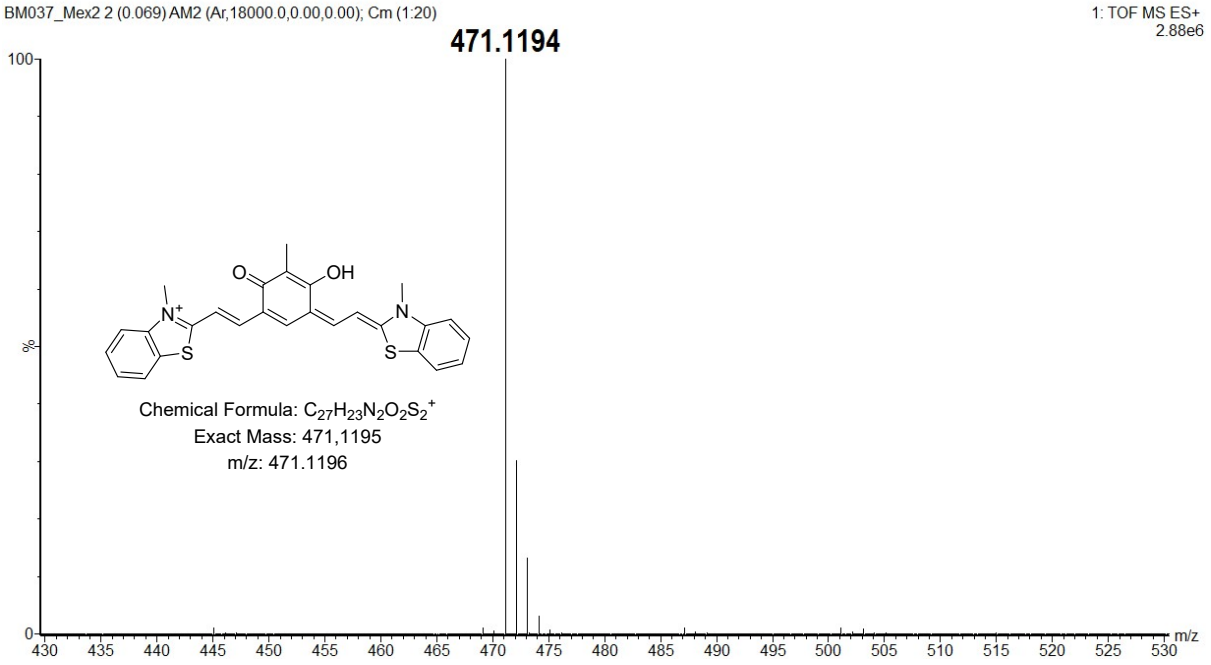


Figure S 50. HRMS spectrum of compound **3•2H^{2+}** (top and bottom spectra correspond to a zoom on two different regions).

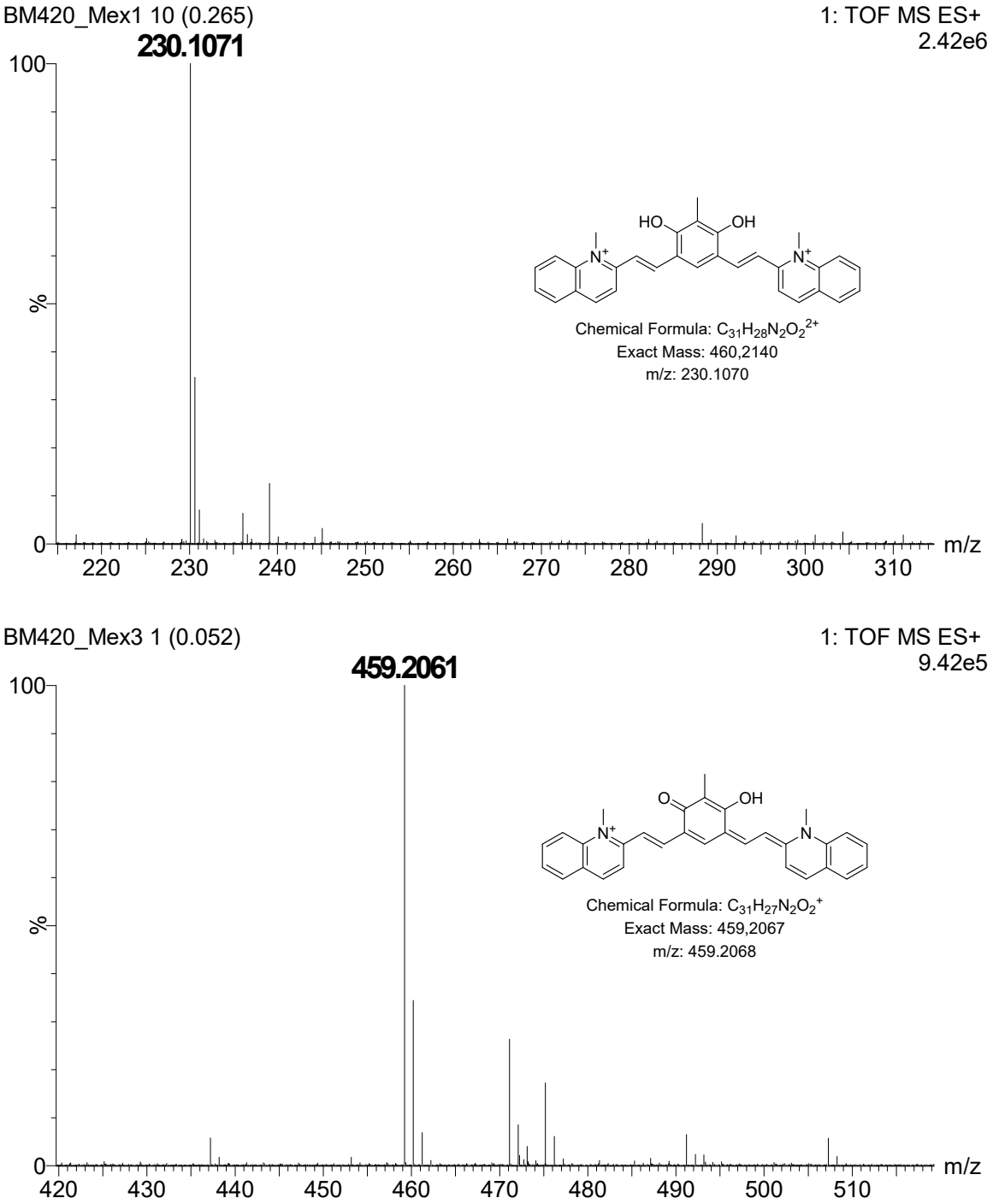


Figure S 51. HRMS spectrum of compound **4•2H²⁺** (top and bottom spectra correspond to a zoom on two different regions).

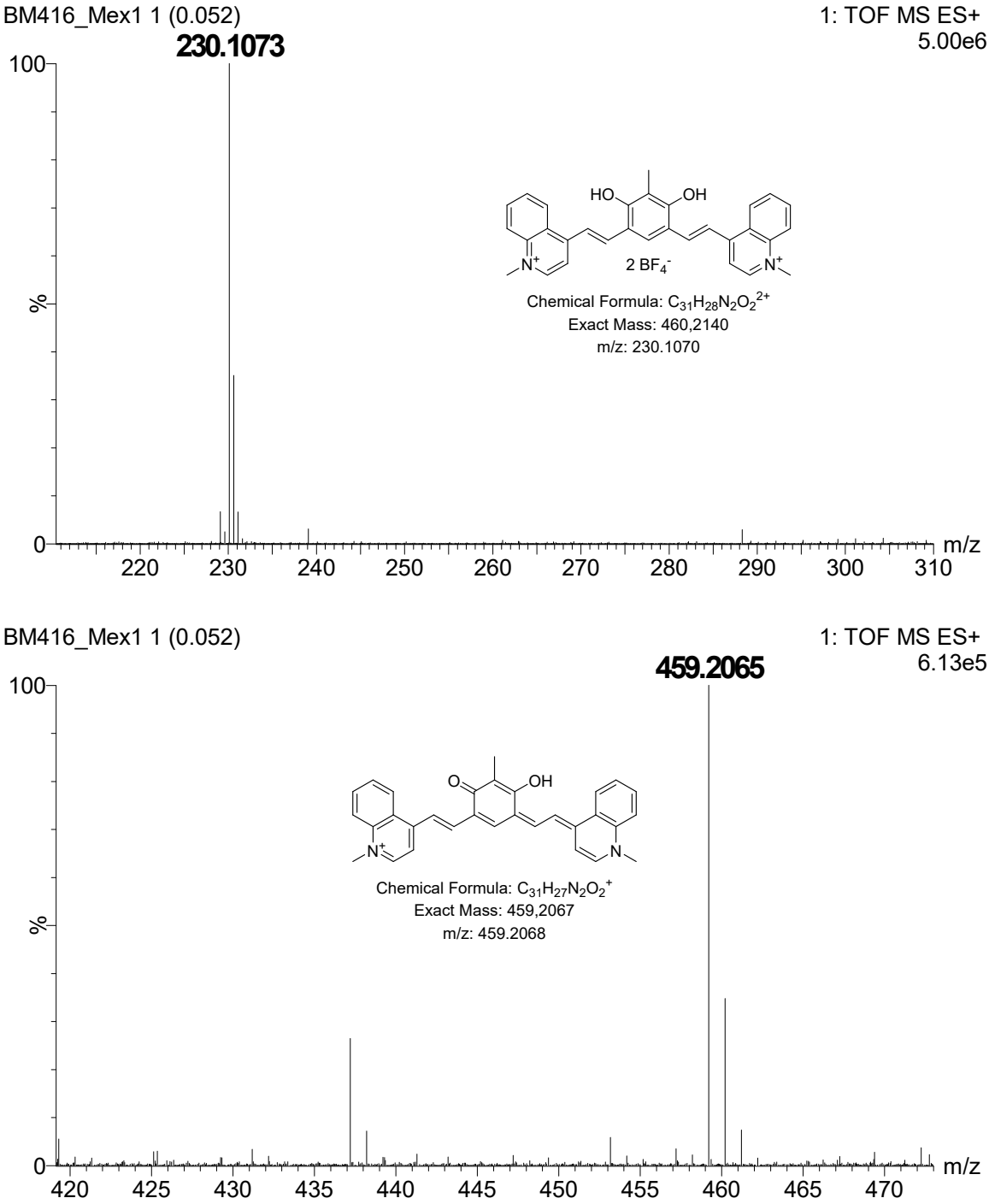


Figure S 52. HRMS spectrum of compound **5•2H^{2+}** (top and bottom spectra correspond to a zoom on two different regions).

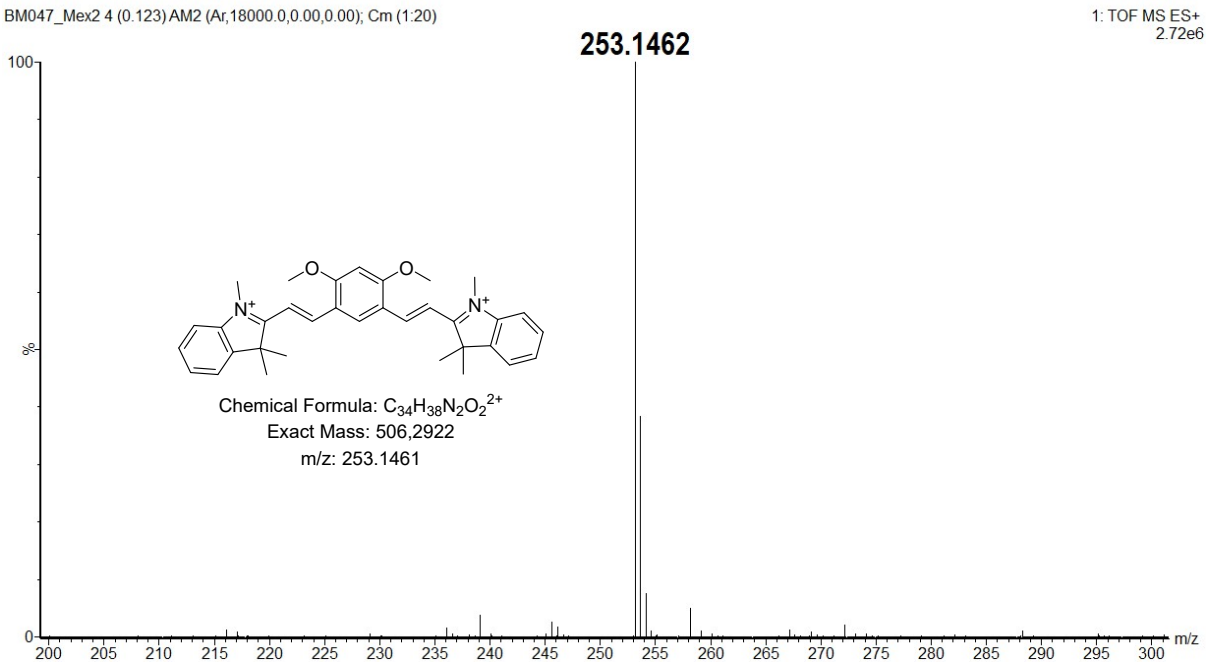


Figure S 53. HRMS spectrum of compound **1'**.

V. INFRARED SPECTRA

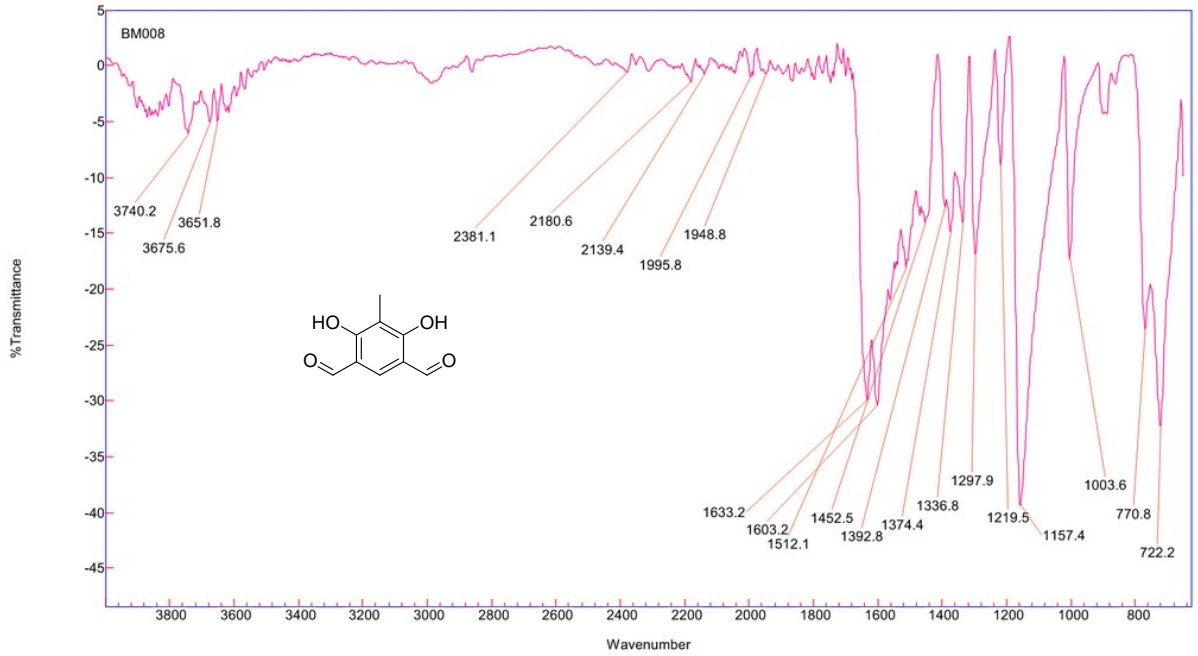


Figure S 54. Infrared spectrum of compound **6** (neat).

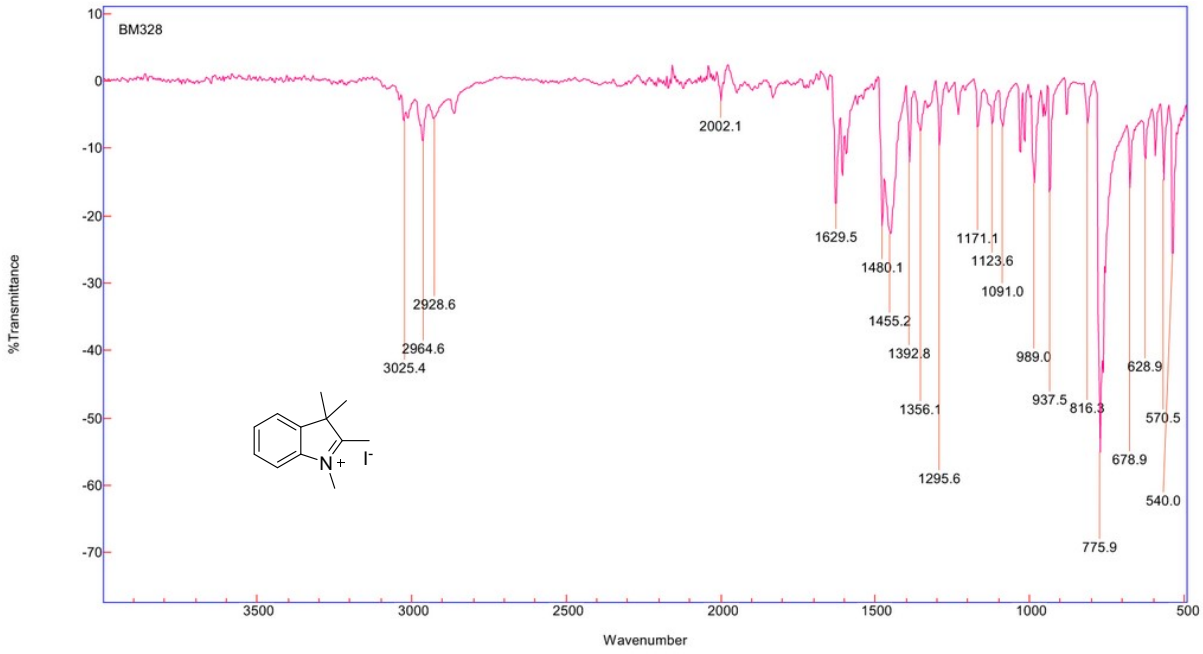


Figure S 55. Infrared spectrum of compound **7** (neat).

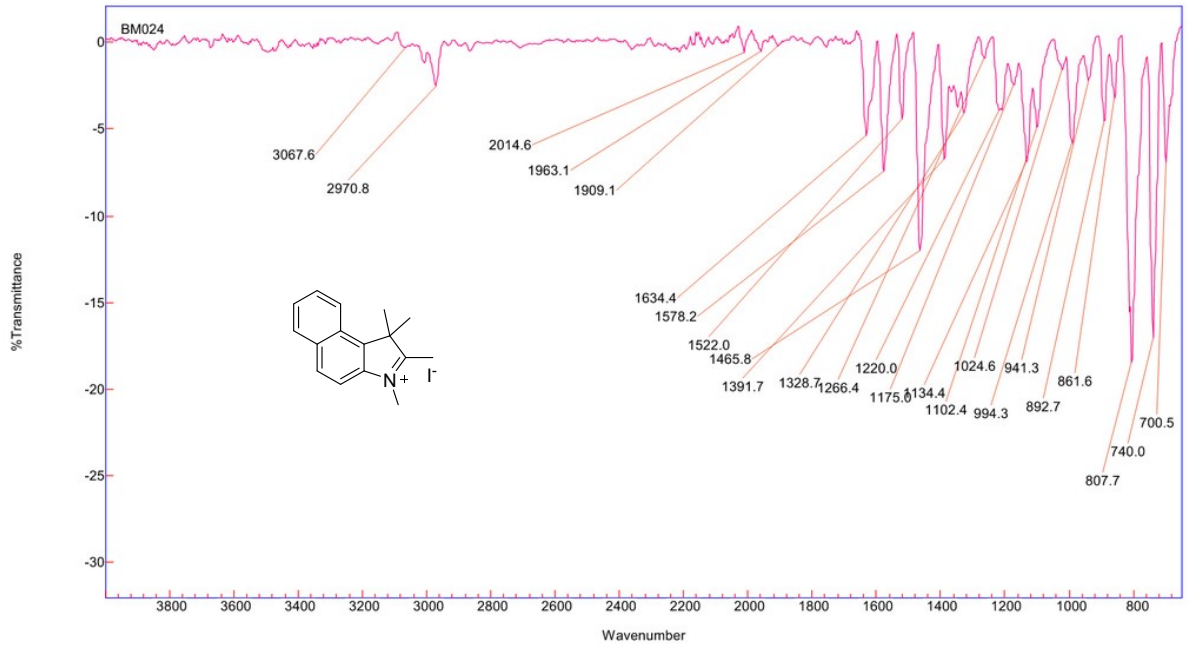


Figure S 56. Infrared spectrum of compound **8** (neat).

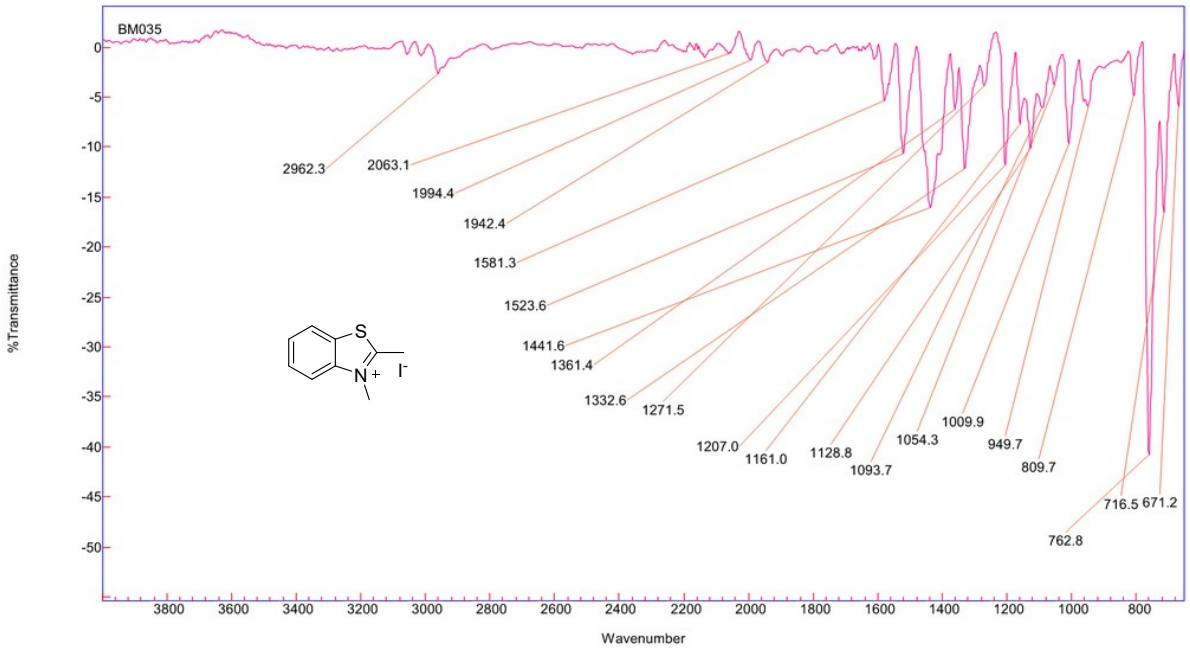


Figure S 57. Infrared spectrum of compound **9** (neat).

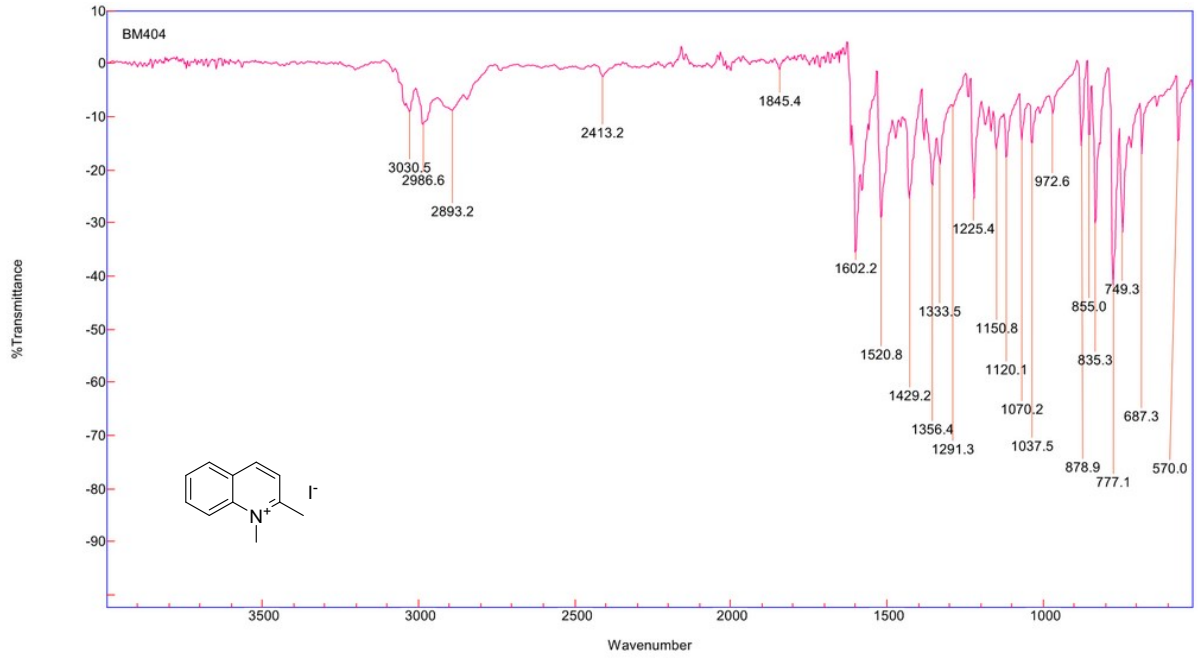


Figure S 58. Infrared spectrum of compound **10** (neat).

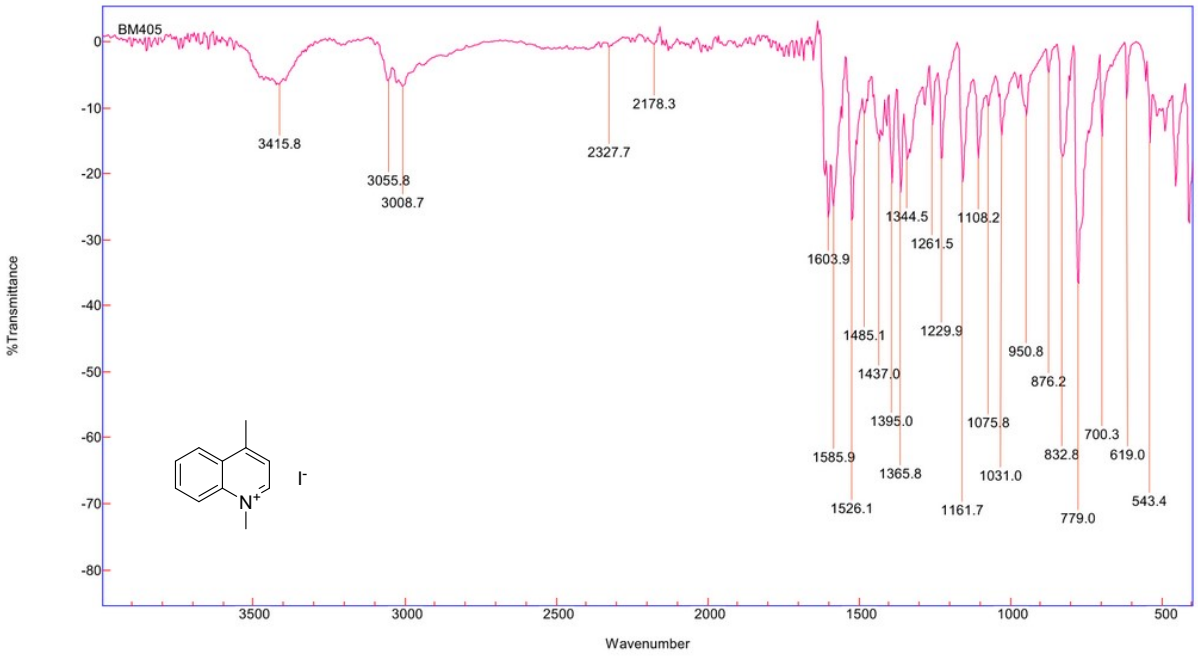


Figure S 59. Infrared spectrum of compound **11** (neat).

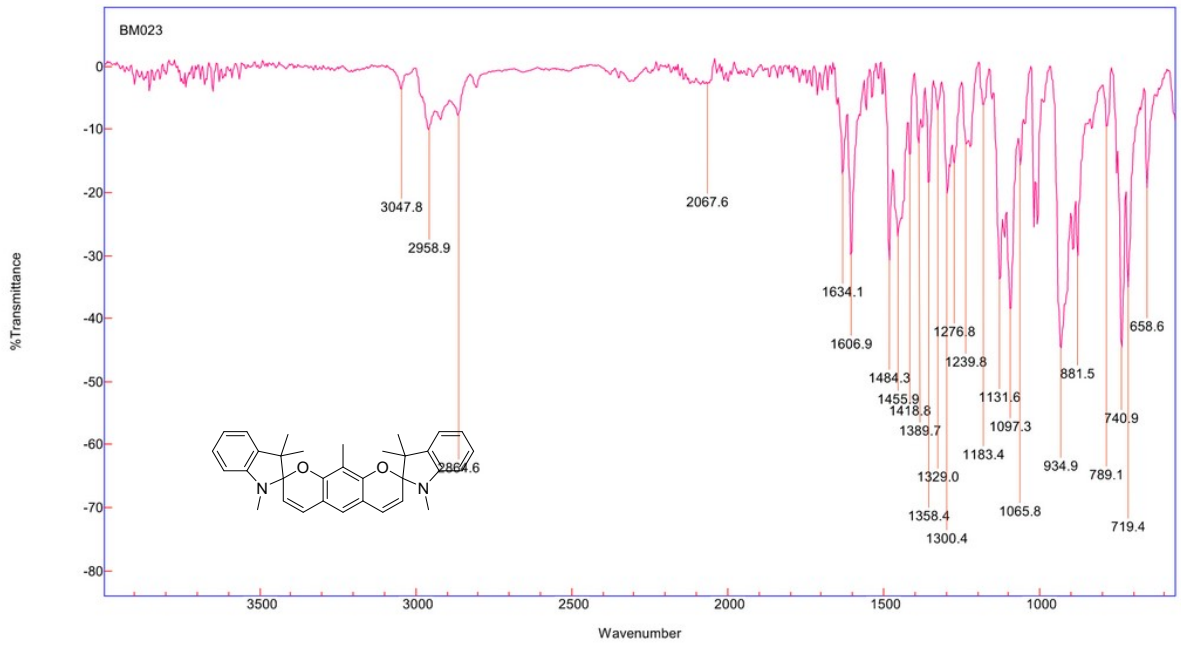


Figure S 60. Infrared spectrum of compound **dsp-1** (neat).

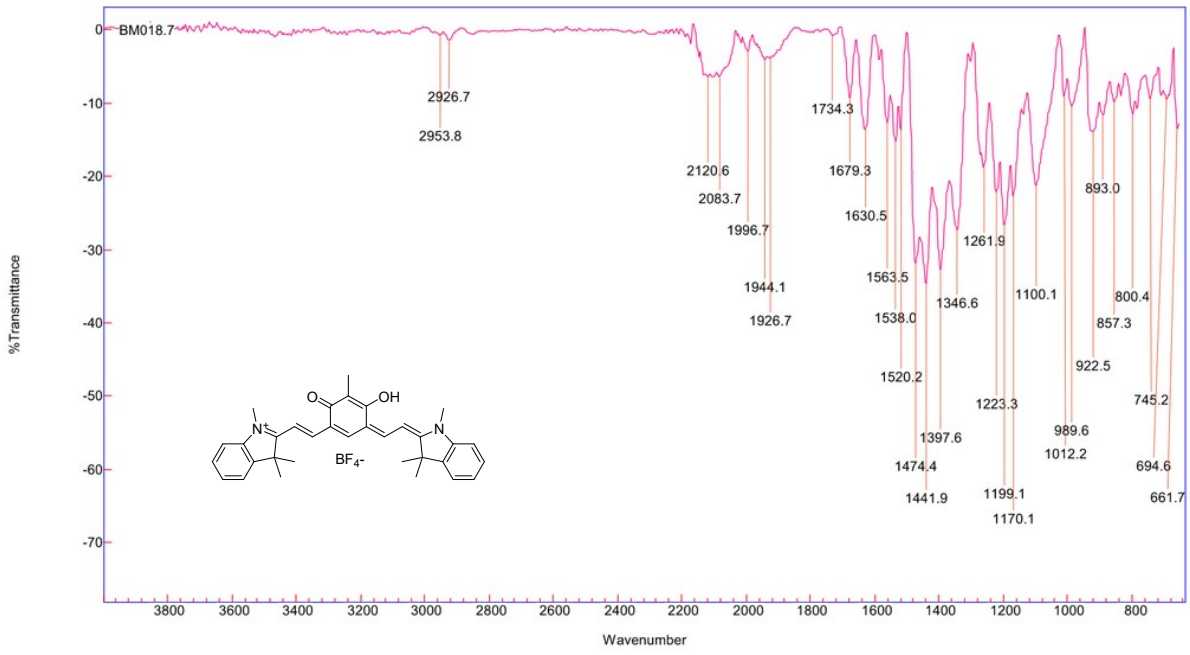


Figure S 61. Infrared spectrum of compound **1•H⁺** (neat).

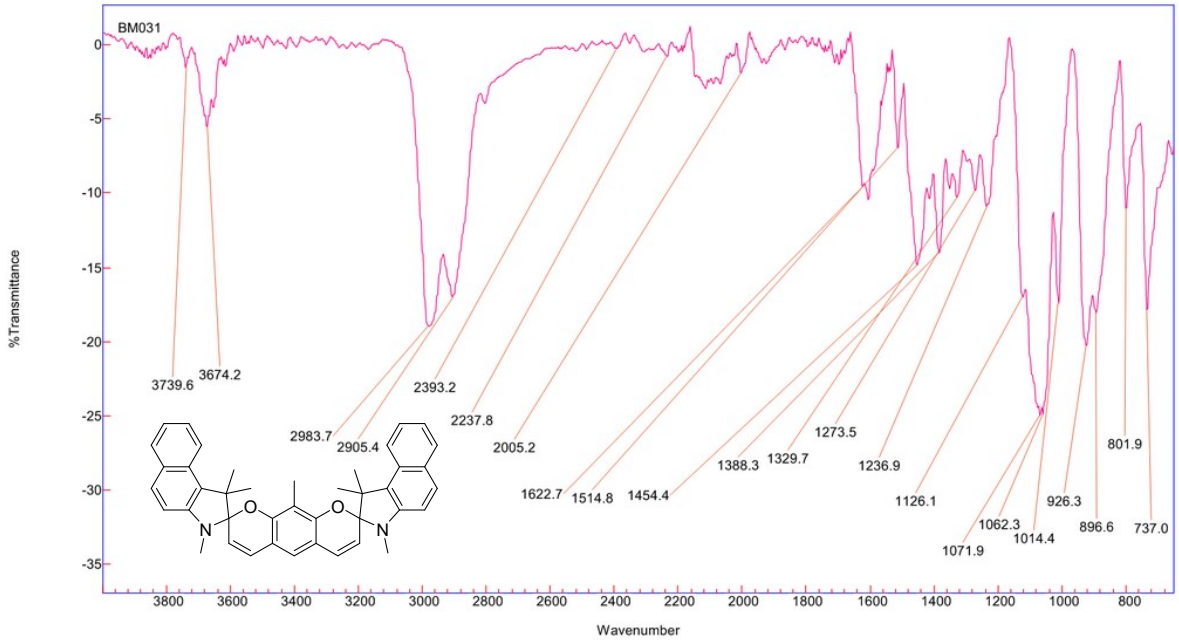


Figure S 62. Infrared spectrum of compound **dsp-2** (neat).

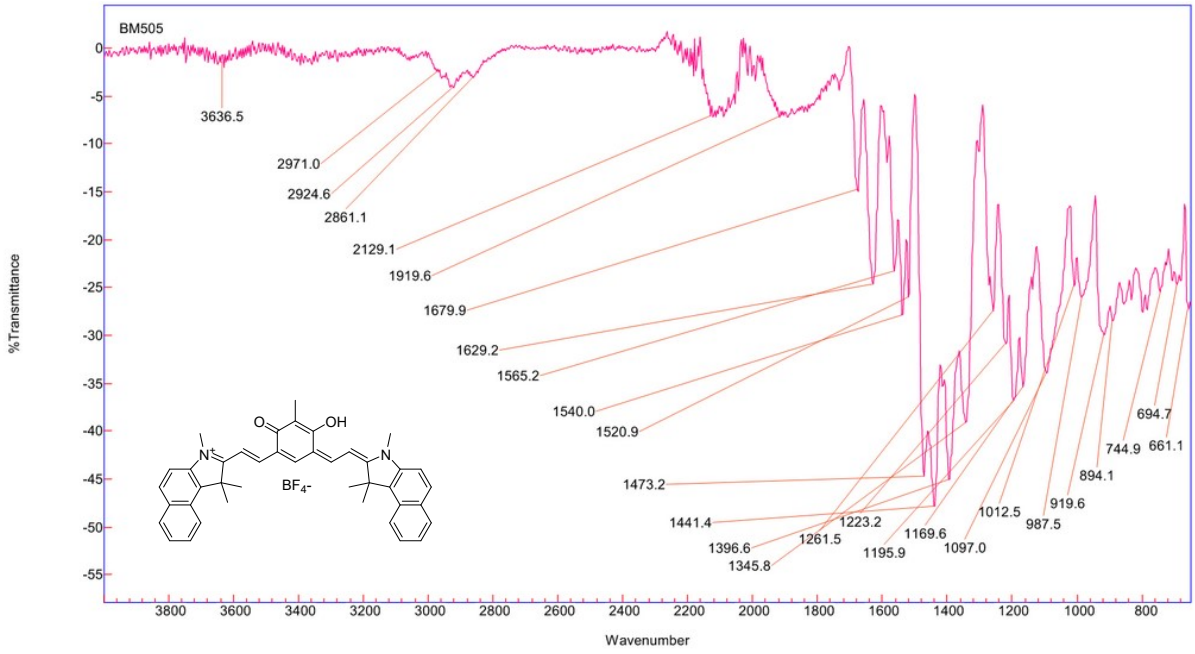


Figure S 63. Infrared spectrum of compound **2•H$^+$** (neat).

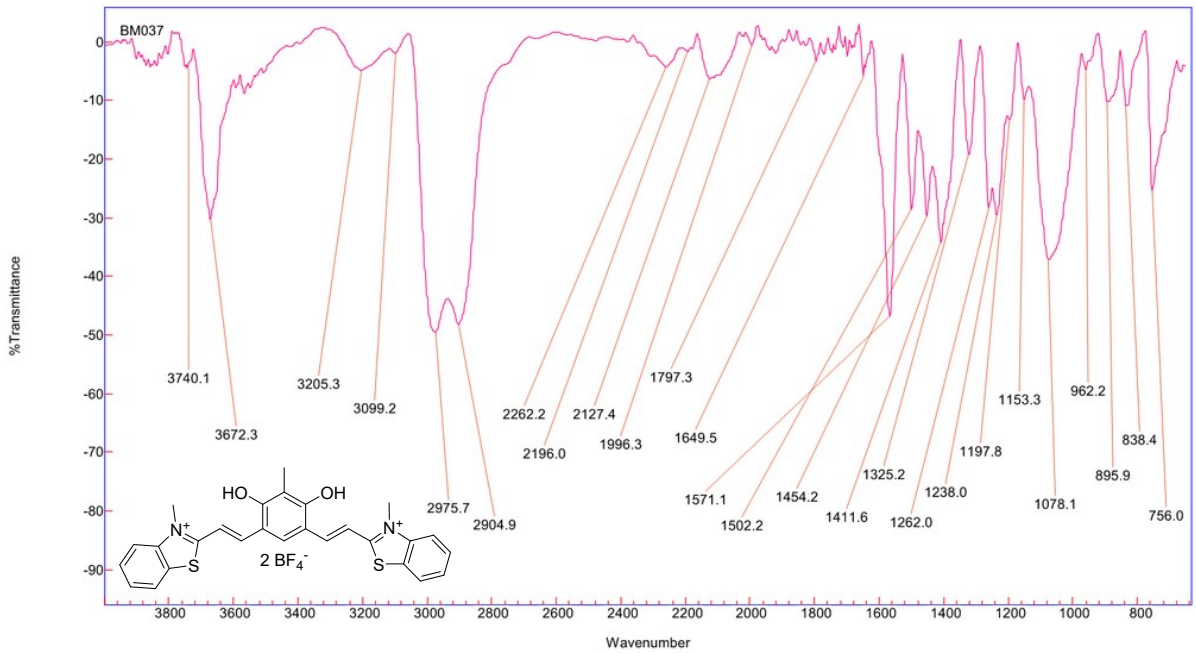


Figure S 64. Infrared spectrum of compound **3•2H^{2+}** (neat).

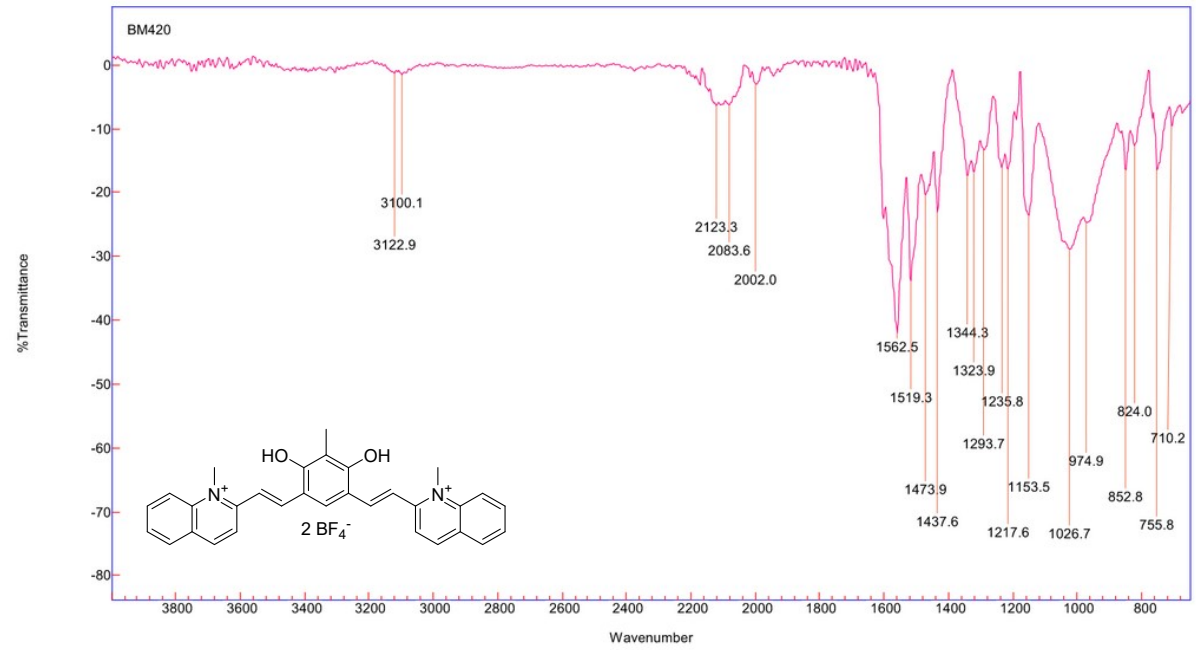


Figure S 65. Infrared spectrum of compound **4•2H^{2+}** (neat).

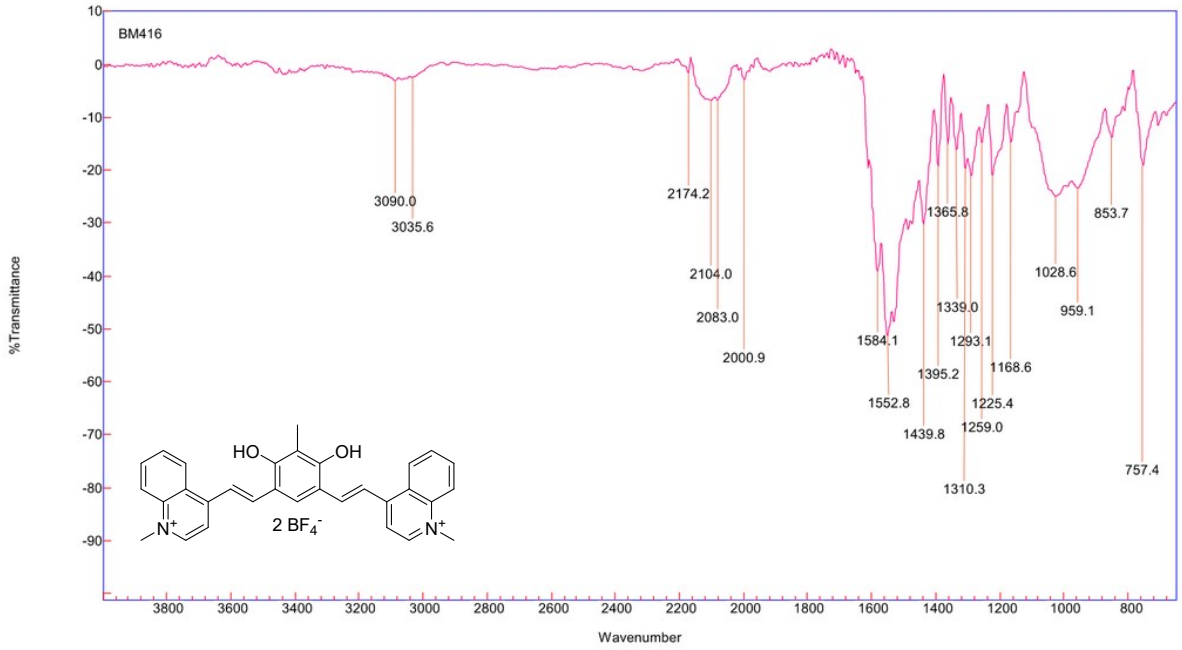


Figure S 66. Infrared spectrum of compound **5•2H^{2+}** (neat).

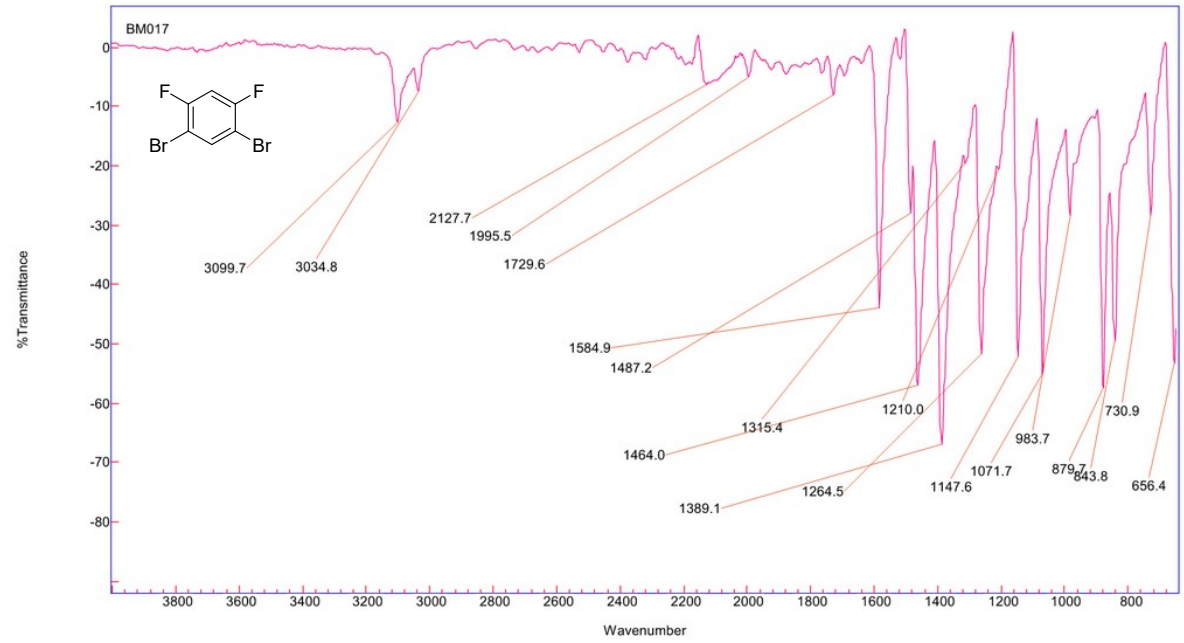


Figure S 67. Infrared spectrum of compound **13** (neat).

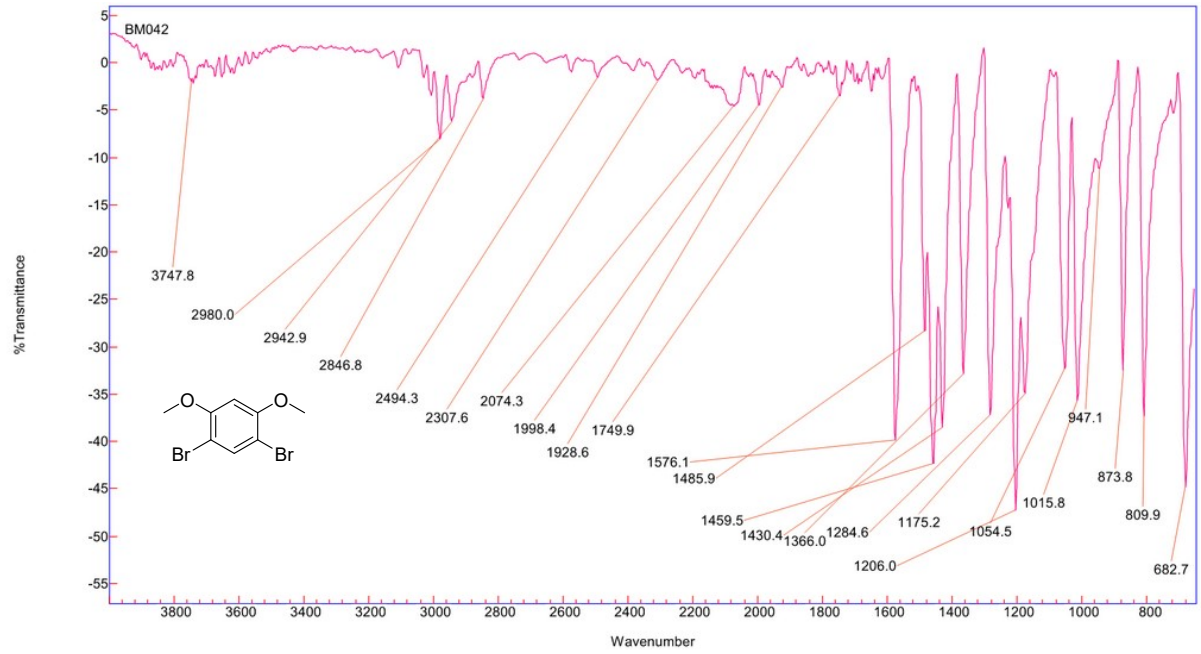


Figure S 68. Infrared spectrum of compound **14** (neat).

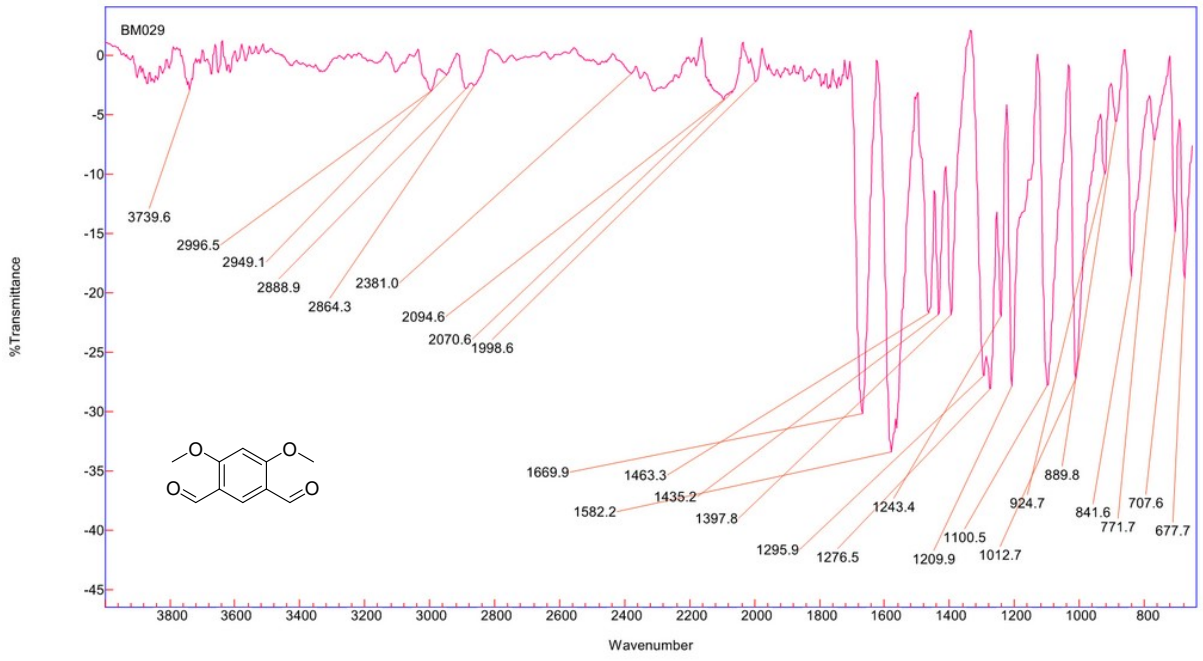


Figure S 69. Infrared spectrum of compound **12** (neat).

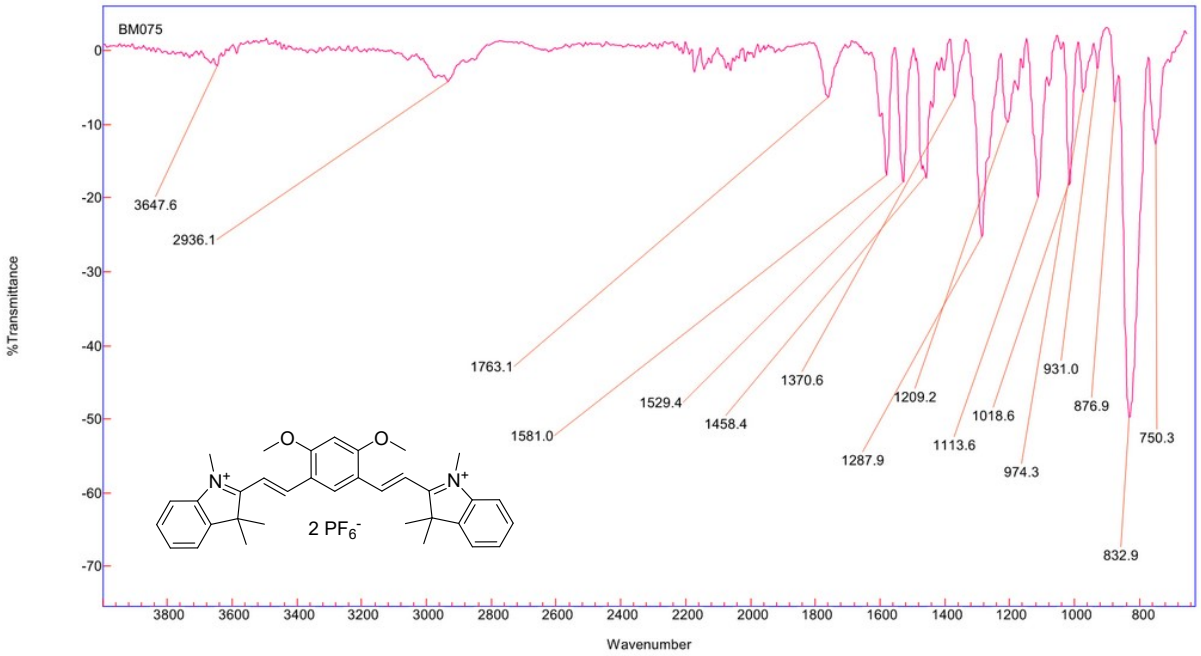
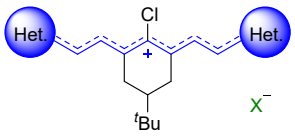


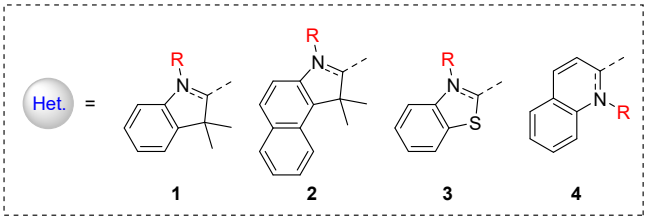
Figure S 70. Infrared spectrum of compound **1'** (neat).

VI. ADDITIONAL PHOTOPHYSICAL DATA

Table S 1. Absorption maxima (λ_{max}), corresponding molar extinction coefficients (ε), emission maxima (λ_{em}), corresponding Stokes shifts (ΔSS), fluorescence quantum yields (ϕ) and lifetimes (τ) of previously reported rigidified cationic heptamethines featuring various heterocyclic extremities.



Cy7-1 Het. = 1; R = $C_{12}H_{25}$; X = Br
Cy7-2 Het. = 2; R = C_2H_5; X = $B(Ph(CF_3)_2)_4$
Cy7-3 Het. = 3; R = CH_2Ph; X = Br
Cy7-4 Het. = 4; R = C_2H_5; X = BPh_4



Dye	Solvent	λ_{max} [nm]	ε [M^{-1} cm^{-1}]	λ_{em} [nm]	ΔSS (cm^{-1})	ϕ	τ (ns)	Reference
Cy7-1	CH_2Cl_2	791	408000	808	266	0.29	1.3	[10]
Cy7-2	$CHCl_3$	826	370000	-	-	-	-	[11]
Cy7-3	CH_3CN	803	188700	823	303	0.12	-	[12]
Cy7-4	CH_2Cl_2	861	200000	-	-	-	-	[13]

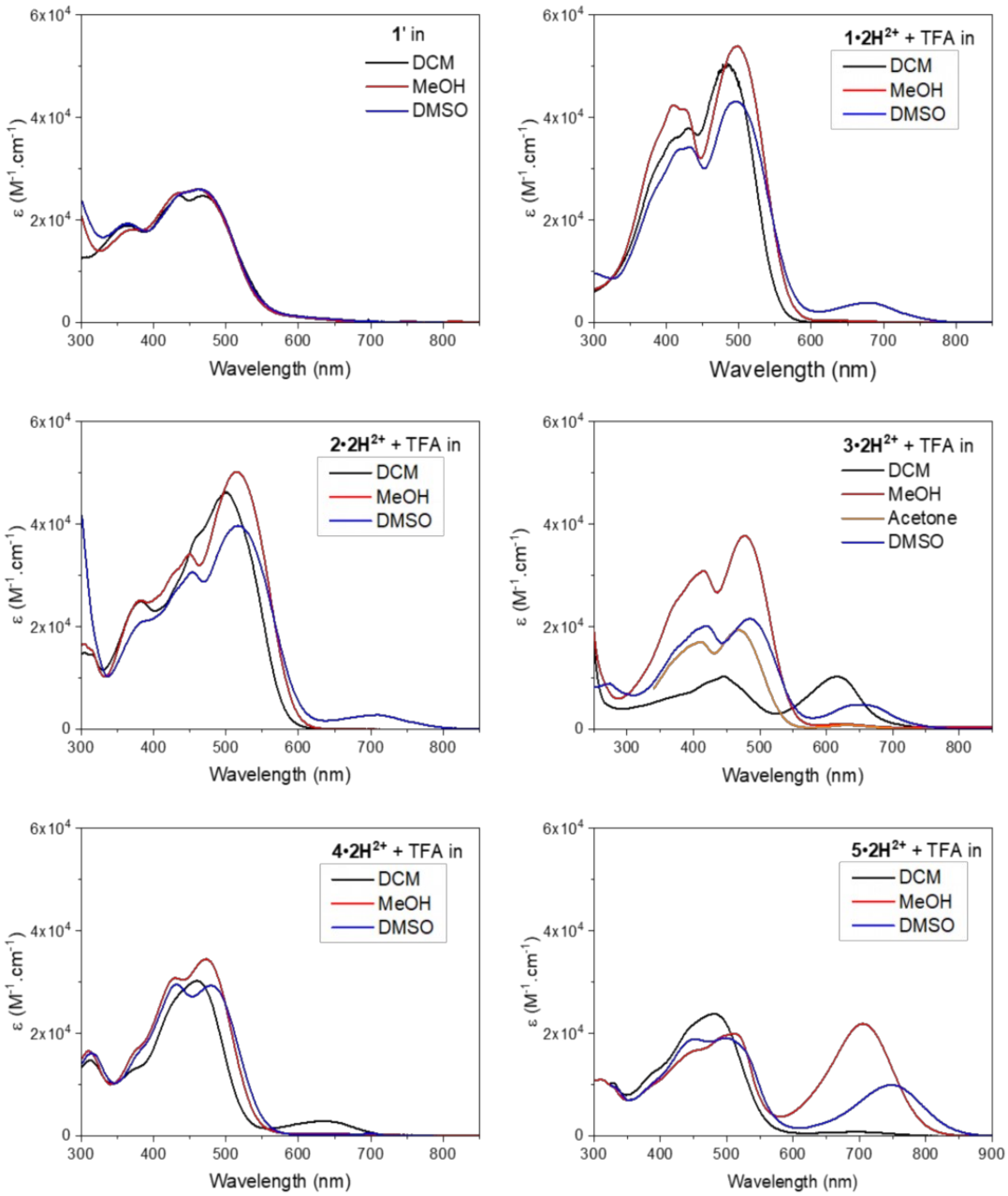


Figure S 71. UV-vis-NIR electronic absorption solvatochromism of dicationic species recorded in various solvents in the presence of TFA (0.1 M). The dications **1•2H^{2+}** and **2•2H^{2+}** were generated *in situ* from **dsp-1** and **dsp-2**. respectively.

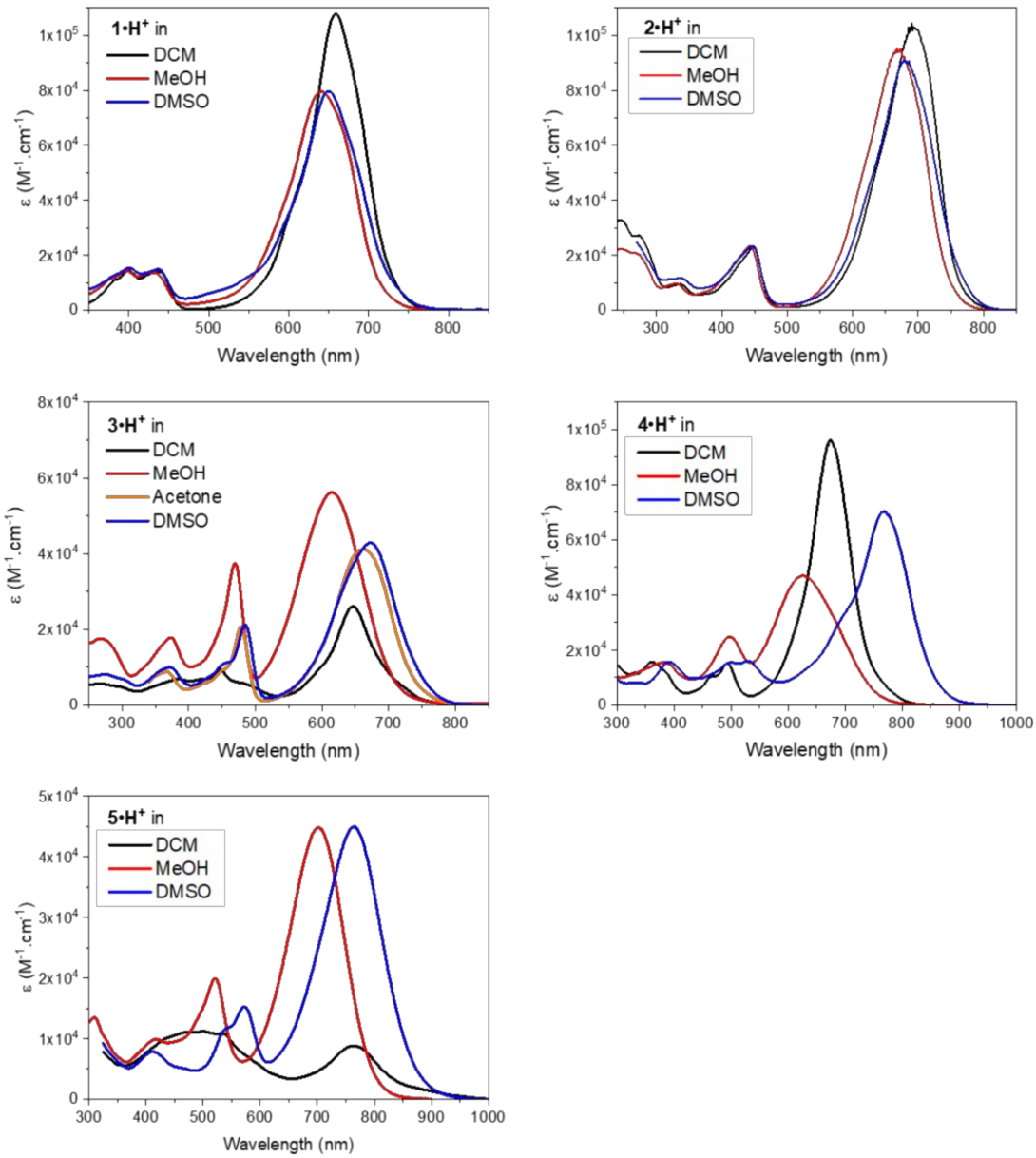


Figure S 72. UV-vis-NIR electronic absorption solvatochromism of cationic species recorded in various solvents. The cations **3•H⁺**, **4•H⁺** and **5•H⁺** were generated by dissolution of compounds **3•2H²⁺**, **4•2H²⁺** and **5•2H²⁺**, respectively.

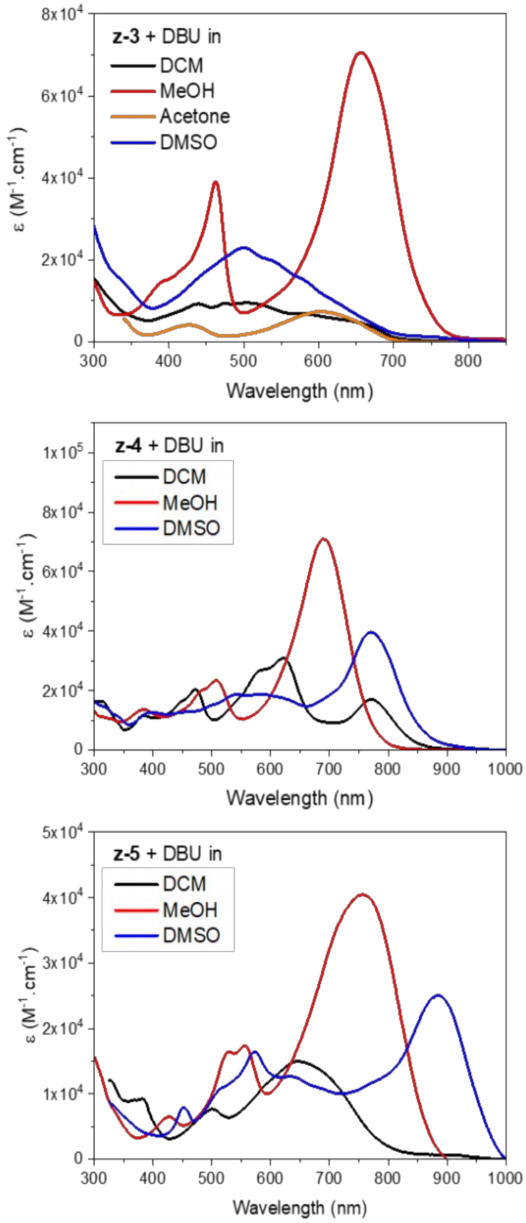


Figure S 73. UV-vis-NIR electronic absorption solvatochromism of zwitterionic species recorded in various solvents in the presence of DBU (0.1 M), generated *in situ* from **3•2H^{2+}**, **4•2H^{2+}** and **5•2H^{2+}**.

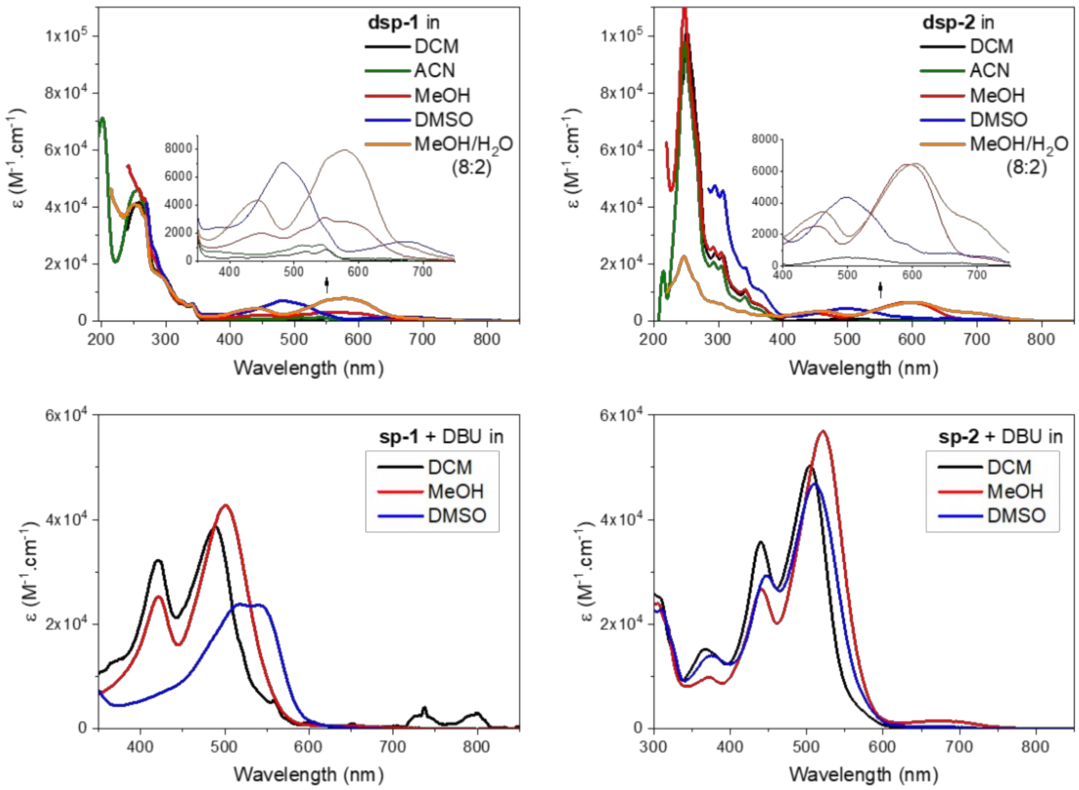


Figure S 74. UV-vis-NIR electronic absorption solvatochromism of spiropyran species recorded in various solvents. Note: the derivatives **sp-1** and **sp-2** were generated *in situ* from **1•H$^+$** and **2•H$^+$**, respectively, in the presence of DBU (0.1 M).

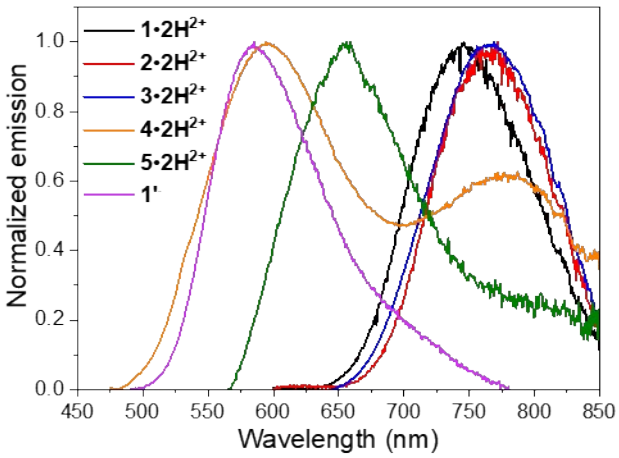


Figure S 75. Normalized emission spectra of the dicationic cationic species of **1–5** and **1'** in methanol. Note: a contribution from the cationic species remains present in the emission spectrum of **4•2H²⁺**, see excitation spectra below (Figure S 79).

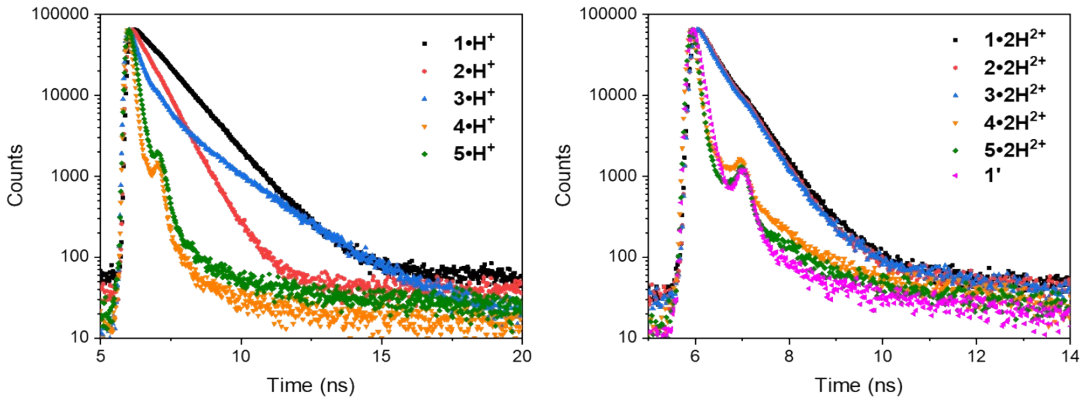


Figure S 76. Fluorescence decays measured by single photon counting of the emissive compounds in methanol solutions.

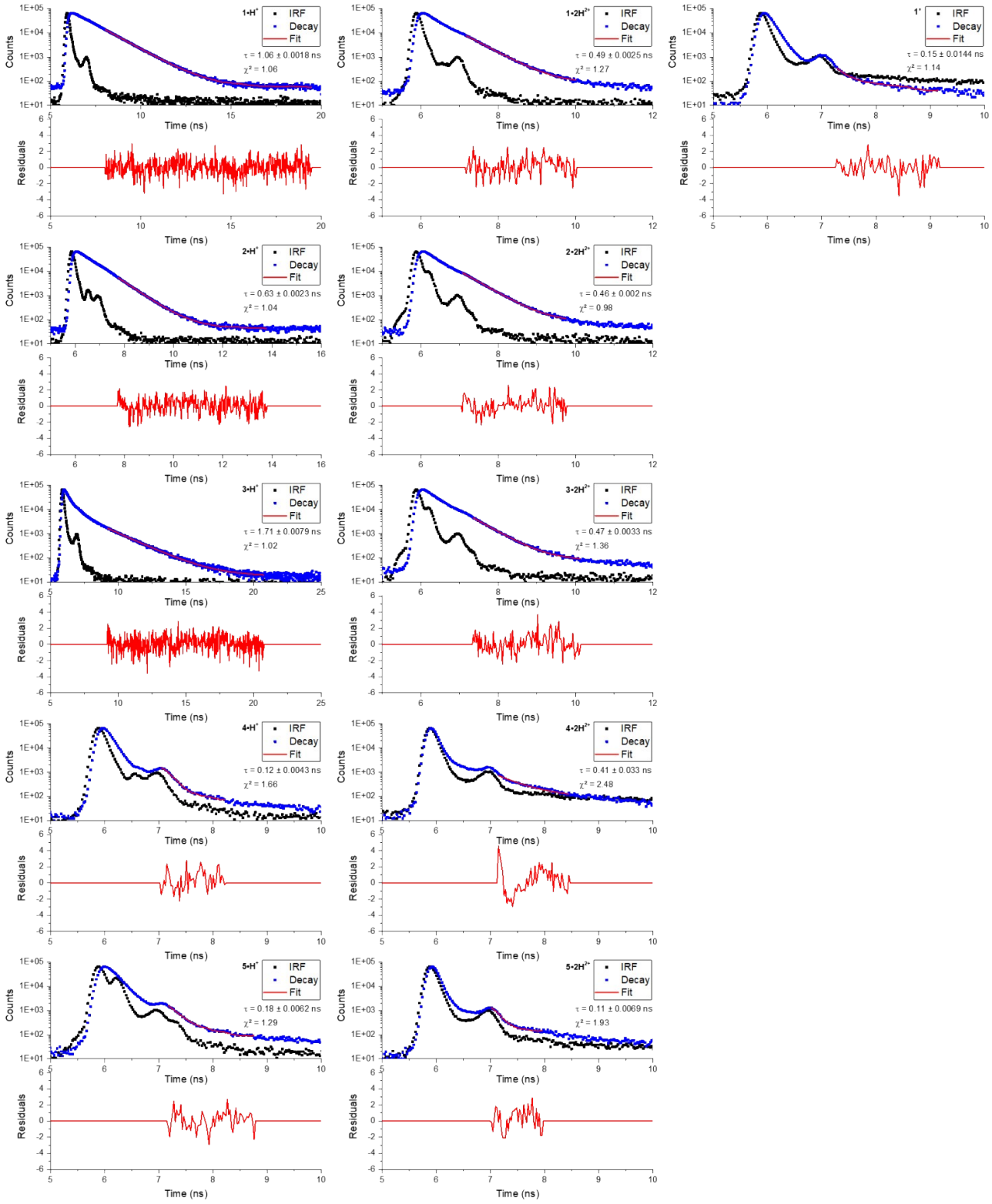


Figure S 77. Time-resolved fluorescence spectroscopy: instrument response function (IRF, black squares), measured fluorescence decay of the compound (blue squares), fit and residuals (red lines). Note: all the measurements were fitted with single exponential decays.

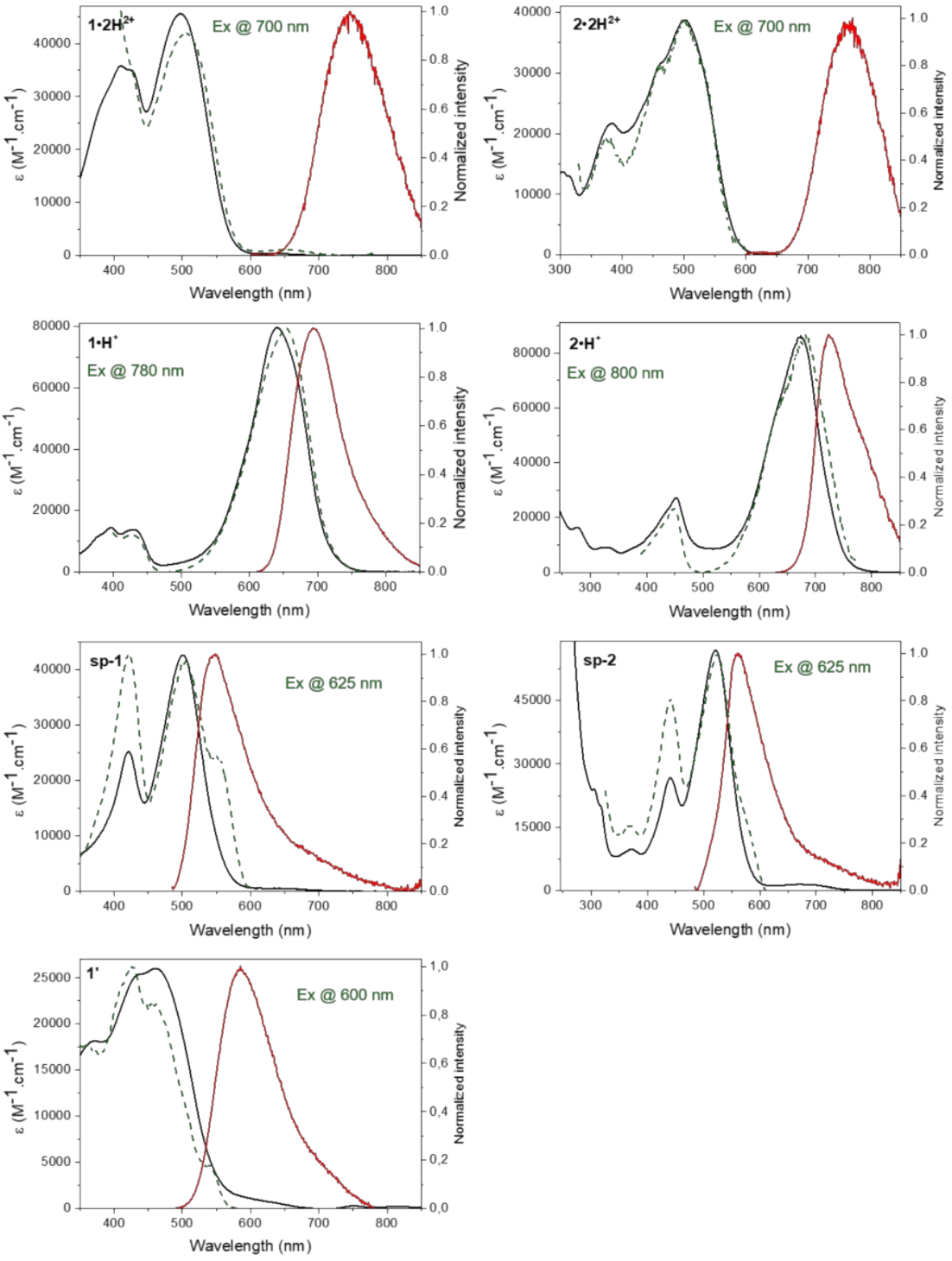


Figure S 78. Electronic absorption (black lines), normalized emission (red lines) and normalized excitation spectra (green dotted lines, with monitoring wavelength specified in green) of the emissive species **1**, **2** and **1'** in MeOH.

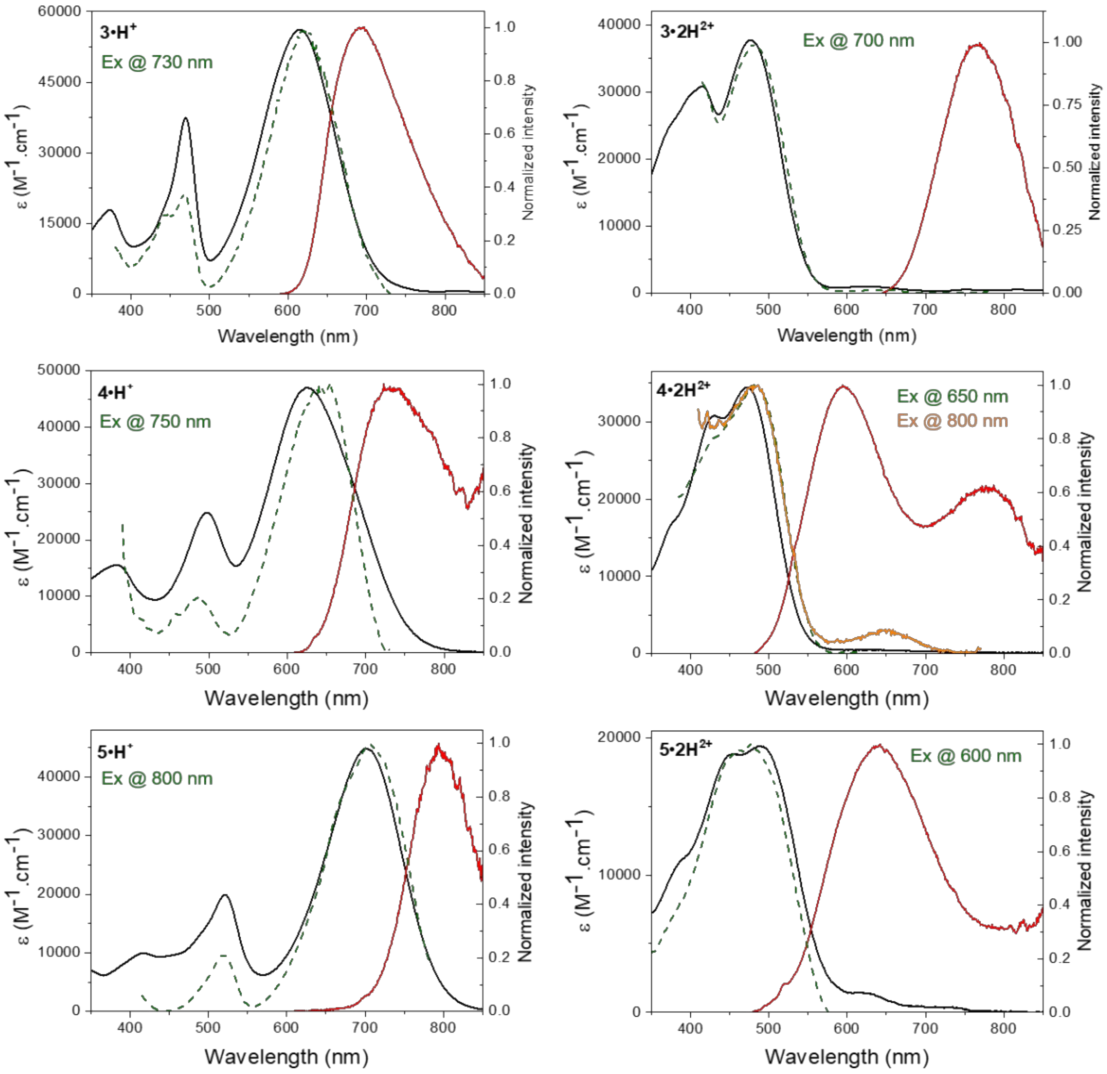


Figure S 79. Electronic absorption (black lines), normalized emission (red lines) and normalized excitation spectra (green dotted lines, with monitoring wavelength specified in green) of the emissive species **3–5** in MeOH. Note: for the emission of **4•2H^{2+}**, the second band found between 700–850 nm is attributed to the presence of **4•H^{+}** in solution, as revealed by the excitation spectrum recorded while monitoring the emission at 800 nm (orange curve).

VII. PHYSICO-CHEMISTRY

Absorption Spectrophotometric Titrations versus pH. A stock solution of the CoPo derivatives (**1–3**) at the mM scale was prepared in pure methanol. An appropriate volume was then diluted in 40 mL of a MeOH/H_2O (80/20 *w/w*) mixture containing 0.1 M of tetrabutylammonium perchlorate (NBu_4ClO_4, Acros organics 98%) in a jacketed cell (METROHM) maintained à 25.0 °C. The free hydrogen ion concentration was measured with a combined glass electrode (METROHM 6.0234.500, Long Life) and an automatic titrator system 794 Basic Titrino. The Ag/AgCl reference glass electrode was filled with NaCl 0.1 M in MeOH/H_2O (80/20 w/w) (VWR Chemicals AnalR NORMAPUR). The combined glass electrode was calibrated[14] as a hydrogen concentration probe by titrating known amounts of perchloric acid (~ 10^{-1} M from $HClO_4$, Prolabo, puriss pa, > 70 %) with CO_2-free tetrabutylammonium hydroxide solution 40% in water (~ 10^{-1} M, VWR Chemicals GPR RECTAPUR). The GLEE program was applied for the glass electrode calibration (standard electrode potential E_0/mV and slope of the electrode/mV pH^{-1}) and to check carbonate levels of the tetrabutylammonium hydroxide solutions used (< 5 %).[14] For the absorption titrations, the initial pH was adjusted to ~ 2-3 with $HClO_4$ and the absorption titrations of **1–3** were carried out by automatic addition of known volumes of tetrabutylammonium hydroxide solutions. After each addition, an absorption spectrum was repeatedly recorded using a CARY 50 (Varian) spectrophotometer fitted with Hellma optical fibers (Hellma, 041.002-UV) and an immersion probe made of quartz suprasil (Hellma, 661.500-QX) and interfaced (Cetrib) with the potentiometric unit.

Analysis and Processing of the Spectroscopic Data. The spectrophotometric data were analyzed with SPECFIT program,[15] which adjusts the absorptivities and the stability constants of the species formed at equilibrium. SPECFIT uses factor analysis to reduce the absorbance matrix and to extract the eigenvalues prior to the multiwavelength fit of the reduced data set according to the Marquardt algorithm.[16,17]

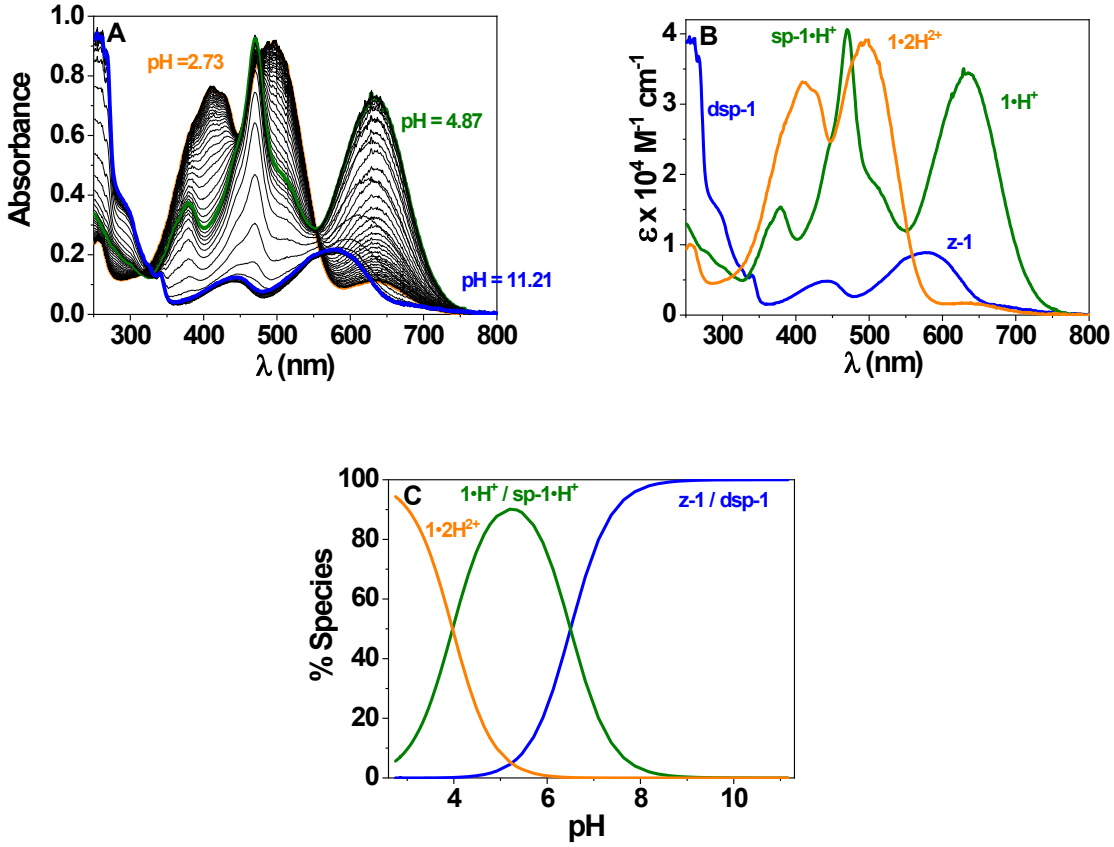


Figure S 80. (A) UV-visible absorption spectrophotometric *versus* pH titration of **1** in CH_3OH/H_2O (80:20 by weight) from acidic to basic pH values; (B) Absorption electronic spectra of **1** (**z-1** and **dsp-1**) and its protonated species **1•H⁺** (**1•H⁺** and **sp-1•H⁺**) et **1•2H²⁺**; (C) Distribution diagrams of the protonated species of **1**. I = 0.1 M NBu_4ClO_4; T = 25.0 ± 0.1 °C; [1] = 2.45 × 10^{-5} M. The absorption spectra are not corrected for the dilution effects. The data have been processed from pH 2.73 to 11.21 with pK_{a1} = 3.79 ± 0.04 and pK_{a2} = 6.16 ± 0.03.

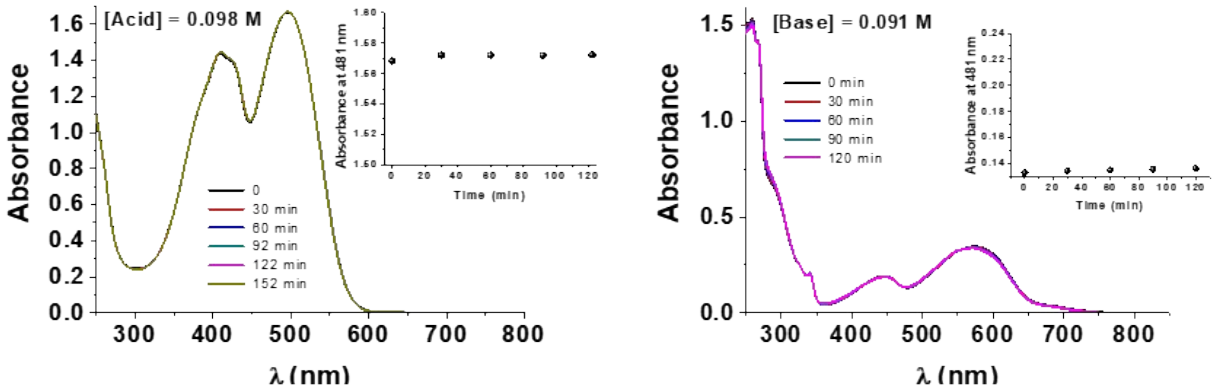


Figure S 81. (A) UV-visible absorption spectra as a function of time measured for **1** in CH_3OH/H_2O (80:20 by weight) under acidic (left) and basic (right) conditions for solutions exposed in the dark. I = 0.1 M NBu_4ClO_4; T = 25.0 ± 0.1 °C; [1] = 2.28 × 10^{-5} M.

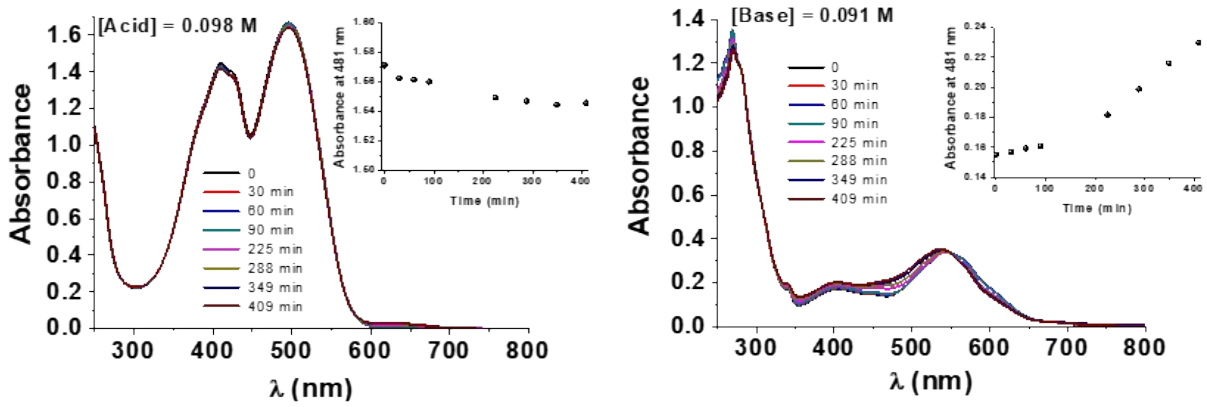


Figure S 82. (A) UV-visible absorption spectra as a function of time measured for **1** in CH_3OH/H_2O (80:20 by weight) under acidic (left) and basic (right) conditions for solutions exposed to daylight. I = 0.1 M NBu_4ClO_4; T = 25.0 ± 0.1 °C; [1] = 2.28 × 10^{-5} M.

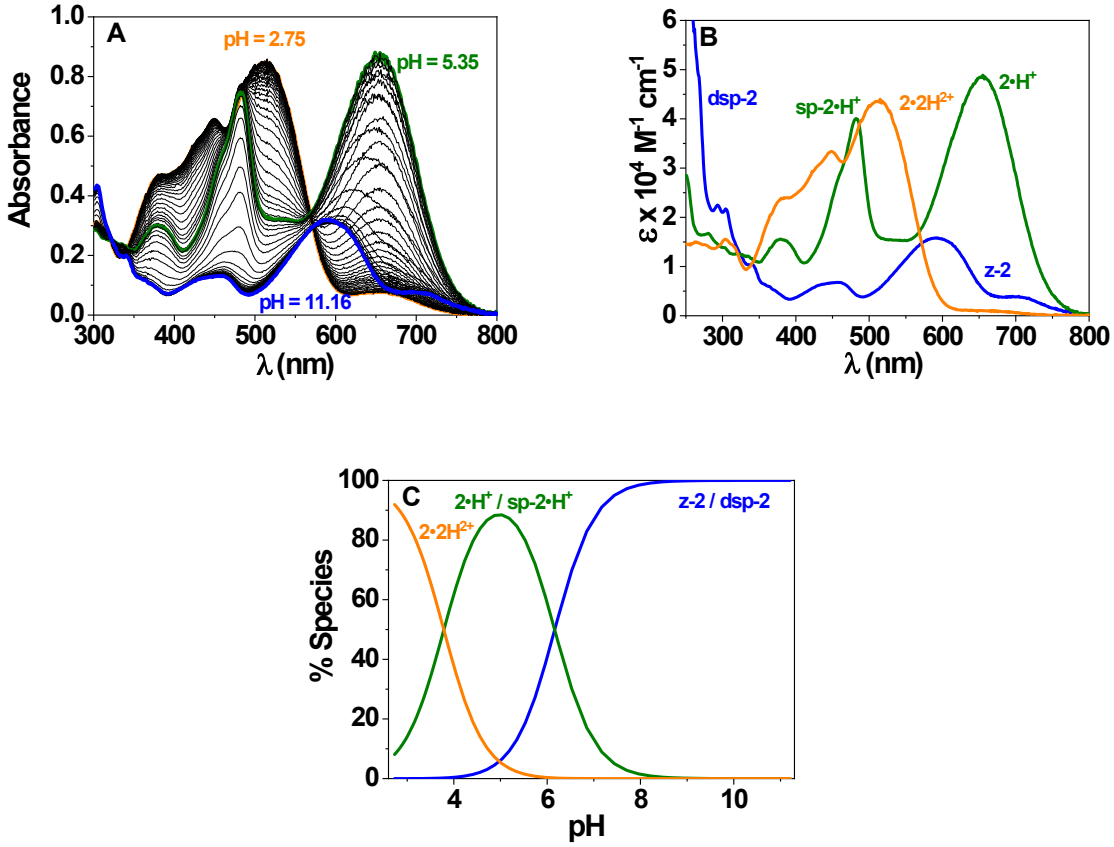


Figure S 83. (A) UV-visible absorption spectrophotometric *versus* pH titration of **2** in CH_3OH/H_2O (80:20 by weight) from acidic to basic pH values; (B) Absorption electronic spectra of **2** (**z-2** and **dsp-2**) and its protonated species **2•H⁺** (**2•H⁺** and **sp-2•H⁺**) and **2•2H²⁺**; (C) Distribution diagrams of the protonated species of **2**. I = 0.1 M NBu_4ClO_4; T = 25.0 ± 0.1 °C; [**2**] = 2.02 × 10^{-5} M. The absorption spectra are not corrected for the dilution effects. The data have been processed from pH 2.75 to 11.16 with pK_{a1} = 3.97 ± 0.03 and pK_{a2} = 6.50 ± 0.02.

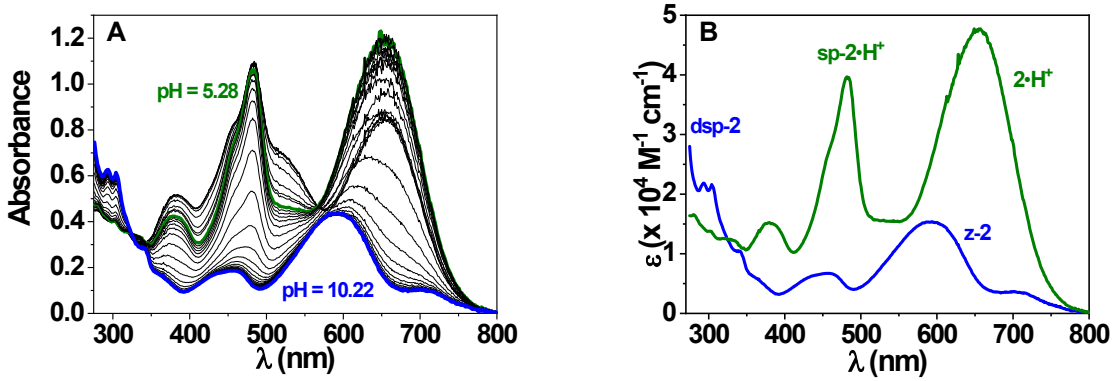


Figure S 84. (A) UV-visible absorption spectrophotometric *versus* pH titration of **2** in CH_3OH/H_2O (80:20 by weight) from acidic to basic pH values; (B) Absorption electronic spectra of **2** (**z-2** and **dsp-2**) and its protonated species **2•H⁺** (**2•H⁺** and **sp-2•H⁺**); I = 0.1 M NBu_4ClO_4; T = 25.0 ± 0.1 °C; [**2**] = 2.81 × 10^{-5} M. The absorption spectra are not corrected for the dilution effects. The data have been processed from pH 4.19 to 10.22 with pK_{a2} = 6.56 ± 0.02.

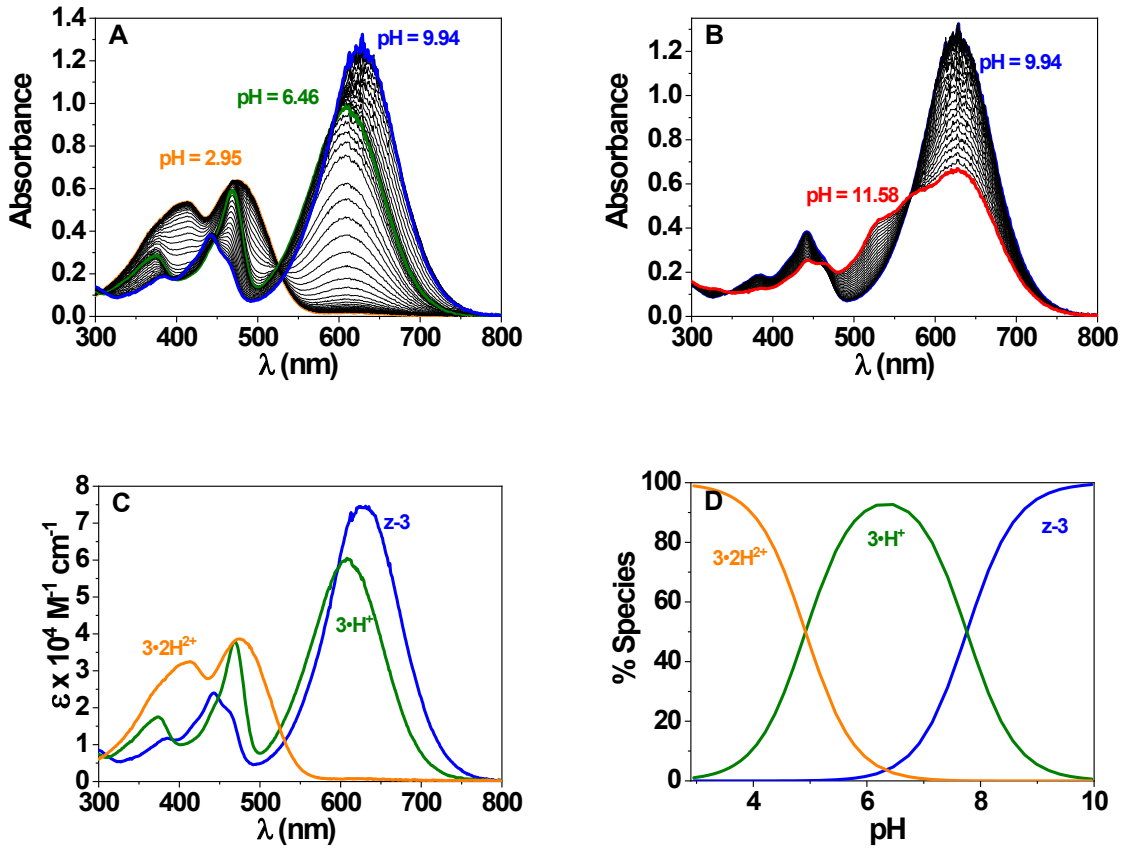


Figure S 85. UV-visible absorption spectrophotometric *versus* pH titration of **3** in CH_3OH/H_2O (80:20 by weight) from acidic to basic pH values: (A) from pH 2.95 to 9.94 and (B) from pH 9.94 to 11.58; (C) Absorption electronic spectra of **3** (**z-3**) and its protonated species **3•H⁺** and **3•2H²⁺**; (D) Distribution diagrams of the protonated species of **3**. I = 0.1 M NBu_4ClO_4; T = 25.0 ± 0.1 °C; [**3**] = 1.66 × 10^{-5} M. The absorption spectra are not corrected for the dilution effects. The data have been processed from pH 2.95 to 9.94 with pK_{a1} = 4.92 ± 0.07 and pK_{a2} = 7.76 ± 0.07.

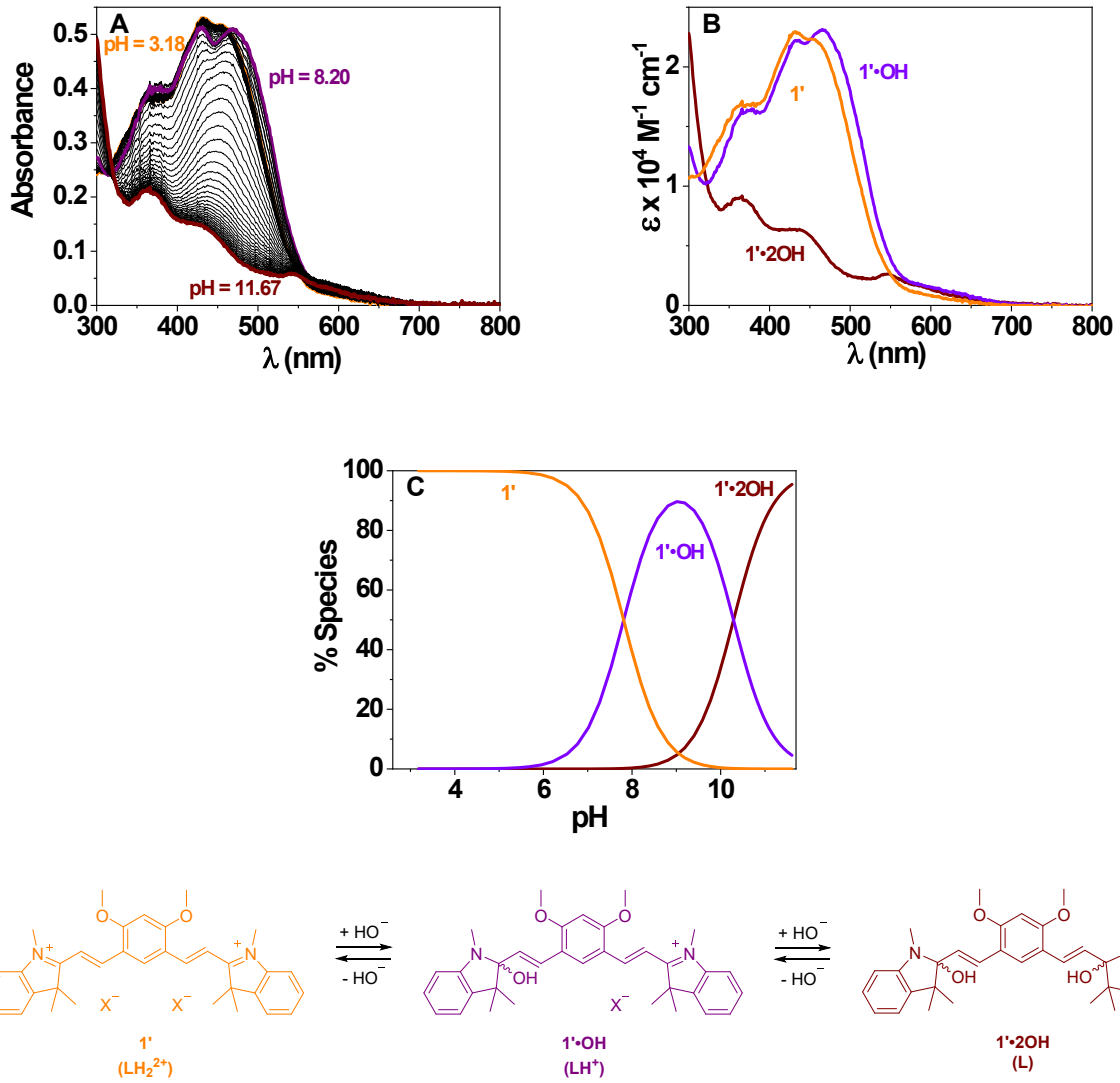
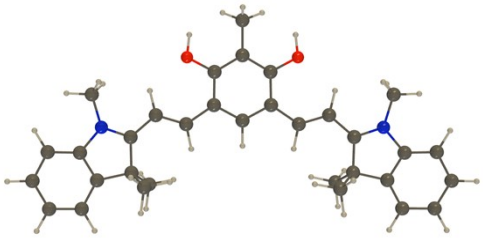


Figure S 86. (A) UV-visible absorption spectrophotometric *versus* pH titration of **1'** in CH_3OH/H_2O (80:20 by weight) from acidic to basic pH values; (B) Absorption electronic spectra of **1'** and its hydroxo species **1'•OH** and **1'•2OH**; (C) Distribution diagrams of the protonated species of **1'**. I = 0.1 M NBu_4ClO_4; T = 25.0 ± 0.1 °C; [**1'**] = 2.30 × 10^{-5} M. The absorption spectra are not corrected for the dilution effects. The data have been processed from pH 3.18 to 11.67 with pK_{a1} = 7.8 ± 0.3 and pK_{a2} = 10.29 ± 0.06. (Bottom) chemical structures of the hydroxylated species with **1'**.

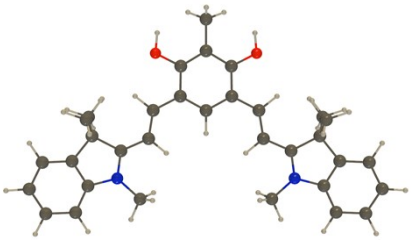
VII. THEORETICAL CALCULATIONS

Methods. In all calculations, no simplifications of the structure were performed, *i.e.*, we modelled exactly the experimental compounds. The ground-state geometries of all compounds were optimized at the M06-2X/6-311G(d,p) level,[18] modelling the solvation effects (MeOH, the solvent used in the UV-vis-NIR measurements) using the well-known PCM model.[19] The very same level of theory was used to next determine the vibrational frequencies on the optimized structures on the basis of analytic determination of the Hessian, and it turned out that all molecules are true minima of the potential energy surface (no imaginary frequencies). These calculations have been performed with the Gaussian16.A03 program[20] applying default algorithms and convergence thresholds, except for: *i)* improved optimization threshold (*tight*); *ii)* tightened SCF convergence (10^{-10} Eh and preventing integral quality variation during the SCF with *novaracc*); *iii*) improved DFT grids (*ultrafine/fine* for energies/eigenvectors in the CPKS process). In a second step, we have used TD-DFT, and more precisely TD-M06-2X/6-311+G(2d,p) to obtain vertical excitation energies to the lowest singlet excited states. During these calculations, we used both the gas-phase and MeOH environments. For the latter, the default linear-response PCM approach[21] in its *non-equilibrium* limit was used; such solvation model is well suited for bright transitions that are our key interest. The excited states have been represented using EDD (Electron Density Difference) plots determined for all key transitions. In the EDD representation, a contour threshold of 0.001 au was used, and the blue and red lobes represent regions of density decrease and increase upon excitation, respectively. Next, being well-aware of the impact of the functional on the TD-DFT results, and of the limitations of TD-DFT for some specific families of states (charge-transfer, cyanine, etc.), we did perform gas CC2/*aug*-cc-pVTDZ calculations[22] with Turbomole 7.3,[23] using DFT determined geometries. These calculations used RI (with the auxiliary basis set corresponding to *aug*-cc-pVDZ) and the frozen-core approximation. Combining the CC2, gas TD-DFT, and PCM-TD-DFT results, one can obtain theoretical best estimates for the vertical transition energies following a procedure described elsewhere.[24] The data in the main text use the CC2 oscillator strengths and those "hybrid" energies. We note that, these vertical transition energies cannot be directly associated to experimental λ_{max}, since vibronic effects are neglected.[24] However, we are here interested in trends in homologous compounds. The NICS reported in the main text have been computed on the structures obtained above using the B3LYP/6-311+G(d,p) level of theory for the NMR (GIAO) part and modelling the solution using PCM(MeOH).[25]

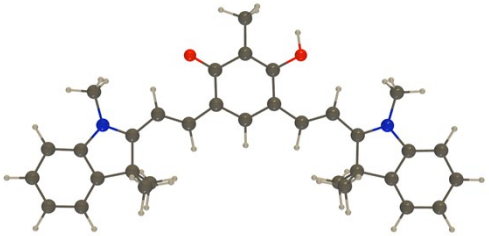
Additional results.



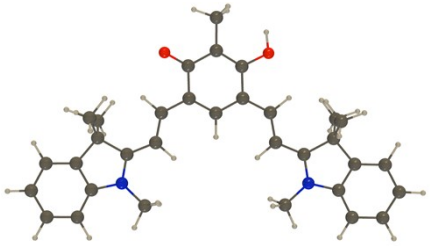
ΔE :0.00 kcal.mol^{-1}



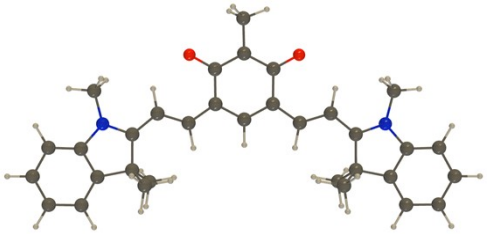
ΔE :-0.21 kcal.mol^{-1}



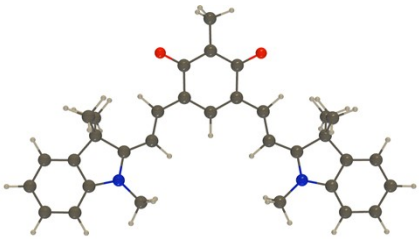
ΔE :0.00 kcal.mol^{-1}



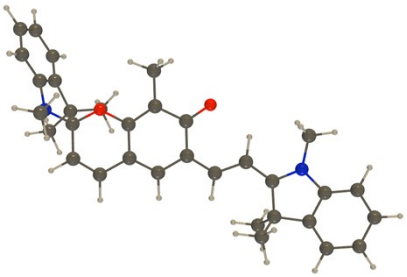
ΔE :+0.85 kcal.mol^{-1}



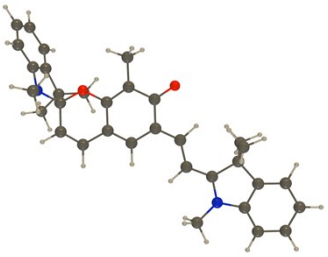
ΔE :0.00 kcal.mol^{-1}



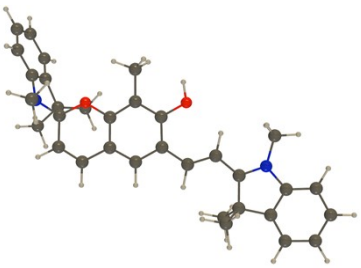
ΔE :+0.53 kcal.mol^{-1}



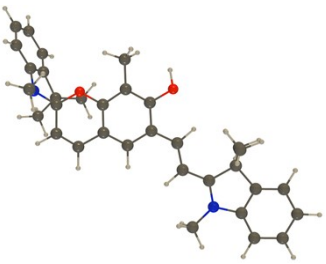
ΔE :0.00 kcal.mol^{-1}



ΔE = -0.03 kcal.mol^{-1}



ΔE :0.00 kcal.mol^{-1}



ΔE = -0.45 kcal.mol^{-1}

Figure S 87. Relative energies of the s-*trans* (left) and -s-*cis* (right) forms for various forms of **1** (from top to bottom: **1•2H^{2+}**, **1•H^{+}**, **z-1**, **sp-1** and **sp-1•H^{+}**). These relative energies have been determined on the E+ZPVE scale, the former being obtained at the PCM- M06-2X/6-311+G(2d,p), and the latter at the PCM-M06-2X/6-311G(d,p) level.

Table S 2. Theoretical vertical excitation wavelength ($\lambda_{vert-abs}^{theo}$ in nm) and corresponding oscillator strength (f, indicated in parentheses) determined in methanol for the *s-trans* or *s-cis* isomers of compound **1**.

	s-*trans*	s-*cis*
1•2H^{2+}	430 (1.88) 384 (0.41)	473 (1.21) 388 (0.72)
1•H^{+}	601 (1.81) 422 (0.58)	687 (1.06) 423 (0.67)
sp-1•H^{+}	471 (1.31) 372 (0.02) 363 (0.28)	486 (1.39) 381 (0.02) 371 (0.18)
sp-1	507 (0.88) 411 (0.06)	516 (0.87) 398 (0.05) 392 (0.65)
z-1	698 (0.03) 636 (0.73)	759 (0.08) 707 (0.44)

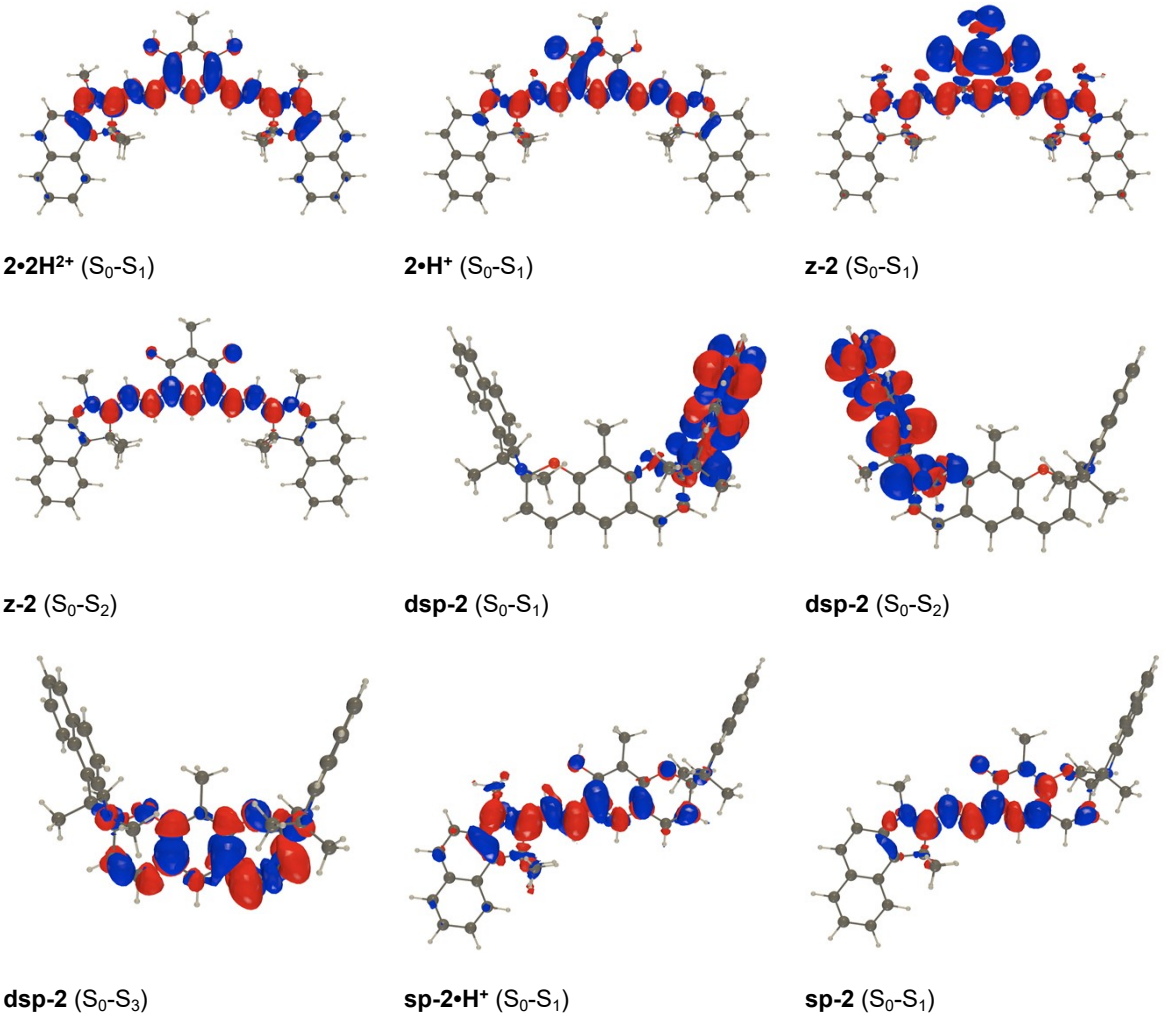
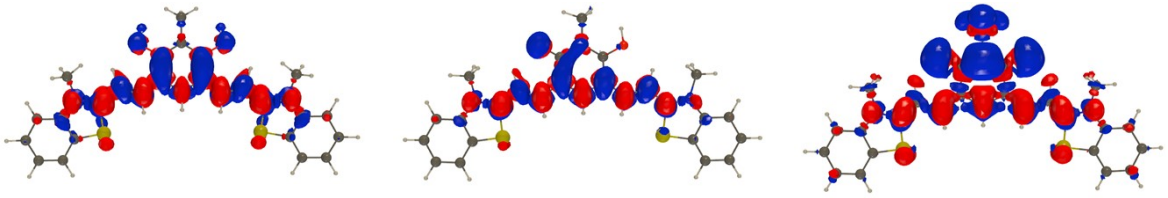
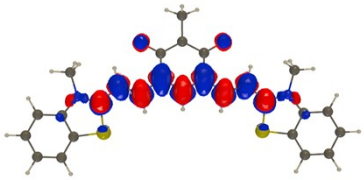


Figure S 88. EDD plots for various forms of **2**. The blue and red lobes indicated decrease and increase of electron density upon photon absorption, respectively. Note that in contrast to **dsp-1** the lowest excited states of **dsp-2** are localized on the side rings. Contour threshold: 0.001 au.

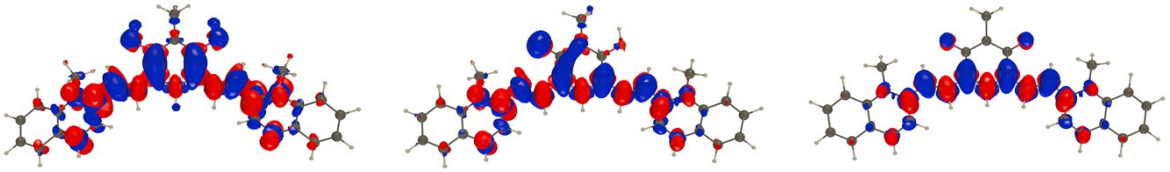


3•2H^{2+} (S_0-S_1) **3•H^{+}** (S_0-S_1) **z-3** (S_0-S_1)



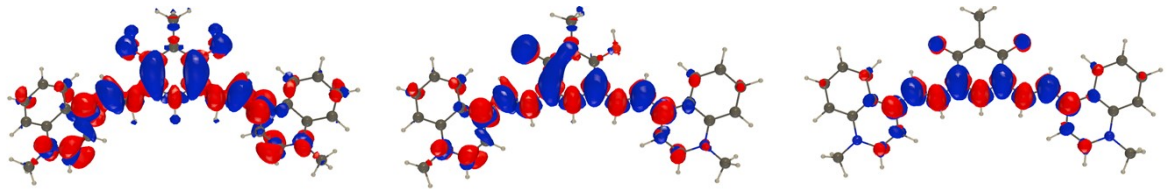
z-3 (S_0-S_2)

Figure S 89. EDD plots for various forms of **3**. See caption of Figure S 88 for more details. Note that as in other case the first and second states of **z-3** have been ordered as given by the CC2-corrected approach, the PCM-TD-DFT "raw" result providing the reversed order (CT state appearing slightly higher in energy than the cyanine state).



4•2H^{2+} (S_0-S_1) **4•H^{+}** (S_0-S_1) **z-4** (S_0-S_1)

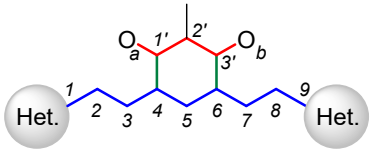
Figure S 90. EDD plots for various forms of **4**. See caption of Figure S 88 for more details.



5•2H^{2+} (S_0-S_1) **5•H^{+}** (S_0-S_1) **z-5** (S_0-S_1)

Figure S 91. EDD plots for various forms of **5**. See caption of Figure S 88 for more details.

Table S 3. Bond lengths (in Å) and absolute value of bond length alternation (BLA) extracted from DFT optimized geometries.



	C1–C2	C2–C3	C3–C4	C4–C5	C5–C6	C6–C7	C7–C8	C8–C9	C1'–C2'	C2'–C3'	Oa–C1'	C3'–Ob	C4–C1'	C6–C3'	BLA (Oa–Ob)	BLA (C1–C5)	BLA (C9–C5)	BLA (C1–C9)
1'	1.433	1.354	1.453	1.397	1.394	1.453	1.354	1.432	1.401	1.394	1.351	1.362	1.413	1.414	0.009	0.067	0.068	0.001
1•2H²⁺	1.429	1.357	1.445	1.394	1.394	1.445	1.358	1.429	1.398	1.398	1.338	1.338	1.420	1.420	0.000	0.062	0.061	0.000
2•2H²⁺	1.431	1.357	1.446	1.394	1.394	1.446	1.357	1.431	1.398	1.398	1.339	1.339	1.419	1.419	0.000	0.063	0.063	0.000
3•2H²⁺	1.439	1.352	1.448	1.393	1.393	1.448	1.352	1.439	1.398	1.398	1.341	1.341	1.417	1.417	0.000	0.071	0.071	0.000
4•2H²⁺	1.458	1.348	1.454	1.393	1.394	1.454	1.348	1.458	1.398	1.399	1.345	1.344	1.414	1.414	0.001	0.085	0.085	0.000
5•2H²⁺	1.457	1.348	1.455	1.394	1.394	1.455	1.348	1.457	1.399	1.399	1.346	1.346	1.414	1.413	0.000	0.085	0.085	0.000
1•H⁺	1.411	1.373	1.422	1.391	1.400	1.416	1.379	1.406	1.458	1.365	1.237	1.352	1.475	1.448	0.104	0.035	0.022	0.007
2•H⁺	1.412	1.373	1.423	1.391	1.400	1.416	1.378	1.407	1.458	1.365	1.237	1.352	1.474	1.448	0.104	0.035	0.023	0.006
3•H⁺	1.418	1.368	1.423	1.390	1.399	1.417	1.373	1.413	1.457	1.366	1.239	1.353	1.473	1.446	0.103	0.042	0.029	0.006
4•H⁺	1.437	1.364	1.430	1.390	1.399	1.424	1.369	1.433	1.456	1.368	1.242	1.356	1.469	1.442	0.101	0.057	0.045	0.006
5•H⁺	1.436	1.364	1.432	1.390	1.400	1.424	1.370	1.429	1.457	1.368	1.242	1.356	1.470	1.442	0.102	0.057	0.041	0.008
z-1	1.395	1.389	1.406	1.396	1.396	1.406	1.389	1.395	1.419	1.418	1.255	1.255	1.496	1.494	0.000	0.008	0.008	0.000
z-2	1.397	1.388	1.407	1.396	1.396	1.406	1.389	1.396	1.419	1.418	1.256	1.255	1.496	1.493	0.000	0.010	0.008	0.001
z-3	1.401	1.383	1.407	1.395	1.395	1.407	1.383	1.401	1.419	1.419	1.256	1.256	1.493	1.493	0.000	0.015	0.015	0.000
z-4	1.417	1.381	1.412	1.395	1.395	1.412	1.381	1.417	1.419	1.419	1.258	1.258	1.491	1.491	0.000	0.027	0.027	0.000
z-5	1.415	1.382	1.412	1.396	1.396	1.412	1.382	1.415	1.419	1.419	1.257	1.257	1.493	1.493	0.000	0.025	0.025	0.000

Cartesian coordinates.

Below we provide the Cartesian coordinates obtained by DFT (in Å), together with the total free energy computed at the DFT level of theory described above. All structures show absence of imaginary frequencies (true minima).

1•2H^{2+} *G= -1538.017788* au

C	-0.0006370	3.5088200	-0.0530360
C	-1.2014840	2.7942630	-0.0144820
C	-1.2269000	1.3746220	-0.0103890
C	0.0006940	0.7144210	-0.0116990
C	1.2275320	1.3758340	-0.0048950
C	1.2006820	2.7953730	-0.0083920
H	0.0012240	-0.3702340	-0.0082460
C	-0.0007090	5.0149960	-0.1206750
H	-0.8620850	5.3916400	-0.6750010
H	-0.0006160	5.4740830	0.8709180
H	0.8607510	5.3912850	-0.6752050
O	-2.3837350	3.4201140	0.0123880
H	-2.2811480	4.3750290	0.0962760
O	2.3821520	3.4224130	0.0240340
H	2.2782020	4.3774010	0.1055620
C	-2.4204970	0.5602040	0.0017260
C	-3.7231600	0.9421880	-0.0084490
H	-2.1997080	-0.5001250	0.0179130
H	-3.9775610	1.9893830	-0.0286510
C	2.4219660	0.5625950	0.0121650
C	3.7242330	0.9453800	0.0230290
H	2.2022140	-0.4980060	0.0168920
H	3.9783780	1.9928130	0.0134520
C	-4.8040790	0.0078570	0.0020830
C	-6.9722330	-0.6597890	0.0004430
C	-6.2403630	-1.8390980	0.0180770
C	4.8048840	0.0102150	0.0325740
C	6.9710910	-0.6627400	0.0424960
C	6.2382080	-1.8389350	-0.0307070
N	6.0561270	0.4242850	0.0885780
N	-6.0550590	0.4265610	-0.0061140
C	-6.4689670	1.8304450	-0.0200270
H	-6.0663270	2.3370490	0.8557220
H	-6.1094790	2.3081320	-0.9304250
H	-7.5517660	1.8776670	0.0065520
C	6.4816090	1.8221460	0.1706810
H	6.3201720	2.3122470	-0.7891680
H	5.9192090	2.3277680	0.9525610
H	7.5362670	1.8510660	0.4226660
C	-8.3572870	-0.6314840	-0.0084600
C	-9.0063620	-1.8642920	0.0023950
H	-8.9254360	0.2883330	-0.0239340
H	-10.0885900	-1.8887480	-0.0042090
C	-6.8944150	-3.0582370	0.0294760
C	-8.2893930	-3.0599080	0.0214570
H	-6.3408080	-3.9900320	0.0444360
H	-8.8233560	-4.0016620	0.0299200
C	6.8915840	-3.0573510	-0.0844290
C	8.2865590	-3.0603630	-0.0672540
H	6.3377920	-3.9874320	-0.1411960
H	8.8199670	-4.0014920	-0.1103400
C	8.3560300	-0.6351830	0.0576780
C	9.0045120	-1.8670630	0.0014700
H	8.9230720	0.2843690	0.1049190
H	10.0866950	-1.8927700	0.0099790
C	4.7639880	-1.5116130	-0.0387140
C	-4.7654210	-1.5148800	0.0223760
C	-4.0982130	-2.0862650	-1.2440470

H	-4.5549650	-1.6694980	-2.1430030
H	-3.0277880	-1.8863060	-1.2695210
H	-4.2422060	-3.1678900	-1.2531010
C	-4.1151510	-2.0478660	1.3143180
H	-3.0471160	-1.8372550	1.3518430
H	-4.5902930	-1.6114860	2.1942590
H	-4.2508070	-3.1300040	1.3491030
C	4.1239230	-1.9990170	-1.3529750
H	3.0584850	-1.7758860	-1.3952440
H	4.6129780	-1.5407280	-2.2139650
H	4.2493980	-3.0808960	-1.4193900
C	4.0849580	-2.1262410	1.2015690
H	4.5273290	-1.7351780	2.1190040
H	3.0126340	-1.9364820	1.2198440
H	4.2373660	-3.2064910	1.1778540

1•H⁺ *G= -1537.592690* au

C	0.0021880	3.5012350	-0.0000080
C	-1.2794810	2.8053230	-0.0000090
C	-1.2311210	1.3313600	-0.0000100
C	0.0029590	0.6899340	-0.0000110
C	1.2318160	1.3597380	-0.0000070
C	1.1771830	2.8068150	-0.0000050
H	0.0185380	-0.3963090	-0.0000120
C	-0.0035230	5.0059730	-0.0000110
H	-1.0331010	5.3567790	-0.0000020
H	0.4904150	5.4177080	0.8862010
H	0.4903990	5.4177030	-0.8862350
O	-2.3473120	3.4296410	-0.0000100
O	2.3718460	3.4400640	-0.0000050
H	2.2408700	4.3952400	0.0000010
C	-2.3962390	0.5157260	-0.0000080
C	-3.7089120	0.9197010	-0.0000130
H	-2.1863140	-0.5484580	-0.0000010
H	-3.9149090	1.9789460	-0.0000210
C	2.4058480	0.5686590	-0.0000050
C	3.7307190	0.9505240	0.0000160
H	2.1948060	-0.4945320	-0.0000220
H	3.9755730	2.0003420	0.0000390
C	-4.7967760	0.0215140	-0.0000060
C	-6.9851070	-0.6007800	-0.0000030
C	-6.2787480	-1.7974090	0.0000130
C	4.7957290	0.0324580	0.0000120
C	6.9720060	-0.6371400	0.0000280
C	6.2402750	-1.8186990	-0.0000160
N	6.0639160	0.4481600	0.0000400
N	-6.0515210	0.4649060	-0.0000130
C	-6.4254010	1.8755860	-0.0000250
H	-6.0286120	2.3609330	0.8914320
H	-6.0286190	2.3609160	-0.8914950
H	-7.5071440	1.9560980	-0.0000210
C	6.4696610	1.8486740	0.0000760
H	6.0856540	2.3444210	-0.8916140
H	6.0856540	2.3443770	0.8917890
H	7.5530130	1.9044230	0.0000760
C	-8.3698910	-0.5501310	-0.0000070
C	-9.0441900	-1.7706710	0.0000080
H	-8.9203220	0.3807380	-0.0000210
H	-10.1269440	-1.7726670	0.0000060
C	-6.9567950	-3.0026730	0.0000270
C	-8.3526460	-2.9801910	0.0000250
H	-6.4201350	-3.9448410	0.0000410
H	-8.9043140	-3.9117650	0.0000360
C	6.8921380	-3.0381690	-0.0000400
C	8.2884280	-3.0468980	-0.0000180
H	6.3349780	-3.9683730	-0.0000770

H	8.8192890	-3.9904770	-0.0000360
C	8.3577520	-0.6177400	0.0000510
C	9.0056790	-1.8527570	0.0000280
H	8.9285830	0.3008690	0.0000870
H	10.0881960	-1.8778770	0.0000450
C	4.7630530	-1.4952020	-0.0000320
C	-4.7957780	-1.5049870	0.0000140
C	-4.1497430	-2.0736050	-1.2772420
H	-4.6073530	-1.6381100	-2.1670750
H	-3.0769810	-1.8866170	-1.3091250
H	-4.3092960	-3.1531600	-1.3001220
C	-4.1497580	-2.0735590	1.2772990
H	-3.0770000	-1.8865540	1.3091960
H	-4.6073900	-1.6380430	2.1671110
H	-4.3092980	-3.1531160	1.3002090
C	4.1071380	-2.0523620	-1.2772250
H	3.0379800	-1.8457220	-1.3116820
H	4.5740260	-1.6264670	-2.1668950
H	4.2457880	-3.1348820	-1.2993670
C	4.1070910	-2.0524510	1.2770980
H	4.5739290	-1.6266030	2.1668150
H	3.0379260	-1.8458400	1.3115210
H	4.2457620	-3.1349700	1.2991800

z-1 *G= -1537.136125* au

C	-0.0013260	3.4923270	-0.0039910
C	-1.2503510	2.8211690	-0.0081350
C	-1.2293440	1.3277440	-0.0044640
C	0.0033690	0.6722360	0.0014480
C	1.2320110	1.3354050	0.0064710
C	1.2542050	2.8314230	0.0092740
H	0.0066730	-0.4159500	0.0025850
C	-0.0349680	4.9951070	-0.0101420
H	-0.6452530	5.3749350	-0.8353230
H	-0.4767980	5.3979200	0.9084970
H	0.9764750	5.3881960	-0.1055830
O	-2.3442220	3.4362540	-0.0150670
O	2.3551330	3.4343200	0.0217300
C	-2.3798760	0.5200230	-0.0046420
C	-3.7089430	0.9236410	-0.0078500
H	-2.1736270	-0.5456960	-0.0008990
H	-3.8994510	1.9864460	-0.0125460
C	2.3847530	0.5296450	0.0073750
C	3.7143540	0.9309790	0.0107910
H	2.1789290	-0.5361250	0.0035300
H	3.9073220	1.9931540	0.0159000
C	-4.7872250	0.0382260	-0.0042960
C	-6.9832370	-0.5789380	-0.0015700
C	-6.2796410	-1.7793590	0.0041120
C	4.7907820	0.0430270	0.0063600
C	6.9857180	-0.5779820	0.0023630
C	6.2800700	-1.7771590	-0.0052250
N	6.0592230	0.4857680	0.0090990
N	-6.0549570	0.4832370	-0.0063160
C	-6.4192310	1.8922500	-0.0119110
H	-6.0175790	2.3827690	0.8755490
H	-6.0200720	2.3752640	-0.9046020
H	-7.5007700	1.9820350	-0.0107290
C	6.4261780	1.8941130	0.0168840
H	6.0270420	2.3864240	-0.8707150
H	6.0263630	2.3768100	0.9094270
H	7.5078850	1.9817700	0.0177840
C	-8.3689790	-0.5323910	-0.0019470
C	-9.0448930	-1.7530300	0.0038180
H	-8.9194960	0.3986700	-0.0064760
H	-10.1278850	-1.7532620	0.0037570

C	-6.9588670	-2.9831640	0.0097850
C	-8.3558180	-2.9630100	0.0096390
H	-6.4215810	-3.9252800	0.0143750
H	-8.9072810	-3.8947320	0.0141310
C	6.9572960	-2.9820920	-0.0130890
C	8.3542750	-2.9642530	-0.0132490
H	6.4184570	-3.9233060	-0.0191900
H	8.9041690	-3.8968920	-0.0195160
C	8.3715270	-0.5337050	0.0024930
C	9.0454000	-1.7554490	-0.0055210
H	8.9235910	0.3964320	0.0084190
H	10.1283890	-1.7574910	-0.0057490
C	4.7952750	-1.4863310	-0.0034000
C	-4.7943580	-1.4911190	0.0030640
C	-4.1505590	-2.0712350	-1.2691570
H	-4.6084510	-1.6413860	-2.1617460
H	-3.0778090	-1.8834640	-1.3036650
H	-4.3095570	-3.1513450	-1.2858300
C	-4.1515010	-2.0583220	1.2816130
H	-3.0788480	-1.8698370	1.3150530
H	-4.6102170	-1.6196030	2.1694550
H	-4.3102670	-3.1382340	1.3090090
C	4.1512020	-2.0503000	-1.2827780
H	3.0788710	-1.8599070	-1.3157130
H	4.6105060	-1.6108830	-2.1699720
H	4.3081210	-3.1304310	-1.3119940
C	4.1508360	-2.0675580	1.2680130
H	4.6095410	-1.6398630	2.1612180
H	3.0783590	-1.8783600	1.3030980
H	4.3082950	-3.1479220	1.2828440

dsp-1 *G= -1537.170447* au

C	0.0172330	-0.4498450	0.5887020
C	-1.1732500	-1.1386490	0.3595730
C	-1.1939690	-2.4601810	-0.1149810
C	0.0136850	-3.1018860	-0.3624110
C	1.2267750	-2.4508710	-0.1524130
C	1.2066340	-1.1357060	0.3304130
H	0.0117080	-4.1248180	-0.7257140
C	0.0339190	0.9702760	1.0781930
H	-0.9116100	1.4615840	0.8513120
H	0.1848260	1.0134420	2.1605890
H	0.8533230	1.5196500	0.6120780
O	-2.3286220	-0.4854510	0.6454960
O	2.3611810	-0.4805580	0.6060900
C	-2.4966060	-3.0914780	-0.2888990
C	-3.6192760	-2.3802160	-0.1821920
H	-2.5294440	-4.1554650	-0.4981170
H	-4.5979310	-2.8293710	-0.2981490
C	2.5274350	-3.0495710	-0.4115560
C	3.6405860	-2.3143320	-0.3617570
H	2.5684400	-4.1020690	-0.6717680
H	4.6061310	-2.7398500	-0.5992490
C	-3.5896250	-0.8972910	0.0533530
C	-4.8663530	0.8913680	0.7176770
C	-4.4224080	1.2272760	-0.5676980
N	-4.6168190	-0.4601580	0.9753860
C	-4.5630240	-0.9305260	2.3477820
H	-4.3286490	-1.9952010	2.3478930
H	-3.8054670	-0.3990500	2.9350230
H	-5.5380580	-0.7958790	2.8176540
C	-5.4643010	1.8347910	1.5417880
C	-5.6240890	3.1319120	1.0403340
H	-5.7925530	1.5848110	2.5433090
H	-6.0862540	3.8849110	1.6681410
C	-4.5827260	2.5090600	-1.0515160

C	-5.1917480	3.4729000	-0.2352680
H	-4.2378390	2.7710780	-2.0466230
H	-5.3194640	4.4855390	-0.5973380
C	-3.8580920	-0.0181910	-1.2189410
C	-2.6005800	0.2177300	-2.0498760
H	-1.8403870	0.7604010	-1.4860900
H	-2.1792580	-0.7341530	-2.3867480
H	-2.8541930	0.8028090	-2.9369640
C	-4.9487220	-0.6614460	-2.0911590
H	-4.5835230	-1.5800110	-2.5568680
H	-5.8377850	-0.8947500	-1.5011010
H	-5.2324640	0.0369510	-2.8809450
C	3.5996910	-0.8458440	-0.0514790
N	3.7533660	-0.0299100	-1.2504230
C	4.7364110	-0.3123620	0.8855750
C	4.2217130	1.2240840	-0.8401160
C	2.7214220	-0.0920370	-2.2700690
C	4.8021890	1.1308570	0.4302530
C	4.4157130	-0.4947490	2.3657350
C	6.0801390	-0.9850340	0.5585530
C	4.1637690	2.4356100	-1.5160760
H	2.4740040	-1.1350240	-2.4671720
H	1.8115750	0.4439360	-1.9669170
H	3.0960920	0.3475790	-3.1950750
C	5.3527520	2.2424920	1.0337070
H	3.5371920	0.0779740	2.6585830
H	4.2356440	-1.5505140	2.5865030
H	5.2671270	-0.1655650	2.9661640
H	6.0970230	-2.0214450	0.9037880
H	6.2844420	-0.9636460	-0.5142940
H	6.8779030	-0.4441860	1.0709480
C	4.7259080	3.5575480	-0.8961240
H	3.6964770	2.5197830	-2.4895580
C	5.3135820	3.4710890	0.3599880
H	5.8023350	2.1702490	2.0187580
H	4.6906620	4.5130710	-1.4064530
H	5.7349460	4.3551120	0.8224120

sp-1 *G= -1537.157054* au

C	1.2521420	1.1554680	-0.4736040
C	1.9609570	-0.0105070	-0.4811290
C	1.3351370	-1.3062040	-0.3845630
C	-0.0234450	-1.3653900	-0.3009480
C	-0.8443840	-0.1975450	-0.2909230
C	-0.2026300	1.1255100	-0.3876450
H	-0.5061350	-2.3370780	-0.2382630
C	1.9125240	2.5001160	-0.5541730
H	2.9888470	2.4179790	-0.4092880
H	1.7290450	2.9721380	-1.5242020
H	1.4923870	3.1661690	0.2023230
O	3.3087590	0.0589130	-0.6334680
O	-0.8466530	2.1879310	-0.3907080
C	2.1971710	-2.4750400	-0.4097590
C	3.5253610	-2.3558480	-0.3566100
H	1.7296950	-3.4522860	-0.4738150
H	4.1815790	-3.2170170	-0.3752800
C	-2.2246640	-0.3713260	-0.1909800
C	-3.2214070	0.6086080	-0.1566530
H	-2.5392430	-1.4084980	-0.1312140
H	-2.9064700	1.6389480	-0.2148940
C	4.1864300	-1.0184310	-0.2129050
C	6.1874420	0.0834250	-0.4520930
C	5.8370820	0.2680580	0.8915270
C	-4.5771530	0.3299360	-0.0486060
C	-6.8047500	0.8113390	0.1007820
C	-6.7404260	-0.5786110	0.1471940

N	-5.4965820	1.3176920	-0.0193720
N	5.3752220	-0.8956810	-1.0317490
C	5.2296330	-0.9429960	-2.4753440
H	4.5332000	-1.7408780	-2.7337750
H	4.8543680	0.0032660	-2.8816110
H	6.1937250	-1.1699580	-2.9323110
C	-5.1656800	2.7303390	-0.1008840
H	-4.5372210	3.0171760	0.7439200
H	-4.6331960	2.9349220	-1.0310230
H	-6.0804650	3.3142290	-0.0797500
C	7.2161630	0.8116450	-1.0338500
C	7.9053070	1.7260820	-0.2286380
H	7.4784480	0.6865890	-2.0773240
H	8.7107390	2.3066760	-0.6633640
C	6.5214340	1.1730650	1.6758380
C	7.5691820	1.9111490	1.1066840
H	6.2501050	1.3178020	2.7166020
H	8.1121820	2.6307720	1.7068190
C	-7.8976910	-1.3248340	0.2643430
C	-9.1229490	-0.6560890	0.3346420
H	-7.8594550	-2.4081610	0.3020000
H	-10.0410260	-1.2225520	0.4268430
C	-8.0078780	1.4976090	0.1700910
C	-9.1704580	0.7343950	0.2880650
H	-8.0624960	2.5775670	0.1373390
H	-10.1265890	1.2400490	0.3448350
C	-5.2947800	-1.0184960	0.0539120
C	4.7153100	-0.6915840	1.2299450
C	3.6331830	-0.1060390	2.1312520
H	3.2631660	0.8465570	1.7499810
H	2.7921920	-0.8007700	2.2206200
H	4.0392590	0.0558840	3.1324940
C	5.3155920	-1.9491360	1.8790980
H	4.5341000	-2.6752510	2.1156430
H	6.0475100	-2.4213110	1.2199620
H	5.8181290	-1.6675610	2.8067000
C	-4.8997030	-1.7831170	1.3297250
H	-3.8635680	-2.1191580	1.2984790
H	-5.0354110	-1.1547350	2.2117430
H	-5.5404960	-2.6616360	1.4303270
C	-5.0885760	-1.8712610	-1.2106090
H	-5.3606410	-1.3057810	-2.1036160
H	-4.0558970	-2.2044410	-1.3115570
H	-5.7285520	-2.7542080	-1.1531690

sp-1•H⁺ *G= -1537.598371* au

C	-1.2456770	1.1865280	0.4596580
C	-1.9698200	-0.0071280	0.4736650
C	-1.3367030	-1.2654160	0.4044030
C	0.0380090	-1.3040530	0.3212510
C	0.8233690	-0.1351010	0.2939930
C	0.1456210	1.1075380	0.3704480
H	0.5354310	-2.2675020	0.2772130
C	-1.9338760	2.5237210	0.5228270
H	-3.0134030	2.3940790	0.5151560
H	-1.6696290	3.0668840	1.4351530
H	-1.6681040	3.1466520	-0.3367780
O	-3.3032320	0.0854230	0.5881790
O	0.8912100	2.2281360	0.3452080
H	0.3353490	3.0125280	0.4198680
C	-2.1822160	-2.4513730	0.4723260
C	-3.5092650	-2.3446280	0.4265390
H	-1.7027330	-3.4185590	0.5738730
H	-4.1562420	-3.2107820	0.4880800
C	2.2474410	-0.2965920	0.1969220
C	3.2241290	0.6532360	0.1410430

H	2.5499930	-1.3365690	0.1640580
H	2.9562670	1.6969390	0.1674090
C	-4.1922470	-1.0233340	0.2339680
C	-6.1913500	0.0783740	0.4527340
C	-5.8613430	0.2051780	-0.9019050
C	4.6066430	0.3368030	0.0396120
C	6.8312240	0.7651430	-0.1199960
C	6.7368640	-0.6199430	-0.1433790
N	5.5188890	1.2946360	-0.0034860
N	-5.3606430	-0.8686330	1.0637250
C	-5.1987510	-0.8635530	2.5067500
H	-4.5040490	-1.6550510	2.7883270
H	-4.8151330	0.0955580	2.8729380
H	-6.1590370	-1.0685390	2.9809950
C	5.2290210	2.7264900	0.0541500
H	4.6522400	3.0200830	-0.8224390
H	4.6704340	2.9496030	0.9620510
H	6.1650250	3.2738040	0.0695740
C	-7.2175350	0.8223670	1.0174280
C	-7.9252990	1.6945130	0.1823550
H	-7.4644250	0.7409250	2.0688360
H	-8.7296550	2.2872120	0.6022090
C	-6.5643510	1.0684860	-1.7164270
C	-7.6095970	1.8223670	-1.1647720
H	-6.3097670	1.1682190	-2.7665540
H	-8.1677430	2.5097240	-1.7882510
C	7.8814250	-1.3893230	-0.2511310
C	9.1123110	-0.7373160	-0.3347750
H	7.8277440	-2.4718600	-0.2715080
H	10.0215910	-1.3187370	-0.4201260
C	8.0391080	1.4385210	-0.2032990
C	9.1862620	0.6544220	-0.3115620
H	8.1100810	2.5175470	-0.1896070
H	10.1511000	1.1407490	-0.3794950
C	5.2854030	-1.0263350	-0.0403510
C	-4.7360190	-0.7594980	-1.2134940
C	-3.6672200	-0.2060410	-2.1510900
H	-3.3051080	0.7685010	-1.8204790
H	-2.8208430	-0.8964970	-2.2188420
H	-4.0846210	-0.0940810	-3.1541660
C	-5.3308150	-2.0506220	-1.7993330
H	-4.5453520	-2.7792170	-2.0142670
H	-6.0512620	-2.4998100	-1.1122950
H	-5.8458100	-1.8133260	-2.7320820
C	4.8660410	-1.7991750	-1.3056150
H	3.8251200	-2.1175010	-1.2639770
H	5.0103990	-1.1876720	-2.1976660
H	5.4913100	-2.6894680	-1.3920170
C	5.0603030	-1.8495310	1.2428250
H	5.3407130	-1.2731270	2.1258100
H	4.0239670	-2.1684610	1.3470800
H	5.6880580	-2.7410900	1.1985500

2•2H^{2+} *G= -1845.157663* au

C	-0.0004390	4.3202550	0.0263950
C	1.2015780	3.6063870	0.0229710
C	1.2273330	2.1872610	0.0366970
C	0.0002560	1.5266190	0.0207910
C	-1.2268440	2.1863850	-0.0195620
C	-1.2004990	3.6051670	-0.0332260
H	0.0005470	0.4419760	0.0306690
C	-0.0068530	5.8273640	0.0718970
H	0.8516530	6.2183800	0.6202590
H	-0.0084840	6.2713910	-0.9265360
H	-0.8711390	6.2068570	0.6202160
O	2.3851550	4.2317180	0.0141000

H	2.2851090	5.1852670	-0.0854510
O	-2.3816420	4.2317340	-0.0973980
H	-2.2757700	5.1858890	-0.1853630
C	2.4204490	1.3707360	0.0600780
C	3.7228390	1.7503770	0.0916490
H	2.1949020	0.3116540	0.0580450
H	3.9739180	2.7983990	0.0926010
C	-2.4196210	1.3697290	-0.0510180
C	-3.7217100	1.7495370	-0.0909790
H	-2.1943240	0.3106490	-0.0408770
H	-3.9726650	2.7976280	-0.0953140
C	4.8108130	0.8213910	0.1050820
C	6.9729470	0.1518870	0.1266590
C	6.2667750	-1.0169450	0.0038830
C	-4.8096960	0.8205580	-0.1064540
C	-6.9718560	0.1515360	-0.1363920
C	-6.2666320	-1.0169430	-0.0050320
N	-6.0565410	1.2344170	-0.2123960
N	6.0583450	1.2353800	0.2026470
C	6.4888450	2.6261920	0.3527120
H	6.4979300	3.1161140	-0.6209290
H	5.8157690	3.1430300	1.0312220
H	7.4859200	2.6366830	0.7809120
C	-6.4852200	2.6247500	-0.3716760
H	-6.4973760	3.1201520	0.5991500
H	-5.8089480	3.1369290	-1.0505970
H	-7.4807060	2.6338440	-0.8035800
C	8.3781550	0.2248040	0.1586660
C	9.0581910	-0.9589710	0.0716320
H	8.9067580	1.1644300	0.2378590
H	10.1416790	-0.9601860	0.0890690
C	6.9557110	-2.2532230	-0.0831850
C	8.3829870	-2.2049910	-0.0459270
C	-6.9563510	-2.2526600	0.0837950
C	-8.3834170	-2.2041840	0.0392480
C	-8.3768620	0.2247180	-0.1756350
C	-9.0576710	-0.9584850	-0.0868830
H	-8.9047740	1.1641670	-0.2613110
H	-10.1410660	-0.9594680	-0.1094900
C	-4.7862710	-0.6970990	0.0176140
C	4.7864090	-0.6967740	-0.0125840
C	4.0871440	-1.3152060	1.2182030
H	4.5251720	-0.9267220	2.1390850
H	3.0187390	-1.1065450	1.2259930
H	4.2187940	-2.3962880	1.2095110
C	4.1512540	-1.1153890	-1.3548520
H	3.0956700	-0.8516820	-1.3994930
H	4.6661550	-0.6295310	-2.1853680
H	4.2374130	-2.1931520	-1.4845920
C	-4.1580220	-1.1105980	1.3647320
H	-3.1024170	-0.8477500	1.4136060
H	-4.6766270	-0.6208460	2.1906410
H	-4.2457740	-2.1877390	1.4985490
C	-4.0810160	-1.3205400	-1.2072040
H	-4.5148560	-0.9362250	-2.1318150
H	-3.0127150	-1.1112190	-1.2107780
H	-4.2121980	-2.4016360	-1.1944810
C	6.3225520	-3.5202240	-0.2053720
C	7.0660900	-4.6681880	-0.2848140
H	5.2440920	-3.5891160	-0.2362900
H	6.5668990	-5.6249370	-0.3771300
C	9.1188490	-3.4144560	-0.1319770
C	8.4785170	-4.6188490	-0.2483410
H	10.2015140	-3.3647800	-0.1037390
H	9.0493430	-5.5367750	-0.3133230
C	-6.3241950	-3.5193140	0.2144940
C	-7.0684760	-4.6667060	0.2952350
H	-5.2459180	-3.5884150	0.2509080

H	-6.5700390	-5.6231950	0.3941000
C	-9.1200600	-3.4130620	0.1267890
C	-8.4806910	-4.6171210	0.2515780
H	-10.2025500	-3.3631890	0.0928780
H	-9.0521110	-5.5345970	0.3176870

2•H⁺ *G= -1844.733255* au

C	0.0099820	4.2938490	-0.0037070
C	1.1859720	3.6006710	-0.0083120
C	1.2420110	2.1541490	-0.0198990
C	0.0135400	1.4837230	-0.0281430
C	-1.2213470	2.1234700	-0.0220330
C	-1.2710750	3.5969570	-0.0093330
H	0.0300640	0.3975210	-0.0373200
C	0.0028930	5.7985770	0.0075140
H	0.4968690	6.2043460	0.8964730
H	0.4959820	6.2173690	-0.8758840
H	-1.0270420	6.1483270	0.0106380
O	2.3799870	4.2356670	-0.0030840
H	2.2475540	5.1905990	0.0035850
O	-2.3395690	4.2208990	-0.0039720
C	2.4165380	1.3626100	-0.0197140
C	3.7407610	1.7448790	-0.0029510
H	2.2027800	0.3003110	-0.0331130
H	3.9806180	2.7957160	0.0112660
C	-2.3854840	1.3051310	-0.0252090
C	-3.6978210	1.7085850	-0.0119420
H	-2.1712210	0.2420630	-0.0382880
H	-3.8985220	2.7687540	0.0019860
C	4.8157290	0.8364030	0.0006700
C	6.9907410	0.1832160	0.0229970
C	6.2914430	-0.9978990	0.0023250
C	-4.7962800	0.8213230	-0.0094760
C	-6.9843170	0.2195550	0.0134720
C	-6.3123040	-0.9772740	0.0003910
N	-6.0444750	1.2782690	0.0029050
N	6.0782350	1.2636860	0.0197890
C	6.4669120	2.6697330	0.0351990
H	6.0768280	3.1683870	-0.8520760
H	6.0741230	3.1507020	0.9311210
H	7.5487250	2.7436810	0.0369650
C	-6.3996070	2.6944910	0.0069140
H	-6.0229660	3.1654720	0.9147920
H	-5.9681750	3.1812420	-0.8671980
H	-7.4787590	2.7937340	-0.0277010
C	8.3968720	0.2549490	0.0442780
C	9.0822750	-0.9296800	0.0428870
H	8.9263420	1.1971070	0.0620210
H	10.1659250	-0.9243300	0.0592580
C	6.9849750	-2.2341070	-0.0004150
C	8.4127990	-2.1826740	0.0205100
C	-7.0345170	-2.1970510	0.0047490
C	-8.4605750	-2.1111890	0.0256940
C	-8.3881110	0.3256360	0.0358720
C	-9.1007490	-0.8426600	0.0416530
H	-8.8950640	1.2801410	0.0510710
H	-10.1839340	-0.8123460	0.0594570
C	-4.8206230	-0.7036020	-0.0166070
C	4.8056020	-0.6902780	-0.0145760
C	4.1253120	-1.2322870	1.2593110
H	4.5879110	-0.7980880	2.1474270
H	3.0609900	-1.0022720	1.2775010
H	4.2380090	-2.3144620	1.3124580
C	4.1604190	-1.2033400	-1.3183010
H	3.0989670	-0.9638300	-1.3635430
H	4.6527350	-0.7559350	-2.1835950

H	4.2666950	-2.2851890	-1.3885430
C	-4.1517060	-1.2519370	1.2605720
H	-3.0830910	-1.0427510	1.2752670
H	-4.6046150	-0.8030960	2.1463870
H	-4.2868070	-2.3312170	1.3196530
C	-4.1835590	-1.2359180	-1.3167180
H	-4.6643990	-0.7828690	-2.1855150
H	-3.1175240	-1.0174710	-1.3588720
H	-4.3118810	-2.3157320	-1.3813860
C	6.3564240	-3.5103460	-0.0227600
C	7.1023630	-4.6593750	-0.0238470
H	5.2779970	-3.5842690	-0.0395990
H	6.6046300	-5.6213410	-0.0412130
C	9.1518270	-3.3939220	0.0187100
C	8.5154540	-4.6055600	-0.0028380
H	10.2347570	-3.3391400	0.0346080
H	9.0884060	-5.5245050	-0.0040600
C	-6.4359170	-3.4874970	-0.0103850
C	-7.2090440	-4.6184900	-0.0045940
H	-5.3594400	-3.5867740	-0.0272150
H	-6.7344990	-5.5921600	-0.0164870
C	-9.2281200	-3.3044170	0.0312800
C	-8.6203970	-4.5307770	0.0165780
H	-10.3093930	-3.2237950	0.0473940
H	-9.2149690	-5.4358740	0.0209760

z-2 *G= -1844.277466* au

C	-0.0007770	4.2724730	0.0050220
C	1.2548810	3.6117660	-0.0119180
C	1.2328790	2.1159890	-0.0095790
C	0.0040450	1.4532330	-0.0024750
C	-1.2289120	2.1081810	0.0065710
C	-1.2498830	3.6013680	0.0117820
H	0.0073990	0.3650440	-0.0043970
C	-0.0344330	5.7752620	0.0123720
H	0.9770250	6.1682510	0.1080000
H	-0.4762770	6.1789890	-0.9058980
H	-0.6447360	6.1542800	0.8378930
O	2.3555430	4.2155940	-0.0271020
O	-2.3435750	4.2172220	0.0220480
C	2.3855890	1.3091280	-0.0126560
C	3.7143310	1.7119860	-0.0185700
H	2.1768440	0.2441410	-0.0084140
H	3.9003770	2.7754080	-0.0245640
C	-2.3793530	1.2992550	0.0081190
C	-3.7075380	1.7044310	0.0150830
H	-2.1701270	0.2343330	0.0022590
H	-3.8909990	2.7684770	0.0223960
C	4.8025000	0.8365790	-0.0152130
C	6.9972890	0.2396110	-0.0136450
C	6.3289690	-0.9609520	-0.0018980
C	-4.7977130	0.8318170	0.0120890
C	-6.9937020	0.2393660	0.0127930
C	-6.3278350	-0.9625850	0.0011110
N	-6.0576560	1.2934330	0.0190260
N	6.0633280	1.2955560	-0.0216800
C	6.4082120	2.7101760	-0.0334670
H	5.9946280	3.1838490	-0.9244750
H	6.0047700	3.1964600	0.8554510
H	7.4874170	2.8196600	-0.0405800
C	-6.3994460	2.7087720	0.0300190
H	-5.9876190	3.1815710	0.9223410
H	-5.9921410	3.1941810	-0.8576070
H	-7.4784230	2.8206800	0.0335620
C	8.4022230	0.3432060	-0.0161950
C	9.1179360	-0.8236540	-0.0059430

H	8.9081920	1.2985190	-0.0254320
H	10.2013760	-0.7908830	-0.0072820
C	7.0537330	-2.1784470	0.0088430
C	8.4804970	-2.0928120	0.0068180
C	-7.0550520	-2.1786240	-0.0079910
C	-8.4816390	-2.0901160	-0.0042280
C	-8.3984290	0.3457580	0.0170700
C	-9.1165000	-0.8196710	0.0085050
H	-8.9024790	1.3020840	0.0265810
H	-10.1998710	-0.7847290	0.0112900
C	-4.8327530	-0.6963840	-0.0003980
C	4.8344280	-0.6916970	-0.0020730
C	4.1855020	-1.2251020	1.2907010
H	4.6565010	-0.7695830	2.1637280
H	3.1189190	-1.0064990	1.3221210
H	4.3131550	-2.3049680	1.3602370
C	4.1813890	-1.2485820	-1.2828440
H	3.1142060	-1.0328760	-1.3140800
H	4.6481820	-0.8075260	-2.1655000
H	4.3109070	-2.3292690	-1.3340950
C	-4.1793540	-1.2539530	1.2798590
H	-3.1117640	-1.0400600	1.3097710
H	-4.6443790	-0.8117120	2.1628560
H	-4.3106800	-2.3343920	1.3317120
C	-4.1861900	-1.2316100	-1.2935930
H	-4.6571620	-0.7755510	-2.1663520
H	-3.1192120	-1.0150970	-1.3261250
H	-4.3160020	-2.3112630	-1.3625360
C	6.4579680	-3.4712420	0.0218990
C	7.2322960	-4.6012740	0.0326300
H	5.3814670	-3.5721070	0.0236480
H	6.7582830	-5.5753650	0.0426280
C	9.2494620	-3.2854020	0.0181180
C	8.6441410	-4.5128520	0.0308420
H	10.3308650	-3.2028340	0.0166170
H	9.2397950	-5.4172460	0.0395590
C	-6.4619210	-3.4726430	-0.0209320
C	-7.2385550	-4.6011130	-0.0298170
H	-5.3856240	-3.5756950	-0.0240710
H	-6.7665270	-5.5761690	-0.0397350
C	-9.2530280	-3.2811570	-0.0136360
C	-8.6502190	-4.5098390	-0.0262200
H	-10.3342570	-3.1963880	-0.0107700
H	-9.2477050	-5.4130370	-0.0334520

dsp-2 *G= -1844.310139* au

C	-0.0242500	-1.0957850	0.4890780
C	-1.2329270	-1.7843930	0.3877330
C	-1.3015930	-3.1095590	-0.0717090
C	-0.1251380	-3.7564360	-0.4309230
C	1.1040110	-3.1075420	-0.3460090
C	1.1330760	-1.7872470	0.1219810
H	-0.1653110	-4.7820810	-0.7842230
C	0.0466820	0.3277670	0.9635740
H	-0.9220880	0.8137260	0.8569830
H	0.3369610	0.3783180	2.0168510
H	0.7964740	0.8779850	0.3928130
O	-2.3505310	-1.1241400	0.7811850
O	2.3077300	-1.1290620	0.2755220
C	-2.6158070	-3.7370670	-0.1199600
C	-3.7225750	-3.0313180	0.1144770
H	-2.6713210	-4.7969370	-0.3448550
H	-4.7057160	-3.4848050	0.0934960
C	2.3720190	-3.7130010	-0.7235430
C	3.4893330	-2.9846380	-0.7788600
H	2.3831150	-4.7659190	-0.9851890

H	4.4257970	-3.4167540	-1.1045560
C	-3.6816970	-1.5564710	0.3896390
C	-4.8733250	0.1741030	1.2913140
C	-4.6645300	0.5641790	-0.0171500
N	-4.5506160	-1.1722760	1.4794390
C	-4.2430870	-1.6674520	2.8105980
H	-3.9802080	-2.7229580	2.7383140
H	-3.4097920	-1.1247980	3.2705990
H	-5.1239810	-1.5803900	3.4471350
C	-5.3760010	1.0570990	2.2700400
C	-5.6844240	2.3384620	1.8894420
H	-5.5094690	0.7346000	3.2951600
H	-6.0648540	3.0441200	2.6199940
C	-5.0119720	1.8684440	-0.4344420
C	-5.5205810	2.7747010	0.5504260
C	-4.1647650	-0.6453010	-0.7963420
C	-3.0158200	-0.4179220	-1.7823740
H	-2.2559360	0.2505310	-1.3748000
H	-2.5444430	-1.3767190	-2.0200130
H	-3.3805320	-0.0042890	-2.7222110
C	-5.3555190	-1.2946870	-1.5209570
H	-5.0380050	-2.1821590	-2.0741440
H	-6.1372020	-1.5803210	-0.8134970
H	-5.7786160	-0.5808980	-2.2310030
C	3.4900930	-1.5158560	-0.4691420
N	3.5636280	-0.7026910	-1.6727330
C	4.6984320	-1.0012980	0.3882520
C	4.0954960	0.5340480	-1.2912280
C	2.4400760	-0.7401540	-2.5940220
C	4.7635770	0.4444970	-0.0865970
C	4.4312960	-1.2383570	1.8778730
C	6.0032490	-1.7033740	-0.0247710
C	4.0044320	1.7435040	-2.0123840
H	2.1535440	-1.7785530	-2.7605280
H	1.5734680	-0.1852260	-2.2106290
H	2.7364190	-0.3153560	-3.5532540
C	5.4394440	1.5679400	0.4393440
H	3.7237390	-0.5164420	2.2841190
H	4.0147730	-2.2401880	2.0150360
H	5.3575060	-1.1918960	2.4512180
H	6.0218210	-2.7381460	0.3258620
H	6.1325720	-1.6918920	-1.1094120
H	6.8475320	-1.1785400	0.4269060
C	4.6284130	2.8527490	-1.5003500
H	3.4538460	1.7977090	-2.9431860
C	5.3559040	2.7998890	-0.2844660
H	4.5711080	3.7986020	-2.0280490
C	6.2040560	1.5487000	1.6419800
C	6.8285050	2.6784840	2.0988970
H	6.2970550	0.6264150	2.1986750
H	7.4071820	2.6389990	3.0143570
C	6.0104790	3.9525280	0.2255710
C	6.7291790	3.9002240	1.3890000
H	5.9313500	4.8798330	-0.3322400
H	7.2262150	4.7850740	1.7674470
C	-4.8986380	2.3354350	-1.7764900
C	-5.2478010	3.6167900	-2.1100210
H	-4.5399150	1.6652760	-2.5453950
H	-5.1560490	3.9475600	-3.1379840
C	-5.8633310	4.0988450	0.1677230
C	-5.7303410	4.5168920	-1.1285130
H	-6.2401700	4.7740710	0.9289350
H	-5.9973110	5.5283090	-1.4094700

sp-2 *G= -1844.297478* au

C	1.4735220	0.8140270	-0.9742230

C	2.0603580	-0.3909190	-0.7159740
C	1.3106400	-1.5518960	-0.3056570
C	-0.0427500	-1.4423590	-0.1894570
C	-0.7404370	-0.2246600	-0.4477110
C	0.0278890	0.9615380	-0.8645980
H	-0.6181570	-2.3136690	0.1116970
C	2.2610710	2.0245640	-1.3803200
H	3.3309130	1.8509500	-1.2752110
H	2.0528960	2.2983270	-2.4188970
H	1.9704450	2.8806620	-0.7674770
O	3.4008950	-0.5016700	-0.8972510
O	-0.5043700	2.0569870	-1.1121630
C	2.0477910	-2.7785780	-0.0601900
C	3.3823090	-2.8011880	-0.0720430
H	1.4808880	-3.6834600	0.1338920
H	3.9419840	-3.7108900	0.1056440
C	-2.1273830	-0.2232110	-0.2915500
C	-3.0175620	0.8363450	-0.4858530
H	-2.5381860	-1.1777120	0.0215060
H	-2.5970160	1.7795560	-0.7981980
C	4.1909480	-1.5596400	-0.2936790
C	6.2624380	-0.8041310	-0.9015750
C	6.0801920	-0.2820510	0.3640850
C	-4.3926960	0.7526020	-0.3031750
C	-6.5415980	1.5044690	-0.2642950
C	-6.6457810	0.1889650	0.1204680
N	-5.1919980	1.8175230	-0.5110420
N	5.3008010	-1.7735800	-1.1962340
C	5.0059450	-2.1075630	-2.5793610
H	4.1996170	-2.8409970	-2.5961930
H	4.6998540	-1.2301410	-3.1598080
H	5.8837590	-2.5575370	-3.0441440
C	-4.7029110	3.1194180	-0.9348620
H	-4.0032080	3.5124350	-0.1955590
H	-4.1970680	3.0311520	-1.8976000
H	-5.5376110	3.8053030	-1.0337430
C	7.3200740	-0.3939380	-1.7404150
C	8.2041230	0.5386900	-1.2600230
H	7.4286080	-0.7999030	-2.7384720
H	9.0231010	0.8806680	-1.8835360
C	7.0023920	0.6505890	0.8885060
C	8.0794130	1.0757120	0.0461890
C	-7.9132800	-0.3647680	0.4266570
C	-9.0503840	0.4947240	0.3172280
C	-7.6513440	2.3653300	-0.3782810
C	-8.8840890	1.8461250	-0.0860540
H	-7.5479330	3.3974290	-0.6839470
H	-9.7645430	2.4740610	-0.1608300
C	-5.2587020	-0.4316170	0.1324620
C	4.8815780	-0.9782510	0.9950290
C	3.8919650	-0.1028300	1.7675570
H	3.7002200	0.8420070	1.2569310
H	2.9423130	-0.6362100	1.8779430
H	4.2544600	0.1061780	2.7737430
C	5.3887480	-2.1174250	1.8945920
H	4.5533640	-2.6547030	2.3503510
H	5.9959490	-2.8254830	1.3261440
H	6.0055640	-1.6993450	2.6931120
C	-4.8745280	-0.8763920	1.5574460
H	-3.8691350	-1.2946240	1.5887540
H	-4.9149440	-0.0257800	2.2403950
H	-5.5684550	-1.6349970	1.9186130
C	-5.1638710	-1.5699980	-0.9025470
H	-5.4023060	-1.1930680	-1.8988870
H	-4.1650700	-2.0040740	-0.9295480
H	-5.8715390	-2.3627680	-0.6611410
C	-10.3407350	-0.0159080	0.6146280
C	-10.5107350	-1.3167770	1.0044350

H	-11.1924470	0.6497710	0.5263380
H	-11.4995290	-1.6969730	1.2293110
C	-8.1273850	-1.7121870	0.8343940
C	-9.3877580	-2.1702540	1.1138370
H	-7.2899860	-2.3898060	0.9276350
H	-9.5270900	-3.1992650	1.4228230
C	6.9346070	1.1865660	2.2076990
C	7.8604930	2.0933260	2.6498420
H	6.1450600	0.8656210	2.8730510
H	7.7900530	2.4837970	3.6583680
C	9.0147410	2.0250890	0.5372480
C	8.9124060	2.5272610	1.8061740
H	9.8200110	2.3416310	-0.1175570
H	9.6330480	3.2489440	2.1709450

sp-2•H⁺ *G= -1844.737636* au

C	1.4572360	0.8915420	-0.9441960
C	2.0577660	-0.3466830	-0.7057730
C	1.3049030	-1.4840970	-0.3489910
C	-0.0624720	-1.3565070	-0.2345870
C	-0.7257440	-0.1344570	-0.4565290
C	0.0695250	0.9817700	-0.8184640
H	-0.6513780	-2.2276210	0.0332760
C	2.2728320	2.1012910	-1.3145340
H	3.3329240	1.8603560	-1.3030760
H	2.0233400	2.4599540	-2.3176440
H	2.1107570	2.9200290	-0.6068050
O	3.3878260	-0.4194760	-0.8566980
O	-0.5592150	2.1531050	-1.0327080
C	2.0236610	-2.7380870	-0.1615150
C	3.3552580	-2.7735240	-0.1859270
H	1.4454710	-3.6436820	-0.0148750
H	3.9036850	-3.6992380	-0.0649100
C	-2.1545660	-0.1200450	-0.3020500
C	-3.0287310	0.9147840	-0.4543250
H	-2.5534080	-1.0879760	-0.0229980
H	-2.6549100	1.8869590	-0.7318940
C	4.1864640	-1.5363190	-0.3459870
C	6.2505800	-0.7676160	-0.9495730
C	6.1017140	-0.3259450	0.3496120
C	-4.4340830	0.7923190	-0.2659940
C	-6.5875710	1.4938780	-0.1910880
C	-6.6604260	0.1635780	0.1362830
N	-5.2305780	1.8354020	-0.4256310
N	5.2646960	-1.7022450	-1.2850680
C	4.9373210	-1.9516290	-2.6791300
H	4.1303280	-2.6831460	-2.7237050
H	4.6202690	-1.0397300	-3.1972610
H	5.8040290	-2.3722860	-3.1892150
C	-4.7788700	3.1764270	-0.7959820
H	-4.0752790	3.5425340	-0.0495540
H	-4.3030990	3.1443370	-1.7754340
H	-5.6342220	3.8407520	-0.8355460
C	7.2972390	-0.3213600	-1.7829560
C	8.2049890	0.5655460	-1.2620200
H	7.3796020	-0.6646020	-2.8066120
H	9.0171740	0.9342350	-1.8790350
C	7.0481590	0.5580750	0.9140660
C	8.1142960	1.0200360	0.0781690
C	-7.9167810	-0.4284290	0.4217640
C	-9.0657610	0.4174210	0.3502010
C	-7.7064650	2.3446960	-0.2688060
C	-8.9266210	1.7891670	0.0040090
H	-7.6227170	3.3899810	-0.5310590
H	-9.8191970	2.4020200	-0.0420080
C	-5.2638410	-0.4248970	0.1203920

C	4.9051660	-1.0428510	0.9604090
C	3.9419910	-0.2034790	1.8041840
H	3.7643690	0.7786940	1.3636910
H	2.9839570	-0.7255900	1.8944790
H	4.3223820	-0.0701760	2.8163680
C	5.4084160	-2.2444990	1.7774220
H	4.5726410	-2.7958660	2.2153380
H	5.9949730	-2.9244760	1.1557420
H	6.0451240	-1.8852280	2.5884460
C	-4.8641280	-0.9135200	1.5288370
H	-3.8566860	-1.3266190	1.5409050
H	-4.9103810	-0.0891830	2.2425070
H	-5.5523520	-1.6895430	1.8610010
C	-5.1438810	-1.5159480	-0.9644040
H	-5.3808220	-1.1019300	-1.9459320
H	-4.1415730	-1.9401170	-0.9996000
H	-5.8453420	-2.3229640	-0.7576740
C	-10.3457910	-0.1270780	0.6280540
C	-10.4900230	-1.4466950	0.9620950
H	-11.2095330	0.5257130	0.5703930
H	-11.4714850	-1.8530940	1.1724880
C	-8.1021980	-1.7944210	0.7712140
C	-9.3540570	-2.2855580	1.0331740
H	-7.2528620	-2.4604970	0.8334480
H	-9.4757580	-3.3287770	1.2978400
C	7.0131320	1.0091190	2.2653710
C	7.9613310	1.8726930	2.7452010
H	6.2318100	0.6572020	2.9248190
H	7.9167390	2.1989910	3.7776480
C	9.0736990	1.9225660	0.6093770
C	9.0032270	2.3440510	1.9094550
H	9.8713230	2.2683970	-0.0397980
H	9.7421780	3.0301490	2.3048690
H	0.0688400	2.8390230	-1.2872210

3•2H^{2+} *G= -2098.730744* au

C	-0.0000000	3.4156340	-0.1998800
C	1.2006830	2.6998410	-0.1808870
C	1.2258780	1.2878970	-0.0638150
C	0.0000010	0.6287750	0.0009190
C	-1.2258780	1.2878950	-0.0638210
C	-1.2006820	2.6998390	-0.1808940
H	0.0000010	-0.4520120	0.0912690
C	-0.0000020	4.9223070	-0.2588160
H	0.8619020	5.3439370	0.2614050
H	-0.0000010	5.2973280	-1.2852240
H	-0.8619090	5.3439340	0.2614040
O	2.3862750	3.3204560	-0.2632470
H	2.2838780	4.2631230	-0.4358240
O	-2.3862750	3.3204540	-0.2632600
H	-2.2838770	4.2631190	-0.4358470
C	2.4263640	0.4805610	-0.0137650
C	3.7222900	0.8629200	-0.0491450
H	2.2158440	-0.5827540	0.0795540
H	3.9996110	1.9018910	-0.1190910
C	-2.4263630	0.4805590	-0.0137710
C	-3.7222880	0.8629170	-0.0491620
H	-2.2158420	-0.5827560	0.0795570
H	-3.9996090	1.9018870	-0.1191200
C	4.7872710	-0.1046790	-0.0097760
S	4.5683960	-1.7746960	-0.3806800
C	6.9276540	-0.9017990	0.2069040
C	6.2628030	-2.0832140	-0.1213170
C	-4.7872690	-0.1046810	-0.0097860
S	-4.5683960	-1.7747020	-0.3806780
C	-6.9276530	-0.9017980	0.2069010

C	-6.2628040	-2.0832160	-0.1213110
N	-6.0538370	0.1871180	0.2726110
N	6.0538390	0.1871180	0.2726230
C	6.5391220	1.5205050	0.6472640
H	7.0127020	1.9902950	-0.2142080
H	5.7114880	2.1234410	1.0036440
H	7.2572990	1.4050340	1.4554940
C	-6.5391230	1.5205060	0.6472450
H	-5.7114880	2.1234530	1.0036020
H	-7.0127250	1.9902810	-0.2142230
H	-7.2572830	1.4050370	1.4554910
C	8.3044680	-0.8894070	0.4296500
C	8.9812220	-2.0918970	0.3209990
H	8.8300010	0.0249090	0.6696700
H	10.0504740	-2.1115670	0.4866770
C	6.9452090	-3.2921570	-0.2271230
C	8.3111570	-3.2802770	-0.0007400
H	6.4228700	-4.2051090	-0.4803600
H	8.8698100	-4.2040410	-0.0774900
C	-6.9452110	-3.2921590	-0.2271050
C	-8.3111590	-3.2802750	-0.0007210
H	-6.4228740	-4.2051140	-0.4803370
H	-8.8698140	-4.2040390	-0.0774640
C	-8.3044660	-0.8894010	0.4296500
C	-8.9812220	-2.0918920	0.3210090
H	-8.8299970	0.0249170	0.6696620
H	-10.0504740	-2.1115580	0.4866890

3•H⁺ *G= -2098.304006* au

C	-0.0030060	3.3909580	-0.0000030
C	-1.2822150	2.6925690	-0.0000020
C	-1.2300950	1.2209290	-0.0000000
C	0.0033040	0.5791360	0.0000000
C	1.2294270	1.2523420	-0.0000000
C	1.1731850	2.6968970	-0.0000010
H	0.0203310	-0.5069670	0.0000010
C	-0.0105930	4.8956860	-0.0000040
H	-1.0409060	5.2445540	-0.0000040
H	0.4826970	5.3084990	0.8861230
H	0.4826960	5.3084970	-0.8861330
O	-2.3540690	3.3131770	-0.0000020
O	2.3689270	3.3300840	-0.0000010
H	2.2383020	4.2852240	-0.0000020
C	-2.4007530	0.4116270	0.0000000
C	-3.7075390	0.8154100	0.0000000
H	-2.2001600	-0.6594860	0.0000010
H	-3.9380840	1.8692670	-0.0000000
C	2.4114340	0.4706190	-0.0000000
C	3.7297260	0.8533300	0.0000000
H	2.2098090	-0.5996880	0.0000010
H	4.0000220	1.8965410	0.0000010
C	-4.7775730	-0.1144950	0.0000000
S	-4.5903860	-1.8386860	-0.0000020
C	-6.9747540	-0.8174700	0.0000020
C	-6.3227990	-2.0525660	-0.0000000
C	4.7763920	-0.0966120	-0.0000000
S	4.5521750	-1.8190530	-0.0000050
C	6.9593840	-0.8500970	0.0000020
C	6.2806590	-2.0706080	-0.0000020
N	6.0765110	0.2344930	0.0000020
N	-6.0670350	0.2467720	0.0000030
C	-6.4675070	1.6566080	0.0000050
H	-6.0793990	2.1446960	0.8928940
H	-6.0794110	2.1446970	-0.8928890
H	-7.5494580	1.7184300	0.0000130
C	6.5098620	1.6333440	0.0000050

H	6.1346360	2.1313970	-0.8931650
H	6.1346410	2.1313920	0.8931810
H	7.5929450	1.6697440	0.0000020
C	-8.3680460	-0.7560900	0.0000030
C	-9.0718130	-1.9500710	0.0000020
H	-8.8971920	0.1861620	0.0000030
H	-10.1537860	-1.9210780	0.0000020
C	-7.0298360	-3.2496920	-0.0000010
C	-8.4143330	-3.1849100	-0.0000000
H	-6.5105680	-4.1990260	-0.0000030
H	-8.9911670	-4.1006350	-0.0000010
C	6.9607890	-3.2826880	-0.0000030
C	8.3469700	-3.2493520	0.0000000
H	6.4204870	-4.2202630	-0.0000060
H	8.9028470	-4.1779460	-0.0000000
C	8.3534780	-0.8201860	0.0000050
C	9.0311780	-2.0297700	0.0000050
H	8.9037850	0.1099890	0.0000080
H	10.1135490	-2.0242080	0.0000070

z-3 *G= -2097.848452* au

C	-0.0000000	3.3863720	-0.0128370
C	-1.2516200	2.7187720	-0.0019360
C	-1.2286350	1.2258760	-0.0126880
C	0.0000000	0.5642640	-0.0172690
C	1.2286350	1.2258760	-0.0126860
C	1.2516200	2.7187720	-0.0019300
H	0.0000000	-0.5237680	-0.0217450
C	-0.0000020	4.8895680	-0.0141720
H	-0.8919140	5.2679540	-0.5157960
H	-0.0000260	5.3105470	0.9995380
H	0.8919310	5.2679550	-0.5157560
O	-2.3512880	3.3255250	0.0141050
O	2.3512890	3.3255240	0.0141060
C	-2.3875430	0.4288910	-0.0131380
C	-3.7099370	0.8331220	-0.0040680
H	-2.1940810	-0.6443900	-0.0215540
H	-3.9265920	1.8903580	0.0048150
C	2.3875430	0.4288910	-0.0131360
C	3.7099370	0.8331220	-0.0040640
H	2.1940810	-0.6443900	-0.0215540
H	3.9265930	1.8903580	0.0048190
C	-4.7662990	-0.0869430	-0.0037490
S	-4.5800620	-1.8220030	-0.0139280
C	-6.9695110	-0.8006720	0.0075790
C	-6.3162520	-2.0360240	-0.0028170
C	4.7663000	-0.0869430	-0.0037450
S	4.5800630	-1.8220030	-0.0139240
C	6.9695110	-0.8006710	0.0075780
C	6.3162520	-2.0360240	-0.0028140
N	6.0676040	0.2659240	0.0054580
N	-6.0676040	0.2659240	0.0054540
C	-6.4663220	1.6724060	0.0133720
H	-6.0806890	2.1576240	0.9097940
H	-6.0727080	2.1688200	-0.8732880
H	-7.5484300	1.7376910	0.0082980
C	6.4663220	1.6724060	0.0133790
H	6.0727340	2.1688160	-0.8732950
H	6.0806630	2.1576290	0.9097870
H	7.5484300	1.7376920	0.0083370
C	-8.3623290	-0.7449480	0.0188920
C	-9.0662510	-1.9410910	0.0188140
H	-8.8934010	0.1964020	0.0282230
H	-10.1483510	-1.9123760	0.0276680
C	-7.0213740	-3.2323760	-0.0030140
C	-8.4081460	-3.1733360	0.0078580

H	-6.4999220	-4.1807350	-0.0112410
H	-8.9819150	-4.0910320	0.0081120
C	7.0213740	-3.2323760	-0.0030130
C	8.4081470	-3.1733350	0.0078500
H	6.4999230	-4.1807350	-0.0112430
H	8.9819150	-4.0910320	0.0080970
C	8.3623290	-0.7449480	0.0188870
C	9.0662520	-1.9410910	0.0188070
H	8.8934010	0.1964020	0.0282190
H	10.1483510	-1.9123760	0.0276630

4•2H^{2+} *G= -1457.097648* au

C	-0.0001600	3.2157940	-0.0182670
C	-1.1991990	2.5009210	0.0665250
C	-1.2259660	1.0871810	0.0521600
C	-0.0007070	0.4273720	-0.0207600
C	1.2257350	1.0872710	-0.0658790
C	1.2015060	2.5013590	-0.0458610
H	-0.0010740	-0.6573640	-0.0327130
C	-0.0078790	4.7233430	-0.0632320
H	-0.8810810	5.1025680	-0.5977550
H	0.0049390	5.1685780	0.9348130
H	0.8427380	5.1145570	-0.6236750
O	-2.3825090	3.1326460	0.1543740
H	-2.2679590	4.0848270	0.2460540
O	2.3894360	3.1312050	-0.0629270
H	2.2877460	4.0800930	0.0685120
C	-2.4295570	0.2738860	0.1065310
C	-3.7205300	0.6577530	0.1646110
H	-2.2219380	-0.7920960	0.0607720
H	-3.9877760	1.7018790	0.1767770
C	2.4289970	0.2728950	-0.1144560
C	3.7199970	0.6560920	-0.1724450
H	2.2203350	-0.7930020	-0.0711550
H	3.9871840	1.7001350	-0.1881480
C	-4.7993680	-0.3208070	0.2265870
C	-7.1016660	-0.8592900	-0.1533780
C	-6.9334920	-2.1065220	0.4893180
C	4.7991670	-0.3223360	-0.2315250
C	7.1012140	-0.8586310	0.1527270
C	6.9349120	-2.1067620	-0.4887100
N	5.9979670	-0.0250580	0.3039520
N	-5.9991530	-0.0252850	-0.3077310
C	-6.1684870	1.1962270	-1.1192700
H	-6.6459620	1.9763430	-0.5265440
H	-5.1996710	1.5293410	-1.4707940
H	-6.7766860	0.9537320	-1.9852470
C	6.1656600	1.1981100	1.1133700
H	6.6472230	1.9758770	0.5208630
H	5.1958500	1.5340020	1.4595140
H	6.7696410	0.9565600	1.9826140
C	-8.3801980	-0.4841070	-0.6133930
C	-9.4385620	-1.3469270	-0.4481090
H	-8.5528880	0.4773750	-1.0722200
H	-10.4183270	-1.0463180	-0.7973660
C	-8.0408920	-2.9715740	0.6346970
C	-9.2753580	-2.6019840	0.1687620
H	-7.8891080	-3.9250880	1.1258260
H	-10.1250620	-3.2626170	0.2802950
C	8.0431970	-2.9711540	-0.6312810
C	9.2766120	-2.6001350	-0.1636980
H	7.8929420	-3.9253220	-1.1216090
H	10.1269870	-3.2602580	-0.2731200
C	8.3786260	-0.4820760	0.6146960
C	9.4378700	-1.3443440	0.4522010
H	8.5497820	0.4799290	1.0730060

H	10.4168000	-1.0427320	0.8029300
C	5.6555670	-2.4446370	-0.9919280
C	4.6236130	-1.5639780	-0.8873570
H	5.5197790	-3.3962920	-1.4925180
H	3.6635830	-1.7781680	-1.3329950
C	-5.6531550	-2.4427840	0.9910580
C	-4.6221310	-1.5613360	0.8841700
H	-5.5158620	-3.3937600	1.4925240
H	-3.6614400	-1.7741030	1.3290440

4•H⁺ *G= -1456.662697* au

C	0.0100330	3.1362710	0.0080210
C	1.2887270	2.4403180	-0.0189190
C	1.2363220	0.9723090	-0.0315080
C	0.0017690	0.3329620	-0.0133040
C	-1.2263170	1.0018430	0.0110740
C	-1.1688250	2.4424710	0.0181480
H	-0.0144570	-0.7534810	-0.0194740
C	0.0167480	4.6413690	0.0219670
H	1.0473670	4.9893230	0.0306300
H	-0.4714640	5.0638070	-0.8627560
H	-0.4813130	5.0469630	0.9090060
O	2.3611410	3.0674020	-0.0289850
O	-2.3624140	3.0846960	0.0372600
H	-2.2226820	4.0382950	0.0360020
C	2.4100570	0.1551990	-0.0514140
C	3.7118700	0.5626250	-0.0510960
H	2.2037500	-0.9125830	-0.0321520
H	3.9116260	1.6213380	-0.0251040
C	-2.4121010	0.2130990	0.0235960
C	-3.7250840	0.5994500	0.0167170
H	-2.2052840	-0.8537440	0.0055850
H	-3.9664760	1.6480140	-0.0186400
C	4.8114210	-0.3611410	-0.0959490
C	7.1761870	-0.7523310	0.1283170
C	7.0288790	-2.0670880	-0.3623880
C	-4.8027570	-0.3432430	0.0697780
C	-7.1668240	-0.7721620	-0.1211090
C	-6.9923420	-2.0846900	0.3658930
N	-6.0457880	0.0317090	-0.3232590
N	6.0410920	0.0361400	0.3089280
C	6.2031790	1.3297850	0.9950080
H	6.5154500	2.1008560	0.2900030
H	5.2626630	1.6064400	1.4571470
H	6.9444470	1.2168830	1.7799780
C	-6.2324390	1.3144810	-1.0212830
H	-6.5132190	2.1000660	-0.3187880
H	-5.3100490	1.5783380	-1.5267450
H	-7.0043260	1.1929840	-1.7744920
C	8.4664180	-0.2638430	0.4107610
C	9.5597520	-1.0834750	0.2327560
H	8.6207030	0.7524980	0.7397290
H	10.5469070	-0.6929370	0.4460230
C	8.1662440	-2.8830380	-0.5258590
C	9.4177780	-2.4035240	-0.2263080
H	8.0282380	-3.8910080	-0.8987130
H	10.2911850	-3.0296770	-0.3532670
C	-8.1140460	-2.9167400	0.5490260
C	-9.3783940	-2.4554470	0.2726210
H	-7.9546710	-3.9227200	0.9188620
H	-10.2400090	-3.0945310	0.4148720
C	-8.4687640	-0.3019220	-0.3779150
C	-9.5474680	-1.1375100	-0.1813030
H	-8.6439740	0.7132160	-0.7003790
H	-10.5437470	-0.7602030	-0.3752110
C	5.7248540	-2.5186710	-0.7060510

C	4.6617380	-1.6851760	-0.6016180
H	5.6016770	-3.5243180	-1.0910800
H	3.6844820	-1.9994880	-0.9353940
C	-5.6749770	-2.5169860	0.6876980
C	-4.6268190	-1.6677380	0.5706830
H	-5.5308240	-3.5211140	1.0693550
H	-3.6418600	-1.9696840	0.8928810

z-4 *G= -1456.204554* au

C	0.0000030	3.0784330	-0.2368710
C	1.2528240	2.4126460	-0.2028800
C	1.2309980	0.9273940	-0.0706270
C	-0.0000050	0.2733880	-0.0062310
C	-1.2309990	0.9274000	-0.0706640
C	-1.2528230	2.4126530	-0.2029420
H	-0.0000090	-0.8103710	0.0934270
C	0.0000370	4.5779950	-0.3449840
H	0.8921500	4.9912910	0.1283280
H	0.0003530	4.9257640	-1.3862590
H	-0.8923480	4.9912820	0.1278150
O	2.3501120	3.0236060	-0.2741500
O	-2.3501150	3.0235970	-0.2742840
C	2.3896280	0.1248860	0.0096250
C	3.7081740	0.5340330	-0.0189240
H	2.1816470	-0.9354490	0.1327660
H	3.8792450	1.5937920	-0.1100330
C	-2.3896360	0.1248970	0.0095810
C	-3.7081800	0.5340430	-0.0189820
H	-2.1816590	-0.9354360	0.1327430
H	-3.8792530	1.5938010	-0.1101080
C	4.8049300	-0.3612990	0.0446010
C	7.2022920	-0.6791610	0.1291050
C	7.0514550	-2.0706740	-0.0455800
C	-4.8049360	-0.3612910	0.0445580
C	-7.2022940	-0.6791580	0.1291100
C	-7.0514580	-2.0706690	-0.0455840
N	-6.0653190	0.1194150	0.2527670
N	6.0653180	0.1194090	0.2527860
C	6.2453940	1.5260160	0.6373650
H	6.4048880	2.1541260	-0.2406670
H	5.3640060	1.8612260	1.1738080
H	7.0950870	1.6010010	1.3085230
C	-6.2453940	1.5260210	0.6373520
H	-5.3639870	1.8612420	1.1737560
H	-6.4049350	2.1541260	-0.2406740
H	-7.0950590	1.6009960	1.3085470
C	8.4982940	-0.1316810	0.1587940
C	9.5971280	-0.9610160	0.0536220
H	8.6537080	0.9340020	0.2337770
H	10.5870510	-0.5222220	0.0711980
C	8.1892290	-2.8908990	-0.1416120
C	9.4529260	-2.3483010	-0.0852010
H	8.0461440	-3.9577820	-0.2682520
H	10.3274270	-2.9813130	-0.1607390
C	-8.1892330	-2.8908970	-0.1415930
C	-9.4529290	-2.3483010	-0.0851500
H	-8.0461480	-3.9577790	-0.2682410
H	-10.3274310	-2.9813150	-0.1606690
C	-8.4982960	-0.1316810	0.1588320
C	-9.5971300	-0.9610170	0.0536830
H	-8.6537100	0.9340020	0.2338250
H	-10.5870540	-0.5222260	0.0712850
C	5.7287760	-2.5996380	-0.1488950
C	4.6583300	-1.7768030	-0.1314200
H	5.6014950	-3.6678220	-0.2818720
H	3.6666620	-2.1759480	-0.2788780

C	-5.7287810	-2.5996300	-0.1489320
C	-4.6583360	-1.7767920	-0.1314750
H	-5.6015000	-3.6678130	-0.2819190
H	-3.6666700	-2.1759330	-0.2789620

5•2H^{2+} *G= -1457.101812* au

C	0.0030230	3.0149720	0.0192340
C	1.1971970	2.2995960	-0.1180440
C	1.2232290	0.8865980	-0.1043060
C	0.0004280	0.2300000	0.0232460
C	-1.2236050	0.8894620	0.1215800
C	-1.1980480	2.3025990	0.0995530
H	0.0003350	-0.8549340	0.0356370
C	0.0114600	4.5226650	0.0651560
H	0.9164840	4.9039620	0.5417930
H	-0.0673020	4.9697190	-0.9292140
H	-0.8023980	4.9106130	0.6801860
O	2.3765910	2.9324650	-0.2618350
H	2.2539630	3.8816750	-0.3696510
O	-2.3831280	2.9371650	0.1731810
H	-2.2819620	3.8860610	0.0425140
C	2.4217060	0.0698320	-0.2253740
C	3.7159760	0.4444310	-0.2721270
H	2.2053480	-0.9956810	-0.2431400
H	3.9840140	1.4859520	-0.1977790
C	-2.4237630	0.0740070	0.2358230
C	-3.7183020	0.4477260	0.2802690
H	-2.2074250	-0.9914540	0.2569950
H	-3.9872420	1.4891220	0.2083100
C	4.7951130	-0.5264090	-0.3986430
C	7.1450590	-1.1965470	-0.0524740
C	-4.7967770	-0.5245100	0.4036460
C	-7.1453480	-1.1960250	0.0509490
C	-5.6607800	-2.6282380	1.1919770
C	-4.6130730	-1.7346900	1.0571480
H	-5.5324070	-3.5684090	1.7102880
H	-3.6692310	-1.9921890	1.5152810
C	5.6579660	-2.6300390	-1.1886310
C	4.6103100	-1.7368090	-1.0514900
H	5.5285540	-3.5705460	-1.7060740
H	3.6653740	-1.9947520	-1.5070980
N	6.8777710	-2.3777840	-0.7200880
N	-6.8794660	-2.3766730	0.7201160
C	-7.9507310	-3.3660810	0.9243390
H	-8.7549750	-2.9151390	1.5030620
H	-8.3222610	-3.7029910	-0.0416410
H	-7.5375590	-4.2080640	1.4698690
C	7.9488140	-3.3669690	-0.9264600
H	7.5343300	-4.2097480	-1.4697540
H	8.7511150	-2.9163310	-1.5081060
H	8.3234100	-3.7026420	0.0387610
C	-6.1028560	-0.2494580	-0.1232330
C	6.1026680	-0.2502920	0.1241930
C	6.3965590	0.9352630	0.8420600
C	7.6539770	1.1722780	1.3310770
H	5.6115850	1.6568180	1.0190280
H	7.8601540	2.0821470	1.8793820
C	8.6795180	0.2295230	1.1275020
C	8.4364630	-0.9398720	0.4518380
H	9.6723580	0.4220040	1.5137660
H	9.2349700	-1.6539020	0.3153900
C	-8.4353030	-0.9401990	-0.4574950
C	-8.6766460	0.2285870	-1.1348310
H	-9.2339550	-1.6544470	-0.3230480
H	-9.6683630	0.4204090	-1.5242980
C	-7.6507790	1.1715140	-1.3361880

C	-6.3947960	0.9353440	-0.8431250
H	-7.8555890	2.0807440	-1.8860590
H	-5.6091230	1.6566220	-1.0183720

5•H⁺ *G= -1456.666208* au

C	0.0079970	2.8913820	-0.0418090
C	1.2884930	2.1999500	-0.1037730
C	1.2415970	0.7311480	-0.0993020
C	0.0092470	0.0907490	-0.0438150
C	-1.2224670	0.7541680	0.0086970
C	-1.1686660	2.1950940	0.0079630
H	-0.0039120	-0.9958710	-0.0415940
C	0.0106520	4.3967210	-0.0373040
H	1.0401480	4.7473540	-0.0596560
H	-0.5032210	4.8126160	-0.9106200
H	-0.4635450	4.8069110	0.8607750
O	2.3562450	2.8327820	-0.1565550
O	-2.3615800	2.8375250	0.0630060
H	-2.2205720	3.7908020	0.0564260
C	2.4170270	-0.0859060	-0.1426950
C	3.7205910	0.3150970	-0.1628370
H	2.2068590	-1.1534020	-0.1264610
H	3.9137640	1.3742890	-0.1336460
C	-2.4034340	-0.0406100	0.0574930
C	-3.7206700	0.3351510	0.0794800
H	-2.1858790	-1.1055420	0.0542200
H	-3.9527910	1.3848310	0.0436410
C	4.8267920	-0.5992390	-0.2019890
C	7.2561420	-1.0610610	0.0030350
C	-4.8031680	-0.5962350	0.1402920
C	-7.2375960	-1.0918570	0.0626700
C	-5.6907760	-2.8194810	0.4914470
C	-4.6220600	-1.9638480	0.4020890
H	-5.5485970	-3.8697060	0.7066930
H	-3.6430430	-2.3832660	0.5762890
C	5.7670010	-2.7915350	-0.5874860
C	4.6803490	-1.9513410	-0.5342470
H	5.6562390	-3.8335490	-0.8546250
H	3.7190630	-2.3687950	-0.7934000
N	7.0147380	-2.3800670	-0.3360310
N	-6.9599390	-2.4185560	0.3388920
C	-8.0499680	-3.3927310	0.4731700
H	-8.7079010	-3.1000210	1.2906520
H	-8.6129540	-3.4490050	-0.4574840
H	-7.6157820	-4.3633600	0.6907240
C	8.1251250	-3.3376810	-0.4266080
H	7.7186560	-4.3065700	-0.6984630
H	8.8305110	-3.0128780	-1.1902430
H	8.6256740	-3.4128270	0.5375910
C	-6.1725300	-0.1611230	-0.0484640
C	6.1708650	-0.1508680	0.0831580
C	6.4578020	1.1817940	0.4646630
C	7.7406120	1.5896490	0.7280990
H	5.6496870	1.8918250	0.5648380
H	7.9342430	2.6135780	1.0200870
C	8.8036930	0.6762690	0.6235780
C	8.5715050	-0.6305510	0.2712770
H	9.8165930	0.9993540	0.8283380
H	9.3997820	-1.3202620	0.2041700
C	-8.5728370	-0.6748410	-0.1111620
C	-8.8480930	0.6393750	-0.4005720
H	-9.3839990	-1.3821320	-0.0217280
H	-9.8765480	0.9506710	-0.5334520
C	-7.8080390	1.5738910	-0.5325780
C	-6.5052500	1.1782220	-0.3608460
H	-8.0334000	2.6046670	-0.7733130

H	-5.7196180	1.9096810	-0.4811360

z-5 *G= -1456.206885* au

C	0.0000000	2.8572200	0.0144020
C	1.2537680	2.1919170	0.0007850
C	1.2327490	0.6994800	0.0073590
C	0.0000000	0.0445260	0.0098600
C	-1.2327490	0.6994810	0.0073600
C	-1.2537680	2.1919170	0.0007890
H	-0.0000000	-1.0438580	0.0113690
C	0.0000010	4.3606810	0.0206780
H	0.8921760	4.7375610	0.5230060
H	0.0000040	4.7859810	-0.9915570
H	-0.8921750	4.7375620	0.5230020
O	2.3493440	2.8086420	-0.0144470
O	-2.3493440	2.8086430	-0.0144390
C	2.3903450	-0.1097340	0.0068270
C	3.7134650	0.2884470	0.0011310
H	2.1767400	-1.1767480	0.0123490
H	3.8848870	1.3513940	-0.0036390
C	-2.3903450	-0.1097320	0.0068280
C	-3.7134660	0.2884490	0.0011320
H	-2.1767410	-1.1767460	0.0123500
H	-3.8848870	1.3513960	-0.0036390
C	4.8093560	-0.6059710	0.0013600
C	7.2676300	-1.0257900	-0.0026880
C	-4.8093560	-0.6059690	0.0013600
C	-7.2676290	-1.0257910	-0.0026930
C	-5.7547680	-2.8393170	0.0028190
C	-4.6674420	-2.0122910	0.0038970
H	-5.6391720	-3.9146810	0.0043720
H	-3.6953230	-2.4807110	0.0060040
C	5.7547710	-2.8393180	0.0028350
C	4.6674430	-2.0122930	0.0039060
H	5.6391770	-3.9146820	0.0043940
H	3.6953250	-2.4807140	0.0060180
N	7.0226090	-2.3883120	-0.0004980
N	-7.0226070	-2.3883120	-0.0005110
C	-8.1329960	-3.3442700	-0.0018680
H	-8.7459810	-3.2068170	0.8885670
H	-8.7422280	-3.2085950	-0.8951490
H	-7.7196700	-4.3481980	-0.0000140
C	8.1330000	-3.3442680	-0.0018460
H	7.7196750	-4.3481970	0.0000160
H	8.7422320	-3.2085980	-0.8951270
H	8.7459840	-3.2068060	0.8885890
C	-6.1801940	-0.1151590	-0.0017250
C	6.1801930	-0.1151590	-0.0017320
C	6.4849850	1.2646070	-0.0036130
C	7.7820740	1.7183880	-0.0065500
H	5.6815570	1.9869130	-0.0024550
H	7.9837890	2.7817440	-0.0078800
C	8.8428830	0.8009830	-0.0077270
C	8.5946550	-0.5514870	-0.0057700
H	9.8665680	1.1540200	-0.0100600
H	9.4235870	-1.2439920	-0.0065590
C	-8.5946560	-0.5514900	-0.0057760
C	-8.8428850	0.8009800	-0.0077180
H	-9.4235860	-1.2439950	-0.0065770
H	-9.8665710	1.1540160	-0.0100520
C	-7.7820780	1.7183870	-0.0065230
C	-6.4849890	1.2646080	-0.0035860
H	-7.9837950	2.7817420	-0.0078370
H	-5.6815620	1.9869150	-0.0024100

VIII. REFERENCES

1 N. A. Voloshin, E. V. Solov'eva, S. O. Bezugliy, A. V. Metelitsa and V. I. Minkin, *Chem Heterocycl Compd*, **48**, 1361–1370.
2 A. M. Brouwer, *Pure Appl Chem*, 2011, **83**, 2213–2228.
3 K. Rurack and M. Spieles, *Anal. Chem.*, 2011, **83**, 1232–1242.
4 S. H. M. Mehr, H. Depmeier, K. Fukuyama, M. Maghami and M. J. MacLachlan, *Org. Biomol. Chem.*, 2017, **15**, 581–583.
5 M. Gerowska, L. Hall, J. Richardson, M. Shelbourne and T. Brown, *Tetrahedron*, 2012, **68**, 857–864.
6 P. Gaur, A. Kumar, G. Dey, R. Kumar, S. Bhattacharyya and S. Ghosh, *ACS Appl. Mater. Interfaces*, 2016, **8**, 10690–10699.
7 J. T. Manka, V. C. McKenzie and P. Kaszynski, *J. Org. Chem.*, 2004, **69**, 1967–1971.
8 L. Babel, T. N. Y. Hoang, L. Guénée, C. Besnard, T. A. Wesolowski, M. Humbert-Droz and C. Piguet, *Chem. – Eur. J.*, 2016, **22**, 8113–8123.
9 K. Benelhadj, J. Massue and G. Ulrich, *New J. Chem.*, 2016, **40**, 5877–5884.
10 S. Pascal, S.-H. Chi, J. W. Perry, C. Andraud and O. Maury, *ChemPhysChem*, 2020, **21**, 2536–2542.
11 I. Davydenko, S. Barlow, R. Sharma, S. Benis, J. Simon, T. G. Allen, M. W. Cooper, V. Khrustalev, E. V. Jucov, R. Castañeda, C. Ordonez, Z. Li, S.-H. Chi, S.-H. Jang, T. C. Parker, T. V. Timofeeva, J. W. Perry, A. K. Y. Jen, D. J. Hagan, E. W. Van Stryland and S. R. Marder, *J. Am. Chem. Soc.*, 2016, **138**, 10112–10115.
12 A. Kurutos, Y. Shindo, Y. Hiruta, K. Oka and D. Citterio, *Dyes Pigments*, 2020, **181**, 108611.
13 Z. Li, S. Mukhopadhyay, S.-H. Jang, J.-L. Brédas and A. K.-Y. Jen, *J. Am. Chem. Soc.*, 2015, **137**, 11920–11923.
14 P. Gans and B. O'Sullivan, *Talanta*, 2000, **51**, 33–37.
15 P. Gans, *Data Fitting in the Chemical Sciences*, Chichester, John Wiley&Sons., 1992.
16 D. W. Marquardt, *J. Soc. Ind. Appl. Math.*, 1963, **11**, 431–441.
17 M. Maeder and A. D. Zuberbuehler, *Anal. Chem.*, 1990, **62**, 2220–2224.
18 Y. Zhao and D. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215–241.
19 J. Tomasi, B. Mennucci and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999–3094.
20 M. J. Frisch et al., Gaussian 16A.03, Gaussian Inc., Wallingford, USA, 2016.
21 R. Cammi and B. Mennucci, *J. Chem. Phys.*, 1999, **110**, 9877–9886.
22 O. Christiansen, H. Koch and P. Jørgensen, *Chem. Phys. Lett.*, 1995, **243**, 409–418.
23 TURBOMOLE, V7.3 2018, a Development of University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989−2007, TURBOMOLE GmbH, since 2007. http://www.turbomole.com.
24 D. Jacquemin, I. Duchemin and X. Blase, *J. Chem. Theory Comput.*, 2015, **11**, 5340–5359.
25 Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta and P. von R. Schleyer, *Chem. Rev.*, 2005, **105**, 3842–3888.