Electronic Supplementary Material (ESI) for Chemical Science.

Supporting information for

Going beyond the borders: pyrrolo[3,2-b]pyrroles with deep red emission

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1. General information

All chemicals were used as received, unless otherwise noted. All reported NMR spectra were recorded on a 500 MHz spectrometer unless otherwise noted. Chemical shifts (δ; ppm) for ^1H and ^{13}C NMR were determined with TMS as the internal reference. *J* values are given in Hz. The absorption and fluorescence spectra of **2a-h** and **1a-l** were recorded in toluene. Mass spectra were obtained with EI ion source and the EBE double focusing geometry mass analyzer or spectrometer equipped with electro-spray ion source with Q-TOF type mass analyzer.

Electrochemical methods used were cyclic voltammetry and differential pulse voltammetry using CH Instruments Electrochemical Analyzer model 620 with the parameters for the first and second techniques, respectively: potential sweep rate of 0.05 V/s; step size of 4 mV, pulse size of 25 mV and frequency of 15 Hz. Setup was in the single-cell with 2 mm^2 - platinum disk (working electrode), platinum coil (counter electrode) and $Ag|Ag^+$ pseudo-reference electrode calibrated with ferrocene|ferrocenium $Fc|Fc^+$ couple as the internal standard. UV-Vis-NIR spectroelectrochemical measurement was performed using Agilent/HP 8453 UV-Visible Spectrophotometer G1103A. A thin-layer optical cell characterized by the optical path of 0.075 mm length was a quartz cuvette containing ITO/quartz electrode (20±5 V/sq, Praezisions Glas & Optic GmbH), $Ag|Ag^+$ pseudo-reference electrode and platinum mesh as a counter electrode. Electron paramagnetic resonance (ESR) spectroelectrochemical measurement was performed using JEOL JES FA-200 X-band spectrometer with the following parameters: 1 mT (modulation width); 1 mW (microwave power); 50 (amplitude) in a system of electrodes: platinum wire (working electrode), platinum coil (counter electrode) and $Ag|Ag^+$ pseudo-reference electrode. Sample concentration was 1.0 mM in dichloromethane or acetonitrile in the presence of 0.1 M Bu_4NBF_4 electrolyte. The solution was deoxygenated by flushing with argon before all electrochemical and spectroelectrochemical measurements.

Tetrabutylammonium tetrafluoroborate (Bu_4NBF_4, 99.0%, Sigma-Aldrich) dried under vacuum, dichloromethane (DCM, for HPLC, 99.8%, Sigma-Aldrich), ferrocene (Fc, 98%, Sigma-Aldrich) and argon (6.0, SIAD Group) were used for the above mentioned studies.

The optical properties have been modelled with DFT and TD-DFT. We used exact experimental structures, but for the side alkyl chains that were replaced by methyl groups for obvious computational reasons. The ground-state geometries have been fully optimized with Gaussian 16[1] using Pople's 6-31G(d) basis set, Truhlar's M06-2X[2] hybrid exchange-correlation functional, and using the PCM[3] model for the environmental effects (toluene). Default or improved convergence parameters have been used. Next, frequency calculations have been systematically achieved - at the very same level of theory - to confirm the minimum nature of the optimized geometries. Starting from these ground-state structures, TD-DFT optimizations and frequency calculations of the lowest singlet states have been performed as well, using the same setting. For the one-photon (vertical) absorption and emission, we next used linear-response TD-DFT, with the same functional, but a diffuse-containing atomic basis set, namely 6-31+G(d,p). The selected solvent model was LR-PCM[4] which is justified as the lowest transition is strongly dipole allowed. We note that in toluene the *equilibrium* and *non-equilibrium* limits of PCM-TD-DFT calculations are essentially equivalent. From these calculations, we deduced 0-0 energies directly, by correcting the adiabatic energies for the differences of ZPVE between the two states.[5] Advantageously, 0-0 energies can be directly compared to the experimentally-available absorption-fluorescence crossing point. For one case, we performed vibrationally resolved calculations of both one-photon absorption and emission. The vibronic spectra have been simulated using the FCclasses3[6] (*Beta* version) code within the time-independent formulation, applying the Franck-Condon model, and using the Adiabatic Hessian (AH) model at 298K. Both properties have been computed with 10^7 integrals and the emission have been broadened using a Lorentzian function (HWHM = 0.03 eV) while using a Gaussian function (HWHM = 0.045 eV) for the absorption. These calculations recovered very large fractions of the FC spectrum (>0.97) indicating a well-converged calculation. Finally, the two-photon cross-sections were simulated using the quadratic response model implemented in Dalton[7] using the optimal geometries. These two-photon calculations were performed with CAM-B3LYP[8] combined to the 6-31G basis set. As a final note, we are well aware of the limits of TD-DFT for boron-containing complexes like "BODIPY" and similar, [9] but the size of the investigated compounds clearly prevents the use of Coupled-Cluster (or similar) schemes.

2. Synthesis

General procedure for the synthesis of pyrrolo[3,2-b]pyrroles

Glacial acetic acid (6 mL), toluene (6 mL), aldehyde (8 mmol) and aniline (8 mmol) were placed in a 50 mL round-bottom flask equipped with a magnetic stir bar. The mixture was stirred at 90 °C for 30 min. After that time, $Fe(ClO4)_3$ (92 mg) was added, followed by diacetyl (350 µL, 4 mmol). The resulting mixture was stirred at 50 °C for 16 h. Solvents were evaporated off. Residue was dissolved in hot ACN and cooled to rt, then in the fridge overnight. The resulting precipitate was filtered off, washed with cold ACN and dried under high vacuum.

1,4-Bis(4-octylphenyl)-2,5-bis(pyrid-2-yl)-1,4-dihydropyrrolo[3,2-b]pyrrole (2a)

Brown solid. Yield: 535 mg (21%). Spectroscopic properties were in agreement with the literature data.[10]

2,5-Bis(6-methylpyrid-2-yl)-1,4-bis(4-octylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (2b)

Brown solid. Yield: 287 mg (11%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.8 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 4H), 7.16 (d, *J* = 8.2 Hz, 4H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.76 (s, 2H), 6.75 (d, *J* = 7.5 Hz, 2H), 2.62 (t, *J* = 7.7 Hz, 4H), 2.46 (s, 6H), 1.64 (q, *J* = 7.3 Hz, 4H), 1.42 - 1.19 (m, 20H), 0.88 ppm (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.9, 151.3, 140.6, 138.1, 136.5, 135.6, 133.4, 128.9, 125.4, 119.8, 119.3, 96.4, 35.5, 31.9, 31.4, 29.5, 29.3, 29.2, 24.6, 22.7, 14.1 ppm. HRMS (EI): *m/z* calculated for $C_{46}H_{56}N_4$: 664.4505 [$M^{\cdot+}$]; found: 664.4498

2,5-Bis(5-bromopyrid-2-yl)-1,4-bis(4-octylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (2c)

Brown solid. Yield: 1340 mg (42%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 2H), 7.53 (d, *J*= 8.5 Hz, 2H), 7.24 - 7.16 (m, 8H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.81 (s, 2H), 2.64 (t, *J*= 7.5 Hz, 4H), 1.65 (quintet, *J* =7.3 Hz, 4H), 1.39 - 1.23 (m, 20H), 0.89 ppm (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 149.8, 141.5, 138.5, 137.3, 135.5, 134.1, 129.3, 125.3, 123.1, 117.0, 97.2, 35.5, 31.9, 31.4, 29.5, 29.3, 22.7, 14.1 ppm. HRMS (EI): *m/z* calculated for $C_{44}H_{50}N_4Br_2$: 792.2402 [$M^{\cdot+}$]; found: 792.2386.

2,5-Bis(4-bromopyrid-2-yl)-1,4-bis(4-octylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (2d)

Yellow solid. Yield: 932 mg (29%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 4.9, 1.1 Hz, 2H), 7.22 (s, 8H), 7.17 – 7.12 (m, 4H), 6.78 (s, 2H), 2.65 (t, *J* = 7.6 Hz, 4H), 1.65 (quintet, *J* = 7.2 Hz, 4H), 1.35 - 1.26 (m, 20H), 0.89 ppm (t, *J* = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 150.0, 141.3, 137.4, 135.4, 133.9, 132.1, 129.2, 125.3, 124.9, 123.5, 97.1, 35.5, 31.9, 31.4, 29.5, 29.3, 29.1, 22.7, 14.1 ppm. HRMS (EI): *m/z* calculated for $C_{44}H_{50}N_4Br_2$: 792.2402 [$M^{\cdot+}$]; found: 792.2388.

2,5-Bis(5-fluoropyrid-2-yl)-1,4-bis(4-octylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (2e)

Brown solid. Yield: 800 mg (30%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.9 Hz, 2H), 7.24 - 7.11 (m, 10H), 6.97 (dd, *J* = 8.9, 4.3 Hz, 2H), 6.70 (s, 2H), 2.63 (t, *J* = 7.7 Hz, 4H), 1.64 (quintet, *J* = 7.1 Hz, 4H), 1.38 - 1.24 (m, 20H), 0.89 ppm (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5 (d, *J* = 255.2 Hz), 148.3 (d, *J* = 3.8 Hz), 141.0, 137.6, 137.4, 135.3, 133.1, 129.1, 125.2, 122.9 (d, *J* = 3.8 Hz), 122.5 (d, *J* = 18.8 Hz), 96.4, 35.5, 31.9, 31.4, 29.5, 29.3, 22.7, 14.1 ppm; ^{19}F NMR (470 MHz, $CDCl_3$) δ -130.92 ppm (dd, *J* = 8.4, 4.6 Hz). HRMS (EI): *m/z* calculated for $C_{44}H_{50}N_4F_2$: 672.4004 [$M^{\cdot+}$]; found: 672.4001.

1,4-Bis(4-octylphenyl)-2,5-bis(quinolin-2-yl)-1,4-dihydropyrrolo[3,2-b]pyrrole (2f)

Brown solid. Yield: 800 mg (28%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (br s, 2H), 7.87 (d, *J* = 9.0 Hz, 2H), 7.68 (d, *J* = 7.9 Hz, 2H), 7.63 (s, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 4H), 7.19 (d, *J* = 7.7 Hz, 6H), 6.98 (br s, 2H), 2.64 (t, *J* = 7.6 Hz, 4H), 1.64 (quintet, *J* = 7.3 Hz, 4H), 1.30 (m, 20H), 0.88 ppm (t, *J* = 6.6 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 129.1, 127.4, 126.3, 125.9, 125.4, 121.2, 35.5, 31.0, 31.4, 29.5, 29.28, 29.24, 22.7, 14.1. HRMS (EI): *m/z* calculated for $C_{52}H_{56}N_4$: 736.4505 [$M^{\cdot+}$]; found: 736.4495.

2,5-Bis(6-chloroquinolin-2-yl)-1,4-bis(4-octylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (2g)

Brown solid. Yield: 1270 mg (39%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 5.1 Hz, 2H), 7.77 (d, *J* = 5.3 Hz, 2H), 7.66 (d, *J* = 2.0 Hz, 2H), 7.54 (dd, *J* = 8.9, 2.3 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 4H), 7.24 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.94 (s, 2H), 2.66 (t, *J* = 7.7 Hz, 4H), 1.66 (quintet, *J* = 7.5 Hz, 4H), 1.37 – 1.24 (m, 20H), 0.90 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9, 146.5, 141.1, 137.9, 136.9, 134.3, 134.2, 131.2, 130.6, 130.3, 129,0 126.9, 126.0, 125.4, 121.7, 97.4, 35.5, 31.9, 31.4, 29.5, 29.3, 29.2, 22.7, 14.1 ppm. HRMS (EI): *m/z* calculated for $C_{52}H_{54}N_4Cl_2$: 804.3726 [$M^{\cdot+}$]; found: 804.3735.

2,5-Bis(isoquinolin-3-yl)-1,4-bis(4-octylphenyl)-1,4-dihydropyrrolo[3,2-b]pyrrole (2h)

Dark brown solid. Yield: 160 mg (7%).^{1}H NMR (500 MHz, $CDCl_3$) δ 9.18 (s, 2H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 2H), 7.50-7.44 (m, 4H), 7.33 (d, *J* = 8.4 Hz, 4H), 7.24 (d, overlapped with a signal of chloroform, *J* = 10.6 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 4H), 6.98 (s, 2H), 2.65 (t, *J* = 7.6 Hz, 4H), 1.65 (quintet, *J* = 7.4 Hz, 4H), 1.39 – 1.21 (m, 20H), 0.89 ppm (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.7, 145.1, 141, 137.9, 136.2, 134.0, 130.6, 129.2, 129.0, 127.7, 126.6, 126.5, 125.5, 117.6, 110.0, 97.1, 35.5, 31.9, 31.4, 29.5, 29.3, 29.2, 22.7, 14.1. HRMS (EI): *m/z* calculated for $C_{52}H_{56}N_4$: 736.4505 [$M^{\cdot+}$]; found: 736.4503.

General procedure for the synthesis of BN-embedded pyrrolo[3,2-b]pyrroles (BN-TAPPs)

The Schenk flask was charged with pyrrolo[3,2-b]pyrrole (0.4 mmol) and $PhBF_3K$ (530 mg, 2.88 mmol). Solids were evacuated and refilled with argon 3 times. Then, solids were dissolved in dry toluene, followed by addition of $SiCl_4$ (92 µL, 0.8 mmol) and Hünig's base (698 µL, 4 mmol). The resulting mixture was stirred at 135 °C overnight. Reaction mixture was cooled down to rt. The formed precipitate was diluted with DCM and the whole mixture was transferred to a round-bottom flask. After adding the proper amount of silica, all solvents were evaporated and the residue was purified by column chromatography (SiO_2, DCM/hexanes). Product was recrystallized from $CHCl_3$/MeOH.

(1a)

Yellow solid. Yield: 201 mg (52%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 5.7 Hz, 2H), 7.51 (t, *J* = 7.8 Hz, 2H), 7.12 - 7.04 (m, 16H), 6.99 (d, *J* = 8.5 Hz, 4H), 6.94 (d, *J* = 8.5 Hz, 2H), 6.92 - 6.88 (m, 8H), 6.82 (t, *J* = 6.6 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 4H), 1.64 (quintet, *J* = 7.3 Hz, 4H), 1.39 - 1.25 (m, 20H), 0.90 ppm (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.8, 149.6, 144.8, 141.9, 140.5, 139.4, 137.4, 136.4, 133.6, 128.9, 127.2, 126.9, 125.2, 116.9, 115.8, 35.6, 32.0, 31.6, 29.6, 29.3, 29.2, 22.7, 14.1 ppm; ^{10}B NMR (54 MHz, $CDCl_3$) δ 49.7 ppm. HRMS (ESI): *m/z* calculated for $C_{68}H_{71}B_2N_4$: 965.5865 [M+H$^+$]; found: 965.5900.

(1b)

Orange solid. Yield: 60 mg (16%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (t, *J* = 8.0 Hz, 2H), 7.11 - 6.98 (m, 16H), 6.88 (d, *J* = 7.6 Hz, 4H), 6.85 - 6.73 (m, 10H), 6.61 (d, *J* = 7.5 Hz, 2H), 2.71 (t, *J* = 7.7 Hz, 4H), 2.07 (s, 6H), 1.77 (quintet, *J* = 7.1 Hz, 4H), 1.51 - 1.28 (m, 20H), 0.90 ppm (t, *J* = 6.5 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.0, 152.1, 147.3, 141.8, 139.4, 136.6, 136.3, 133.5, 128.8, 127.6, 126.9, 124.7, 118.8, 113.3, 35.7, 32.0, 31.9, 29.6, 29.3, 29.2, 22.7, 22.5, 14.1 ppm; ^{10}B NMR (54 MHz, $CDCl_3$) δ 133.9 ppm; HRMS (ESI): *m/z* calculated for $C_{70}H_{75}B_2N_4$: 993.6178 [M+H$^+$]; found: 993.6196.

(1c)

Orange solid. Yield: 110 mg (10%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.1 Hz, 2H), 7.58 (dd, *J* = 8.9, 2.1 Hz, 2H), 7.14 - 7.02 (m, 16H), 6.98 (d, *J* = 8.0 Hz, 4H), 6.92 - 6.85 (m, 8H), 6.79 (d, *J* = 8.9 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 4H), 1.64 (quintet, *J* = 7.3 Hz, 4H), 1.39 - 1.25 (m, 20H), 0.91 ppm (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 145.8, 142.32, 142.27, 140.9, 137.2, 135.9, 134.7, 133.5, 131.1, 129.0, 127.9, 127.1, 125.5, 116.6, 111.2, 35.6, 32.0, 31.6, 29.5, 29.3, 29.2, 22.7, 14.1 ppm; ^{10}B NMR (54 MHz, $CDCl_3$) δ 42.6 ppm. HRMS (ESI): *m/z* calculated for $C_{68}H_{69}B_2N_4Br_2$: 1121.4075 [M+H$^+$]; found: 1121.4098.

(1d)

Orange solid. Yield: 130 mg (29%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 6.2 Hz, 2H), 7.13 - 6.99 (m, 22H), 6.96 (dd, *J* = 6.2, 1.9 Hz, 2H), 6.90 - 6.84 (m, 8H), 2.66 (t, *J* = 7.5 Hz, 4H), 1.65 (quintet, *J* = 6.8 Hz, 4H), 1.38 - 1.25 (m, 20H), 0.90 ppm (t, *J* = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.1, 145.2, 142.5, 141.0, 136.9, 136.6, 135.7, 133.4, 129.1, 127.1, 127.1, 125.5, 120.3, 119.0, 35.5, 32.0, 31.6, 29.6, 29.3, 29.1, 22.7, 14.1 ppm; ^{10}B NMR (54 MHz, $CDCl_3$) δ 105.0 ppm. HRMS (ESI): *m/z* calculated for $C_{68}H_{69}B_2N_4Br_2$: 1121.4075 [M+H$^+$]; found: 1121.4099.

(1e)

Orange solid. Yield: 168 mg (42%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (t, *J* = 2.6 Hz, 2H), 7.37 - 7.30 (m, 2H), 7.14 - 7.04 (m, 16H), 6.99 (d, *J* = 8.2 Hz, 4H), 6.93 - 6.86 (m, 10H), 2.63 (t, *J* = 7.6 Hz, 4H), 1.64 (quintet, *J* = 7.5 Hz, 4H), 1.40 - 1.27 (m, 20H), 0.91 (t, *J* = 6.9 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1 (d, *J* = 247.0 Hz), 148.1, 142.2, 140.3, 136.5, 136.1, 133.5, 133.2, 129.0, 127.9 (d, *J* = 19.8 Hz), 127.1, 125.5, 116.1 (d, *J* = 5.2 Hz), 35.6, 32.0, 31.6, 29.5, 29.3, 29.2, 22.7, 14.1 ppm; ^{19}F NMR (470 MHz, $CDCl_3$) δ -132.54 – -132.61 ppm (m). ^{10}B NMR (54

MHz, $CDCl_3$) δ -28.1 ppm. HRMS (ESI): *m/z* calculated for $C_{68}H_{69}B_2N_4F_2$: 1001.5676 [$M+H^+$]; found: 1001.5705.

(1f)

Maroon solid. Yield: 77 mg (18%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.0 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.60 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.23 - 7.17 (m, covered by a signal from $CHCl_3$, 4H), 7.15 (d, *J* = 8.9 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 4H), 7.05 - 6.93 (m, 16H), 6.79 - 6.75 (m, 8H), 2.76 (t, *J* = 7.5 Hz, 4H), 1.80 (quintet, *J* = 4H), 1.52 - 1.30 (m, 20H), 0.91 (t, *J* = 7.0 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9, 148.7, 142.9, 142.4, 140.8, 140.2, 139.1, 136.4, 133.7, 131.1, 129.1, 128.2, 127.9, 126.9, 125.5, 124.7, 124.6, 122.9, 115.4, 35.8, 31.9, 31.8, 29.6, 29.4, 29.3, 22.7, 14.1 ppm. ^{10}B NMR (54 MHz, $CDCl_3$) δ 39.4 ppm. HRMS (ESI): *m/z* calculated for $C_{76}H_{75}B_2N_4$: 1065.6178 [$M+H^+$]; found: 1065.6211.

(1g)

Dark red solid. Yield: 107 mg (24%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 9.1 Hz, 2H), 7.65 (d, *J* = 9.3 Hz, 2H), 7.60 (d, *J* = 2.3 Hz, 2H), 7.19 (d, *J* = 9 Hz, 2H), 7.18 (dd, *J* = 9.5, 2.5 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 4H), 7.08 - 6.98 (m, 12H), 6.96 (d, *J* = 8.3 Hz, 4H), 6.79 - 6.70 (m, 8H), 2.76 (t, *J* = 7.6 Hz, 4H), 1.80 (quintet, *J* = 7.45 Hz, 4H), 1.53 - 1.30 (m, 20H), 0.92 (t, *J* = 7 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.7, 142.6, 141.3, 141, 139.3, 139.2, 136.2, 133.6, 131.8, 130.4, 129.2, 127.8, 127, 126.8, 126.2, 125, 124.3, 116.5, 35.8, 31.95, 31.9, 29.6, 29.3, 29.25, 22.7, 14.1 ppm. ^{10}B NMR (54 MHz, $CDCl_3$) δ -30.8 ppm. HRMS (ESI): *m/z* calculated for $C_{76}H_{73}B_2N_4Cl_2$: 1133.5398 [$M+H^+$]; found: 1133.5417.

(1h)

Orange solid. Yield: 16 mg (8%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (s, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 4H), 7.12 - 7.05 (m, 14H), 7.02 (d, *J* = 8.0 Hz, 4H), 6.98 (d, *J* = 6.1 Hz, 8H), 2.69 (t, *J* = 7.5 Hz, 4H), 1.70 (quintet, *J* = 6.4 Hz, 4H), 1.36 (m, 20H), 0.92 (t, *J* = 6.4 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.3, 149.0, 144.9, 141.7, 140.2, 138.3, 136.7, 136.6, 133.6, 133.1, 129.2, 128.8, 127.3, 127.0, 126.5, 125.9, 125.2, 124.2, 109.8, 35.6, 32.0, 31.7, 29.6, 29.4, 29.2, 22.7, 14.2 ppm. ^{10}B NMR (54 MHz, $CDCl_3$) δ 29.43 ppm. HRMS (ESI): *m/z* calculated for $C_{76}H_{75}B_2N_4$: 1065.6178 [$M+H^+$]; found: 1065.6227.

Synthesis of compound 1i

The Schlenk flask was charged with **3c** (74 mg, 0.065 mmol), 4-ethynylbenzonitrile (24 mg, 0.19 mmol), Cs_2CO_3 (69 mg, 0,21 mmol), palladium (II) acetate (1.3 mg, 6.6 µmol) and triphenylphosphine (6.2 mg, 26.4 mmol). After three vacuum/argon cycles, reagents were dissolved in anhydrous DMSO (5 ml). The resulting mixture was stirred at 80 °C for 24 hours. The mixture was cooled to room temperature and evaporated. The residue was purified by column chromatography (SiO_2, DCM/hexanes, 2:3). Product was recrystallized from $CHCl_3$/MeOH.

Red solid. Yield: 75 mg (95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 1.8 Hz, 2H), 7.64 - 7.55 (m, 6H), 7.50 (d, *J* = 8.5 Hz, 4H), 7.15 - 7.05 (m, 16H), 7.03 - 6.98 (m, 4H), 6.94 - 6.87 (m, 10H), 2.65 (t, *J* = 7.6 Hz, 4H), 1.66 (quintet, *J* = 7.3 Hz, 4H), 1.39 - 1.27 (m, 20H), 0.91 ppm (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.3, 148.5, 147.8, 142.5, 141.64, 141.60, 138.6, 135.7, 133.6, 132.1, 131.9, 129.1, 127.12, 127.10, 127.08, 125.6, 118.3, 115.6, 112.3, 112.0, 110.0, 91.6, 89.5, 35.6, 32.0, 31.6, 29.6, 29.3, 29.2, 22.7, 14.2 ppm; ^{10}B NMR (54 MHz, $CDCl_3$) δ -53.2 ppm. HRMS (EI): *m/z* calculated for $C_{86}H_{76}B_2N_6$: 1214.6318 [$M^{\cdot+}$]; found: 1214.6331.

Synthesis of compound 1j

The Schlenk flask was charged with **3c** (56 mg, 0.05 mmol), bis(4-methoxyphenyl)amine (34.4 mg, 0.15 mmol), bis(tri-*tert*-butylphosphine)palladium(0) (1.27 mg, 2.5 µmol) and sodium *tert*-butoxide (48.1 mg, 0.5 mmol). After three vacuum/argon cycles, reagents were dissolved in anhydrous toluene (5 ml). The resulting mixture was stirred at 100 °C for 24 hours. Reaction mixture was cooled to rt and quenched with a few drops of water. All solvents were evaporated off, and the residue was purified by column chromatography (SiO_2, DCM/hexanes, 1:1). Product was recrystallized from $CHCl_3$/MeOH.

Red solid. Yield: 50 mg (70%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.84 (br s, 2H), 7.15 - 6.97 (m, 18H), 6.96 - 6.82 (m, 20H), 6.78 - 6.61 (m, 10H), 3.74 (s, 12H), 2.56 (t, *J* = 7.7 Hz, 4H), 1.59 (quintet, *J* = 7Hz, 4H), 1.36 - 1.20 (m, 20H), 0.87 ppm (t, *J* = 6.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 150.1, 141.5, 139.8, 139.2, 138.1, 136.6, 133.6, 128.7, 127.1, 126.8, 125.7, 125.0, 114.9, 55.5, 35.5, 31.9, 31.7, 29.5, 29.3, 29.2, 22.7, 14.1 ppm; ^{10}B NMR (54 MHz, $CDCl_3$) δ 40.6 ppm. HRMS (ESI): *m/z* calculated for $C_{96}H_{97}B_2N_6O_4$: 1419.7757 $[M+H^+]$; found: 1419.7809.

Synthesis of compound 1k

The Schlenk flask was charged with **2g** (52.1 mg, 45.9 mmol), 4-ethynylbenzonitrile (22.9 mg, 180 mmol), Cs_2CO_3 (78 mg, 239 mmol), XPhos (6.6 mg, 14 µmol) and bis(acetonitrile)dichloropalladium(II) (1.2 mg, 4.6 µmol). After three vacuum/argon cycles, reagents were dissolved in anhydrous dioxane (5 mL). The resulting mixture was stirred at 90 °C for 16 hours. Reaction mixture was cooled to room temperature. Solvent was evaporated off, and the residue was purified by column chromatography (SiO_2, DCM/hexanes, 2:3).

Maroon solid. Yield: 56% (42 mg). ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.2 Hz, 2H), 7.82 (d, *J* = 1.4 Hz, 2H), 7.70 (d, *J* = 9.1 Hz, 2H), 7.57 (dd, *J* = 35.9, 8.2 Hz, 8H), 7.34 (dd, *J* = 9.1, 1.6 Hz, 2H), 7.19 (d, *J* = 9.1 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 4H), 7.08 - 6.99 (m, 12H), 6.98 (d, *J* = 8.0 Hz, 4H), 6.78 (d, *J* = 6.9 Hz, 8H), 2.78 (t, *J* = 7.6 Hz, 4H), 1.88 - 1.75 (quintet, *J* = 7.6 Hz, 4H), 1.53 - 1.30 (m, 20H), 0.92 (t, *J* = 6.7 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.1, 143.4, 138.03, 138.01, 136.7, 135.1, 135.0, 131.1, 129.1, 128.9, 127.29, 127.26, 126.9, 124.5, 123.04, 123.01, 122.32, 120.5, 120.3, 118.3, 113.7, 111.6, 106.9, 88.1, 84.5, 31.0, 27.2, 27.1, 24.9, 24.6, 24.5, 18.0 ppm. ^{10}B NMR (54 MHz, $CDCl_3$) δ 46.1 ppm. HRMS (APCI): *m/z* calculated for $C_{94}H_{81}B_2N_6$: 1315.6709 $[M+H]^{\cdot+}$; found: 1315.6750.

Synthesis of compound 1l

The Schlenk flask was charged with **2g** (104 mg, 92 mmol), 4-ethynyl-N,N-dimethylaniline (13 mg, 90 mmol), Cs_2CO_3 (156 mg, 478 mmol), XPhos (13.2 mg, 28 µmol) and bis(acetonitrile)dichloropalladium(II) (2,4mg, 9.2 µmol). After three vacuum/argon cycles, reagents were dissolved in anhydrous dioxane (10 mL). The resulting mixture was stirred at 90 °C for 16 hours. Reaction mixture was cooled to room temperature. Solvent were evaporated off, and the residue was purified by column chromatography (SiO_2, DCM/hexanes, 2:3).

Brown solid. Yield: 100mg (80%). ^1H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 9.1 Hz, 2H), 7.74 (d, *J* = 1.4 Hz, 2H), 7.65 (d, *J* = 9.1 Hz, 2H), 7.35 (d, *J* = 8.9 Hz, 4H), 7.32 (dd, *J* = 9.2, 1.7 Hz, 2H), 7.16 (d, *J* = 9.0 Hz, 2H), 7.11 (d, *J* = 8.0 Hz, 4H), 7.08 - 6.96 (m, 16H), 6.79 (d, *J* = 6.8 Hz, 8H), 6.64 (d, *J* = 8.3 Hz, 4H), 2.98 (s, 12H), 2.78 (t, *J* = 7.5 Hz, 4H), 1.82 (quintet, *J* = 7.7 Hz, 4H), 1.53 - 1.30 (m, 20H), 0.93 (t, *J* = 6.8 Hz, 6H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.3, 150.2, 148.4, 142.5, 142.1, 141.1, 139.5, 139.5, 136.3, 134.0, 133.7, 132.7, 130.2, 129.2, 127.8, 127.0, 125.5, 124.8, 122.7, 120.6, 115.9, 111.8, 109.5, 92.5, 86.7, 40.2, 35.8, 32.0, 31.9, 29.6, 29.3, 29.3, 22.7, 14.1 ppm. ^{10}B NMR (54 MHz, $CDCl_3$) δ -123.7 ppm. HRMS (APCI): *m/z* calculated for $C_{96}H_{93}B_2N_6$: 1351.7648 $[M+H]^{\cdot+}$; found: 1351.7673.

3. Crystallographic data

Single crystal of **1a** suitable for x-ray diffraction analysis was obtained by slowly diffusing hexanes into its tetrahydrofuran solution. A total of 4584 frames were collected. The total exposure time was 61.12 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm.

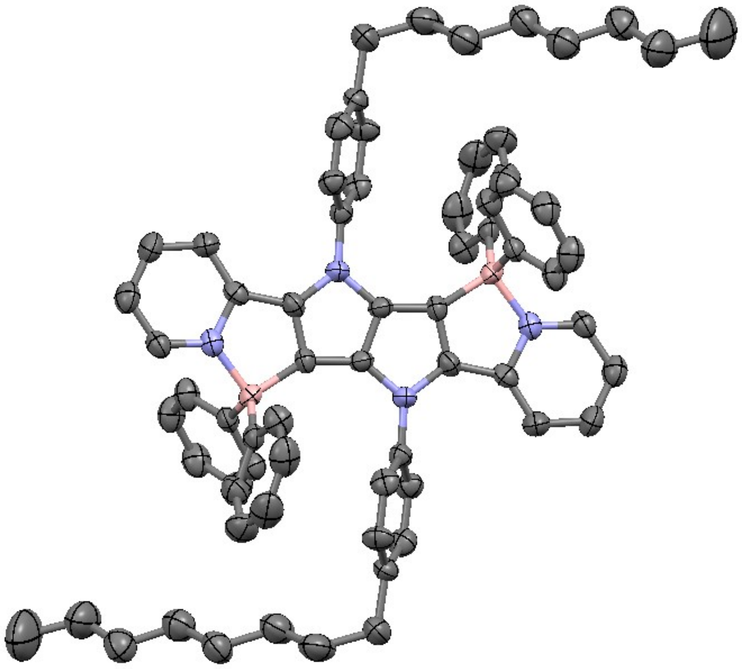


Fig. S1. Crystal structure of **1a** with thermal ellipsoids, shown at 50% probability. The hydrogen atoms in the structure were omitted for clarity

Table S1. Crystallographic data for 1a

Chemical Formula	$C_{68}H_{70}B_2N_4$	
Formula weight	964.90 g/mol	
Temperature	296(2) K	
Wavelength	1.54178 Å	
Crystal size	0.114 x 0.204 x 0.310 mm	
Crystal habit	fluorescent yellow plate	
Crystal system	monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 16.0079(13) Å	α = 90°
	b = 12.8244(9) Å	β = 90.002(6)°
	c = 13.7166(11) Å	γ = 90°
Volume	2815.9(4) $Å^3$	
Z	2	
Diffractometer	Bruker APEX-II CCD	
Radiation source	fine-focus sealed tube	
Reflections collected	50300	
Independent reflections	4258 [R(int) = 0.1183]	
Tmax, Tmin	0.9460, 0.8620	

Absorption correction	numerical	
Refinement method	Full-matrix least-squares on F^2	
Function minimized	$\Sigma\ w(F_o^2 - F_c^2)^2$	
Data/restraints/parameters	4258 / 0 / 380	
Goodness-of-fit on F2	1.107	
Final R indices	1801 data; I>2σ(I)	R1 = 0.0838, wR2 = 0.1338
	all data	R1 = 0.2420, wR2 = 0.1690
Largest diff. Peak and hole	0.243 and -0.237 eÅ^{-3}	

4. Spectroscopic properties

When dissolved in toluene, pyridyl-substituted TAPPs **2a**-**2e** strongly absorb UV-light, with absorption maxima in the 375-394 nm region and extinction coefficient in the 23000 - 57000 $M^{-1}\cdot cm^{-1}$ range, whereas their emission maxima are observed between 419 - 436 nm (Table S2). Changing the substituent to quinoline (compounds **2f** and **2g**) leads to ca. 50 nm bathochromic shift of both absorption and emission maxima. This effect is much less pronounced in the case of isoquinoline substituted pyrrolo[3,2-*b*]pyrrole **2h**. All TAPPs exhibit moderate Stokes shifts in the 1730-3150 cm^{-1} with fluorescence quantum yields (Φ_{fl}) typically higher than 0.4, indicative of rigid structure undergoing small structural changes after absorption. The only exception to this trend is compound **2d** bearing bromine substituents which shows smaller emission yield, very likely due to the heavy atom effect, which, interestingly, is less marked for similar dibromo-derivative **2c**.

Table S2. Spectroscopic properties of compounds 2a-2h

Compound	Solvent	λ_{abs}^{max} [nm]	ε_{max} [$M^{-1}\cdot cm^{-1}$]	λ_{em}^{max} [nm]	Stokes shift [cm^{-1}]	Φ_{fl}
2a	toluene	377	46000	419	2660	0.66[a]
2b	toluene	382	30900	421	2430	0.69[a]
2c	toluene	394	29200	436	2440	0.60[a]
2d	toluene	390	27100	428	2280	0.12[a]
2e	toluene	375	30300	419	2800	0.56[a]
2f	toluene	432	56600	467	1730	0.44[b]
2g	toluene	443	46900	477	1610	0.48[b]
2h	toluene	401	23700	459	3150	0.45[a]

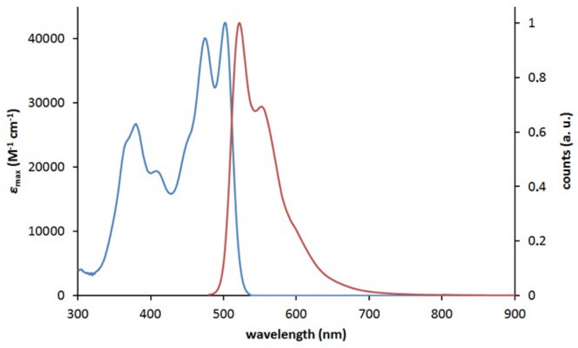
[a] Determined with quinine sulfate in H_2SO_4 (0.5 M) as a standard. [b] Determined with coumarin 153 in ethanol as a standard.

Photostability measurements

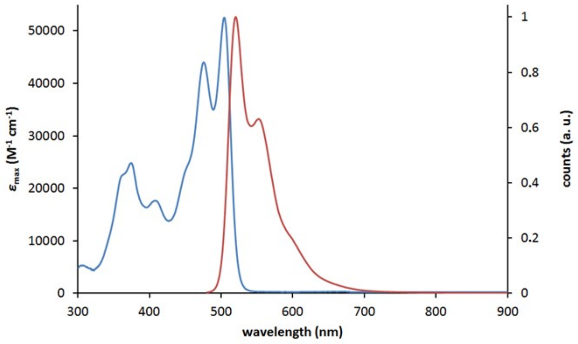
Photostability of compounds **1a** and **2a** was determined through the variation in absorption of each sample at the appropriate absorption maximum wavelength (λ_{abs}) with respect to irradiation time. Toluene was selected as the solvent. Concentrations giving similar optical densities (A ≈ 1) were used. Quartz cells of samples were irradiated with a 300 W Xe lamp (Asahi spectra MAX-350, light power: 0.115 W/cm^2) for 180 min at 25 °C equipped with a UV/vis mirror module through a glass fiber. The absorption spectra were measured at appropriate times during the irradiation. BODIPY (difluoro{2-[1-(3,5-dimethyl-2*H*-pyrrol-2-ylidene-*N*)ethyl]-3,5-dimethyl-1*H*-pyrrolato-*N*}boron), DPP (2,5-dimethyl-3,6-bis(3,4-dimethoxyphenyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione) and Alexa Fluor 555 were used as references.

5. Absorption (blue line) and normalized emission (red line) spectra measured in toluene.

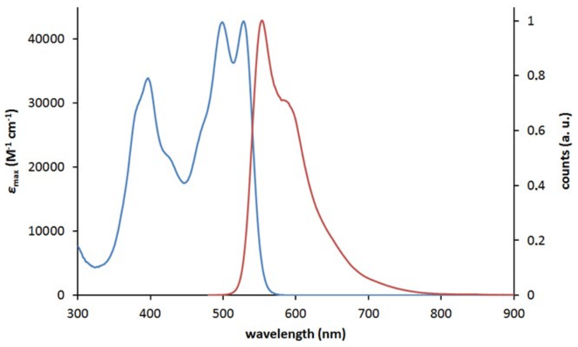
1a



1b



1c



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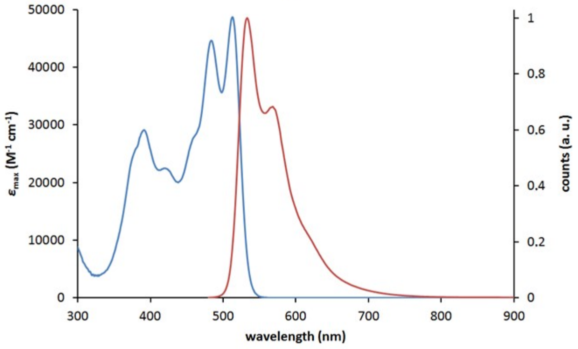

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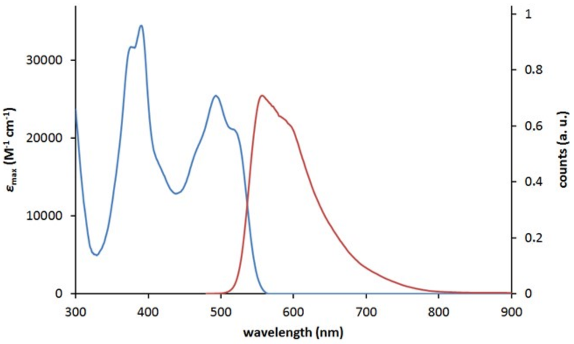

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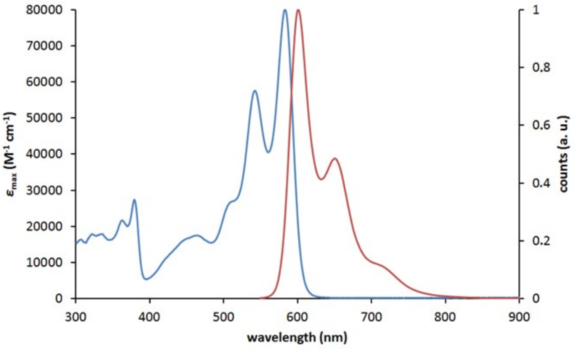

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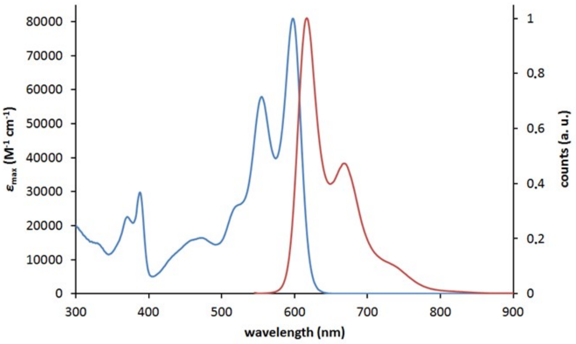

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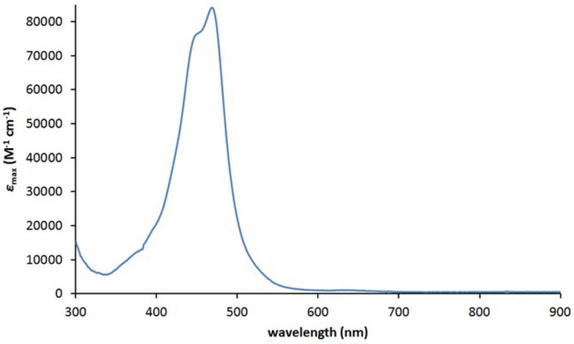
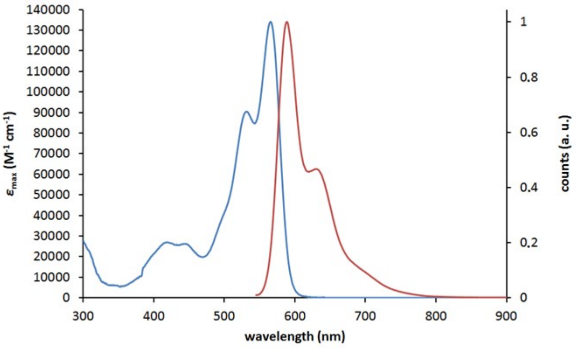


1i



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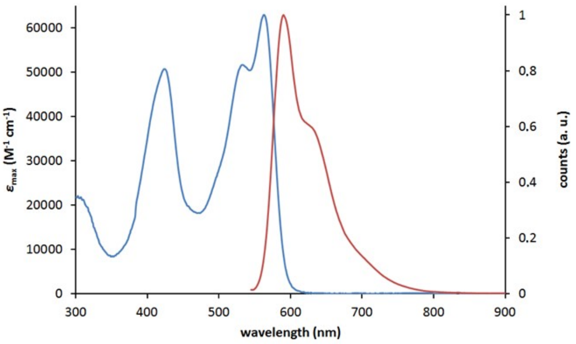
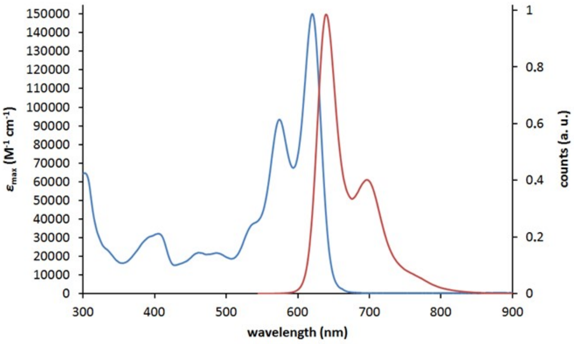


1k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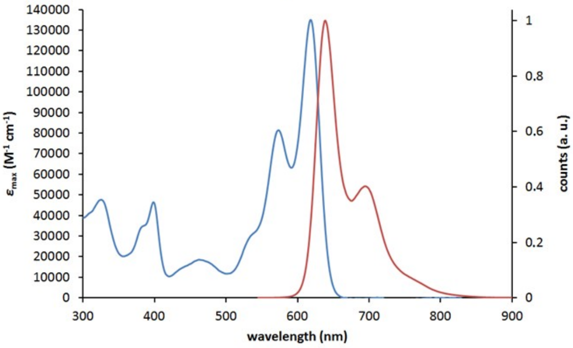
1l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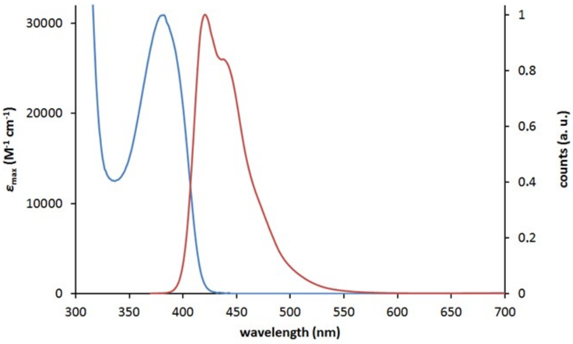
2b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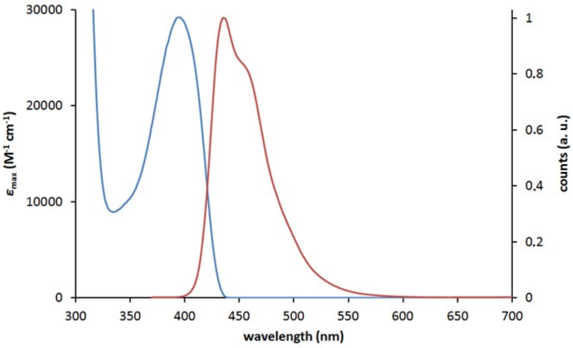
2c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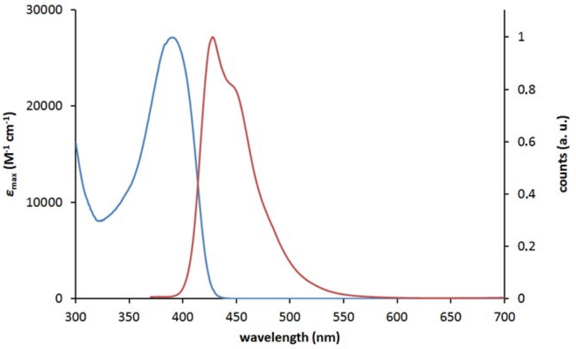
2d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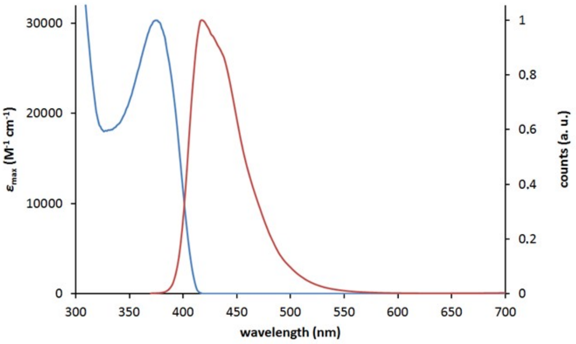
2e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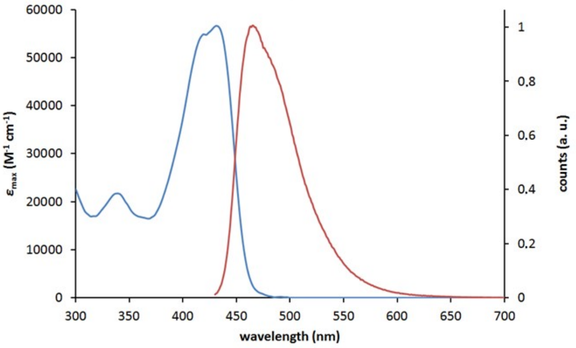
2f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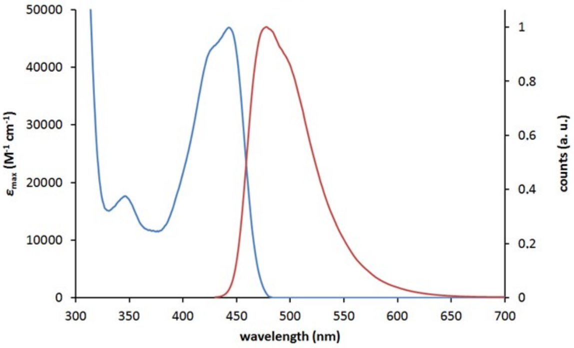
2g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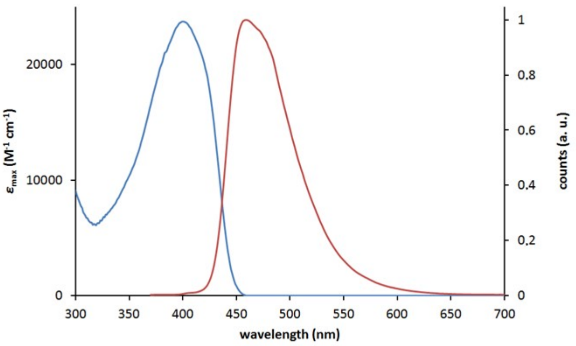
wavelength (nm)

2h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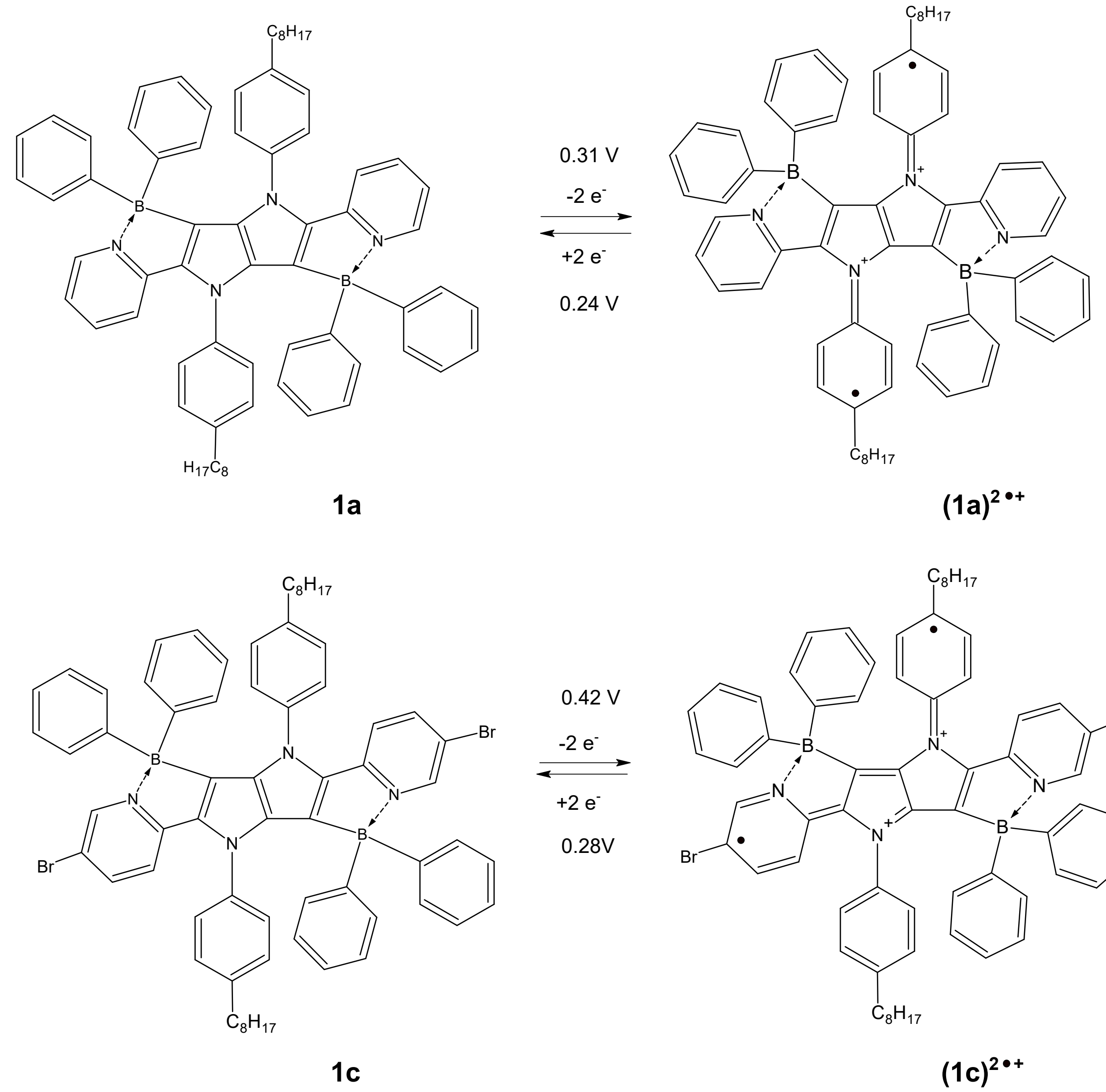
wavelength (nm)

6. Electrochemical properties



Scheme S1. Structural changes during the oxidation of **1a** and **1c** under the polarization of the first reversible oxidation peak

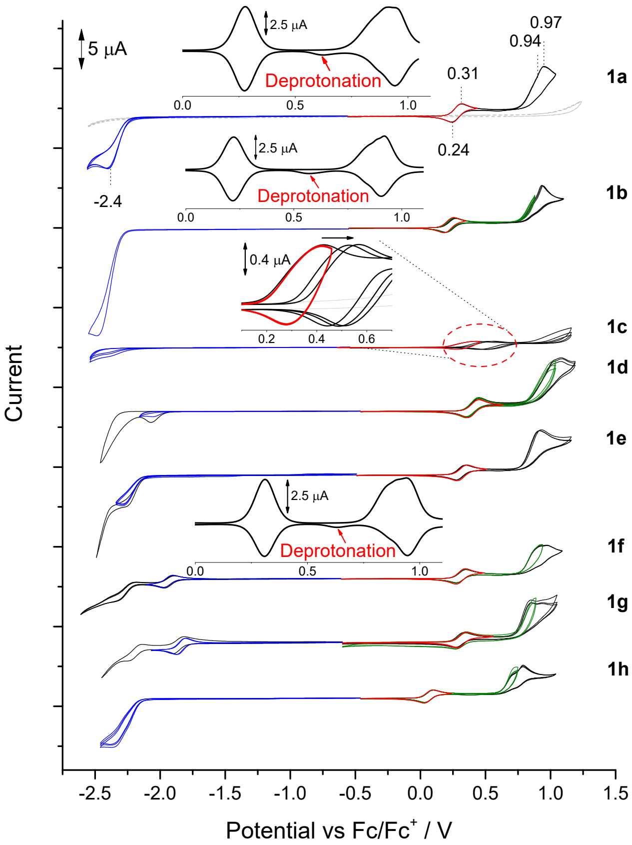


Fig. S2. Cyclic voltammograms in the solution of BN-TAPP-series compounds (1 mM) in 0.1 M Bu4NBF4/DCM. Oxidation (red, black CVs), reduction (blue, black CVs), second oxidation (green, black CVs).

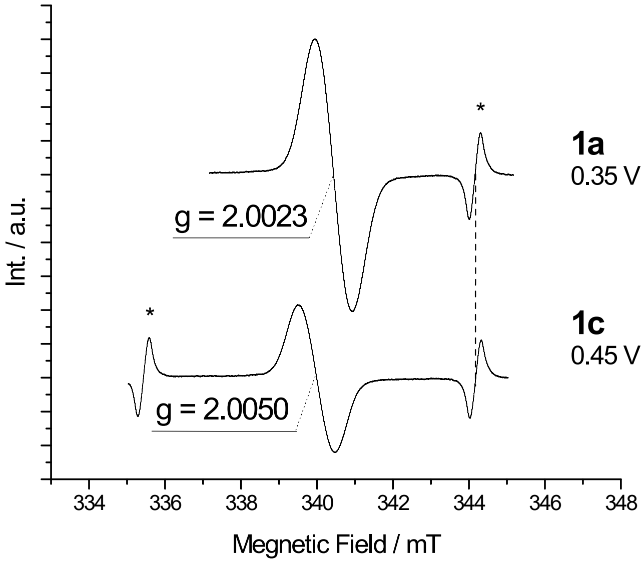


Fig. S3. In-situ ESR spectra of **1a** and **1c** in 0.1 M Bu_4NBF_4/DCM under the polarization of the first reversible oxidation peak; 1 mT, Amp. 50, 1mW.

7. Calculations

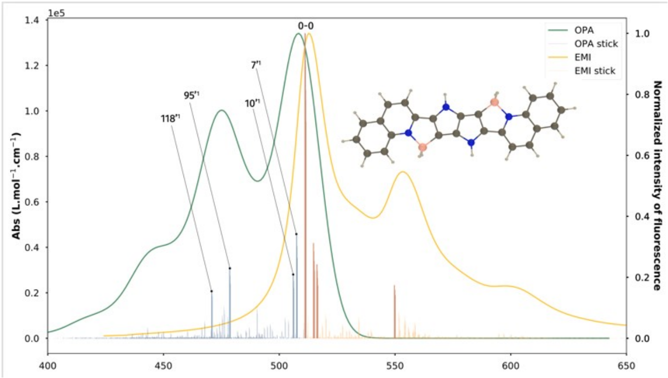
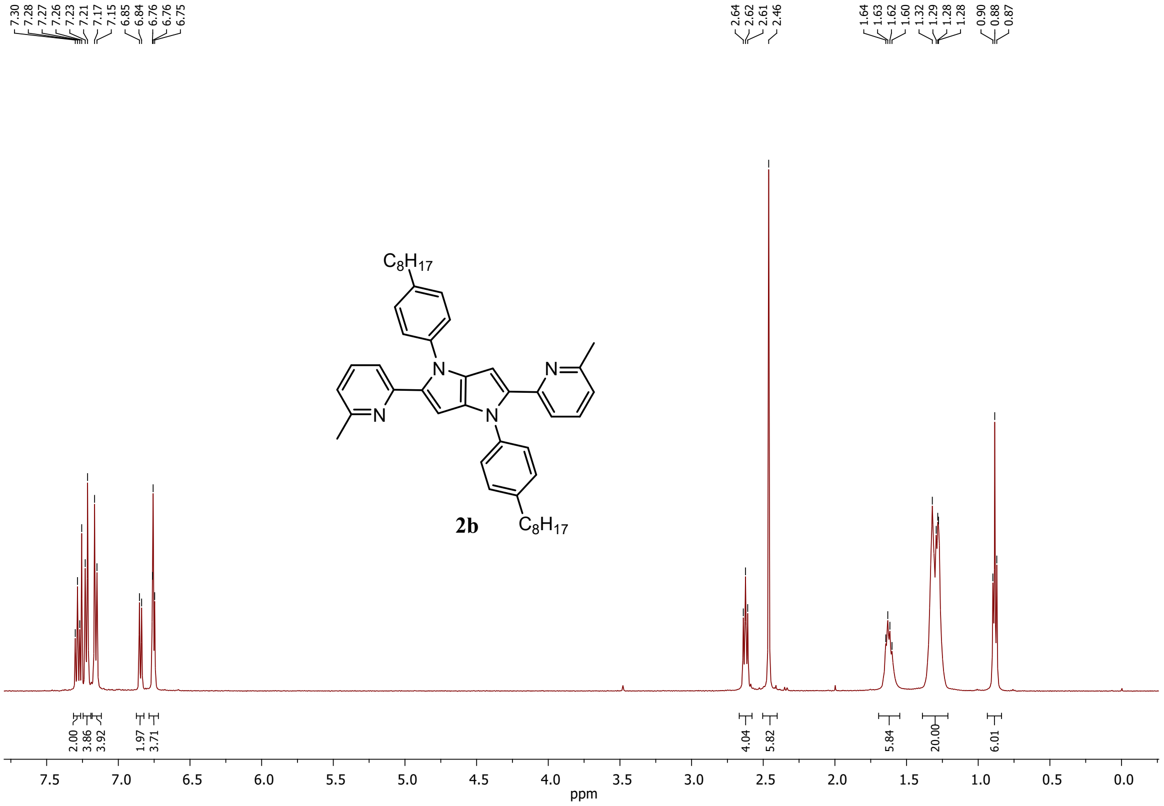
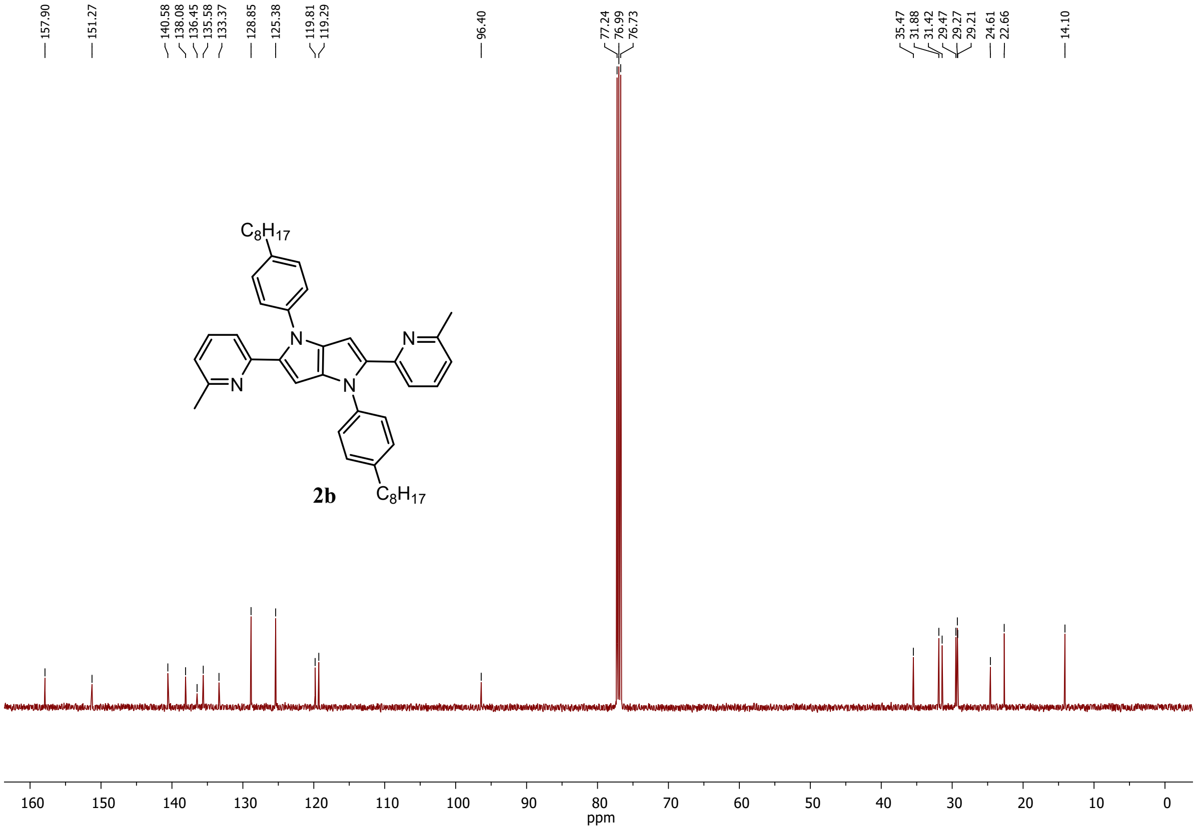
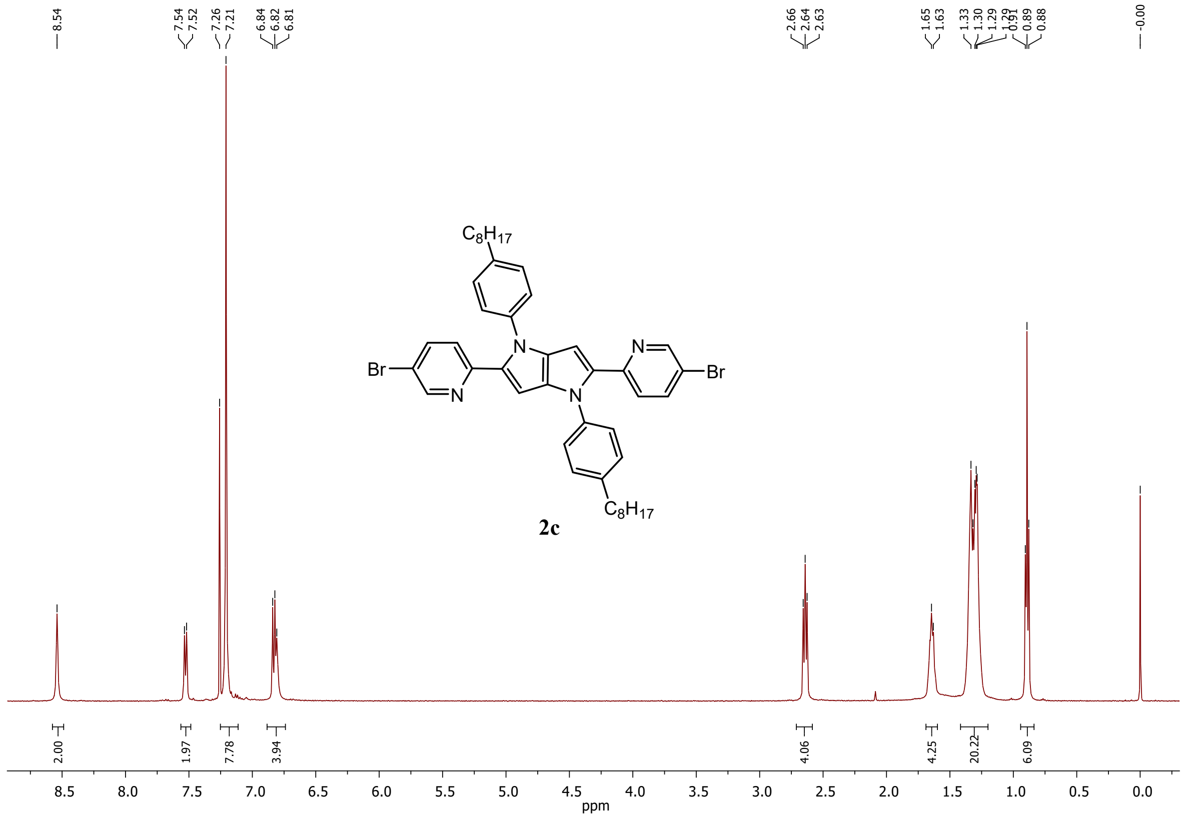


Fig. S4. Vibrationally resolved one-photon absorption and emission spectra for a model of compound of **1f**

8. ^{1}H, ^{13}C, ^{19}F and ^{10}B NMR spectra



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1.63
1.33
1.30
1.29
1.29
0.91
0.89
0.88
-0.00
C8H17
Br
N
N
N
N
Br
C8H17
2c
2.00
1.97
7.78
3.94
4.06
4.25
20.22
6.09
8.5
8.0
7.5
7.0
6.5
6.0
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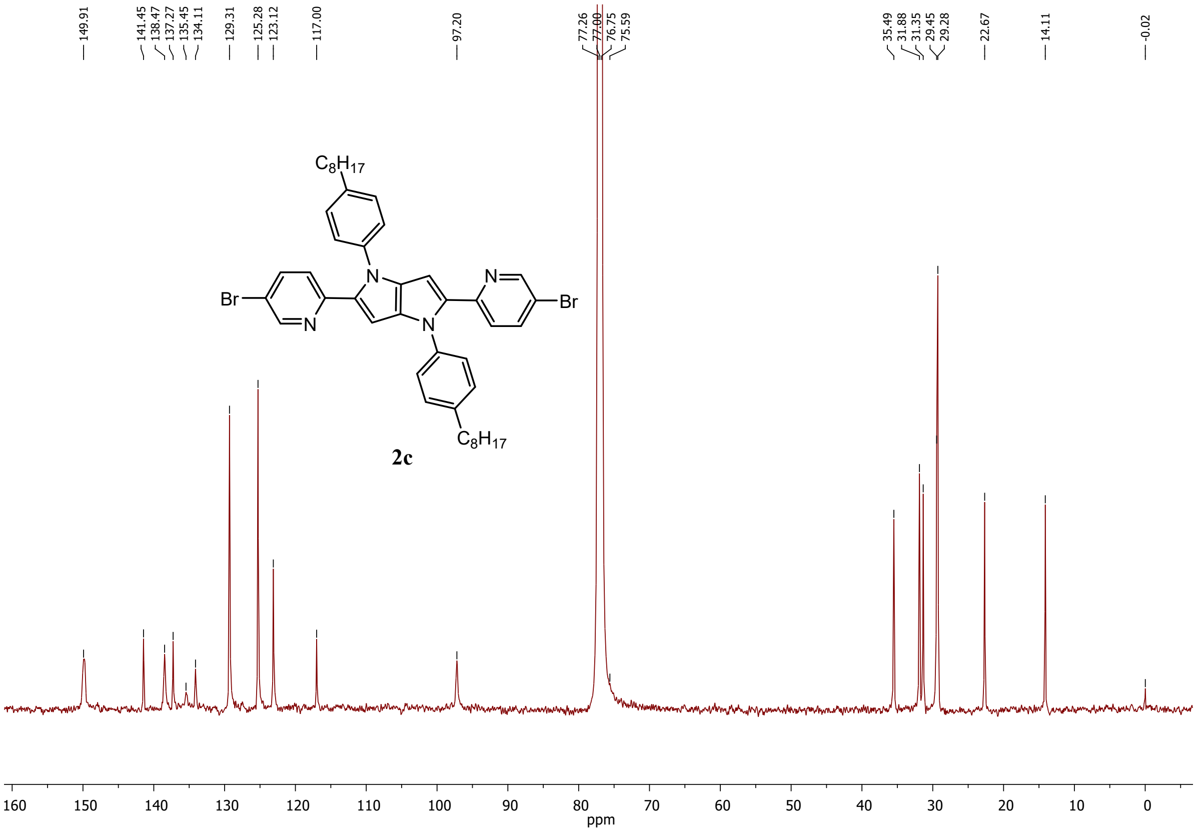
ppm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125.28
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77.00
76.75
75.59
35.49
31.88
31.35
29.45
29.28
22.67
14.11
-0.02
C8H17
Br
N
N
N
N
Br
C8H17
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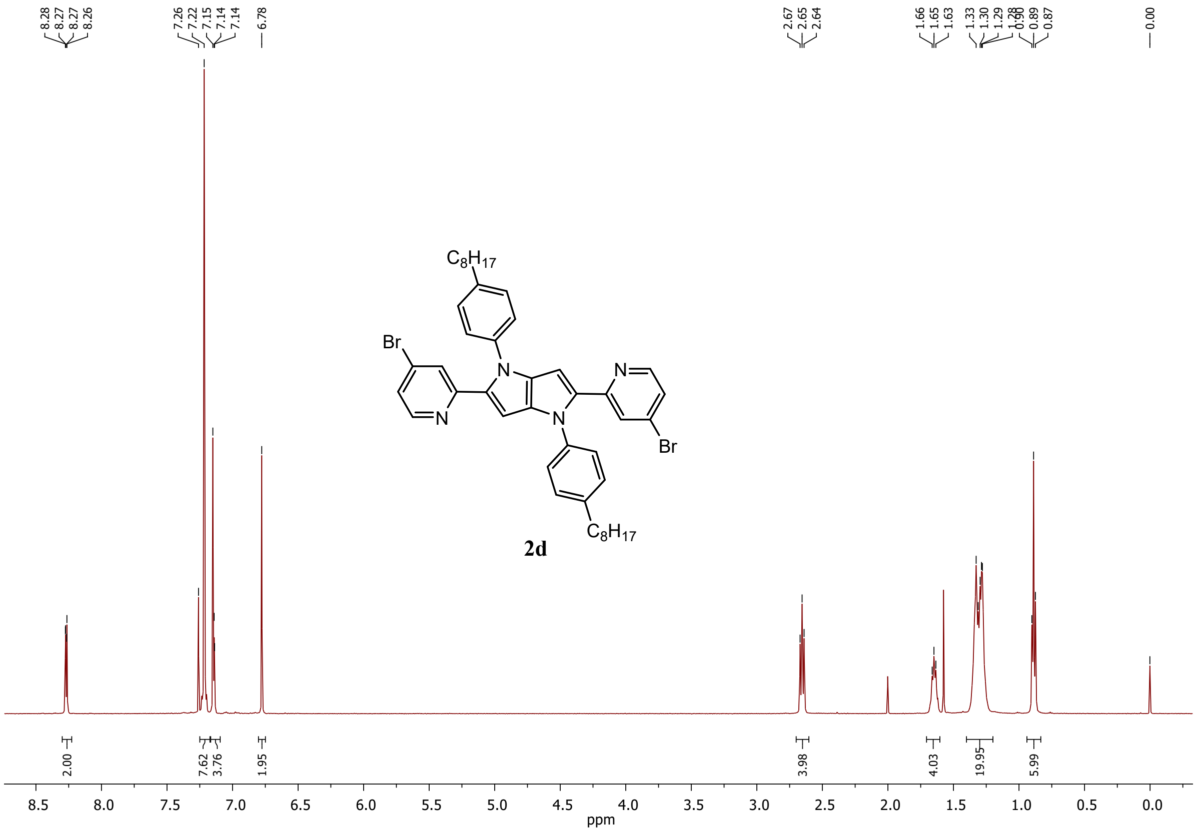
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7.14
7.14
6.78
2.67
2.65
2.64
1.66
1.65
1.63
1.33
1.30
1.29
1.28
0.90
0.89
0.87
0.00
C_8H_{17}
Br
N
N
N
N
Br
C_8H_{17}
2d
2.00
7.62
3.76
1.95
3.98
4.03
19.95
5.99
8.5
8.0
7.5
7.0
6.5
6.0
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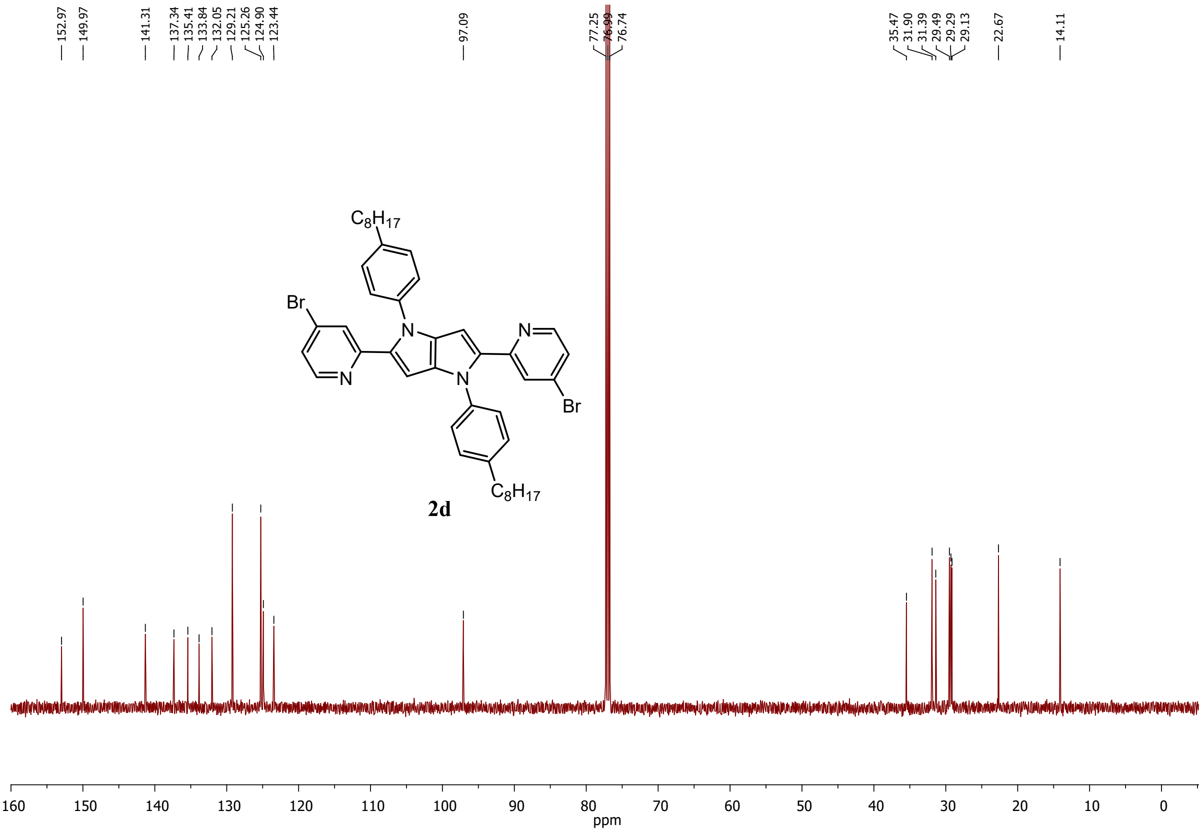
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77.25
76.99
76.74
35.47
31.90
31.39
29.49
29.29
29.13
22.67
14.11
C_8H_{17}
Br
N
N
N
N
Br
C_8H_{17}
2d
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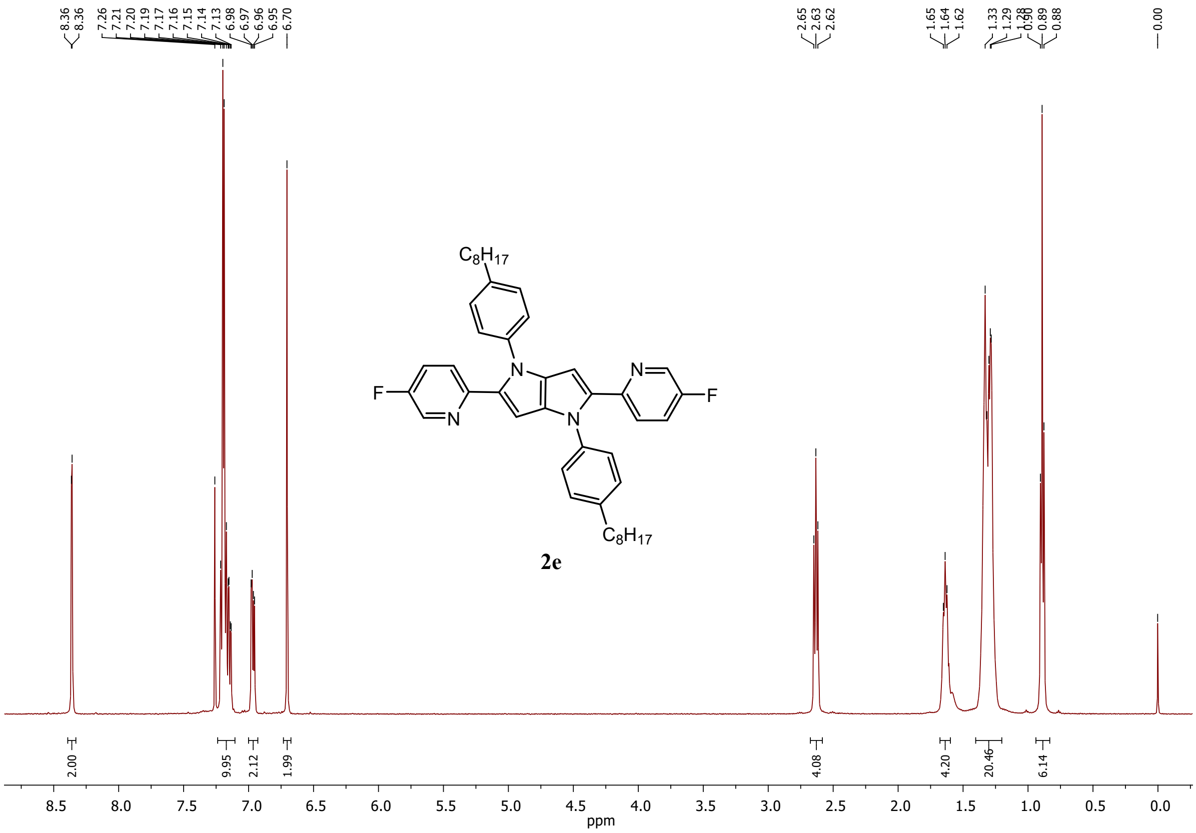
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7.16
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7.14
7.13
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6.96
6.95
6.70
2.65
2.63
2.62
1.65
1.64
1.62
1.33
1.29
1.28
0.90
0.89
0.88
0.00
C8H17
F
N
N
N
N
F
C8H17
2e
2.00
9.95
2.12
1.99
4.08
4.20
20.46
6.14
8.5
8.0
7.5
7.0
6.5
6.0
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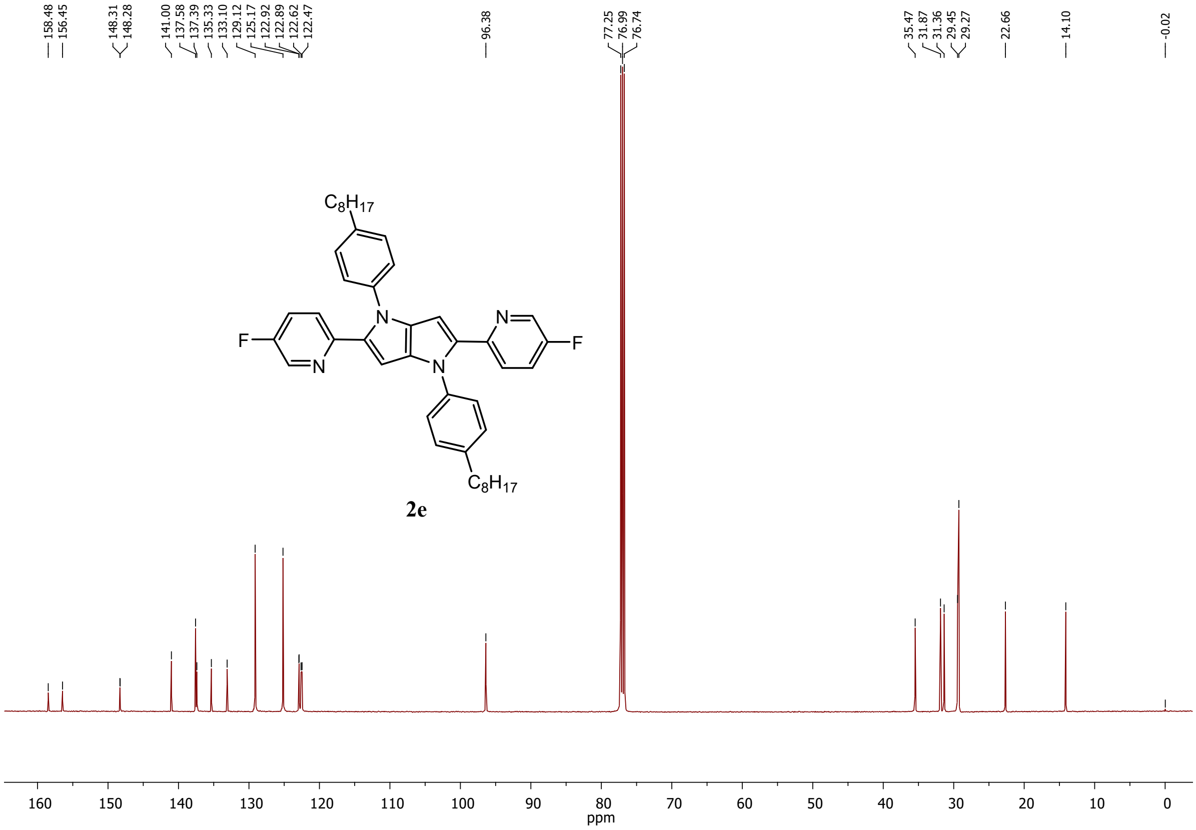
ppm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122.92
122.89
122.62
122.47
96.38
77.25
76.99
76.74
35.47
31.87
31.36
29.45
29.27
22.66
14.10
-0.02
C8H17
F
N
N
N
N
F
C8H17
2e
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100
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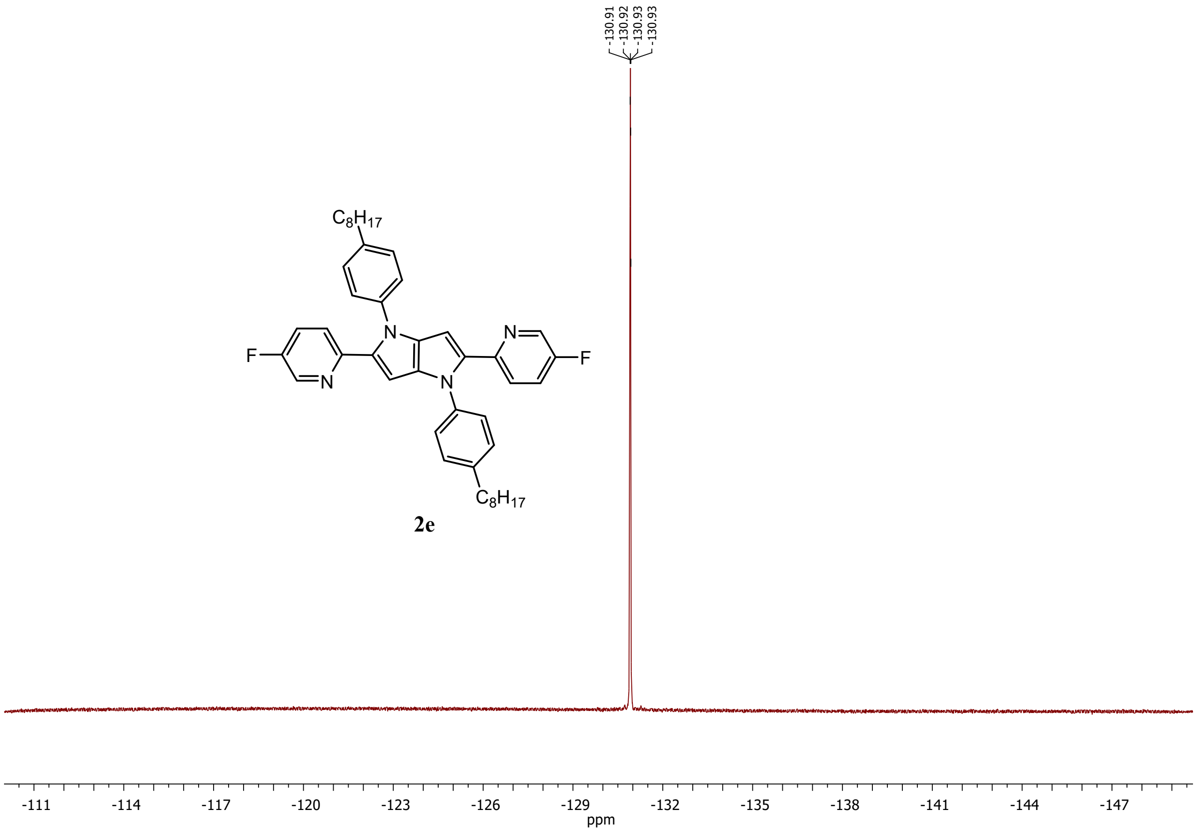

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-130.93
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C8H17
F
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N
N
N
F
C8H17
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-120
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-126
-129
-132
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-138
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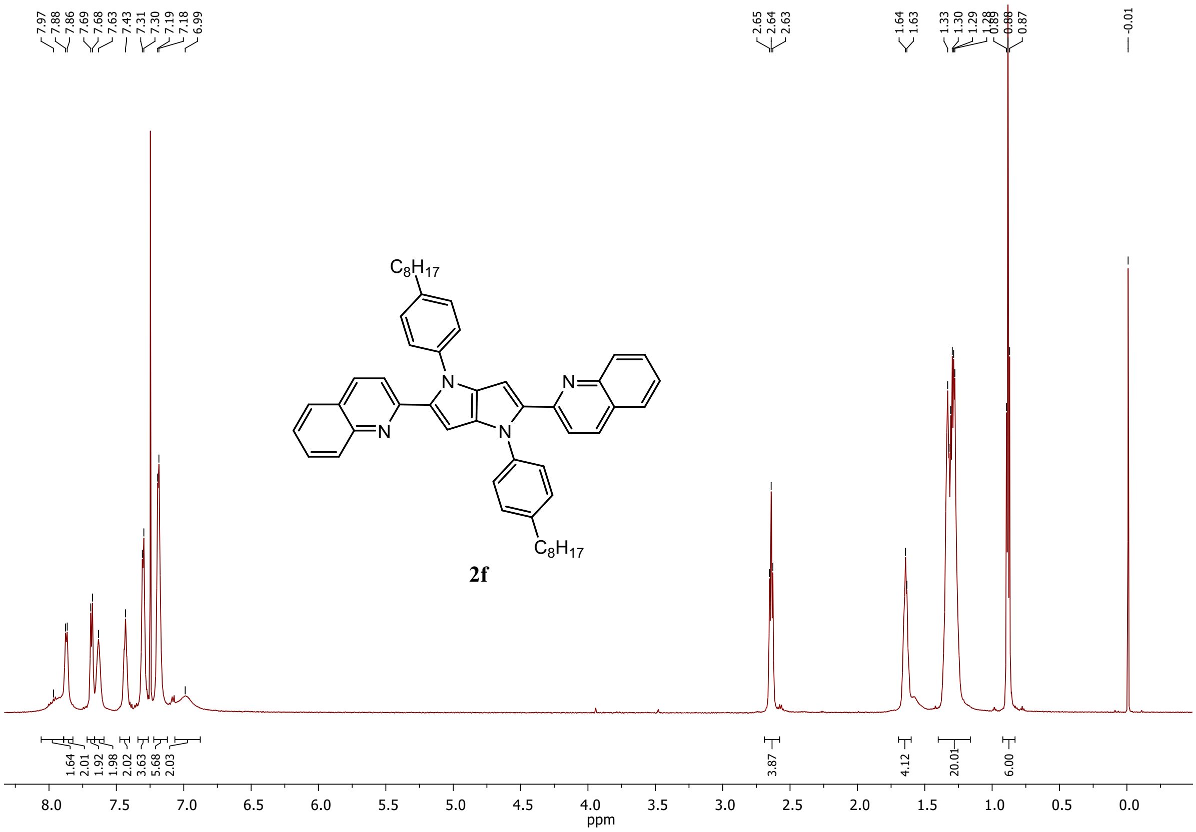
-144
-147
ppm

2e



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7.63
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7.31
7.30
7.19
7.18
6.99
2.65
2.64
2.63
1.64
1.63
1.33
1.30
1.29
1.28
0.89
0.88
0.87
-0.01
C8H17
N
N
N
N
C8H17
1.64
2.01
1.92
1.98
2.02
3.63
5.68
2.03
3.87
4.12
20.01
6.00
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
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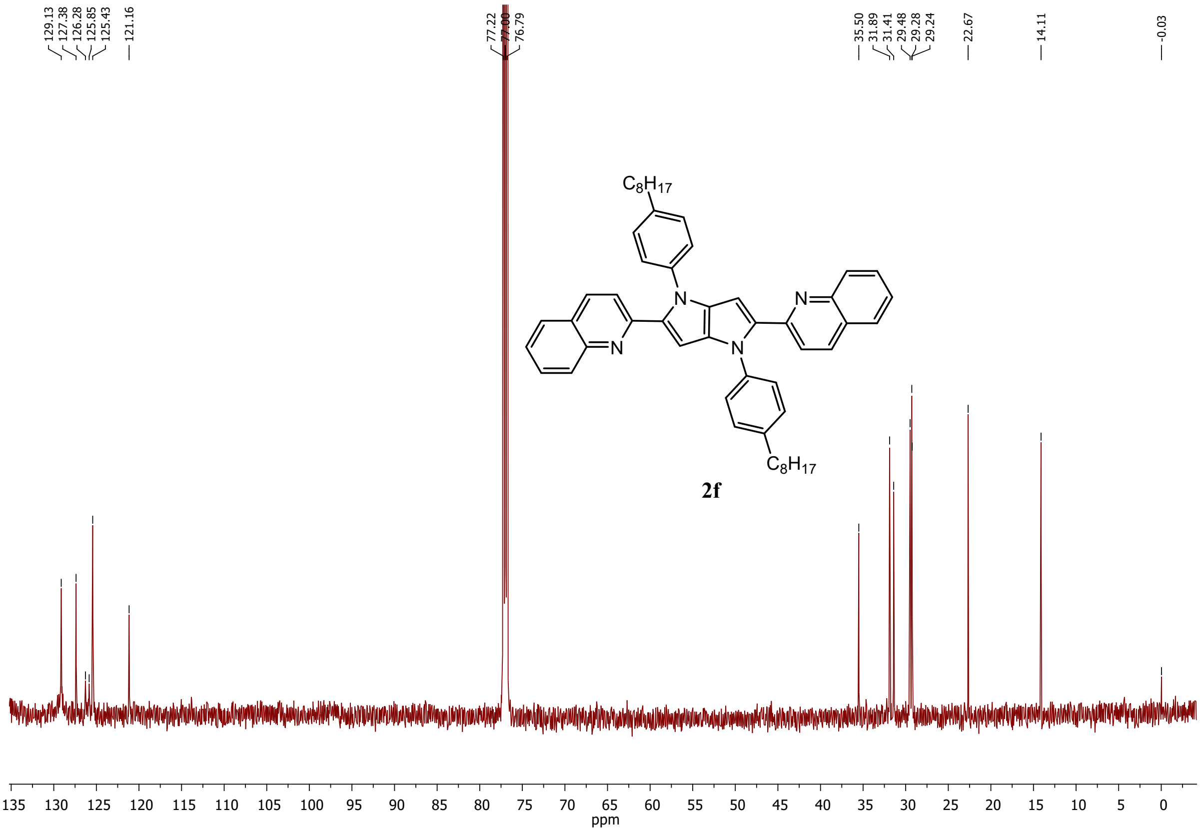
ppm

2f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126.28
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121.16
77.22
77.00
76.79
35.50
31.89
31.41
29.48
29.28
29.24
22.67
14.11
-0.03
C_8H_{17}
N
N
N
N
C_8H_{17}
135
130
125
120
115
110
105
100
95
90
85
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65
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55
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45
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35
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25
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5
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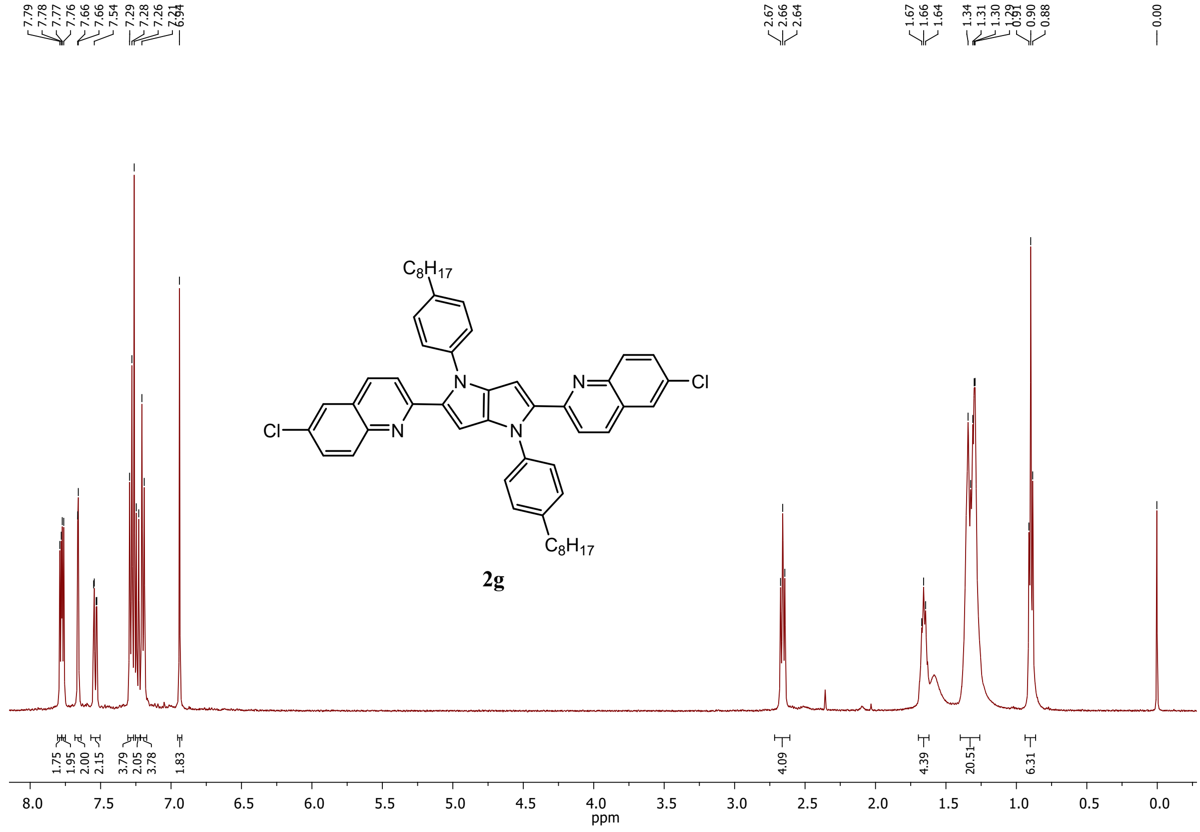
ppm

2f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7.66
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7.26
7.21
6.94
2.67
2.66
2.64
1.67
1.66
1.64
1.34
1.31
1.30
1.29
0.91
0.90
0.88
0.00
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Cl
N
N
N
N
Cl
C_8H_{17}
1.75
1.95
2.00
2.15
3.79
2.05
3.78
1.83
4.09
4.39
20.51
6.31
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
2.5
2.0
1.5
1.0
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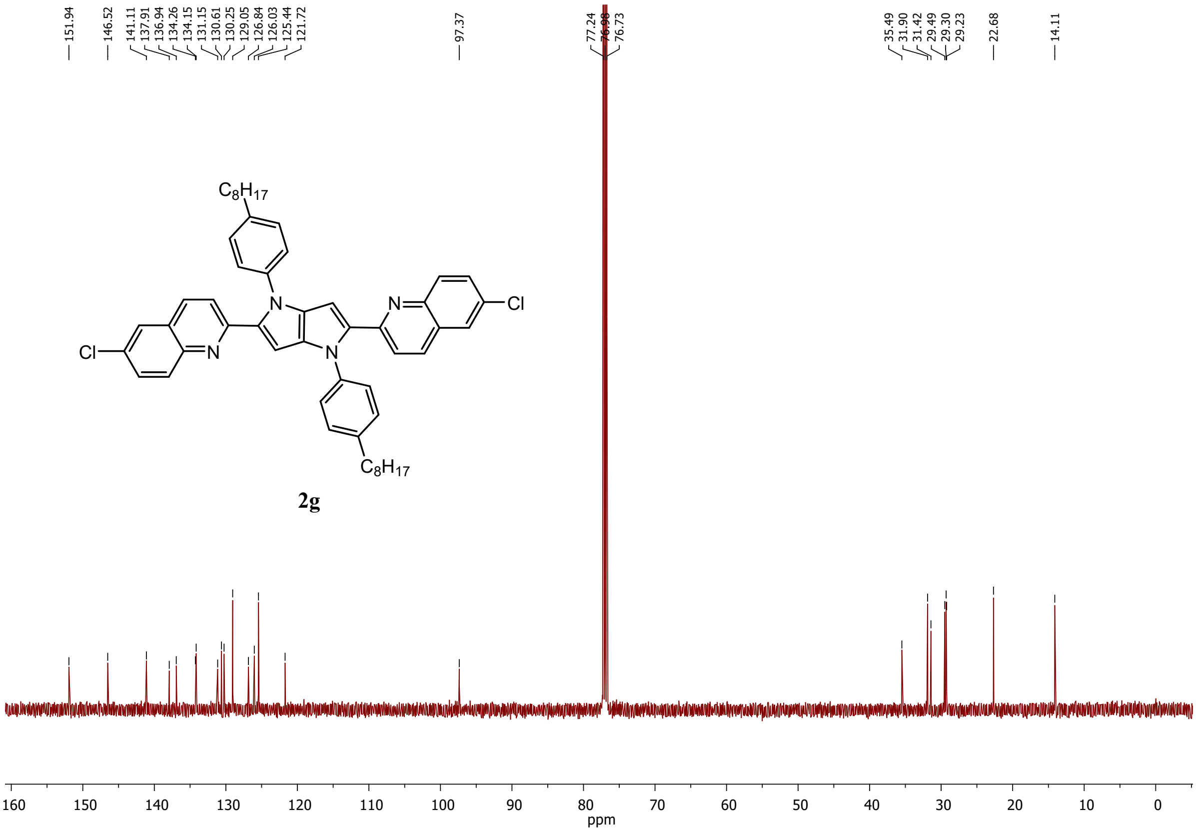
0.0
ppm

2g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130.25
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126.84
126.03
125.44
121.72
97.37
77.24
76.98
76.73
35.49
31.90
31.42
29.49
29.30
29.23
22.68
14.11
C_8H_{17}
N
N
Cl
Cl
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140
130
120
110
100
90
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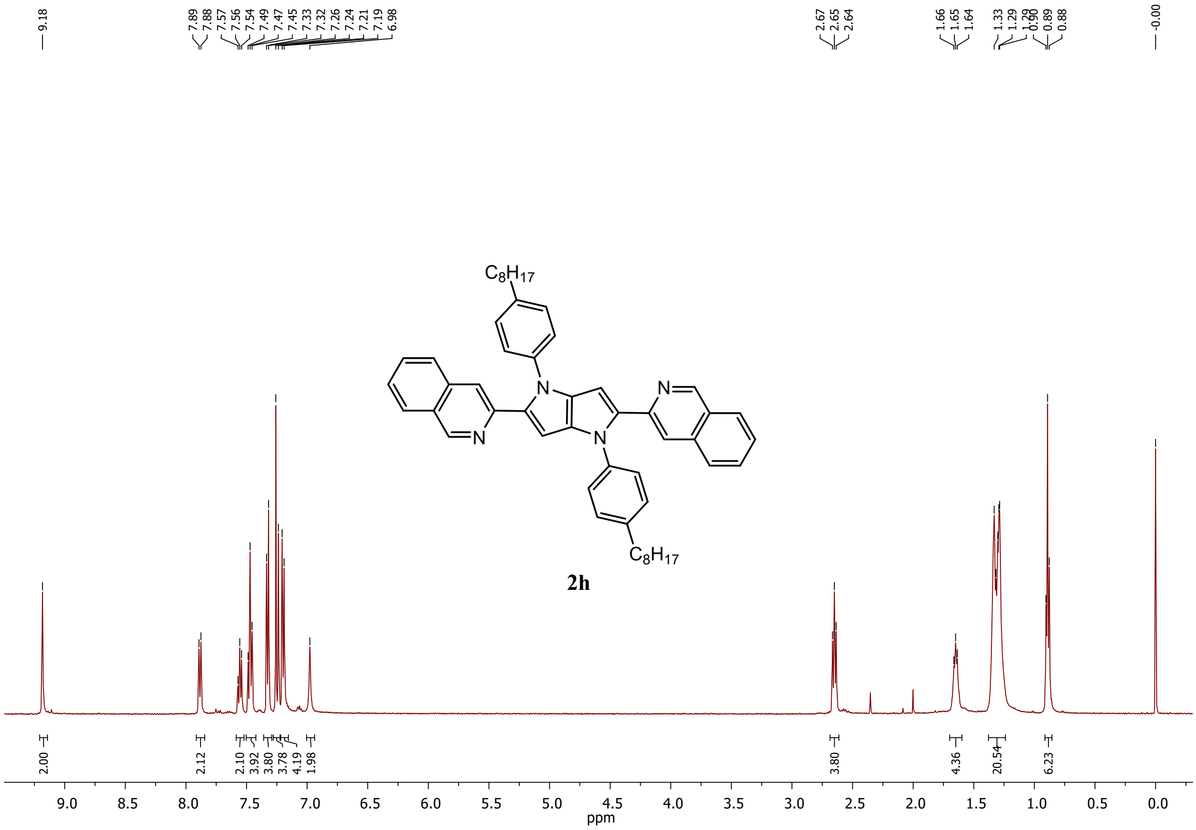
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7.89
7.88
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7.54
7.49
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7.45
7.33
7.32
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7.24
7.21
7.19
6.98
2.67
2.65
2.64
1.66
1.65
1.64
1.33
1.29
1.29
0.90
0.89
0.88
-0.00
C_8H_{17}
N
N
2.00
2.12
2.10
3.92
3.80
3.78
4.19
1.98
3.80
4.36
20.54
6.23
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.0
3.5
3.0
2.5
2.0
1.5
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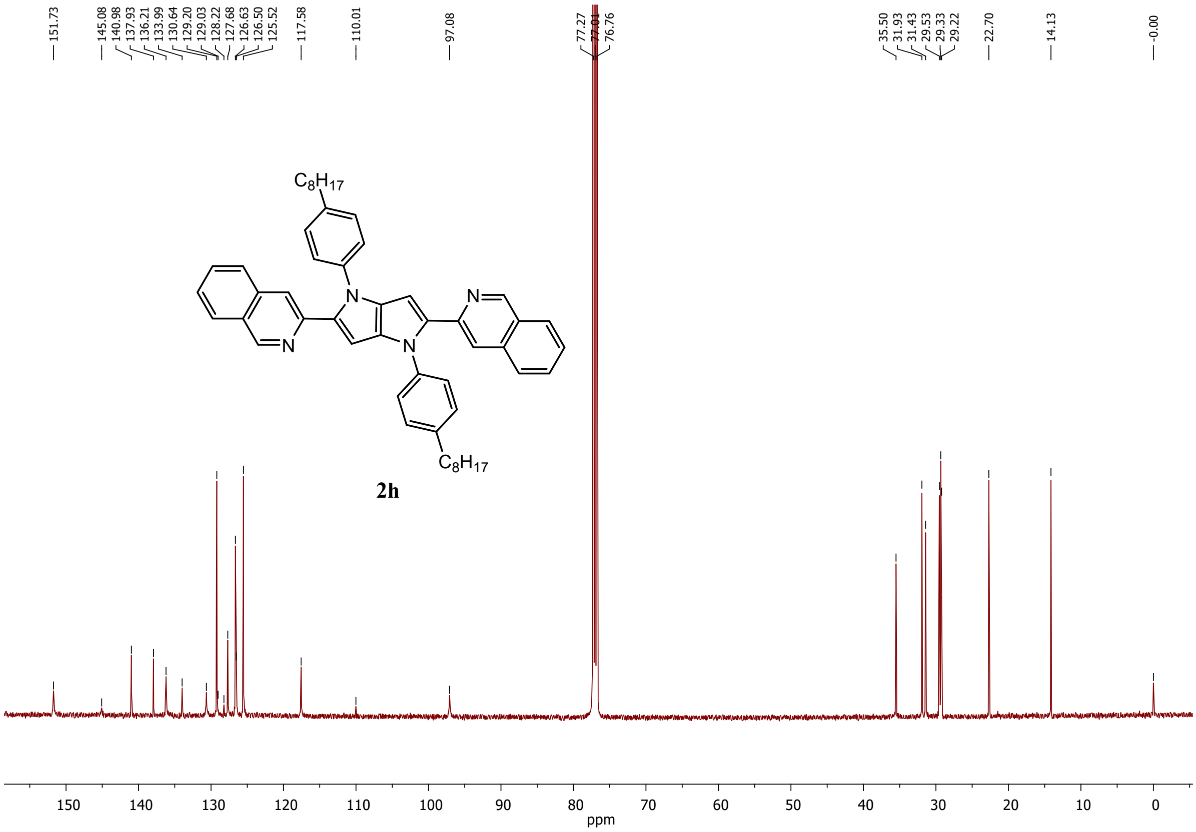
ppm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125.52
117.58
110.01
97.08
77.27
77.01
76.76
35.50
31.93
31.43
29.53
29.33
29.22
22.70
14.13
-0.00
C8H17
N
N
N
N
C8H17
2h
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140
130
120
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20
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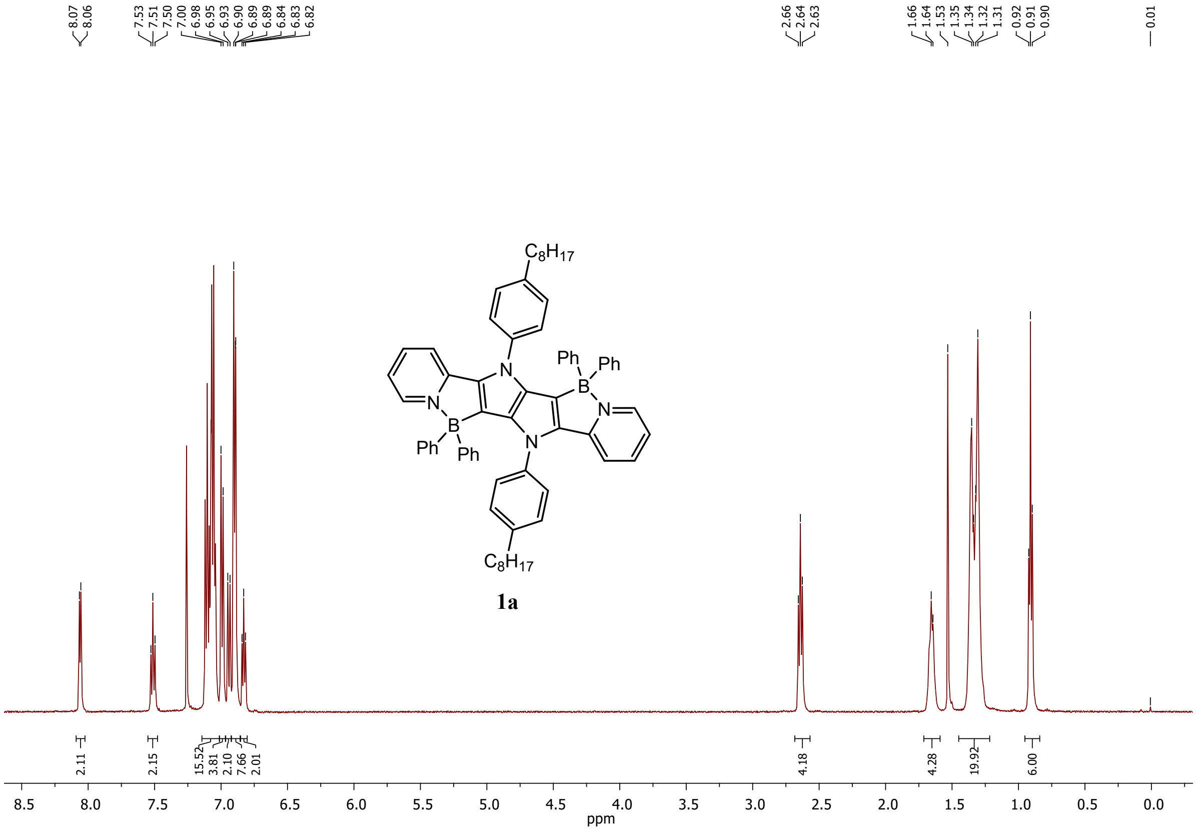
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6.84
6.83
6.82
2.66
2.64
2.63
1.66
1.64
1.53
1.35
1.34
1.32
1.31
0.92
0.91
0.90
0.01
C8H17
Ph
Ph
B
N
N
N
N
B
Ph
Ph
C8H17
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2.15
15.52
3.81
2.10
7.66
2.01
4.18
4.28
19.92
6.00
8.5
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7.0
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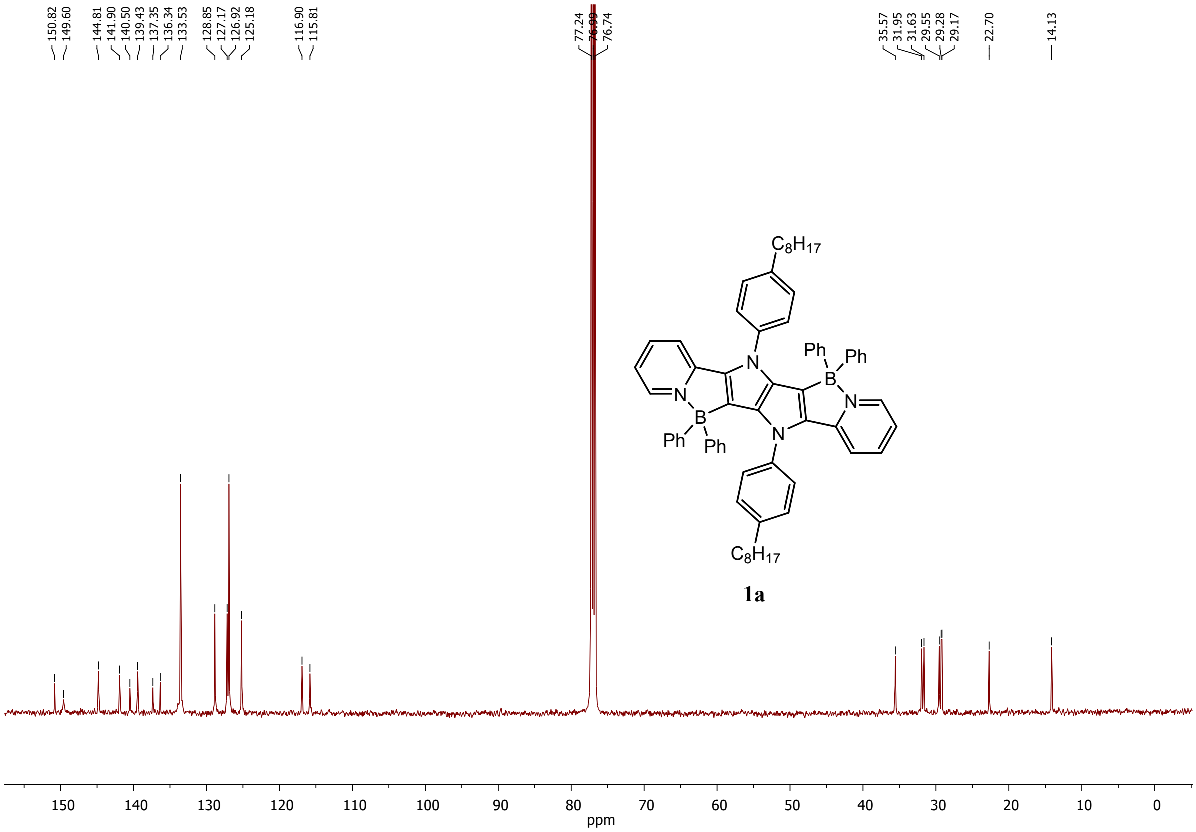
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125.18
116.90
115.81
77.24
76.99
76.74
35.57
31.95
31.63
29.55
29.28
29.17
22.70
14.13
C8H17
N
Ph
Ph
B
N
N
B
Ph
Ph
N
C8H17
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20
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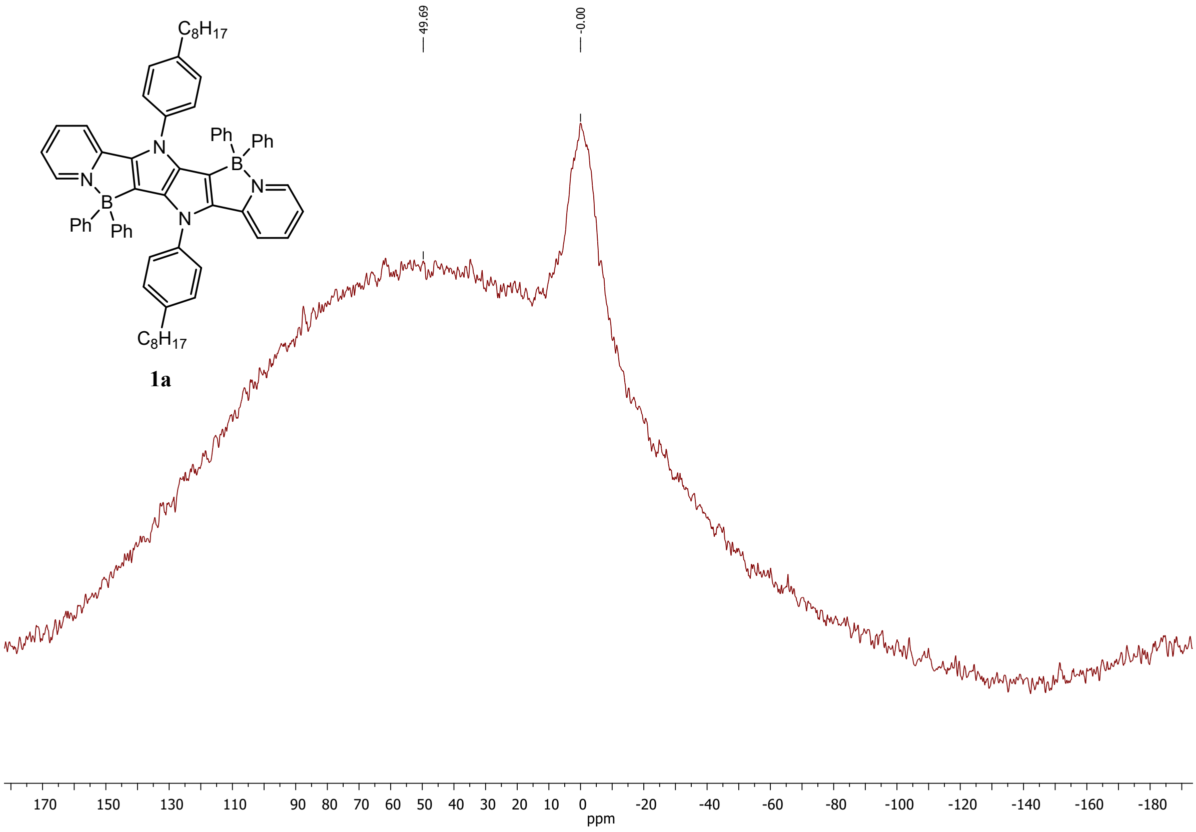
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150
130
110
90
80
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-60
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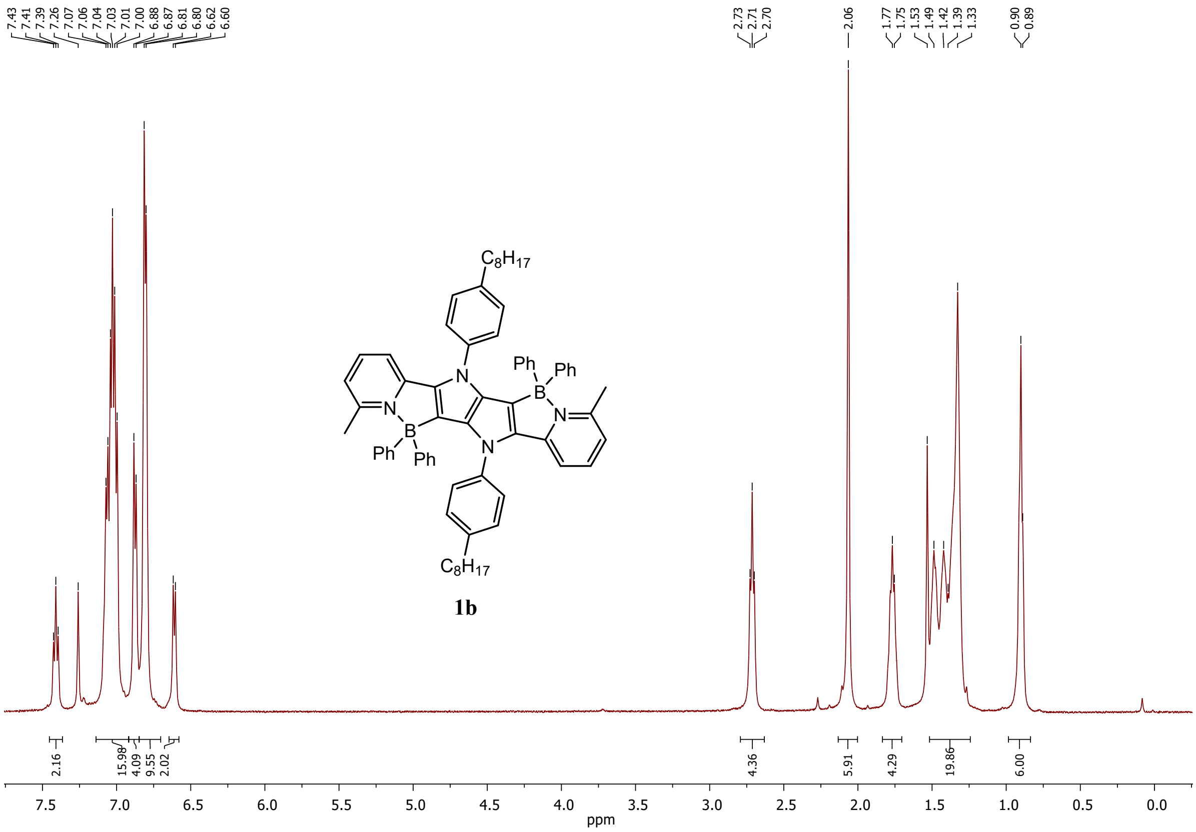
-180
ppm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6.81
6.80
6.62
6.60
2.73
2.71
2.70
2.06
1.77
1.75
1.53
1.49
1.42
1.39
1.33
0.90
0.89
C_8H_{17}
N
Ph
Ph
B
N
N
B
Ph
Ph
N
C_8H_{17}
1b
2.16
15.98
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5.91
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6.5
6.0
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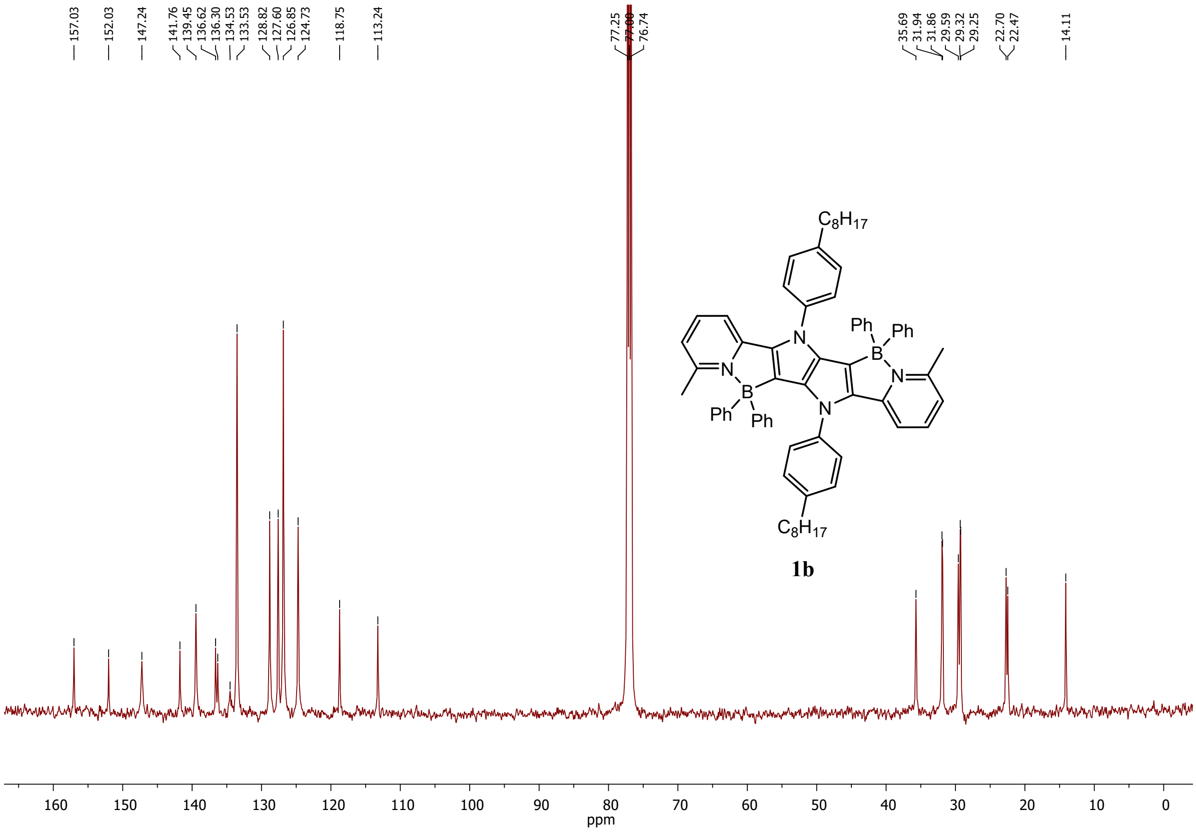
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127.60
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124.73
118.75
113.24
77.25
77.00
76.74
35.69
31.94
31.86
29.59
29.32
29.25
22.70
22.47
14.11
C_8H_{17}
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Ph
Ph
B
N
N
B
Ph
Ph
N
C_8H_{17}
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120
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60
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20
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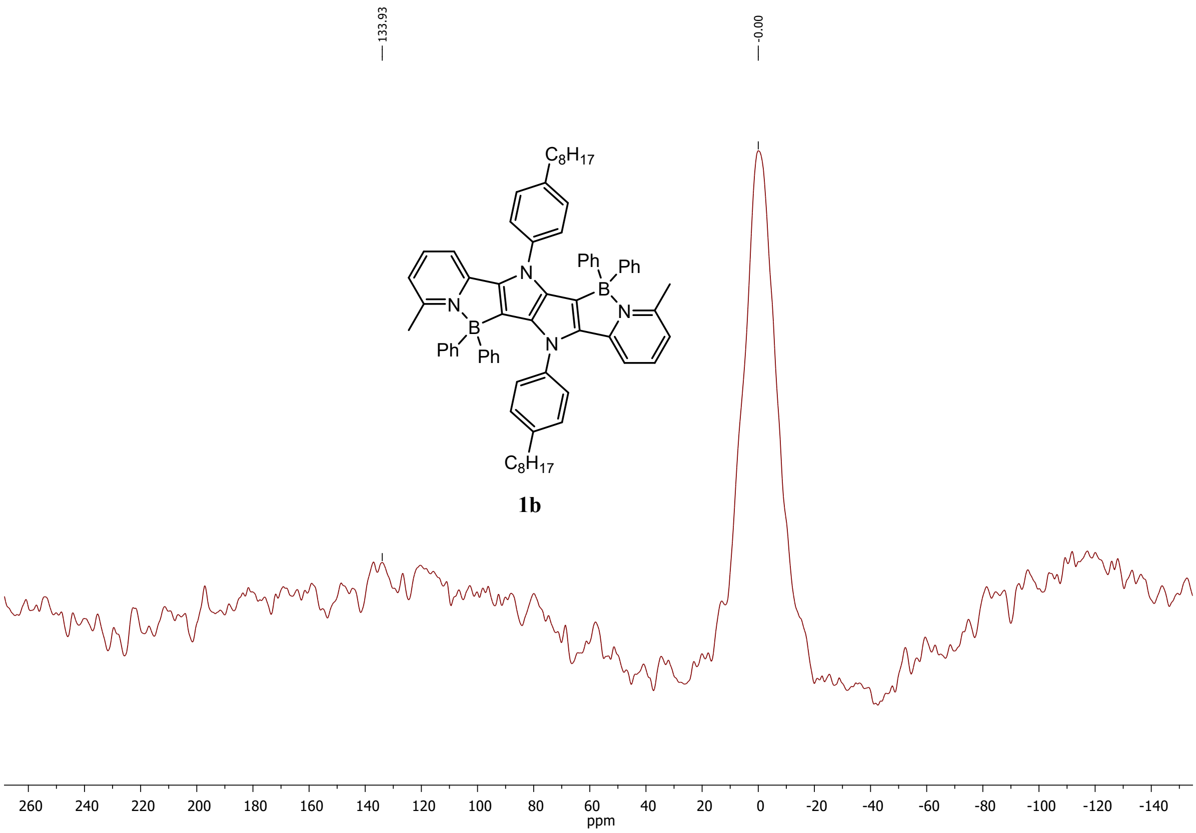
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B
Ph
Ph
N
N
C_8H_{17}
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240
220
200
180
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60
40
20
0
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-40
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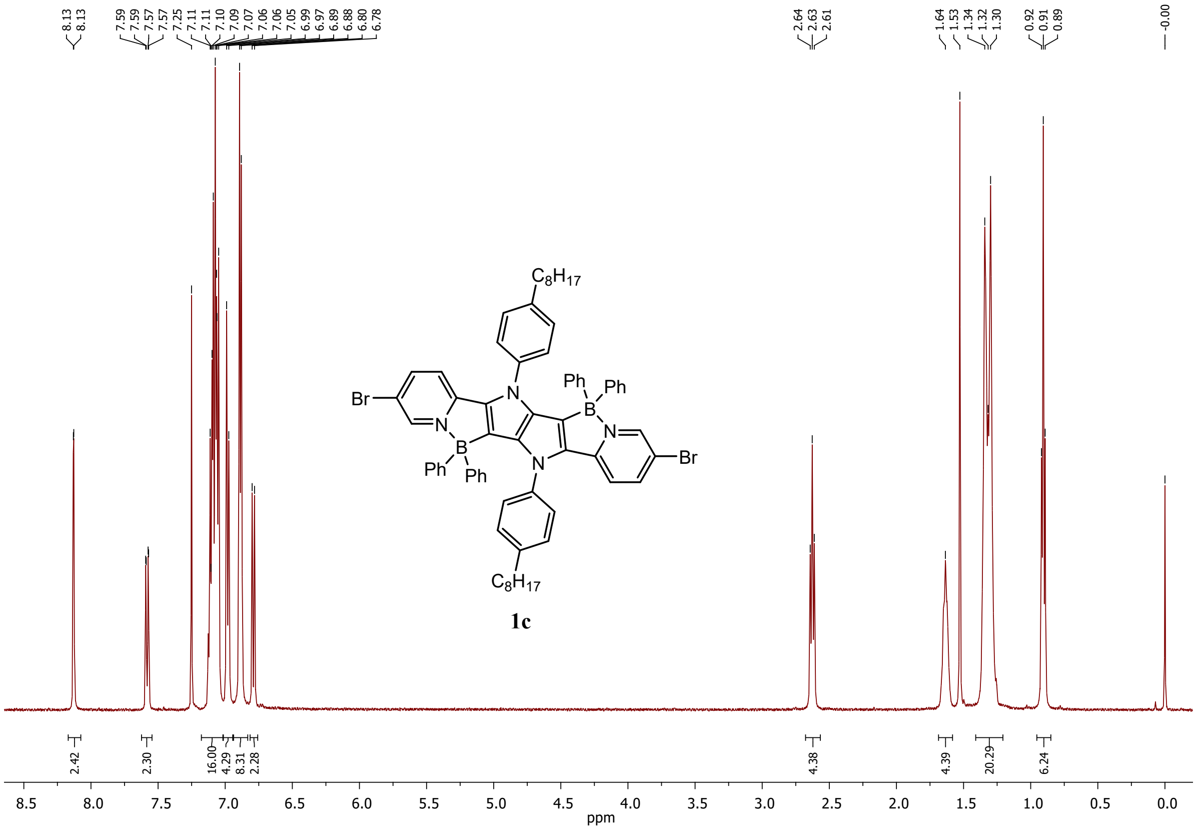
-80
-100
-120
-140
ppm

1b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7.10
7.09
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7.06
7.05
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6.89
6.88
6.80
6.78
2.64
2.63
2.61
1.64
1.53
1.34
1.32
1.30
0.92
0.91
0.89
-0.00
C_8H_{17}
Br
N
Ph
B
Ph
N
B
Ph
Ph
N
N
Br
C_8H_{17}
2.42
2.30
16.00
4.29
8.31
2.28
4.38
4.39
20.29
6.24
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
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1.0
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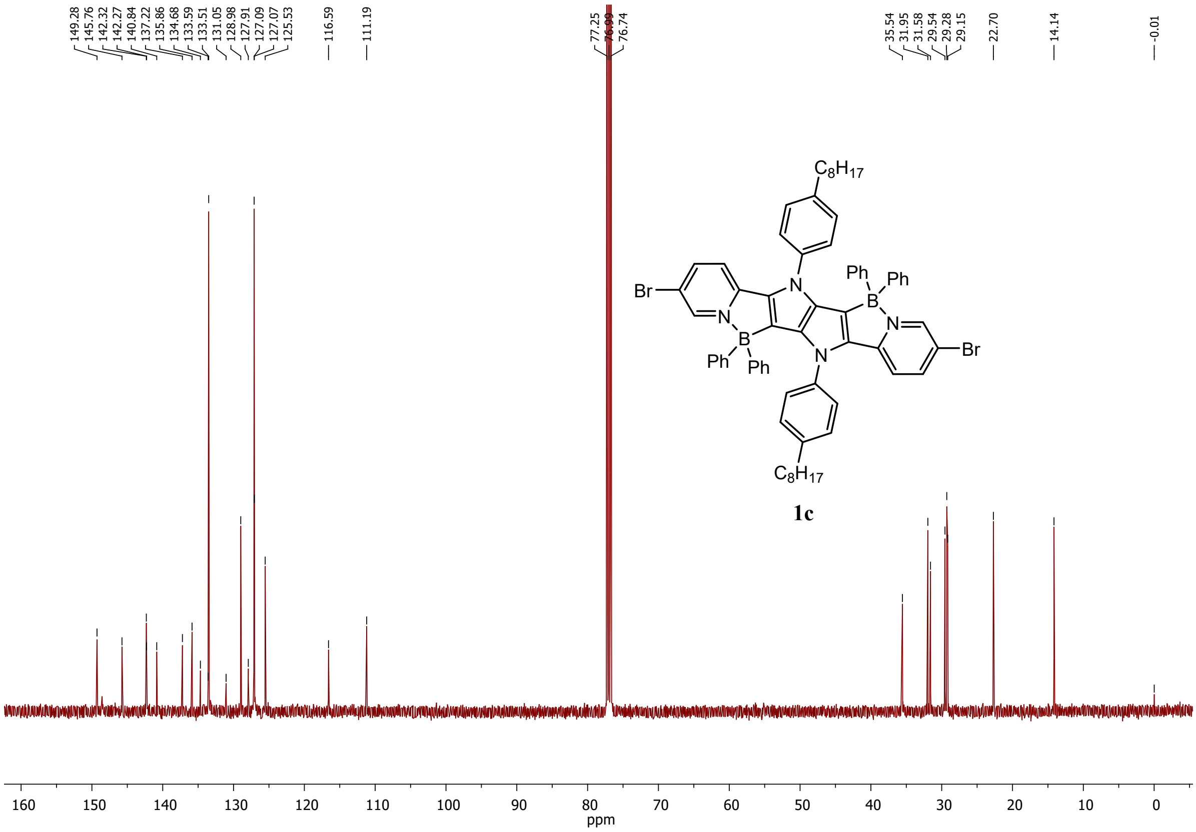
0.0
ppm

1c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111.19
77.25
76.99
76.74
35.54
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29.54
29.28
29.15
22.70
14.14
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C_8H_{17}
Br
N
Ph
B
N
Ph
Ph
B
Ph
N
N
Br
C_8H_{17}
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50
40
30
20
10
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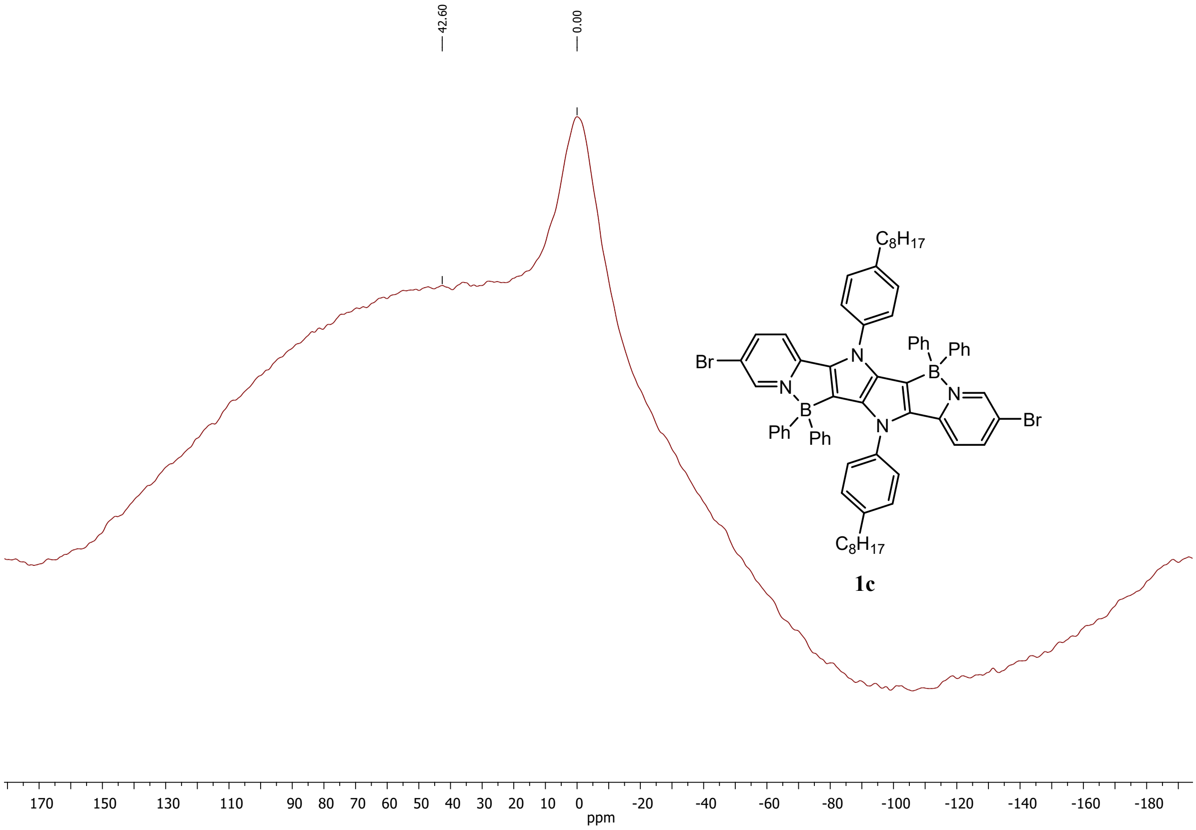
ppm

1c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Ph
Ph
B
N
B
Ph
Ph
N
N
Br
C_8H_{17}
170
150
130
110
90
80
70
60
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-120
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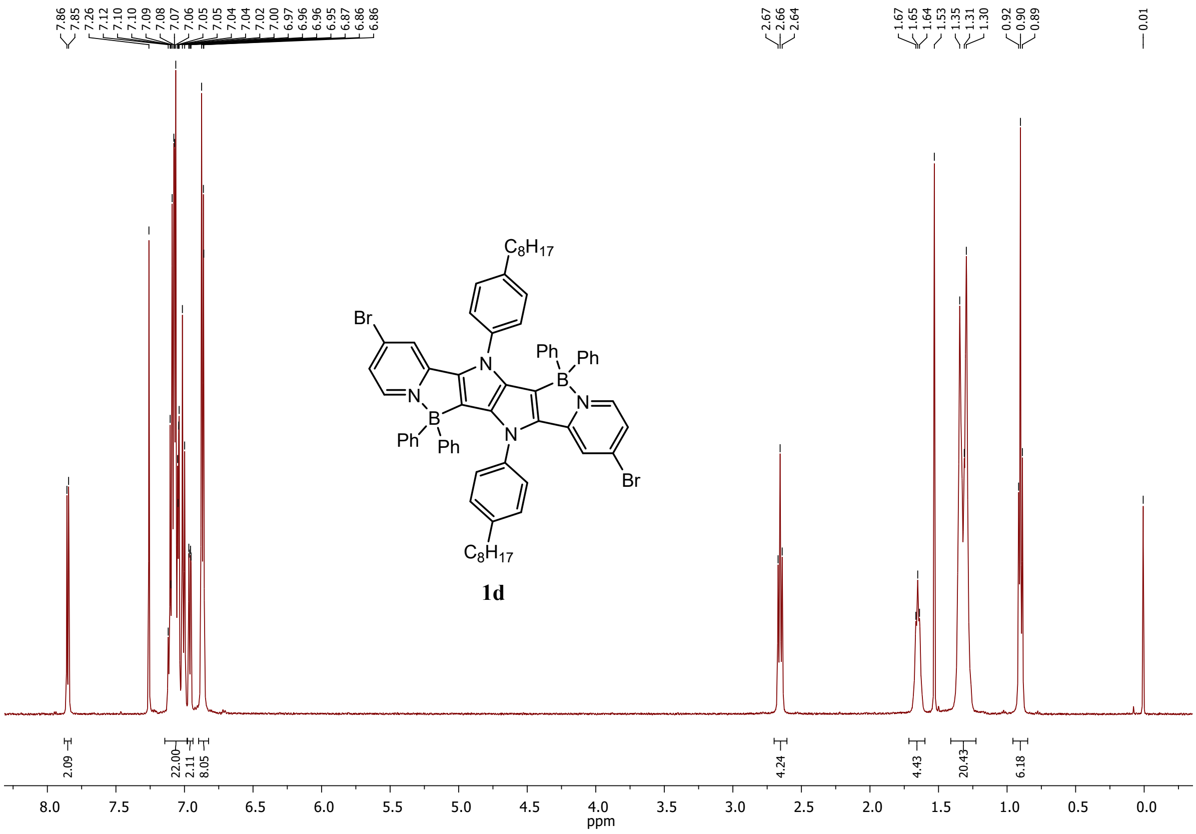
-160
-180
ppm

1c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7.05
7.05
7.04
7.04
7.02
7.00
6.97
6.96
6.96
6.95
6.87
6.86
6.86
2.67
2.66
2.64
1.67
1.65
1.64
1.53
1.35
1.31
1.30
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0.90
0.89
0.01
2.09
22.00
2.11
8.05
4.24
4.43
20.43
6.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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1.5
1.0
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C8H17
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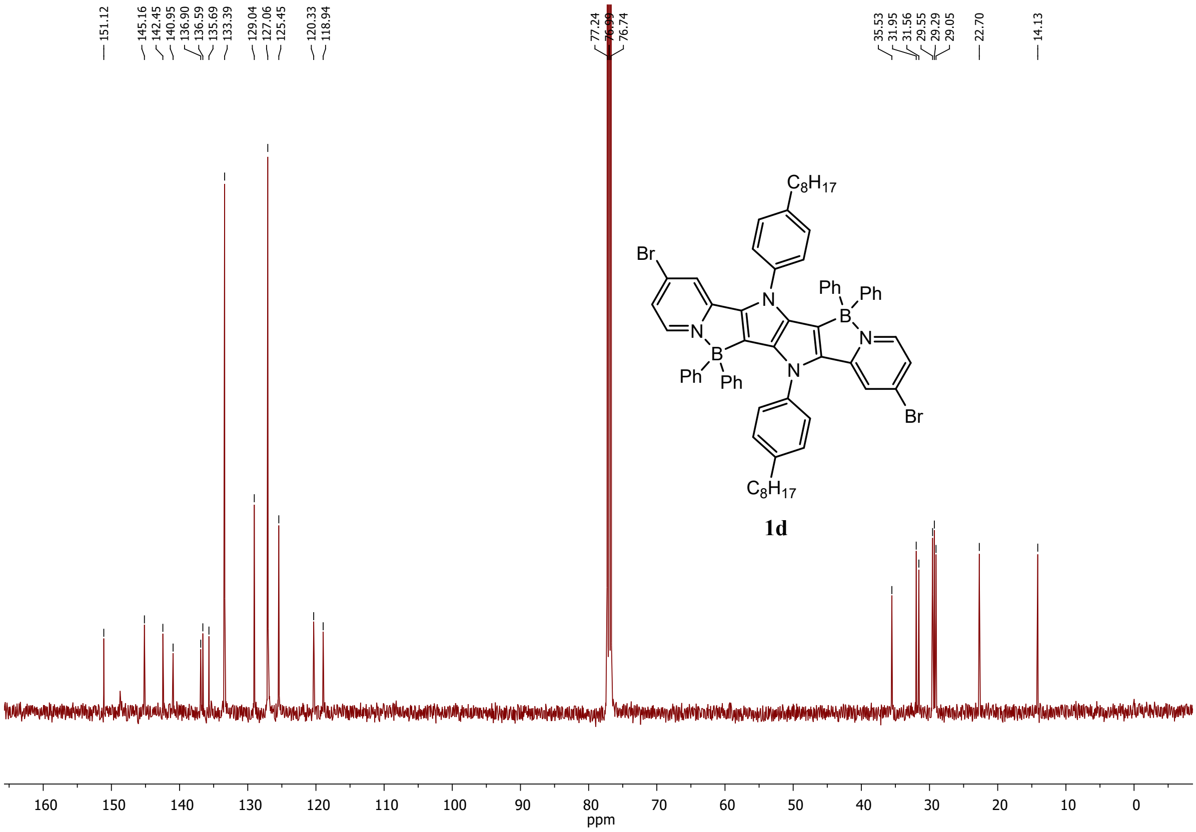
N
Ph
B
1d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127.06
125.45
120.33
118.94
77.24
76.99
76.74
35.53
31.95
31.56
29.55
29.29
29.05
22.70
14.13
160
150
140
130
120
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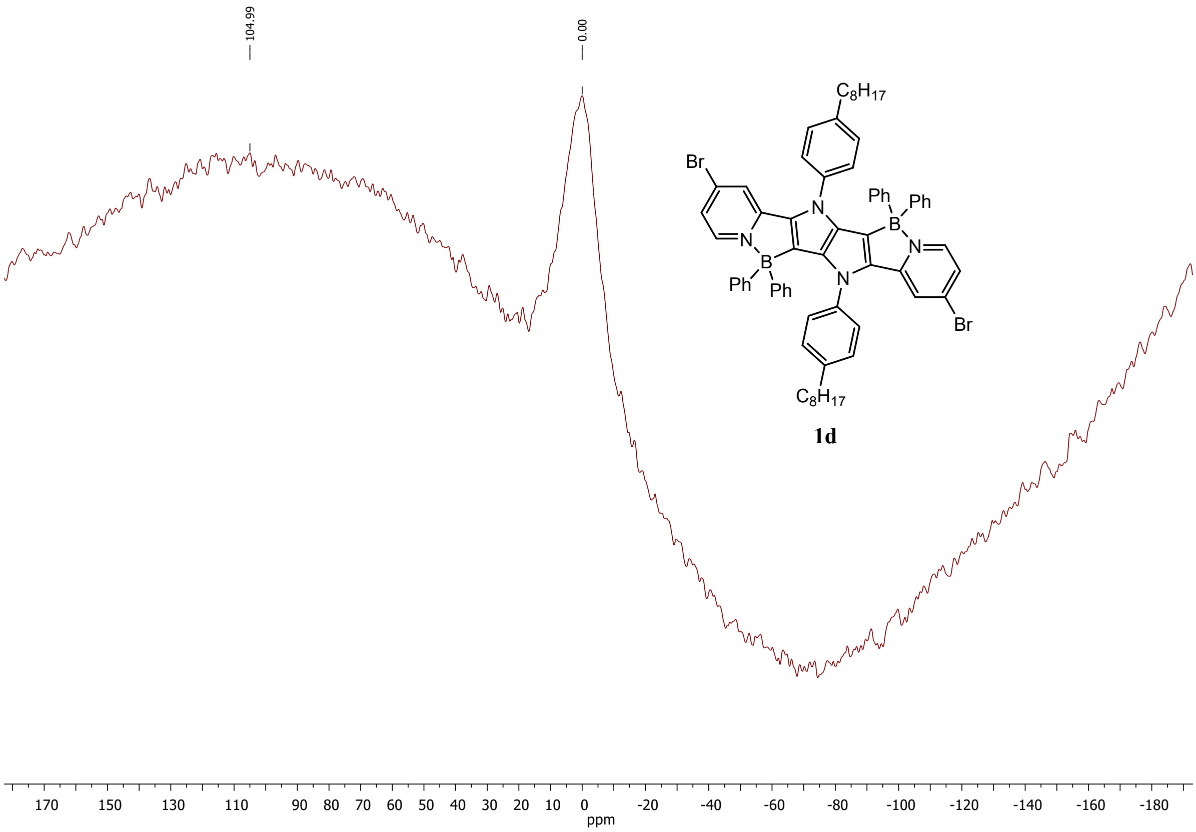
N
Ph
B
1d



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Ph
B
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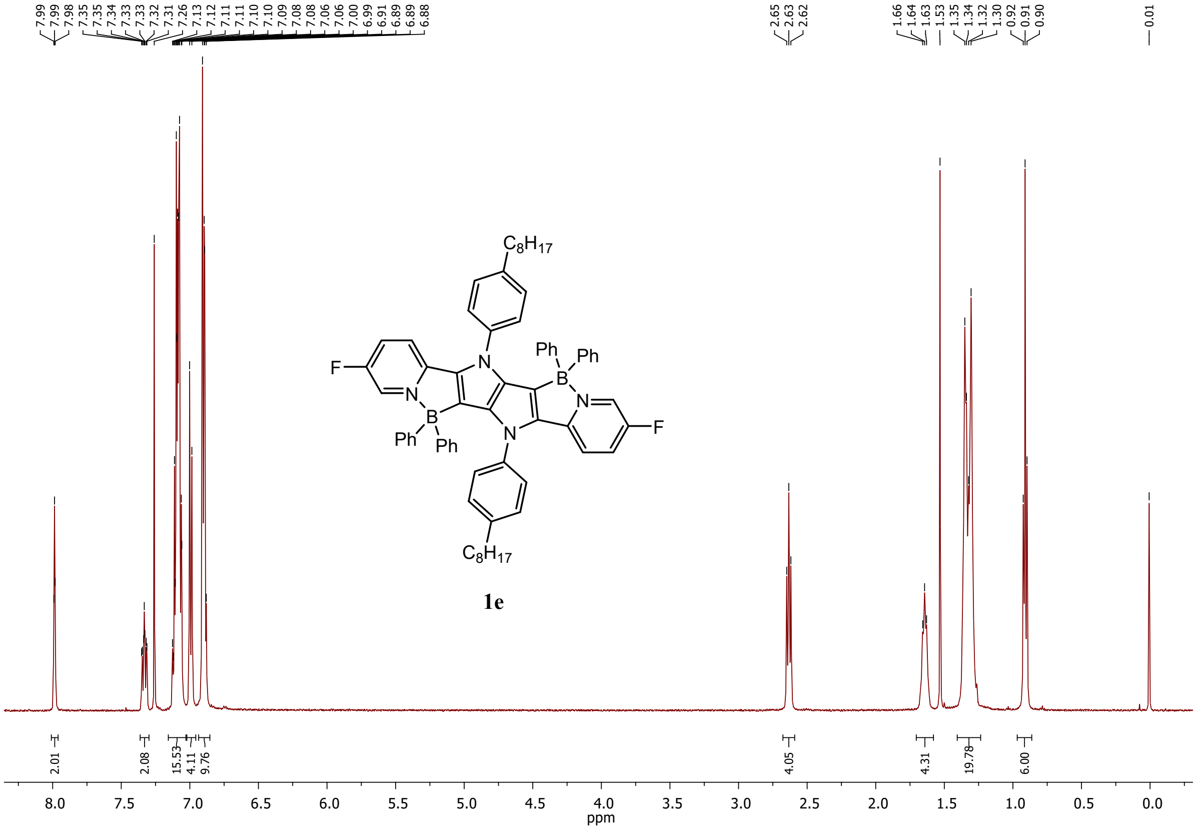
-160
-180
ppm

1d



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7.32
7.31
7.26
7.13
7.12
7.11
7.11
7.10
7.10
7.09
7.08
7.08
7.06
7.06
7.00
6.99
6.91
6.89
6.89
6.88
2.65
2.63
2.62
1.66
1.64
1.63
1.53
1.35
1.34
1.32
1.30
0.92
0.91
0.90
-0.01
C8H17
F
N
Ph
B
2.01
2.08
15.53
4.11
9.76
4.05
4.31
19.78
6.00
8.0
7.5
7.0
6.5
6.0
5.5
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2.5
2.0
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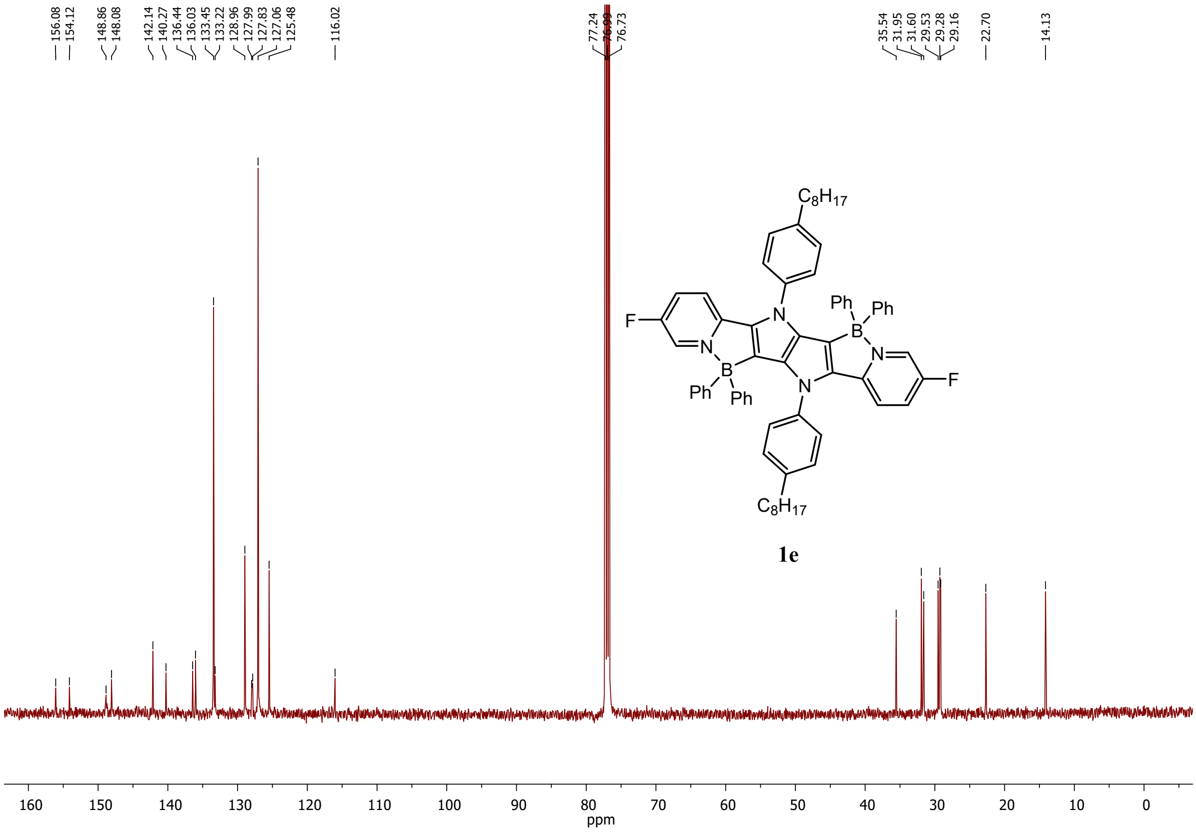
1.0
0.5
0.0
ppm

1e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133.22
128.96
127.99
127.83
127.06
125.48
116.02
77.24
76.99
76.73
35.54
31.95
31.60
29.53
29.28
29.16
22.70
14.13
C_8H_{17}
F
N
Ph
B
N
F
C_8H_{17}
1e
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140
130
120
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100
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20
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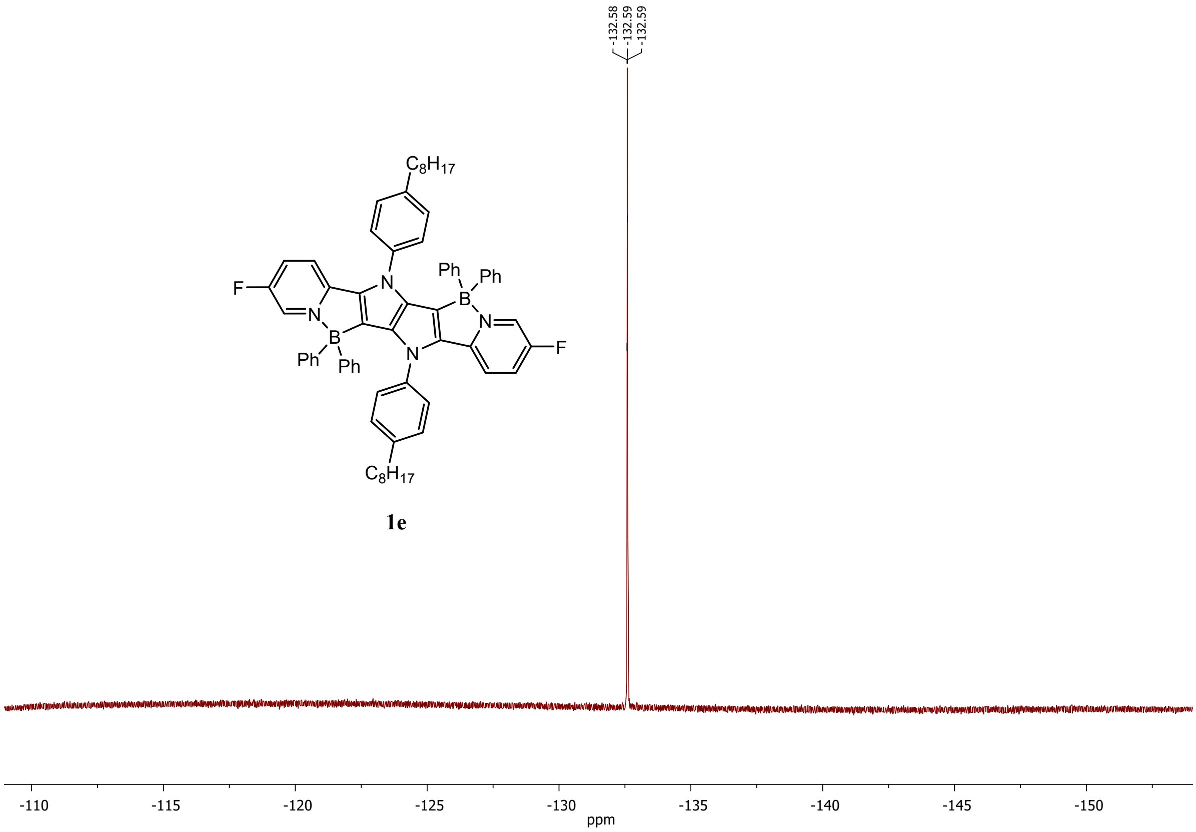
0
ppm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-132.59
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N
Ph
B
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F
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-120
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-140
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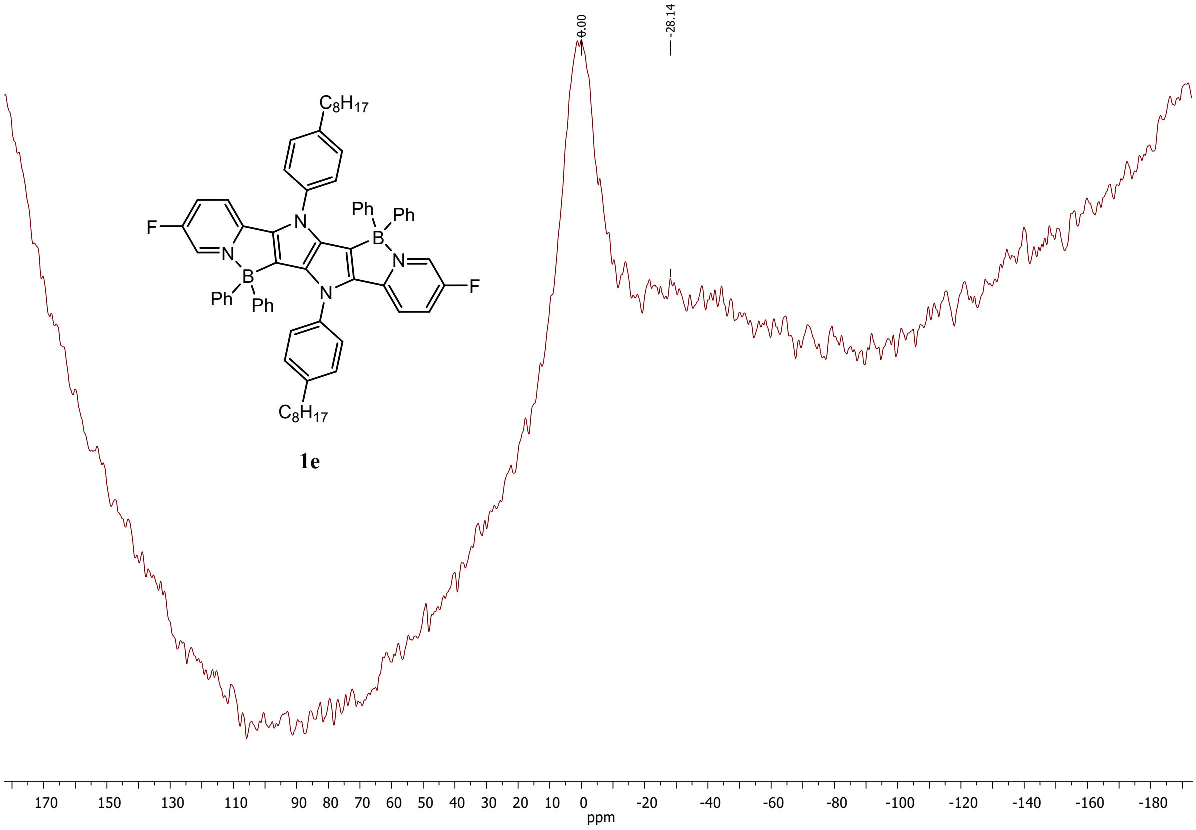
-150
ppm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N
B
Ph
Ph
N
Ph
Ph
B
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N
F
C_8H_{17}
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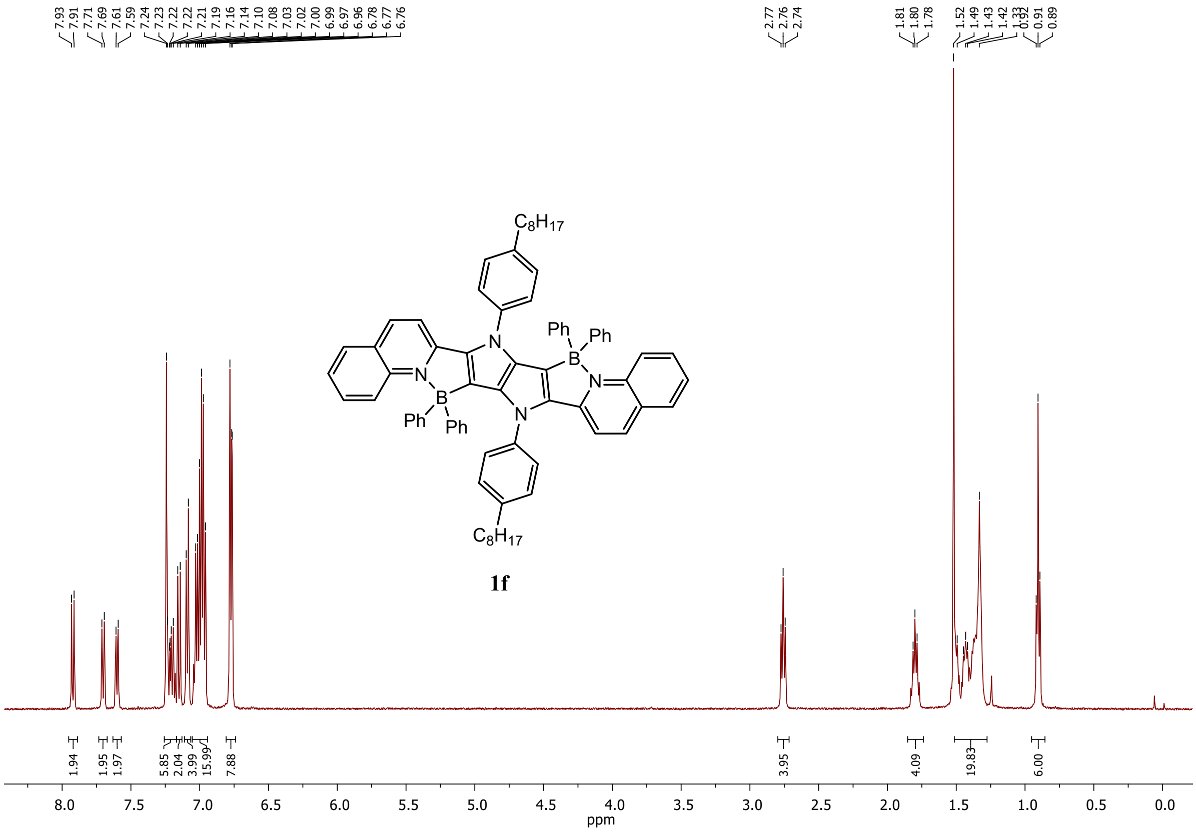
ppm

1e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7.22
7.21
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7.16
7.14
7.10
7.08
7.03
7.02
7.00
6.99
6.97
6.96
6.78
6.77
6.76
2.77
2.76
2.74
1.81
1.80
1.78
1.52
1.49
1.43
1.42
1.33
1.32
0.91
0.89
C_8H_{17}
Ph
Ph
B
N
N
B
N
N
Ph
Ph
C_8H_{17}
1.94
1.95
1.97
5.85
2.04
3.99
15.99
7.88
3.95
4.09
19.83
6.00
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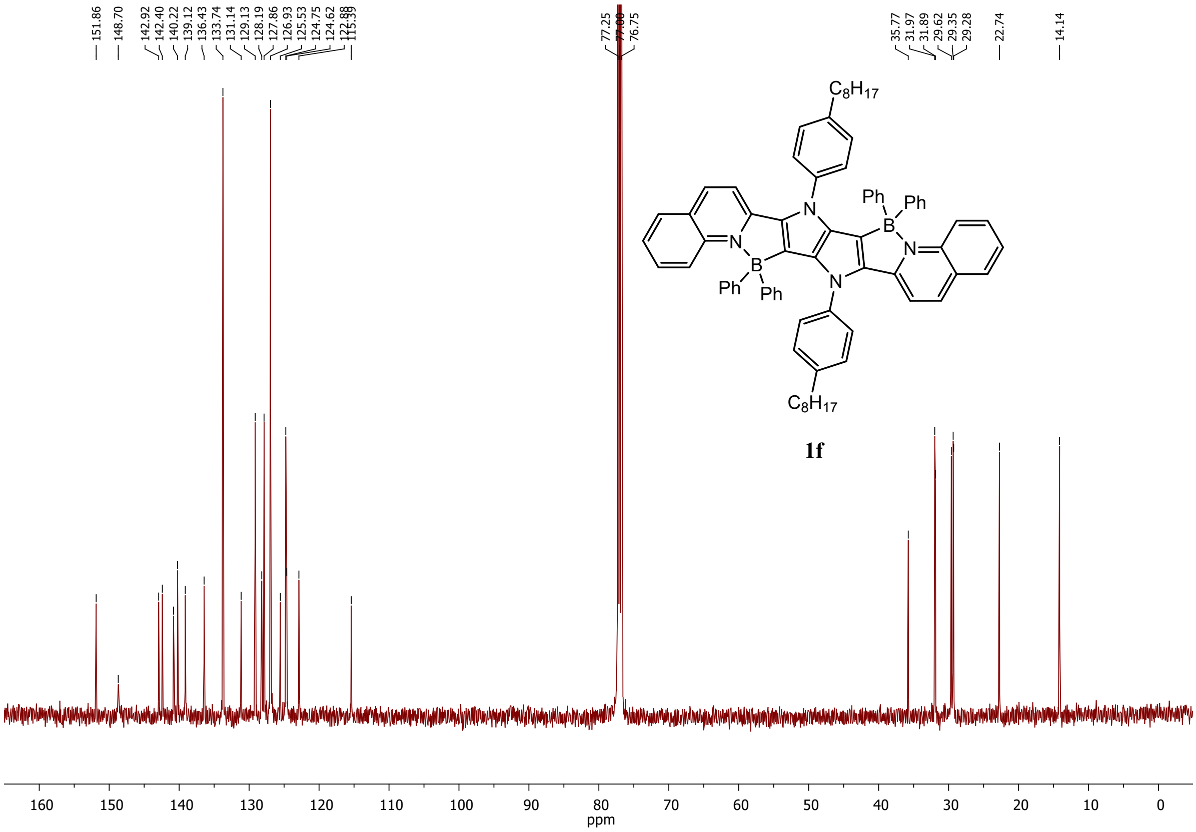
ppm

1f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133.74
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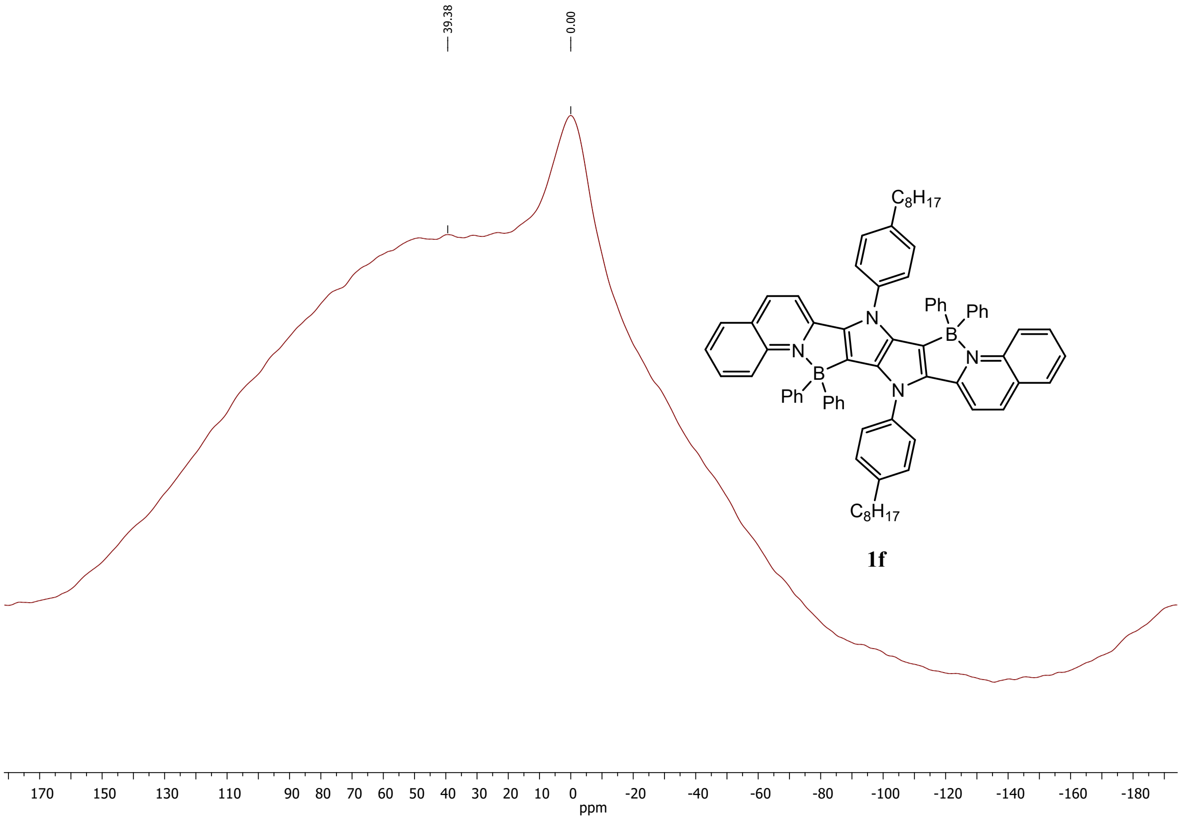
129.13
128.19
127.86
126.93
125.53
124.75
124.62
122.88
115.59
77.25
77.00
76.75
35.77
31.97
31.89
29.62
29.35
29.28
22.74
14.14
C_8H_{17}
N
B
Ph
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

1f


39.38
0.00
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Ph
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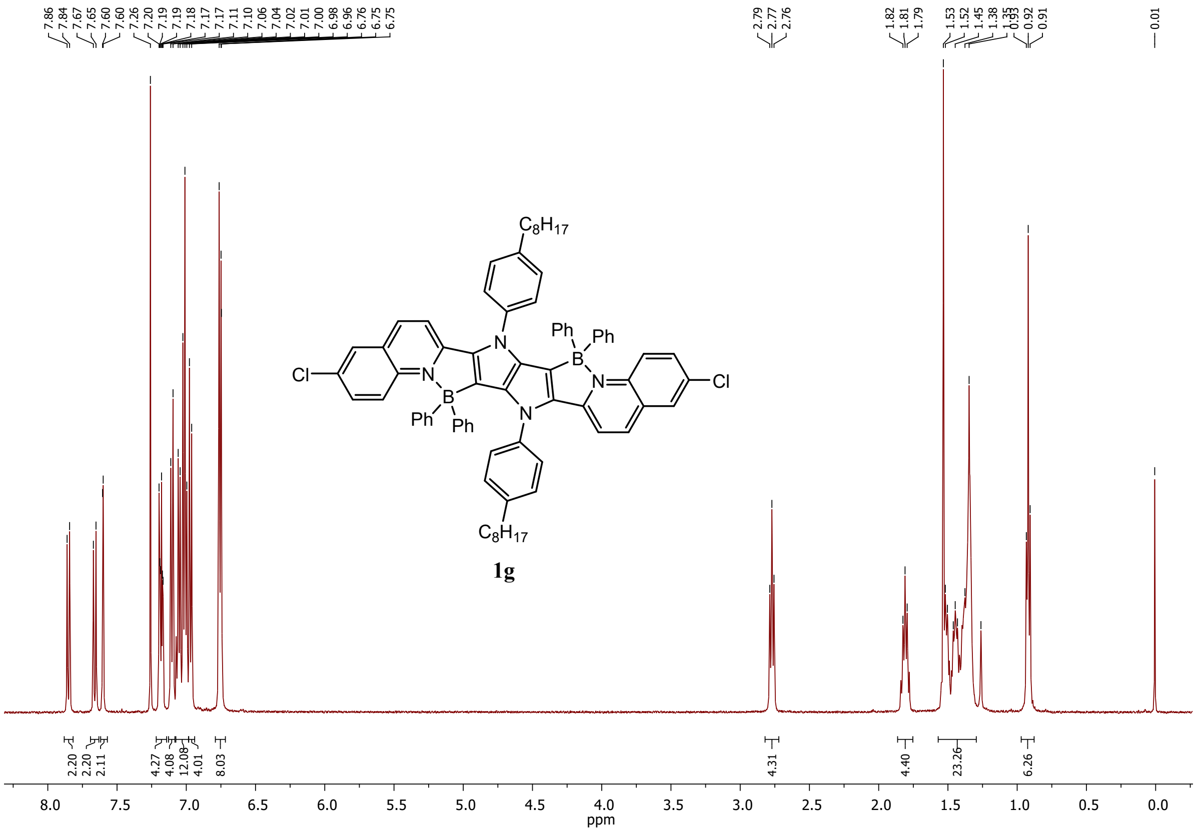
ppm

1f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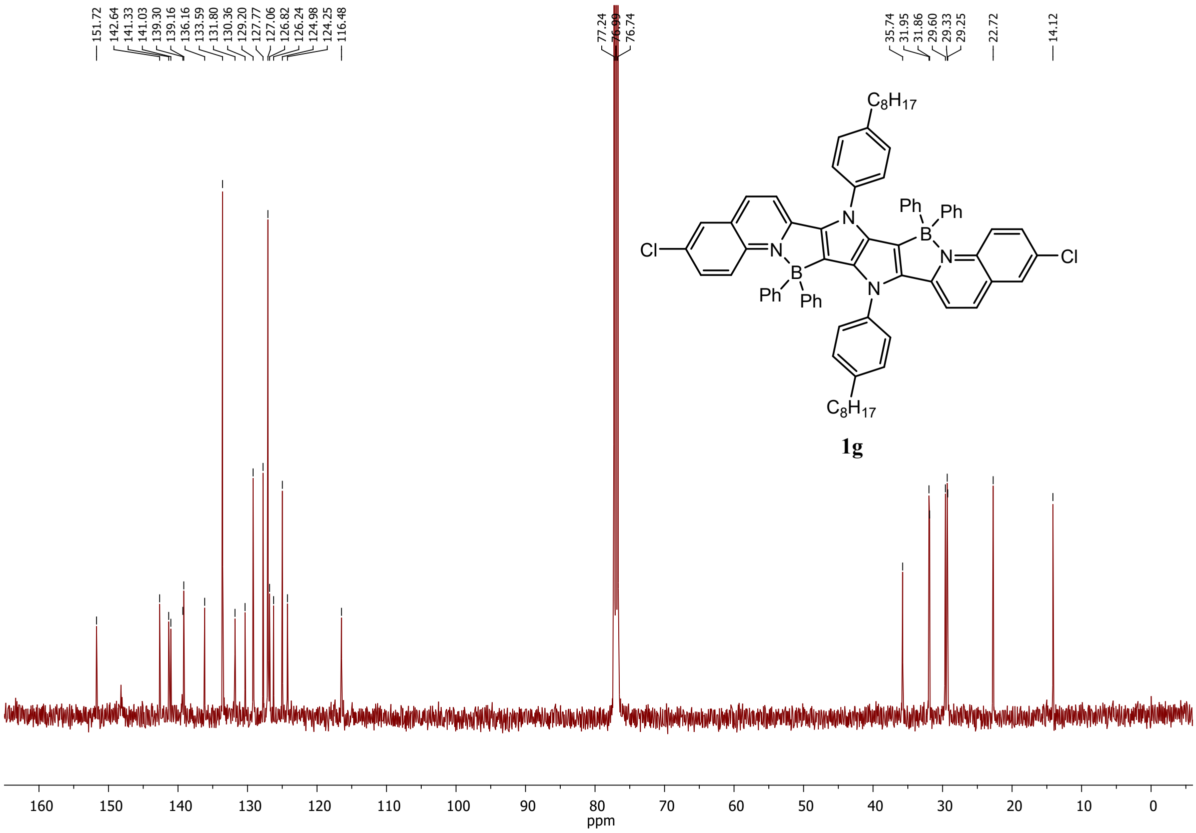
7.19
7.19
7.18
7.17
7.17
7.11
7.10
7.06
7.04
7.02
7.01
7.00
6.98
6.96
6.76
6.75
6.75
2.79
2.77
2.76
1.82
1.81
1.79
1.53
1.52
1.45
1.38
1.35
0.93
0.92
0.91
0.01
2.20
2.20
2.11
4.27
4.08
12.08
4.01
8.03
4.31
4.40
23.26
6.26
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
C_8H_{17}
Ph
Ph
Cl
N
B
N
N
B
N
Cl
Ph
Ph
C_8H_{17}
1g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130.36
129.20
127.77
127.06
126.82
126.24
124.98
124.25
116.48
77.24
76.99
76.74
35.74
31.95
31.86
29.60
29.33
29.25
22.72
14.12
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm
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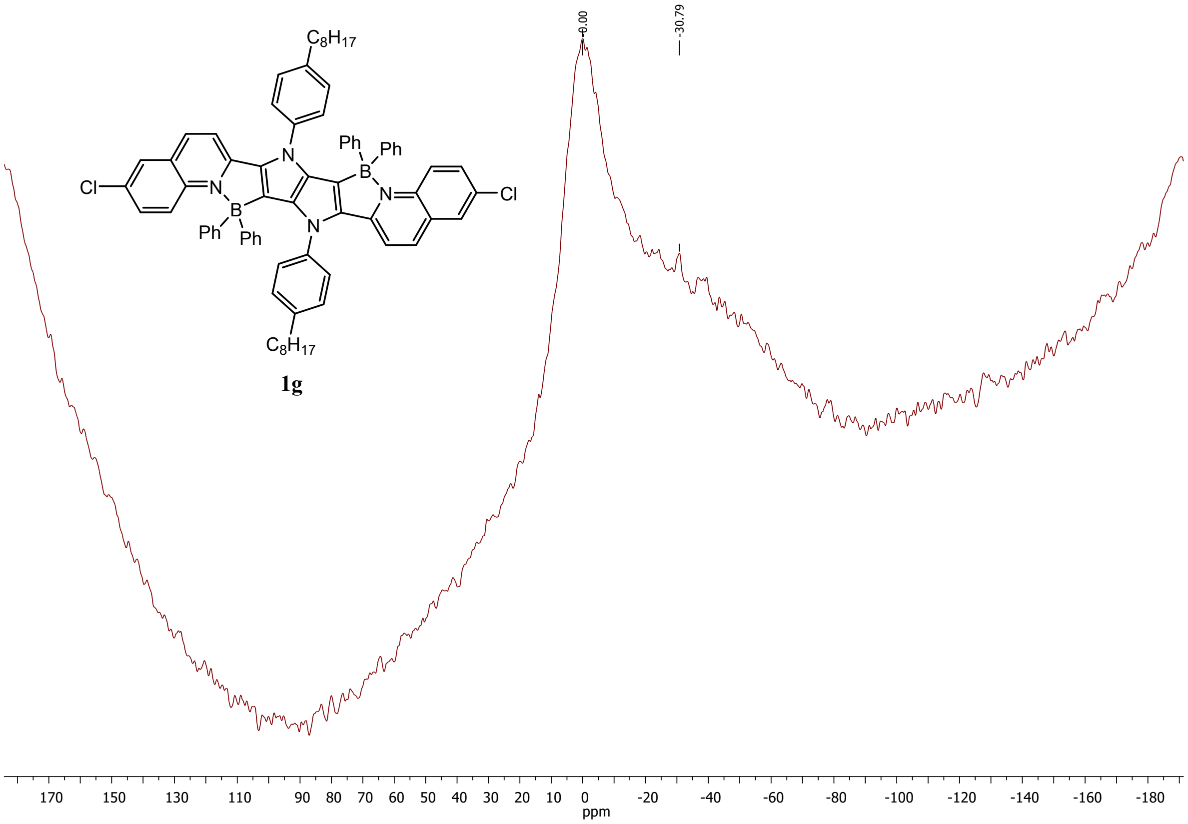
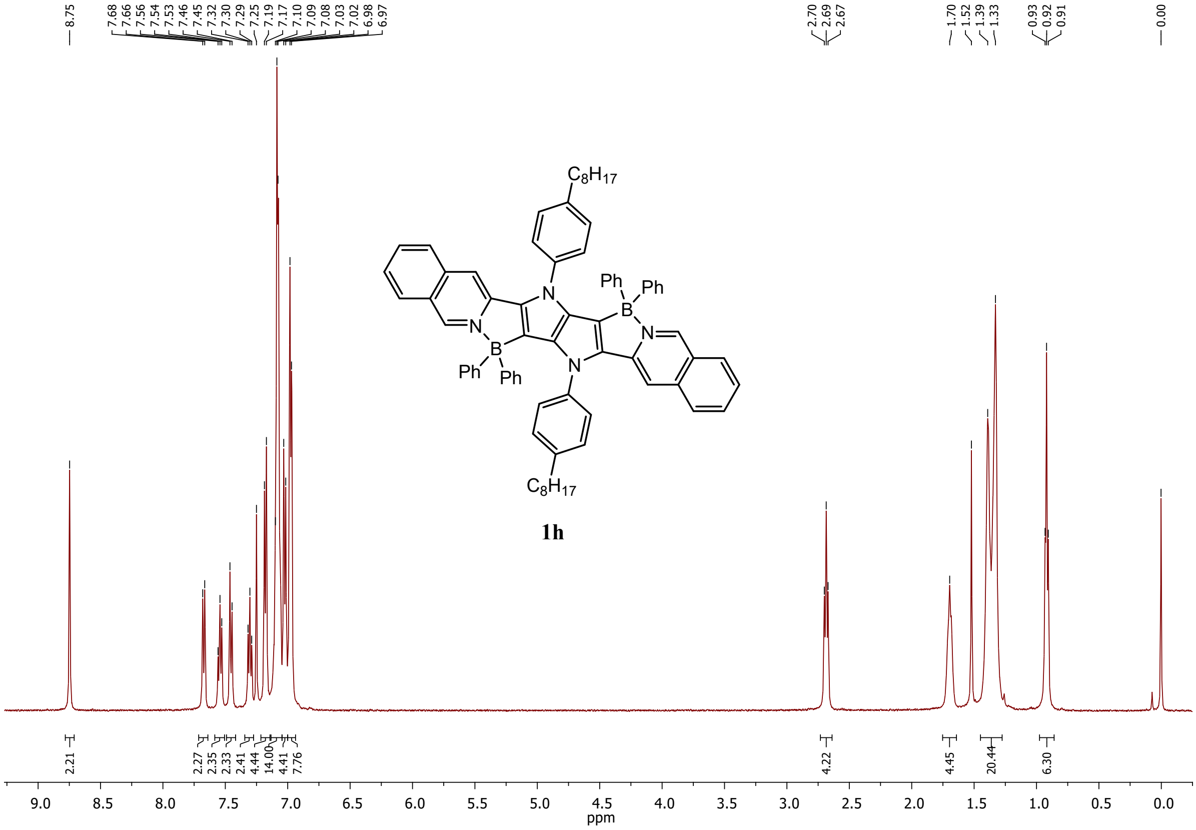
Ph
Ph
Cl
N
B
N
N
B
N
Cl
Ph
Ph
C_8H_{17}
1g


C8H17
Cl
N
B
Ph
Ph
Ph
Ph
1g
0.00
-30.79
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm


8.75
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7.53
7.46
7.45
7.32
7.30
7.29
7.25
7.19
7.17
7.10
7.09
7.08
7.03
7.02
6.98
6.97
2.70
2.69
2.67
1.70
1.52
1.39
1.33
0.93
0.92
0.91
0.00
C8H17
N
B
Ph
Ph
Ph
Ph
1h
2.21
2.27
2.35
2.33
2.41
4.44
14.00
4.41
7.76
4.22
4.45
20.44
6.30
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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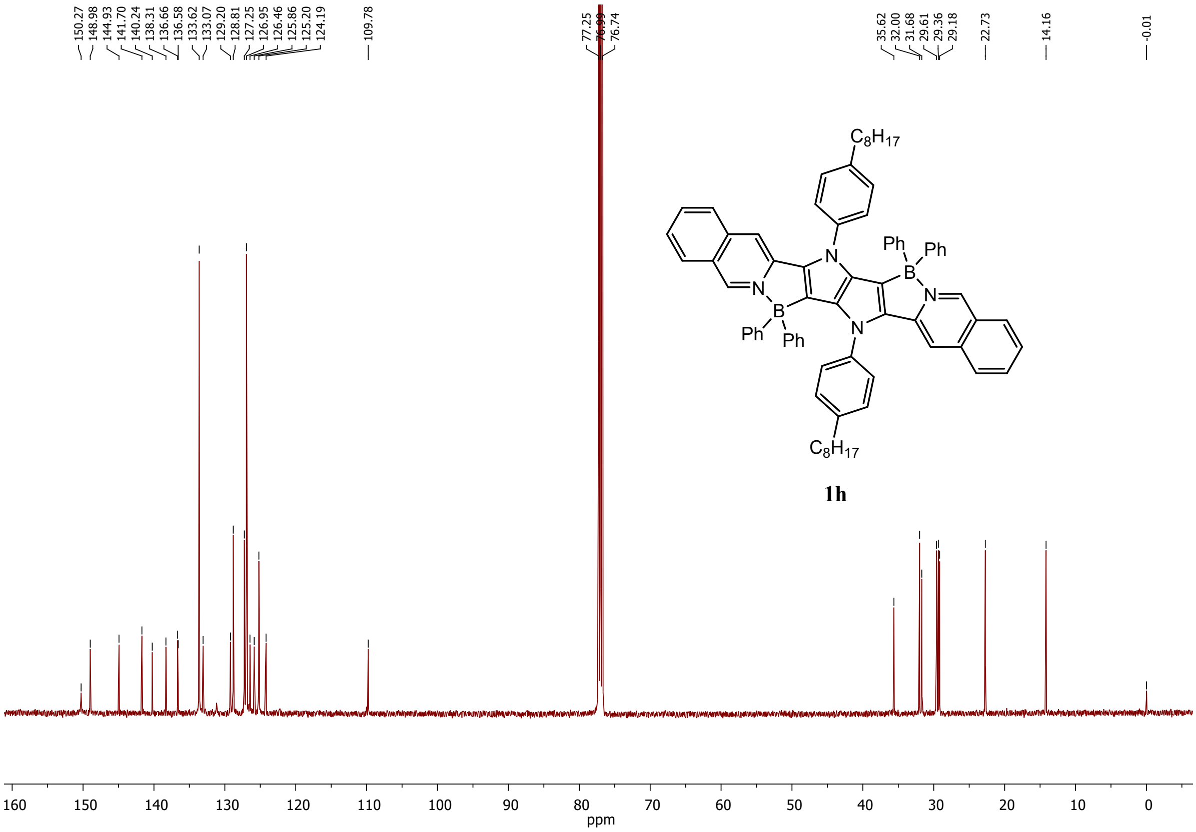
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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136.58
133.62
133.07
129.20
128.81
127.25
126.95
126.46
125.86
125.20
124.19
109.78
77.25
76.99
76.74
35.62
32.00
31.68
29.61
29.36
29.18
22.73
14.16
-0.01
C8H17
N
Ph
Ph
B
N
N
B
Ph
Ph
N
C8H17
1h
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140
130
120
110
100
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60
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20
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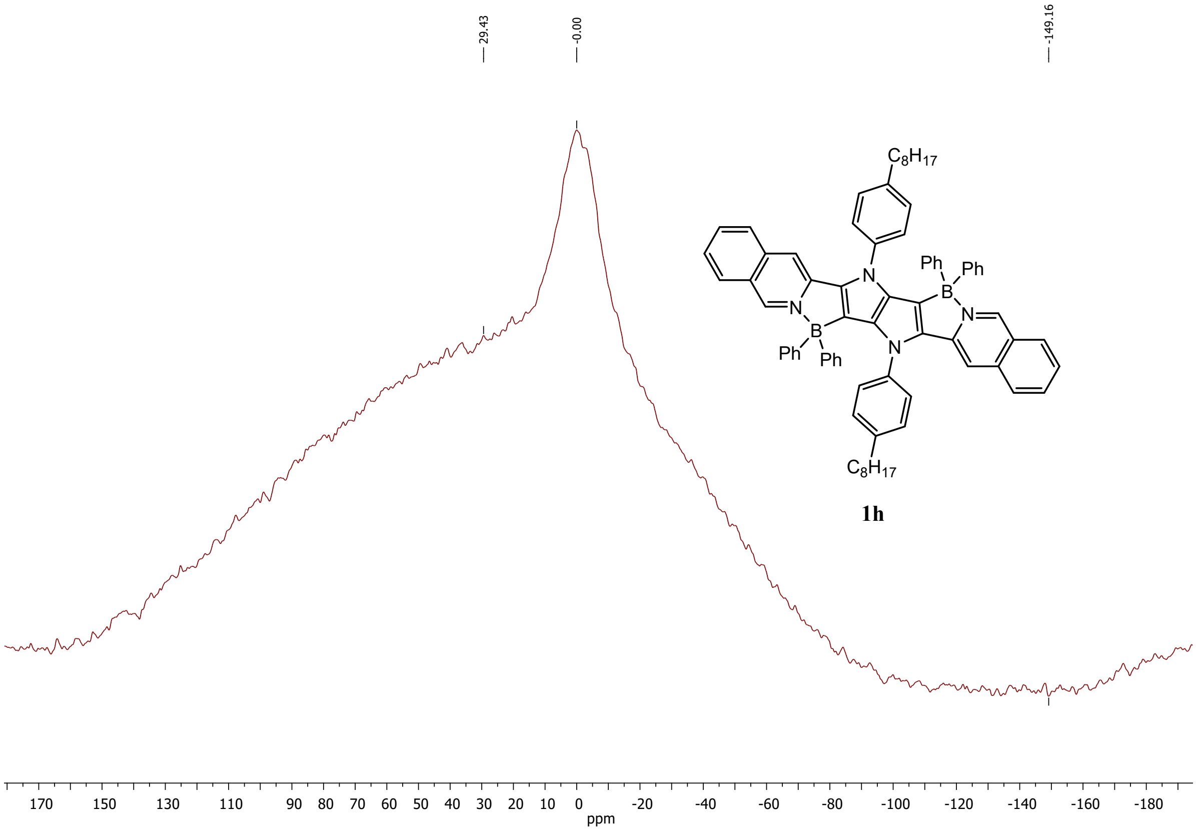
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N
Ph
Ph
B
N
N
B
Ph
Ph
N
C8H17
1h
170
150
130
110
90
80
70
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50
40
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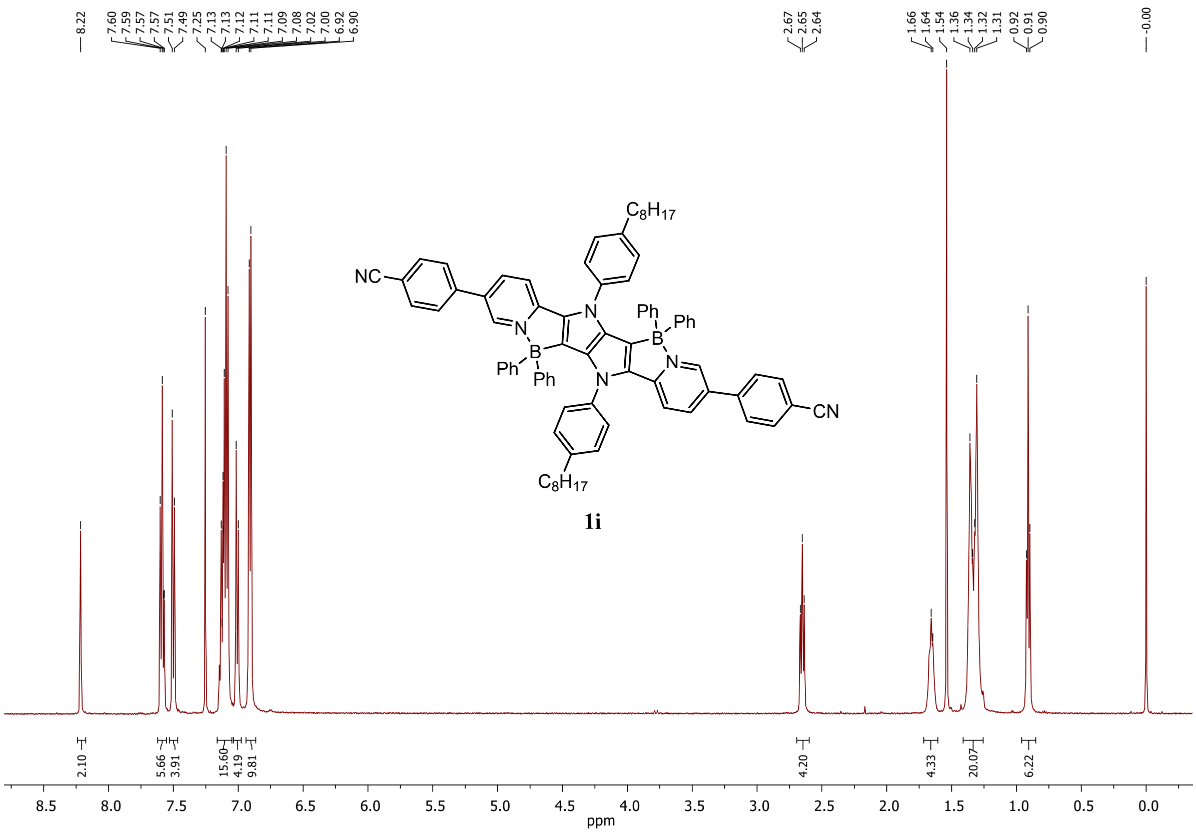
20
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm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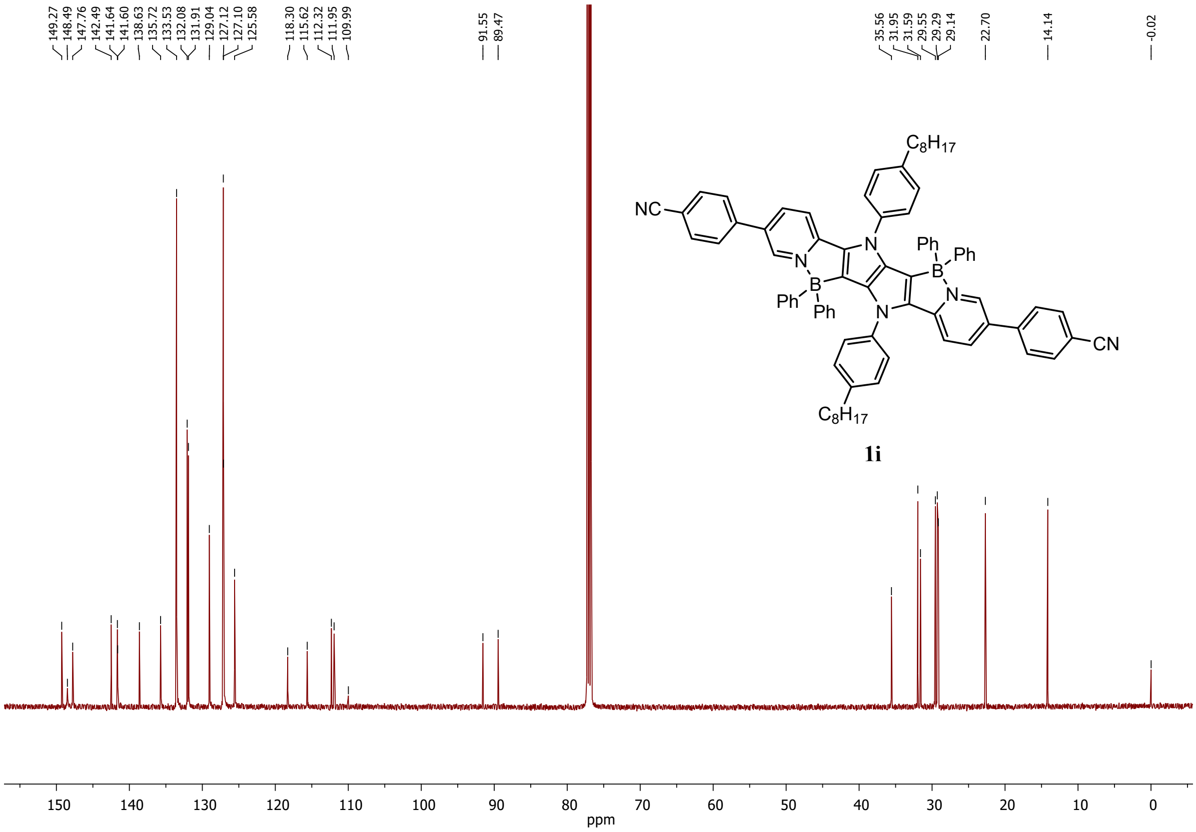
7.51
7.49
7.25
7.13
7.13
7.12
7.11
7.11
7.09
7.08
7.02
7.00
6.92
6.90
2.67
2.65
2.64
1.66
1.64
1.54
1.36
1.34
1.32
1.31
0.92
0.91
0.90
-0.00
NC
CN
N
Ph
B
C_8H_{17}
1i
2.10
5.66
3.91
15.60
4.19
9.81
4.20
4.33
20.07
6.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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132.08
131.91
129.04
127.12
127.10
125.58
118.30
115.62
112.32
111.95
109.99
91.55
89.47
35.56
31.95
31.59
29.55
29.29
29.14
22.70
14.14
-0.02
NC
CN
N
Ph
B
C_8H_{17}
1i
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140
130
120
110
100
90
80
70
60
50
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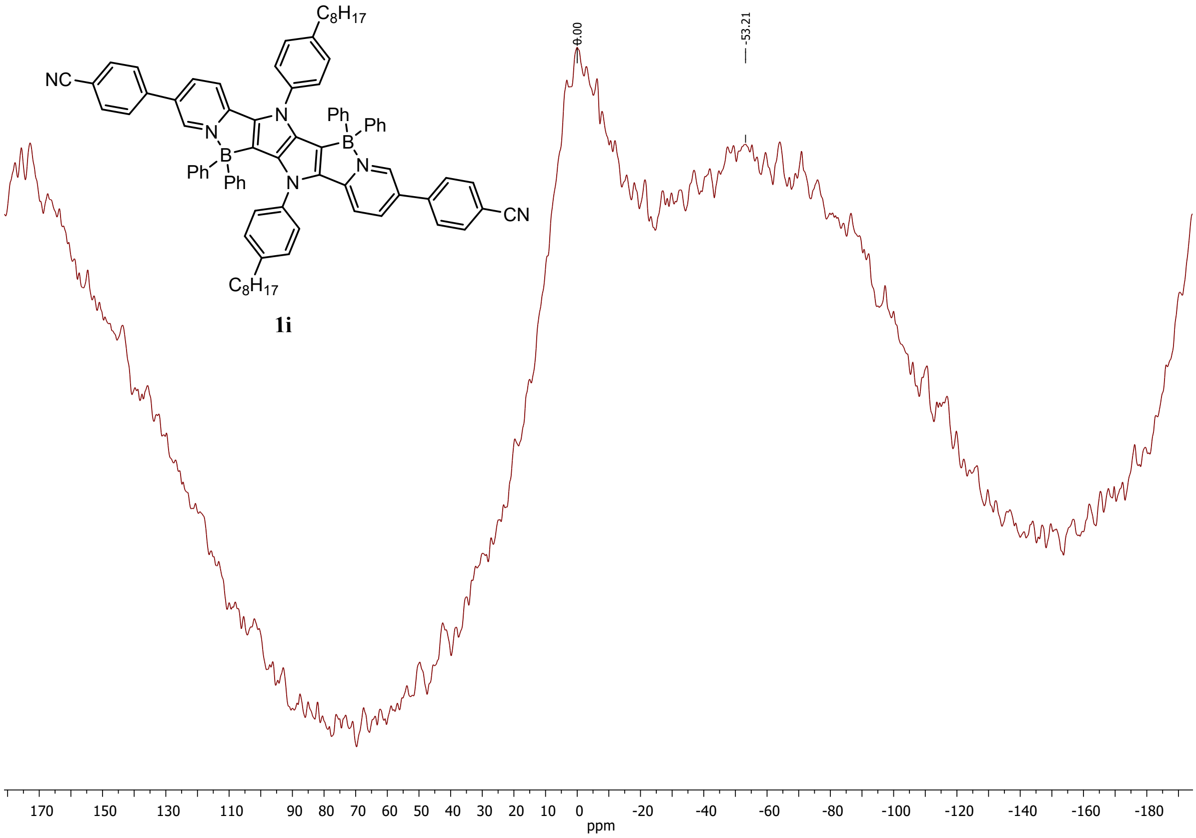
30
20
10
0
ppm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-53.21
NC
CN
C8H17
Ph
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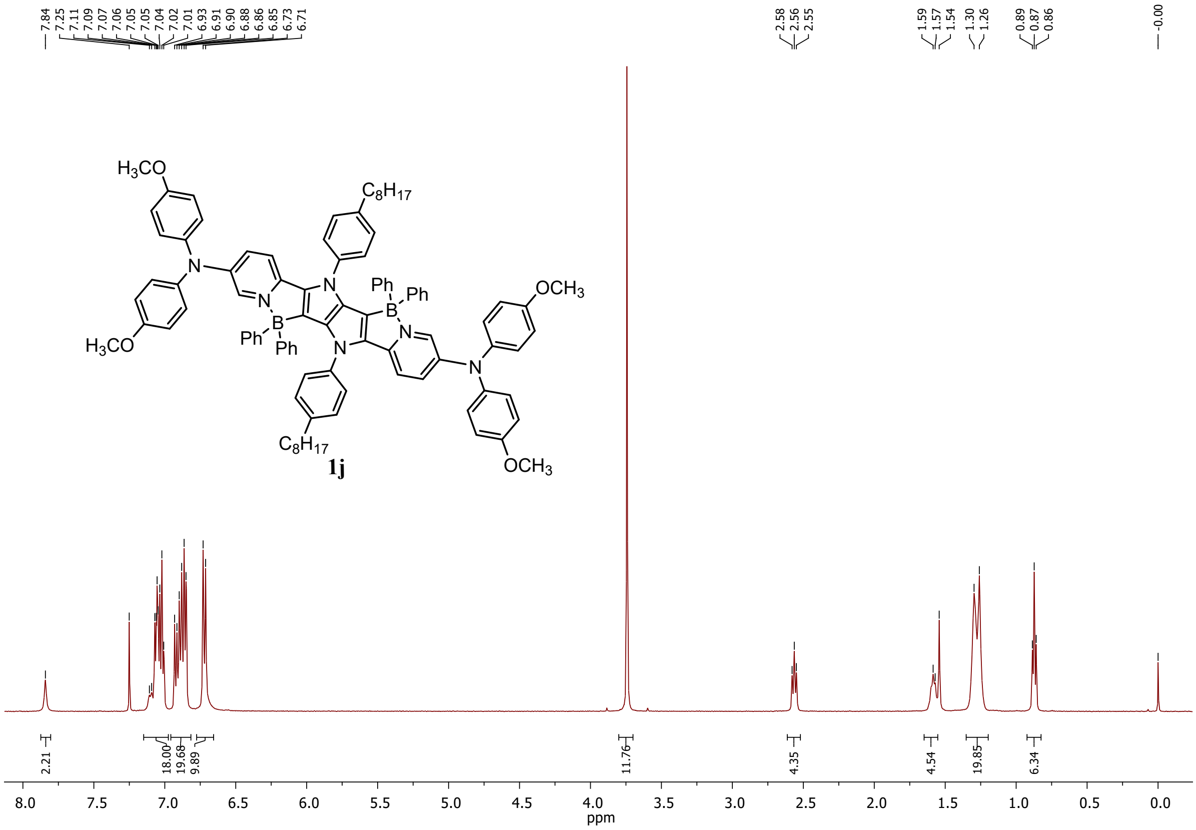
N
1i
170 150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180
ppm

(1j)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7.07
7.06
7.05
7.05
7.04
7.02
7.01
6.93
6.91
6.90
6.88
6.86
6.85
6.73
6.71
2.58
2.56
2.55
1.59
1.57
1.54
1.30
1.26
0.89
0.87
0.86
-0.00
H3CO
OCH3
C8H17
Ph
B
N
1j
2.21
18.00
19.68
9.89
11.76
4.35
4.54
19.85
6.34
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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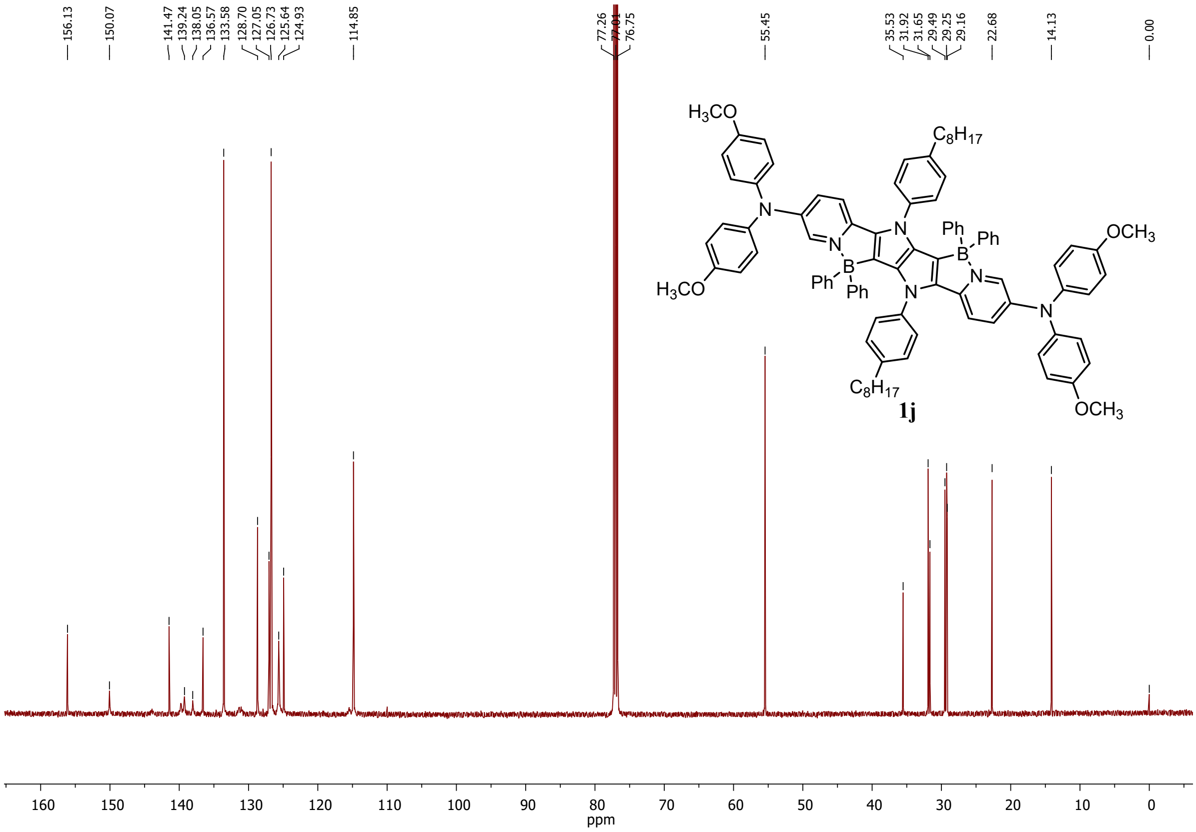
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150.07
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139.24
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136.57
133.58
128.70
127.05
126.73
125.64
124.93
114.85
77.26
77.01
76.75
55.45
35.53
31.92
31.65
29.49
29.25
29.16
22.68
14.13
0.00
H3CO
C8H17
N
N
N
Ph
Ph
B
N
OCH3
B
Ph
Ph
N
H3CO
N
C8H17
OCH3
1j
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140
130
120
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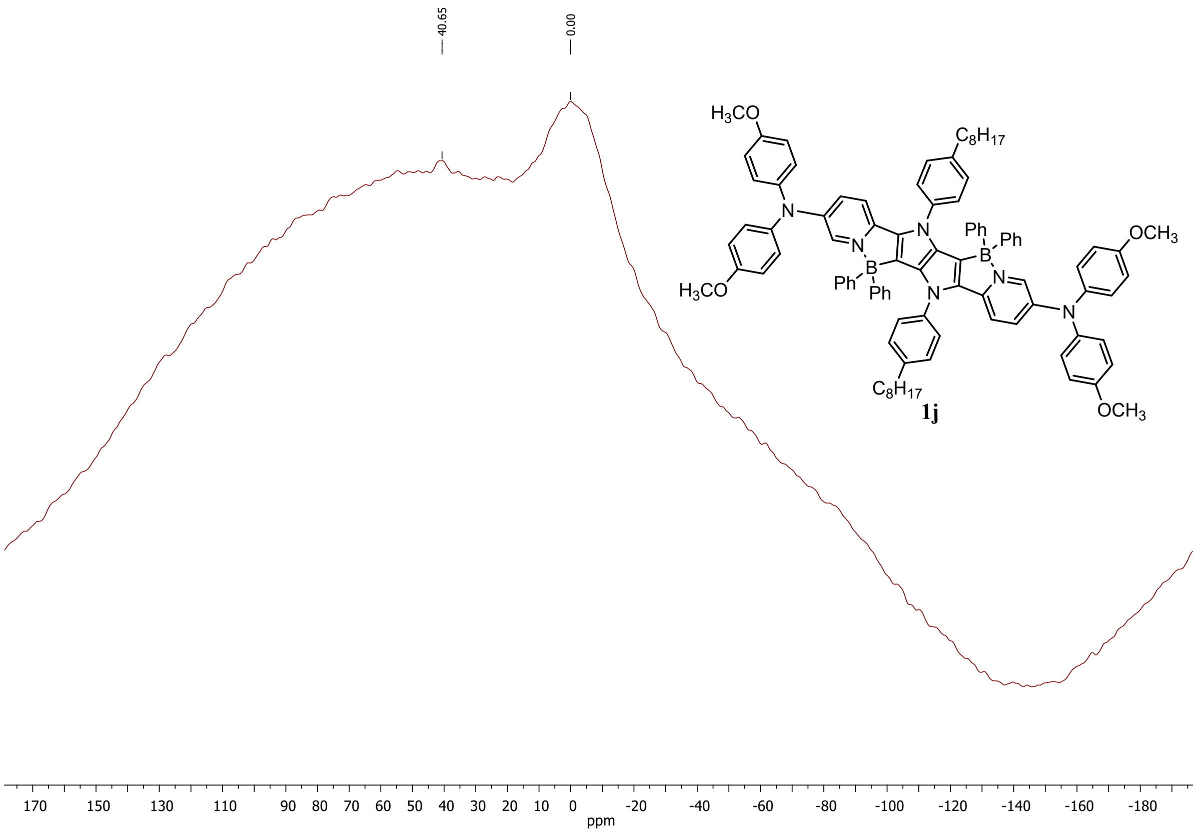
100
90
80
70
60
50
40
30
20
10
0
ppm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C8H17
N
N
N
Ph
Ph
B
N
OCH3
B
Ph
Ph
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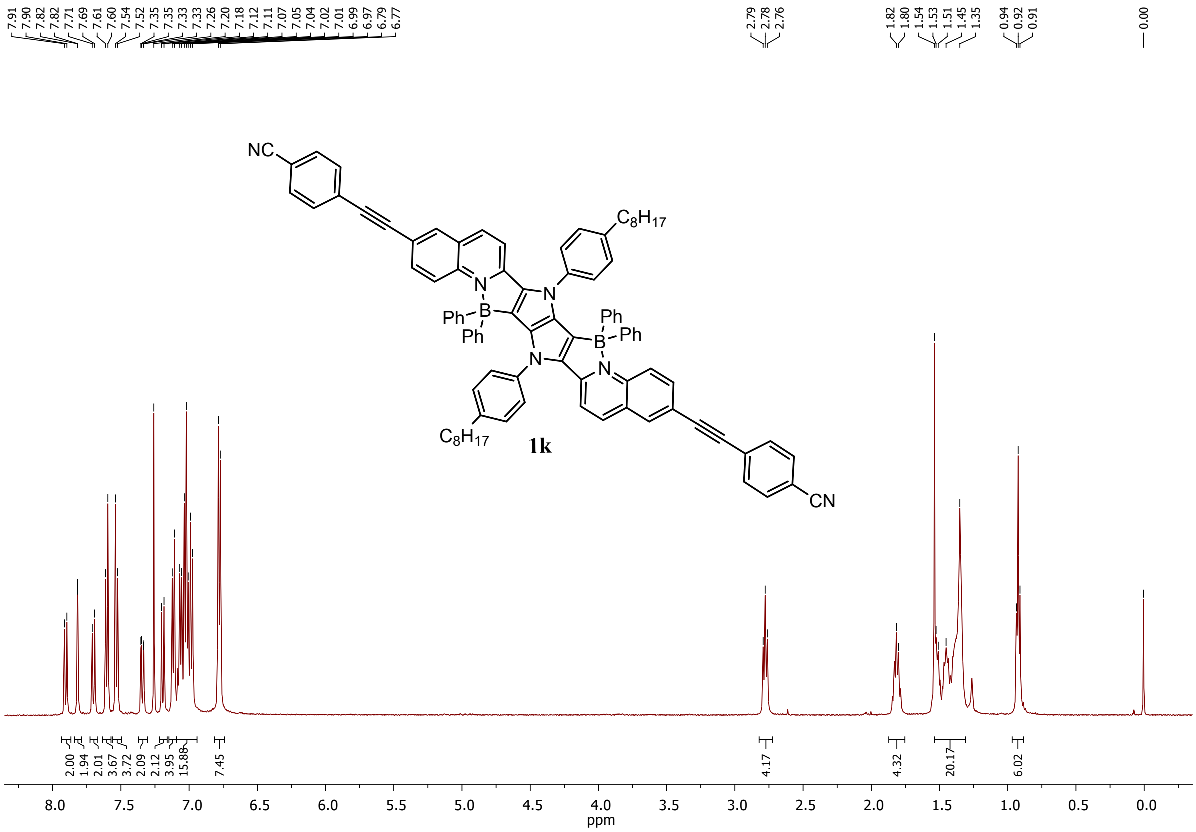
H3CO
N
C8H17
OCH3
1j
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

(1k)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7.82
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7.61
7.60
7.54
7.52
7.35
7.35
7.33
7.33
7.26
7.20
7.18
7.12
7.11
7.07
7.05
7.04
7.02
7.01
6.99
6.97
6.79
6.77
2.79
2.78
2.76
1.82
1.80
1.54
1.53
1.51
1.45
1.35
0.94
0.92
0.91
0.00
NC
C_8H_{17}
Ph
B
N
Ph
B
Ph
C_8H_{17}
1k
CN
2.00
1.94
2.01
3.67
3.72
2.09
2.12
3.95
15.88
7.45
4.17
4.32
20.17
6.02
8.0
7.5
7.0
6.5
6.0
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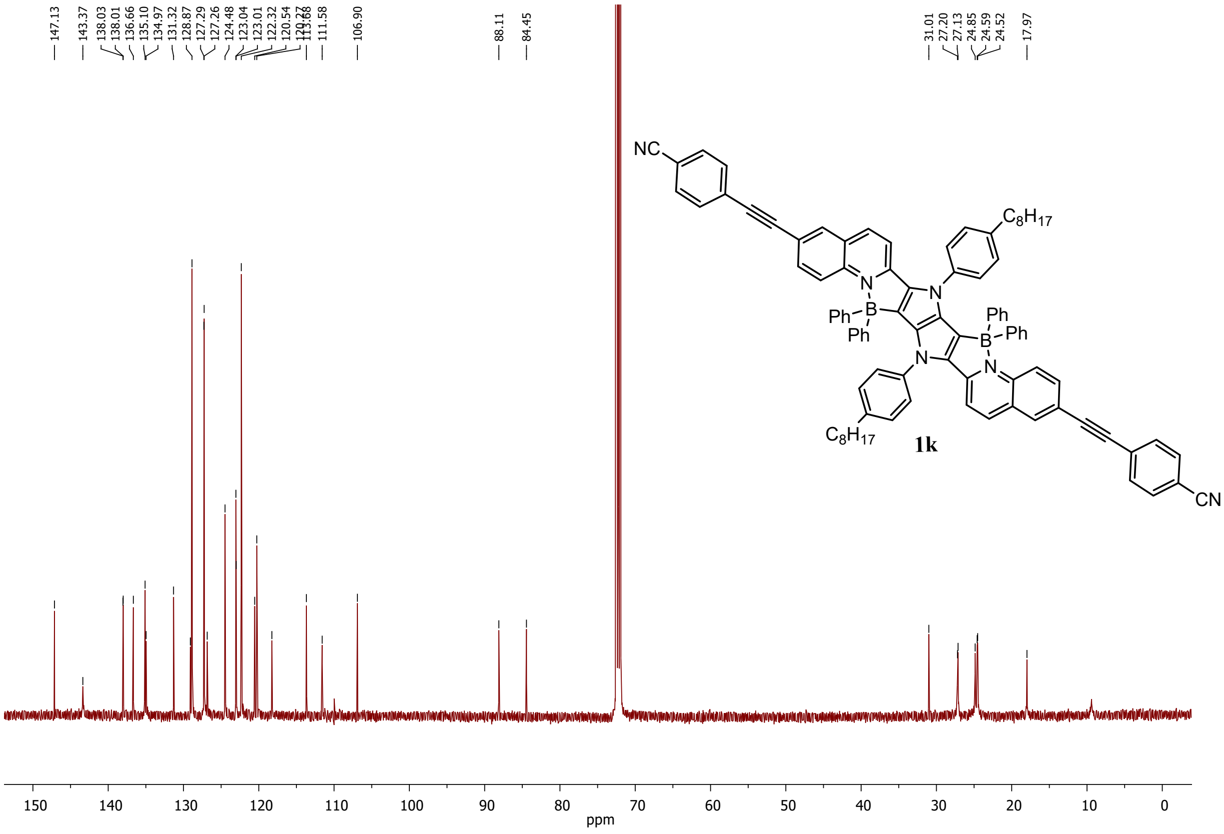
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


147.13
143.37
138.03
138.01
136.66
135.10
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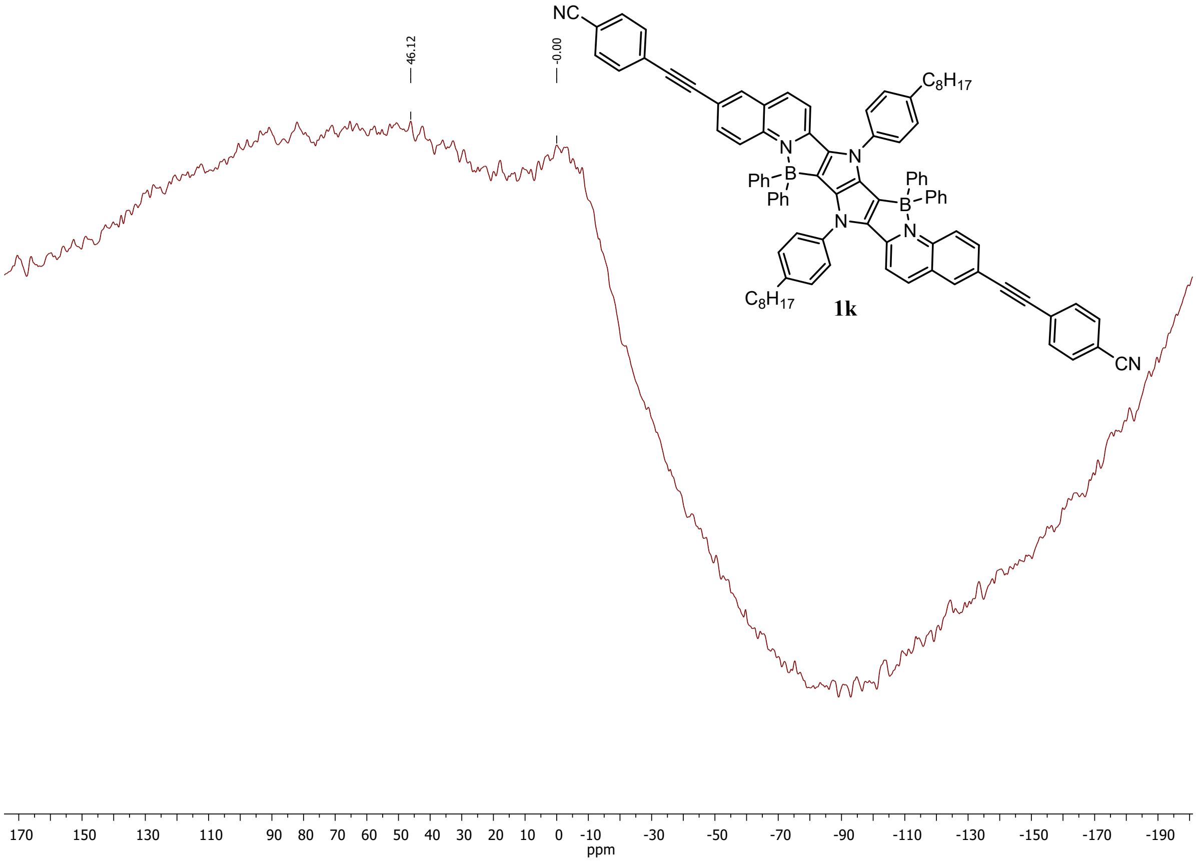
131.32
128.87
127.29
127.26
124.48
123.04
123.01
122.32
120.54
120.27
113.68
111.58
106.90
88.11
84.45
31.01
27.20
27.13
24.85
24.59
24.52
17.97
NC
C_8H_{17}
Ph
B
N
Ph
B
Ph
C_8H_{17}
1k
CN
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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-0.00
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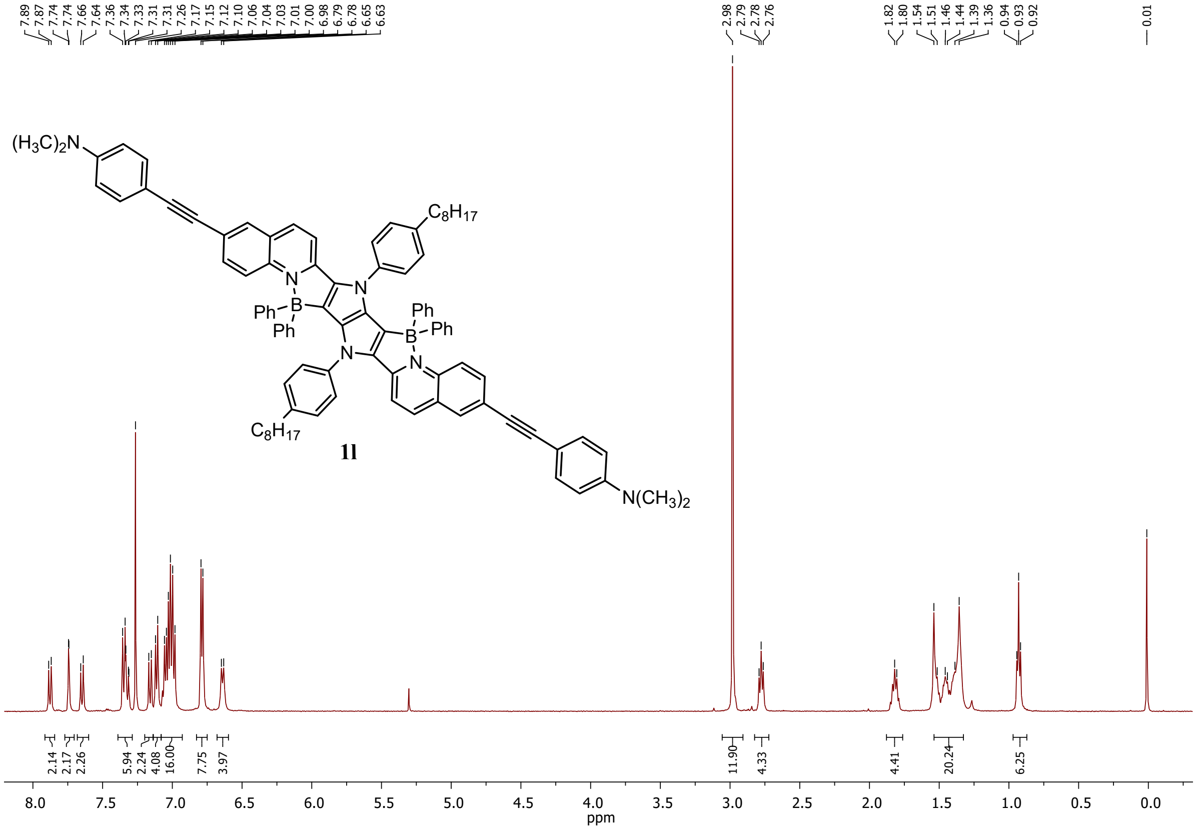
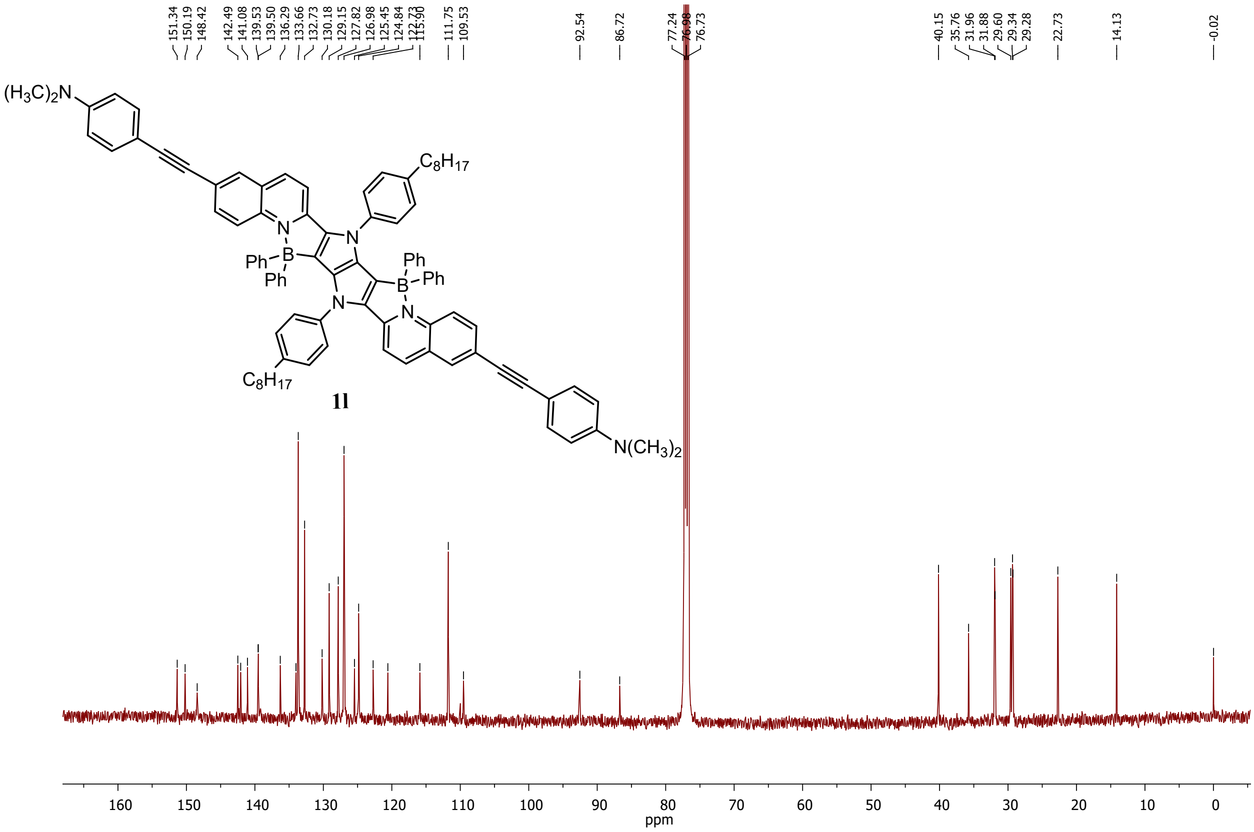
C8H17
N
B
Ph
Ph
Ph
Ph
N
N
B
N
C8H17
CN
170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190
ppm

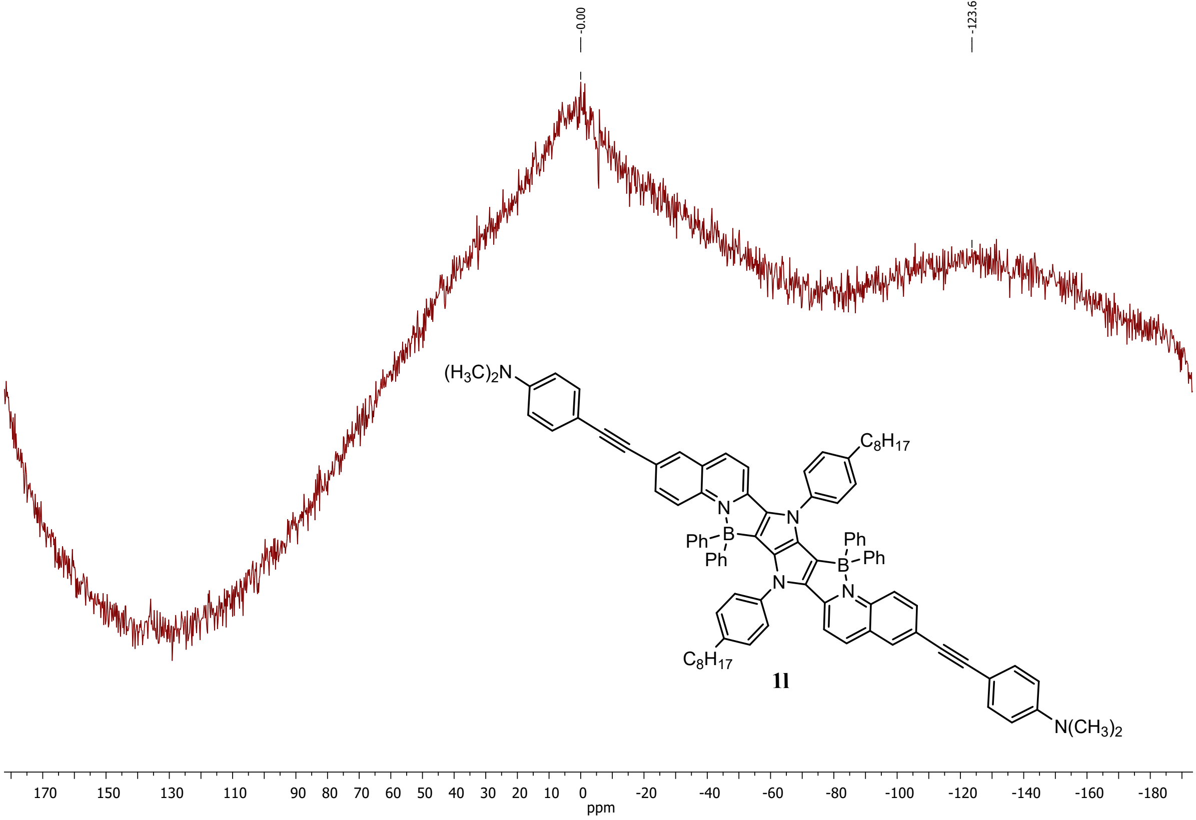
1k


7.89
7.87
7.74
7.74
7.66
7.64
7.36
7.34
7.33
7.31
7.31
7.26
7.17
7.15
7.12
7.10
7.06
7.04
7.03
7.01
7.00
6.98
6.79
6.78
6.65
6.63
2.98
2.79
2.78
2.76
1.82
1.80
1.54
1.51
1.46
1.44
1.39
1.36
0.94
0.93
0.92
0.01
(H3C)2N
C8H17
N
B
Ph
Ph
N
Ph
B
Ph
N
N
C8H17
N(CH3)2
2.14
2.17
2.26
5.94
2.24
4.08
16.00
7.75
3.97
11.90
4.33
4.41
20.24
6.25
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

1l


151.34
150.19
148.42
142.49
141.08
139.53
139.50
136.29
133.66
132.73
130.18
129.15
127.82
126.98
125.45
124.84
122.73
115.90
111.75
109.53
92.54
86.72
77.24
76.98
76.73
40.15
35.76
31.96
31.88
29.60
29.34
29.28
22.73
14.13
-0.02
(H3C)2N
C8H17
N
N
Ph
B
Ph
Ph
B
Ph
N
N
C8H17
N(CH3)2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

1l


-0.00
-123.65
(H3C)2N
C8H17
N
N
Ph
B
Ph
Ph
B
Ph
N
N
C8H17
N(CH3)2
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

1l

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