

# Highly substituted Bodipy dyes with Spectroscopic Features sensitive to the Environment

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Supporting Information (24 pages)

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## **1) General Methods.**

All reactions were performed under a dry atmosphere of argon using standard Schlenk tube techniques. All chemicals were used as received from commercial sources without further purification unless otherwise stated. CH<sub>3</sub>CN was distilled from P<sub>2</sub>O<sub>5</sub> under an argon atmosphere. The 200, 300,

400 ( $^1\text{H}$ ) and 50, 75, 100 MHz ( $^{13}\text{C}$ ) NMR spectra were recorded at room temperature using perdeuterated solvents as internal standards:  $\%$  (H) in ppm relative to residual protiated solvent;  $\%$  (C) in ppm relative to the solvent. Mass spectra were measured with a ESI-MS mass spectrometer. Chromatographic purifications were performed using 40-63  $\mu\text{m}$  silica gel. TLC was performed on silica gel plates coated with fluorescent indicator.

Electronic absorption and emission spectra were measured under ambient conditions using commercial instruments. Fluorescence spectra were recorded with a spectrophotometer. Solvents for spectroscopy were spectroscopic grade and were used as received after checking for impurities. A wide variety of excitation wavelengths were used, according to the species under investigation. Spectral titrations were carried out with excitation at isosbestic points. Luminescence lifetimes were measured using the time-correlated, single photon counting mode coupled to a Stroboscopic system. The excitation source was a thyatron-gated flash lamp filled with nitrogen gas. No filter was used for the excitation. The instrumental response function was determined with a scattering solution. Fluorescence quantum yields were measured relative to Rhodamine 6G and Cresyl Violet<sup>1</sup> and tetramethoxy-bis-isoindolodipyrromethene-difluoroborate<sup>2</sup> as a standard.

The following equation was used to determine the relative fluorescence quantum yield:

$$\Phi_{\text{F}}(\text{x}) = (A_{\text{S}}/A_{\text{X}})(F_{\text{X}}/F_{\text{S}})(n_{\text{X}}/n_{\text{S}})^2\Phi_{\text{F}}(\text{s})$$

Where  $A$  is the absorbance (in the range 0.01-0.1 A.U.),  $F$  is the area under the emission curve,  $n$  is the refractive index of the solvents (at 25 °C) used in measurements, and the subscripts s and x represent standard and unknown, respectively.

## **2) Preparative experimental part**

All anhydrous reactions were carried out under dry argon by using Schlenk tube techniques. All reagents were used directly as obtained commercially unless otherwise noted. were purchased from different commercial sources. compound **3**<sup>3</sup>, **5**<sup>4</sup> and **4-(2-methoxyethoxy)ethoxy)benzaldehyde**<sup>5</sup> were

obtained according to the respective references.



**Figure S1.** TLC plate (silica) of the regio-isomer mixture of compound **9**. Right part spots obtained for the pure compound **9**. Left spot of the crude reaction mixture obtained at the end of the reaction leading to compound **10**. Central part, overlapping of compound **9** and reaction mixture leading to cmpd **10**. Solvent of elution dichloromethane 98/ethylacetate 2 v/v.

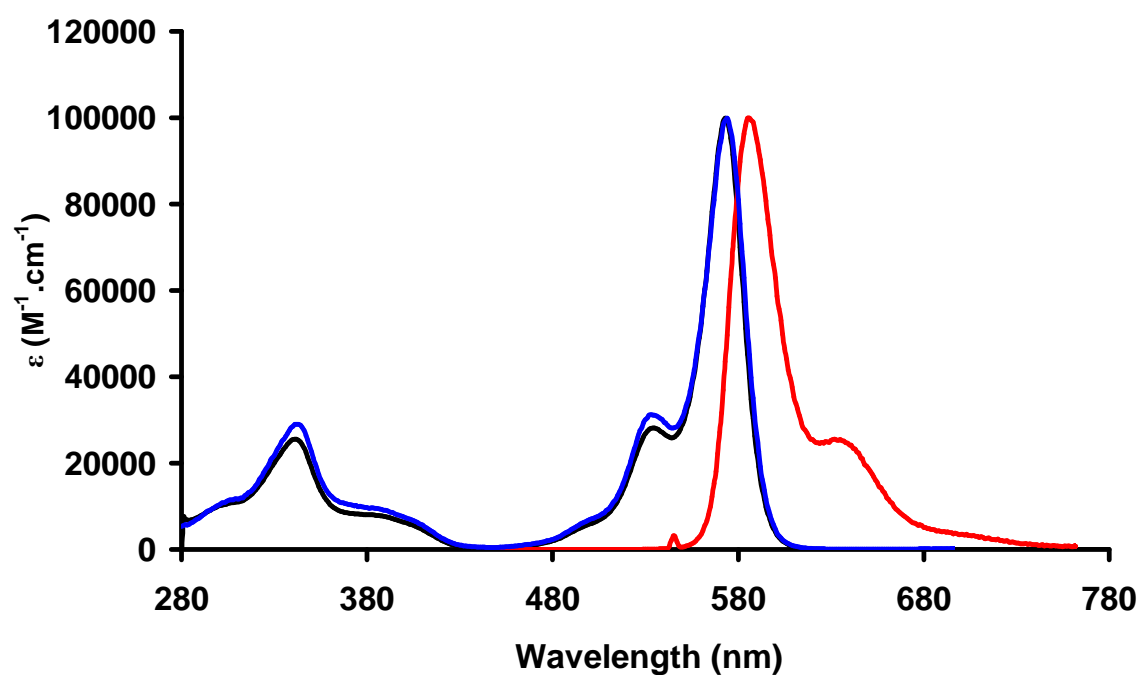
### **3) X-ray Structure Determination of compound 6.**

Reflection data were collected on a Nonius-Bruker Kappa CCD diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. *Crystal Data*: C<sub>59</sub> H<sub>58</sub> B F<sub>2</sub> I N<sub>2</sub> O<sub>8</sub>, FW = 1098.78, *data collection*<sup>6</sup>:  $\varphi + \omega$  scan frames with 2°/frame and exposure times of 120 s/frame, *data reduction*<sup>7</sup>: Triclinic, P  $\bar{1}$ ,  $a = 10.672(3)$ ,  $b = 15.083(3)$ ,  $c = 17.585(4) \text{ \AA}$ ,  $\alpha = 86.626(4)$ ,  $\beta = 72.898(5)$ ,  $\gamma = 80.806(4)^\circ$ ,  $V = 2670.5(11) \text{ \AA}^3$ , Absorption correction = Multi-scan method<sup>8</sup>,  $D = 1.366 \text{ Mg/m}^3$ , 48751 collected reflections up to  $\theta_{\max} = 23.3^\circ$ , 7675 unique ( $R_{\text{int}} = 0.023$ ), *structure solution*<sup>3</sup>: direct methods, *model refinement*<sup>9</sup>: on  $F^2$  by full matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms; All hydrogen atoms were located on difference Fourier syntheses but were refined with a riding model and with  $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$  (1.5 for a methyl group).  $R_1 = 0.080$ ,  $wR_2 = 0.149$ , ( $R_1 = 0.052$ ,  $wR_2 = 0.129$  for  $I > 2\sigma(I)$ ), goodness-of-fit = 1.040. Concerted orientational disorder observed at the terminal part of both ethyleneglycol side chains and for one anisole group within the molecular packing was treated with a split atom model of two components with site-occupancy factors constrained to unity. Geometries and

anisotropic displacement parameters for the disordered atoms were restrained to be similar by applying adequate SHELXL instructions. The final site-occupation factor of the major conformation was 0.529(8).

Structural data have been deposited with the Cambridge Crystallographic Data Centre (CIF file) as supplementary publication number **CCDC 762202**. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB21, EZ, UK [fax: +44-1-223-336-033 or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)]

#### **4) Spectroscopy: spectra traces**



**Figure S2:** Absorption(black), emission(red) and excitation(blue) spectra of **2a** in dioxane.

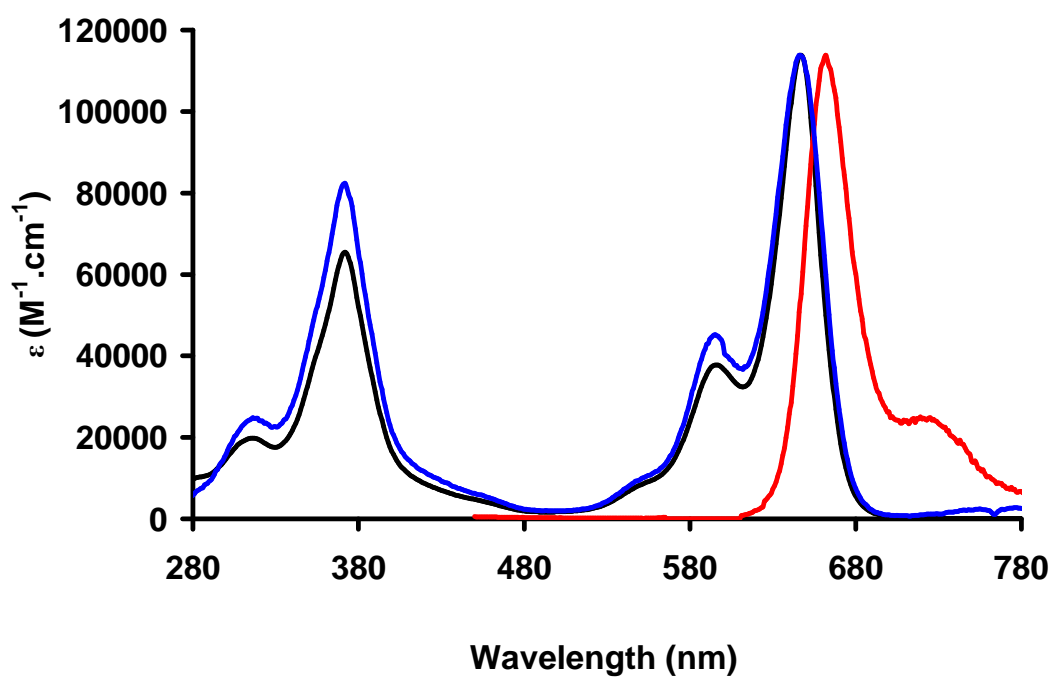


Figure S3: Absorption(black), emission(red) and excitation(blue) spectra of **2b** in dioxane.

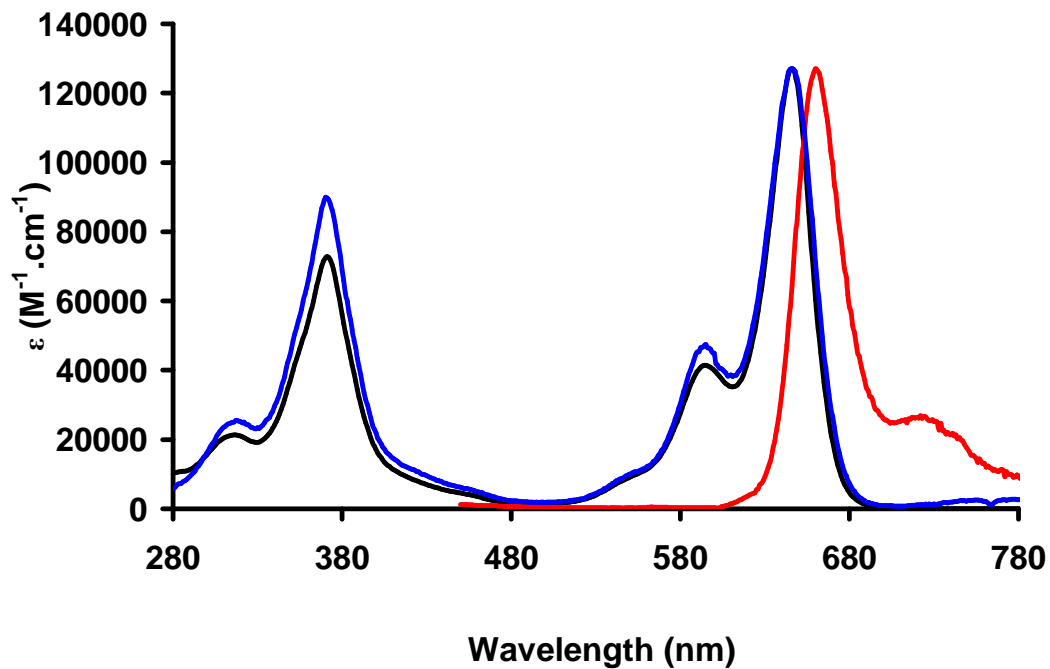
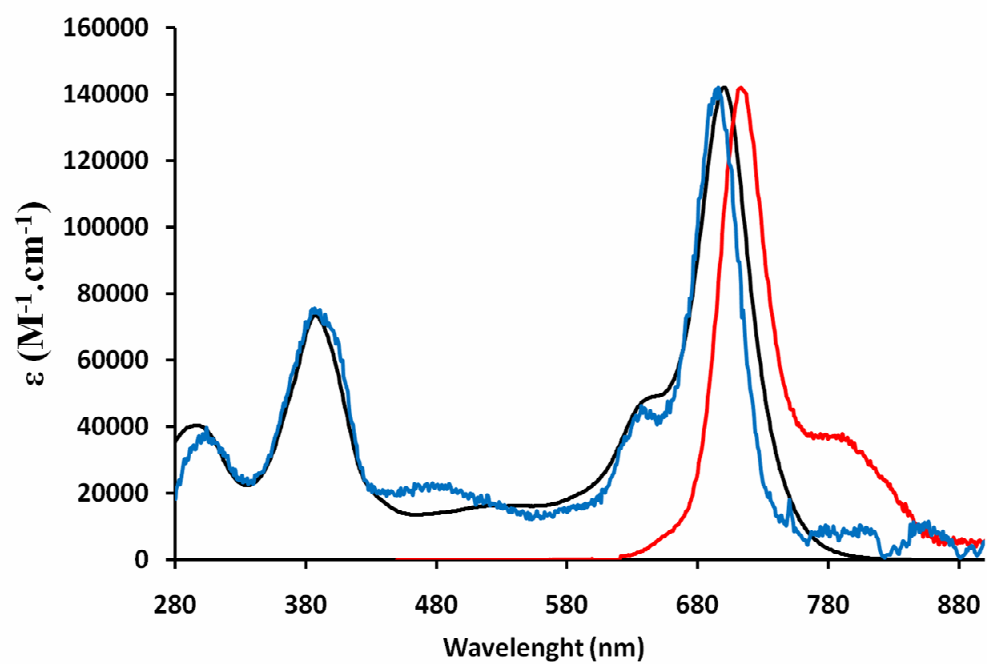


Figure S4: Absorption(black), emission(red) and excitation(blue) spectra of **7** in dioxane.



**Figure S5:** Absorption(black), emission(red) and excitation(blue) spectra of **10** in dioxane.

## **5) NMR Spectra**

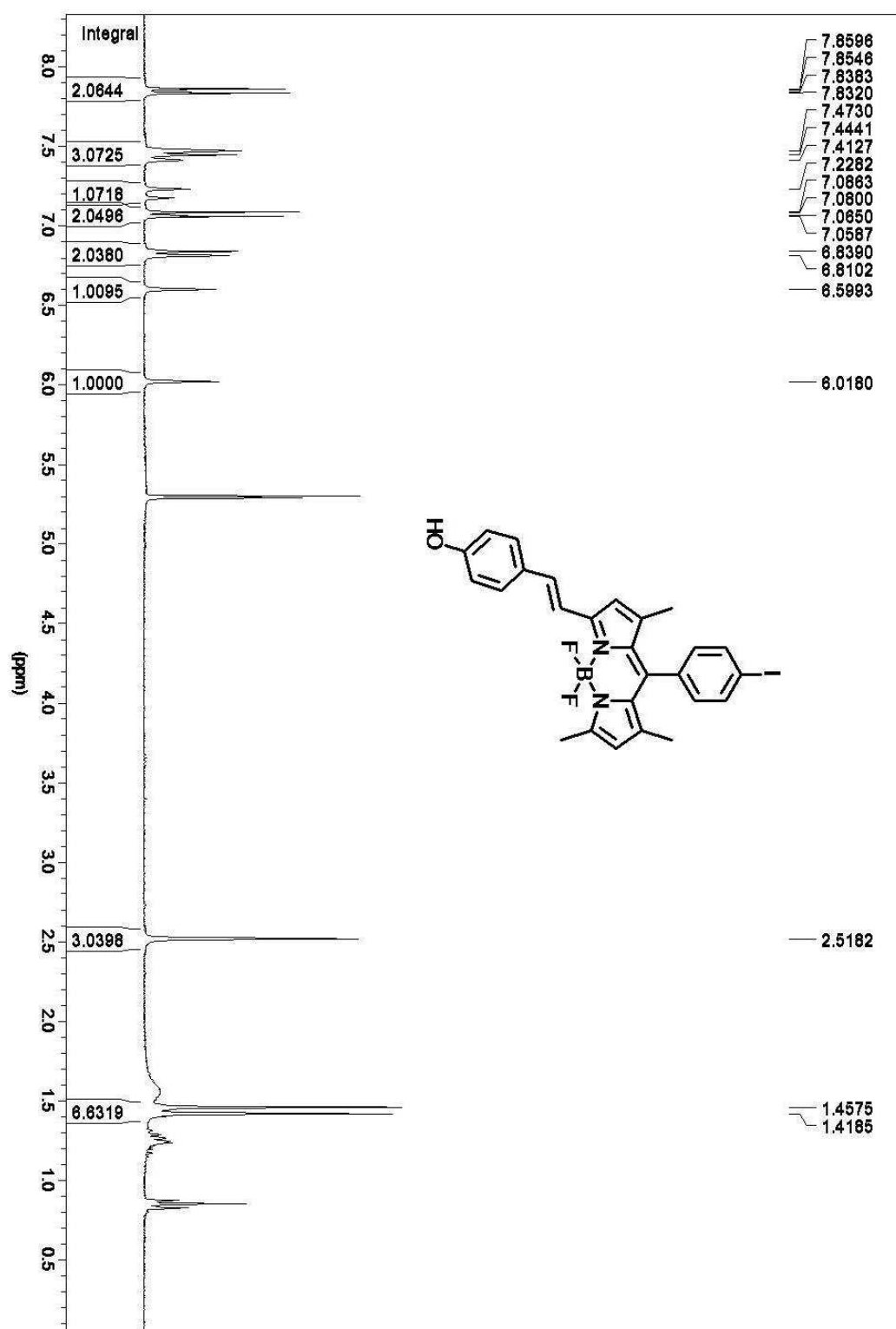


Figure S6: NMR spectra  $^1\text{H}$  of compound **2a** in  $\text{CD}_2\text{Cl}_2$ .

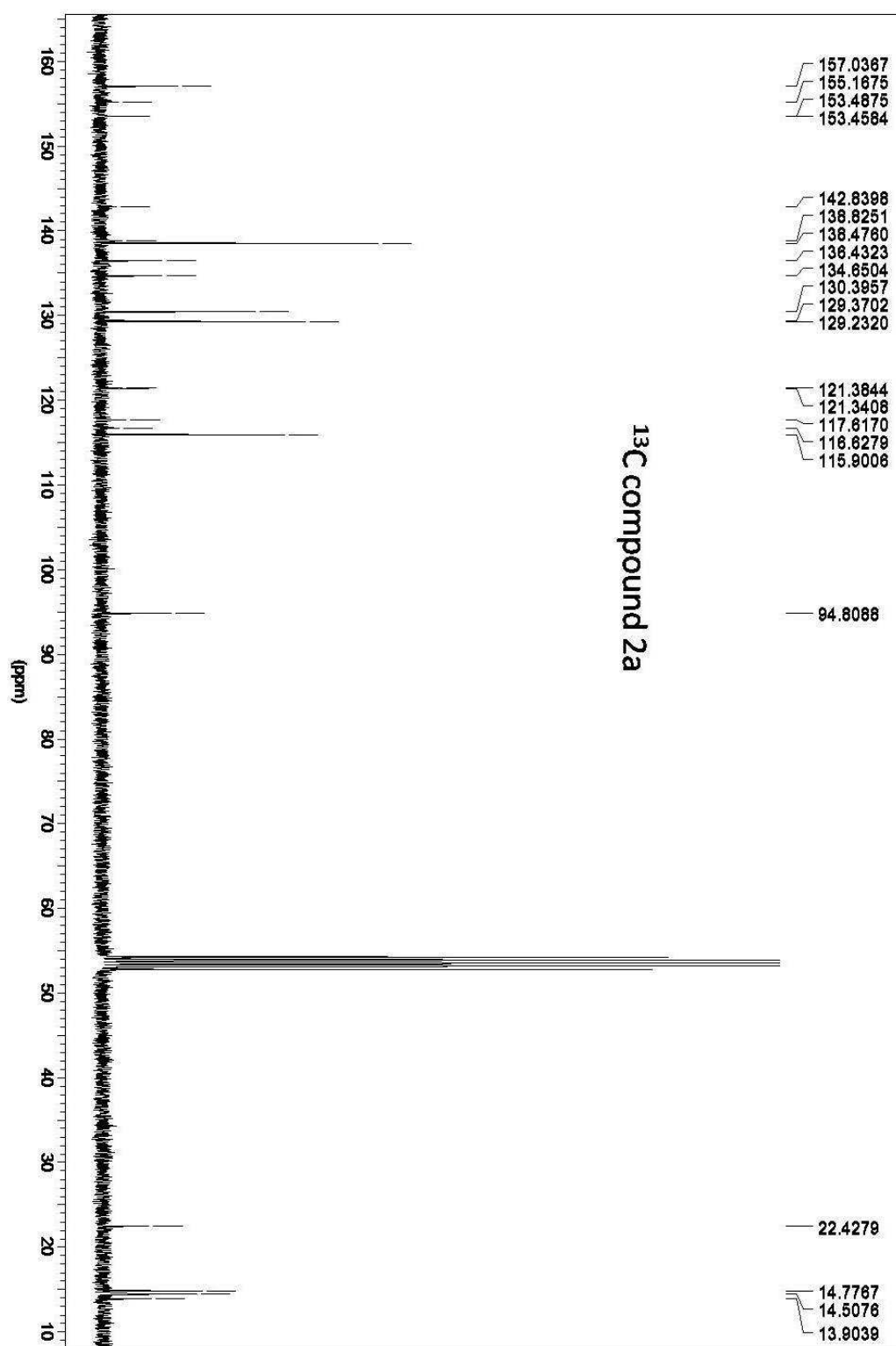
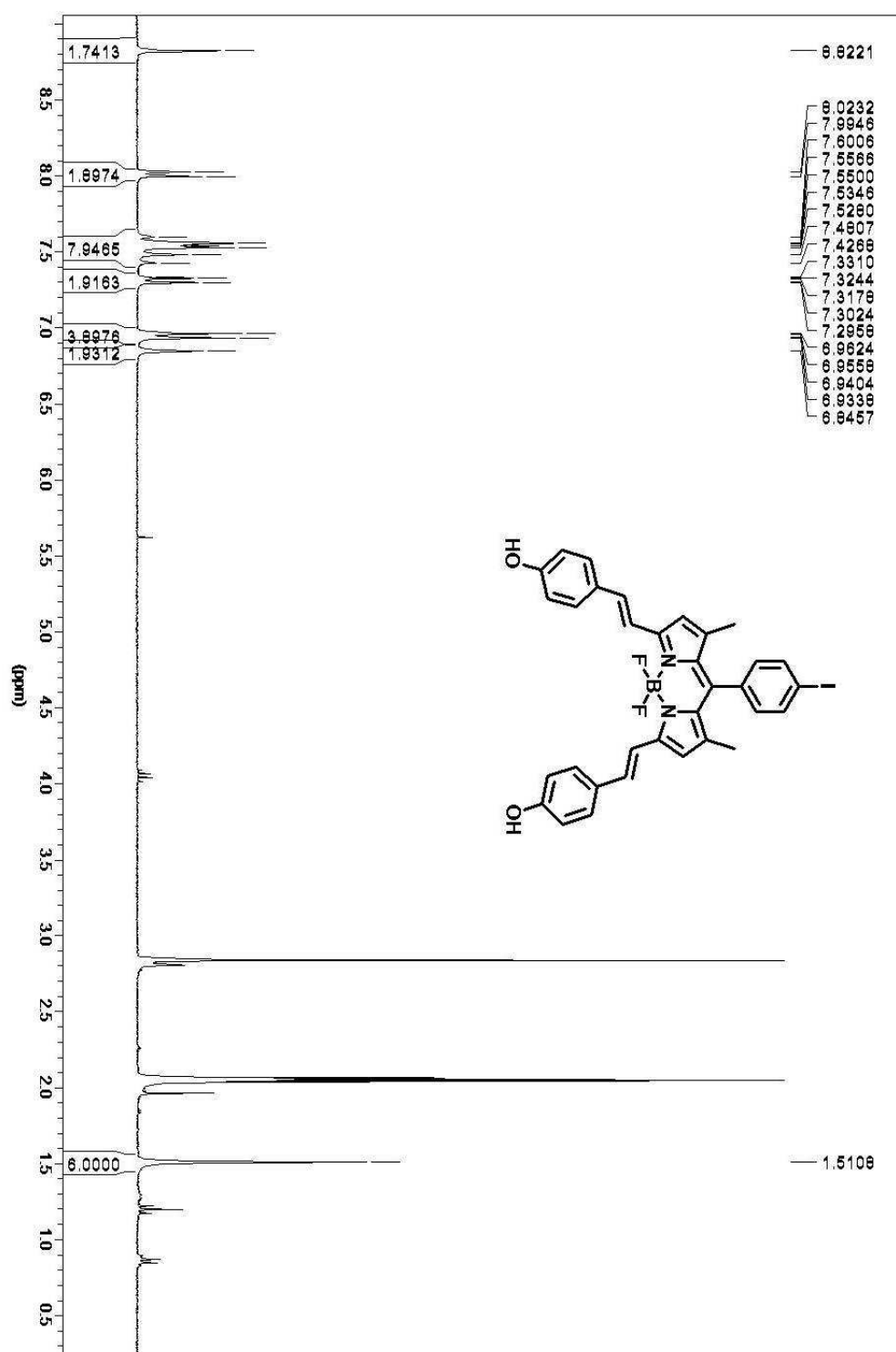
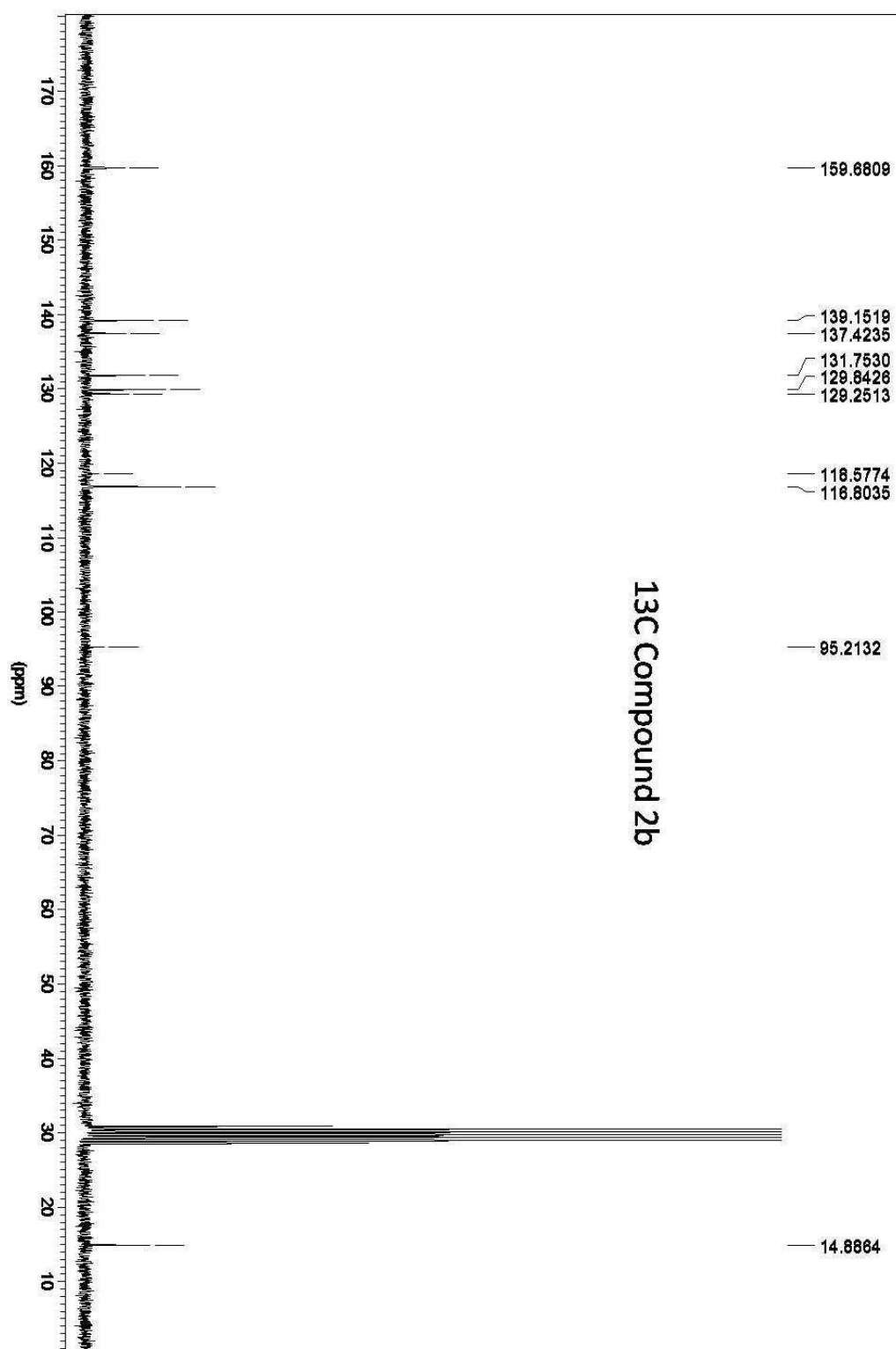


Figure S7: NMR spectra <sup>13</sup>C of compound **2a** in CD<sub>2</sub>Cl<sub>2</sub>.





**Figure S8:** NMR spectra <sup>1</sup>H of compound **2b** in (CD<sub>3</sub>)<sub>2</sub>CO.



**Figure S9:** NMR spectra  $^{13}\text{C}$  of compound **2b** in  $(\text{CD}_3)_2\text{CO}$ .

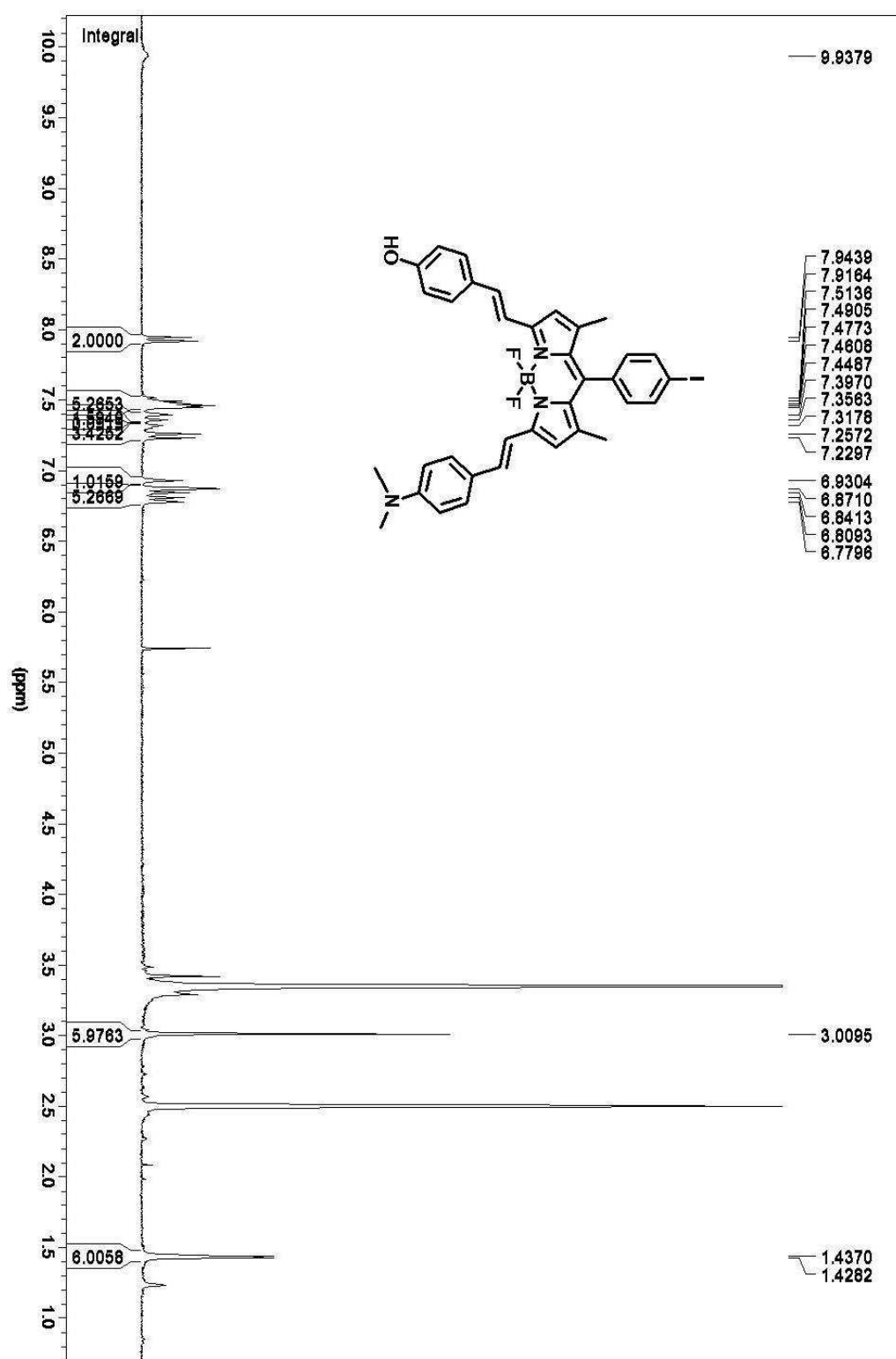


Figure S10: NMR spectra  $^1\text{H}$  of compound 4 in DMSO- $\text{d}_6$ .

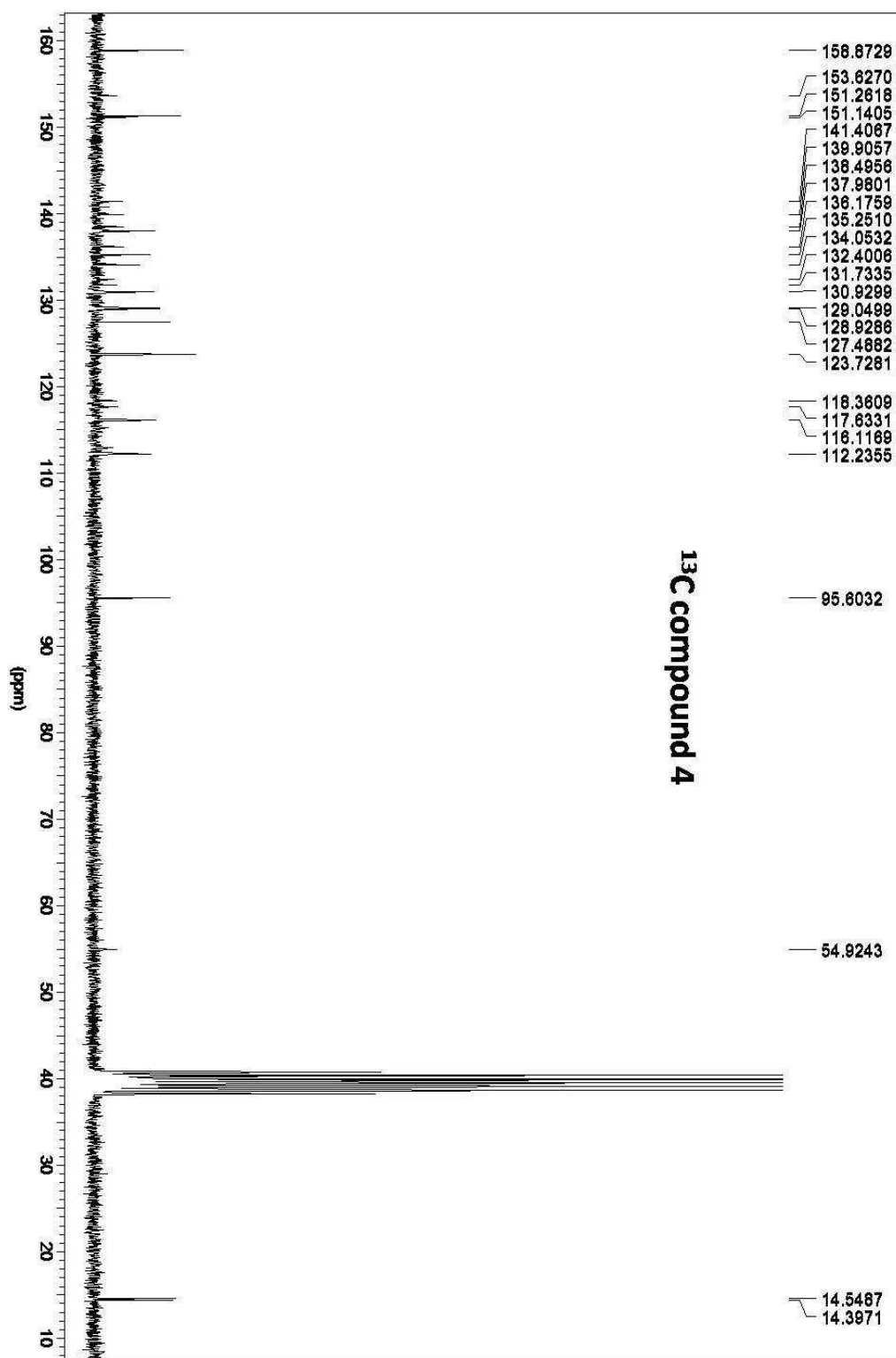


Figure S11: NMR spectra  $^{13}\text{C}$  of compound **4** in DMSO- $\text{d}_6$ .

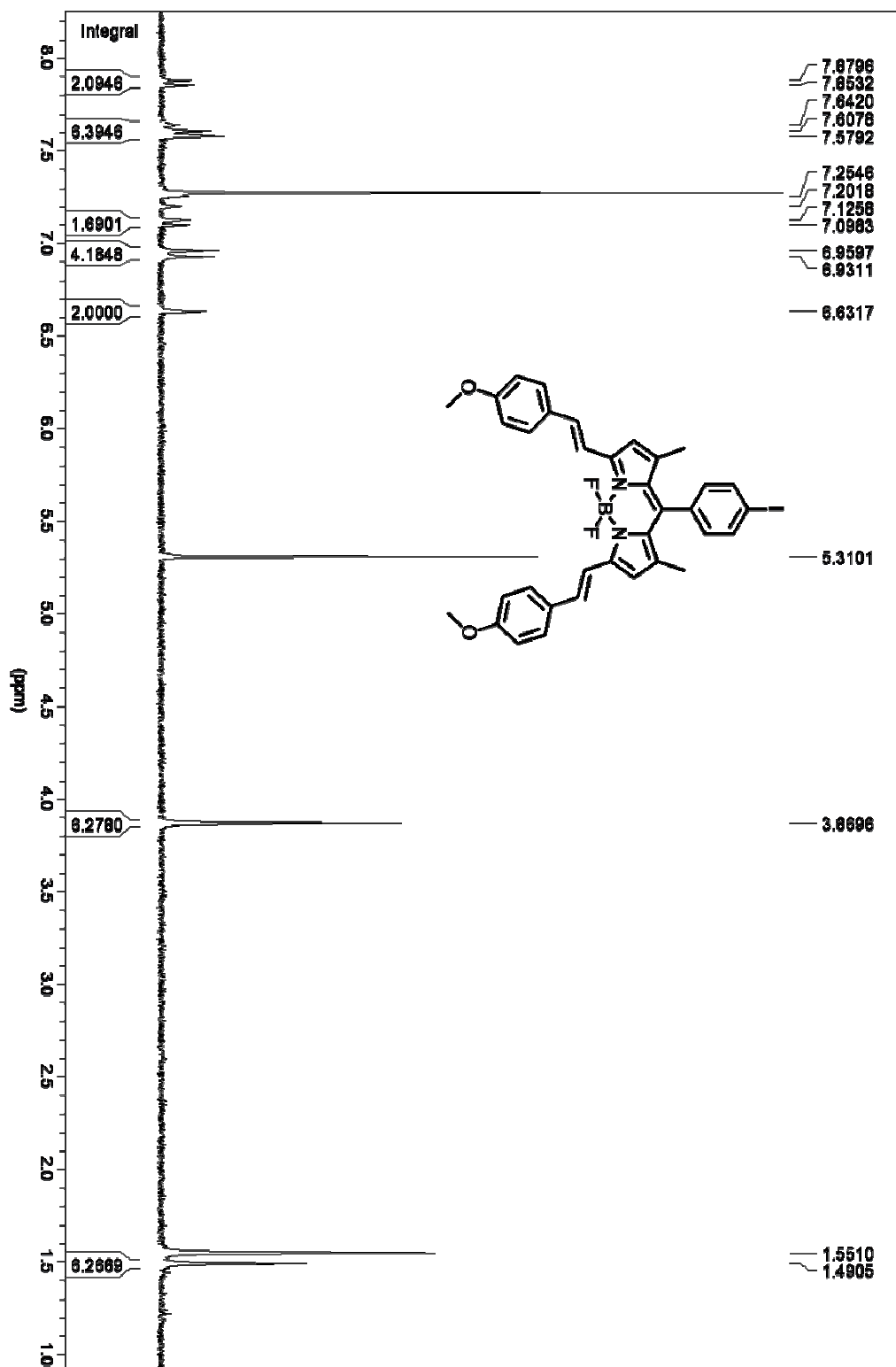
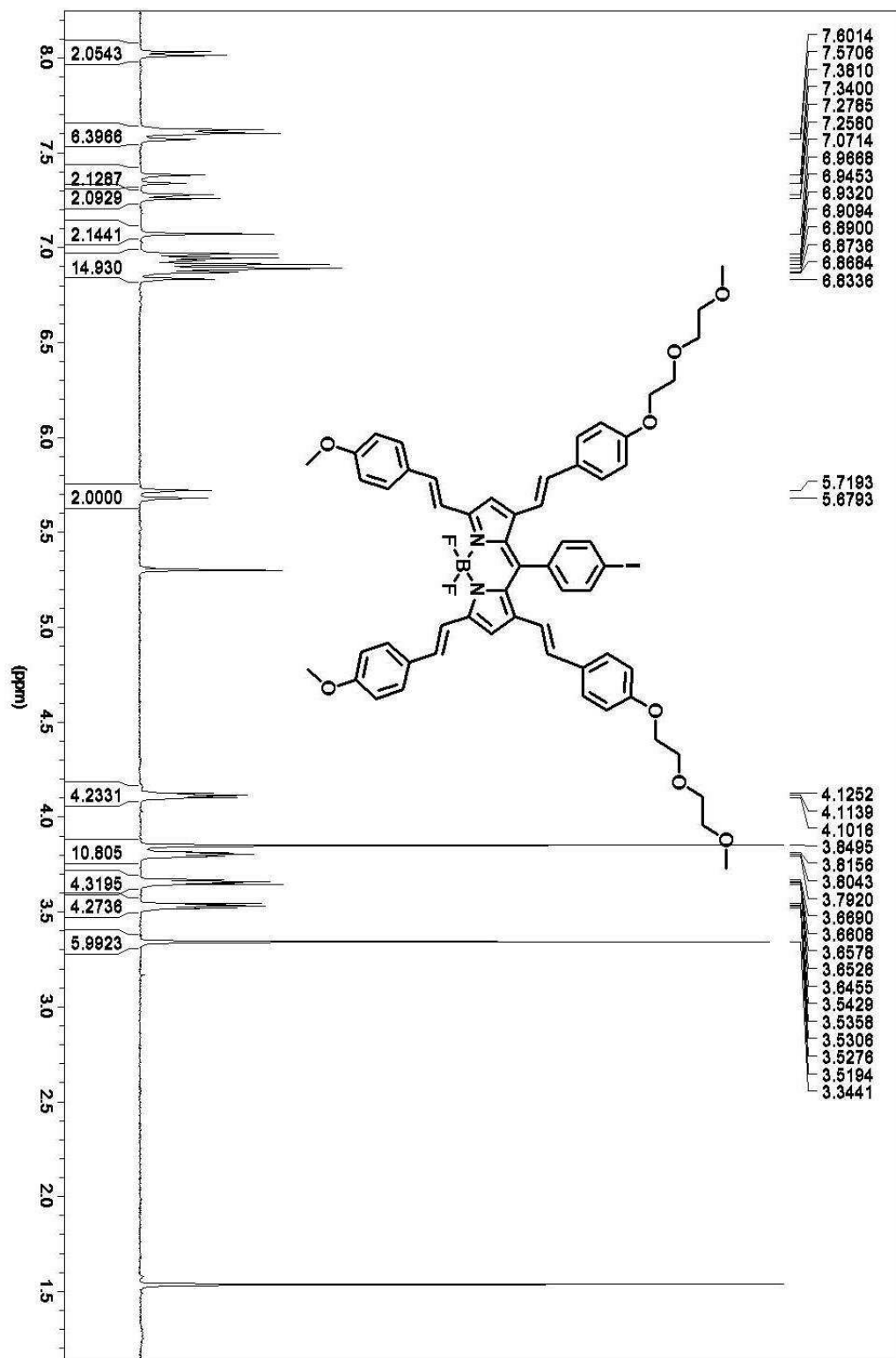


Figure S12: NMR spectra <sup>1</sup>H of compound **5** in CDCl<sub>3</sub>.



**Figure S13:** NMR spectra <sup>1</sup>H of compound **6** in CD<sub>2</sub>Cl<sub>2</sub>.

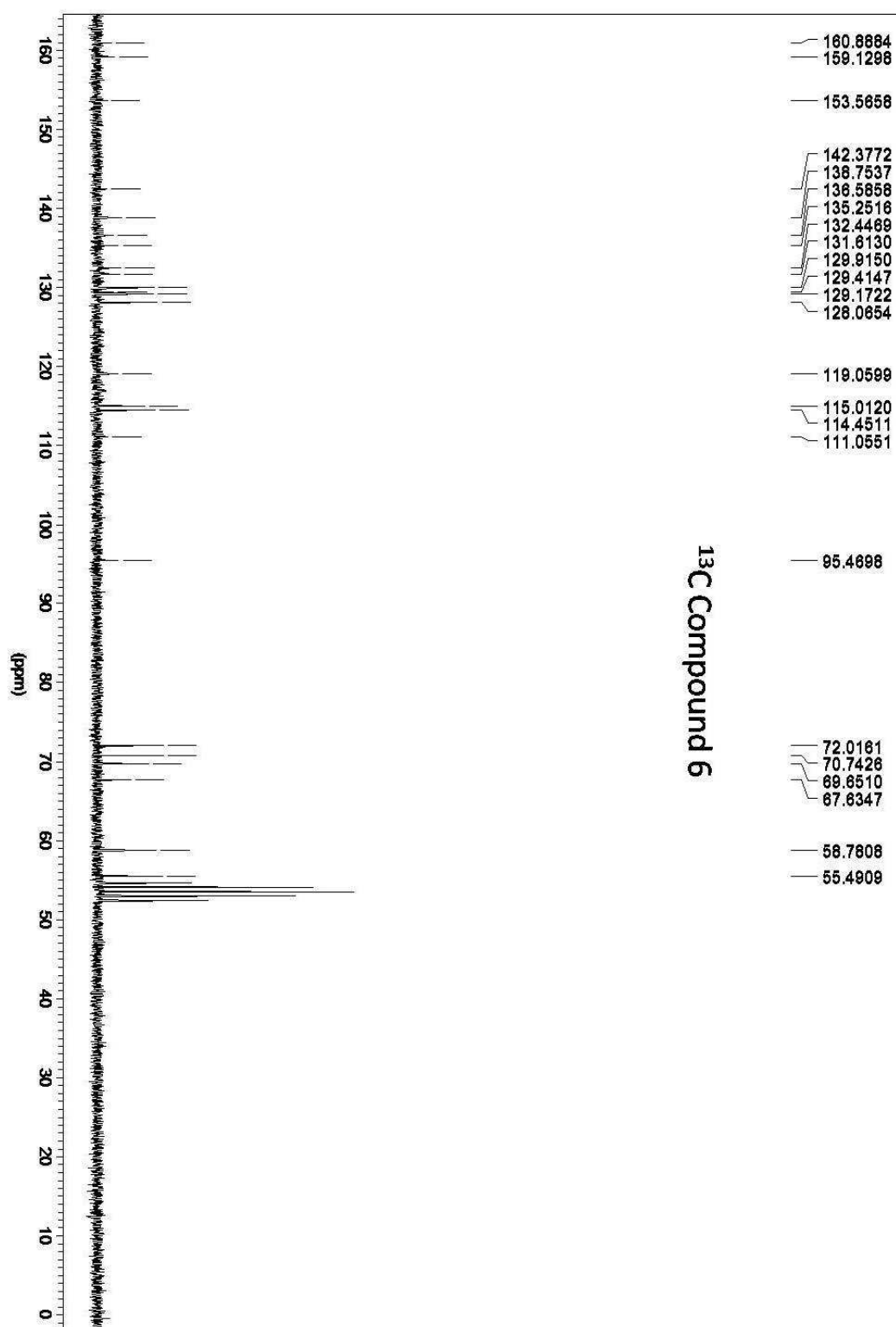


Figure S14: NMR spectra <sup>13</sup>C of compound **6** in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure S15:** NMR spectra  $^1\text{H}$  of compound **7** in  $(\text{CD}_3)_2\text{CO}$ .



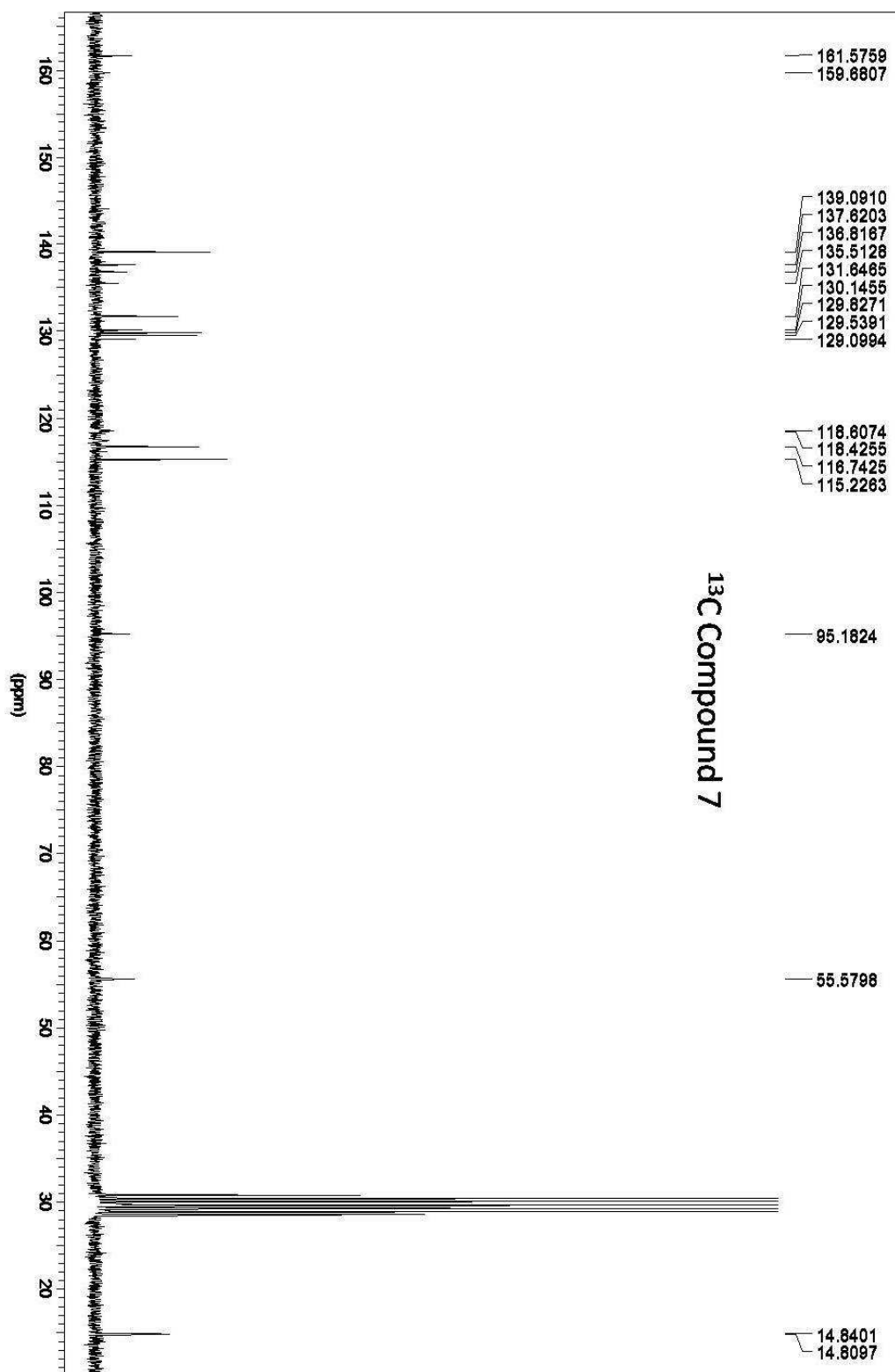


Figure S16: NMR spectra  $^{13}\text{C}$  of compound 7 in  $(\text{CD}_3)_2\text{CO}$ .

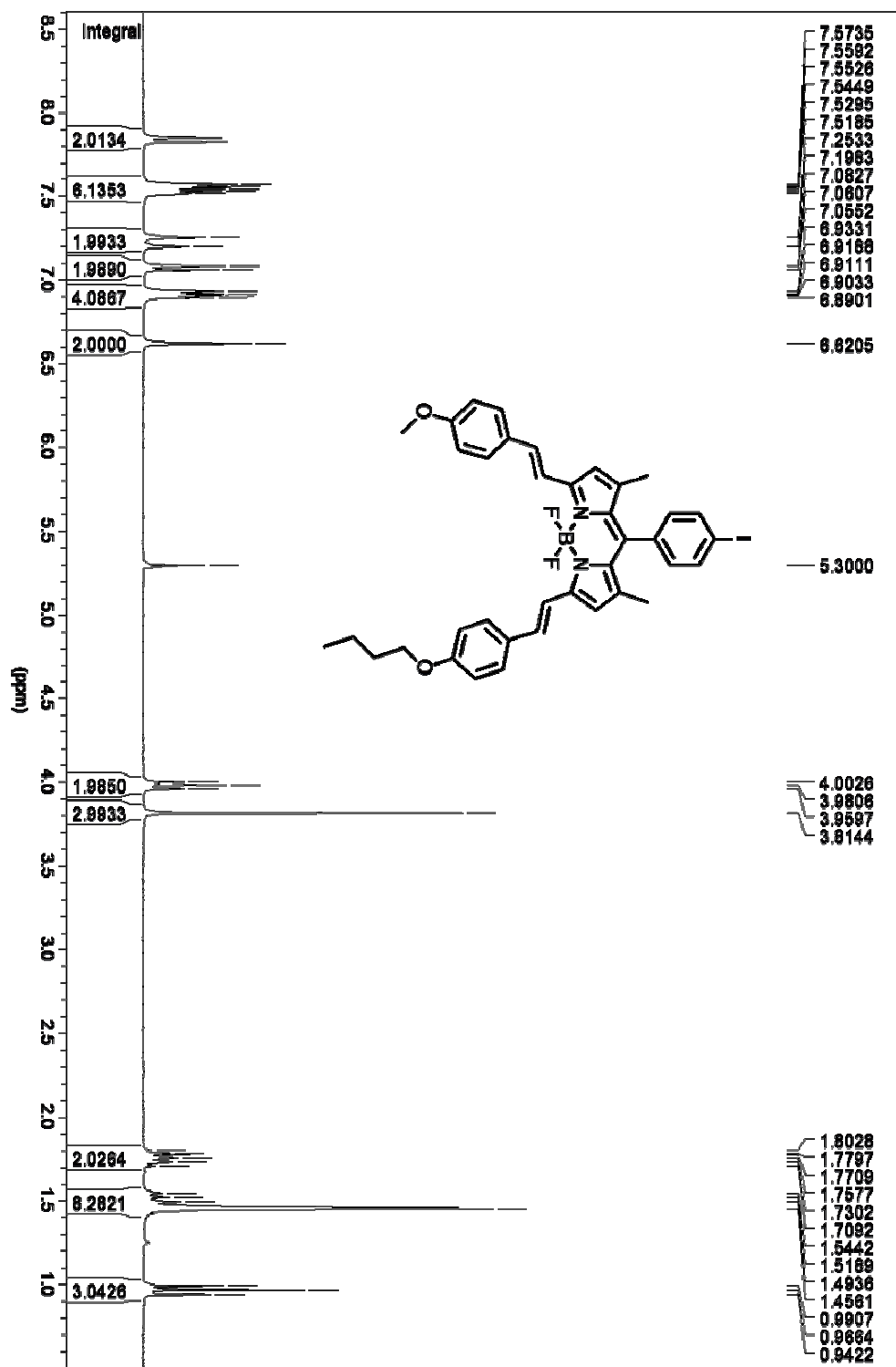
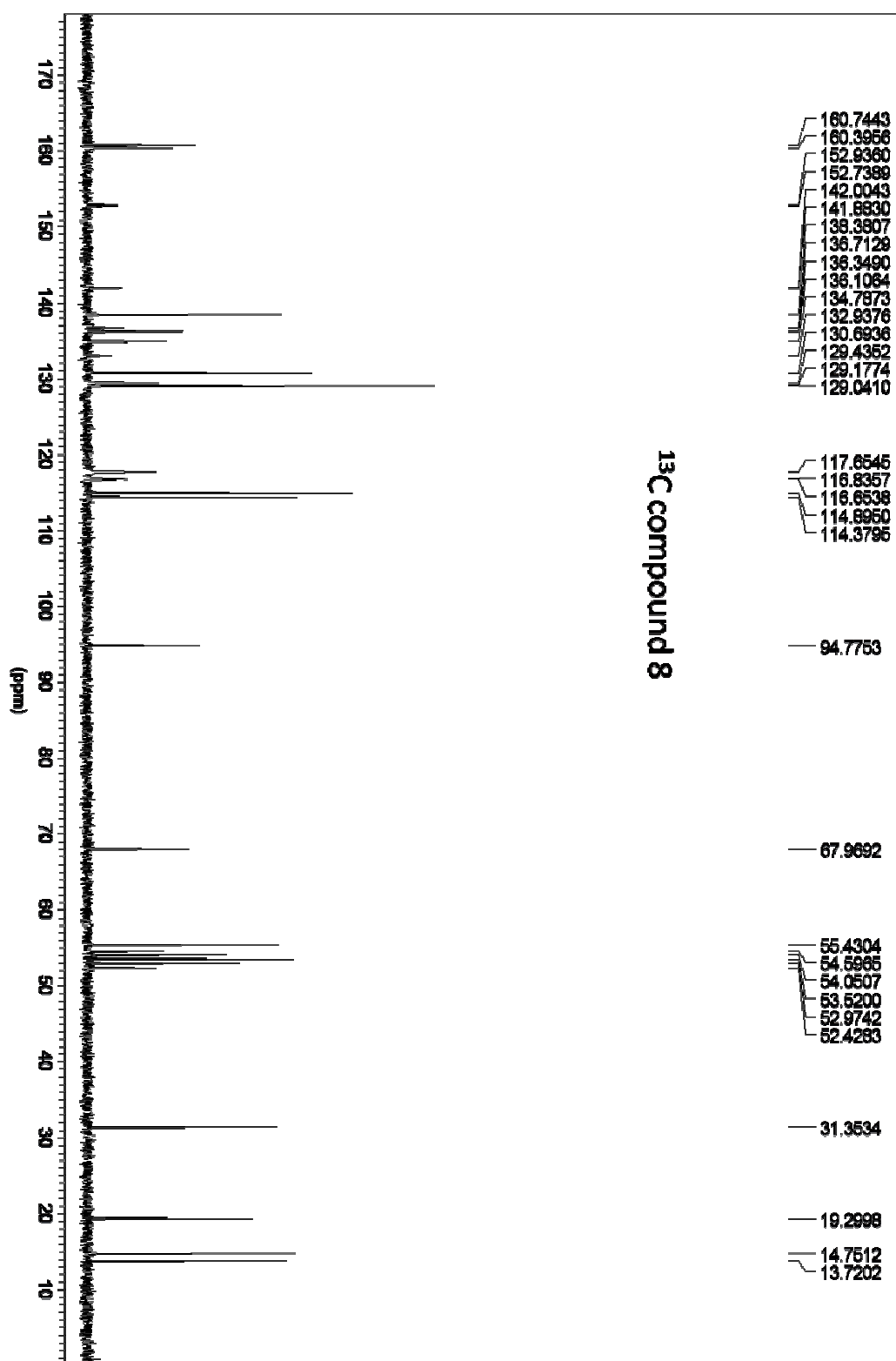


Figure S17: NMR spectra <sup>1</sup>H of compound **8** in CD<sub>2</sub>Cl<sub>2</sub>.



**Figure S18:** NMR spectra  $^{13}\text{C}$  of compound **8** in  $\text{CD}_2\text{Cl}_2$ .

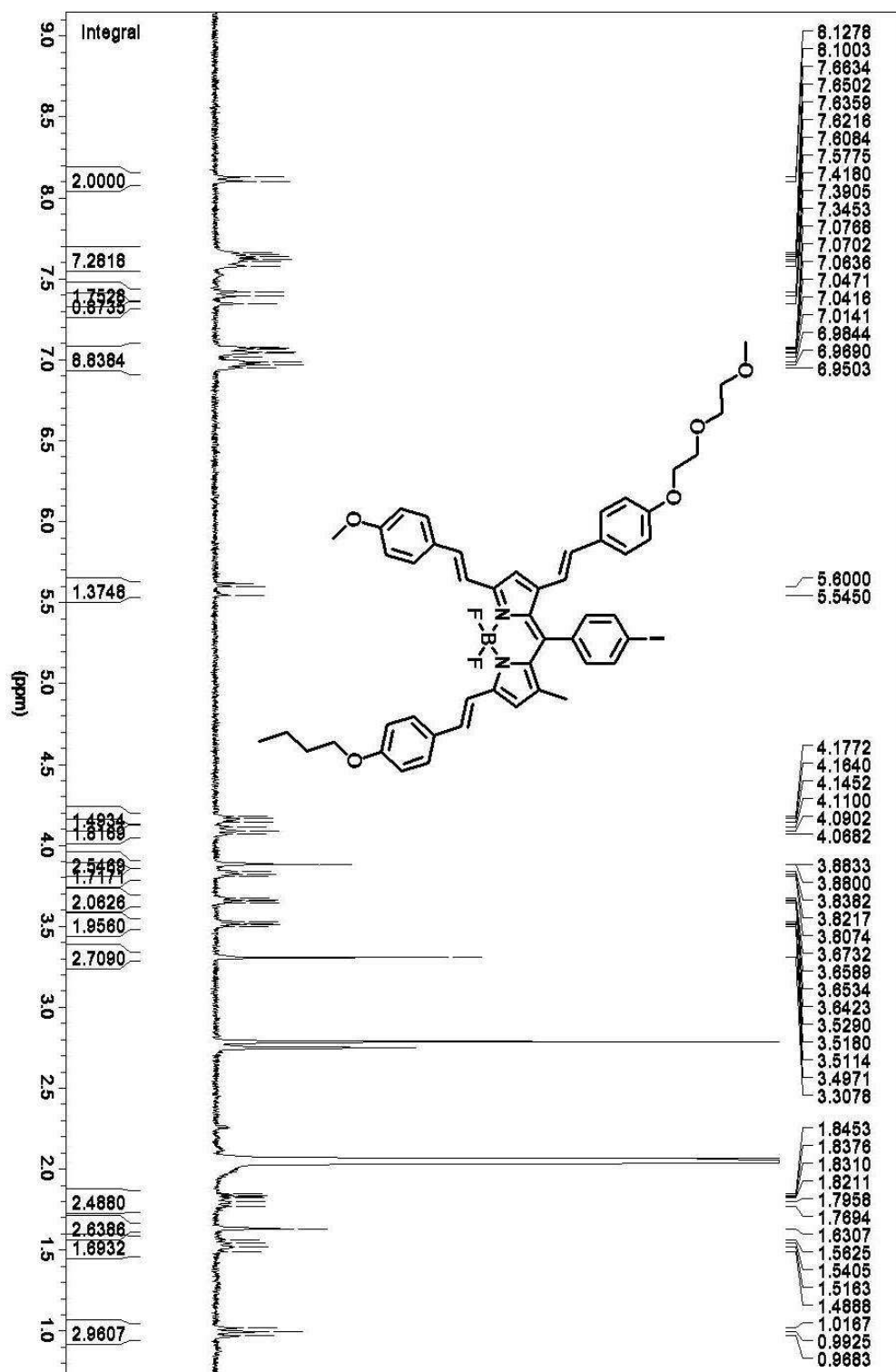


Figure S19: NMR spectra  $^1\text{H}$  in  $(\text{CD}_3)_2\text{CO}$  of compound **9**.

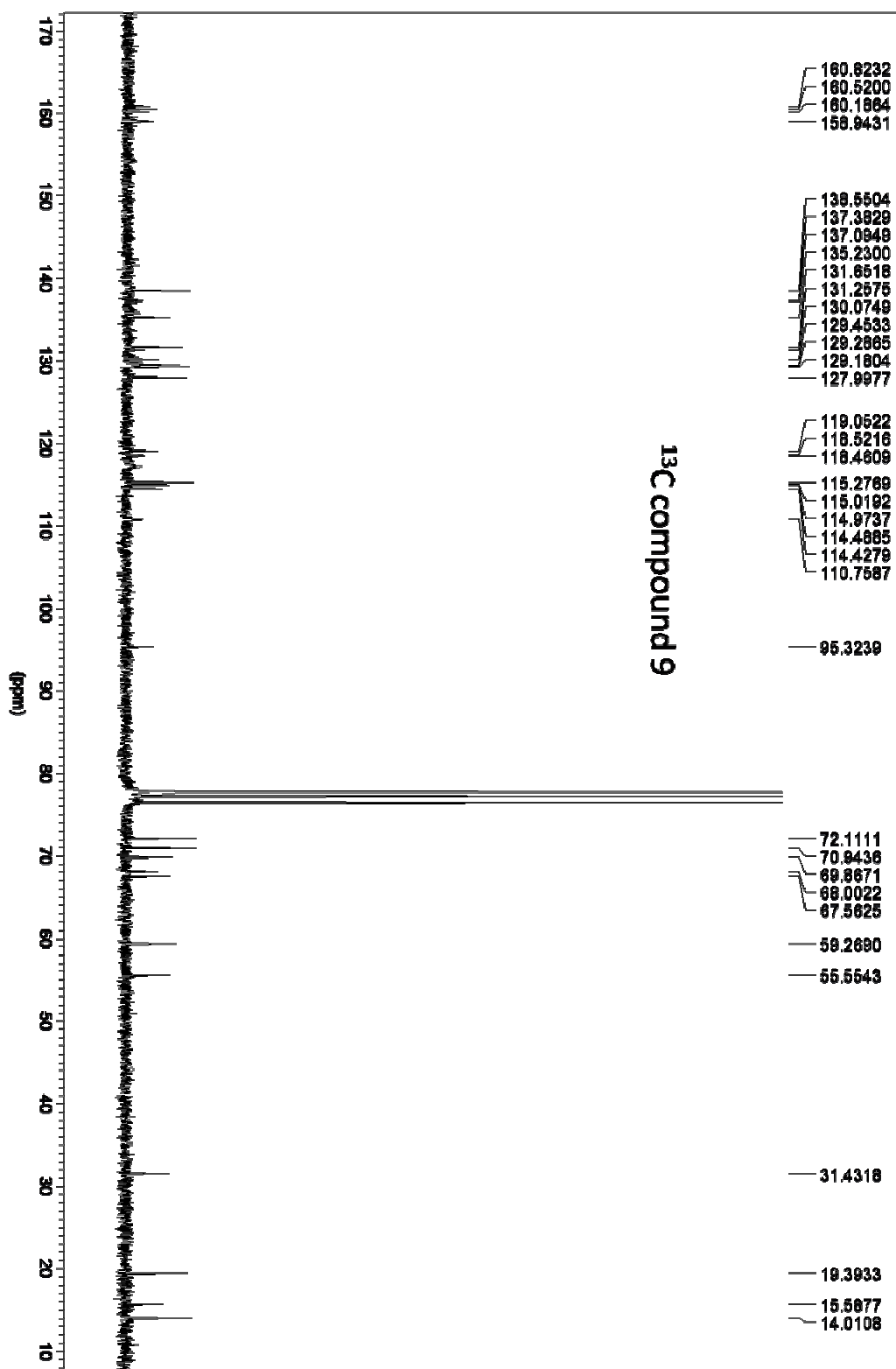


Figure S20: NMR spectra <sup>13</sup>C of compound 9 in CDCl<sub>3</sub>.

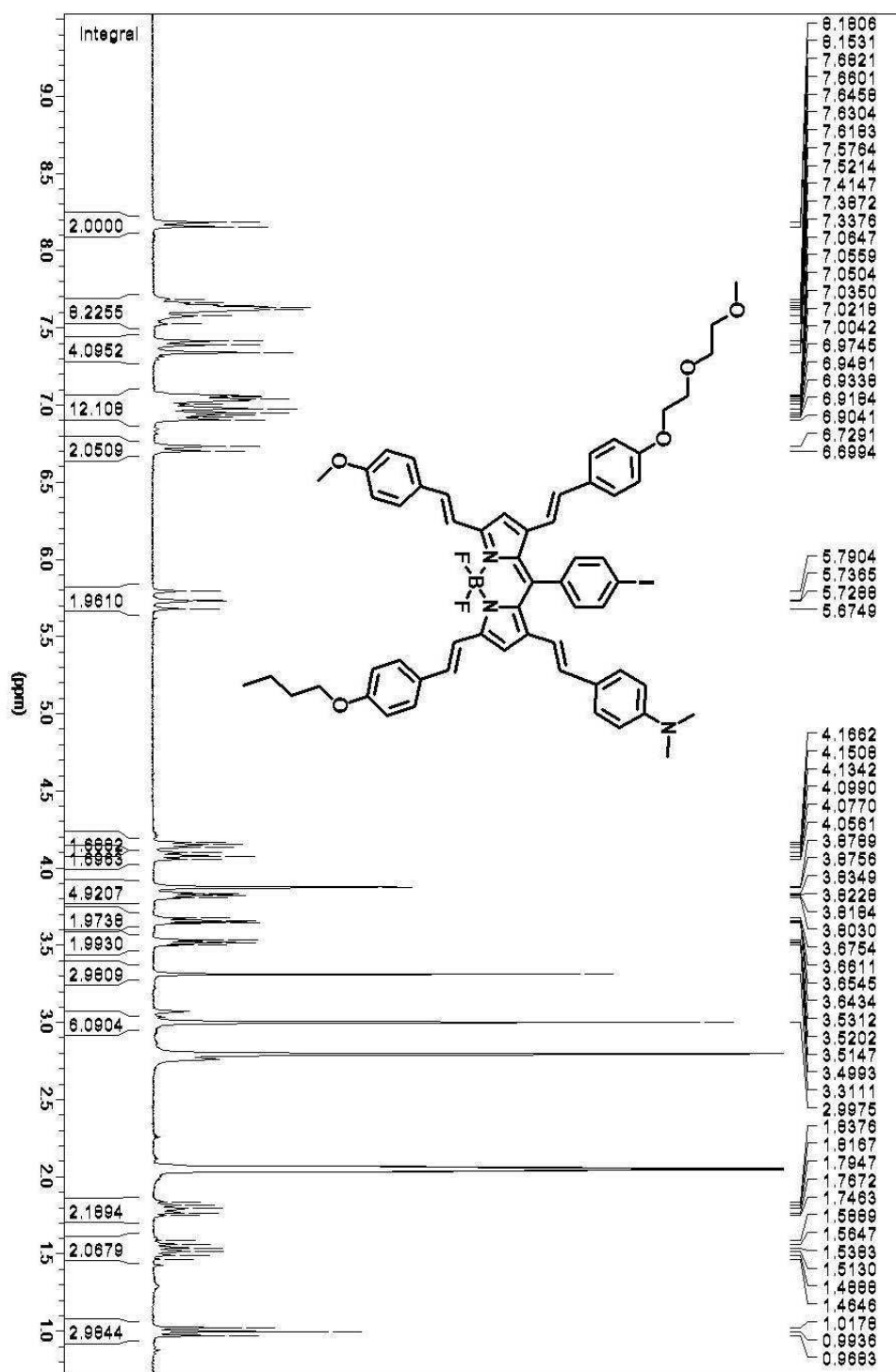


Figure S21: NMR spectra  $^1\text{H}$  of compound **10** in  $(\text{CD}_3)_2\text{CO}$ .

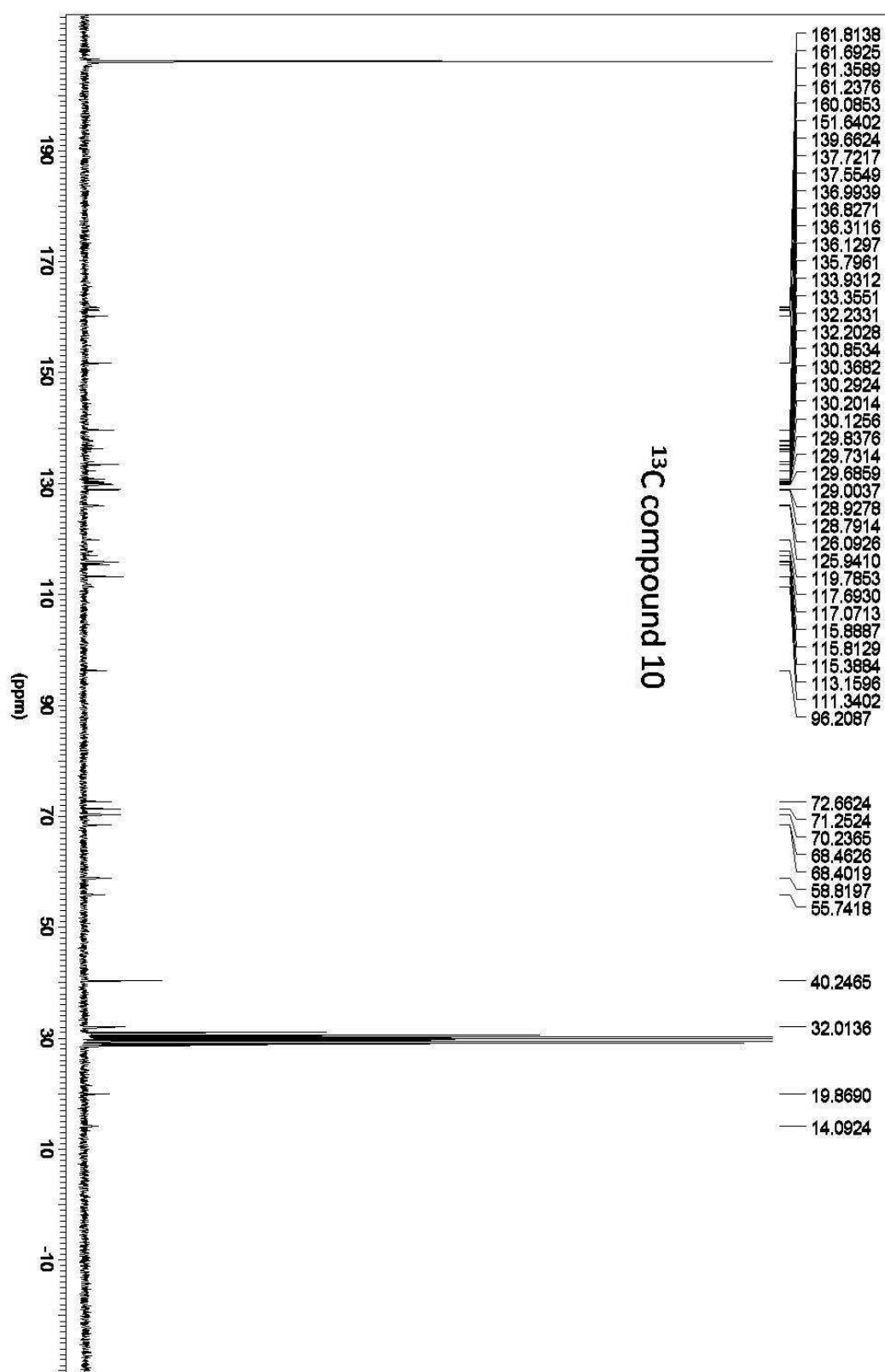


Figure S22: NMR spectra <sup>13</sup>C of compound **10** in (CD<sub>3</sub>)<sub>2</sub>CO.

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- <sup>4</sup> (a) Niu, S-L; Ulrich, G; Retailleau, P; Harrowfield, J; Ziesse R. *Tetrahedron Lett.* **2009**, *42*, 2097–2099. (b) Mula, S; Ulrich, G; Ziesse R. *Tetrahedron Lett.* **2009**, *50*, 6383-6388.
- <sup>5</sup> Rousseau, T; Cravino, A; Bura, T; Ulrich, G; Ziesse R; Roncali, J. *Chem. Commun* **2009**, *13*, 1673-1675.
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- <sup>7</sup> Otwinowski, Z. and Minor, W. (1997) *Processing of X-ray Diffraction Data Collected in Oscillation Mode*, *Methods in Enzymology*, Volume **276**: *Macromolecular Crystallography*, part A, p.307-326, C.W. Carter, Jr. & R.M. Sweet, Eds., Academic Press.
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