

Synthesis and Electronic Properties of π -Extended Flavins

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a) General experimental conditions

Reagents, catalysts, ligands were purchased reagent grade and used without further purification. The used solvents were dried and distilled according to standard procedures.¹ Column chromatography: silica gel 60, mesh 70-230. TLC: silica gel plates.

Analytical characterization of the synthesized compounds was done by common methods. Melting Points were determined on Büchi SMP or a Lambda Photometrics OptiMelt MPA 100 and are uncorrected. IR Spectra were recorded with a Bio-Rad FT-IR Excalibur FTS 3000 equipped with a Specac *Golden Gate* Diamond Single Reflection ATR-System. NMR spectra were recorded in CDCl₃ and TFA_d on Bruker Avance 300 (¹H: 300.1 MHz, ¹³C: 75.5 MHz, T = 300 K) relative to external standards unless stated otherwise. The assignments of quaternary C, CH, CH₂ and CH₃ have been made by using DEPT spectra. Electro spray mass spectra were performed on a Finnigan MAT TSO 7000 ESI-spectrometer. Other Mass Spectra were recorded on Varian CH-5 (EI), Finnigan MAT 95 (CI; FAB and FD); Xenon serves as the ionization gas for FAB.

Fluorescence spectra

Luminescence spectra were performed with UV-grade solvents (Baker or Merck) in 1 cm quartz cuvettes (Hellma and recorded using a Fluorolog 3-22 (Horiba Jobin Yvon) spectrophotometer. Emission decay times were measured with a cooled photomultiplier (RCA C7164R) combined with a FAST ComTec multichannel scaler PCI card with a time resolution of 250 ps. For absolute measurements of photoluminescence quantum yields at ambient temperature and at 77 K a Hamamatsu Photonics (C9920-02) system was used.

Cyclic voltammograms (CVs) were recorded in dimethyl sulfoxide (DMSO) solutions containing 0.2 M *n*-Bu₄NPF₆ as the supporting electrolyte. Voltammetric experiments were controlled with a computer-controlled Eco Chemie Autolab PGSTAT 100 with an ADC fast scan generator. The working electrode was a 1 mm diameter planar Pt disk, the auxiliary electrode a Pt wire and the reference electrode was an Ag wire separated from the test solution with a salt bridge containing 0.5 M *n*-Bu₄NPF₆ in acetonitrile. Test solutions were thoroughly deoxygenated by purging with Ar gas prior to voltammetric analysis.

b) Synthesis of the amines 2a – 2c

General procedure for the syntheses of amines (GP2)

In a dry Schlenk flask was added, under inert atmosphere and continuous stirring, sodium *tert*-butoxide (1.2 mole), palladium acetate (0.005 mole), anhydrous 1,4-dioxane, tri-*tert*-butylamine (0.005 mole), bromo-derivative (1 mole) and *n*-butylamine (1.2 mole). The reaction mixture was moved in to preheated oil bath at 80°C and stirred for 19 h. After cooling to room temp., the solution was diluted with deionized water and methylene chloride. The aqueous phase was extracted with small portions of methylene chloride, the combined organic phases were dried over anhydrous MgSO₄ and the solvents were removed *in vacuo*. The residue was chromatographed on silica gel (petroleum ether : ethyl acetate; 100:1) to furnish the products **2a – 2c** as solids or resins.

N-Butylpyren-4-amine (2a)

This compound was synthesized according to **GP 2** and after purification by flash-chromatography on silica gel (petroleum ether : ethyl acetate; 100:1) compound **2a** (340 mg, 70%) was obtained as a yellow solid. Mp. 77-79°C. *R_f* (petroleum ether: ethyl acetate; 10:1): 0.50.

¹H-NMR (300 MHz, CDCl₃, δ ppm): 1.07 (t, *J* = 6 Hz, 3 H), 1.62 (m, 2 H), 1.89 (m, 2 H), 3.50 (t, *J* = 6 Hz, 2 H), 4.53 (s, 1 H), 7.13 (s, 1 H), 7.93 (t, *J* = 6 Hz, 2 H), 8.01 (m, 4 H), 8.13 (d, *J* = 9 Hz, 1 H), 8.18 (d, *J* = 9 Hz, 1 H). ¹³C-NMR (300 MHz, CDCl₃, δ ppm): 14.40 (CH₃), 20.98 (CH₂), 31.91 (CH₂), 44.35 (CH₂), 102.03 (CH), 117.26 (C_{quat}), 120.27 (C_{quat}), 121.80 (C_{quat}), 123.27 (CH), 125.25 (CH), 125.43 (CH), 125.50 (CH), 125.66 (CH), 126.62 (CH), 127.28 (CH), 128.11 (CH), 131.18 (C_{quat}), 132.09 (C_{quat}), 133.21 (C_{quat}), 142.40 (C_{quat}). IR (ν, cm⁻¹): 3369 (w), 3046 (m), 2952 (m), 2926 (m), 2860 (m), 1468 (m), 1169 (m), 1129 (w), MS (ES-MS) *m/z*: 274 (M⁺+H). Anal. calcd. f. C₂₀H₁₉N: C 87.87, H 7.01, N 5.12, found: C 87.68, H 6.90, N 5.07.

N-Butylanthracen-2-amine (2b)

This compound was synthesized according to **GP 2** and after purification by flash-chromatography on silica gel (petroleum ether : ethyl acetate; 100:1) compound **2b** (272 mg, 61 %) was obtained as a as a yellow solid. Mp. 300 °C decomp. *R_f* (petroleum ether: ethyl acetate, 10:1): 0.44. ¹H-NMR (300 MHz, CD₂Cl₂, δ ppm): 0.99 (t, *J* = 6 Hz, 3 H), 1.51 (m, 2 H), 1.70 (m, 2 H), 3.25 (t, *J* = 6 Hz, 2 H), 3.95 ppm (s, 1H), 6.81 (s, 1 H), 6.91 (dd, *J* = 3 Hz, *J* = 9 Hz, 1 H), 7.33 (m, 2 H), 7.76 (d, *J* = 9 Hz, 1 H), 7.87 (m, 2 H), 8.08 (s, 1 H), 8.21 (s, 1 H). ¹³C-NMR (300 MHz, CD₂Cl₂, δ ppm): 13.80 (CH₃), 20.50 (CH₂), 31.47 (CH₂),

43.62 (CH₂), 100.74 (CH), 120.56 (C_{quat}), 122.22 (CH), 123.49 (C_{quat}), 125.31 (CH), 126.05 (C_{quat}), 127.31 (CH, CH), 128.22 (CH), 129.16 (CH, CH), 132.60 (C_{quat}), 133.97 (C_{quat}), 145.62 (C_{quat}), IR (ν , cm⁻¹): 3393 (w), 3065 (w), 2918 (m), 1480 (m), 1461 (m), 1277 (m), 1136 (w), MS (ES-MS) m/z : 250 (M⁺+H).

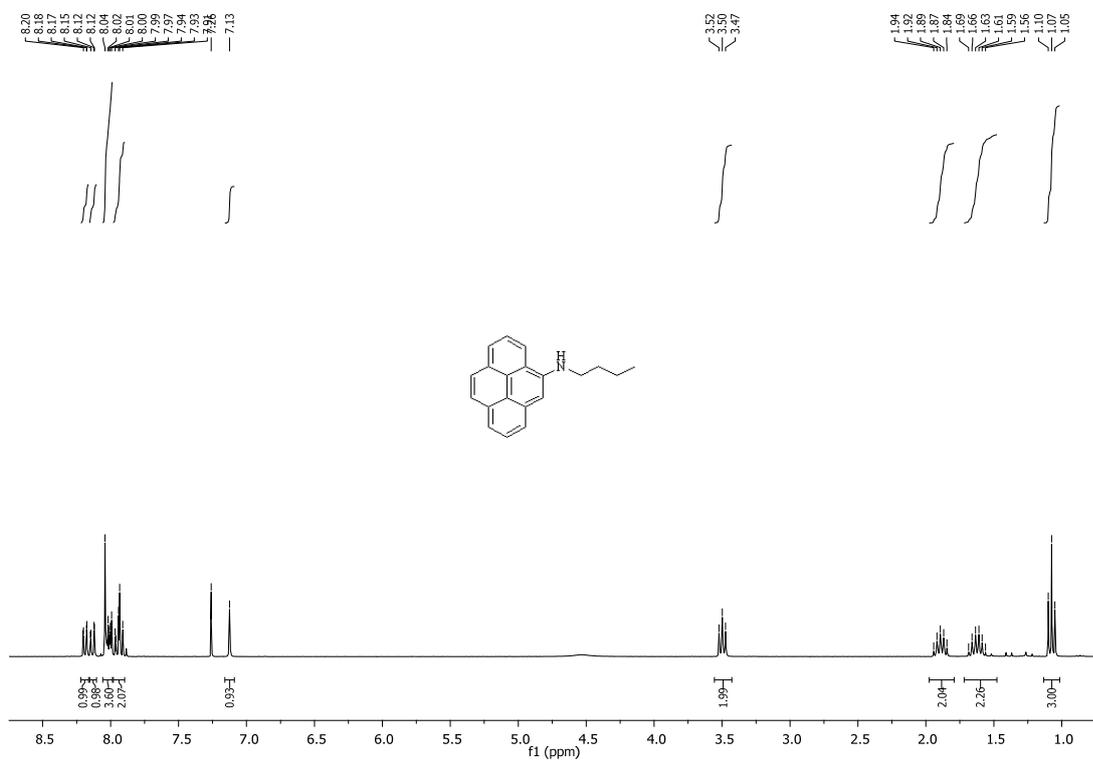
***N*-Butylnaphthalen-2-amine (2c)²**

This compound was synthesized according to **GP 2** and after purification by flash-chromatography on silica gel (petroleum ether : ethyl acetate; 100:1) compound **2c** (370 mg, 77 %) was obtained as a white solid. Mp. 65 - 70 °C. R_f (petroleum ether : ethyl acetate; 10:1): 0.64.

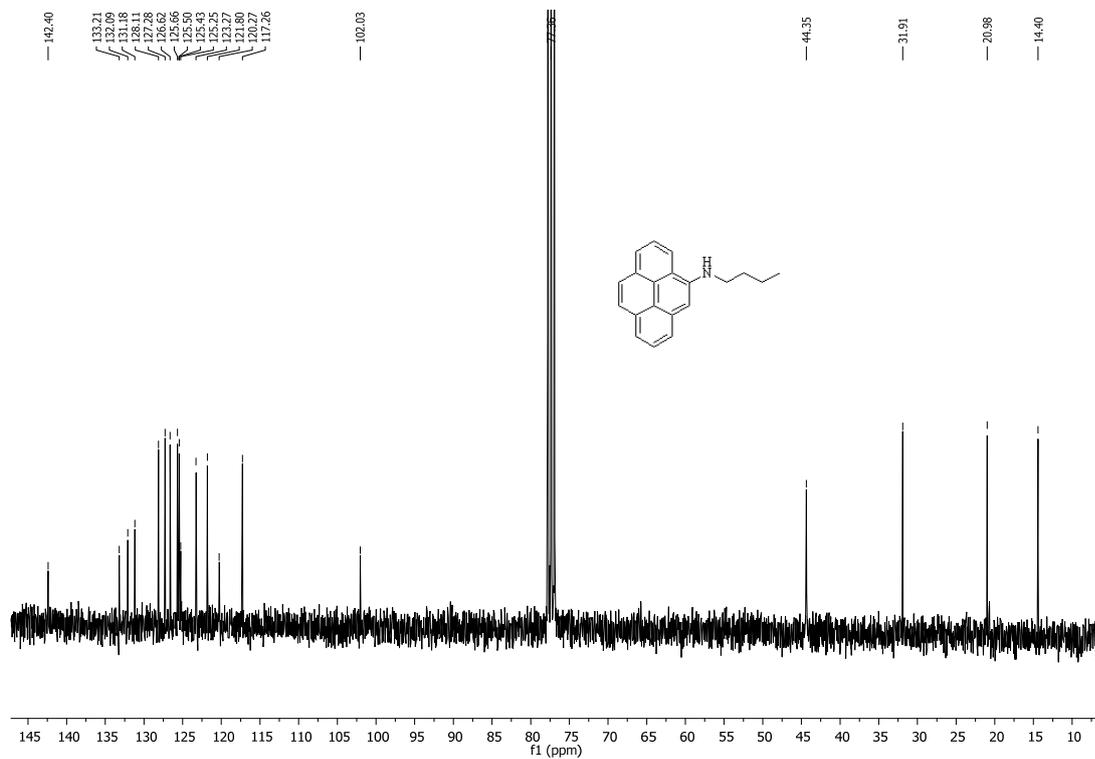
¹H-NMR (300 MHz, CD₂Cl₂, δ ppm): 0.99 (t, J = 6 Hz, 3 H), 1.48 (m, 2 H), 1.67 (m, 2 H), 3.20 (t, J = 6 Hz, 2 H), 3.86 (s, 1 H), 6.78 (s, 1 H), 6.87 (dd, J = 3 Hz, J = 9 Hz, 1 H), 7.16 (t, J = 6 Hz, 1 H), 7.34 (t, J = 6 Hz, 1 H), 7.61 (d, J = 9 Hz, 2 H), 7.65 (d, J = 6 Hz, 1 H). ¹³C-NMR (300 MHz, CD₂Cl₂, δ ppm): 13.81 (CH₃), 20.47 (CH₂), 31.59 (CH₂), 43.71 (CH₂), 103.81 (CH), 118.09 (CH), 121.69 (CH), 125.80 (CH), 126.27 (CH), 127.39 (CH), 127.60 (C_{quat}), 128.74 (CH), 135.50 (C_{quat}), 146.49 (C_{quat}). IR (ν , cm⁻¹): 3048 (w), 2956 (m), 2927 (m), 1602 (m), 1473 (m), 1359 (m), 1080 (w). MS (ES-MS) m/z : 200 (M⁺+H).

c) ^1H and ^{13}C NMR spectra of 2a – 2c

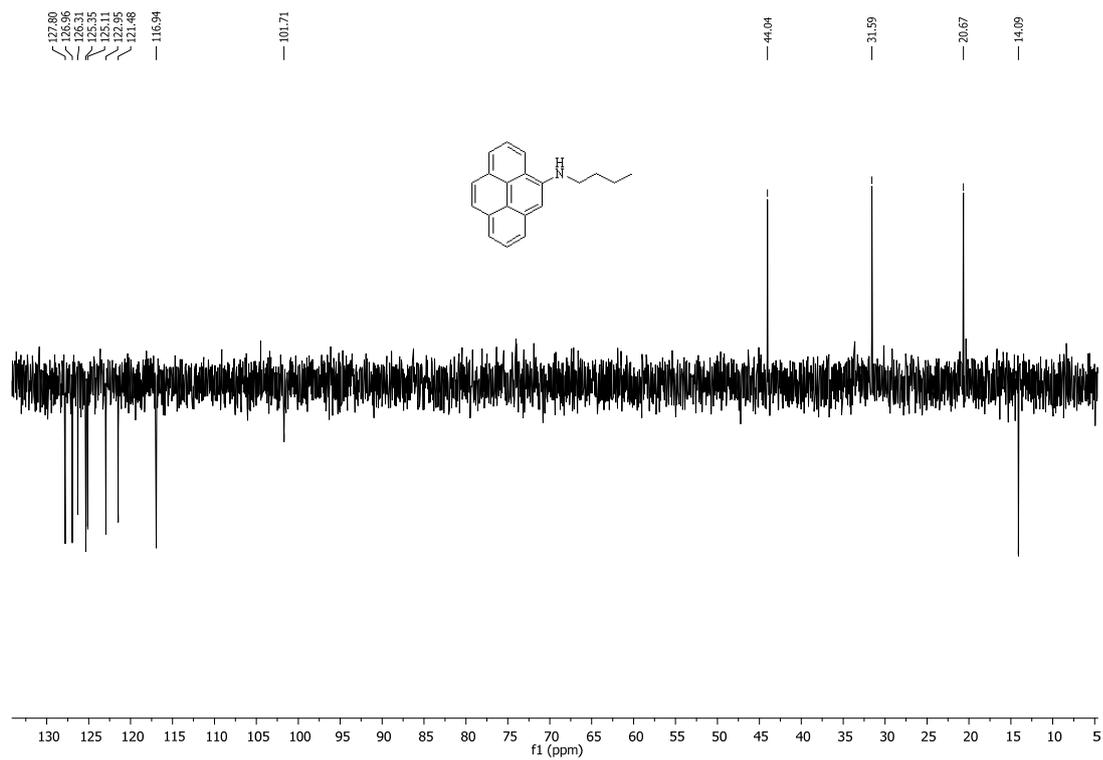
^1H NMR spectra of 2a recorded in CDCl_3 (298K, 300 MHz)



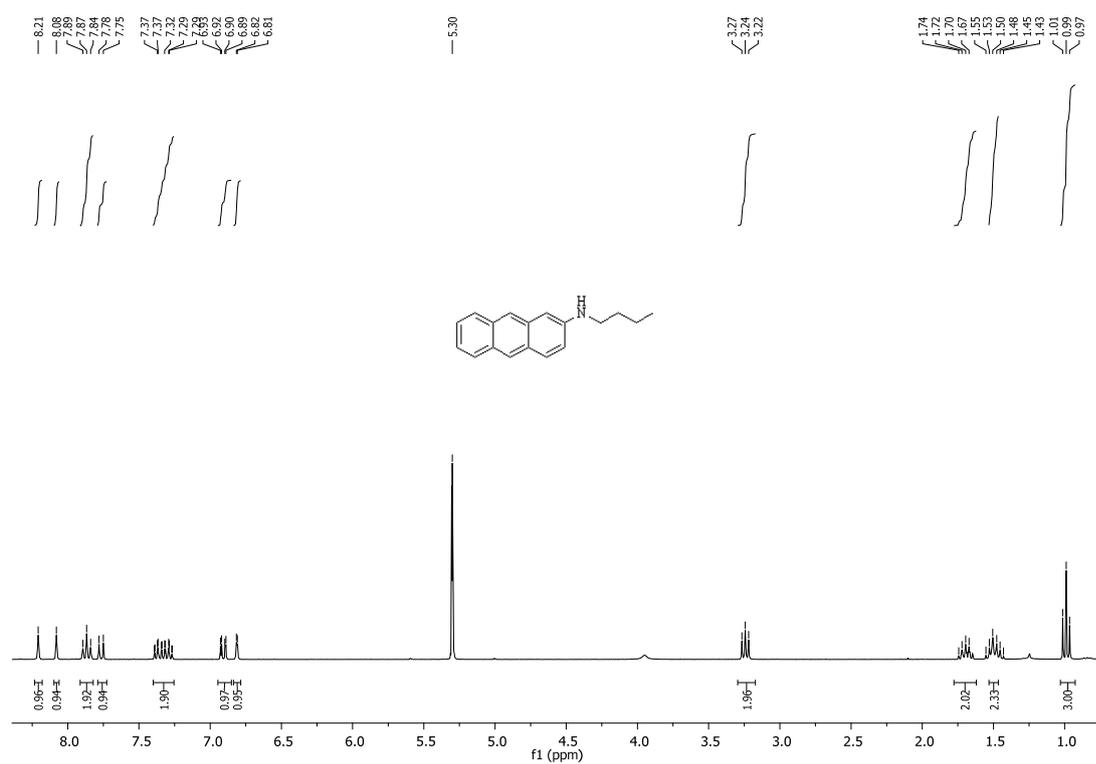
^{13}C NMR spectra of 2a recorded in CDCl_3 (298K, 75 MHz)



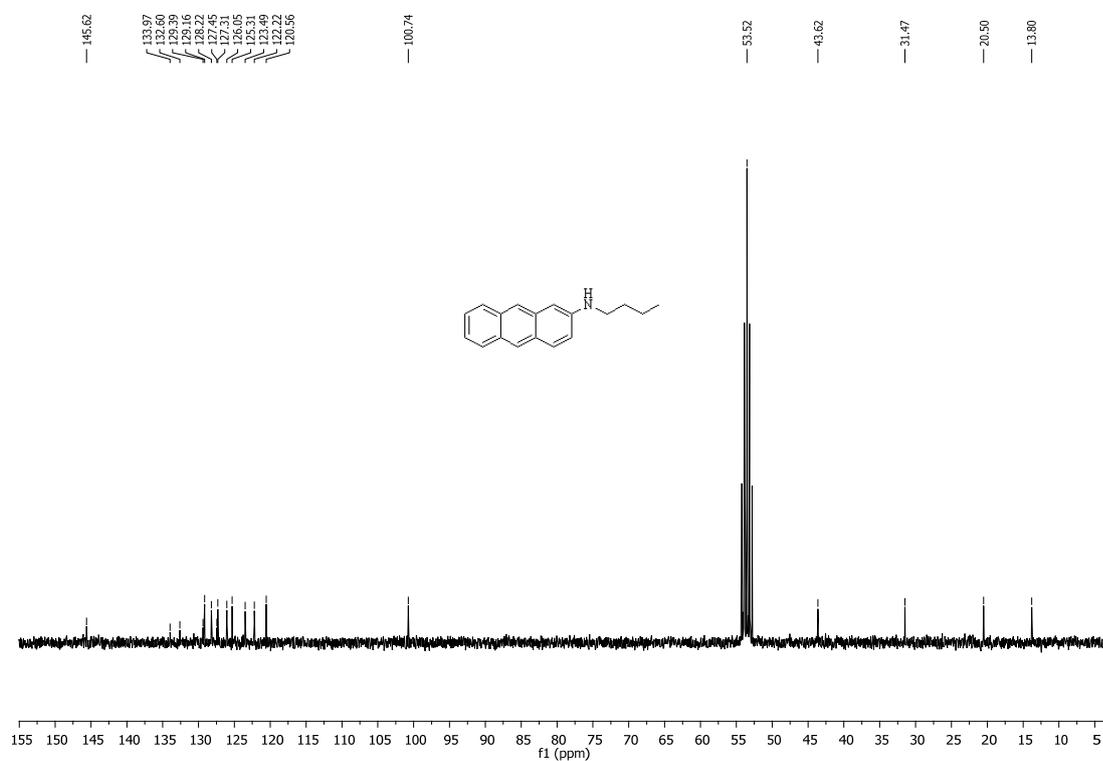
DEPT NMR spectra of **2a** recorded in CDCl₃ (298K, 75 MHz)



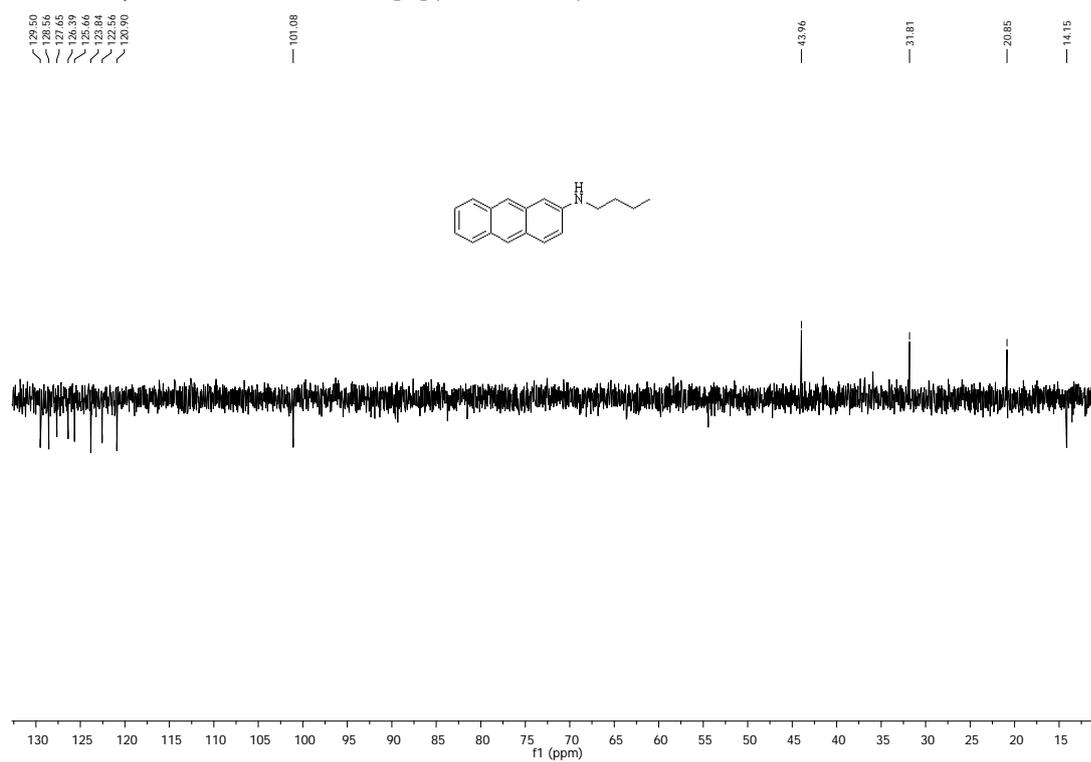
¹H NMR spectra of **2b** recorded in CD₂Cl₂ (298K, 300 MHz)



¹³C NMR spectra of **2b** recorded in CH₃Cl (298K, 75 MHz)

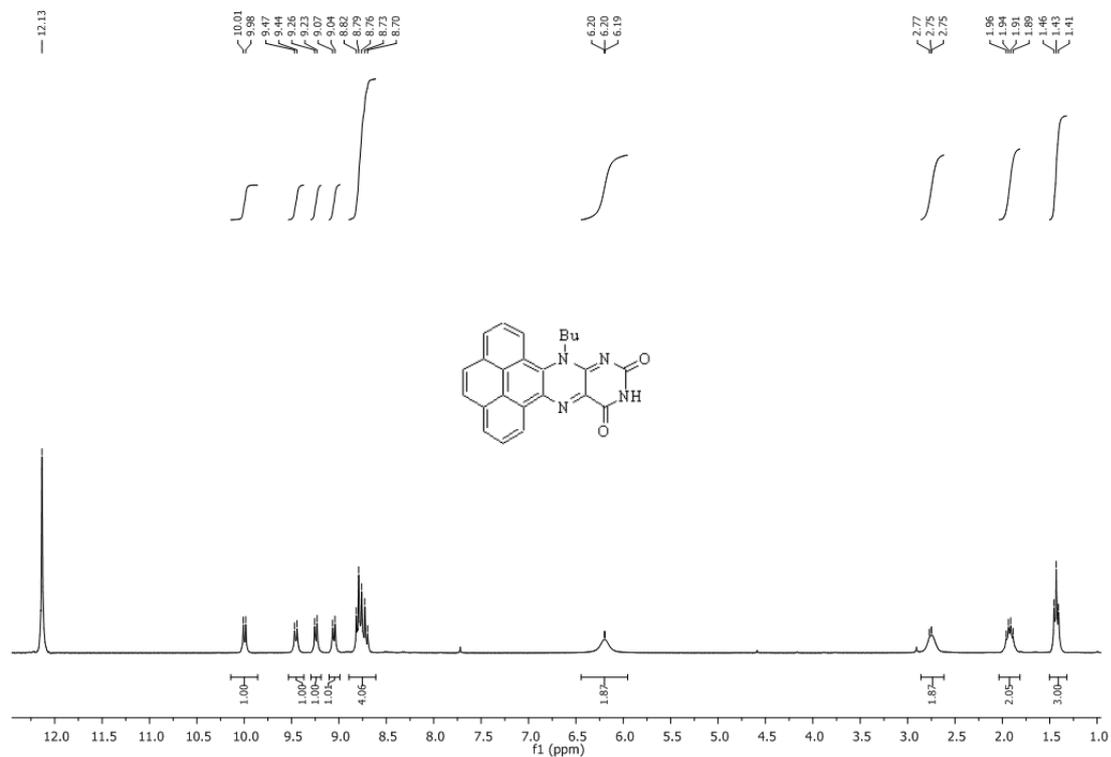


DEPT NMR spectra of **2b** recorded in CD₂Cl₂ (298K, 75 MHz)

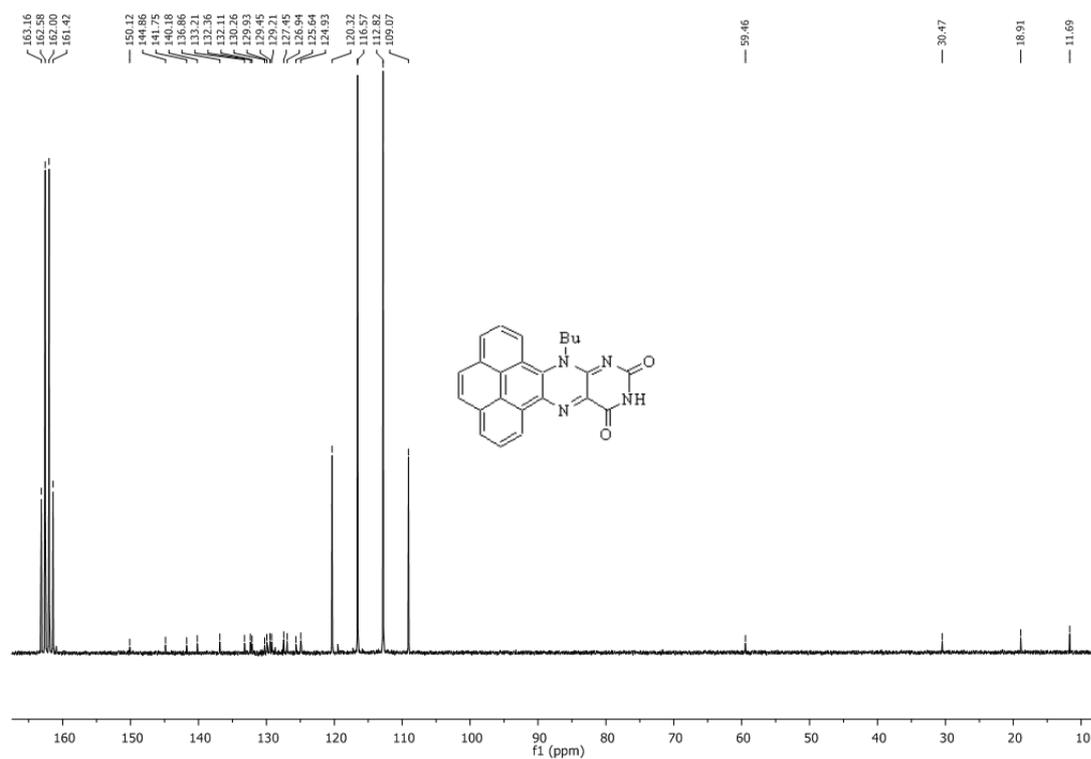


d) ^1H and ^{13}C NMR spectra of **3a** – **3c**

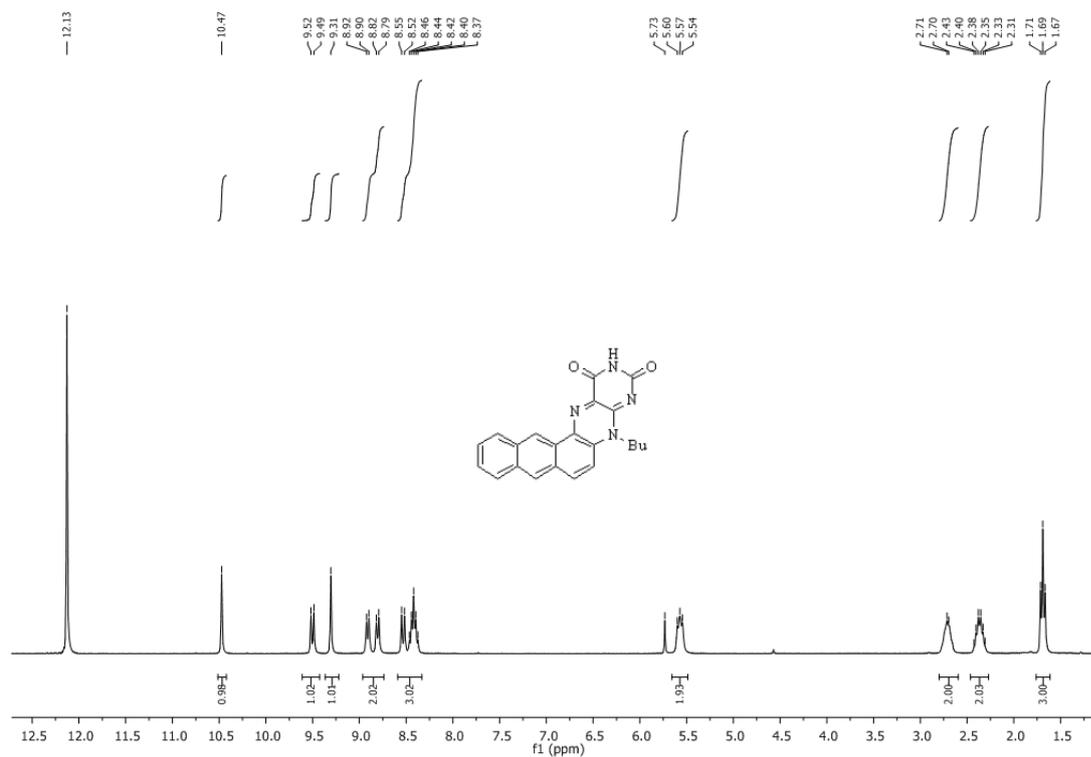
^1H NMR spectra of **3a** recorded in CF_3COOD (298K, 300 MHz)



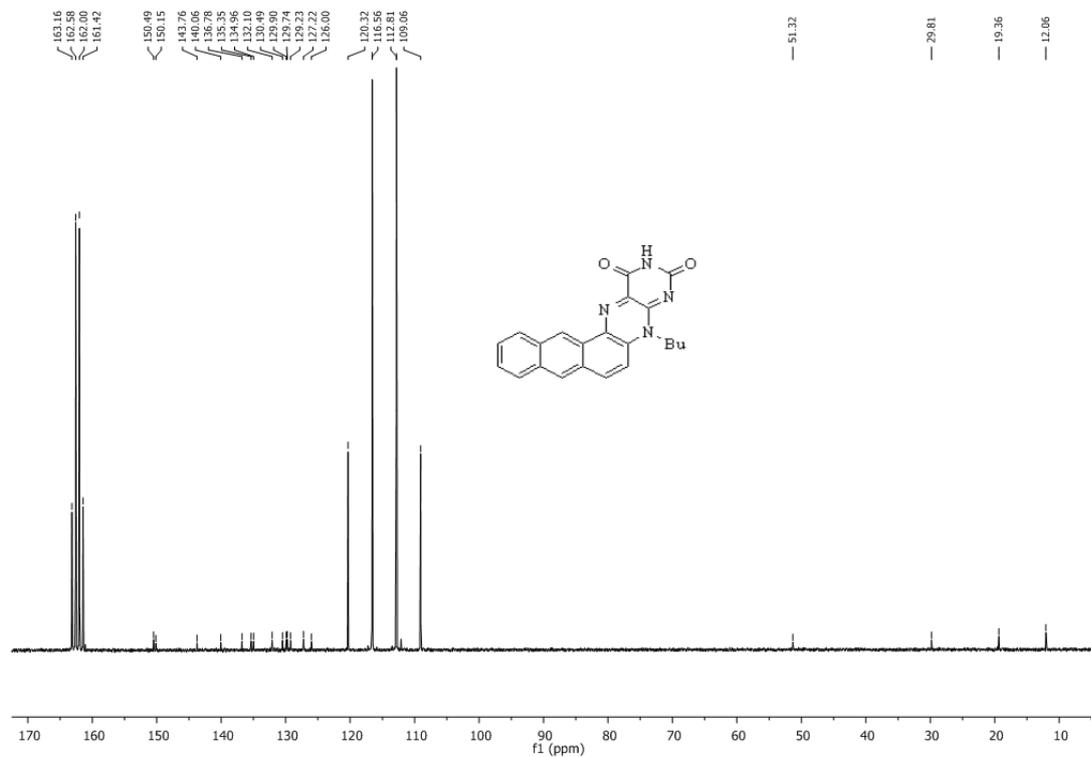
^{13}C NMR spectra of **3a** recorded in CF_3COOD (298K, 75 MHz)



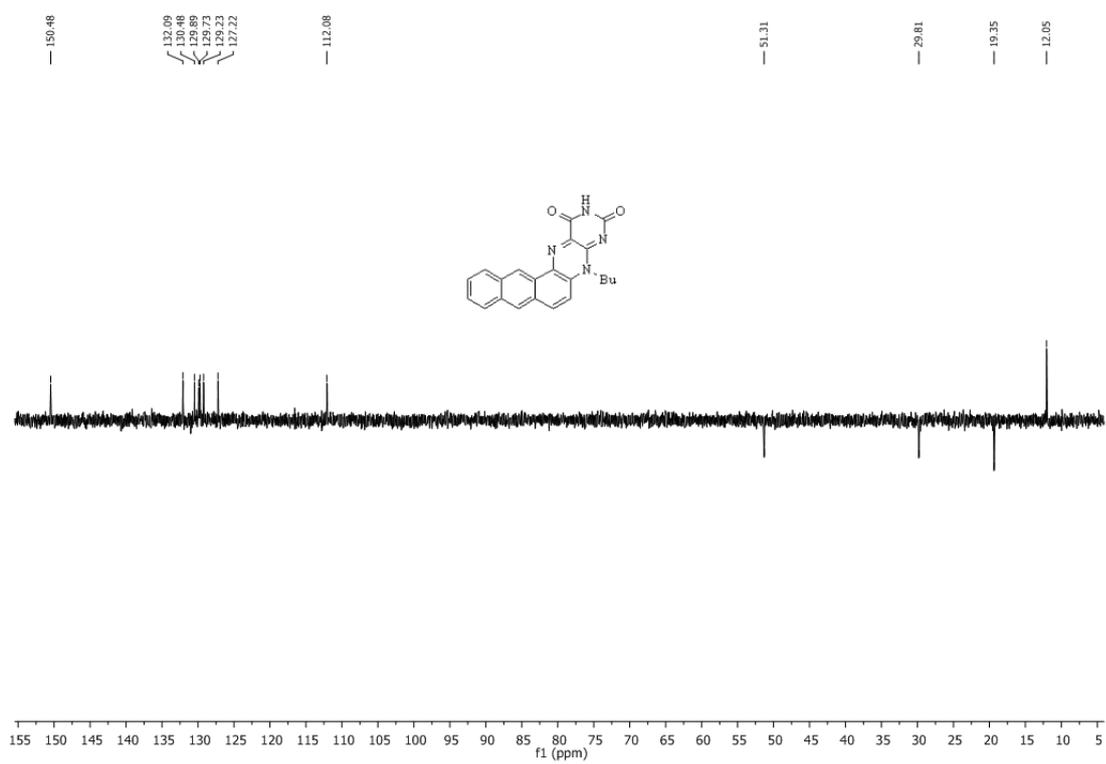
^1H NMR spectra of **3b** recorded in CF_3COOD (298K, 300 MHz)



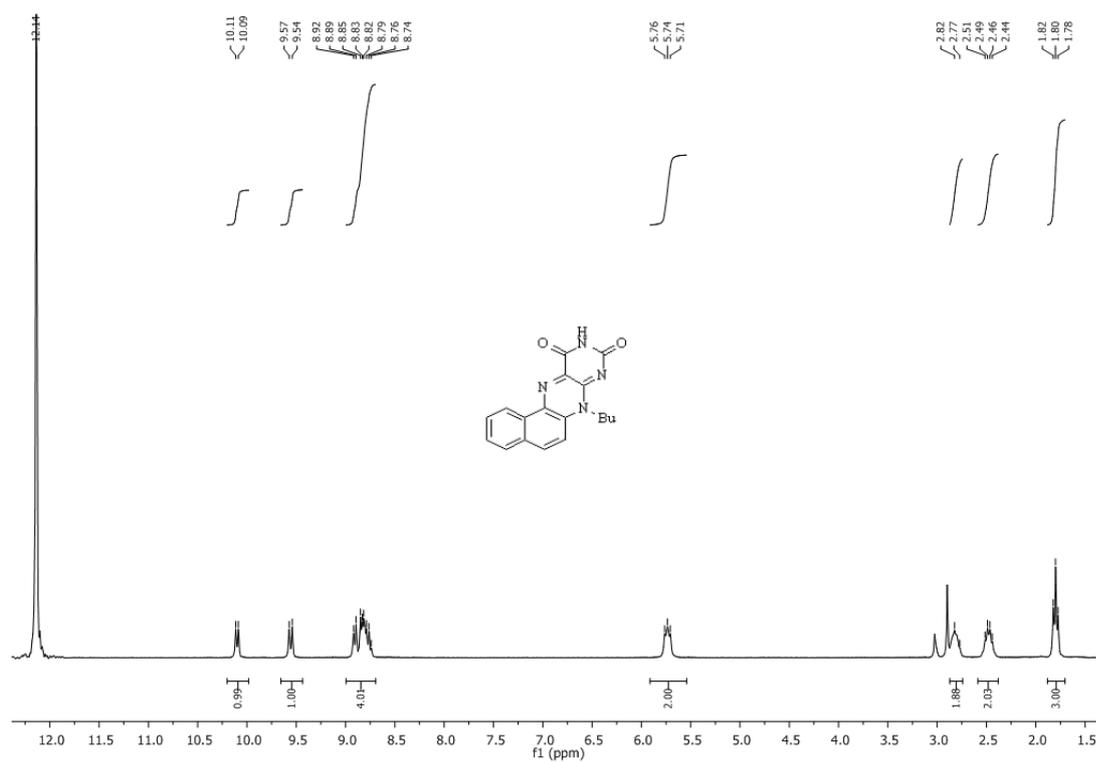
^{13}C NMR spectra of **3b** recorded in CF_3COOD (298K, 75 MHz)



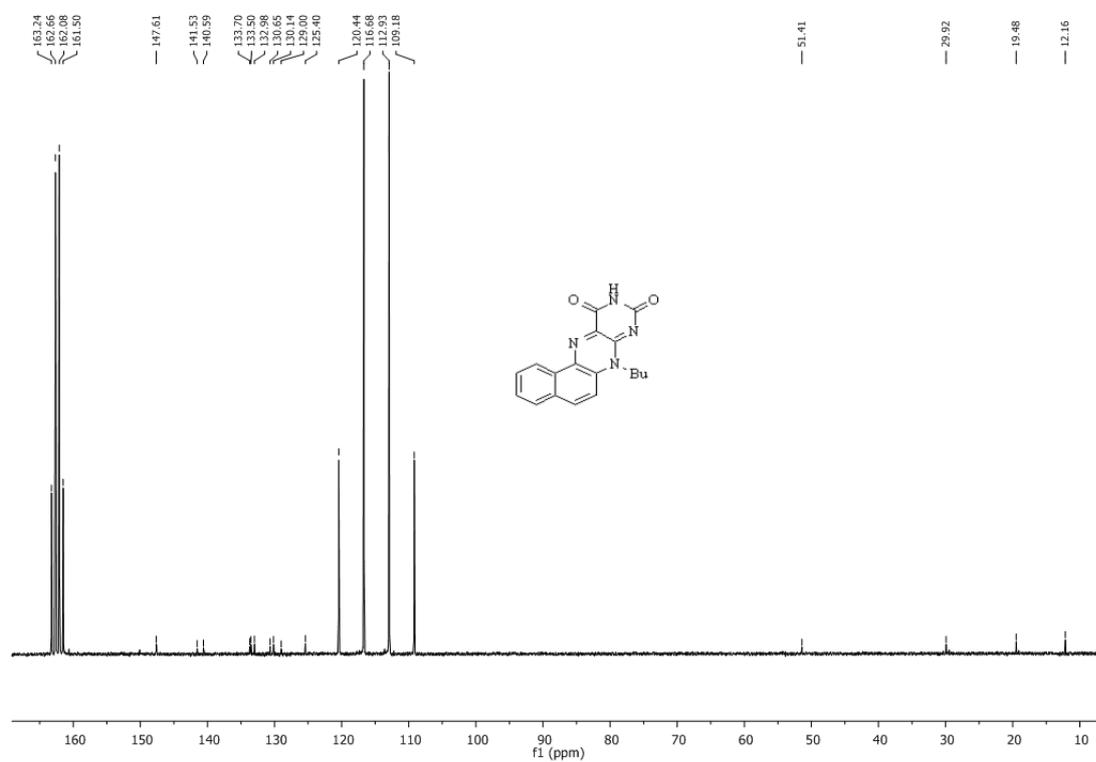
DEPT spectra of **3b** recorded in CF₃COOD (298K, 75 MHz)



^1H NMR spectra of **3c** recorded in CF_3COOD (298K, 300 MHz)

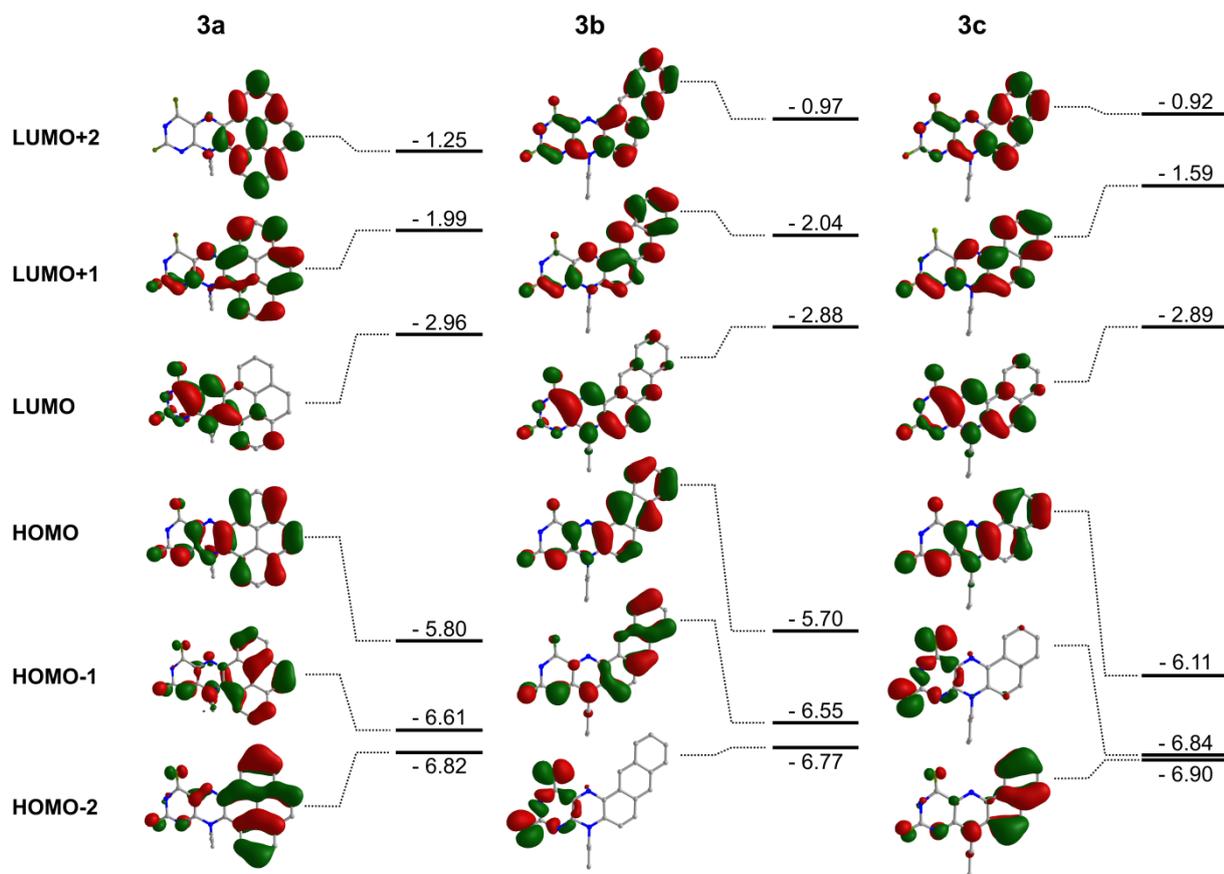


^{13}C NMR spectra of **3c** recorded in CF_3COOD (298K, 75 MHz)



e) Selected molecular orbitals for compounds 3a, 3b, and 3c.

For each molecular orbital, its energy in eV is given.



f) References

1. H. G. O. Becker, W. Berger, G. Domschke, E. Fanghänel, J. Faust, M. Fischer, F. Gentz, K. Gewalt, R. Gluch, R. Mayer, K. Müller, D. Pavel, H. Schmidt, K Schollberg, K. Schwetlick, E. Seiler and G. Zeppenfeld, *Organikum*, Johann Ambrosius Barth Verlag, Heidelberg, Leipzig, 1996.
2. J.H. Huang and L.-M. Yang, *Org. Lett.* 2011, **13**, 3750-3753.