

Unprecedented, One-Pot, Sequential Thiolate Substitutions of 8-methylthio-BODIPY under Mild Conditions leading to a Red Emissive BODIPY Dye 3,5,8-tris(PhS)-BODIPY.

Electronic Supplementary Information

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Experimental

Compound 2 was synthesized by reacting **1** (50 mg, 0.21 mmol purchased from Cuantico de Mexico, (Guanajuato, Mexico) with 1.5 eq. of PhSH in dry dichloromethane under nitrogen atmosphere. After 6 hours of stirring at room temperature silica gel thin-layer chromatography indicated that the reaction was finished. The product was purified by silica gel column chromatography using a 30/70% EtOAc/Hexanes solvent system. The final product was recrystallized from a dichloromethane/hexane mixture.

Compounds 3 and 4 were synthesized by reacting **1** (50 mg, 0.21 mmol) with 3 eq. of phenylthiol in dry tetrahydrofuran under nitrogen atmosphere. After 6 hours of stirring at room temperature silica gel thin-layer chromatography indicated that compound **3** was formed. Further stirring for 48 hours produced compound **4**. The products were purified by silica gel column chromatography using 30/70% EtOAc/Hexanes. The final products were recrystallized from a dichloromethane/hexane mixture. The same results were obtained by reacting **2** with PhSH under identical conditions.

Compound 5 was synthesized by reacting **1** (50 mg, 0.21 mmol purchased from Cuantico de Mexico, Guanajuato, Mexico) with 1.5 eq. of EtSH in tetrahydrofuran under nitrogen atmosphere. After 6 hours of stirring at room temperature silica gel thin-layer chromatography indicated that the reaction was finished. The product was purified by silica gel column chromatography using 30/70% EtOAc/Hexane solvent system. The final products were recrystallized from a dichloromethane/hexane mixture.

2: Orange crystals, yield 94%, 59.2 mg; m.pt. 134-135°C; ¹H NMR (CDCl₃) δ 6.37-6.38 (d, 2H, J = 5.28 Hz), 6.95 (d, 2H, J = 4.08 Hz), 7.40-7.45 (m, 3H), 7.60 (d, 2H, J = 7.56 Hz), 7.75 (s, 2H). ¹³C NMR (CDCl₃) 118.0 (CH), 126.8 (CH), 130.0 (CH), 130.3 (CH), 131.9 (C), 133.1 (CH), 134.2 (C), 142.1 (CH), 150.0 (C). ¹⁹F NMR (CDCl₃) -145.5 (m). Anal. Calcd. for C₁₅H₁₁BF₂N₂S: C, 60.03; H, 3.69. Found: C, 60.14; H, 3.95.

3: Red crystals, yield 59%, 51.4 mg; m.p. 163-164°C; ¹H NMR (CDCl₃) δ 5.78 (d, 1H, J = 4.8 Hz), 6.34 (s, 1H), 6.92 (d, 1H, J = 3.42 Hz), 7.07 (d, 1H, 4.8 Hz), 7.30-7.32 (m, 3H), 7.42-7.47 (m, 5H), 7.62-7.65 (m, 3H). ¹³C NMR (CDCl₃) 116.7 (CH), 119.7 (CH), 126.2 (CH), 128.5 (CH), 128.9 (C), 129.8 (CH), 129.9 (CH), 130.3 (CH), 130.4 (CH), 131.2 (CH), 134.3 (C), 134.4

(C), 135.3 (CH), 138.7 (C), 139.1 (CH), 139.9 (C), 152.4 (C). ^{19}F NMR (CDCl_3) -147.6 (m). Anal. Calcd. for $\text{C}_{21}\text{H}_{15}\text{BF}_2\text{N}_2\text{S}_2$: C, 61.78; H, 3.70. Found: C, 61.86; H, 3.85.

4: Red crystals, yield 19%, 20.5 mg; m.pt. 92-93°C; ^1H NMR (CDCl_3) δ 5.79 (d, 2H, $J = 4.8$ Hz), 6.98 (d, 2H, $J = 4.14$ Hz), 7.22 (d, 1H, $J = 7.56$ Hz), 7.25-7.27 (m, 2H), 7.36-7.37 (d, 2H, $J = 8.22$ Hz), 7.40-7.44 (m, 6H), 7.65 (d, 2H, $J = 8.64$ Hz). ^{13}C NMR (CDCl_3) δ 118.5 (CH), 127.8 (CH), 128.1 (CH), 129.6 (CH), 129.7 (CH), 129.8 (CH), 129.9 (CH), 130.0 (CH), 133.3 (C), 135.0 (CH), 135.5 (C), 138.1 (C), 157.5 (C). ^{19}F NMR (CDCl_3) δ -147.5 (m). Anal. Calcd. for $\text{C}_{27}\text{H}_{19}\text{BF}_2\text{N}_2\text{S}_3$: C, 62.79; H, 3.71. Found: C, 61.41; H, 3.66. *Note: The isolated yield of the reaction was poor due to the presence of trace compounds with similar R_f values in the chromatography purification process.*

5: Orange crystals, yield 82%, 43.3 mg (0.17 mmol); m.p. 92-93°C; ^1H NMR (CDCl_3) δ 1.40–1.42 (t, 3H, $J = 7.74$ Hz), 3.34-3.38 (q, 2H, $J = 7.56$), 6.51 (d, 2H, $J = 4.14$ Hz), 7.41 (d, 2H, $J = 4.14$ Hz), 7.79 (s, 2H). ^{13}C NMR (CDCl_3) δ 14.9 (CH_3), 32.5 (CH_2), 118.0 (CH), 128.5 (CH), 135.1 (C), 142.2 (CH), 151.4 (C). ^{19}F NMR (CDCl_3) -145.8 (m). Anal. Calcd. for $\text{C}_{11}\text{H}_{11}\text{BF}_2\text{N}_2\text{S}$: C, 52.41; H, 4.40. Found: C, 52.74; H, 4.25.

The new compounds were characterized by NMR spectroscopy using a Bruker 600 MHz NMR; UV-vis spectroscopy recorded in a Cary 50 spectrometer; fluorescence spectroscopy recorded on an Olis DM 45 fluorometer. Rhodamine B ($\Phi = 0.70$ in ethanol) and cresyl violet perchlorate ($\Phi = 0.54$ in ethanol) were used as standards for the calculation of the quantum yields.

Solvent	2				3				4			
	λ_{max} Abs (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	λ_{max} Em (nm)	ϕ	λ_{max} Abs (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	λ_{max} Em (nm)	ϕ	λ_{max} Abs (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	λ_{max} Em (nm)	ϕ
Hexane	497	24,000	542	0.61	554	83,000	593	0.39	609	63,000	630	0.24
DCM	495	24,000	N.D.		551	83,000	598	0.05	609	57,500	634	0.23
THF	493	21,000	N.D.		553	74,000	598	0.05	609	51,000	632	0.22
Acetone	493	23,000	N.D.		548	69,000	595	0.02	603	50,000	628	0.18
MeOH	497	24,000	N.D.		545	75,000	593	0.02	603	49,000	628	0.19

Table 1. Summary of the optical properties of BODIPYs 2-4.

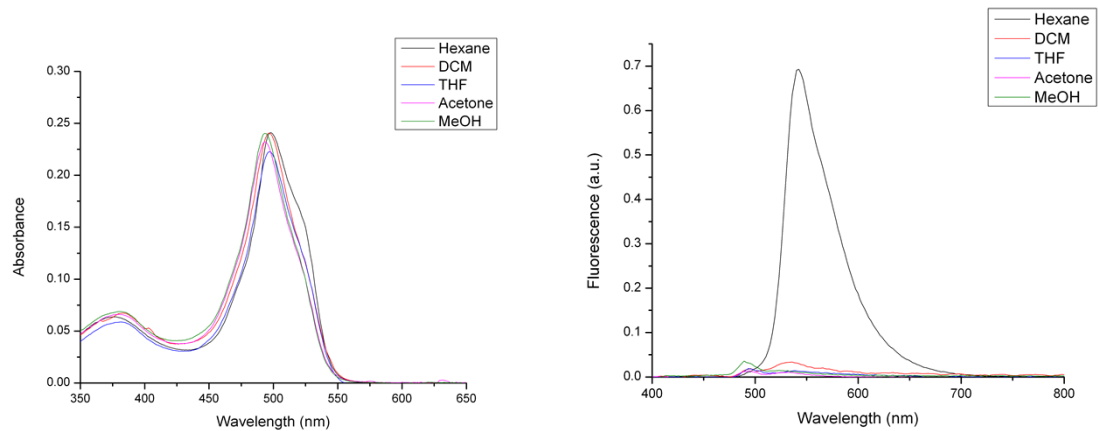


Figure 1. Absorbance (left) and emission spectra of **2**

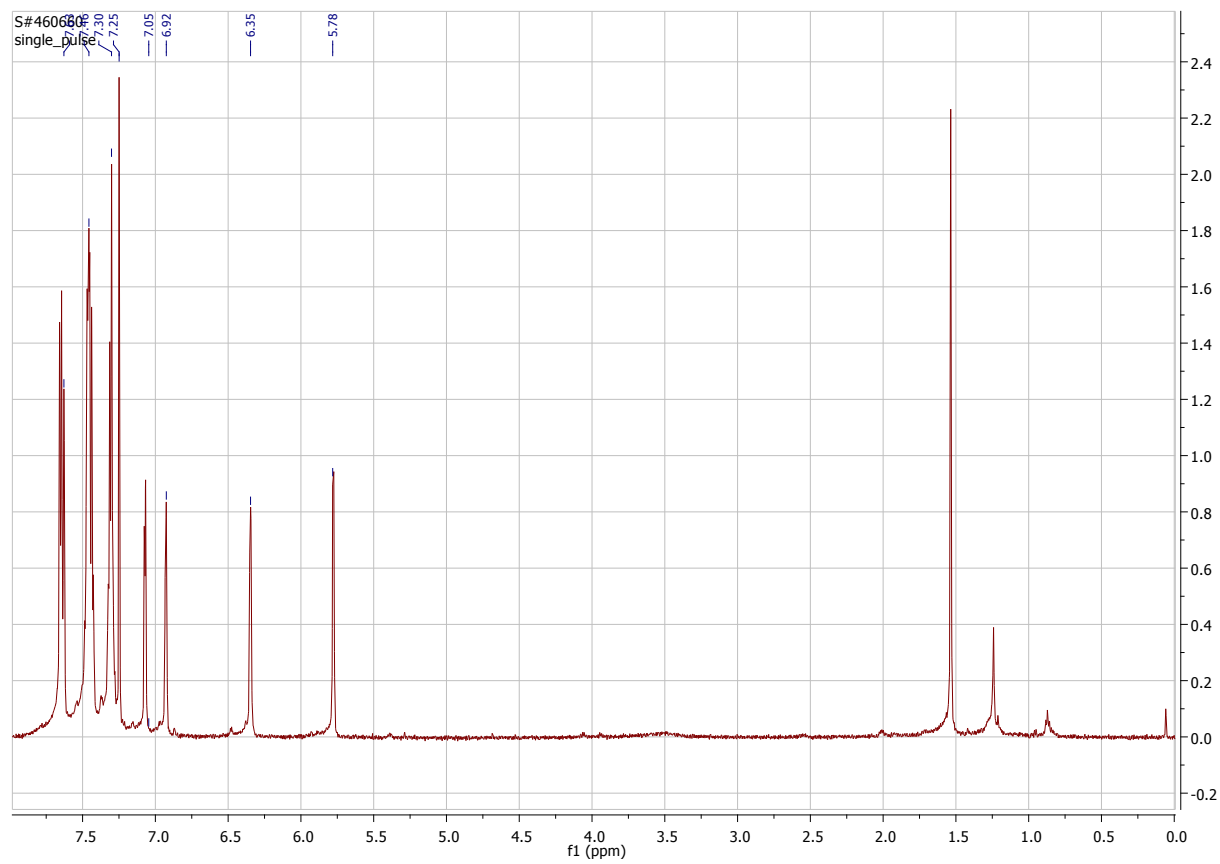


Figure 2. 3,8-bis(phenylthio)BODIPY **3**; ^1H NMR

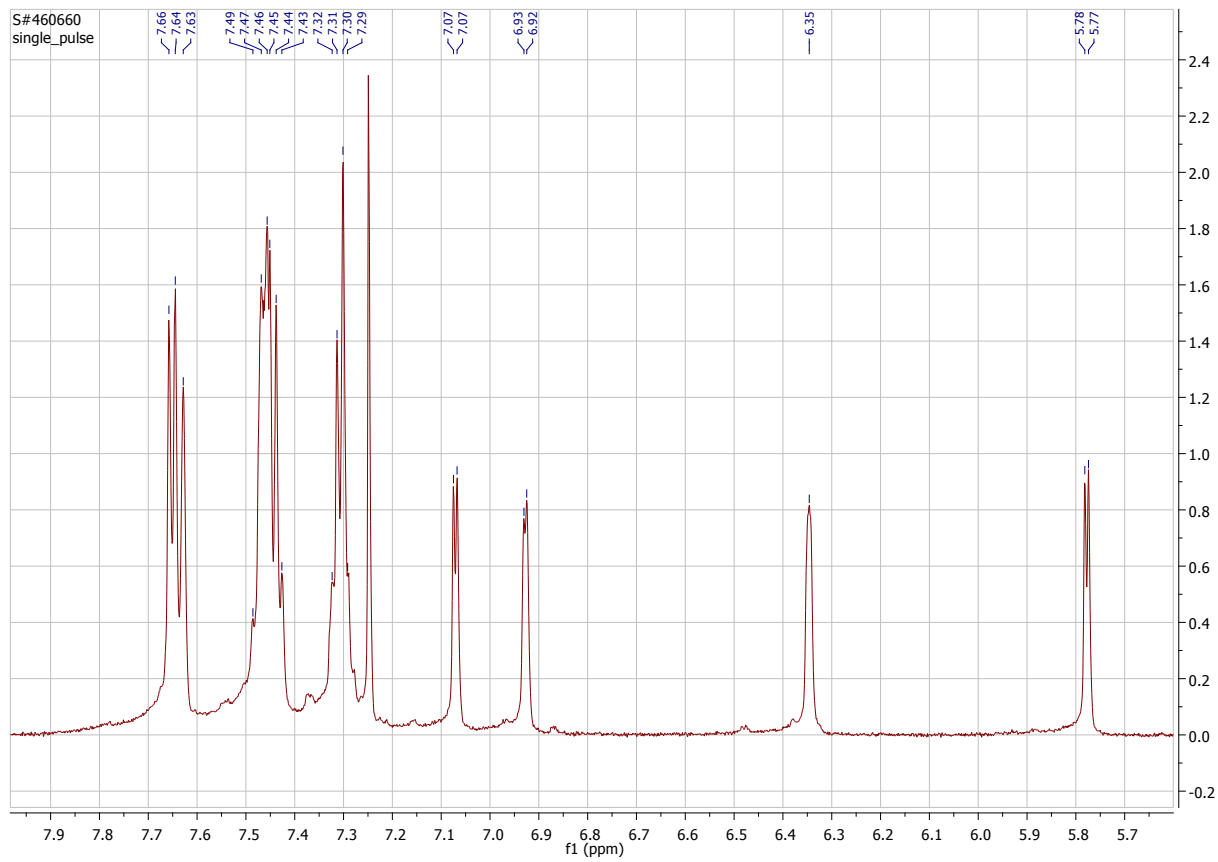


Figure 3. 3,8-bis(phenylthio)BODIPY **3**; ^1H NMR expanded

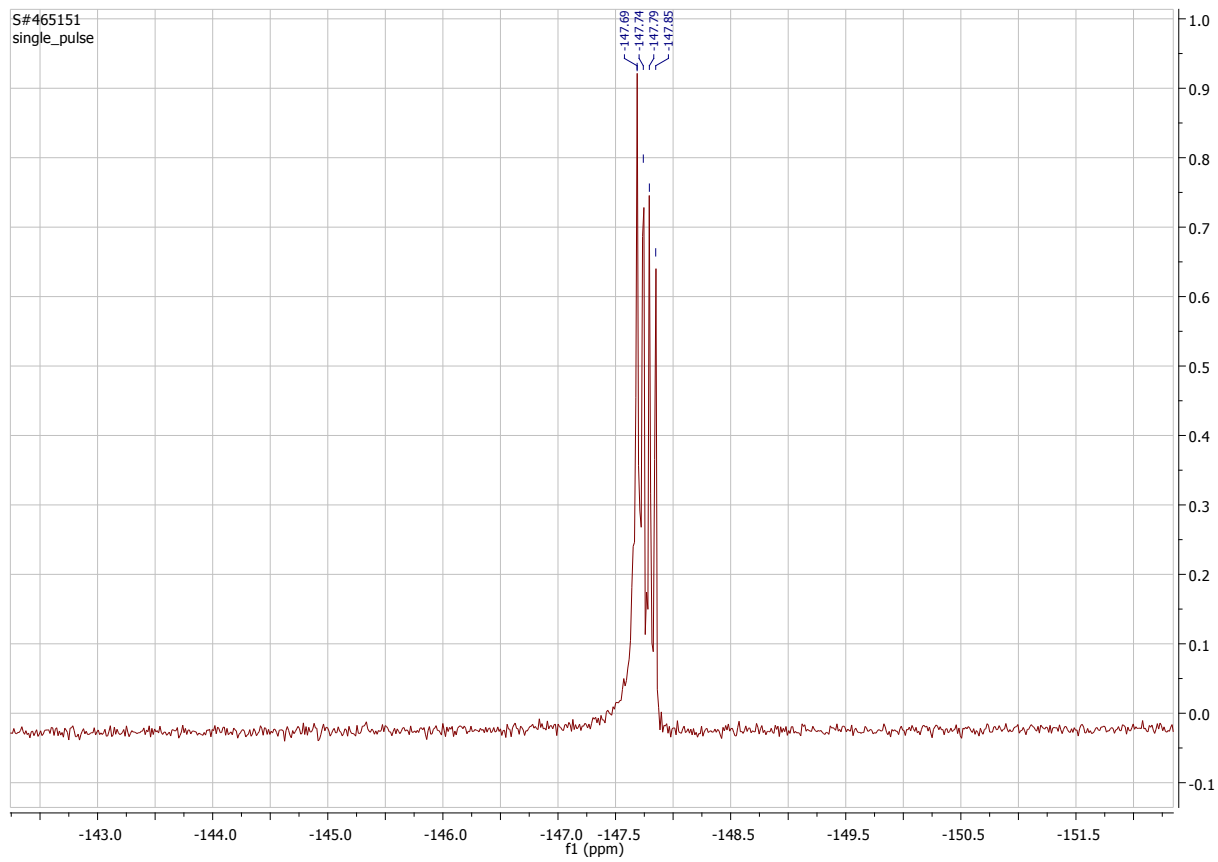


Figure 4. 3,8-bis(phenylthio)BODIPY **3**; ^{19}F NMR

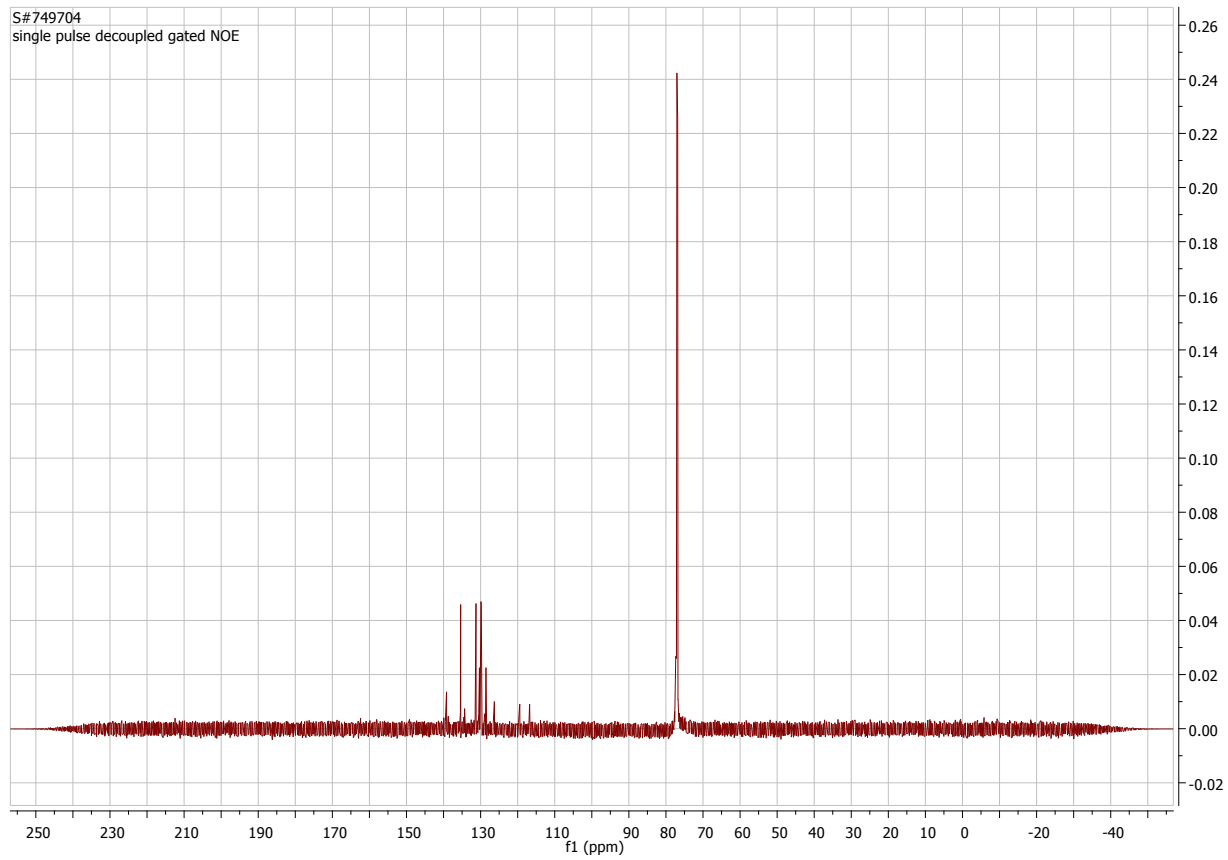


Figure 5. 3,8-bis(phenylthio)BODIPY **3**; ^{13}C NMR

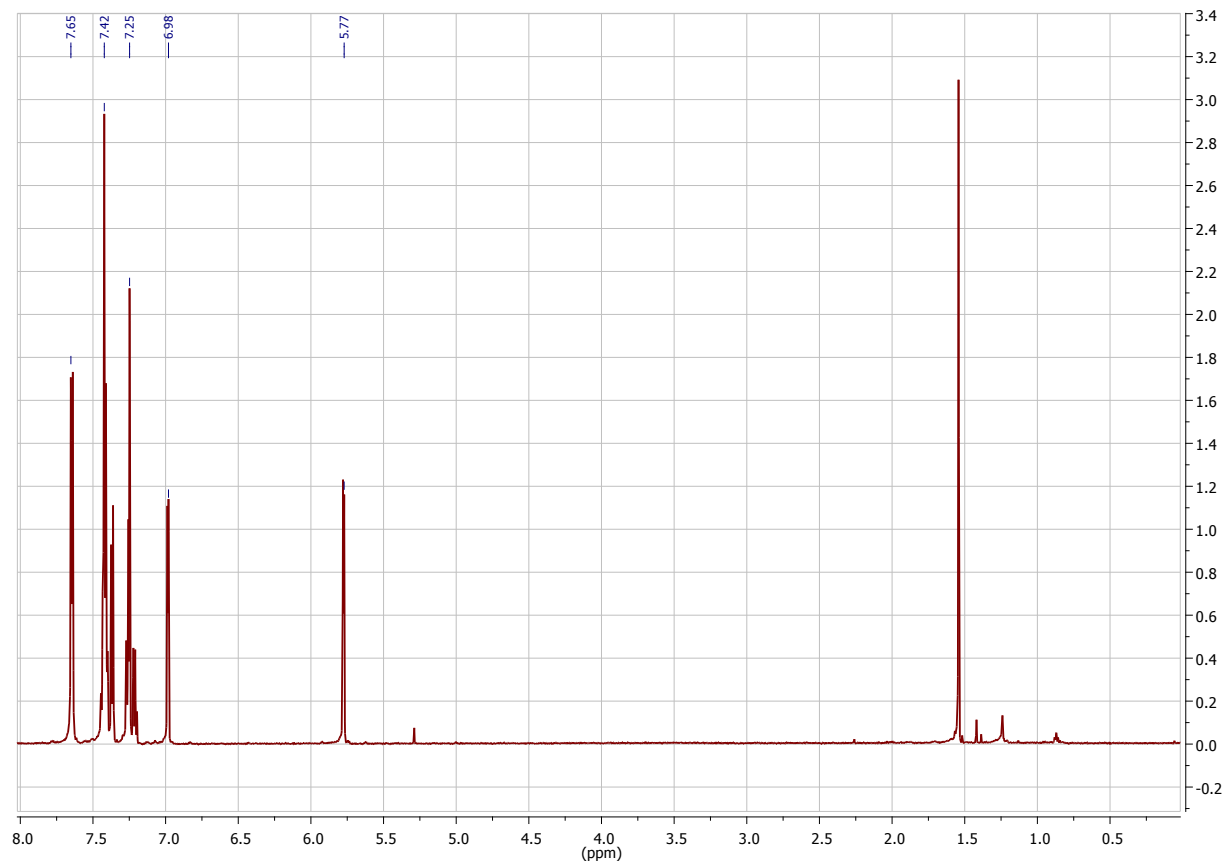


Figure 6. 3,8-bis(phenylthio)BODIPY **4**; ¹H NMR

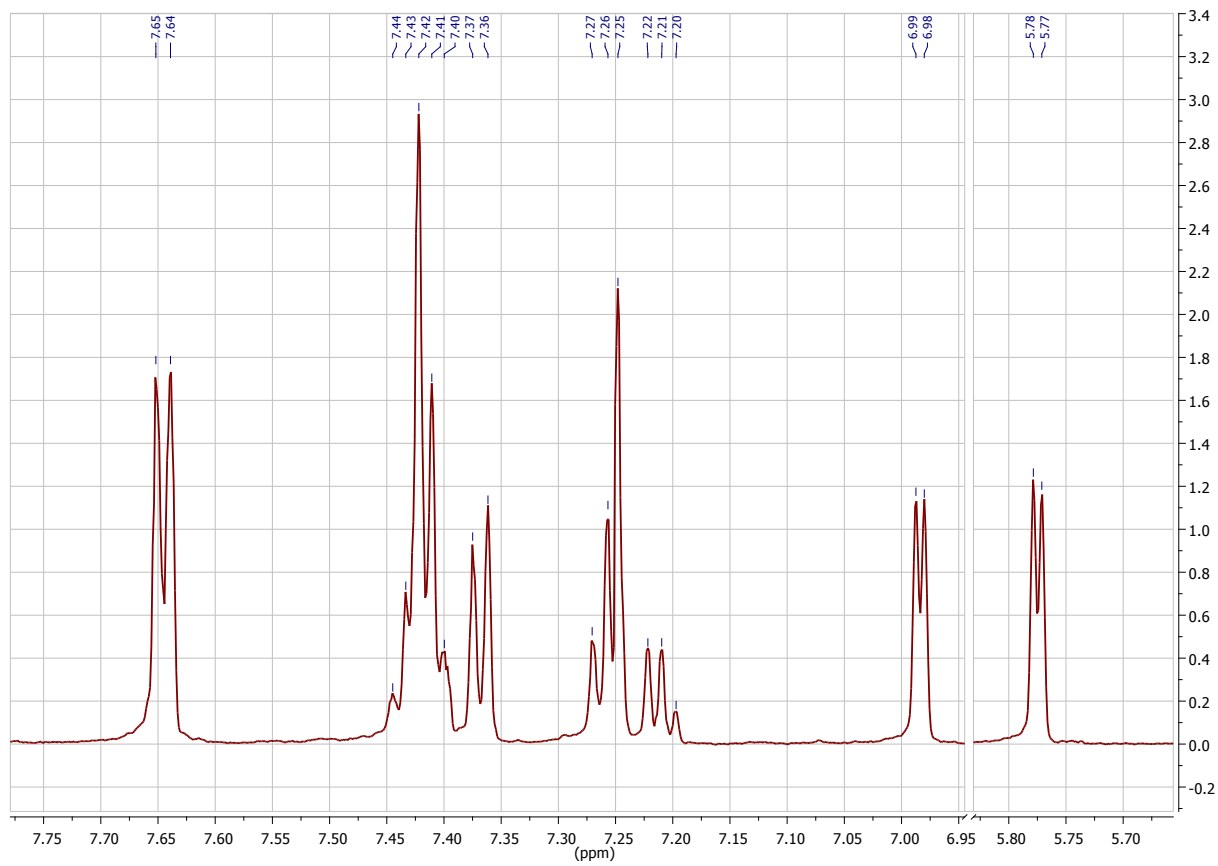


Figure 7. 3,5,8-tris(phenylthio)BODIPY **4**; ¹H NMR expanded.

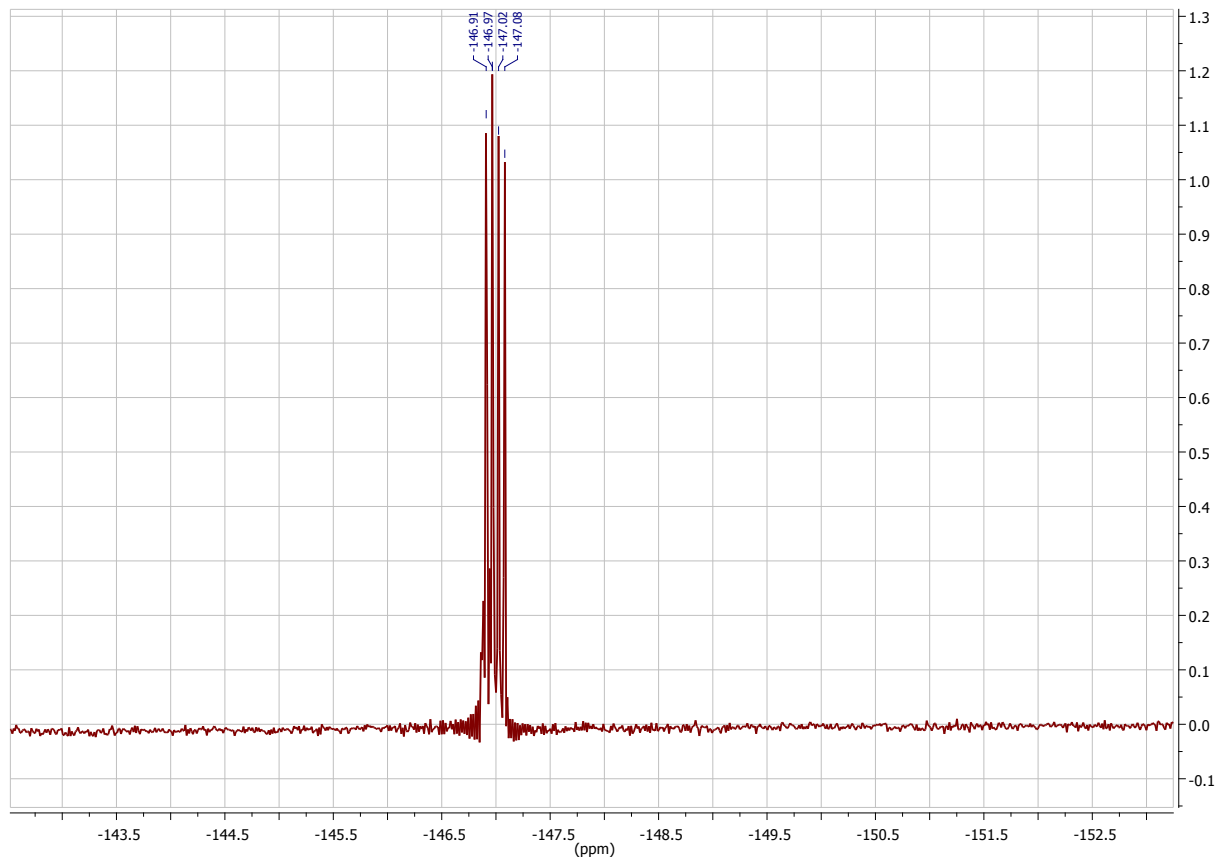


Figure 8. 3,5,8-tris(phenylthio)BODIPY 4; ^{19}F NMR

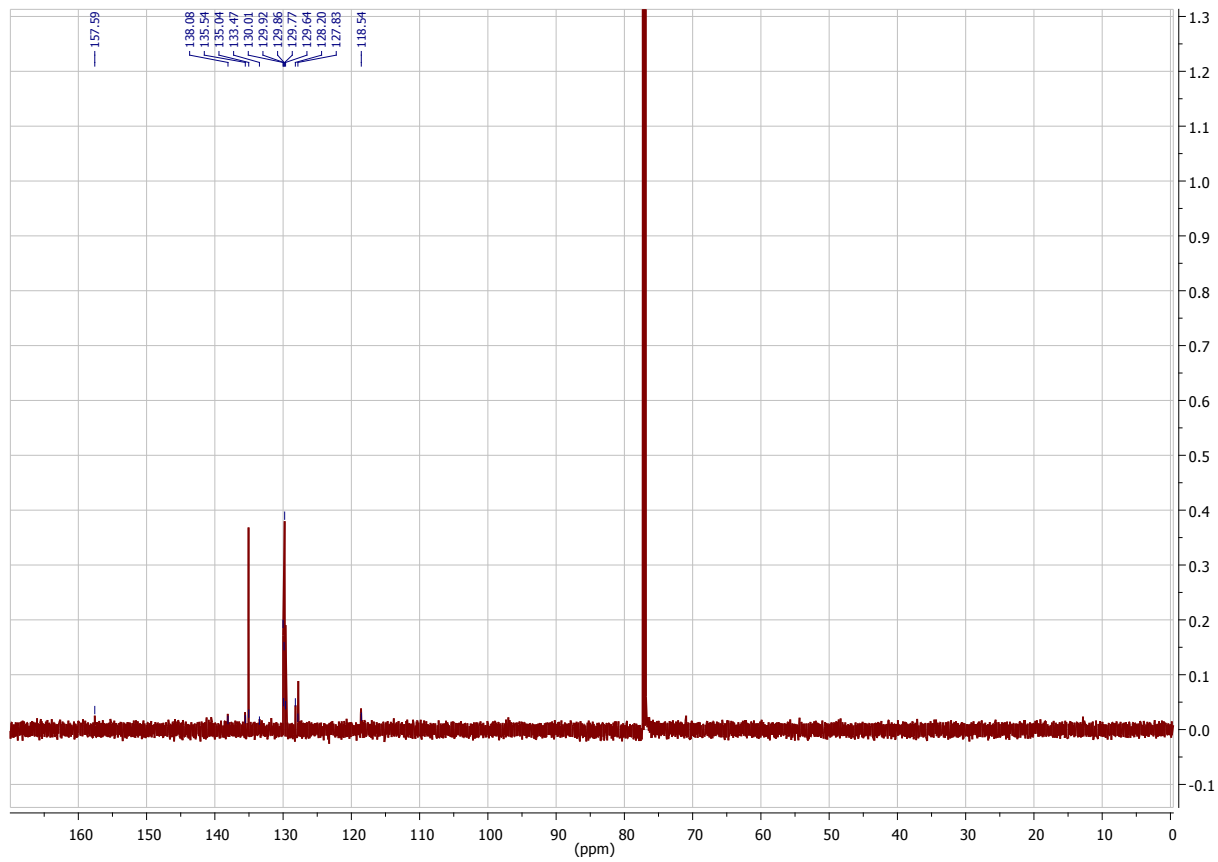


Figure 9. 3,5,8-tris(phenylthio)BODIPY 4; ^{13}C NMR

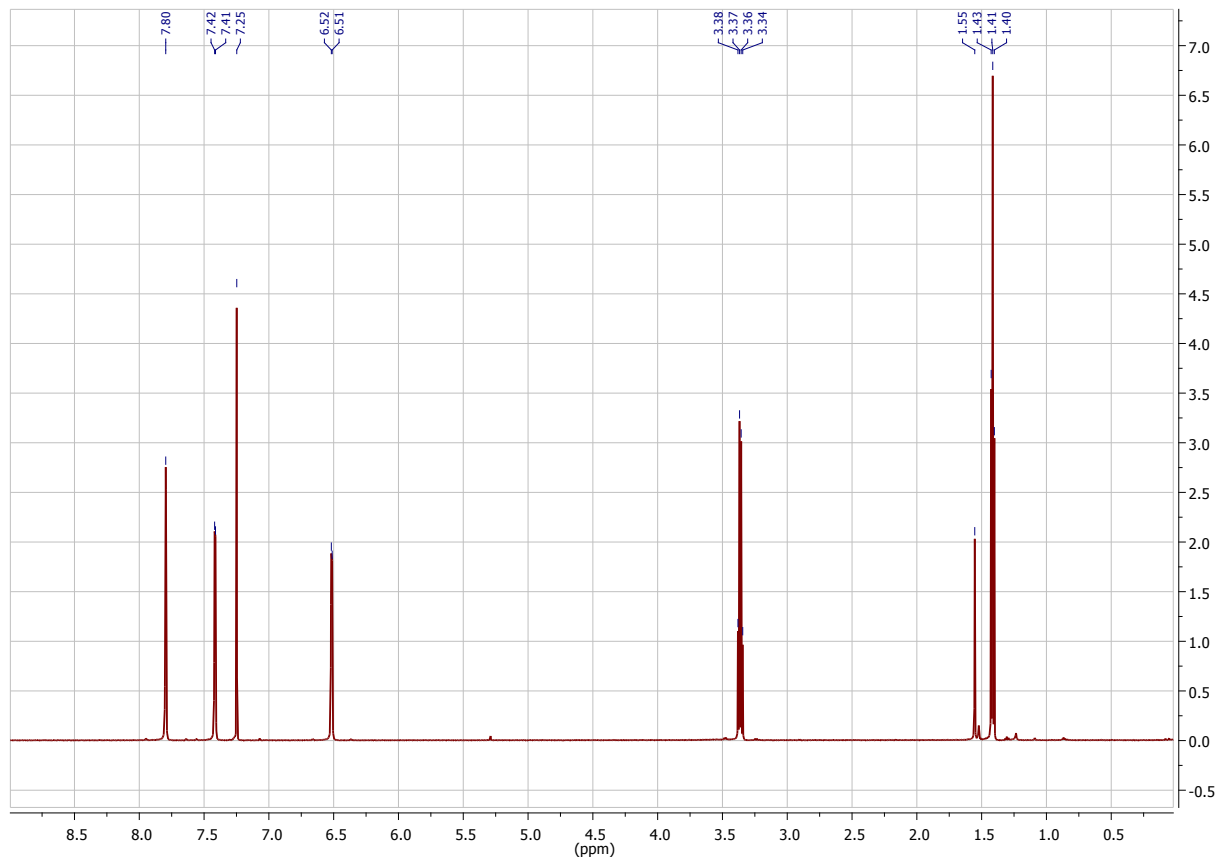


Figure 10. 8-ethylthio-BODIPY 5, ^1H NMR

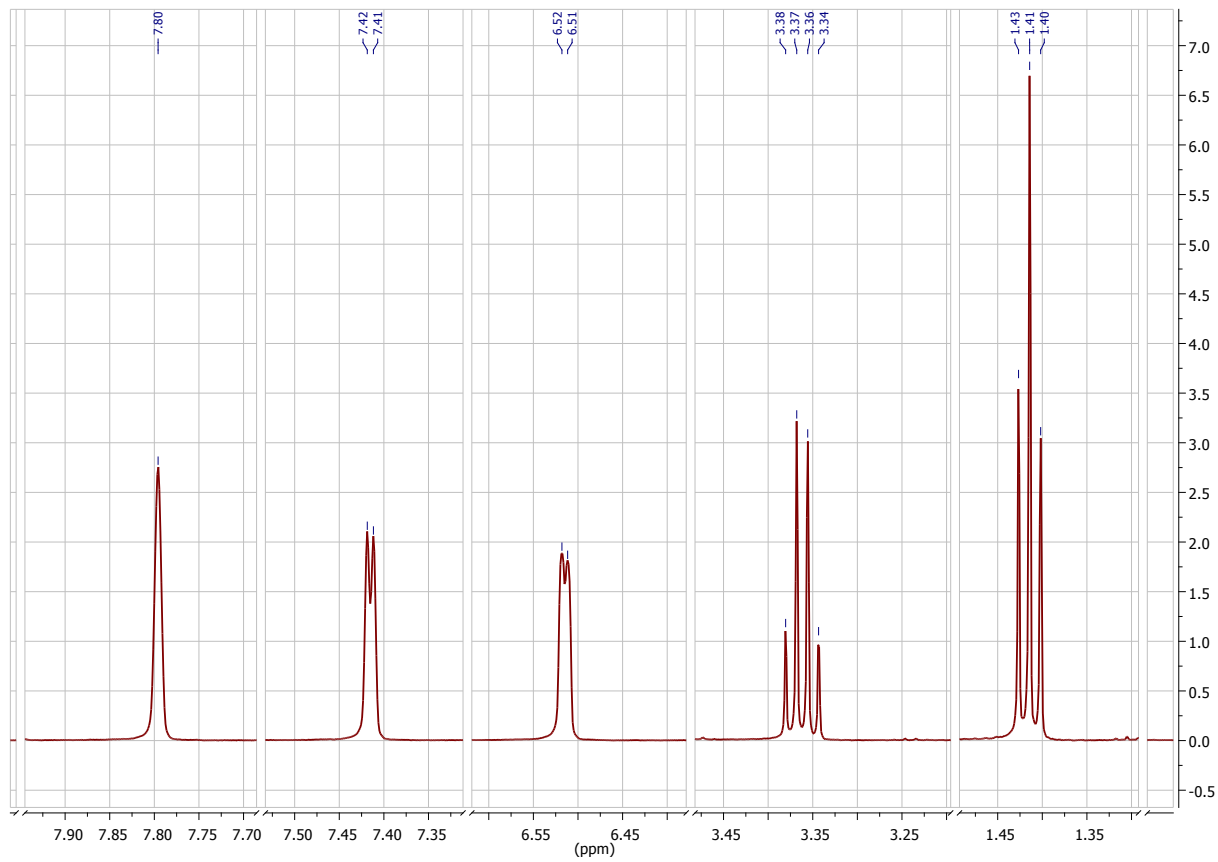


Figure 11. 8-ethylthio-BODIPY 5, ^1H NMR zoom

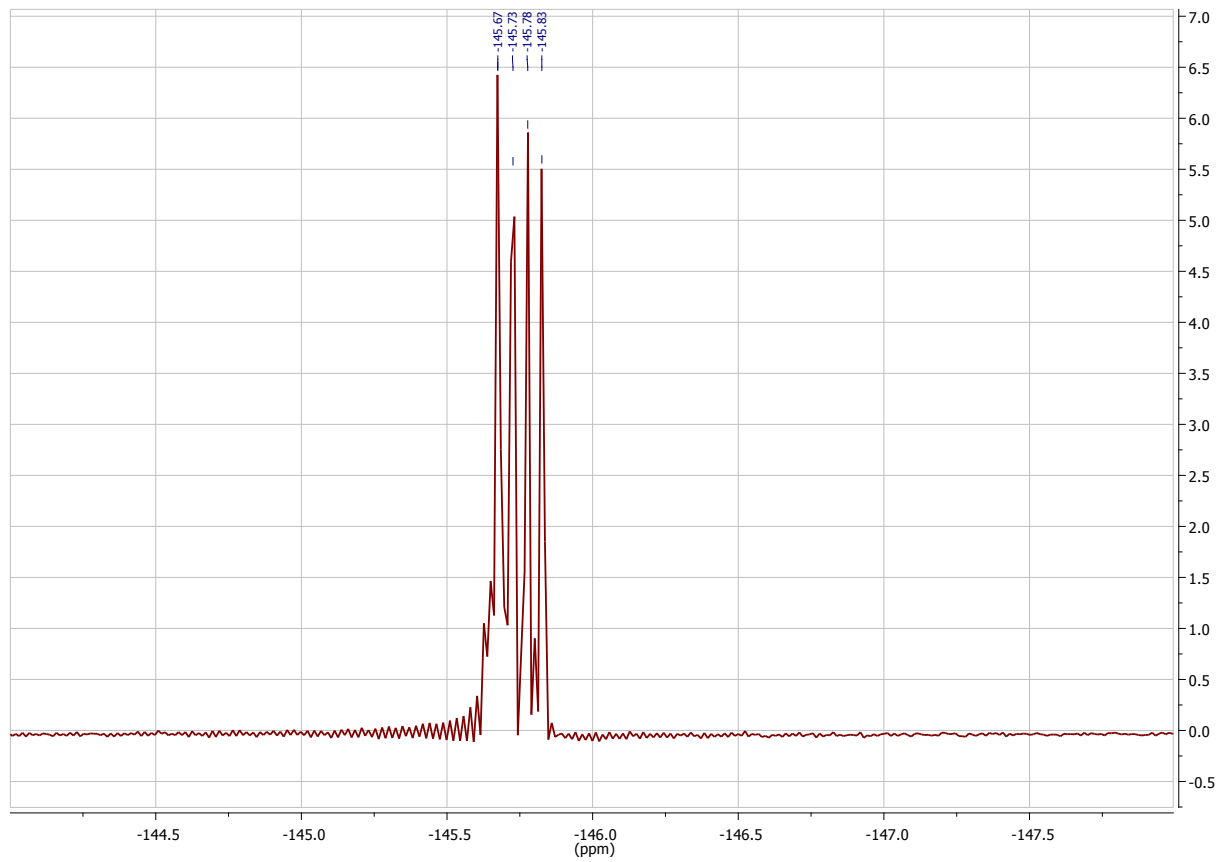


Figure 12. 8-ethylthio-BODIPY 5, ^{19}F NMR

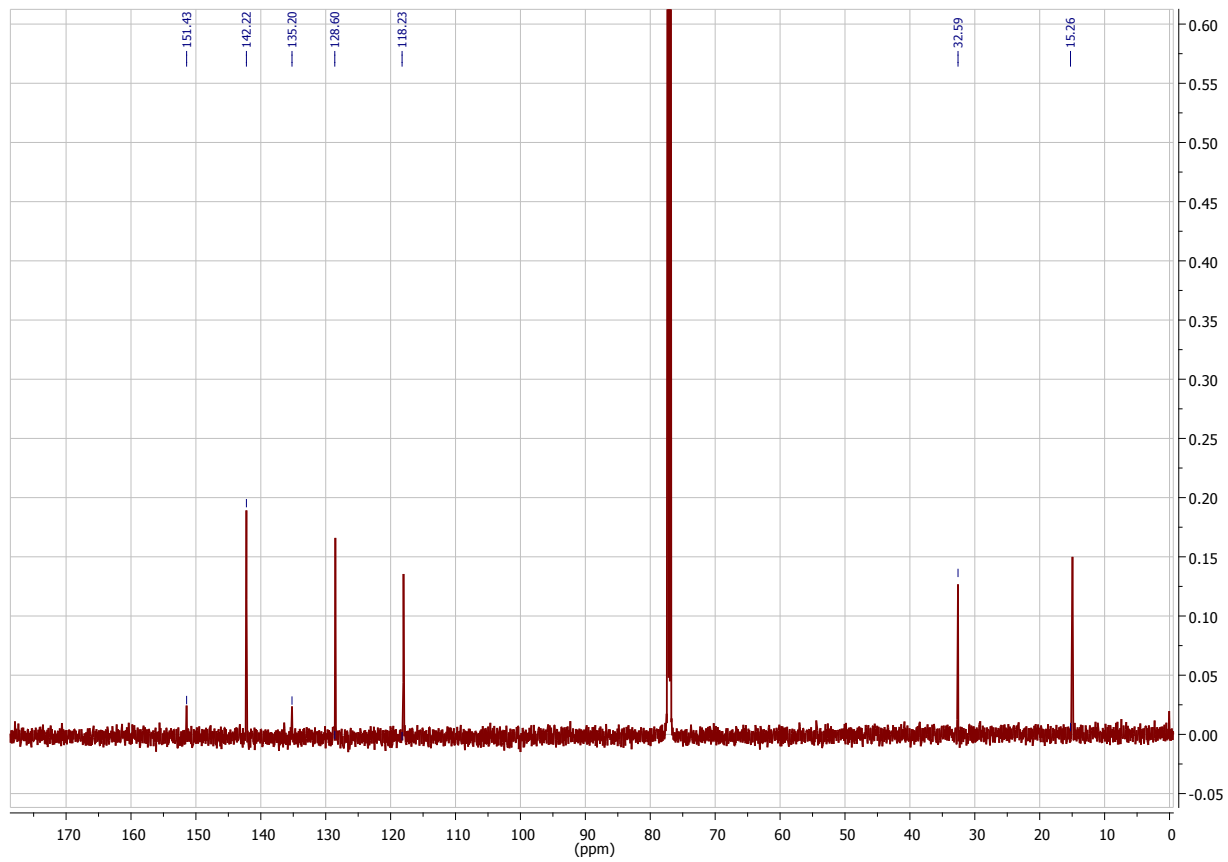


Figure 13. 8-ethylthio-BODIPY 5, ^{13}C NMR

Crystal Packing aspects of 2, 3 and 4

In the case of the monothio BODIPY **2**, in the crystal structure can be observed the formation of ribbons or chains by the HB between the F atoms and two hydrogens in the aromatic ring (F1...H13 [2.635 Å] and F2...H11 [2.395 Å], Figure9). These chains are then interlinked by more HB through the F atoms (F1...H12 [2.514 Å] and F2...H1 [2.440 Å]) generating a 2-D structure (Figure9).

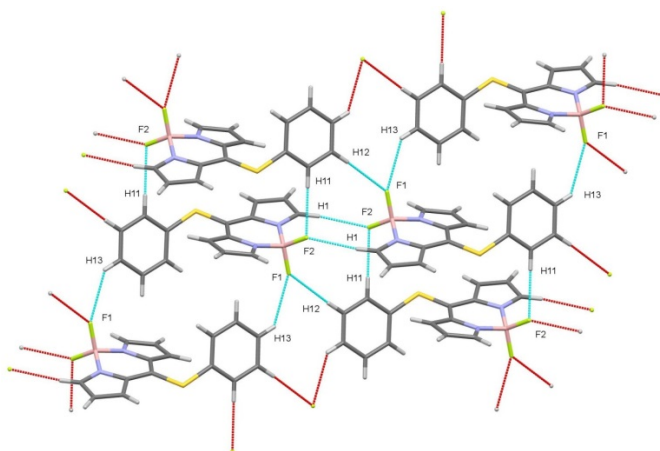


Figure 14

On the other hand, the presence of the second phenyl ring on the bis-adduct **3** blocks the interactions with the hydrogen on the bodipy core generating a chain motif along axis *b* through F2...H11 [2.605 Å] and F2...H20 [2.558 Å], Figure10a. Another structural change in the crystal is the formation of dimers (Figure10b), not observed in the mono-adduct, with a distance of 3.493 Å between the mean planes of each bodipy with a close interaction of the F and S atoms of 3.054 Å, probably the driving force, because that distance is shorter than the Van der Waal's distance by 0.216 Å. This F...S interactions interlock chain motifs generating a 2-D structure.

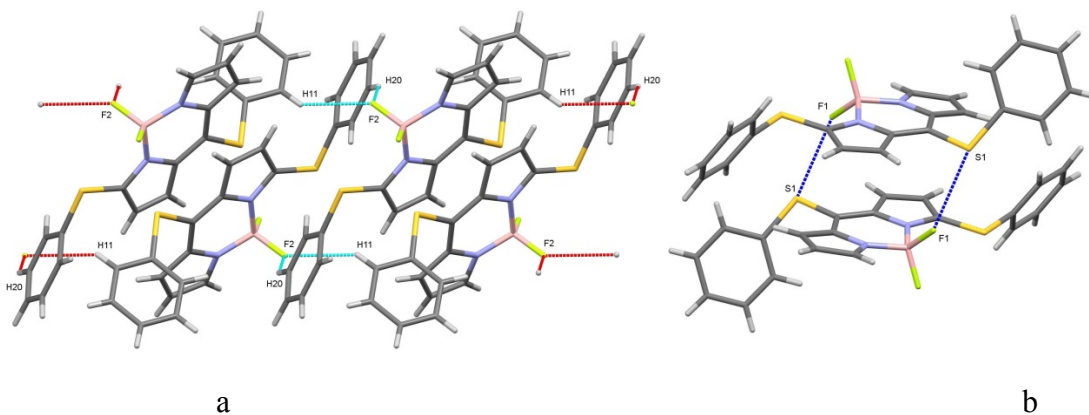


Figure 15

In the case of the tris adduct, **4**, the formation of dimers is also observed (Figure 11), the distance between them (mean planes) is 3.531 Å, as expected a little longer than the bis adduct due to the increased molecular volume. Due to the same reason the F⋯S interactions are slightly longer (3.158 Å), but still below the sum of VdW radii by 0.112 Å. But in this molecule, the F⋯S interaction is not necessary as in the bis-adduct to expand the order of the architecture to 2-D, but they are collaborating with the F⋯H network, F1⋯H25 [2.551 Å], F2⋯H26 [2.464 Å], Figures 12 and 13.

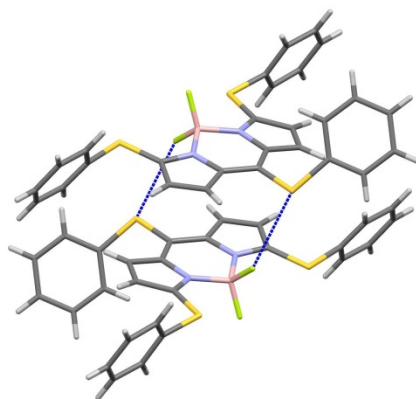


Figure 16. Dimer for **4**

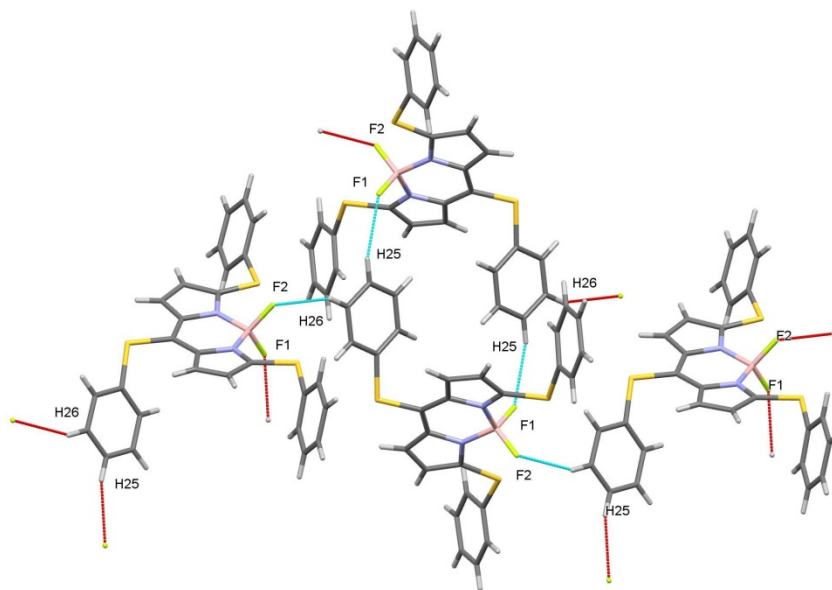


Figure 17. Partial HB network generated from a central molecule of **4**

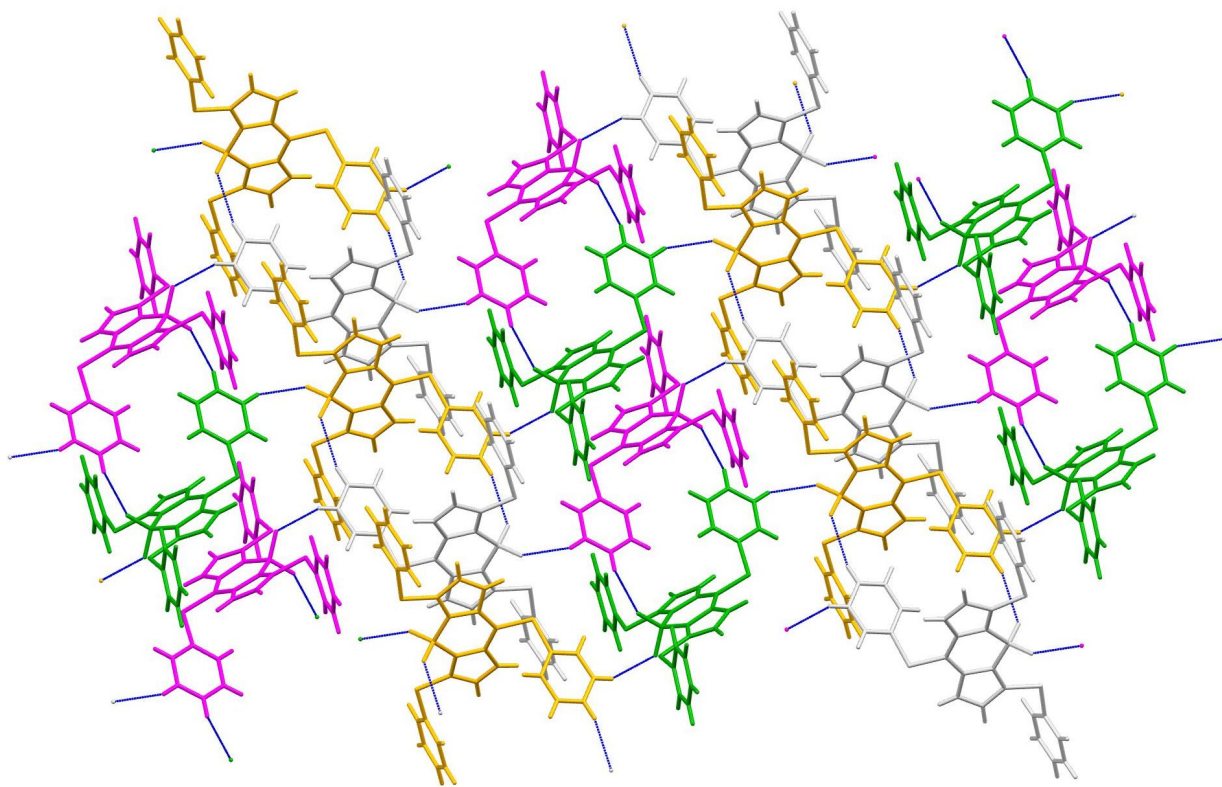


Figure 18. HB network molecules of **4** in different color to increase clarity