Supporting Information for

Tuning the optical properties of BODIPY dyes by N-rich heterocycles conjugation using a combined synthetic and computational approach

Jean Michel Merkes[a,b,c], Tobias Ostlender[a], Fufang Wang[d], Fabian Kiessling[b], Haitao Sun*[d], and Srinivas Banala*[a,b,c]

[a] Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany
[b] Institute for Experimental Molecular Imaging (ExMI), University Clinic, RWTH Aachen University, Forkenbeckstrasse 55, 52074 Aachen, Germany
[c] Fraunhofer Institute for Digital Medicine MEVIS, Max-von-Lauestrasse 2, 28359 Bremen, Germany.
[d] State Key Laboratory of Precision Spectroscopy, School of Physics and Electronic Science, East China Normal University, Shanghai 200241, P. R. China.

1. General

All the reactions, work-up and chromatography were performed under protection from light using by wrapping an alumina foil. All the glassware for the reactions was oven dried at 100 °C and cooled under high vacuum (HV) before use and kept under argon. Absolute solvents were prepared by distillation over calcium hydride (DCM), Solvona Sodium (THF, Toluene). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator (water bath temp $\leq$ 37°C) under protection from light, by covering the round bottomed flask with a black cloth. Thin-layer chromatography was carried out using Merck silica gel 60 F254 aluminium plates with F-254 indicator and separated bands were visualized under UV light (254 nm, 320 nm). Column chromatography was performed using Merck silica gel 60 (230-400 mesh) or fine silica gel (70-230 mesh). Technical grade solvents, dichloromethane (CH_2Cl_2), ethyl acetate (EtOAc), hexane, and methanol were distilled before their use for in column chromatography. Reagent grade chemicals were obtained from various vendors (Sigma Aldrich, Fisher Acros, ABCR, ChemPur), and used as received. Cremophore EL was purchased from Fisher Acros, eluted over basic Alox column with THF and removed solvent, and used for encapsulation application. Cancer cell lines were obtained from ATCC, growth media (DMEM, RPMI), FCS media, and XTT kit were purchased from Gibco Life Tech.

Spectroscopy: (^{1}H- ^{19}F-, and ^{13}C-) NMR spectra were recorded on a Varian AV400 or AV600 spectrometer (in ^{19}F: 376, 564, in ^{13}C: 100 or 125 MHz) in $CDCl_3$ and were reported relative to the solvent residual signal (^{1}H: C*H*Cl_3, δ(H) 7.26, δ(^{13}CHCl_3)=77.2 ppm). For ^{19}F NMR, $CFCl_3$ was used as external standard in $CDCl_3$ and reported data with set reference δ(C*F*Cl_3)= 0.0. Data were reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet); coupling constants (*J*) are in Hertz (Hz), rounded to the

nearest 0.1 Hz. UV/Vis spectroscopy: *PerkinElmer Lambda 35 spectrometer*, in 10 mm quartz cells, reported λ_{max} in nm, and *TECAN* infinite 200 used for XTT measurements. Fluorescence spectroscopy: *PerkinElmer LS45* excitation (λ_{exc}) and emission wavelengths (λ_{Em} (intensity)) λ in nm. Mass Spectrometry: ESI Thermo Fisher LTQ-Orbitrap XL, positive ion mode, *m/z* (rel. intensity %) or a Finnigan SSQ 7000 mass spectrometer (EI or CI).

Fluorescence quantum yields were measured relative to methyleneblue in MeOH as a reference ($\Phi_{(r)}$ = 0.03). The following equation was used to determine the relative fluorescence quantum yield:

$$\Phi_{(x)} = (A_r/A_x)(F_x/F_r)(n_x/n_r)^2\Phi_{(r)}$$

The subscript *r* represents reference and *x* for the unknown.

A is the absorbance, F is the area under the emission curve, n is the refractive index of the solvents used.

2. XTT Cell viability Assay

In a 96-well plate, cells ($5x10^3$ to $10x10^3$) were seeded and added RPMI media supplemented with 10% FCS, 1% penicillin/streptomycin (P/S) for PC3, or DMEM media supplemented with 10% FCS, 1% P/S for A549. The cells were incubated at 37 °C (in 5% CO_2 incubator) for up to 16-24 h to let the cells attach to the well plate surface. The substances in DMEM or RPMI media (conc. 0.001 µmol/ml to 0.1 µmol/ml) were added to the above well plates, and further incubated at 37 °C in 5% CO_2 incubator for 24 h. XTT-solution (5 mL) was freshly prepared (by XTT test kit, from Gibco) by adding 100 µL XTT activator (N-methyl dibenzopyrazine methyl sulfate), and 50 µL of this mixture was added to each well of the above cells. After 24 h the absorption was measured in TECAN-reader at 475 nm wavelength using 660 nm as reference.

3. Computational studies

The ground-state (S_0) geometries of (N_n-Het)BODIPYs and (N_0-(OMe)Ph)BODIPY were optimized using density functional theory at the B3LYP[1,2]-D3(BJ)[3]/6-311+G(d,p)[4,5] level. The HOMO and LUMO orbitals, absorption excitation energies of these molecules were obtained at the time-dependent (TD)-LC-ωPBE*[6]/6-311+G(d,p) level based on their optimized S_0 geometries. The emission excitation energies of these molecules were calculated at the same level based on their optimized lowest singlet excited state (S_1) geometries. The corresponding range-separation parameter (ω, in $Bohr^{-1}$) for each molecule was optimally tuned according to "GAP-Tuning" approach[6,7] and listed in Table S1. The SMD[8] model was employed to take into account the effects of the DMF solvent. All the calculations were performed using the Gaussian 16 software.[9]

Table S1. Calculated absorption / emission wavelength (in nm) or excitation energies (in eV) of molecules obtained at the TD-tuned LC-ωPBE*/6-311+G(d,p) level based on their optimized S_0 / S_1 geometries, respectively. The corresponding range-separation parameters ω* are also listed.

Molecule	ω*	λ_{01} (nm)	E_{01} (eV)	Electronic configuration	λ_{10} (nm)	E_{10} (eV)	Exp (abs/em)
N_0-(OMe)Ph)BODIPY	0.153	640	1.94	H → L 97%	683	1.82	
(N_1-Het)BODIPY	0.157	668	1.86	H → L 97%	707	1.75	
(N_2-Het)BODIPY (**2**)	0.160	633	1.95	H → L 97%	665	1.86	680/707 (1.82/1.75)
(N_3-Het)BODIPY	0.160	595	2.08	H → L 98%	623	1.99	
(N_4-Het)BODIPY	0.163	577	2.15	H → L 98%	602	2.06	

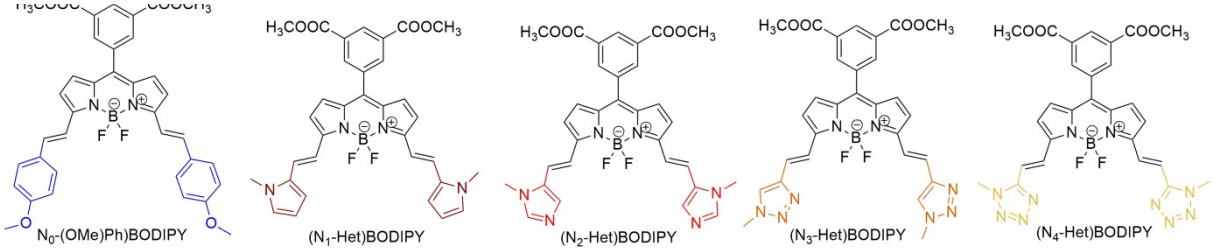


Table S2. Calculated HOMO and LUMO energy levels for N_0-(OMe)Ph)BODIPY, (N_n-Het)BODIPY and corresponding N_n-Het molecules at the tuned LC-ωPBE*/6-311+G(d,p) level.

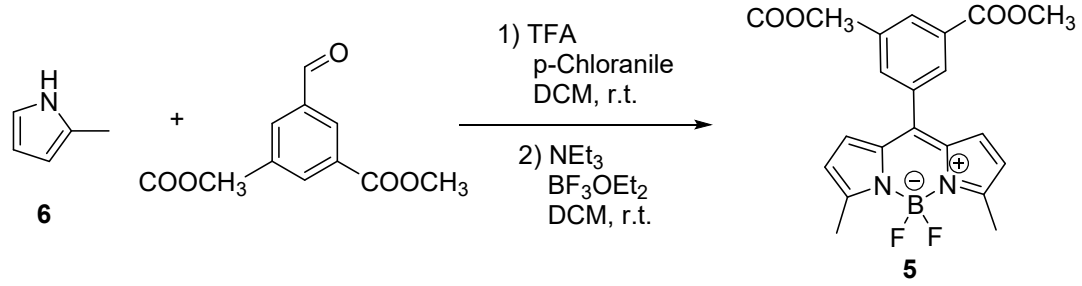
Mol	HOMO	LUMO	H-L GAP
N_0-(OMe)Ph)BODIPY	-6.27	-2.05	4.22
(N_1-Het)BODIPY	-6.12	-1.97	4.15
(N_2-Het)BODIPY (**2**)	-6.38	-2.07	4.31
(N_3-Het)BODIPY	-6.60	-2.09	4.51
(N_4-Het)BODIPY	-7.08	-2.42	4.66
N_1-Het	-8.13 (-8.09 ± 0.01) [a]	-1.31	6.82
N_2-Het	-8.80 (-8.66) [a]	-1.17	7.63
N_3-Het	-9.87 (-9.50) [a]	-1.07	8.80
N_4-Het	-10.80 (-10.30) [a]	-0.92	9.88

[a] Values in parentheses are experimentally determined data in gas phase taken from NIST database (https://webbook.nist.gov/cgi/).

4. Experimental Procedures

All reactions were performed under argon protection atmosphere as long as not otherwise stated. BODIPY starting material **6** was obtained by literature known procedure [10] in 2 steps as followed:

Synthesis of 10-(3,5-bis(methoxycarbonyl)phenyl)-5,5-difluoro-3,7-dimethyl-5H-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide (5)



Step 1: 1.054 g(13.0 mmol, 2.1 eq) of 2-methylpyrrole and 1.375 g (6.19 mmol) dimethyl-5-formylisophthalate were dissolved in 200 mL of dry DCM under argon atmosphere. The reaction was catalyzed initiated by addition of 1 drop (*ca.* 10 µL) of TFA, and mixture was stirred for 90 min at room temperature. To this mixture 1.522 g (6.19 mmol, 1.0 eq) of p-chloranil was added and stirred for another 90 min at r.t., and was quenched by addition of saturated $NAaHCO_3$. The mixture was extracted with DCM and dried over Na_2SO_4. The crude was concentrated in vacuum and purified by column filtration, adsorbing mixture on 20 g of alumina (neutral). This alumina absorbed mixture was loaded over a 15 cm alumina (neutral Al_2O_3) column, and product was eluted with (hexane:ethyl acetate, 4:1), and product contained fractions collected, solvents removed under reduced pressure to obtain dipyrromethene product as a yellow solid.

Step 2: To the above product, 400 mL dry DCM was added under argon, followed by 24 mL (18.133 g, 179.2 mmol, 35.0 eq) of NEt_3. This mixture was stirred for 15 min at room temperature, and was added 30 mL (34.881 g, 245.8 mmol, 48.0 eq) of $BF_3.OEt_2$. The reaction was stirred for further 60 min at r.t., and after full conversion the reaction was quenched by addition of saturated $NaHCO_3$. The reaction mixture was extracted with DCM (3x), and the combined organic phases were dried over Na_2SO_4, and the solvent was removed under reduced pressure to obtain product **3** as a red solid (1.73 g, 68 %).

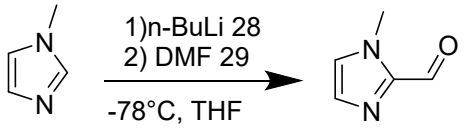
^{1}H-NMR (600 MHz, $CDCl_3$) δ [ppm]: 6.91 (s, *J* = 9.4 Hz, 1H), 6.41 (s, 2H), 5.34 (s, 1H), 4.68 (d, *J* = 4.0 Hz, 2H), 4.37 (d, *J* = 4.1 Hz, 2H), 2.05 (s, 6H), 0.74 (s, 6H).

^{13}C-NMR (151 MHz, $CDCl_3$) δ [ppm]: 163.56, 156.79, 137.56, 133.05, 132.91, 132.37, 129.88, 129.02, 128.09, 118.12, 50.78, 13.06.

^{19}F-NMR (564 MHz, $CDCl_3$) δ [ppm]: -149.49.

ESI-MS(THF): calculated m/z for [$C_{21}H_{19}BF_2N_2O_4$]: 412.14059; found m/z: 365.14899 ([M-BF_2+H+H]$^+$).

1-methylimidazolaldehyde 7



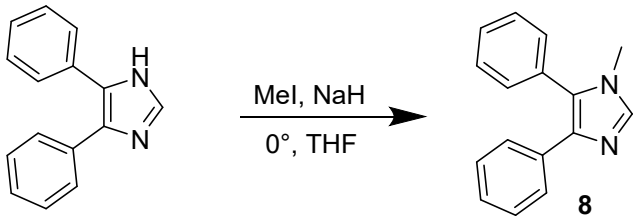
7

11.75 mL (18.825 mmol, 1.5 eq) of a 1.6 M n-BuLi in hexane was added drop-wise to a solution of 1 mL (1.03 g, 12.55 mmol) 1-methylimidazol in 20 mL absolute THF at -78°C. After full addition the mixture was stirred for 30 min before 3.91 mL (3.71 g, 50.2 mmol, 4 eq) DMF were added slowly. The reaction was continued for 20 min more.

After full conversion on TLC, the mixture was quenched by addition of 30 mL saturated sodium bicarbonate solution and extracted three times with ethyl acetate. The combined organic solvents were dried over sodium sulfate and concentrated in vacuum. The crude was purified by column chromatography (silica, hexane: ethyl acetate 4:1) to obtain the product as pale yellow solid (716.2 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ [ppm] = 9.78 (d, *J* = 0.9 Hz, 1H), 7.23 (d, *J* = 0.9 Hz, 1H), 7.07 (s, 1H), 3.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ [ppm] = 182.1, 131.4, 127.2, 34.9.

1-Methyl-4,5-diphenylimidazol 8



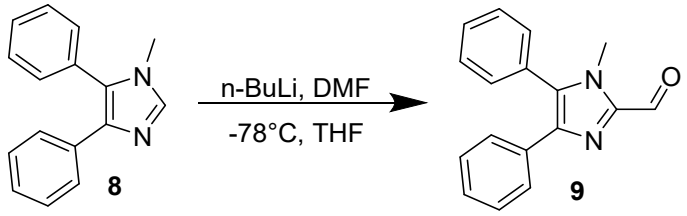
8

59.9 mg (2.50 mmol, 1.1 eq) NaH (60 % in mineral oil) were added to a solution of 500 mg (2.27 mmol, 1.0 eq) 4,5-diphenylimidazol in 20 mL absolute THF at 0°C. The solution was stirred for 20 min and 424 µL (6.81 mmol, 3.0 eq) methyliodid were added drop-wise. The reaction was allowed to warm to room temperature and stirred for 72 h.

The reaction mixture was quenched with 30 mL saturated sodium bicarbonate solution and extracted with ethyl acetate three times. The combined organic layers were dried over sodium sulfate and concentrated under vacuum. The crude was purified by column chromatography (silica, hexane: ethyl acetate 1:2 to 1:4) to obtain the product as a white solid (172.9 mg, 33%).

^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 7.59 (s, 1H), 7.50 – 7.42 (m, 5H), 7.36 – 7.33 (m, 2H), 7.23 – 7.19 (m, 2H), 7.16 – 7.12 (m, 1H), 3.49 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ [ppm] = 138.2, 137.4, 134.6, 130.6, 129.0, 128.6, 128.1, 126.6, 126.3, 32.2.

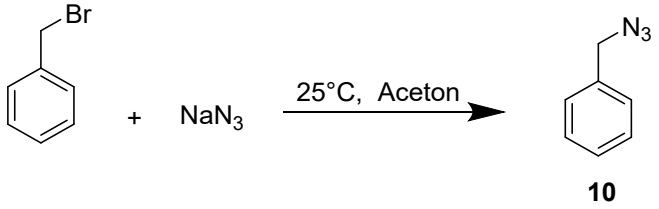
1-Methyl-4,5-diphenylimidazolaldehyde 9



330 µL (0.608 mmol, 1.2 eq) of a 1.6 M n-BuLi in hexane were added drop-wise to a solution of 112.7 mg (0.507 mmol, 1.0 eq) 1-methyl-4,5-diphenylimidazol in 10 mL absolute THF at -78°C. After full addition the reaction mixture was stirred for 30 min. Then 158 µL (149.5 mg, 2.028 mmol, 4.0 eq) DMF were added and the reaction was stirred for 20 min more. After full conversion the reaction mixture was quenched by addition of 30 mL saturated sodium bicarbonate solution. The mixture was extracted three times with ethyl acetate. The combined organic layers were dried over sodium sulfate and concentrated under vacuum. The crude was purified by column chromatography (silica, hexane: ethyl acetate 1:2 to 1:4) to obtain the product as a white solid (101 mg, 76%).

^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 9.94 – 9.91 (m, 1H), 7.52 – 7.49 (m, 3), 7.48 – 7.45 (m, 2H), 7.36 – 7.32 (m, 2H), 7.26 – 7.20 (m, 3H), 3.84 (s, 3H).^{13}C NMR (151 MHz, $CDCl_3$) δ [ppm] = 182.3, 143.0, 141.3, 135.7, 133.2, 130.4, 129.6, 129.2, 128.7, 128.3, 127.4, 127.1, 32.9.

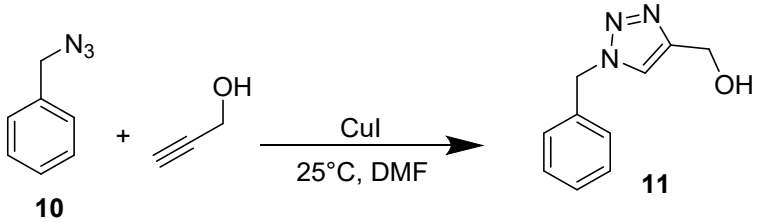
Benzylazid 10



To a solution of 50 mL distilled acetone and 2.38 mL (3.420 g, 20 mmol) benzyl bromide 2.925 g (45 mmol, 2.5 eq) sodium azide was added. The reaction mixture was stirred overnight at room temperature. After full conversion the volatile solvents were removed in vacuum and the crude was taken up in water and ethyl acetate. The aqueous layer was extracted three times with ethyl acetate. The combined organic layers were dried over sodium sulfate and concentrated under vacuum to obtain a white solid (1.633 g, 61%).

^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 7.57 – 7.35 (m, 5H), 4.44 – 4.33 (m, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ [ppm] = 135.6, 128.9, 128.4, 54.8.

(1-Benzyl-1,2,3-triazol-4-yl)methanol 11

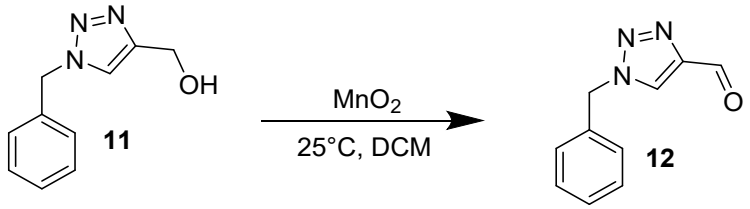


798.9 mg (6.0 mmol, 1.0 eq) benzyl azide were dissolved in 25 mL DMF. To this 690 µL (672.7 mg, 12.00 mmol, 2.0 eq) 2-propyn-1-ol were added, followed by 114.3 mg (0.6 mmol, 0.1 eq) copper iodide. The solution was stirred for 72 h at room temperature.

After full conversion the reaction mixture 30 mL saturated sodium bicarbonate solution was added. The mixture was extracted three times with ethyl acetate. The combined organic layers were dried over sodium sulfate and concentrated under vacuum. The crude was purified by column chromatography (silica, hexane: ethyl acetate 2:1) to obtain the product as a white solid (378 mg, 33 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 7.44 (s, 1H), 7.41 – 7.34 (m, 3H), 7.30 – 7.24 (m, 2H), 5.52 (s, 2H), 4.77 (s, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ [ppm] = 134.4, 129.1, 128.8, 128.1, 121.5, 56.6, 54.2.

1-Benzyl-1*H*-1,2,3-triazol-4-carboxaldehyd 12



189.2 mg (1.0 mmol, 1.0 eq) 1-benzyl-1,2,3-triazolmethanol were dissolved in 15 mL abs CH_2Cl_2. 899.4 mg (10.0 mmol, 10.0 eq) MnO_2 were added and the reaction was stirred for 1 h at room temperature. After full conversion the mixture on TLC, the reaction was filtrated over celite and the filtrate concentrated in vacuum. The crude was purified by column chromatography (silica, hexane: ethyl acetate 2:1) to obtain a white solid (34.6 mg, 19%).

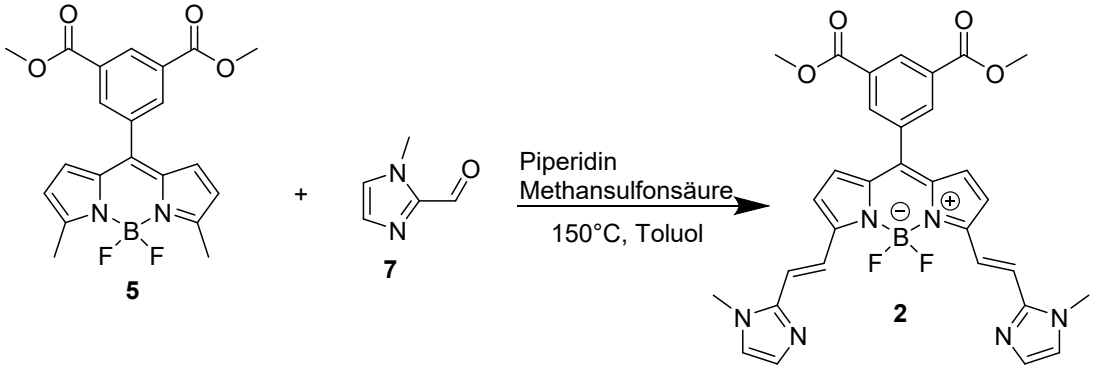
^{1}H NMR (600 MHz, $CDCl_3$) δ [ppm] = 10.12 (s, 1H), 7.99 (s, 1H), 7.45 – 7.38 (m, 3H), 7.34 – 7.29 (m, 2H), 5.59 (s, 2H).^{13}C NMR (151 MHz, $CDCl_3$) δ[ppm] = 185.1, 148.0, 133.3, 129.4, 129.3, 128.4, 125.0, 54.6.

General Procedure for Knoevenagel condensation

1.0 eq of BODIPY was dissolved in 3 mL of abs toluene, added 2.0 eq of corresponding aldehyde, 0.5 mL piperidine and 2 drops of methyl sulfonic acid. The reaction was heated in a Dean-Stark setup in pre-heated oilbath at 150 °C and distilled to dryness. The reaction was repeated once more with the addition of 2.0 eq aldehyde, 0.5 mL piperidine, 2 drops of methyl sulfonic acid in 3 mL of toluene. The crude was taken up in CH_2Cl_2 and washed with saturated sodium bicarbonate. The aqueous layer is extracted with DCM three times and the combined organic extracts were dried over sodium sulfate and concentrated in vacuum.

The crude is purified by column chromatography. All steps are conducted under protection from light.

Methylimidazol BODIPY 2



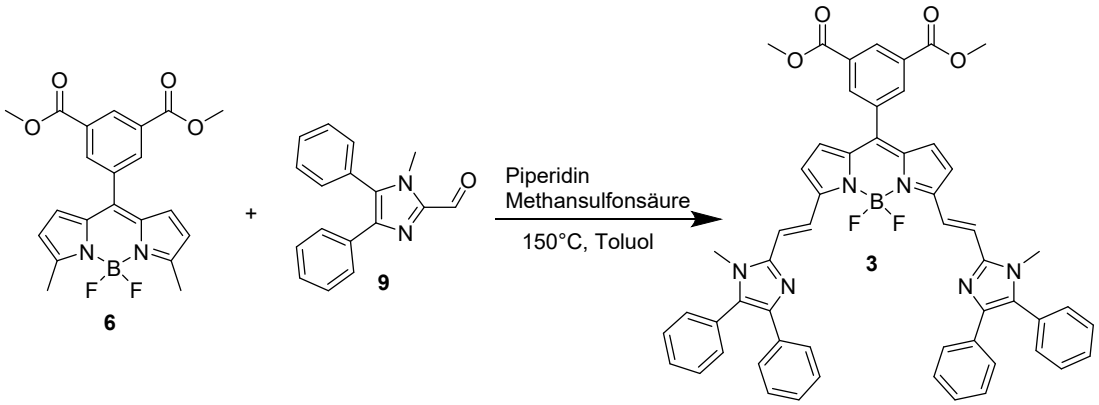
5 + 7 → 2

10.3 mg (0.025 mmol, 1.0 eq) starting BODIPY **5**, 10.0 mg (0.1 mmol , 4.0 eq) **7**.

The crude was purified by column chromatography (silica, ethyl acetate: methanol 1:0 to 9:1) to obtain **2** as a blue solid (7.1 mg, 48%).

^{1}H NMR (600 MHz, CD_2Cl_2) δ [ppm] = 8.82 (t, *J* = 1.6 Hz, 1H), 8.36 (d, *J* = 1.6 Hz, 2H), 7.98 (d, *J* = 16.1 Hz, 2H), 7.44 (d, *J* = 16.1 Hz, 2H), 7.33 (d, *J* = 10.3 Hz, 2H), 7.30 (s, 2H), 7.12 (d, *J* = 4.5 Hz, 2H), 6.80 (t, *J* = 6.4 Hz, 2H), 3.97 (s, 6H), 3.90 (s, 6H).^{19}F NMR (564 MHz, CD_2Cl_2) δ [ppm] = -140.0 (dd, *J* = 65.5, 34.1 Hz). ESI-MS [m/z]: found: 597.22510; calculated for [P+H$^+$] = 597.22349.

Diphenylimidazol-BODIPY 3



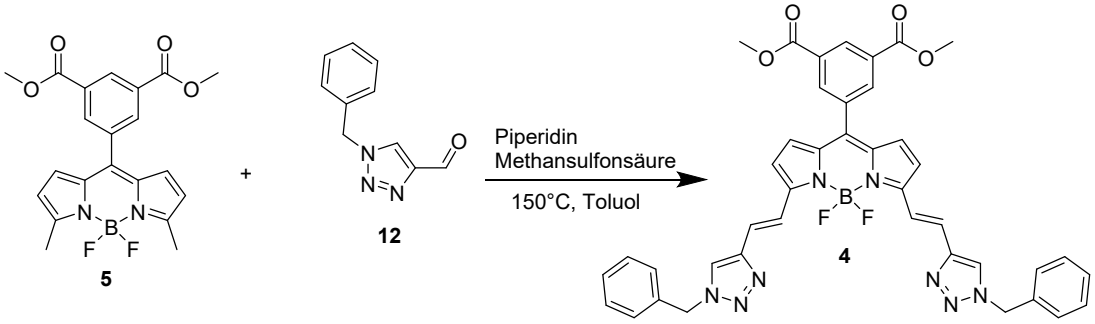
6 + 9 → 3

10.3 mg (0.025 mmol, 1.0 eq) starting BODIPY **6**, 19.7 mg (0.075 mmol , 3.0 eq) **9**.

The crude was purified by column chromatography (silica, ethyl acetate: hexane 3:1 to 0:1 to ethyl acetate: hexane 1:4 to 1:1) to obtain **3** as a blue solid (5.0 mg, 22 %).

^{1}H NMR (600 MHz, CD_2Cl_2) δ [ppm] = 8.85 (t, *J* = 1.6 Hz, 1H), 8.38 (d, *J* = 1.7 Hz, 2H), 8.23 (d, *J* = 16.1 Hz, 2H), 7.60 – 7.50 (m, 11H), 7.42 – 7.35 (m, 5H), 7.27 – 7.20 (m, 7H), 7.16 (d, *J* = 4.5 Hz, 2H), 6.82 (d, *J* = 4.5 Hz, 2H), 3.99 (s, 6H).^{19}F NMR (564 MHz, CD_2Cl_2) δ [ppm] = -141.4 (br dd). ESI-MS [m/z]: found: 901.35065; calculated for [P+H$^+$] = 901.34405.

Triazol BODIPY 4



10.3 mg (0.025 mmol, 1.0 eq) starting BODIPY **5**, 16.0 mg (0.086 mmol , 3.6 eq) **12**.

The crude was purified by column chromatography (silica, ethyl acetate: hexane 3:1 to 0:1 to ethyl acetate: hexane 1:5 to 1:1) to obtain **4** as a blue solid (2.9 mg, 30 %).

^{1}H NMR (600 MHz, CD_2Cl_2) δ [ppm] = 8.82 (t, *J* = 1.6 Hz, 1H), 8.37 (d, *J* = 1.6 Hz, 2H), 7.86 (s, 2H), 7.73 (d, *J* = 16.5 Hz, 2H), 7.47 – 7.28 (m, 13H), 6.98 (d, *J* = 4.5 Hz, 2H), 6.76 (d, *J* = 4.5 Hz, 2H), 5.60 (s, 4H), 3.97 (s, 6H).^{13}C NMR (151 MHz, CD_2Cl_2) δ [ppm] = 154.9, 145.9, 134.9, 134.7, 131.5, 129.1, 128.7, 128.1, 125.7, 122.2, 120.1, 116.9.^{19}F NMR (564 MHz, CD_2Cl_2) δ [ppm] = -139.4 (dd, *J* = 65.9, 32.8 Hz). ESI-MS [m/z]: found: 683.25830; calculated for [$C_{34}H_{27}BF_2N_8Na0_4$] = 683.21141.

5. UV-vis spectra

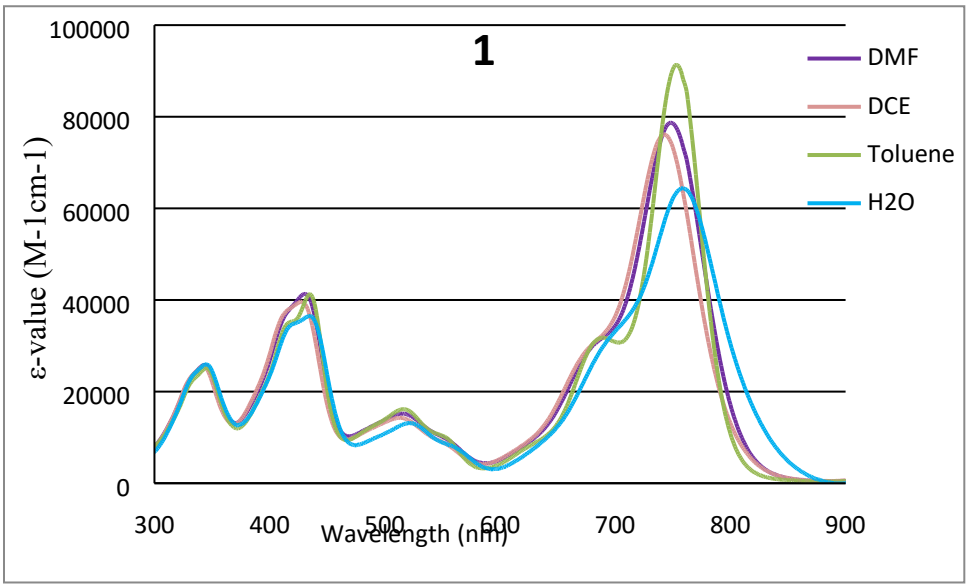


Figure S1. Overlay of UV-vis absorption spectra of compound **1** (in DMF, 1,2-DCE, Toluene and H_2O solutions); For dissolving compound **1** in H_2O, it was formulated in cremophore EL (1-2 mg/µmol).

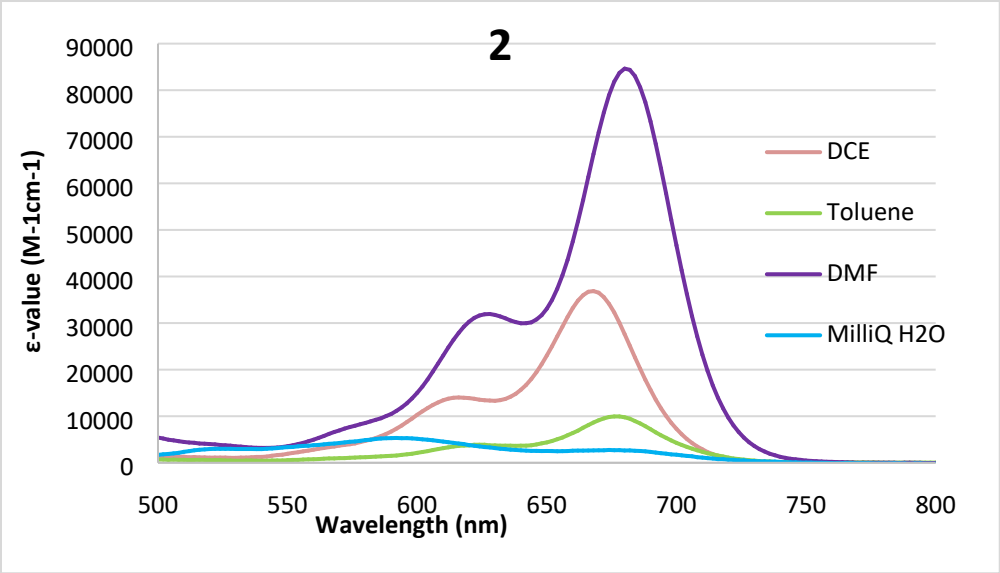


Figure S2. Overlay of UV-vis absorption spectra of compound **2** (DMF, 1,2-DCE, Toluene and H_2O solutions); For dissolving compound **2** in H_2O, it was formulated in cremophore EL (1-2 mg/µmol).

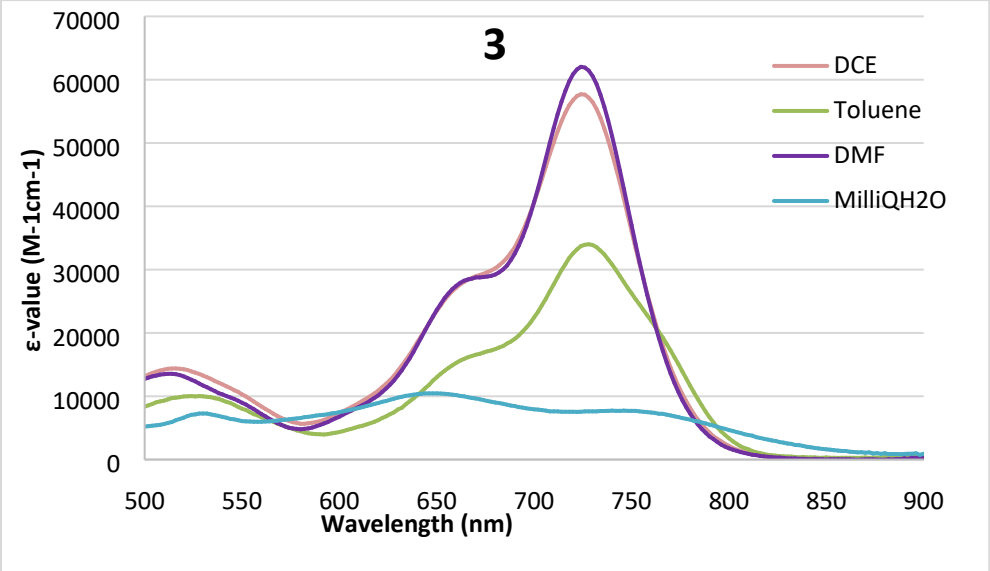


Figure S3. Overlay of UV-Vis absorption spectra of compound **3** (DMF, 1,2-DCE, Toluene and H_2O solutions); For dissolving compound **3** in H_2O, it was formulated in cremophore EL (1-2 mg/µmol).

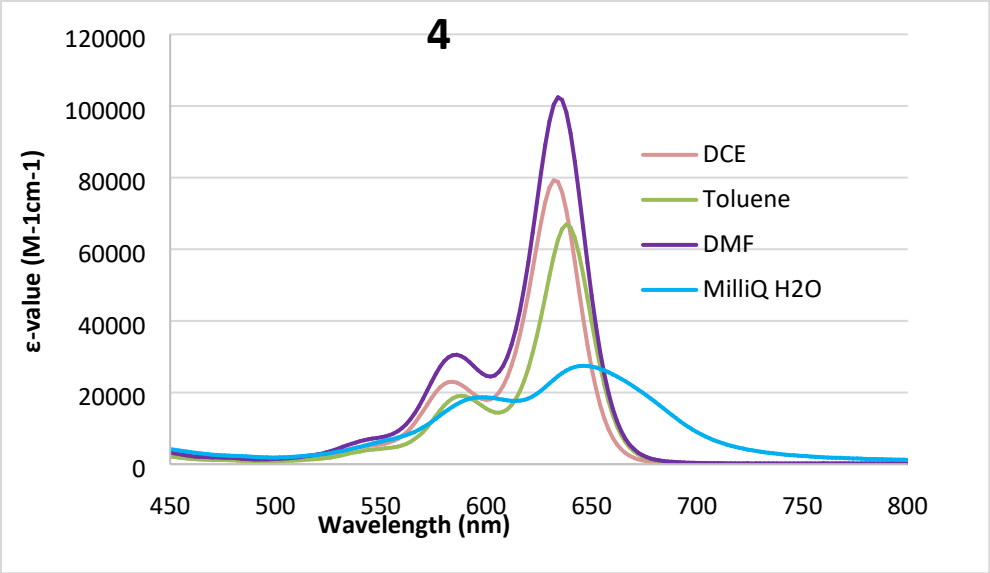


Figure S4. Overlay of UV-vis absorption spectra of compound **4** (DMF, 1,2-DCE, Toluene and H_2O solutions); For dissolving compound **4** in H_2O, it was formulated in cremophore EL (1-2 mg/µmol).

6. Fluorescence emission spectra

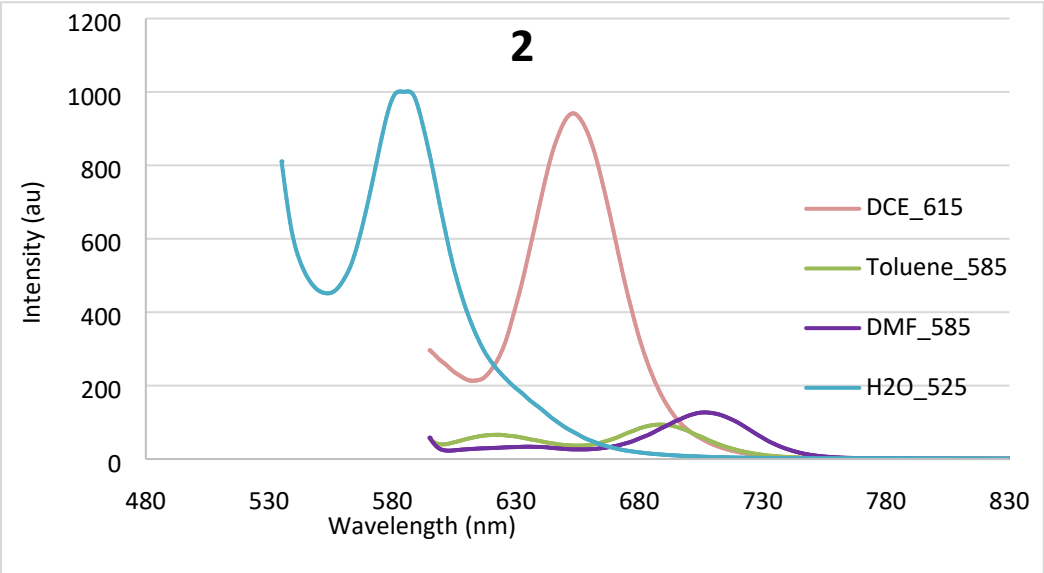


Figure S5: Fluorescence emission spectra of compound **2** in various solvents (conc. = 5 µM) at the following excitation wavelengths: (DCE: 615 nm; Toluene: 585 nm; DMF: 585 nm; H2O: 525 nm).

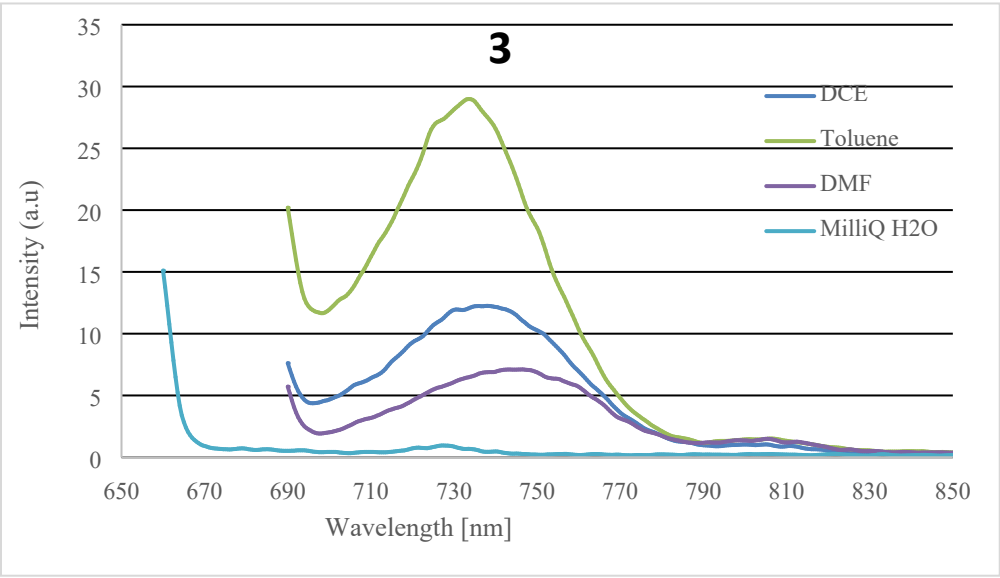
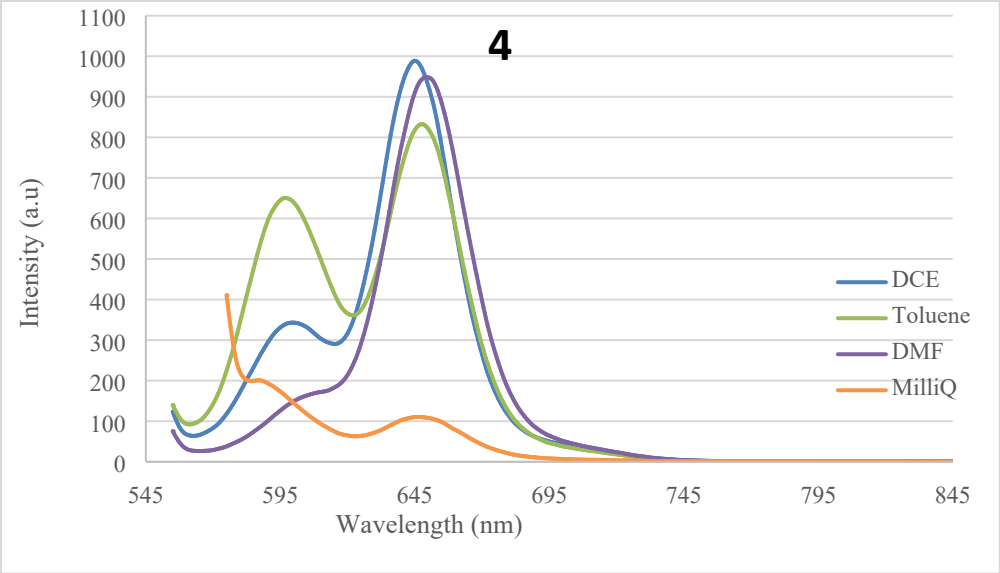


Figure S6: Fluorescence emission spectra of compound **3** in various solvents (conc. = 5 µM) at the following excitation wavelengths: (DCE: 680 nm; Toluene: 680 nm; DMF: 680 nm; H2O: 650 nm).



Fluorescence emission spectra of compound **4** in various solvents (conc. = 5 µM) at the following excitation wavelengths: (DCE: 545 nm; Toluene: 545 nm; DMF: 545 nm; H2O: 565 nm).

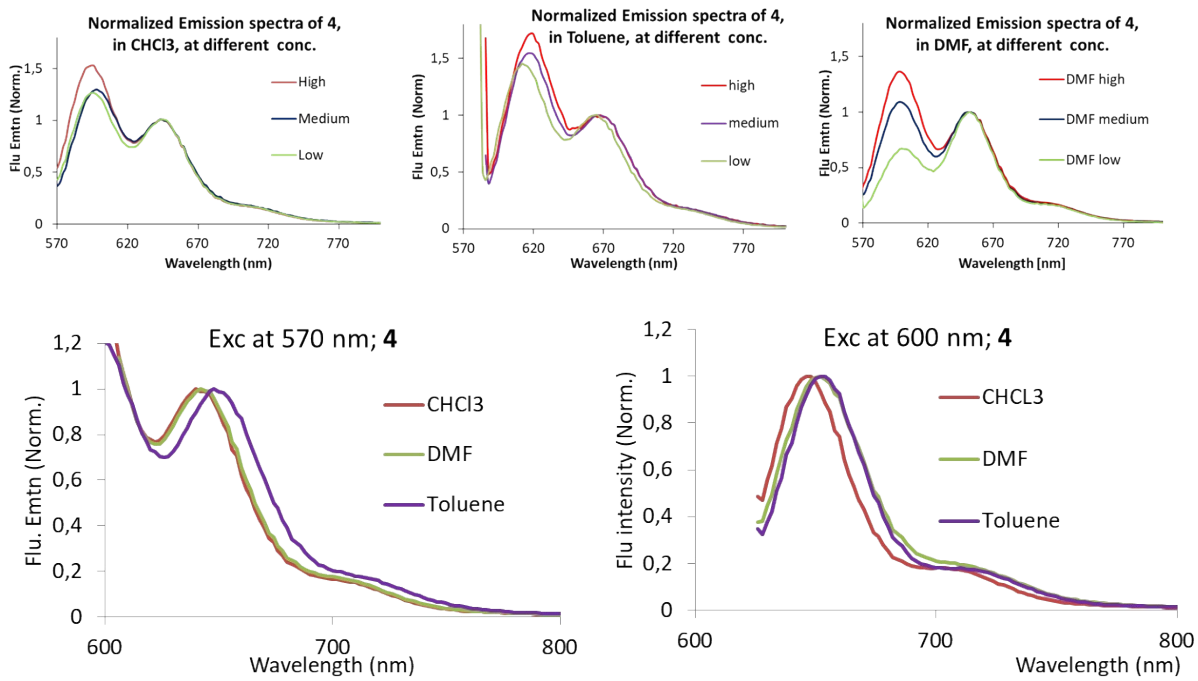
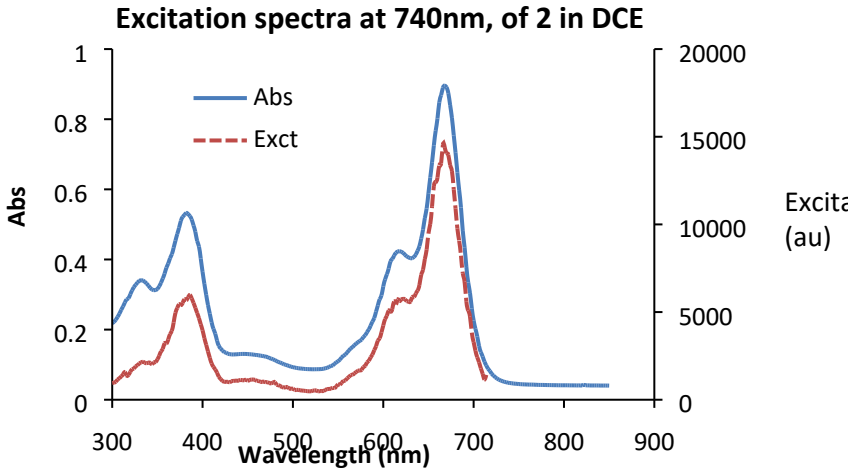
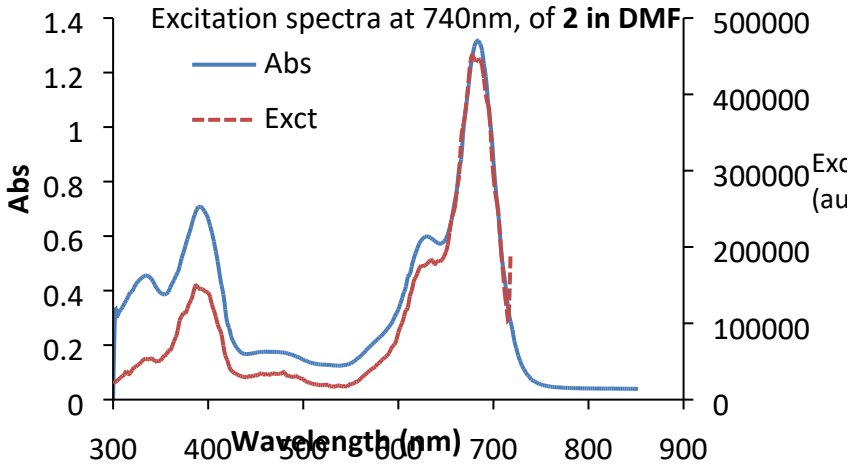
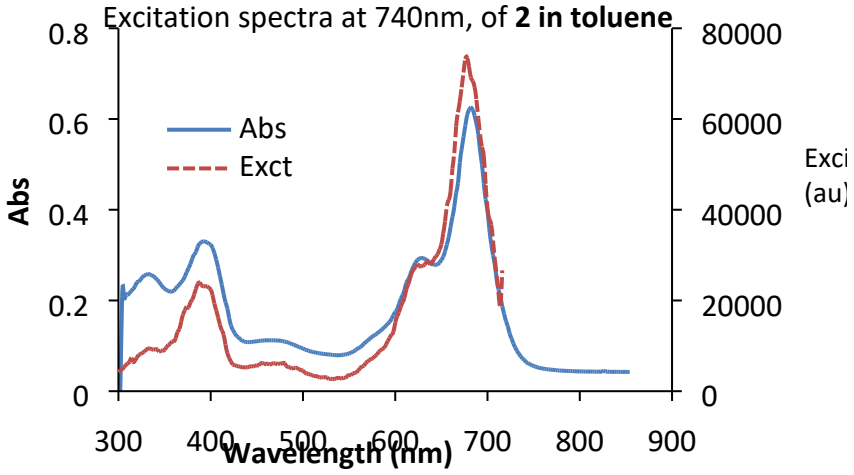


Figure S7: Fluorescence emission spectra of compound **4** in various solvents ($CHCl_3$, Toluene and DMF); top different concentrations for the excitation wavelengths 540 nm) and bottom: excitation at 570 nm and 600 nm.

7. Excitation spectra







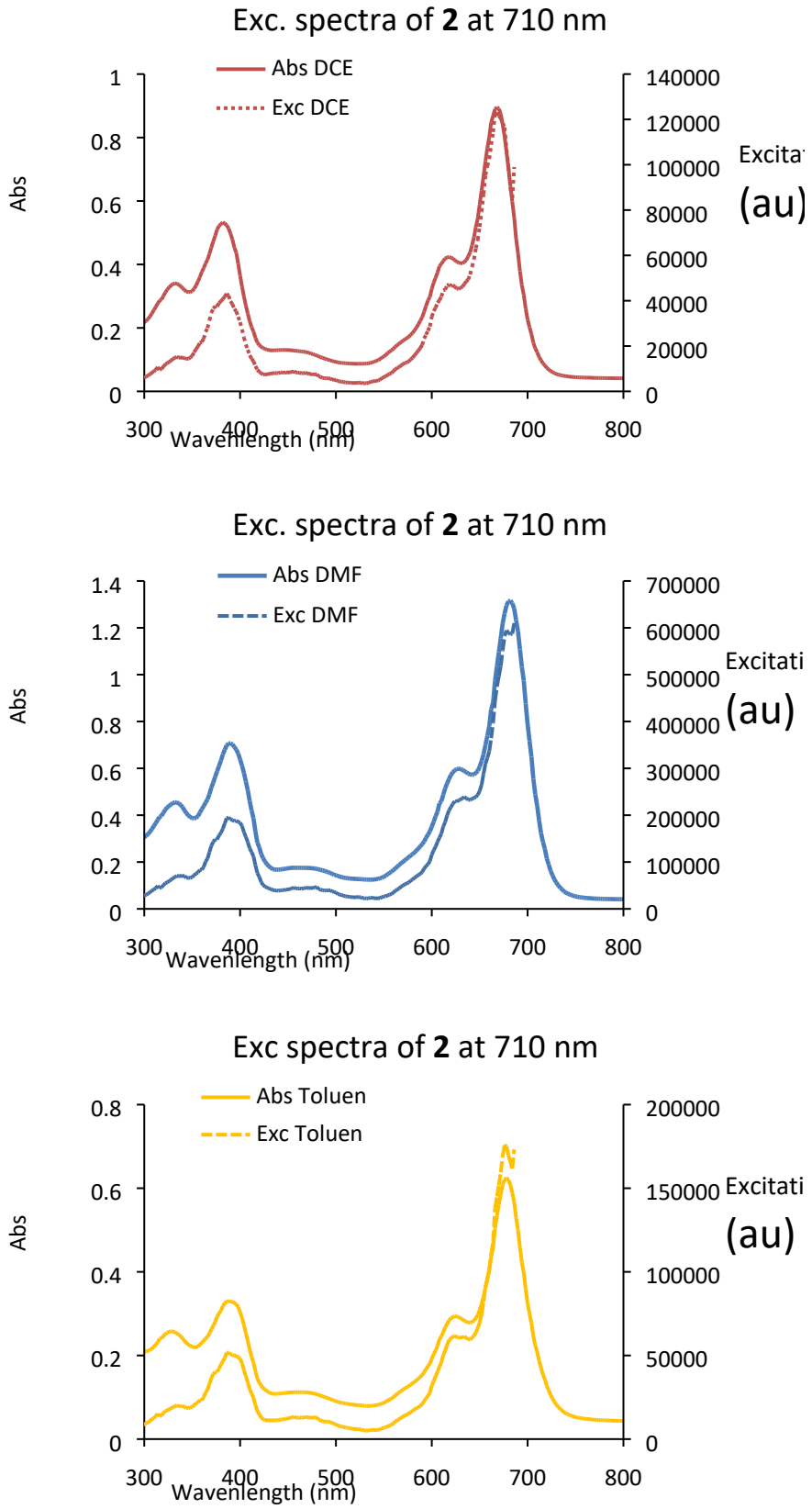


Figure S8: Overlay of excitation spectra (for λ_{Em} at 740 nm, and λ_{Em} at 710 nm) along with absorption spectra of compound **2** in various solvents.

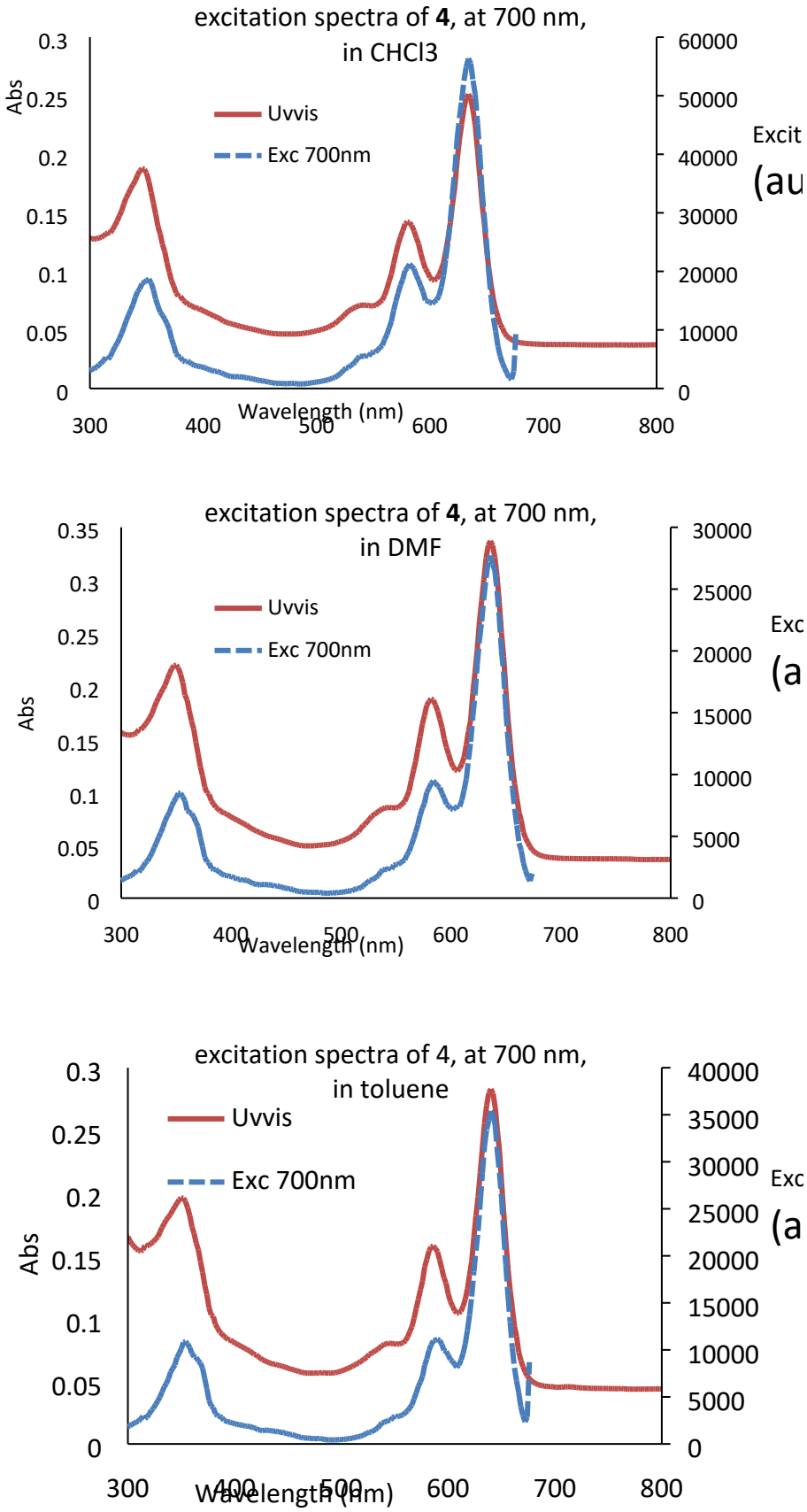


Figure S9: Overlay of excitation spectra (for λ_{Em} at 700 nm) and absorption of spectra of compound **4** in various solvents.

8. HPLC chromatograms

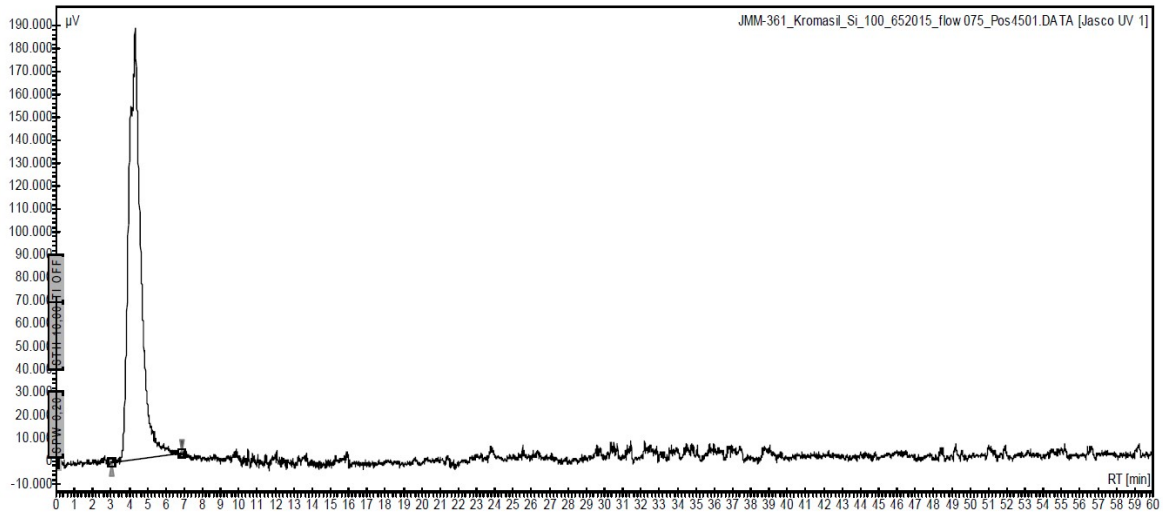
Method: Kromasil Si-100 (unmodified silica, 7 µM particle size), 250 x 4.6 mm column

Gradient: Hexane/^{i}PrOH/EtOH: 65:20:15 (at 0 min) to 20:40:40 (in 15 min), and constant afterwards.

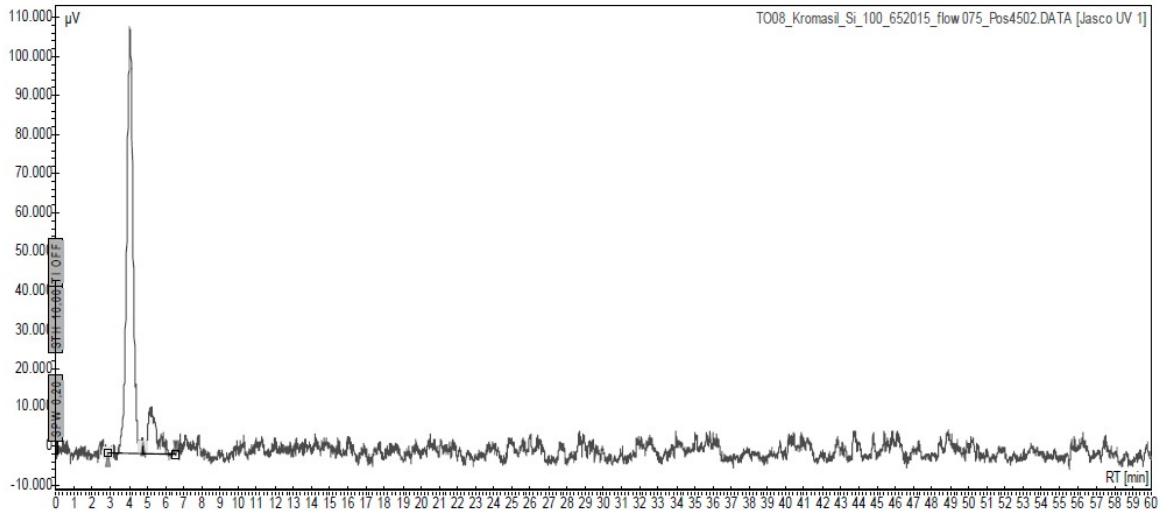
Flow rate: 1 mL/min

DAD detection: 254 nm, 400 nm and 600 nm.

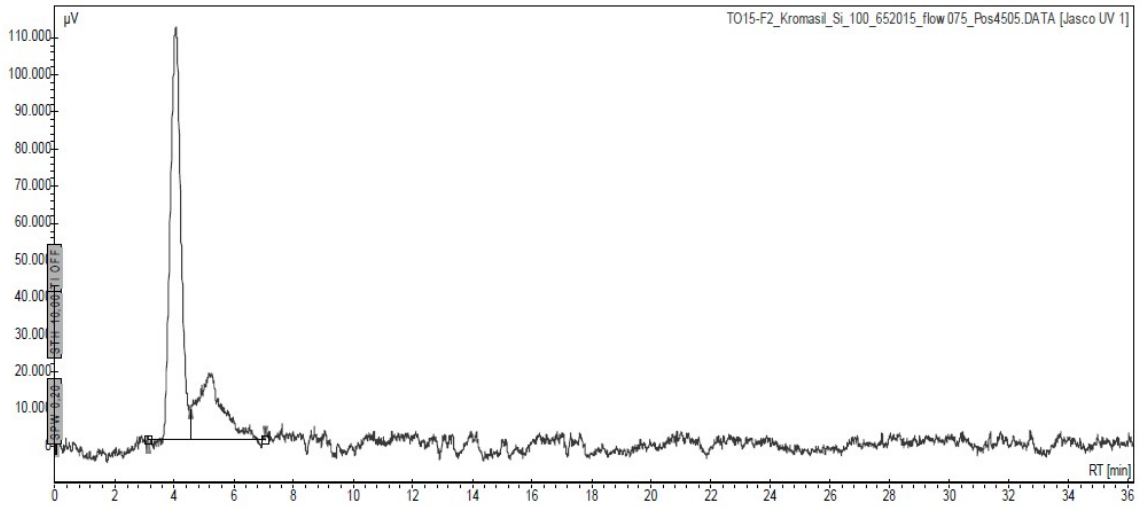
a) (N_1-Het)BODIPY (**1**)



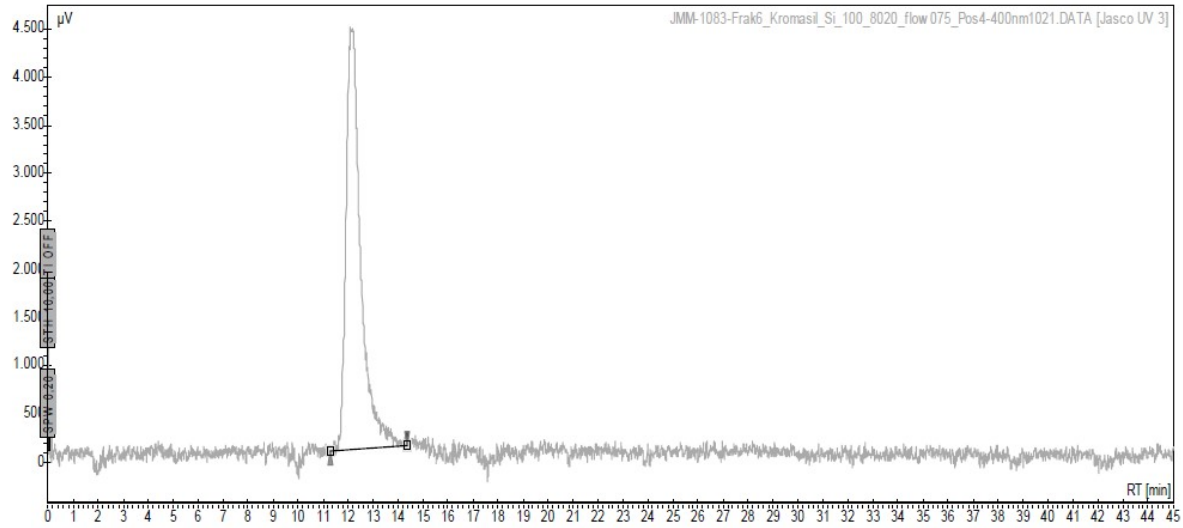
b) (N_2-Het)BODIPY **(2)**



c) (N_2-Het)BODIPY **(3)**

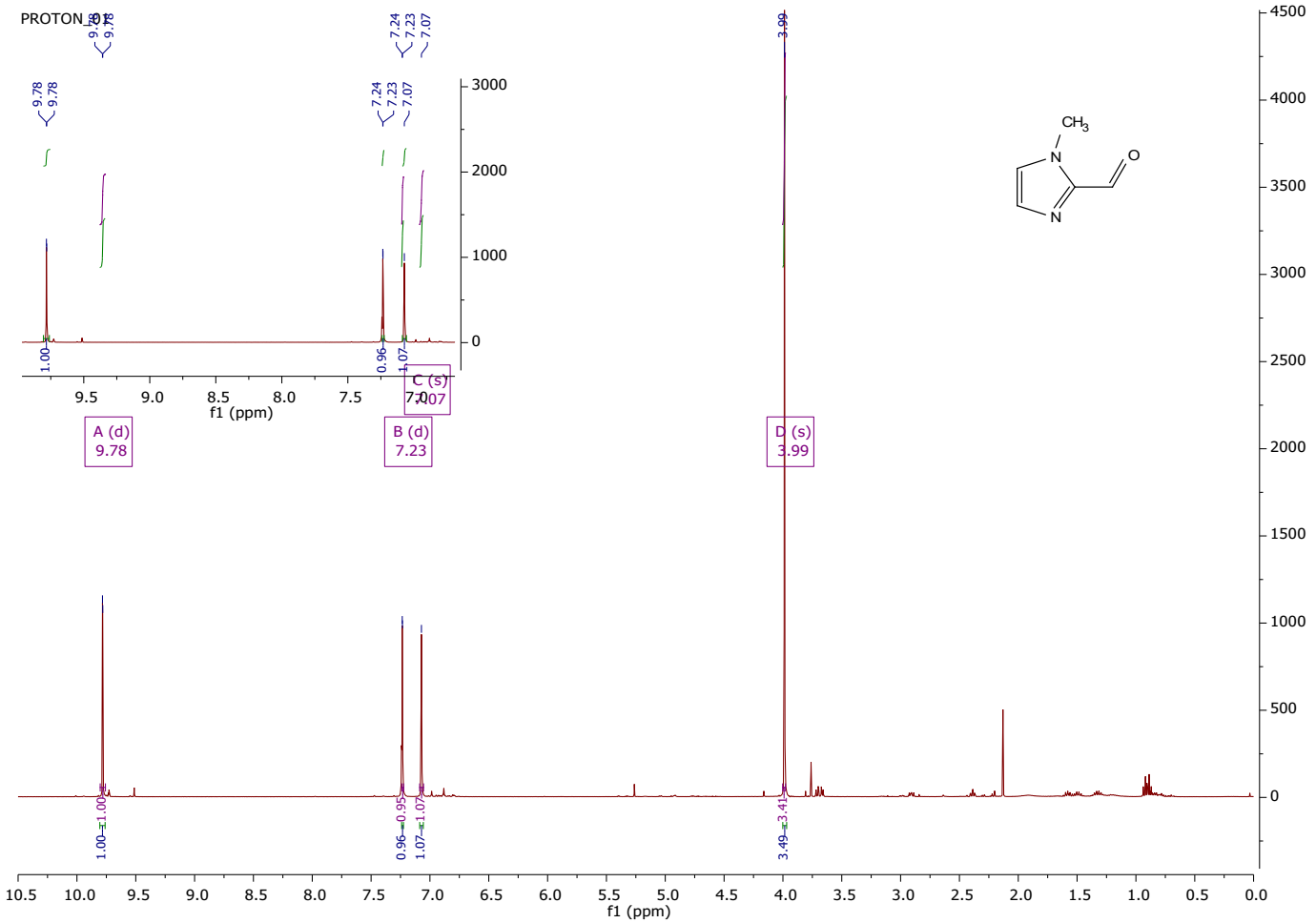


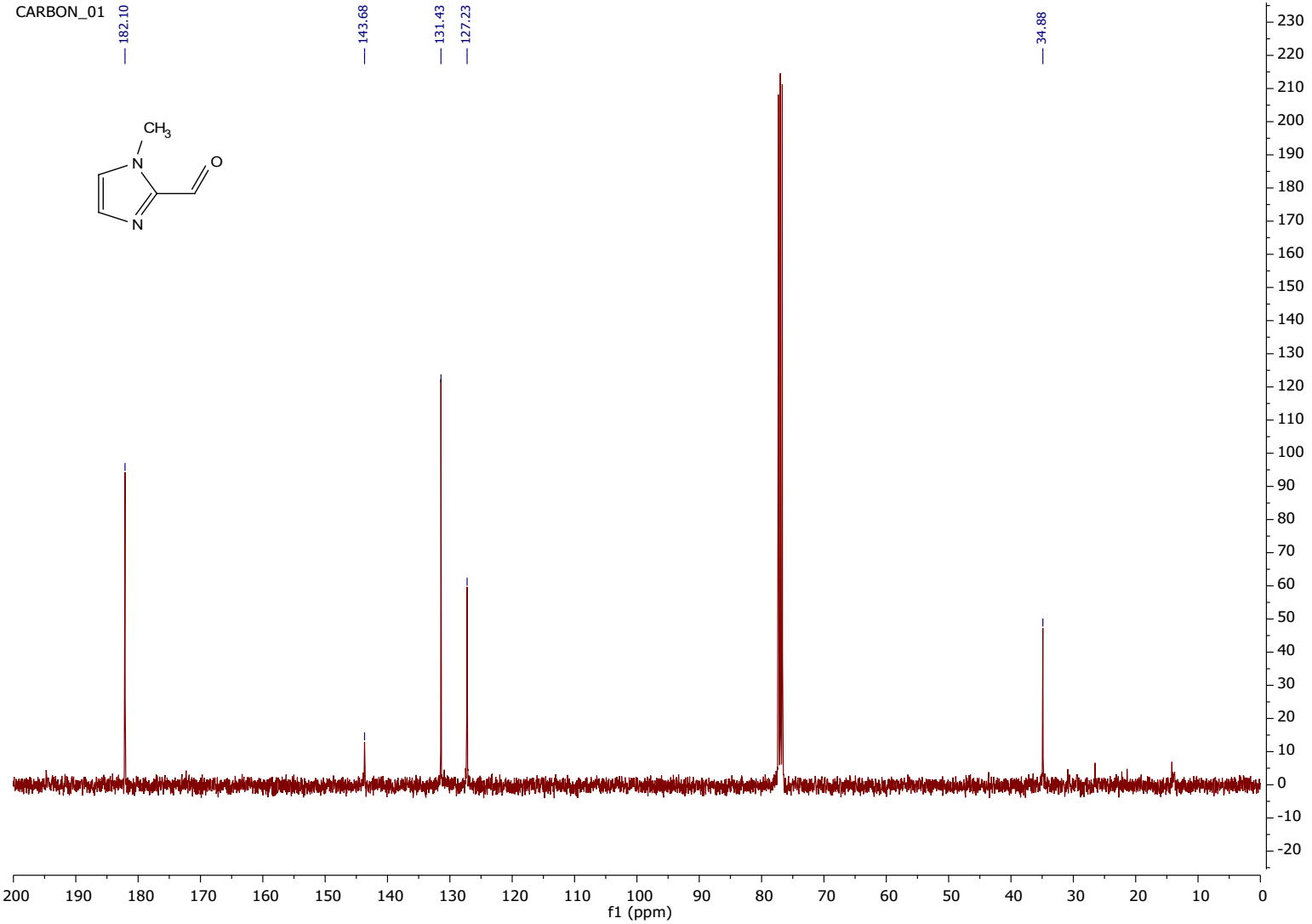
d) (N_3-Het)BODIPY **(4)**



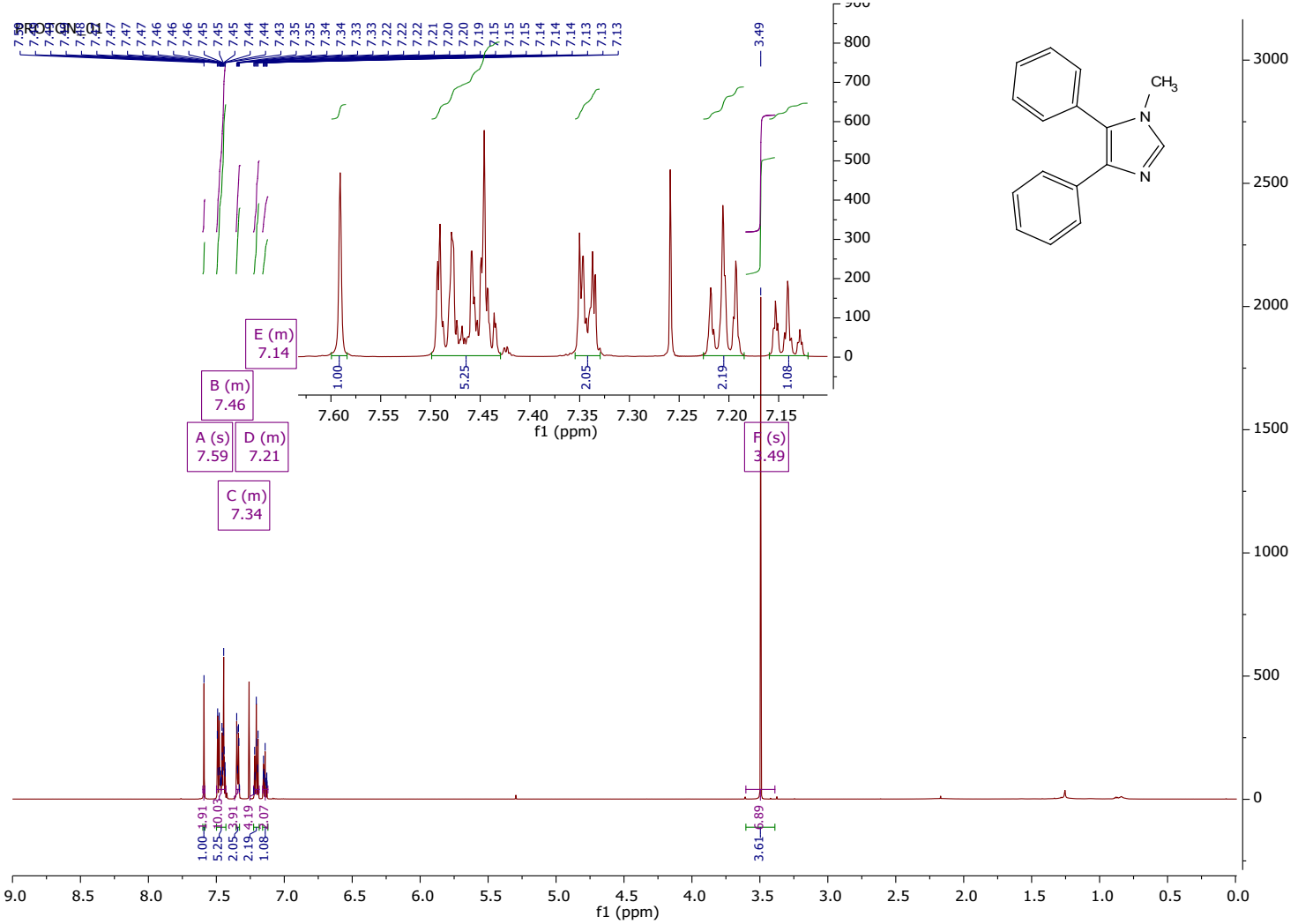
9. NMR spectra

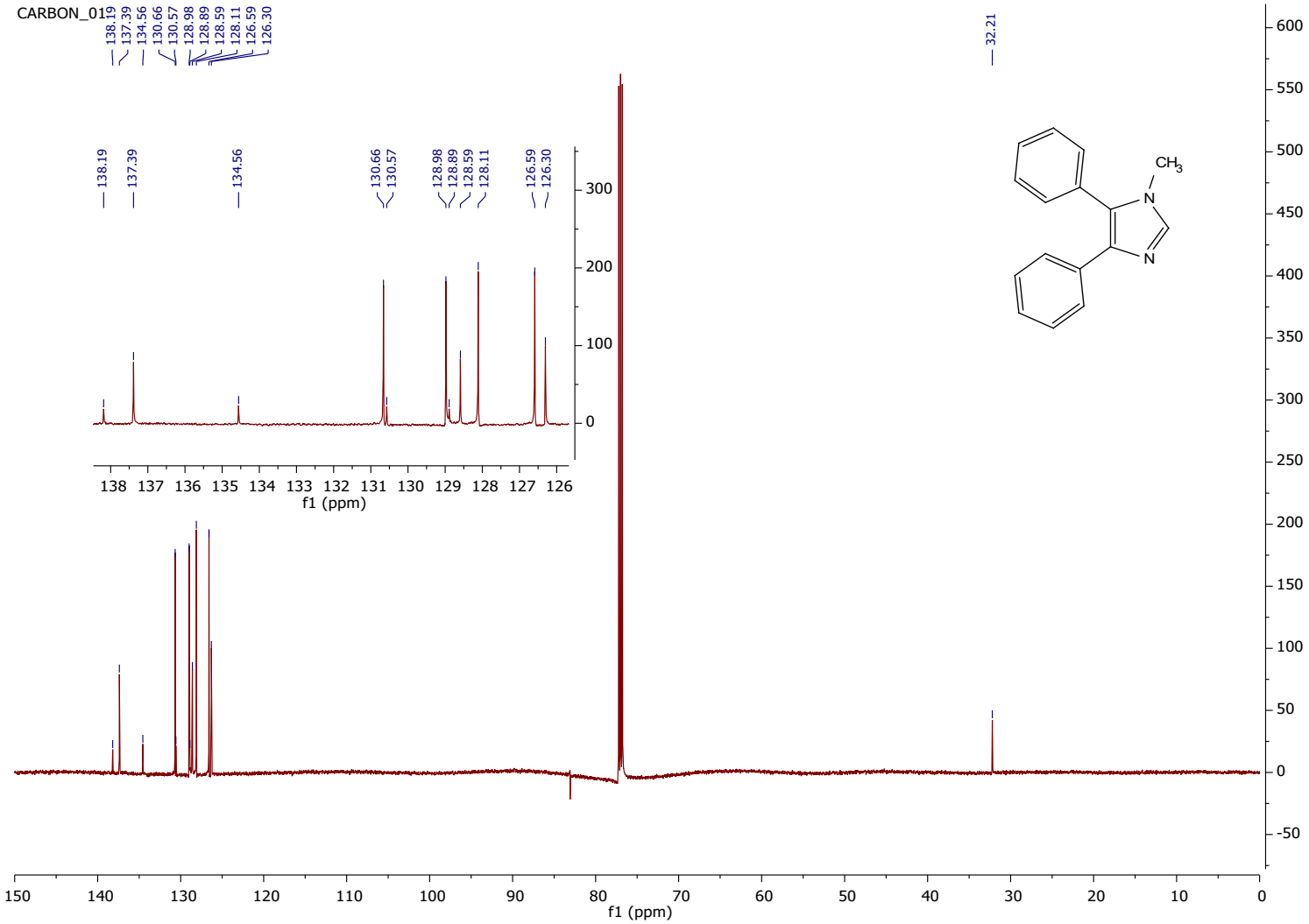
1-methylimidazolaldehyde 7



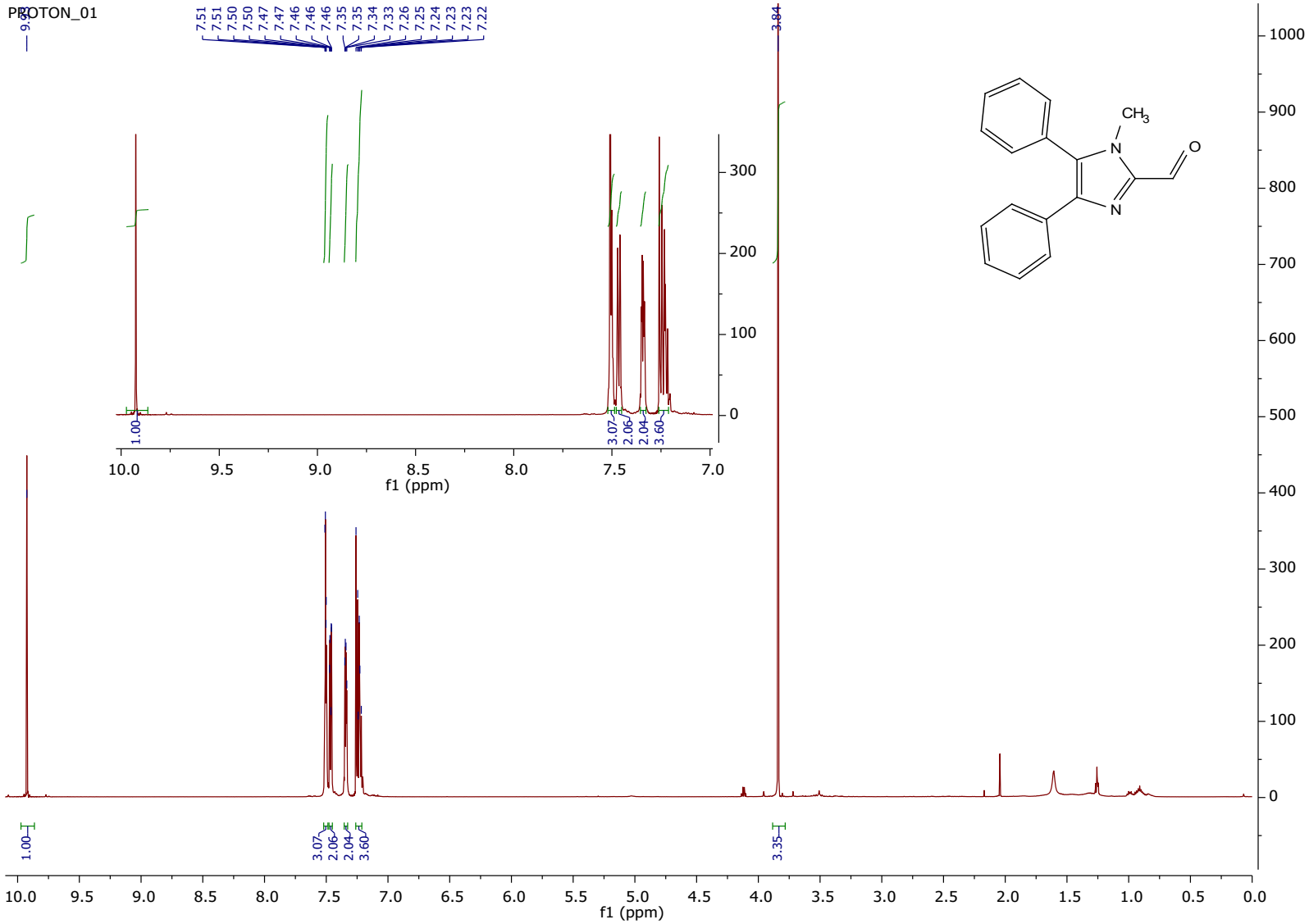

CARBON_01
182.10
143.68
131.43
127.23
34.88
CH3
N
N
O
f1 (ppm)

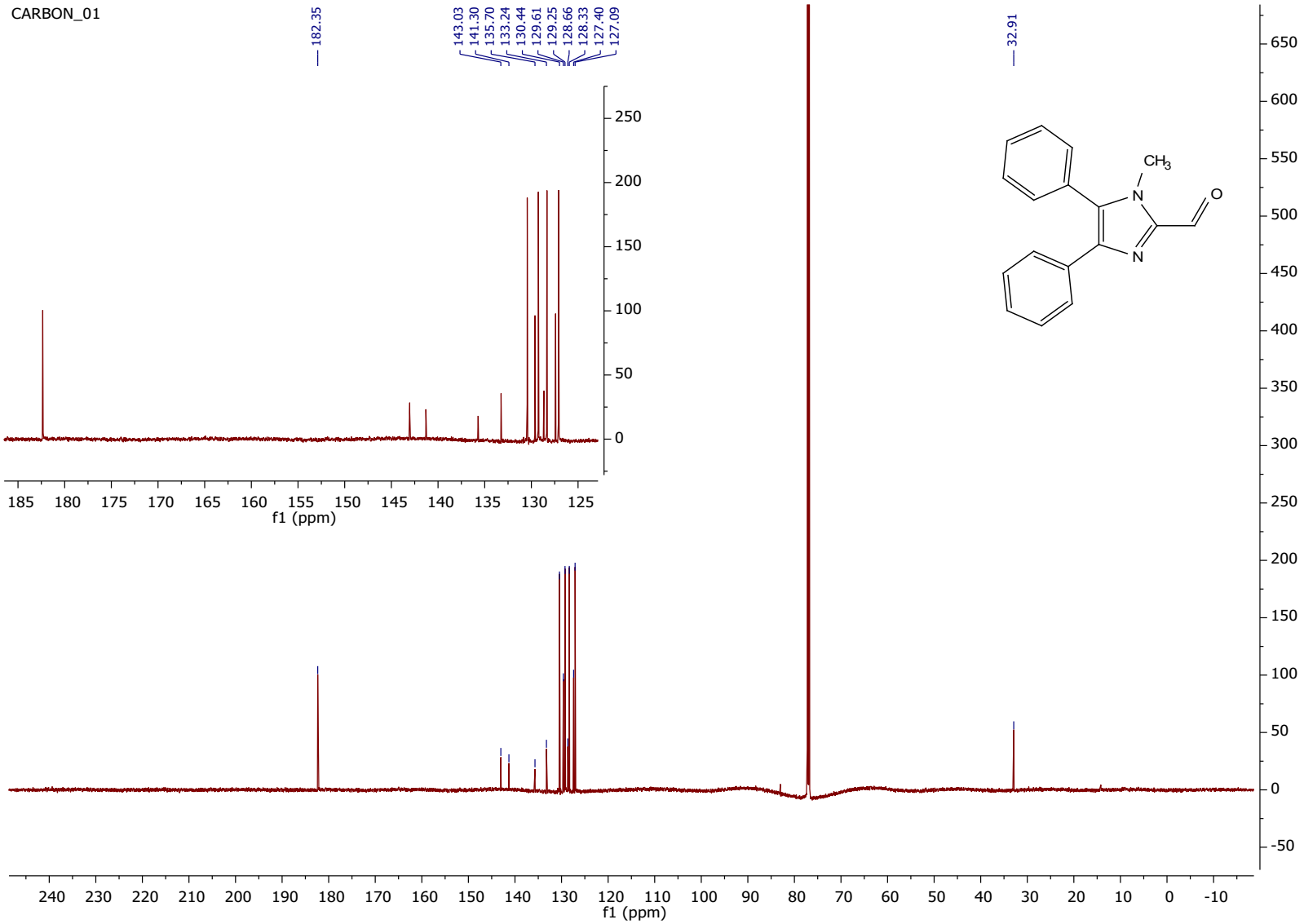
1-Methyl-4,5-diphenylimidazol 8



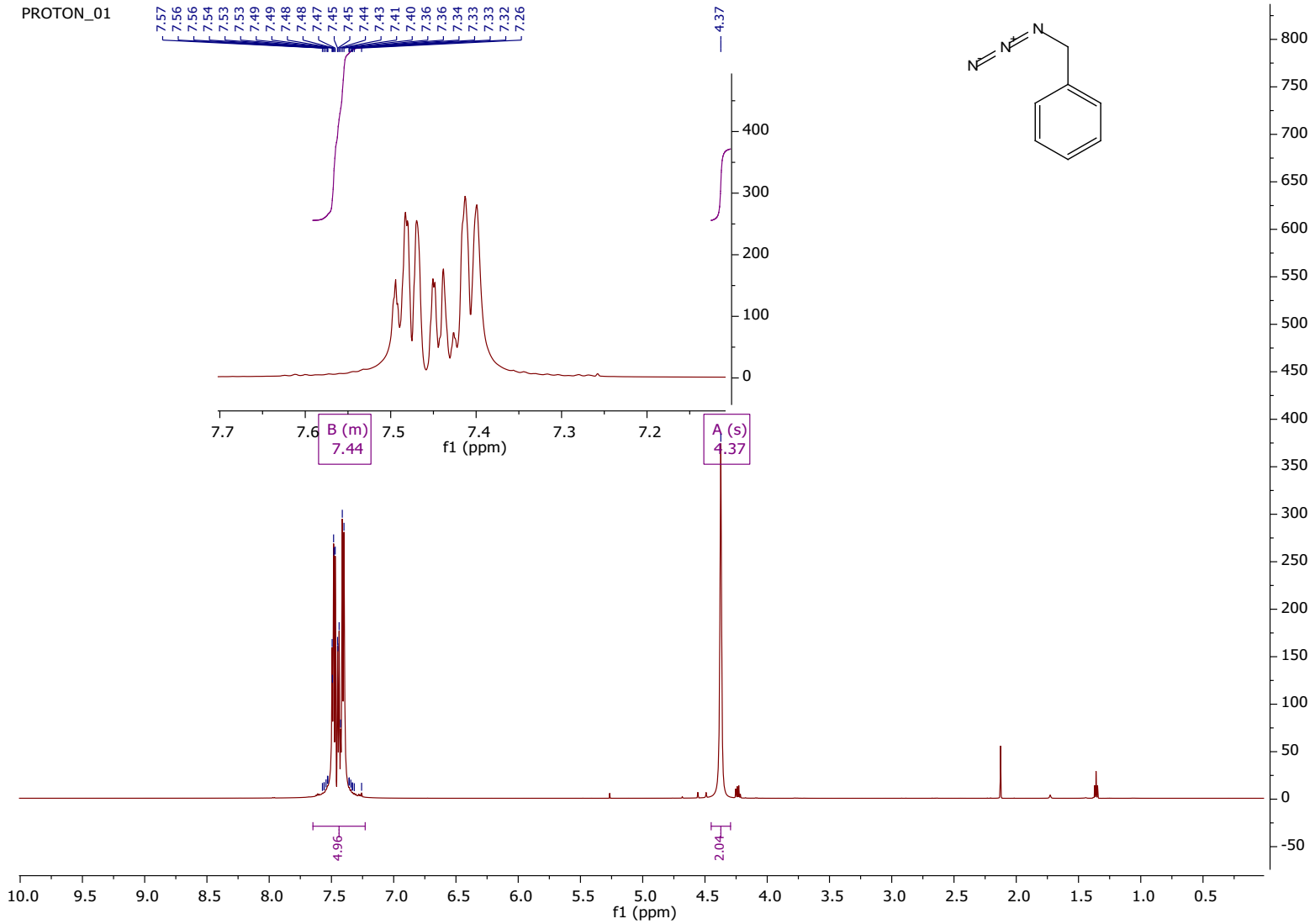

CARBON_01
138.19
137.39
134.56
130.66
130.57
128.98
128.89
128.59
128.11
126.59
126.30
32.21
CH3
N
N
f1 (ppm)
f1 (ppm)

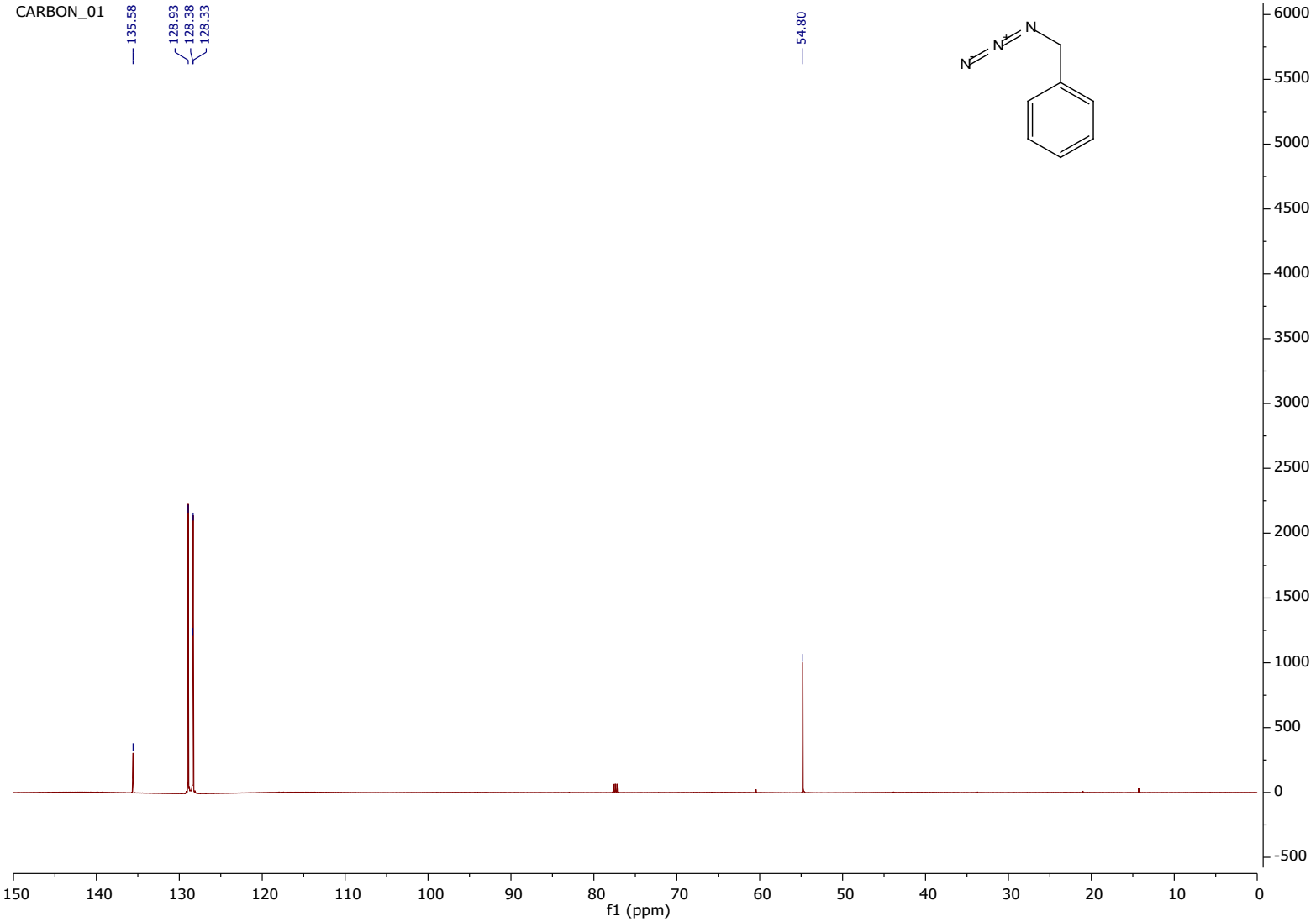
1-Methyl-4,5-diphenylimidazolaldehyde 9



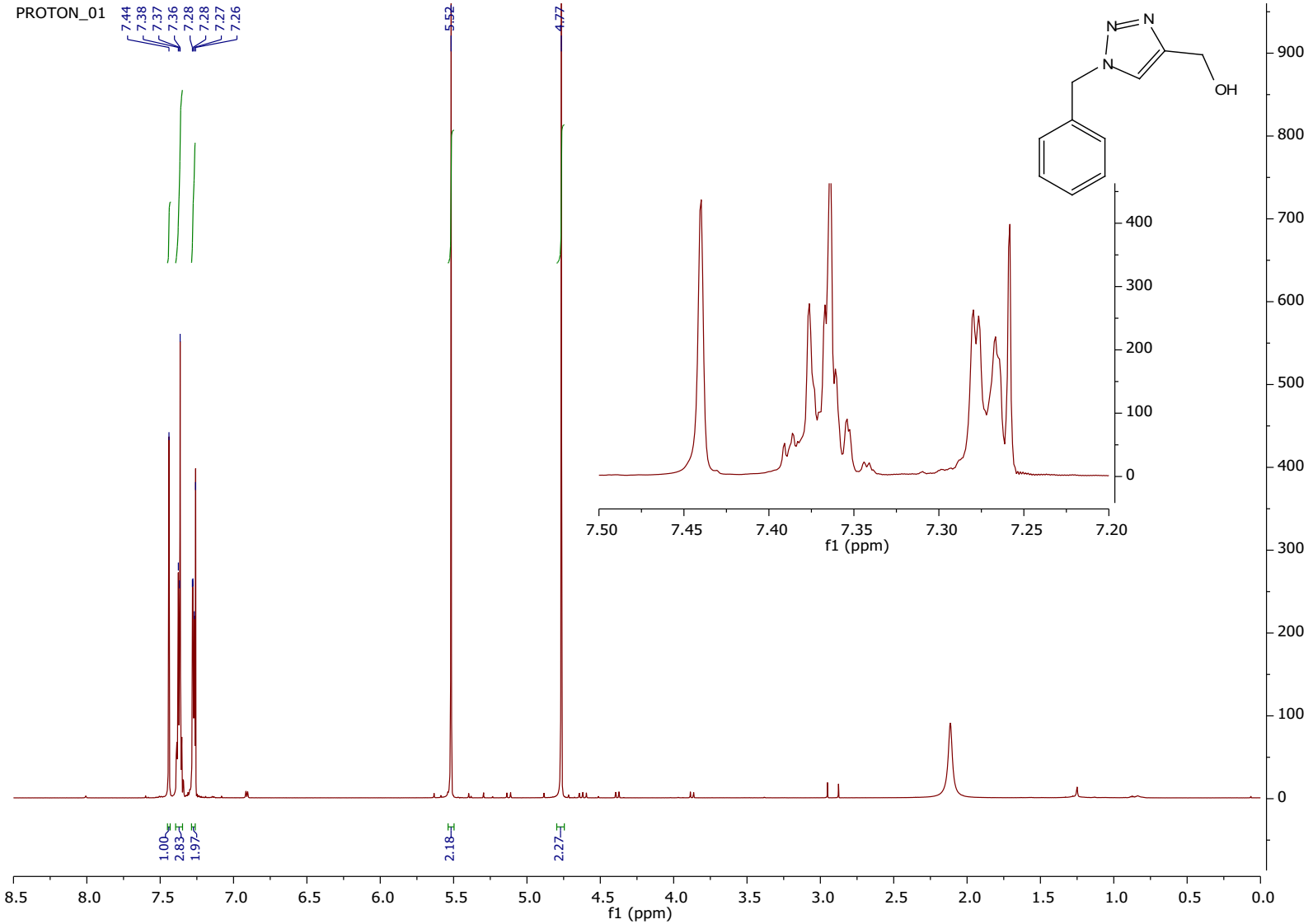

CARBON_01
182.35
143.03
141.30
135.70
133.24
130.44
129.61
129.25
128.66
128.33
127.40
127.09
32.91
CH3
N
N
O
f1 (ppm)
f1 (ppm)

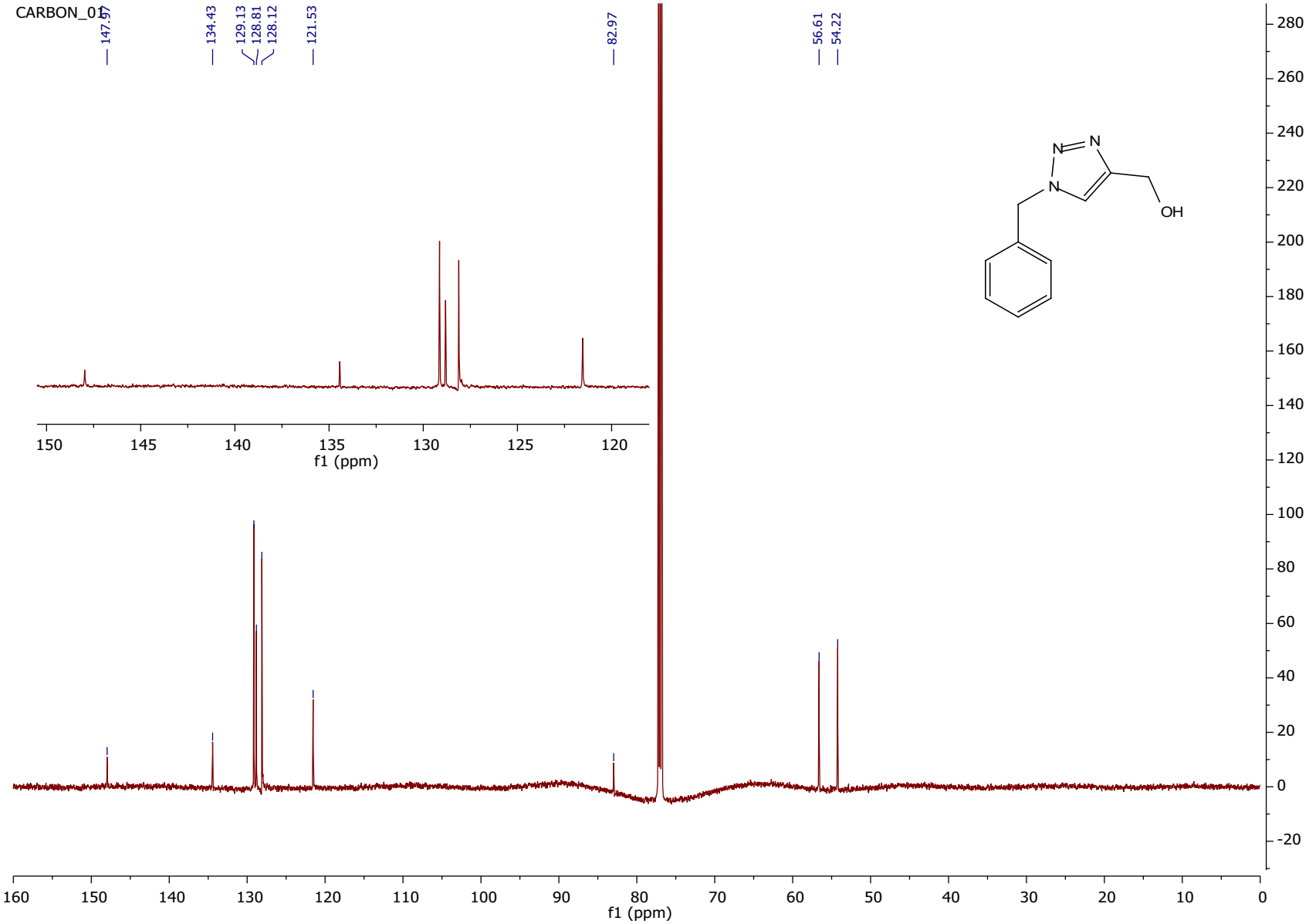
Benzylazid 10



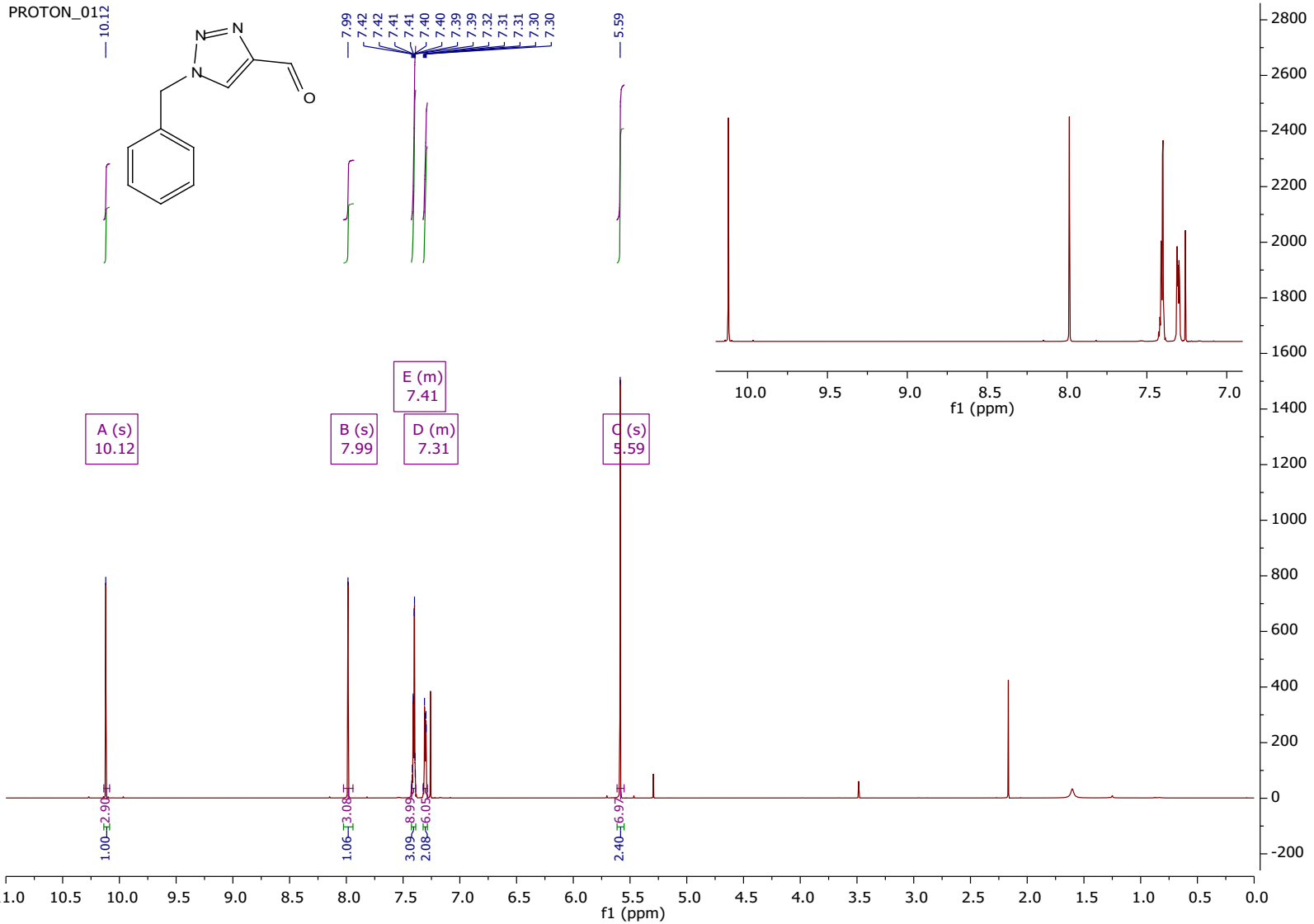

CARBON_01
135.58
128.93
128.38
128.33
54.80
N
N
N
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

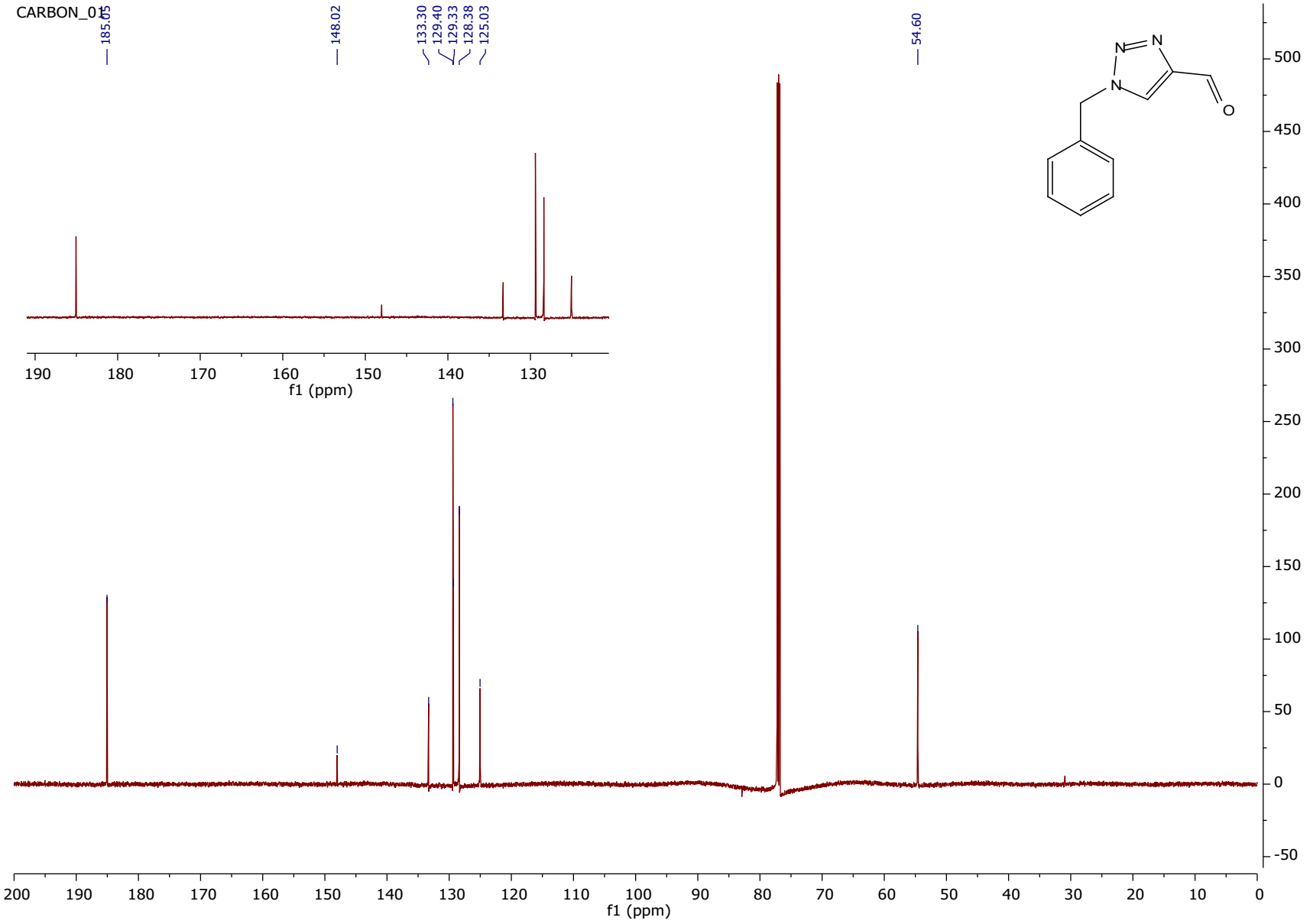
(1-Benzyl-1,2,3-triazol-4-yl)methanol 11



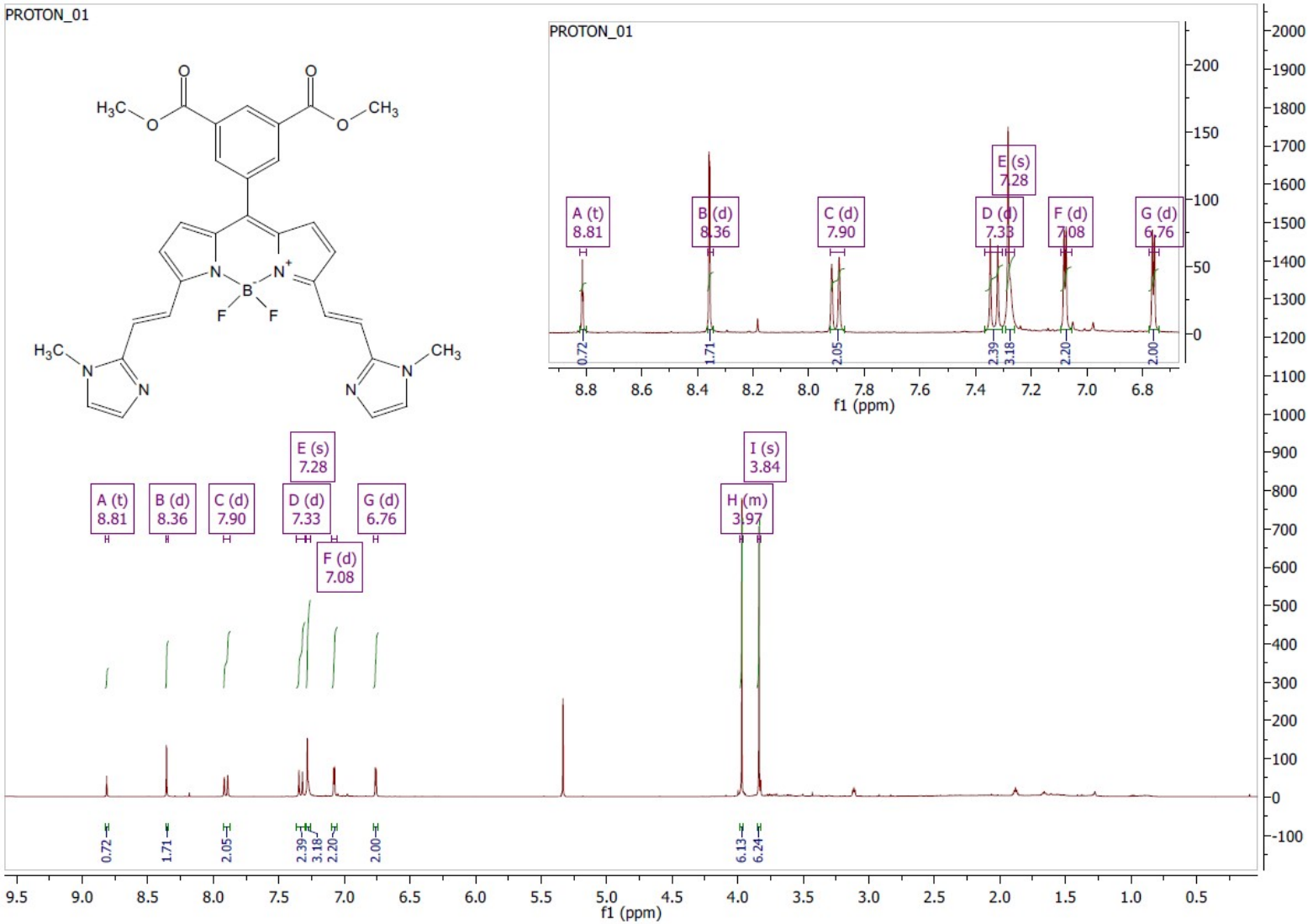

CARBON_01
147.97
134.43
129.13
128.81
128.12
121.53
82.97
56.61
54.22
N
N
N
OH
150
145
140
135
130
125
120
f1 (ppm)
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

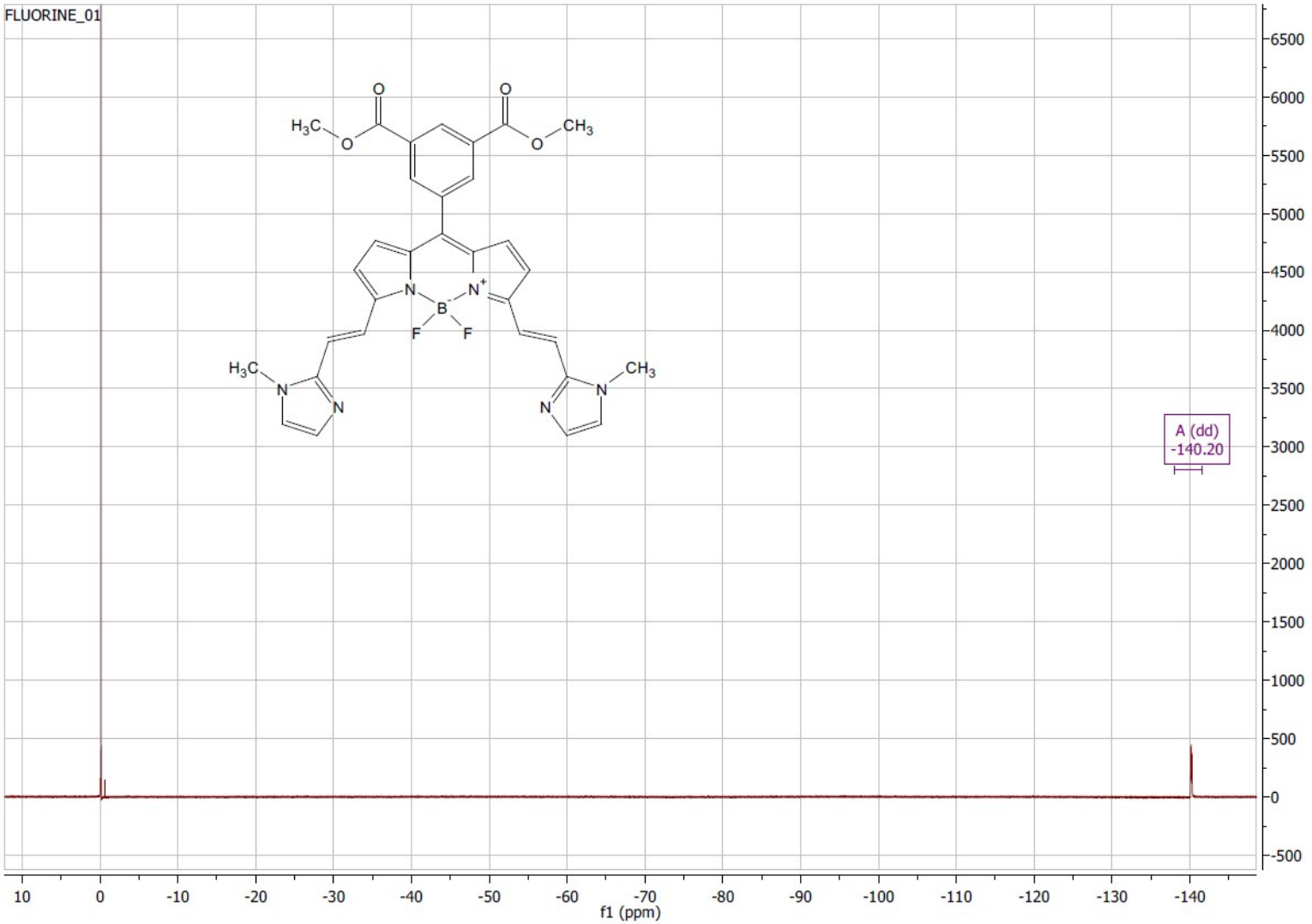
1-Benzyl-1*H*-1,2,3-triazol-4-carboxaldehyd 12

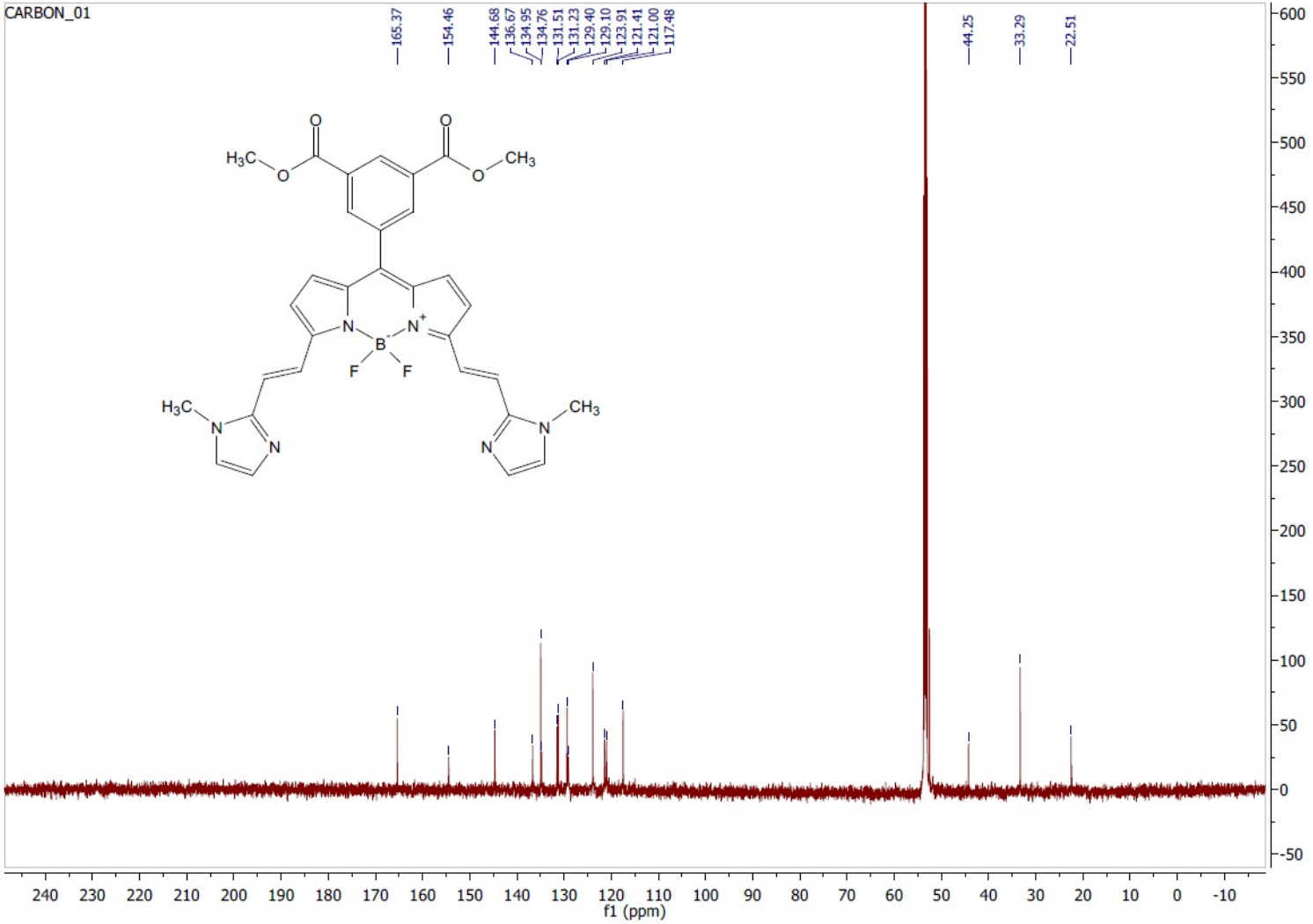



CARBON_01
185.05
148.02
133.30
129.40
129.33
128.38
125.03
54.60
N
N
N
O
f1 (ppm)
f1 (ppm)

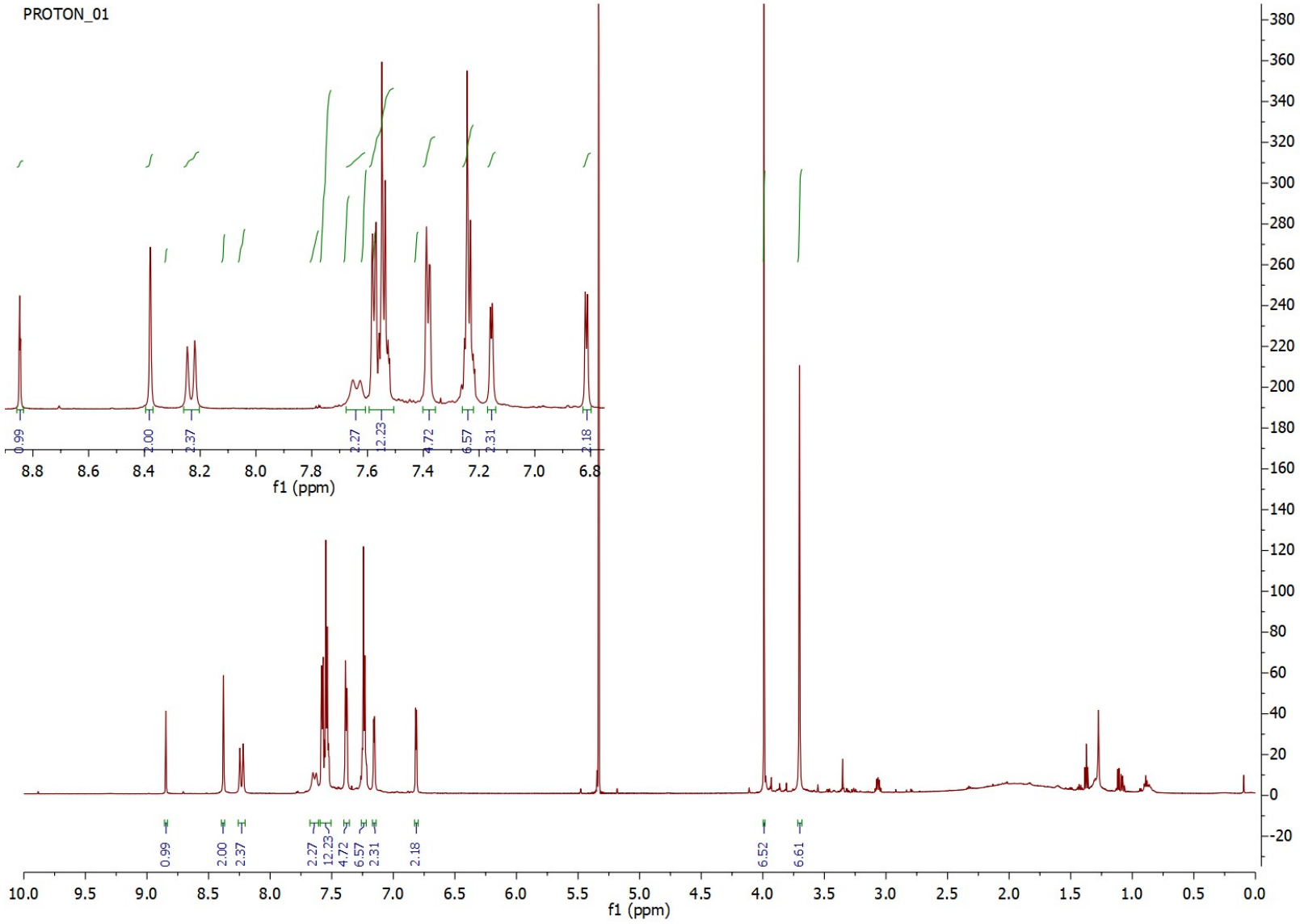
Methylimidazol BODIPY 2

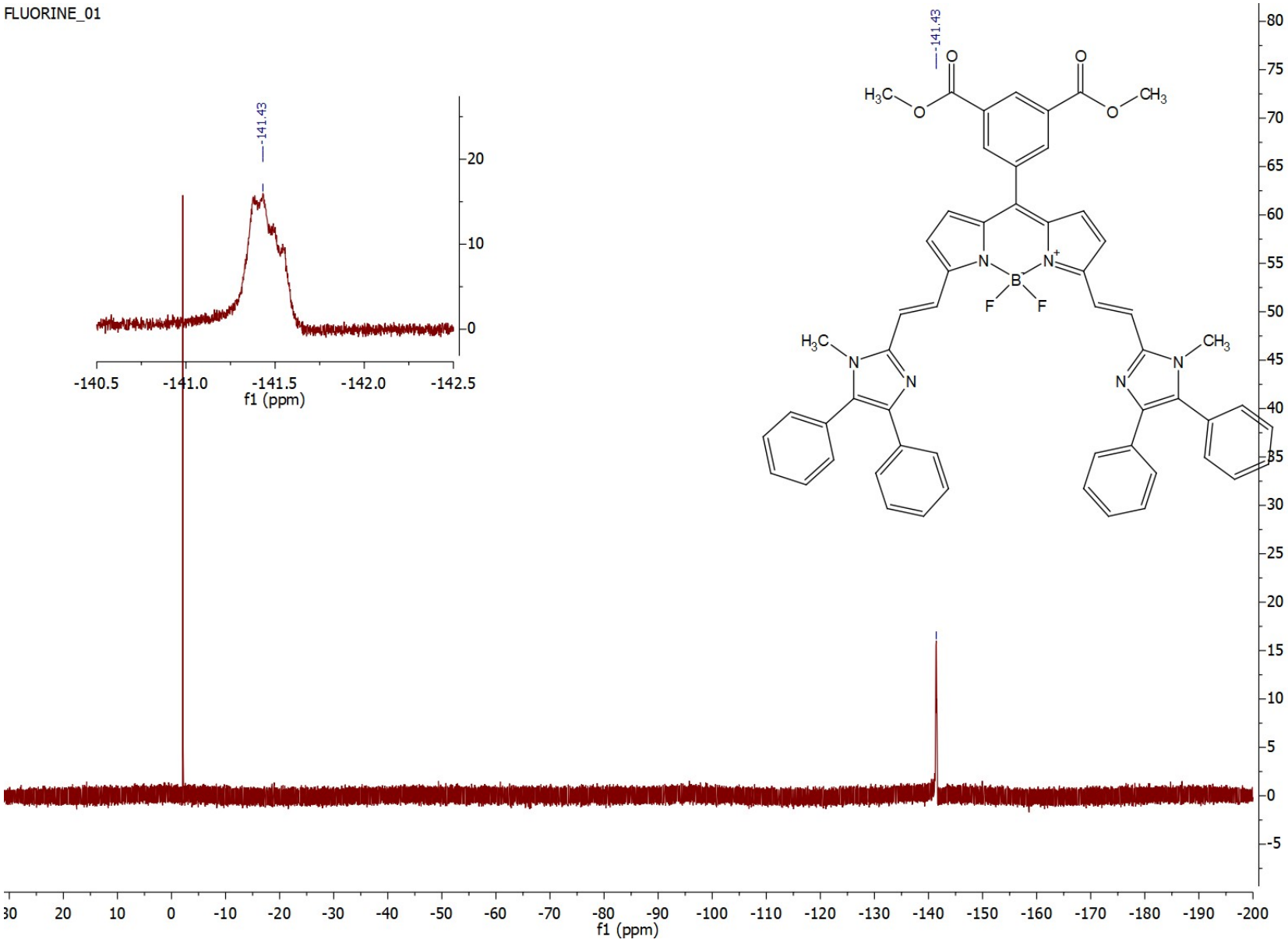


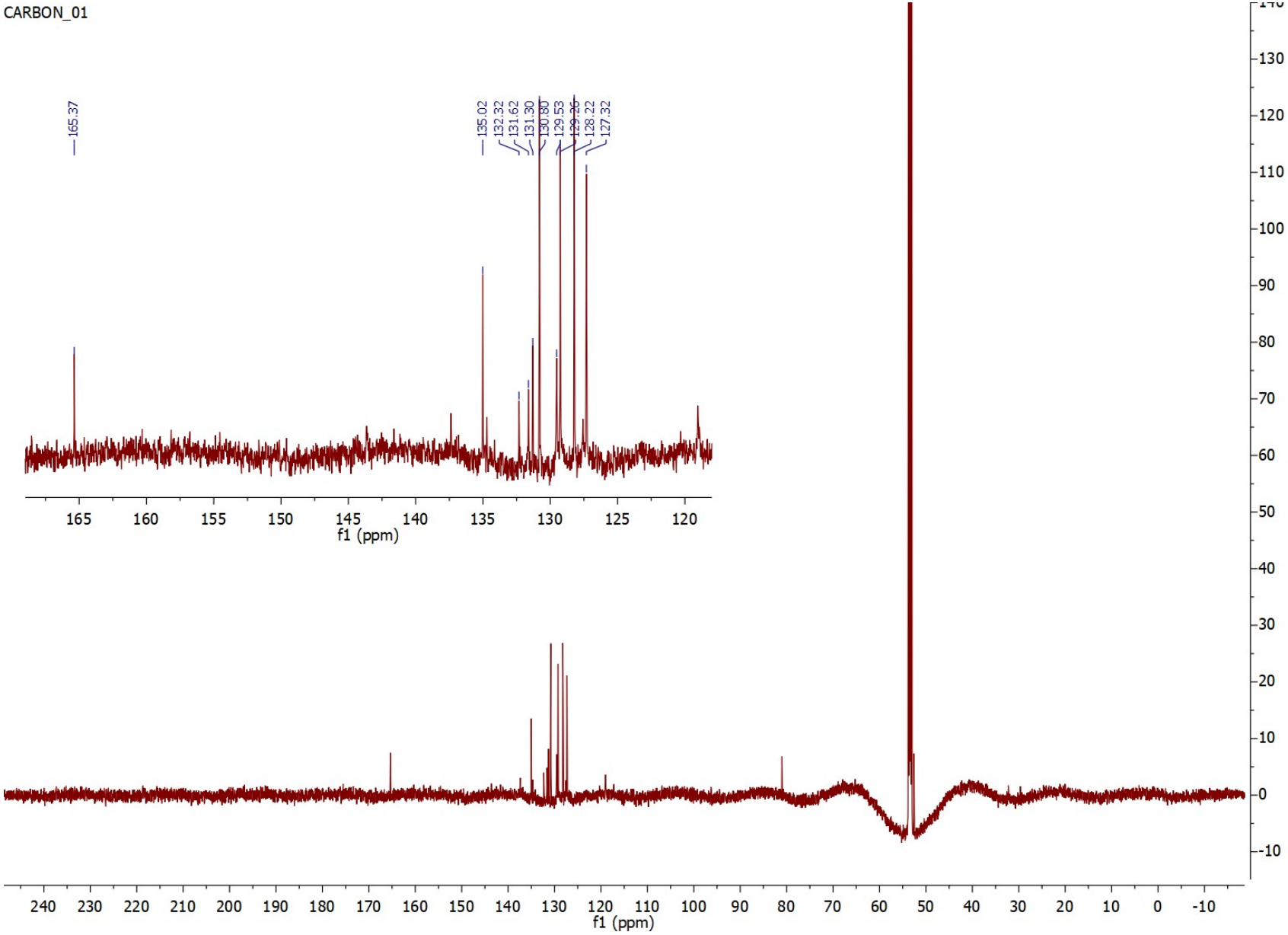

FLUORINE_01
A (dd)
-140.20
f1 (ppm)


CARBON_01
165.37
154.46
144.68
136.67
134.95
134.76
131.51
131.23
129.40
129.10
123.91
121.41
121.00
117.48
44.25
33.29
22.51
f1 (ppm)

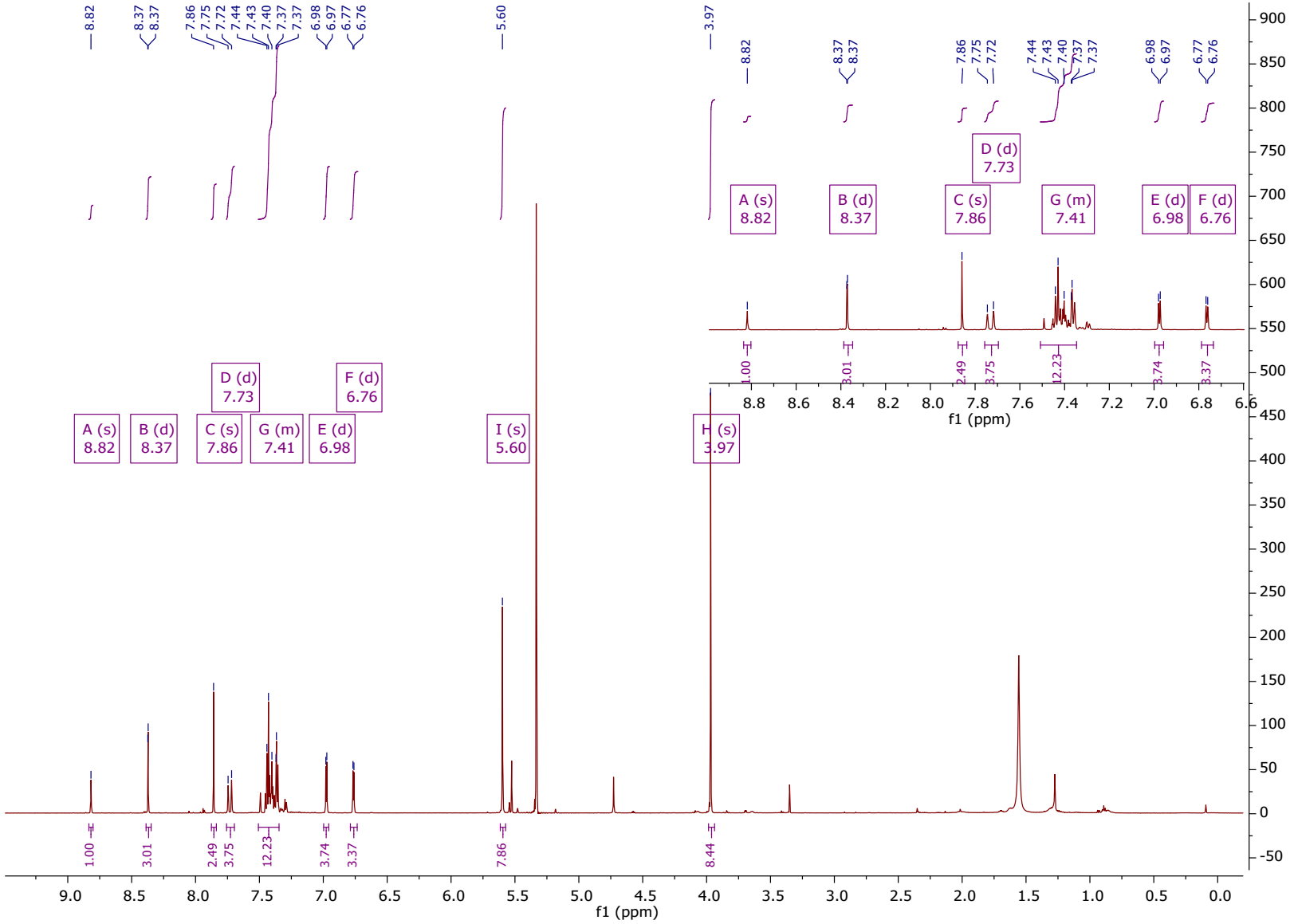
Diphenylimidazol-BODIPY 3

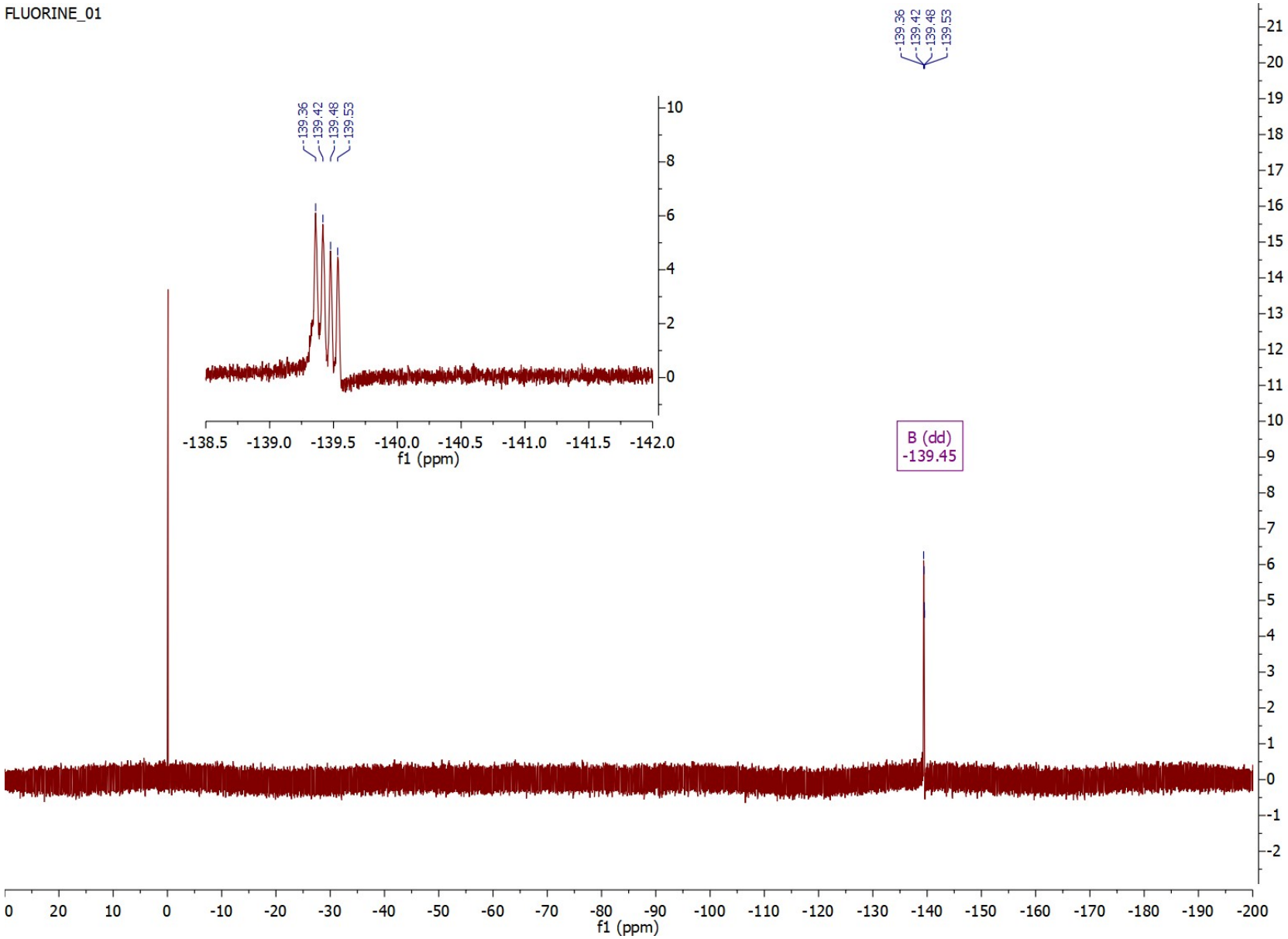


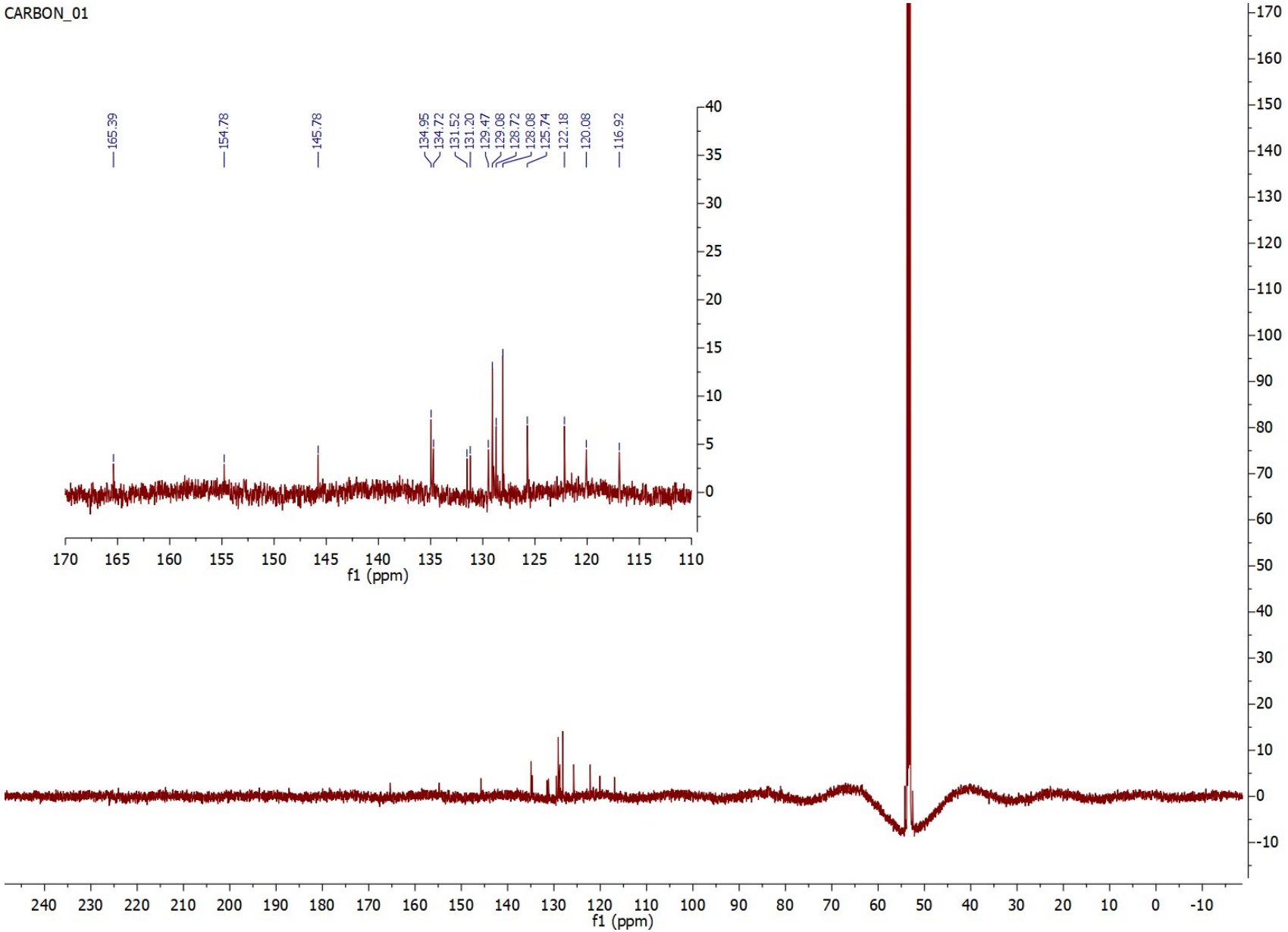

FLUORINE_01
-141.43
-140.5
-141.0
-141.5
-142.0
-142.5
f1 (ppm)
-141.43
f1 (ppm)


CARBON_01
165.37
135.02
132.32
131.62
131.30
130.80
129.53
129.26
128.22
127.32
165 160 155 150 145 140 135 130 125 120
f1 (ppm)
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

Triazol BODIPY 4




FLUORINE_01
-139.36
-139.42
-139.48
-139.53
B (dd)
-139.45
f1 (ppm)


CARBON_01
165.39
154.78
145.78
134.95
134.72
131.52
131.20
129.47
129.08
128.72
128.08
125.74
122.18
120.08
116.92
f1 (ppm)
f1 (ppm)

8. References

1. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B,* **1988**, *37*, 785.
2. A. D. Becke, *J. Chem. Phys.,* **1993**, *98*, 5648-5652.
3. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.,* **2011**, *32*, 1456-1465.
4. M. J. Frisch, J. A. Pople and J. S. Binkley, *J. Chem. Phys.*, **1984**, *80*, 3265-3269.
5. R. Krishnan, J. S. Binkley, R. Seeger and J. A. Pople, *J. Chem. Phys.,* **1980**, *72*, 650-654.
6. H. Sun, C. Zhong and J. L. Bredas, *J. Chem. Theory Comput.,* **2015**, *11*, 3851-3858.
7. H. Sun and J. Autschbach, *J. Chem. Theory Comput.* **2014**, *10*, 1035.
8. A. V. Marenich, C. J. Cramer, and D. G. Truhlar, *J. Phys. Chem. B,* **2009**, *113*, 6378-6396.
9. M. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, G. Petersson, H. Nakatsuji and et al. Gaussian 16 Rev. A.03; Gaussian Inc., Wallingford, CT, 2016.
10. J. M. Merkes, T. Lammers, R. Kancherla, M. Rueping, F. Kiessling, S. Banala, *Adv. Opt. Mater.* **2020**, *1902115*.