

Electronic Supplementary Information for

**Water-solubilised BF<sub>2</sub>-chelated tetraarylazadipyrromethenes**

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## Synthetic Procedures

### Compound 4:

Compound **3** (481 mg, 1 mmol), methyl bromoacetate (368  $\mu$ L, 4 mmol), NaI (300 mg, 2 mmol) and  $K_2CO_3$  (550 mg, 4 mmol) were placed in round bottom flask. Acetone (100 mL) was added and the reaction mixture heated under reflux for 16 hr. The solvent was removed, the residue was dissolved in  $CH_2Cl_2$ , washed with water, dried over  $Na_2SO_4$  and evaporated to dryness. Crystallization from ethyl acetate/cyclohexane gave **4** as dark solid (554 mg, 89%), m.p. 194-196  $^{\circ}C$ .  $\delta_H$  (500 MHz,  $CDCl_3$ ): 8.03 (d,  $J = 7.4$ , 4H), 7.85 (d,  $J = 8.3$ , 4H), 7.40 (t,  $J = 7.4$ , 4H), 7.34 (t,  $J = 7.1$ , 2H), 7.09 (s, 2H), 7.03 (d,  $J = 8.3$ , 4H), 4.72 (s, 4H), 3.85 (s, 6H).  $\delta_C$  (100 MHz,  $CDCl_3$ ): 169.0, 159.3, 154.1, 149.4, 142.3, 133.8, 129.0, 128.20, 128.15, 127.9, 126.1, 115.3, 114.4, 65.3, 52.4. HRMS (ESI) calcd for  $C_{38}H_{32}N_3O_6$   $[M + H]^+$ : 626.2291, found 626.2304. IR (KBr disc)  $cm^{-1}$ : 1767, 3055  $cm^{-1}$ .

### Compound 5:

Compound **4** (275 mg, 0.44 mmol) was dissolved in dry  $CH_2Cl_2$  (80 mL) DIEA was added (0.8 mL, 4.6 mmol) followed by  $BF_3 \cdot OEt_2$  (1 mL, 8.12 mmol) and the reaction mixture was stirred at r.t. for 24 hr under  $N_2$  atmosphere. The reaction mixture was washed twice with water, the organic phase separated, dried and evaporated. The residue was purified by silica gel column chromatography (eluent,  $CH_2Cl_2/AcOEt$  95:5) affording **5** as red solid (215 mg, 73%), m.p. 206-208  $^{\circ}C$ .  $\delta_H$  (500 MHz,  $CDCl_3$ ): 8.04 – 8.09 (m, 8H), 7.54 – 7.36 (m, 6H), 7.07 – 6.94 (m, 6H), 4.71 (s, 4H), 3.84 (s, 6H).  $\delta_C$  (100 MHz,  $CDCl_3$ ): 168.9, 160.0, 158.1, 145.4, 143.5, 132.4, 131.7, 129.33, 129.30, 128.6, 125.2, 118.7, 114.9, 65.2, 52.4. HRMS (ESI) calcd for  $C_{38}H_{31}BN_3O_6F_2$   $[M + H]^+$ : 674.2274, found 674.2277. IR (KBr disc): 1602, 1732, 1763  $cm^{-1}$ .

### Compound 6:

Compound **5** (248 mg, 400  $\mu$ mol) and potassium trimethylsilanolate (600 mg, 4.8 mol) were stirred in dry THF for 3h. 2N HCl (12.5 mL) was added, THF was removed under the reduced pressure and the resulting mixture was extracted with 25% isopropanol in  $CH_2Cl_2$ . Organic phase was washed with water, dried and evaporated. Subsequent preparative RP-HPLC (C-18; acetonitrile-water, 90:10; retention time: 8 min) afforded **6** as dark powder (86 mg, 34%), m. p. 214-216  $^{\circ}C$ .  $\delta_H$  (500 MHz, acetone- $d_6$ ): 8.04 – 8.09 (m, 8H), 7.54 – 7.36 (m, 6H), 7.07 –

6.94 (m, 6H), 4.71 (s, 4H), 3.84 (s, 6H).  $^{13}\text{C}$  NMR (100 MHz, acetone- $d_6$ ): 168.9, 160.71, 158.2, 145.2, 143.0, 132.4, 131.8, 129.4, 129.3, 128.6, 124.5, 119.4, 114.8, 64.5. HRMS (ESI) calcd for  $\text{C}_{36}\text{H}_{25}\text{BN}_3\text{O}_6\text{F}_2$   $[\text{M} - \text{H}^+]^+$ : 644.1804, found 644.1824. IR (KBr disc): 1023, 1035, 1266, 1472, 1503, 1604  $\text{cm}^{-1}$ .

### Compound 8:

Compound 7 (168 mg, 320  $\mu\text{mol}$ ), propane-1,3-sultone (97 mg, 800  $\mu\text{mol}$ ) and  $\text{K}_2\text{CO}_3$  (110 mg, 800  $\mu\text{mol}$ ) were heated under reflux in acetone (60 mL) for 6 hr, under a  $\text{N}_2$  atmosphere. The resulting precipitate was filtered, washed with acetone and cold methanol. Preparative RP-HPLC (C-18; acetonitrile-water, 60:40; retention time: 3 min) afforded 7 (102 mg, 41%) as a green solid m.p.  $> 300$   $^\circ\text{C}$ . For NMR analysis the compound was transformed into tetrabutylammonium salt by extraction of aqueous solution of 8 with  $\text{CHCl}_3$  in presence of tetrabutylammonium chloride. The organic phase was washed with water twice, dried and evaporated.  $\delta_{\text{H}}$  of  $\mathbf{8}\cdot(\text{NBu}_4)_2$  (500 MHz,  $\text{CDCl}_3$ ): 8.11 - 8.00 (m, 8H), 7.51 - 7.35 (m, 6H), 7.04 (s, 2H), 6.99 (d,  $J = 9.0$ , 4H), 4.25 (t,  $J = 6.4$ , 4H), 3.32 - 3.17 (m, 16H), 2.98 (t,  $J = 7.3$ , 4H), 2.42 - 2.28 (m, 4H), 1.61 (dt,  $J = 12.0$ , 7.8, 16H), 1.51 - 1.31 (m, 16H), 0.98 (t,  $J = 7.3$ , 24H).  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ): 161.7, 158.0, 145.2, 142.9, 132.5, 131.6, 129.21, 129.18, 128.5, 123.7, 118.6, 114.8, 67.4, 58.7, 48.2, 25.6, 23.9, 19.7, 13.7. HRMS (ESI) calcd for  $\text{C}_{38}\text{H}_{33}\text{BN}_3\text{O}_8\text{F}_2\text{S}_2$   $[\text{M} - \text{H}^+]^-$ : 772.1770, found 772.1757. IR (KBr disc)  $\text{cm}^{-1}$ : 1505, 1603  $\text{cm}^{-1}$ .

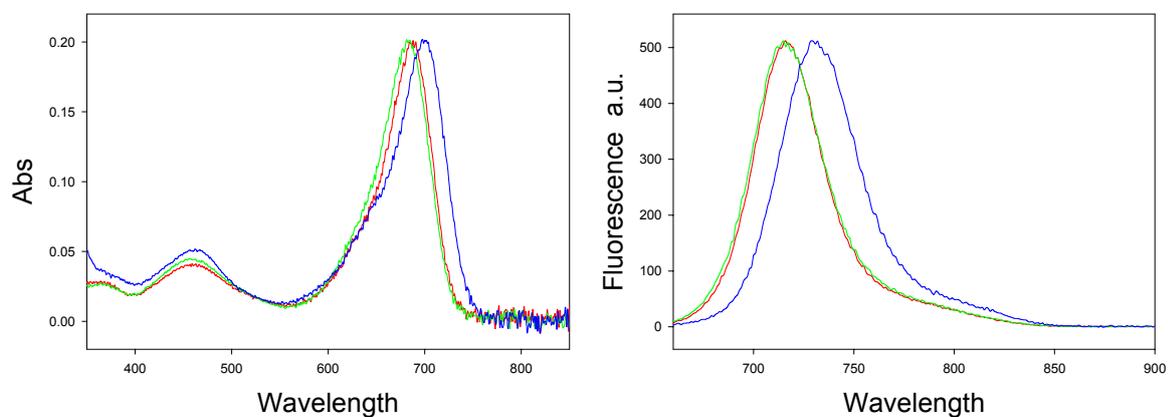
### Compound 10:

3-(4-Diethylaminomethylphenyl)-1-(4-methoxyphenyl)-4-nitrobutan-1-one 9 (7.88 g, 20.5  $\mu\text{mol}$ ), ammonium acetate (55.22 g, 0.72 mol) and ethanol (200 mL) were heated under reflux for 48 hr. The reaction was allowed to cool to room temperature, the solvent was removed and the residue partitioned between  $\text{CH}_2\text{Cl}_2$  (200 mL) and  $\text{H}_2\text{O}$  (150 mL). The aqueous layer was basified with 1 M NaOH and extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 100 mL). The organic fractions were combined and the solvent evaporated. Column chromatography on alumina with  $\text{CH}_2\text{Cl}_2$ /ethyl acetate (7:1) as eluent gave 10 as a red metallic solid (2.50 g, 36%), m.p. 172-173  $^\circ\text{C}$ .  $\delta_{\text{H}}$  (300 MHz,  $\text{CDCl}_3$ ): 8.01 (d,  $J = 8.2$  Hz, 4H), 7.87 (d,  $J = 8.8$  Hz, 4H), 7.38 (d,  $J = 8.2$  Hz, 4H), 7.10 (s, 2H), 7.03 (d,  $J = 8.8$  Hz, 4H), 3.90 (s, 6H), 3.64 (s, 4H), 2.58 (q,  $J = 7.2$  Hz, 8H), 1.10 (t,  $J = 7.2$  Hz, 12H), NH not observed.  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ): 161.4, 154.4, 149.6, 142.3, 139.8, 132.7, 129.2, 129.0, 128.3, 125.3, 114.8, 114.1, 57.7, 55.7, 47.0, 12.1. ES-MS:  $m/z$  680  $[\text{M} + \text{H}^+]^+$ . HRMS (ESI) calcd for  $\text{C}_{44}\text{H}_{50}\text{N}_5\text{O}_2$   $[\text{M} + \text{H}^+]^+$ : 680.3965, found 680.3967. IR (KBr disk): 3455, 3421, 1606  $\text{cm}^{-1}$ .

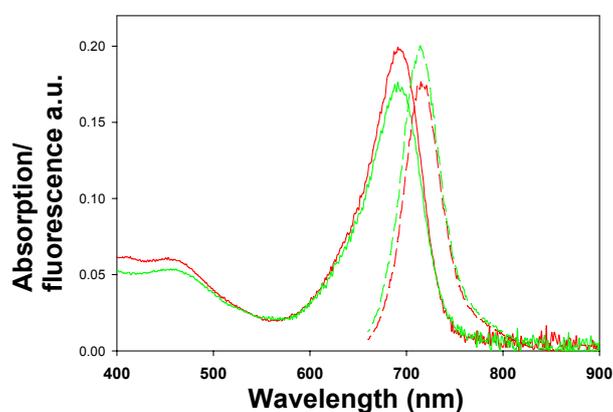
**Compound 11:**

Compound **10** (0.45 g, 0.66 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (80 mL) under N<sub>2</sub>, treated with diisopropylethylamine (0.86 g, 6.6 mmol) and BF<sub>3</sub>·Et<sub>2</sub>O (1.32 g, 9.3 mmol) and stirred at room temperature for 24 hr. The resultant green solution was washed with water (3 x 50 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The crude material was columned on alumina eluting with CH<sub>2</sub>Cl<sub>2</sub>/ethylacetate (8:1) to give **11** as a metallic red solid (0.35 g, 72%), m.p. 198-200 °C. δ<sub>H</sub> (500 MHz CDCl<sub>3</sub>): 8.09-8.11 (m, 4H), 8.05 (d, *J* = 8.1 Hz, 4H), 7.46 (d, *J* = 8.1 Hz, 4H), 7.01-7.04 (m, 6H), 3.90 (s, 6H), 3.68 (s, 4H), 2.61 (q, *J* = 7.2 Hz, 8H), 1.12 (t, *J* = 7.2 Hz, 12H). δ<sub>C</sub> (125 MHz CDCl<sub>3</sub>): 162.1, 158.3, 145.6, 143.4, 141.6, 131.8, 131.3, 129.3, 129.3, 124.5, 118.5, 114.5, 57.6, 55.7, 47.1, 12.0. ESI-MS: *m/z* 728 [M+H]<sup>+</sup>. HRMS calcd for C<sub>44</sub>H<sub>49</sub>BF<sub>2</sub>N<sub>5</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 728.3947, found: 728.3936. IR (KBr disk): 3419, 2966, 1602 cm<sup>-1</sup>. λ<sub>max</sub> abs (CHCl<sub>3</sub>): 691 nm (ε = 76,000 Lmol<sup>-1</sup> cm<sup>-1</sup>).

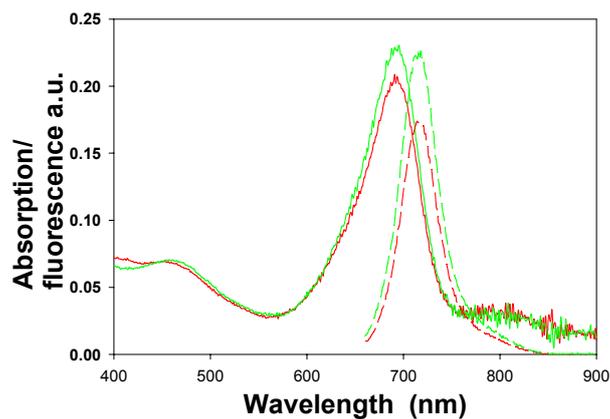
## Spectroscopic properties of 6, 8 and 12.



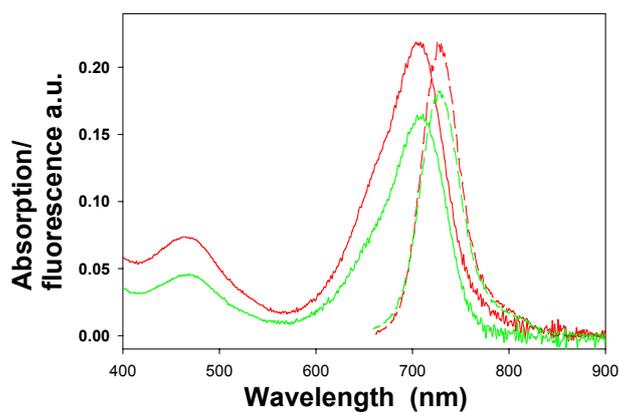
**Fig 1.** The absorption (left) and fluorescence (right) of **6** (green line), **8** (red line), and **12** (blue line) in methanol. Fluorescence spectra were taken after excitation at 640 nm.



**Fig 2.** The stability of **6** in PBS (pH = 7.0) containing 3% of BSA. Spectra were taken after 24 hr (red line) and 48 hr (green line) exposure to the sun light. Solid and dashed lines represent relative absorption and fluorescence respectively.



**Fig 3.** The stability of **8** in PBS (pH = 7.0) containing 3% of BSA. Spectra were taken after 24 hr (red line) and 48 hr (green line) exposure to the sun light. Solid and dashed lines represent relative absorption and fluorescence respectively.



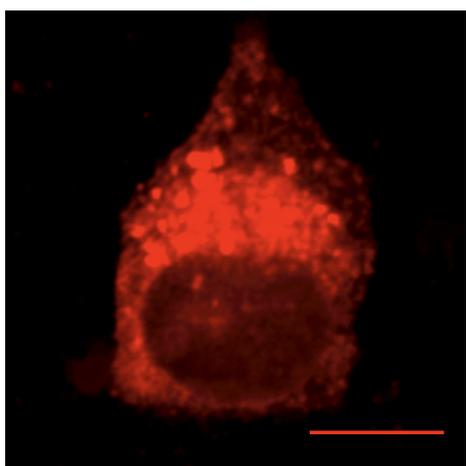
**Fig 4.** The stability of **12** in PBS (pH = 7.0) containing 3% of BSA. Spectra were taken after 24 hr (red line) and 48 hr (green line) exposure to the sun light. Solid and dashed lines represent relative absorption and fluorescence respectively.

### MDA-MB-231 Cell and bacteria incubation conditions

MDA-MB-231 cells were seeded into a 8 well chambered microscopy slide and they were grown overnight in DMEM media at 37 °C in the presence of 5% CO<sub>2</sub>. The media was then removed and **6** and **8** (5 µM) was added, followed by an incubation period of 1 hour in the dark. Cells were then washed with PBS to remove excess compound. Prior to visualization, cells were fixed in 3.7% formaldehyde solution, co-stained with DAPI and a coverslip was mounted onto the microscopy slide. In a similar way, *E. coli* cells were incubated with **12** (4 µM) in the dark for 10 minutes. The bacterial cells were washed with PBS and An aliquot of this solution was suspended onto a microscopy slide and allowed to dry. Before imaging, a coverslip was mounted onto the microscopy slide.

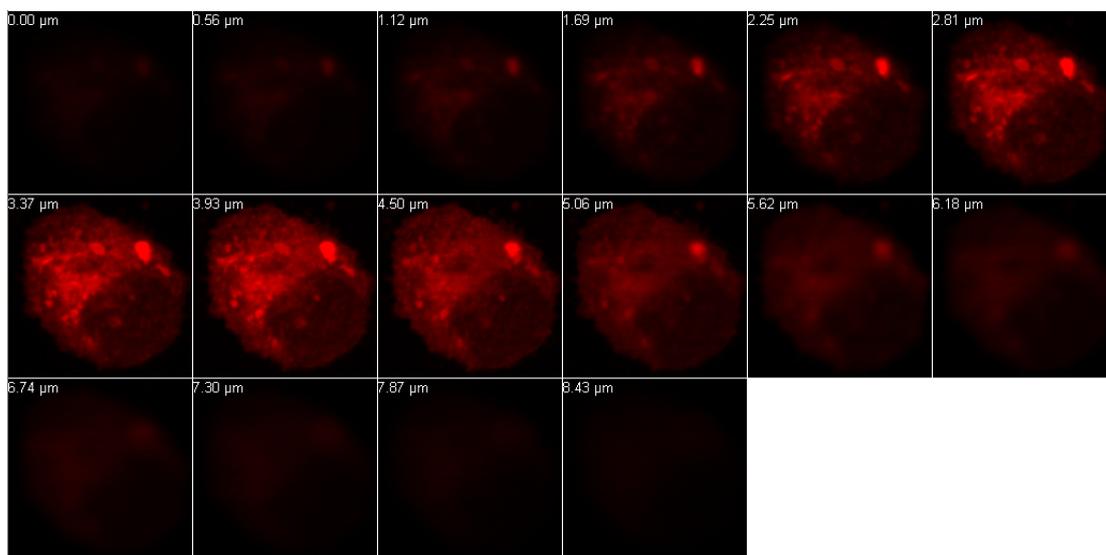
Images were obtained using an LSM510 META confocal laser scanning microscope equipped with 63× numerical aperture 1.4 objective. DAPI was excited at 364 nm and detected with a band-pass filter 385-470 nm, whilst **6**, **8** and **12** were excited at 633 nm and their fluorescence was detected through a 650 nm long-pass filter.

### Individual MDA-MB-231 cell following incubation with **6**

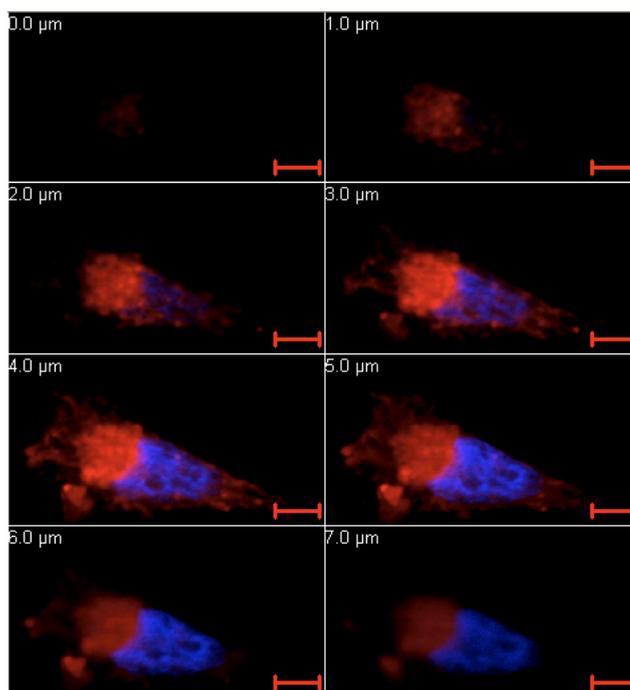


Scale bar 10 µm

### CLSM Z-Stack Analysis of 6 in MDA-MB-231 cells

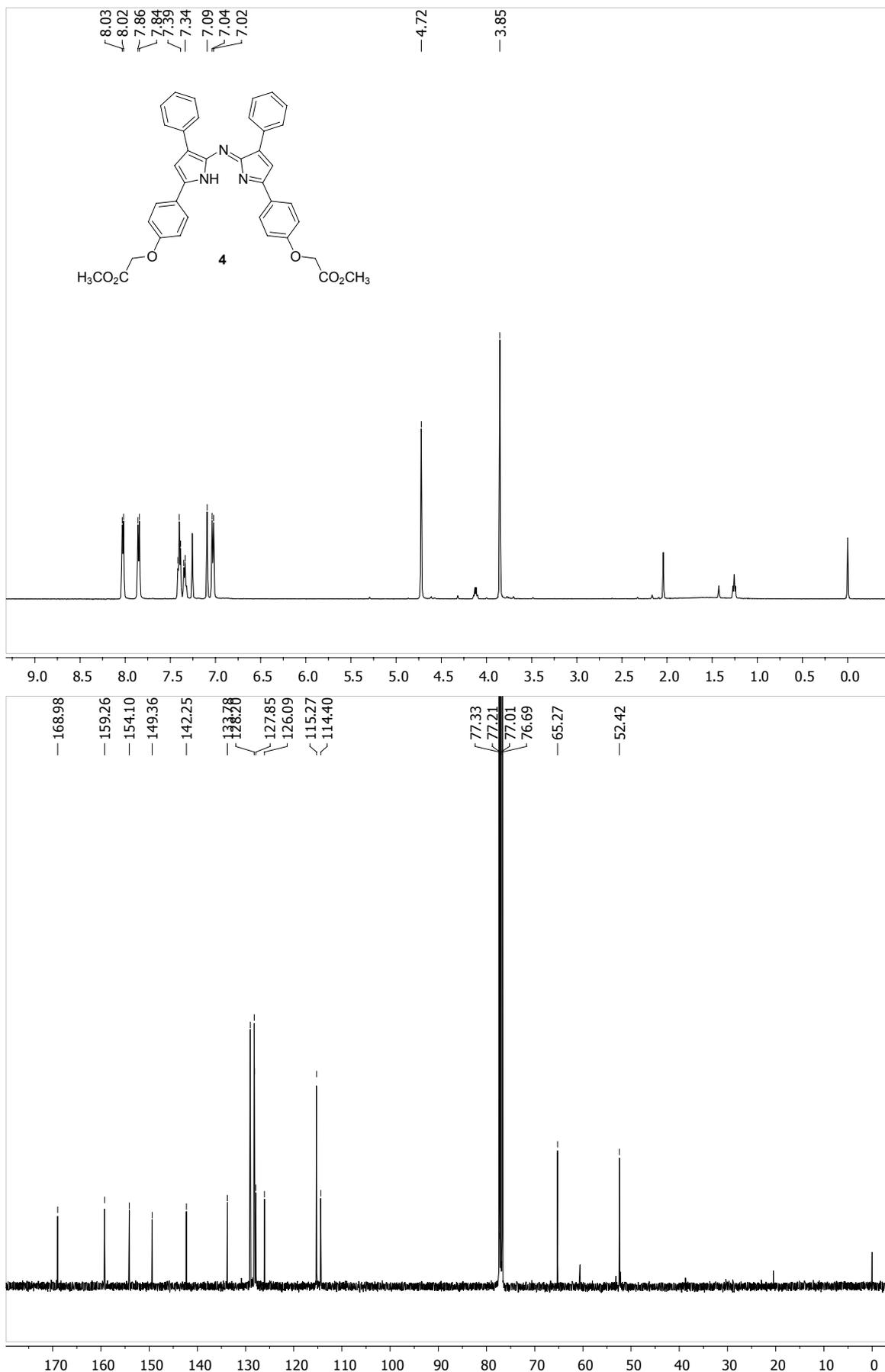


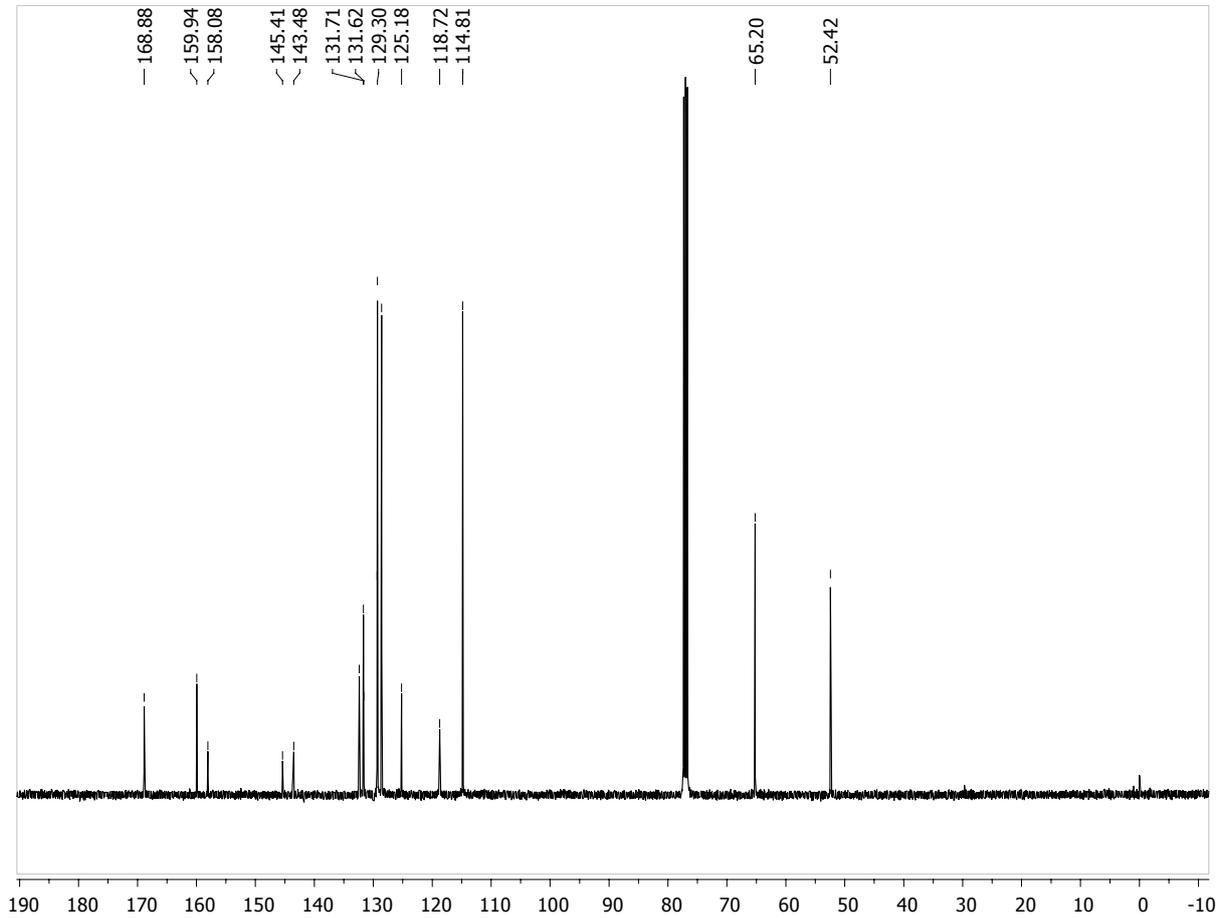
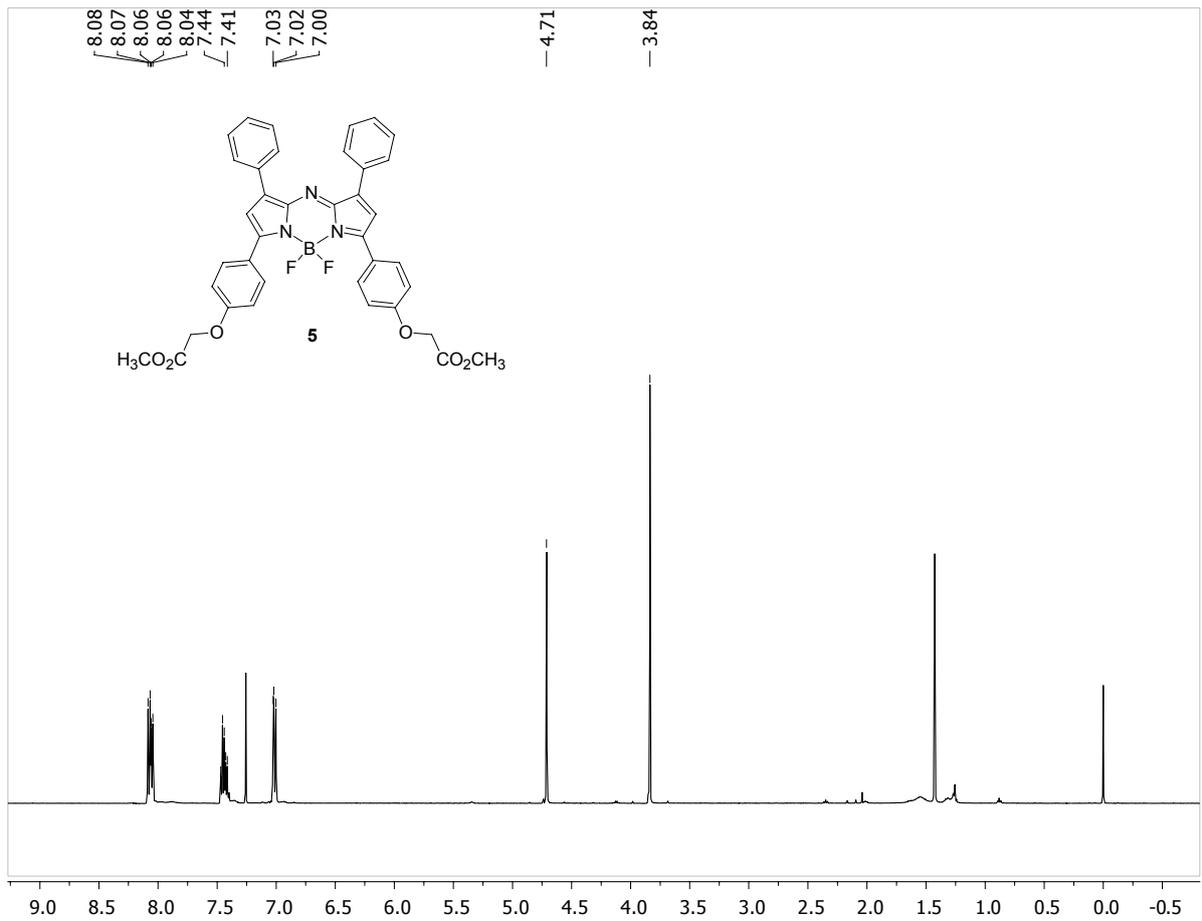
### CLSM Z-Stack Analysis of 8 in MDA cells and nuclear co-staining with DAPI (blue colour)

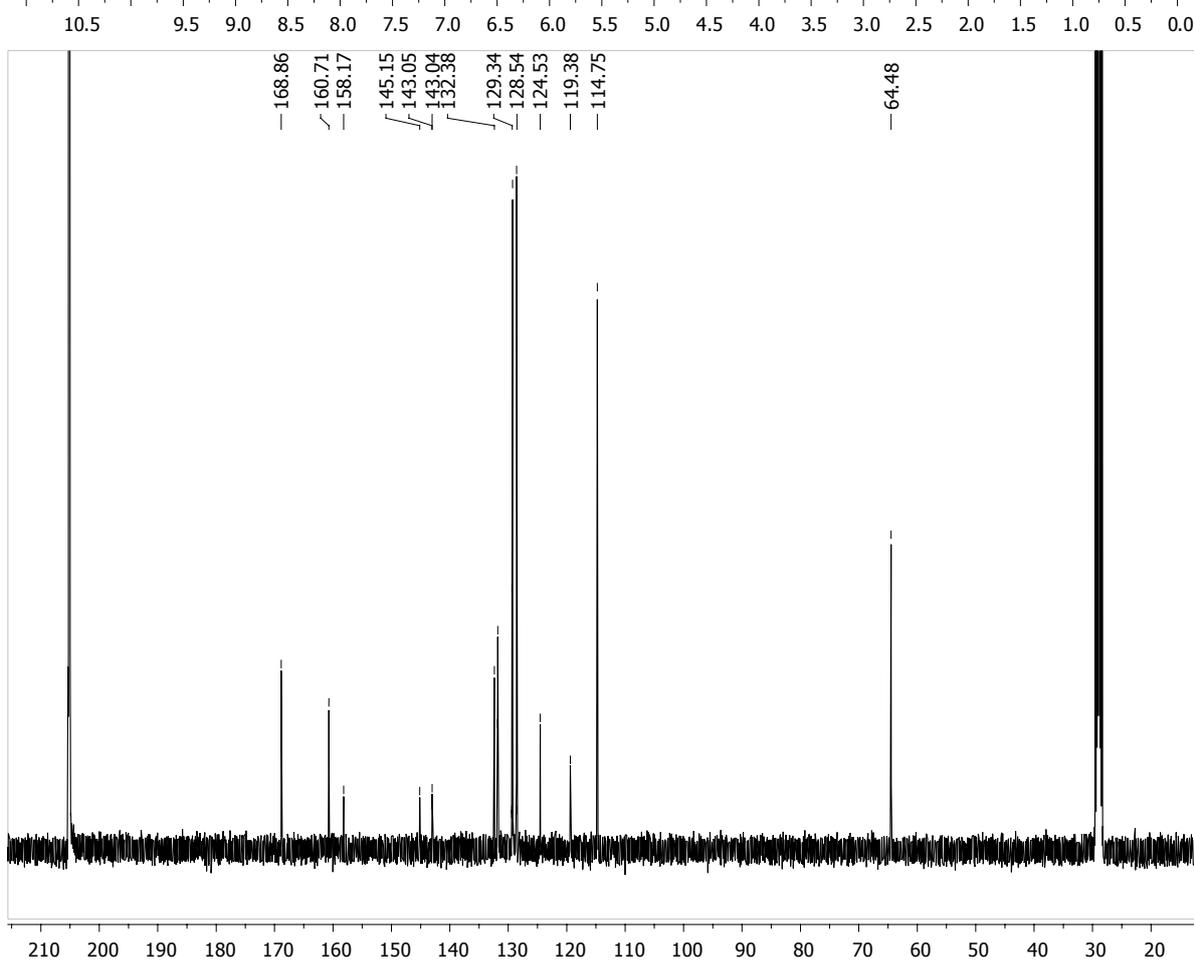
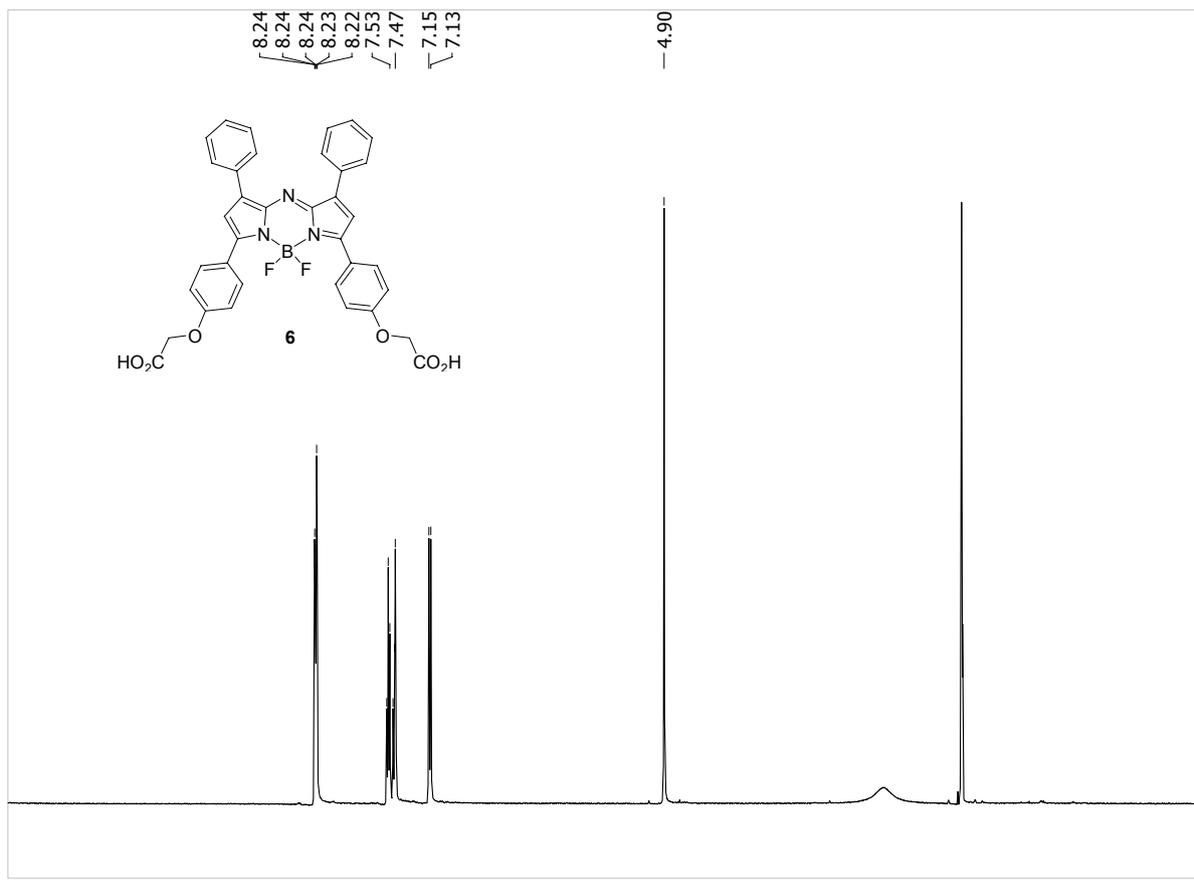


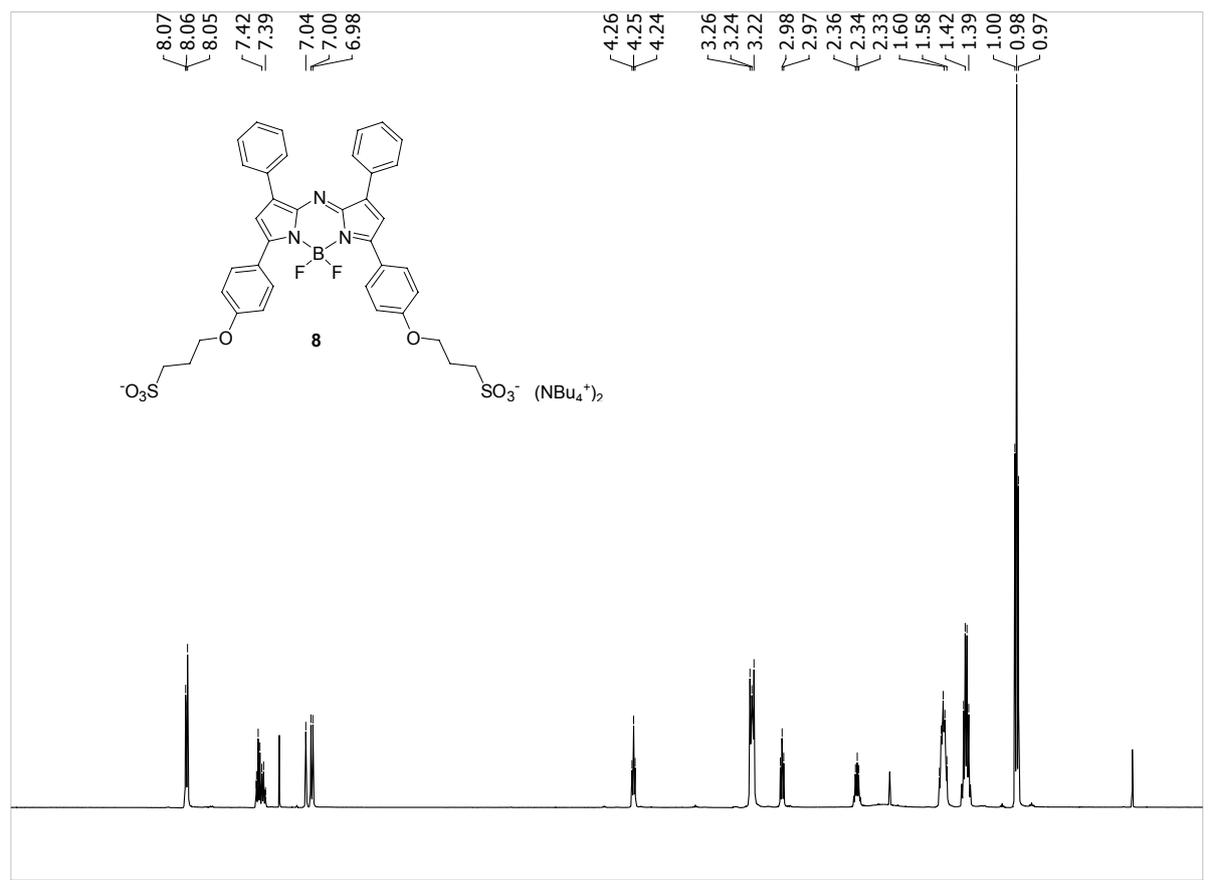
scale bar 5μm

# NMR spectra

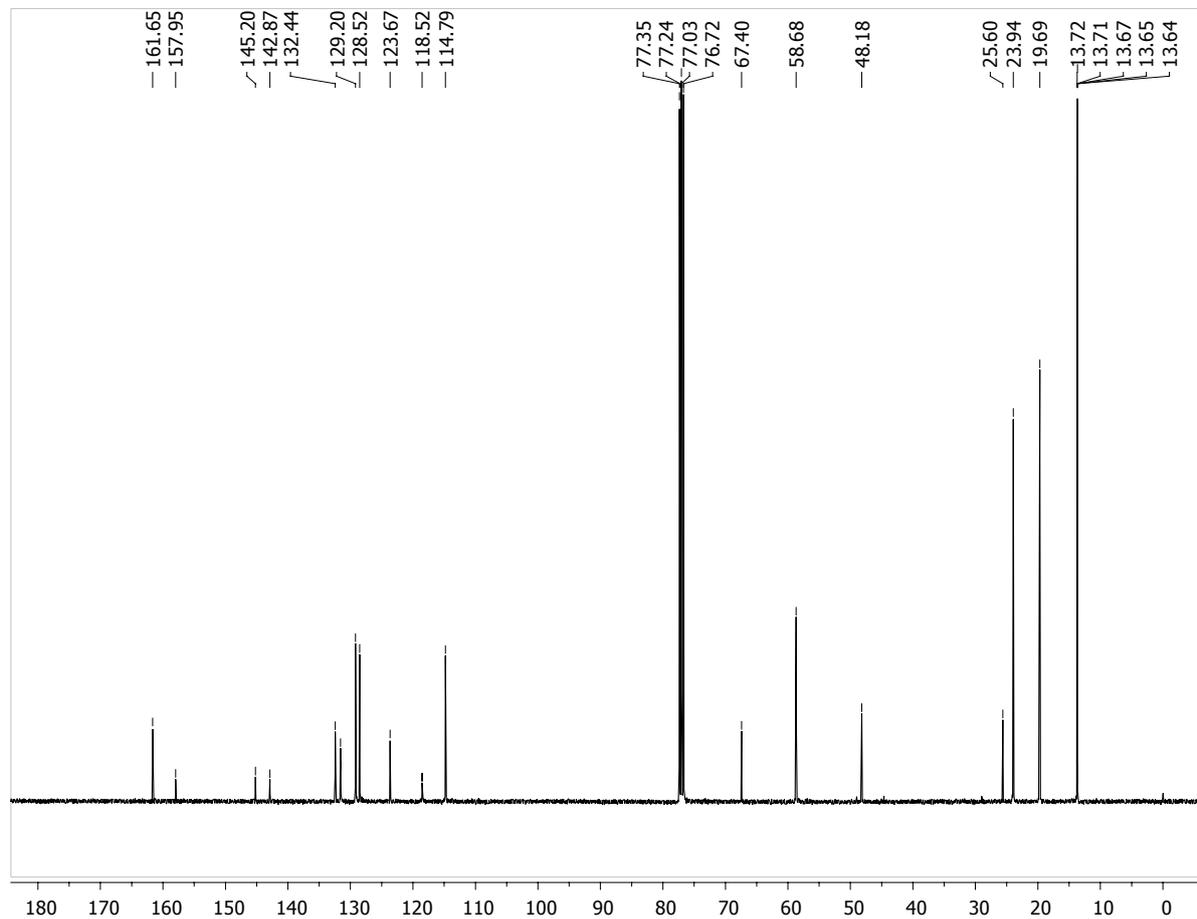








9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5



180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

