

## Supporting Information

### Photo-Labile BODIPY Protecting Groups for Glycan Synthesis

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# 1 General Information

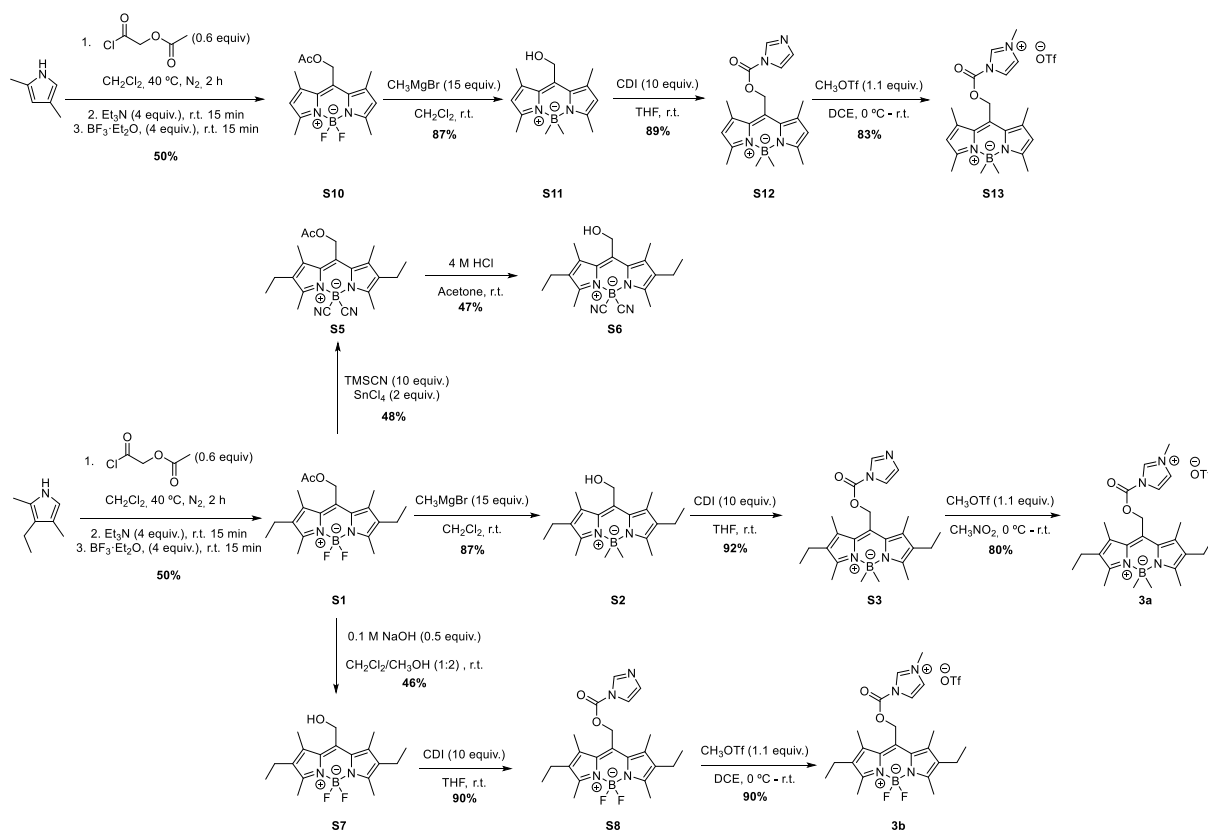
All **chemicals** were reagent grade and used as supplied unless otherwise noted. All **solvents** for chemical reactions were commercially purchased in p.a. quality. If stated, they were dried in a Solvent Dispensing System (J.C. Meyer). For HPLC and MS spectrometry, solvents with corresponding quality were used. Water was used from a Milli Q-station from Millipore.

Reaction completion, identity, and purity of all compounds were determined by low resolution mass spectrometry (**ESI-LRMS**) or analytical thin-layer chromatography (**TLC**). TLC was performed on Merck silica gel 60 F<sub>254</sub> plates (0.25 mm). Compounds were visualized by UV irradiation (254 nm) or stained (5% sulfuric acid in ethanol or Hanessian's Stain: 235 mL of distilled water, 12 g of ammonium molybdate, 0.5 g of ceric ammonium molybdate, and 15 mL sulfuric acid). **Flash column chromatography** was performed on Kieselgel 60 with 230-400 mesh (Sigma-Aldrich, St. Louis, USA and Merck 60). Analysis and purification by normal and reverse phase **HPLC** and ESI-LRMS was performed by using an Agilent 1200 series. <sup>1</sup>H, <sup>13</sup>C, COSY and HSQC **NMR spectra** were recorded in parts per million ( $\delta$ ) relative to the resonance of the solvent on a Varian 400-MR (400 MHz), Varian 600-MR (600 MHz), or Bruker Biospin AVANCE700 (700 MHz) spectrometer. Assignments were supported by COSY and HSQC experiments. High resolution mass spectra (**HRMS**) were obtained using 6210 or 6540 ESI-TOF mass spectrometer (Agilent). For photolysis, a 500 W halogen lamp or green LED lamp (525 nm) from Kessil Lightning were used.

## 2 Compound Preparation and Analytical Data

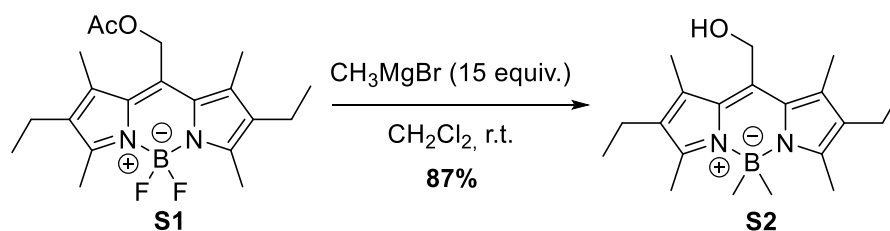
### 2.1 BODIPY Precursors

#### Synthesis scheme



Compounds **S1** & **S7**<sup>i</sup>, **S5**<sup>ii</sup>, **S10**<sup>iii</sup>, **S11**<sup>iv</sup> were synthesized according to the procedures described previously. All spectra for these compounds matched those previously reported.

## Synthesis of S2



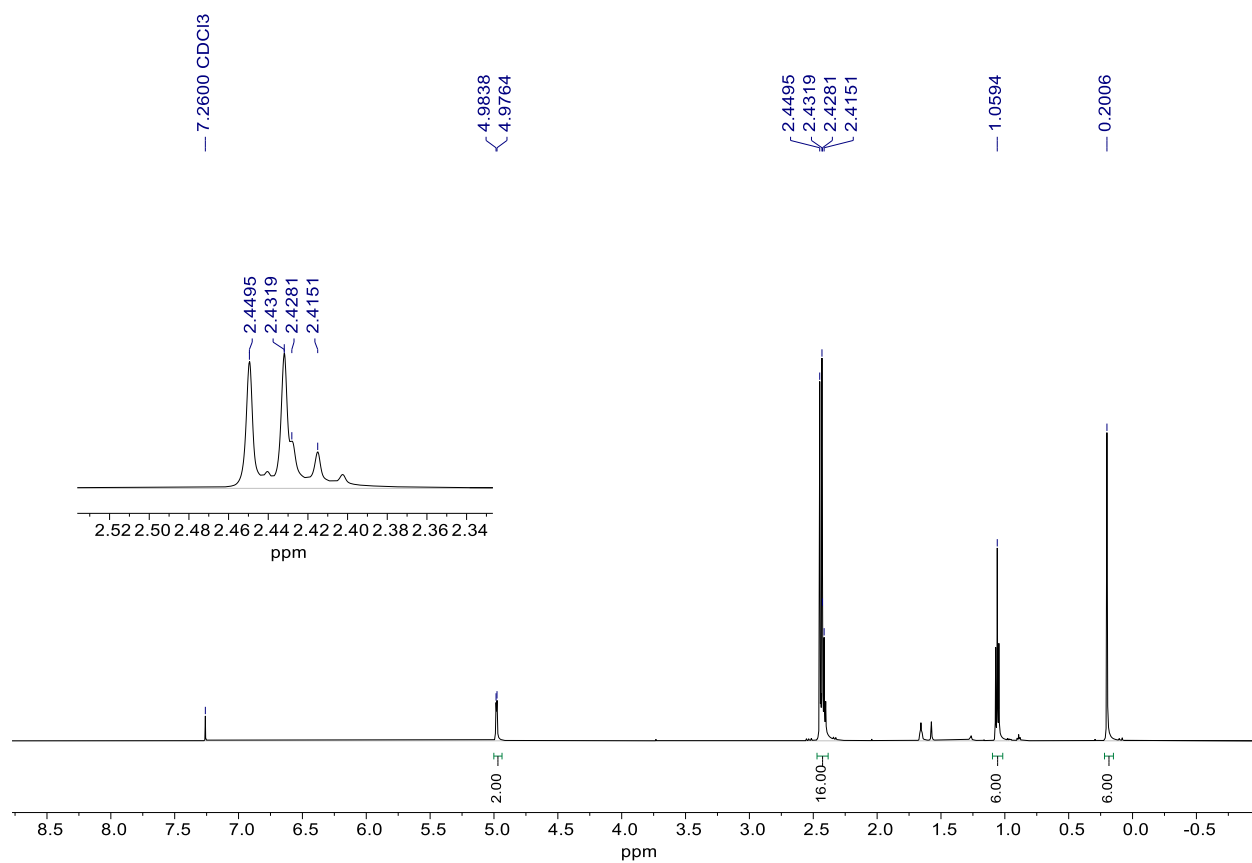
To a solution of **S1** (0.55 g, 1.5 mmol, 1 equiv.) in anhydrous dichloromethane (50 mL), 3 M methyl magnesium bromide (3.0 mL, 9 mmol, 4 equiv.) was added under a  $\text{N}_2$  atmosphere and the reaction was stirred until the starting material was consumed. Reaction was then quenched with ammonium chloride. Organic layer was washed with ammonium chloride and brine followed by drying over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the solid residue was purified with flash column chromatography (10% - 20% ethyl acetate in hexane).

$^1\text{H NMR}$  (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.98 (s, 1H), 4.98 (s, 1H), 2.45 (s, 6H), 2.43 (s, 6H), 2.41 (q,  $J = 7.5$  Hz, 4H), 1.06 (t,  $J = 7.6$  Hz, 6H), 0.20 (s, 6H) ppm.

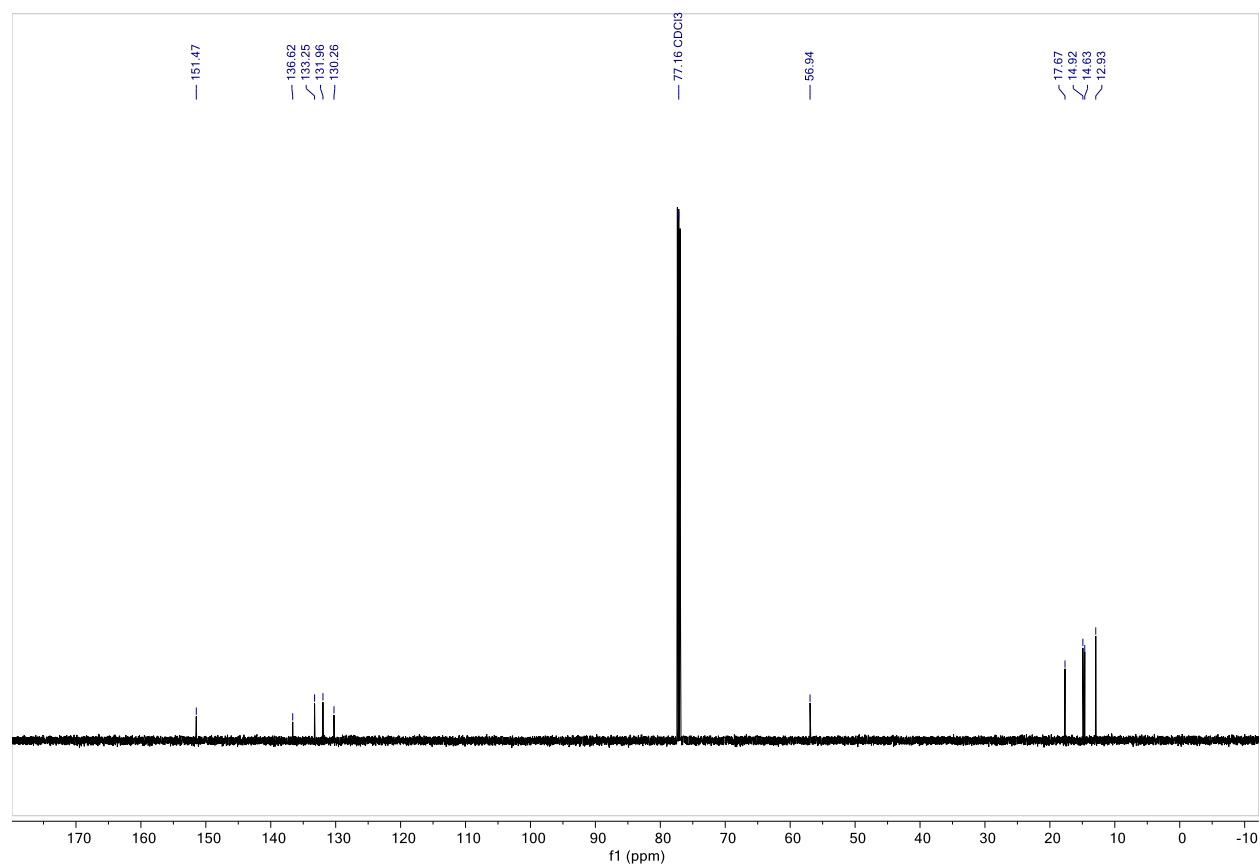
$^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.5, 136.6, 133.3, 132.0, 130.3, 57.0, 17.7, 14.9, 14.6, 12.9 ppm.

**HRMS/ESI<sup>+</sup>** For compound **S2**  $[\text{M}+\text{H}]^+$ , 327.2607 was calculated and 327.2601 was found.

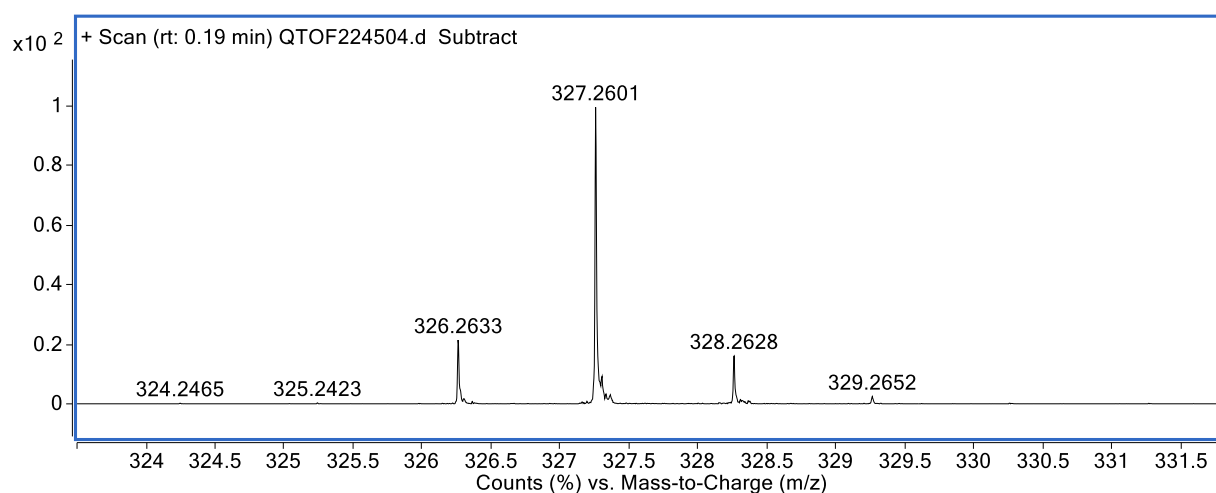
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **S2**:



$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **S2**:



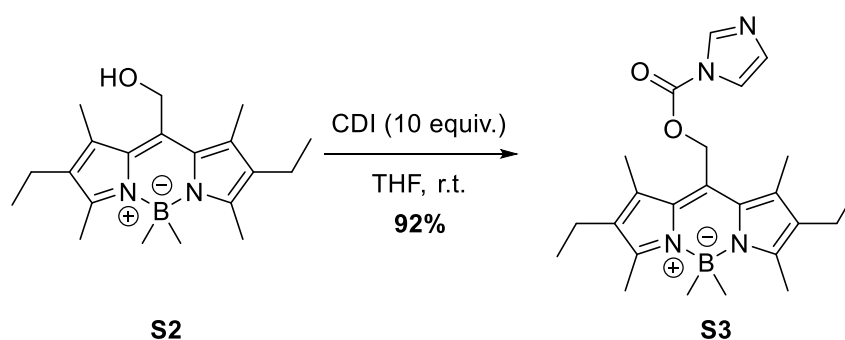
## HRMS/ESI<sup>+</sup> For compound **S2**:



## General procedure for the synthesis of **S3**, **S8**, **S12**

Carbonyldiimidazole (CDI) (10 equiv.) was added to a solution either of **S2**, **S7** or **S11** (1 equiv.) in anhydrous THF (20 mL) followed by stirring at room temperature until the starting material was consumed. Reaction was then diluted with dichloromethane and washed three times with water and three times with brine, respectively. After drying the organic layer over anhydrous sodium sulfate, solvent was removed under reduced pressure. Solid residue was then purified with flash column chromatography (hexane/ethyl acetate).

## Synthesis of **S3**



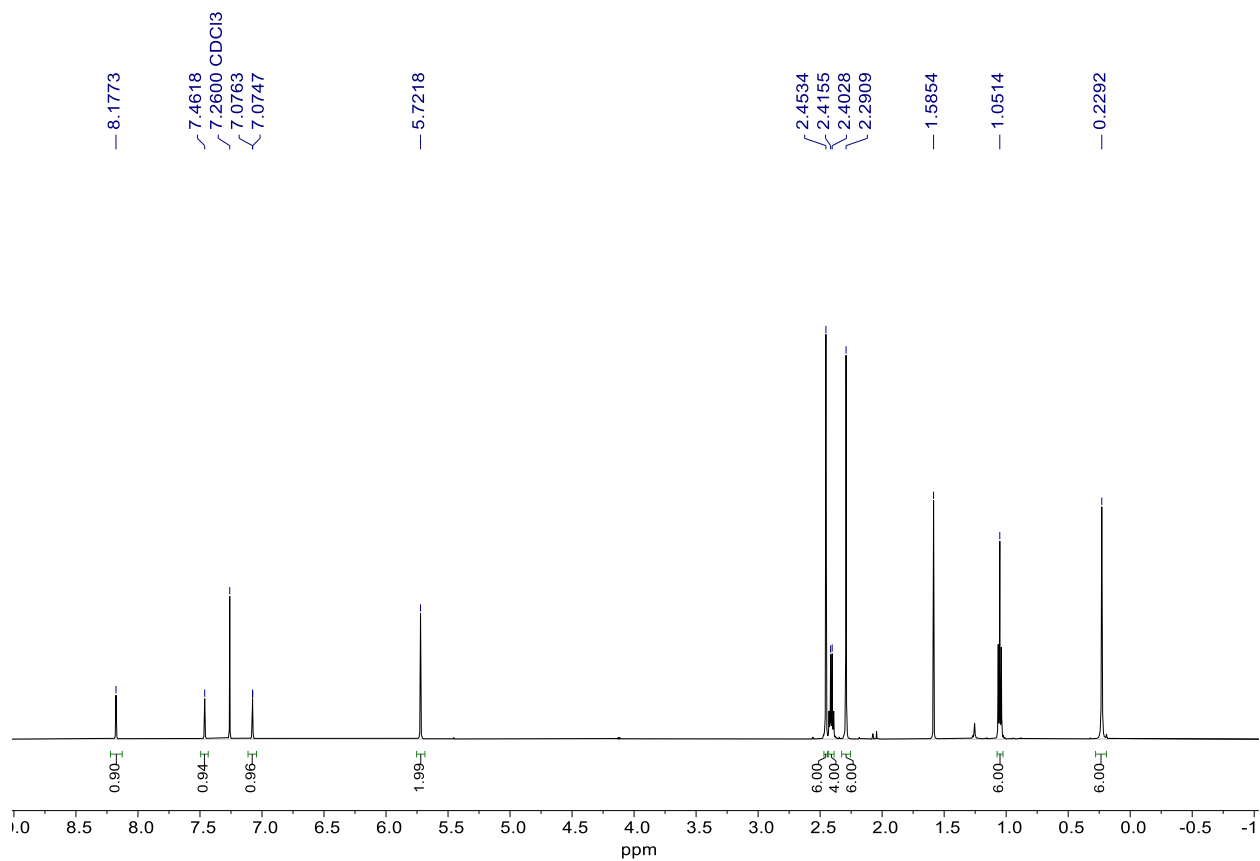
To a solution of **S2** (0.42 g, 1.3 mmol, 1 equiv.), CDI (2.10 g, 13 mmol, 10 equiv.) was added and stirred at room temperature for one hour. Product was purified via flash column chromatography with 30% ethyl acetate in hexane as the eluent. Compound **S3** was obtained as a bright orange solid (0.50 g, 92%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.18 (s, 1H), 7.46 (s, 1H), 7.08 (d, *J* = 0.9 Hz, 1H), 5.72 (s, 2H), 2.45 (s, 6H), 2.41 (q, *J* = 7.6 Hz, 4H), 2.29 (s, 6H), 1.05 (t, *J* = 7.6 Hz, 6H), 0.23 (s, 6H) ppm.

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.7, 148.7, 137.4, 134.0, 131.7, 131.1, 131.0, 128.8, 117.4, 62.7, 17.6, 14.9, 14.8, 13.0 ppm.

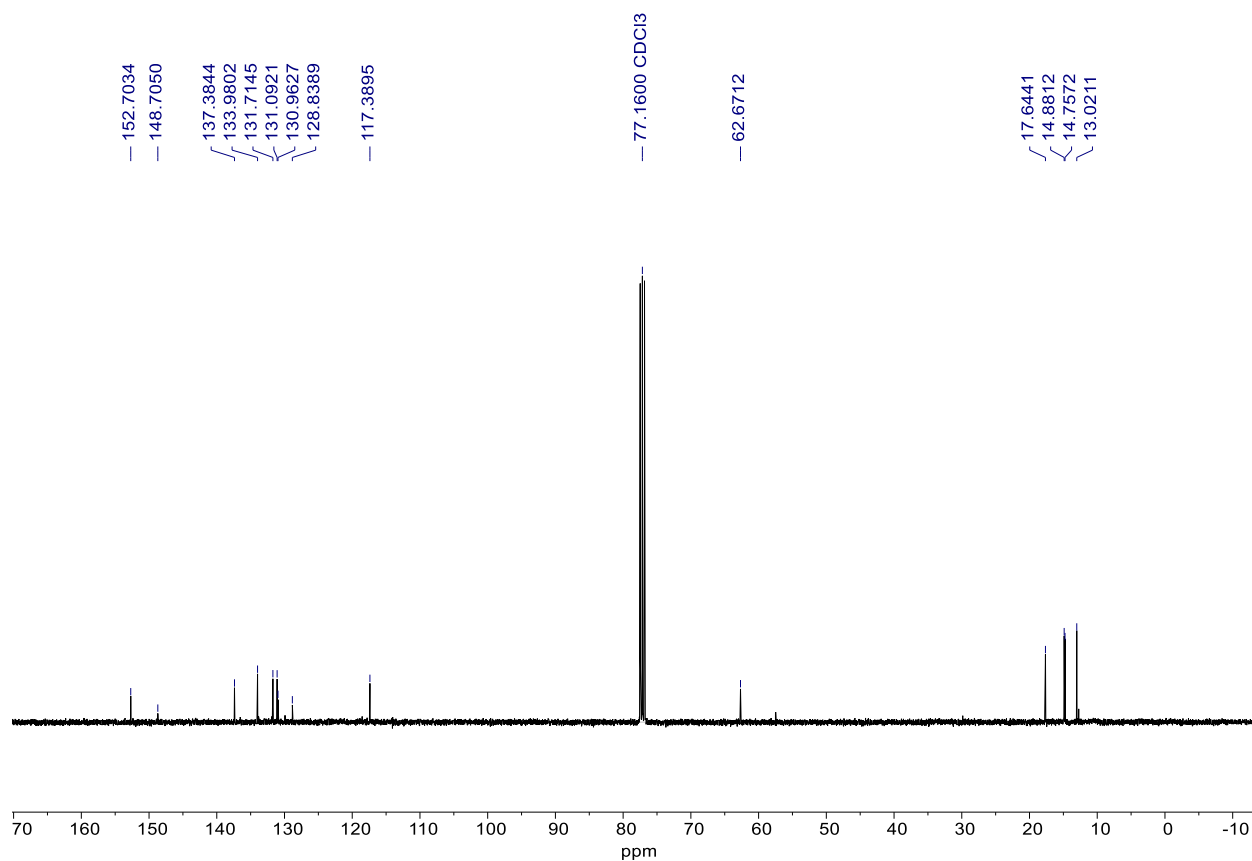
HRMS/ESI<sup>+</sup> For compound **S3**  $[\text{M}+\text{H}]^+$  421.2775 was calculated and 421.2770 was found

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **S3**:

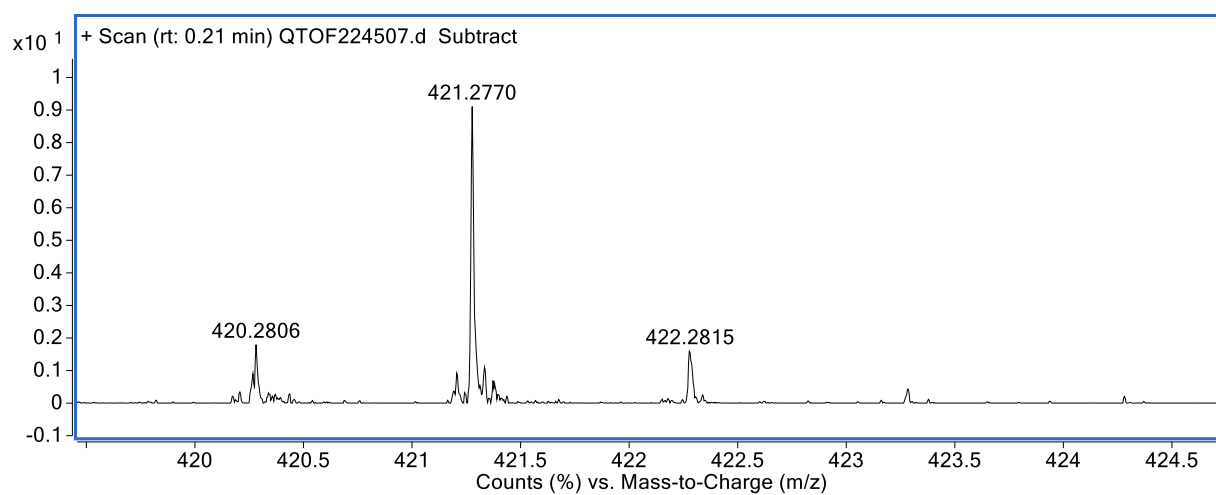




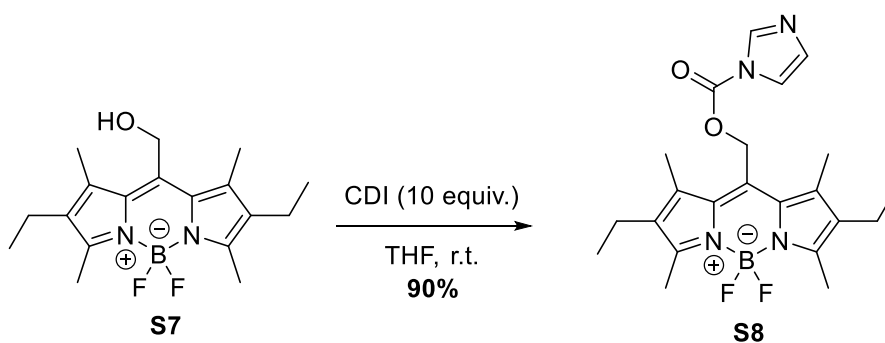
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **S3**:



HRMS/ESI<sup>+</sup> of **S3**:



## Synthesis of **S8**



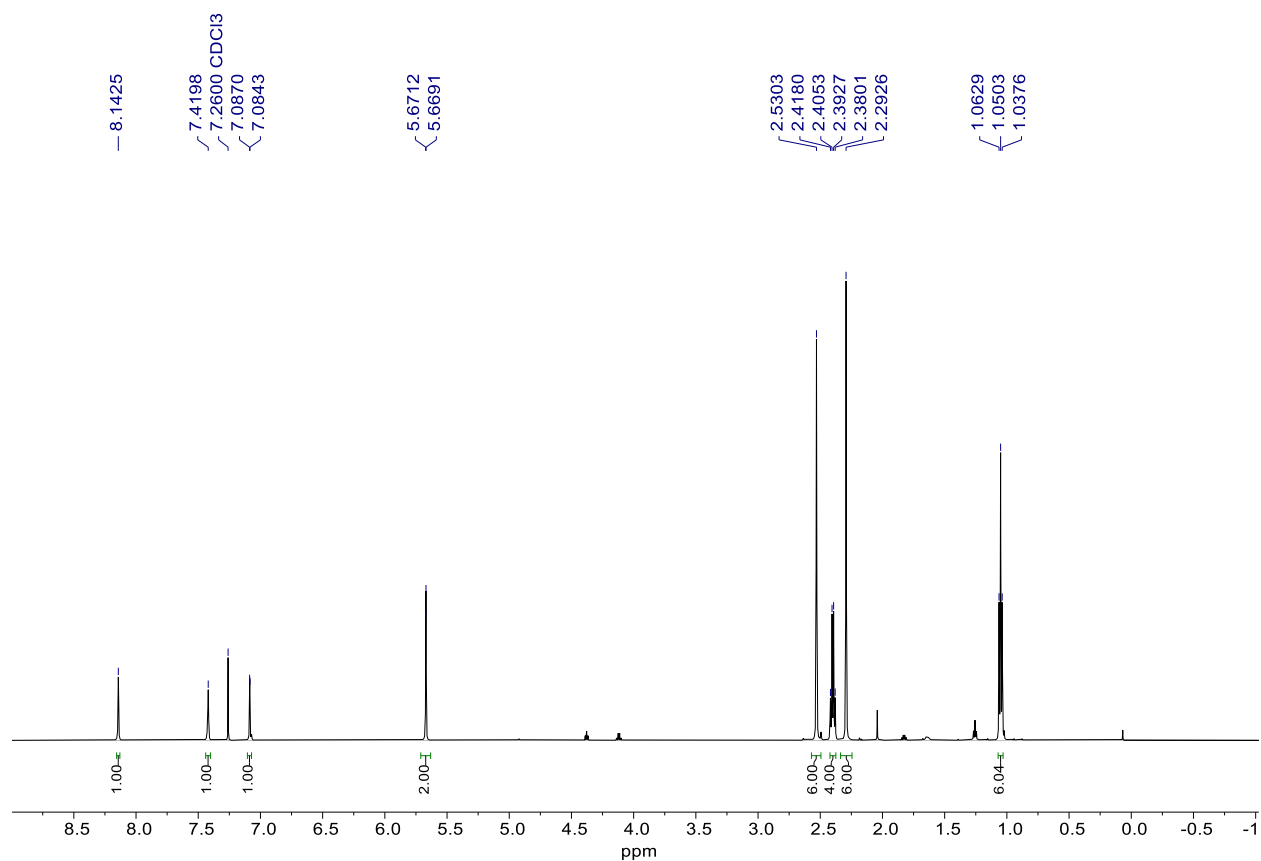
To a solution of **S7** (0.20 g, 0.6 mmol, 1 equiv.), CDI (0.10 g, 6 mmol, 10 equiv.) was added and stirred at room temperature for one hour. Product was purified via flash column chromatography with 20% - 50% ethyl acetate in hexane as the eluent. Compound **S8** was obtained as a red solid (0.105 g, 90%).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):** δ 8.14 (s, 1H), 7.42 (s, 1H), 7.09 (d, *J* = 1.6 Hz, 1H), 5.67 (d, *J* = 1.3 Hz, 2H), 2.53 (s, 6H), 2.40 (q, *J* = 7.6 Hz, 4H), 2.29 (s, 6H), 1.05 (t, *J* = 7.6 Hz, 6H) ppm.

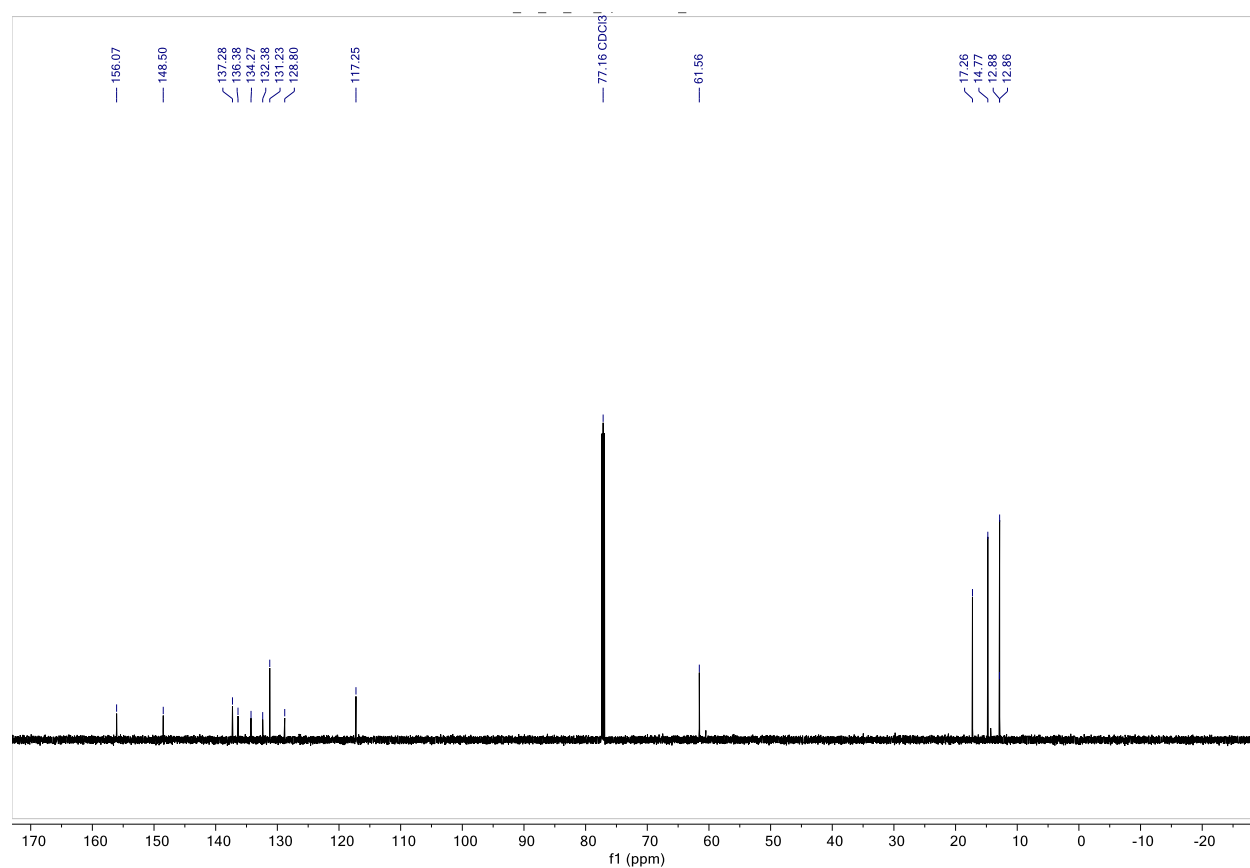
**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):** δ 156.1, 148.5, 137.3, 136.4, 134.3, 132.4, 131.2, 128.8, 117.3, 61.6, 17.3, 14.8, 12.9, 12.9 ppm.

**HRMS/ESI<sup>+</sup>** For compound **S8** [M+H]<sup>+</sup> 429.2273 was calculated and 429.2270 was found.

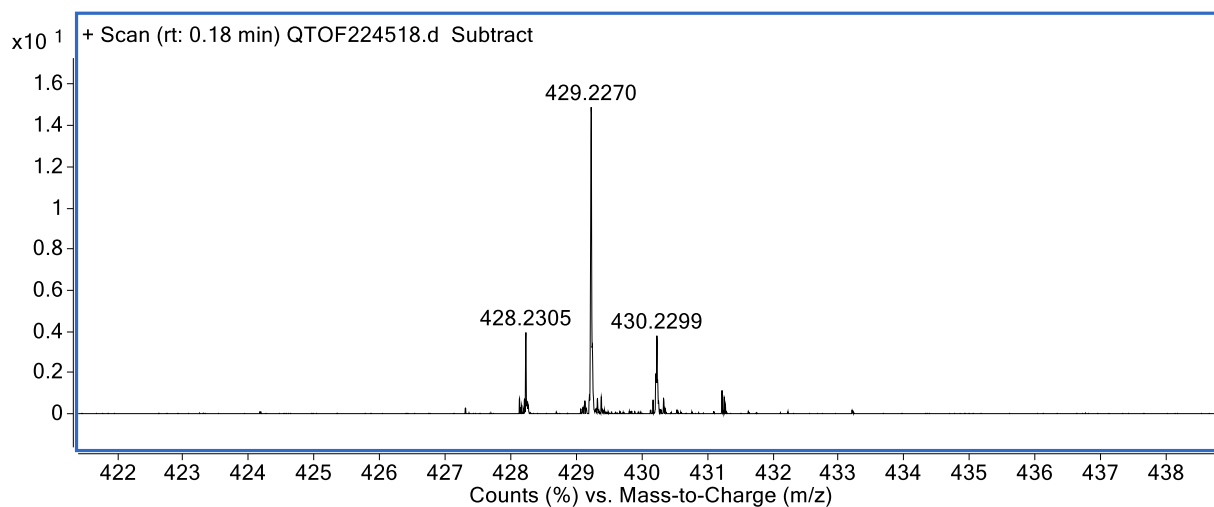
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **S8**:



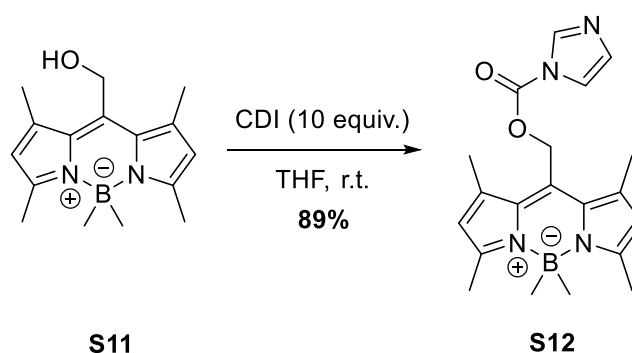
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **S8**:



### HRMS/ESI<sup>+</sup> of compound **S8**:



### Synthesis of **S12**



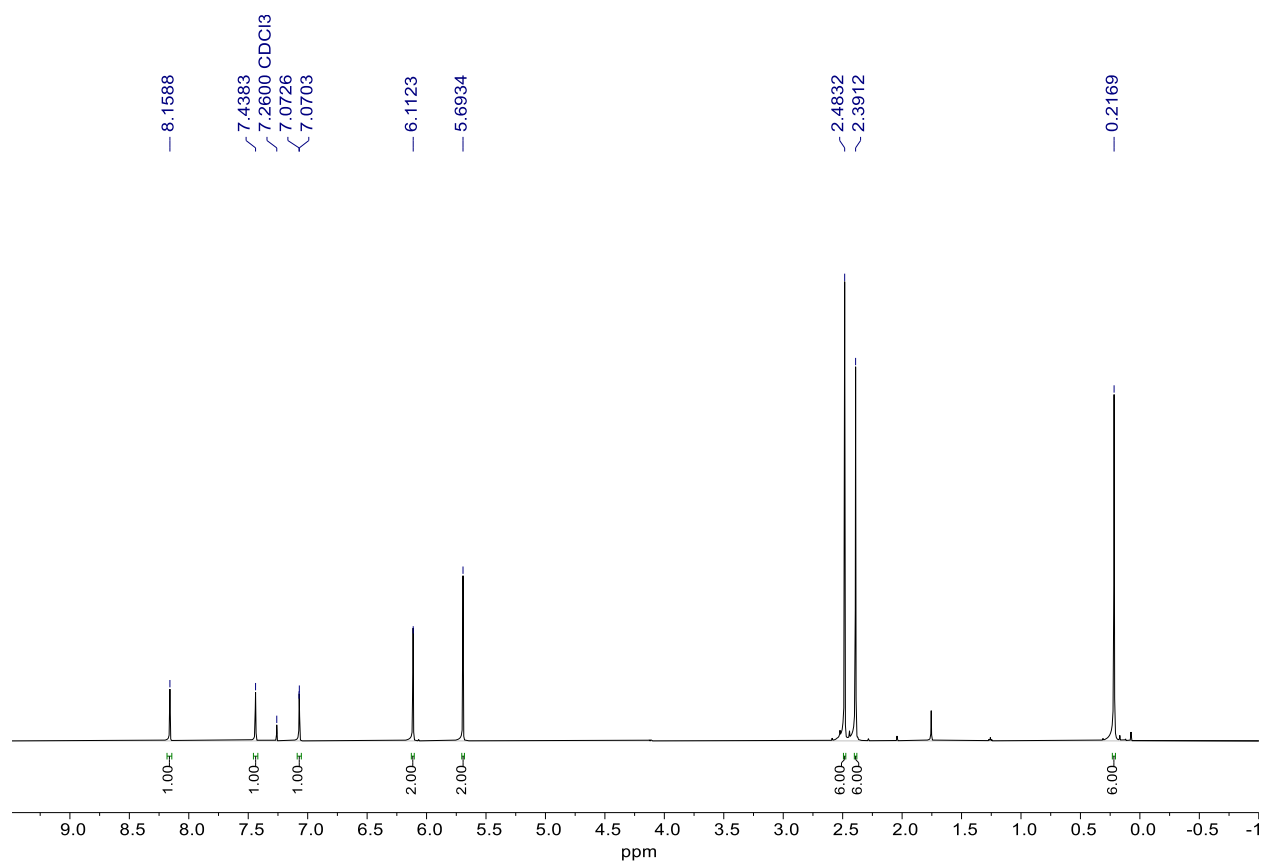
To a solution of **S11** (1.00 g, 3.7 mmol, 1 equiv.), CDI (6.01 g, 37 mmol, 10 equiv.) was added and stirred at room temperature for one hour. Product was purified via flash column chromatography with 10%- 30% ethyl acetate in hexane as the eluent. Compound **S12** was obtained as a red solid (1.20 g, 89%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 8.16 (s, 1H), 7.44 (s, 1H), 7.07 (d, *J* = 1.4 Hz, 1H), 6.11 (s, 2H), 5.69 (s, 2H), 2.48 (s, 6H), 2.39 (s, 6H), 0.22 (s, 6H) ppm.

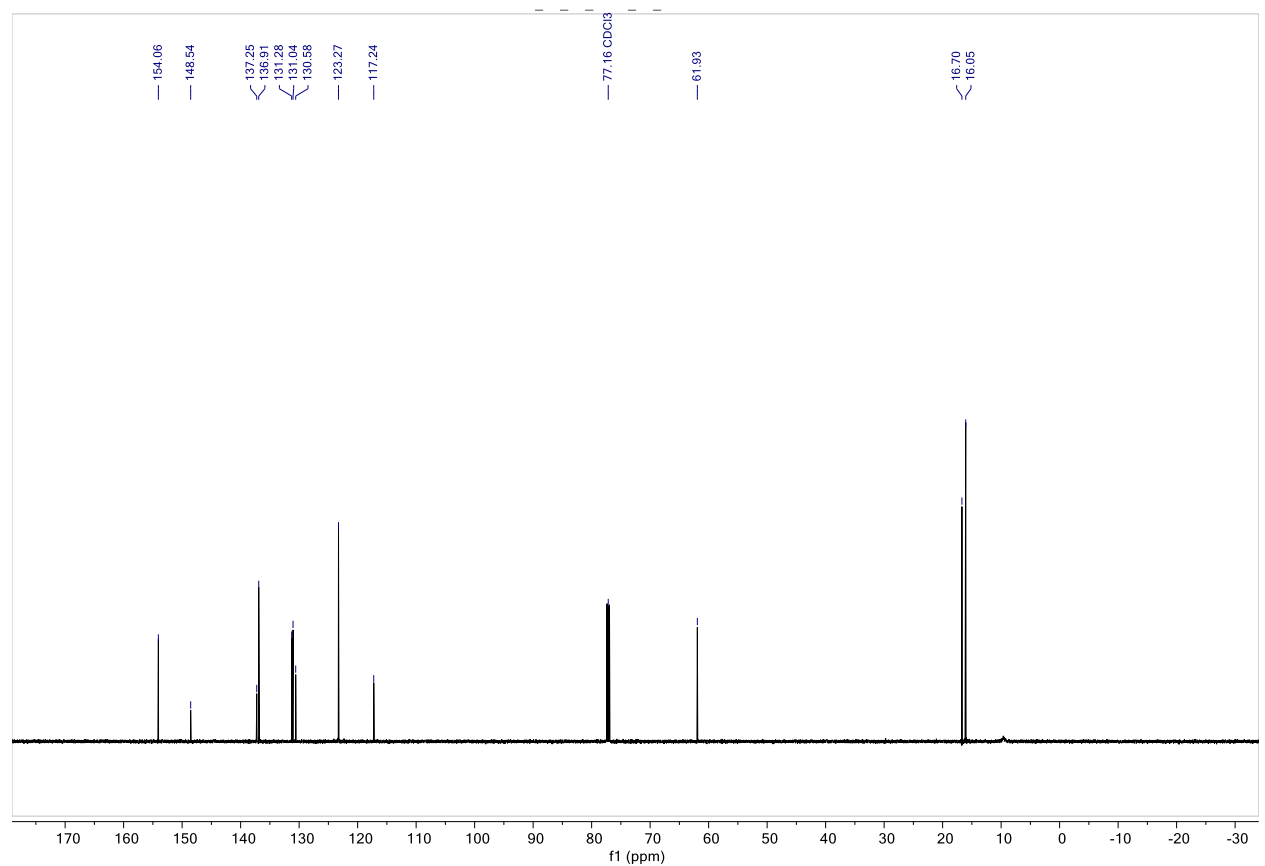
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 154.1, 148.5, 137.2, 136.9, 131.3, 131.0, 130.6, 123.3, 117.2, 61.9, 16.7, 16.1 ppm.

HRMS/ESI<sup>+</sup> For compound **S12** [M+H]<sup>+</sup> 365.2148 was calculated and 365.2151 was found.

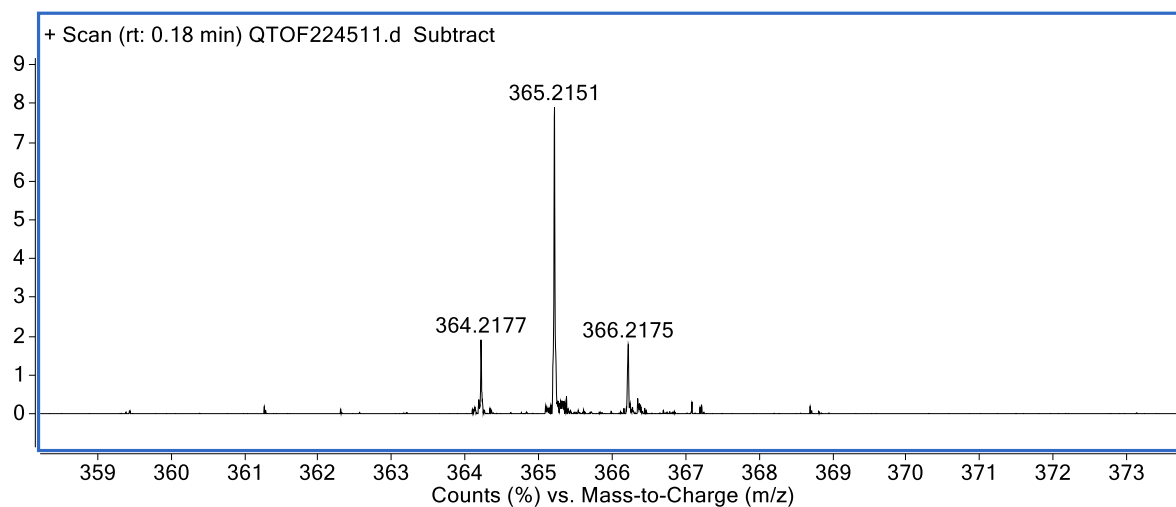
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **S12**:



$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **S12**:



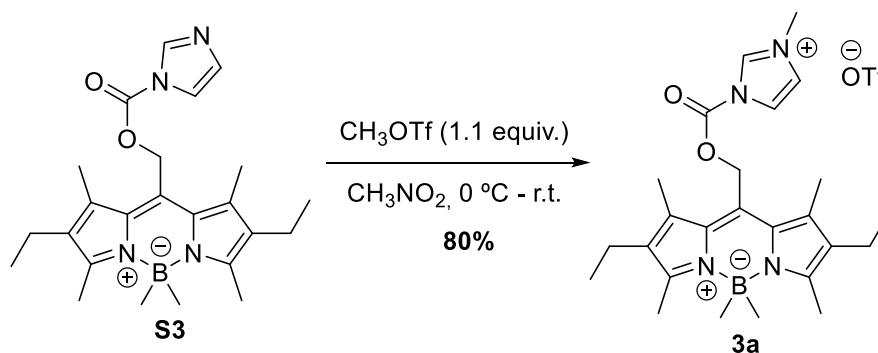
## HRMS/ESI<sup>+</sup> of **S12**:



## General procedure for the synthesis of **3a**, **3b**, **S13**

Methyl triflate (1.1 equiv.) was added to a solution of compound **S3** or **S8** in DCE at 0°C and stirred for 15 minutes. The reaction was then allowed to come to room temperature. The solid crashed out and was then filtered and washed with hexane.

## Synthesis of **3a**



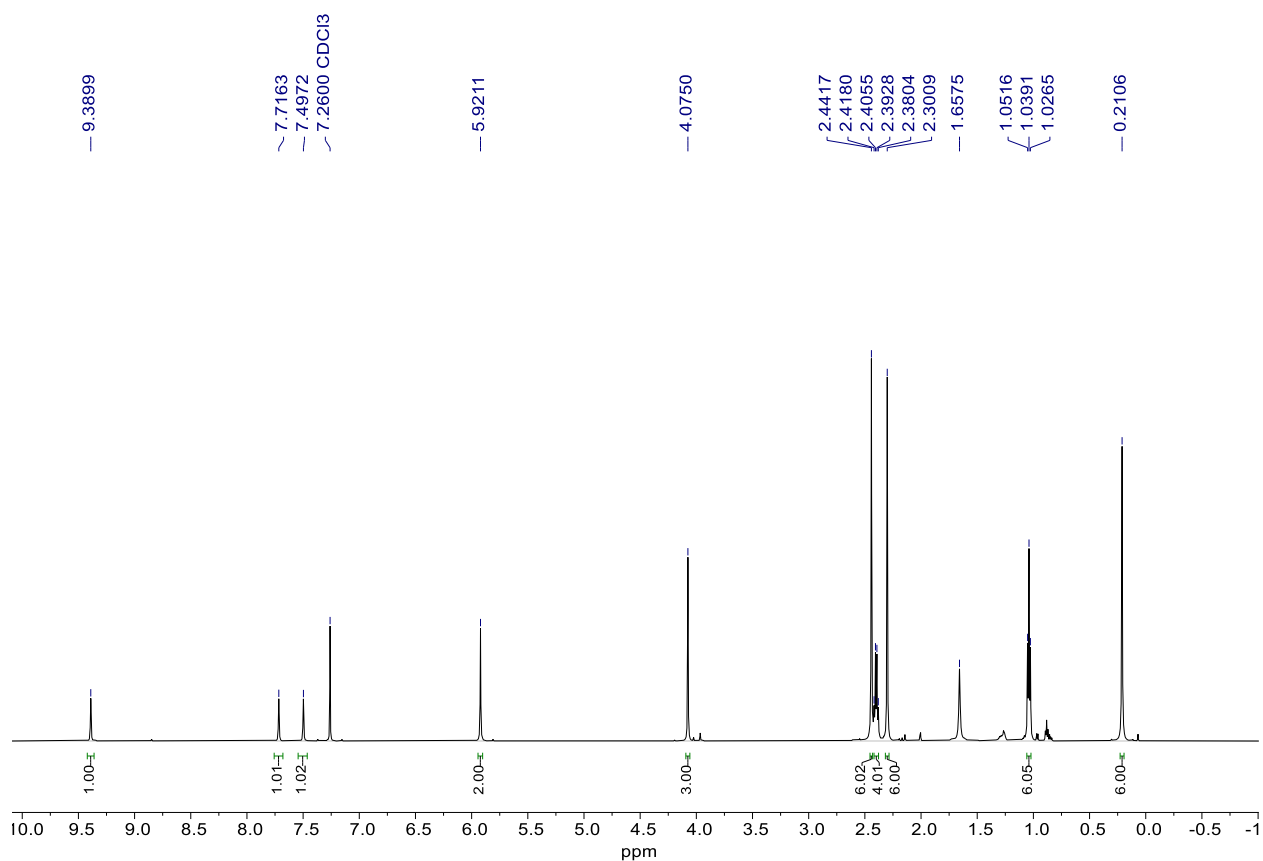
To an ice-cold solution of compound **S3** (0.50 g, 1.19 mmol, 1 equiv.) in DCE (5.0 mL), methyl triflate was added (0.14 mL, 1.31 mmol, 1.1 equiv.) and the reaction was stirred for 15 minutes before letting it come to room temperature. A red solid crashed out which was isolated by filtering followed by washing with hexane (0.556 g, 80%).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):** δ 9.39 (s, 1H), 7.72 (s, 1H), 7.50 (s, 1H), 5.92 (s, 2H), 4.08 (s, 3H), 2.44 (s, 6H), 2.40 (q, *J* = 7.5 Hz, 4H), 2.30 (s, 6H), 1.04 (t, *J* = 7.5 Hz, 6H), 0.21 (s, 6H) ppm.

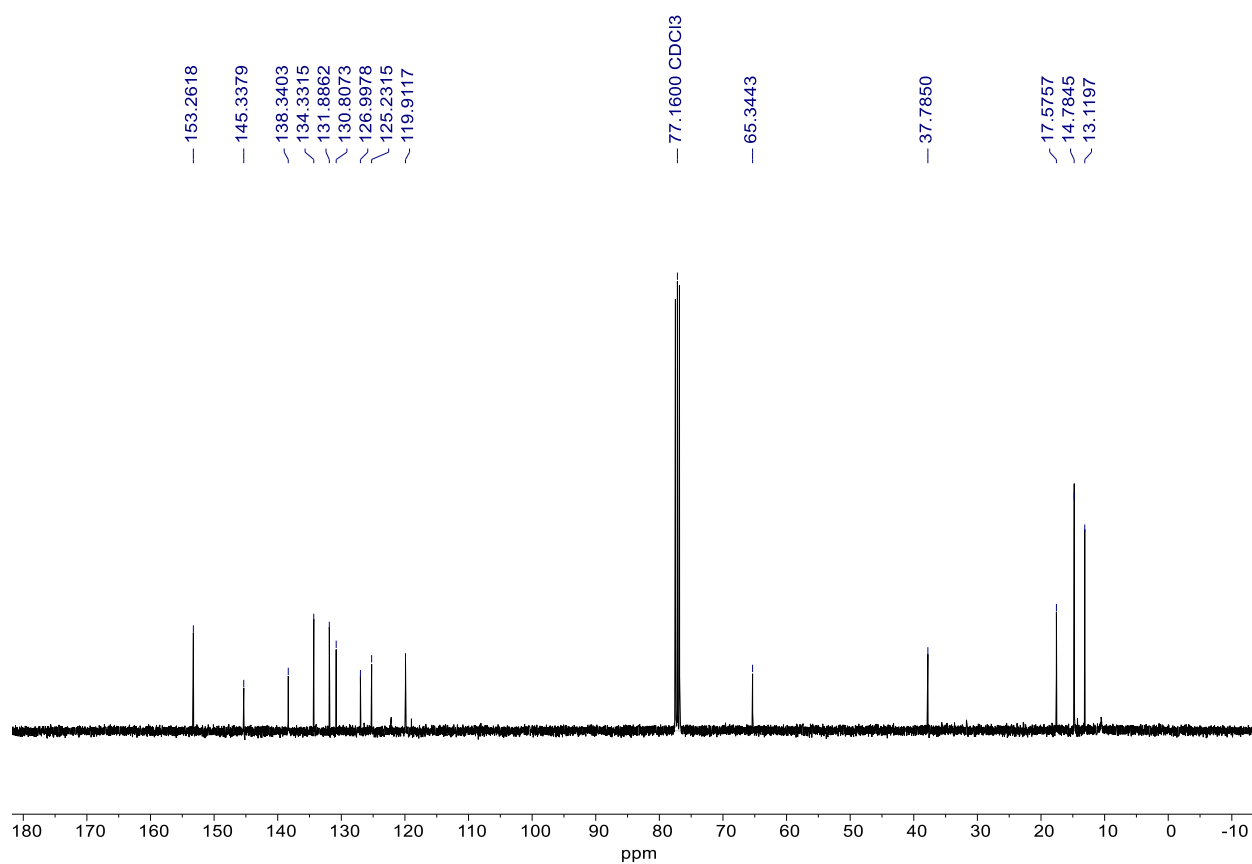
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.3, 145.3, 138.3, 134.3, 131.9, 130.8, 127.0, 125.2, 119.9, 65.3, 37.8, 17.6, 14.8, 13.1 ppm.

HRMS/ESI<sup>+</sup> For compound **3a**  $[\text{M}]^+$  435.2931 was calculated and 435.2918 was found.

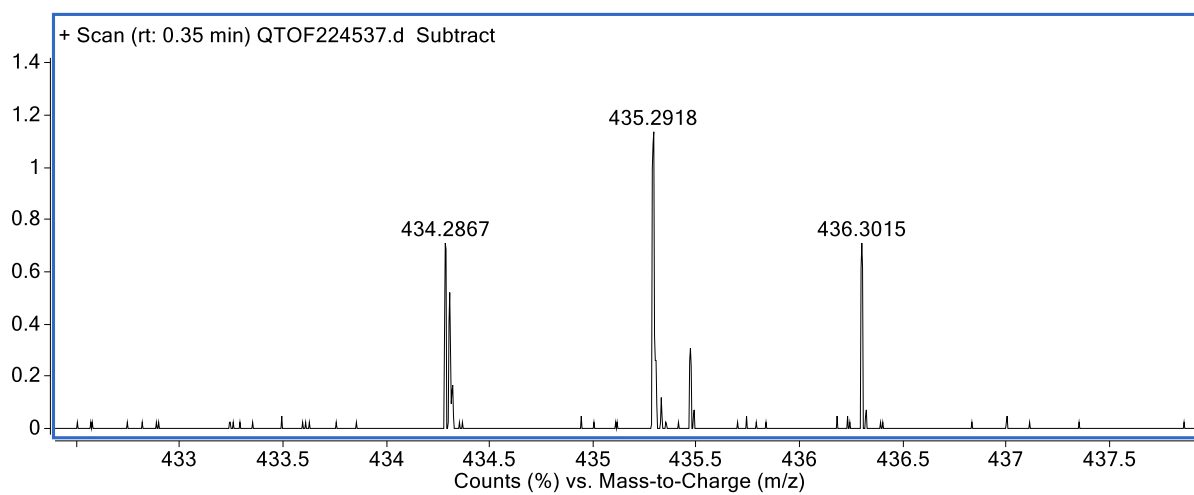
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **3a**:



<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of **3a**:

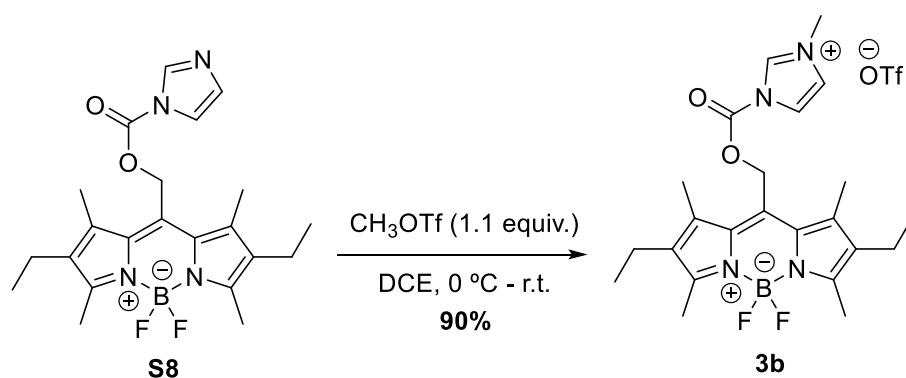


HRMS/ESI<sup>+</sup> of **3a**:





## Synthesis of 3b



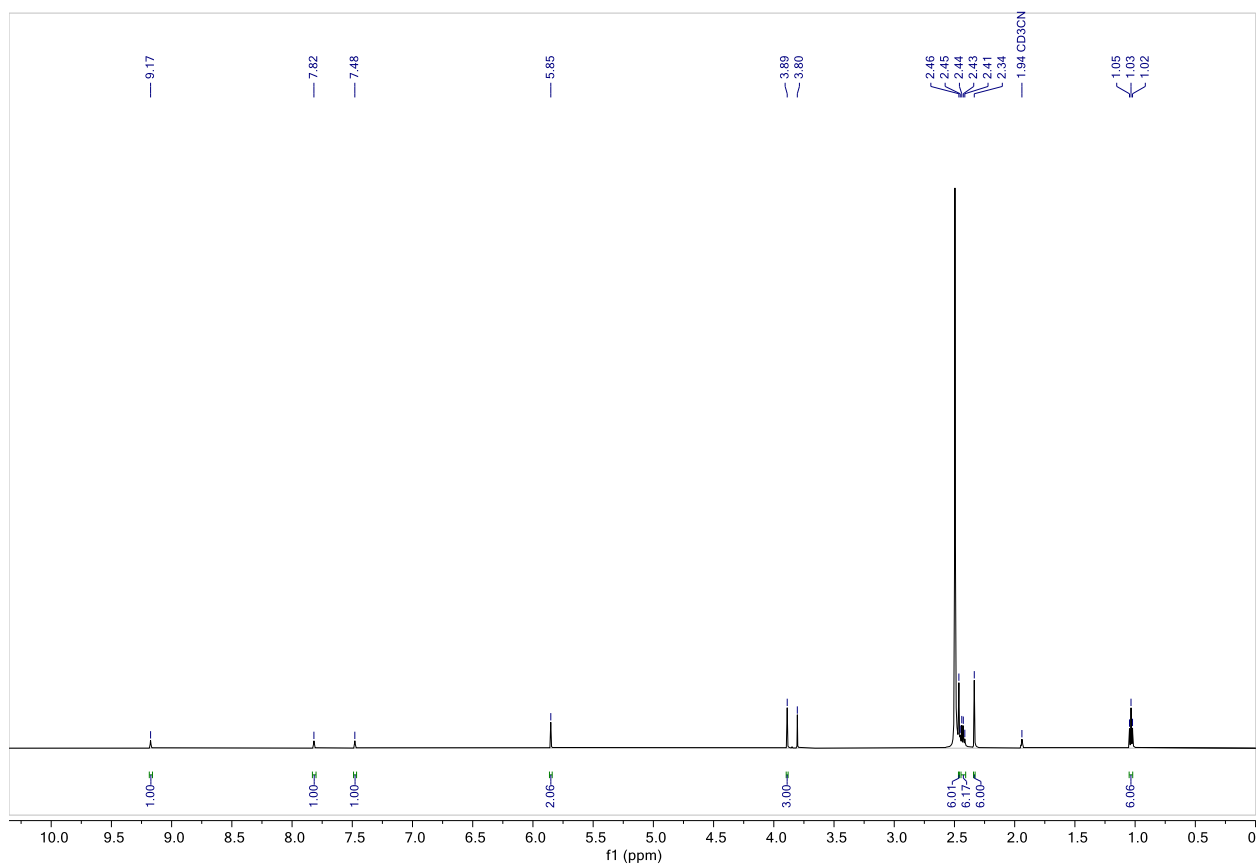
To an ice-cold solution of compound **S8** (0.15 g, 0.35 mmol, 1 equiv.) in DCE (5.0 mL), methyl triflate was added (0.06 mL, 0.51 mmol, 1.1 equiv.) and reaction was stirred for 15 minutes before letting it come to room temperature. A red solid crashed out which was isolated by filtering followed by washing with hexane (0.2 g, 90%).

**$^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta$  9.17 (s, 1H), 7.82 (s, 1H), 7.48 (s, 1H), 5.85 (s, 2H), 3.89 (s, 3H), 2.46 (s, 6H), 2.43 (q,  $J = 7.6$  Hz, 6H), 2.34 (s, 6H), 1.03 (t,  $J = 7.5$  Hz, 6H) ppm.

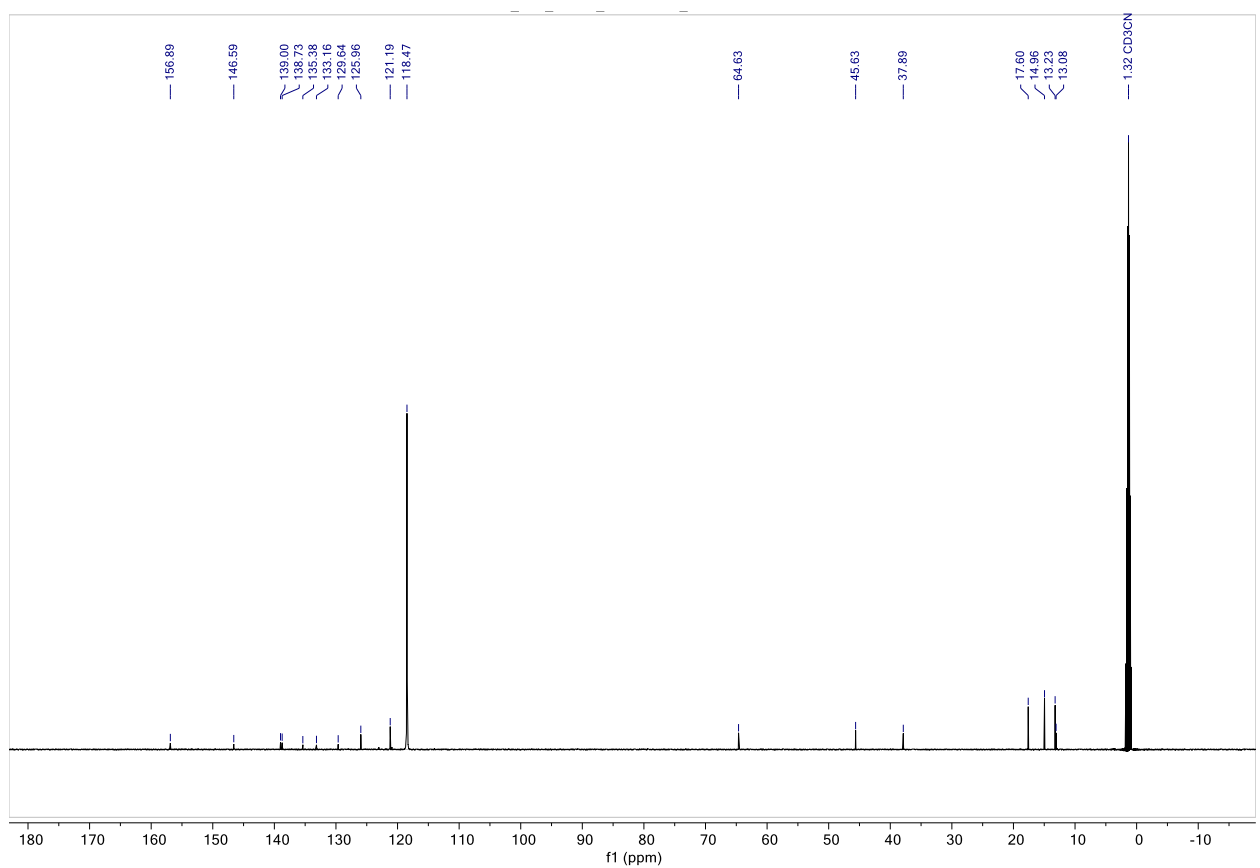
**$^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_3\text{CN}$ ):**  $\delta$  156.9, 146.6, 139.0, 138.7, 135.4, 133.2, 129.6, 126.2, 121.2, 64.6, 45.6, 37.9, 17.6, 15.0, 13.2 ppm.

**HRMS/ESI<sup>+</sup>** of **3b**  $[\text{M}]^+$  443.2429 was calculated and 443.2435 was found.

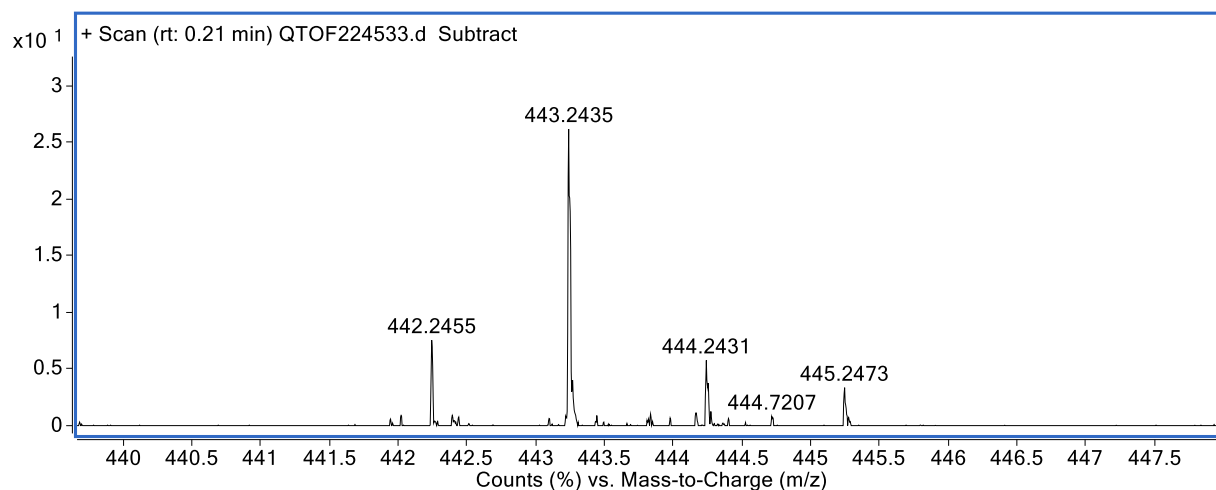
$^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{CN}$ ) of **3b**:



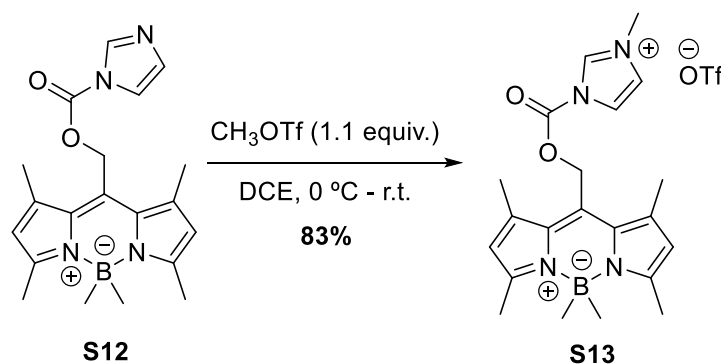
$^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_3\text{CN}$ ) of **3b**:



### HRMS/ESI<sup>+</sup> of **3b**:



### Synthesis of **S13**



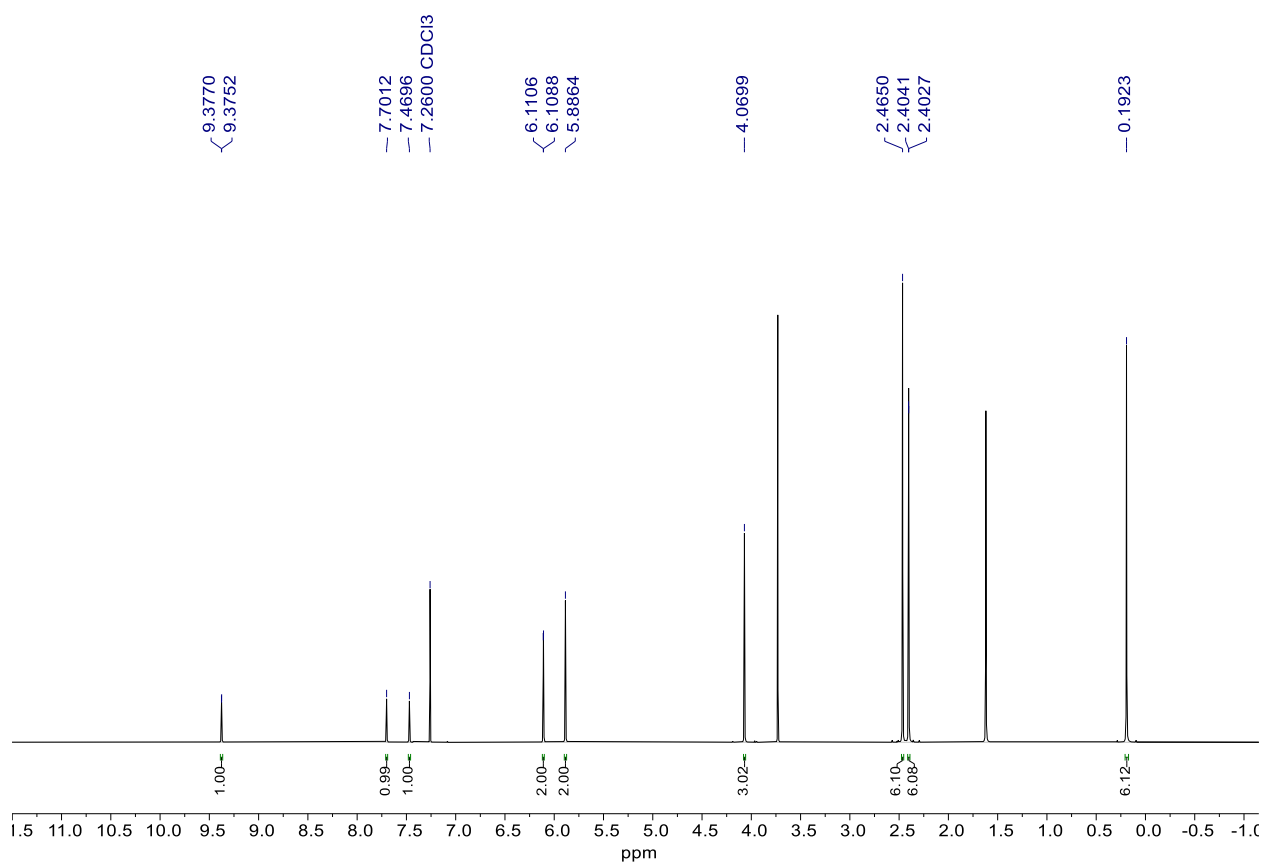
To an ice-cold solution of compound **S12** (0.15 g, 0.35 mmol, 1 equiv.) in DCE (5.0 mL), methyl triflate was added (0.06 mL, 0.51 mmol, 1.1 equiv.) and reaction was stirred for 15 minutes before letting it come to room temperature. A red solid crashed out which was isolated by filtering followed by washing with hexane (0.2 g, 90%).

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 9.38 (d, *J* = 1.1 Hz, 1H), 7.70 (s, 1H), 7.47 (s, 1H), 6.11 (d, *J* = 1.1 Hz, 2H), 5.89 (s, 2H), 4.07 (s, 3H), 2.46 (s, 6H), 2.40 (s, 6H), 0.19 (s, 6H) ppm.

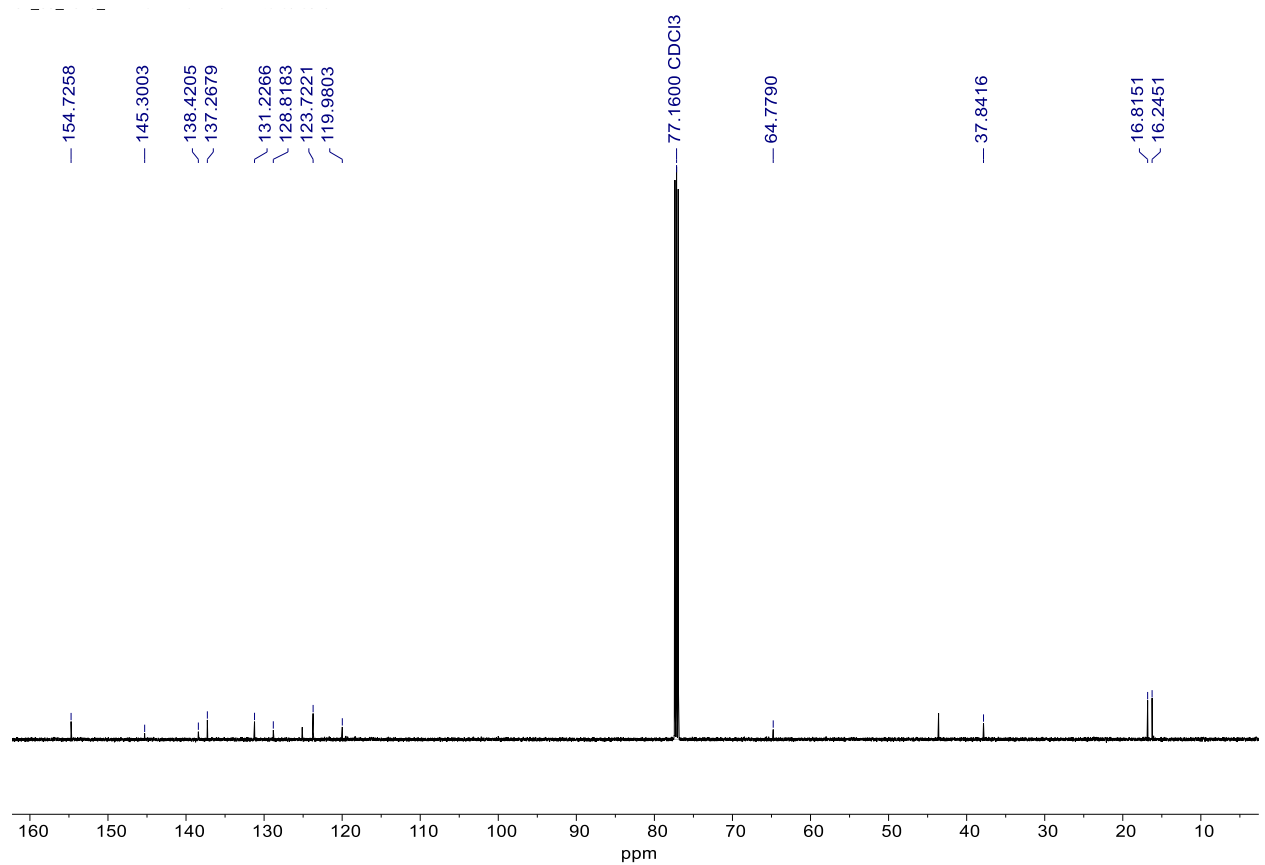
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>): δ 154.7, 145.3, 138.4, 137.3, 131.2, 128.8, 123.7, 120.0, 64.8, 37.8, 16.8, 16.3 ppm.

HRMS/ESI<sup>+</sup> For compound **S13** [M]<sup>+</sup> 379.2305 was calculated and 379.2288 was found.

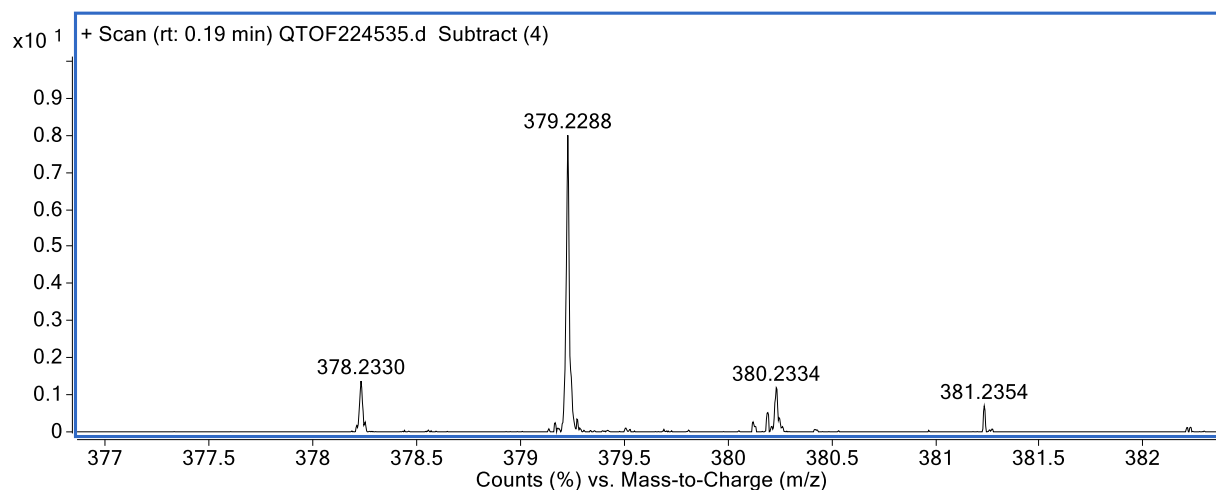
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **S13**:



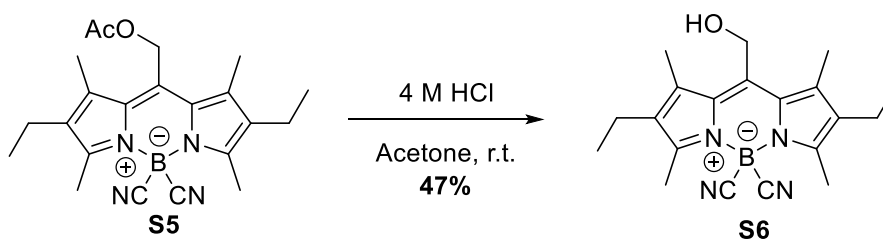
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **S13**:



## HRMS/ESI<sup>+</sup> of **S13**:



## Synthesis of **S6**



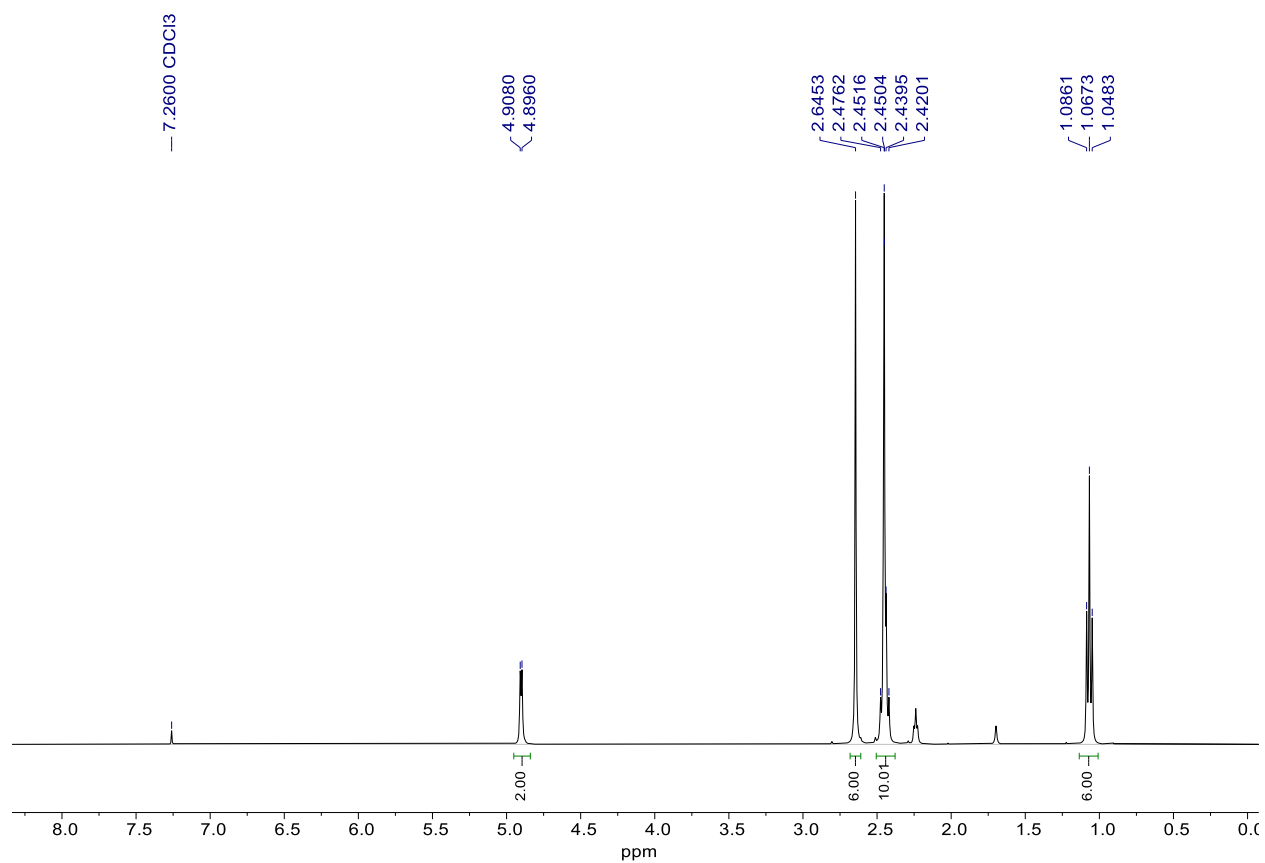
A portion of 4 M HCl was added to a solution of **S5** (0.250 g, 0.64 mmol, 1 equiv.) 0.02 M in acetone until the final concentration of HCl was 1.3 M. The reaction mixture was then stirred at 40°C under N<sub>2</sub> until the starting material was consumed. Upon completion of the reaction, the mixture was diluted with ethyl acetate followed by washing three times with brine and drying over anhydrous sodium sulfate. Solvent was evaporated under reduced pressure and the solid residue was purified using flash column chromatography with hexane/ethyl acetate as eluent. An orange solid was obtained (0.109 g, 47%).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):**  $\delta$  4.90 (s, 1H), 4.90 (s, 1H), 2.65 (s, 6H), 2.51 – 2.38 (m, 10H), 1.07 (t,  $J = 7.6$  Hz, 6H) ppm.

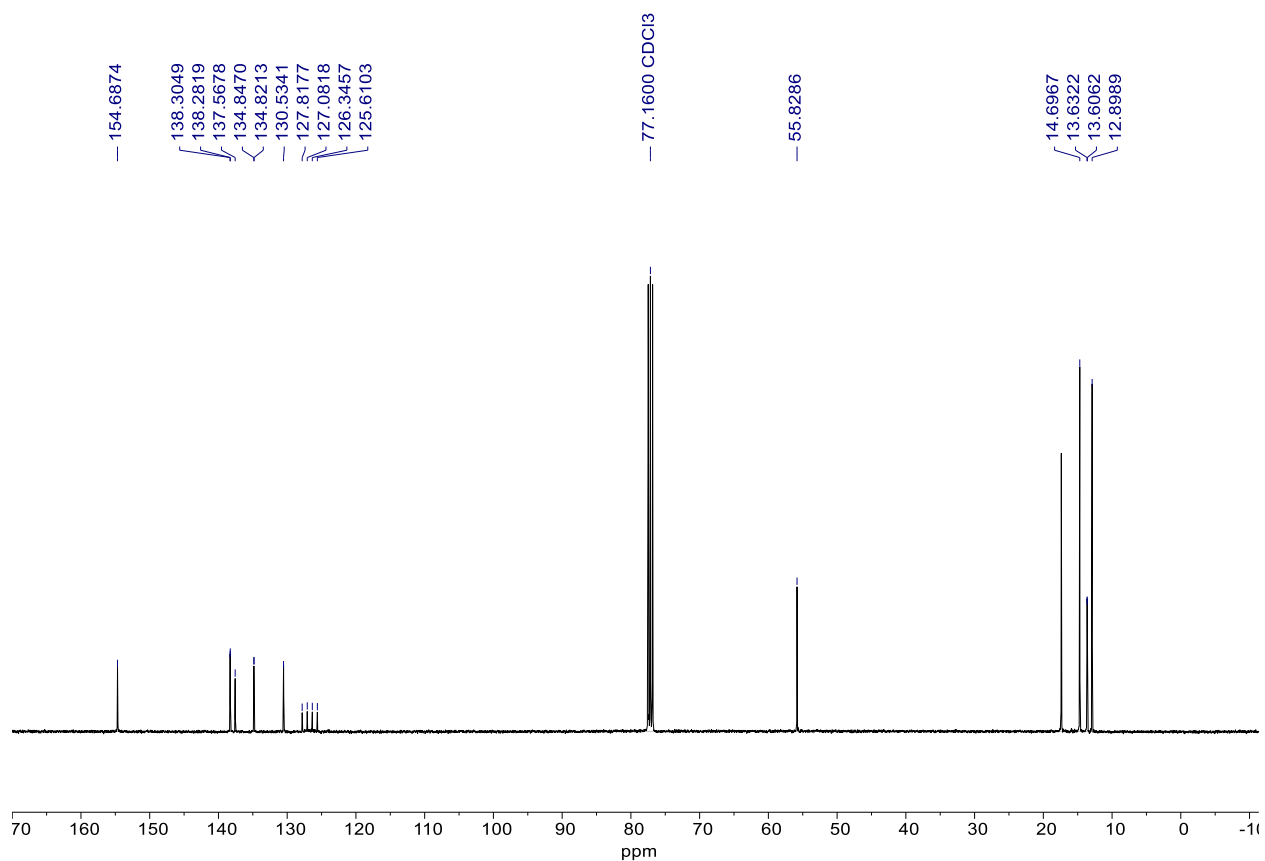
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):**  $\delta$  154.7, 138.3, 138.3, 137.6, 134.9, 134.8, 130.5, 127.8, 127.1, 126.4, 125.6, 55.8, 14.7, 13.6, 13.6, 12.9 ppm.

**HRMS/ESI<sup>-</sup>** For compound **S6** [M-H]<sup>-</sup> 347.2043 was calculated and 347.2039 was found.

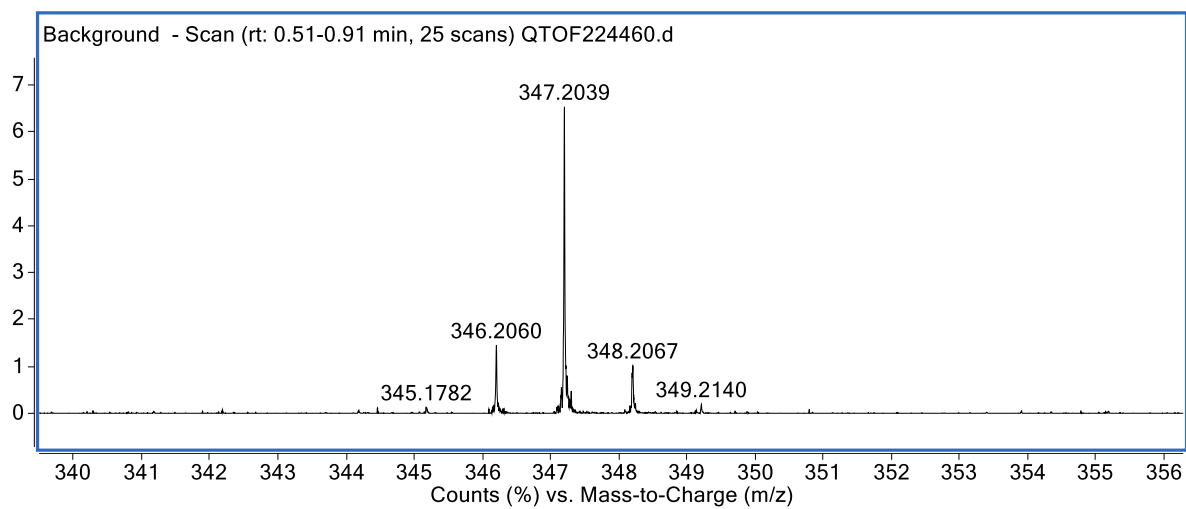
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **S6**:



$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **S6**:

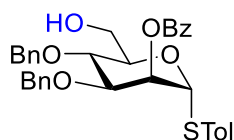


**HRMS/ESI<sup>-</sup> of S6:**



## 2.2 BODIPY Glycan Building Blocks

### *p*-Tolyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-1-thio- $\alpha$ -D-mannopyranoside (**2**)<sup>V</sup>



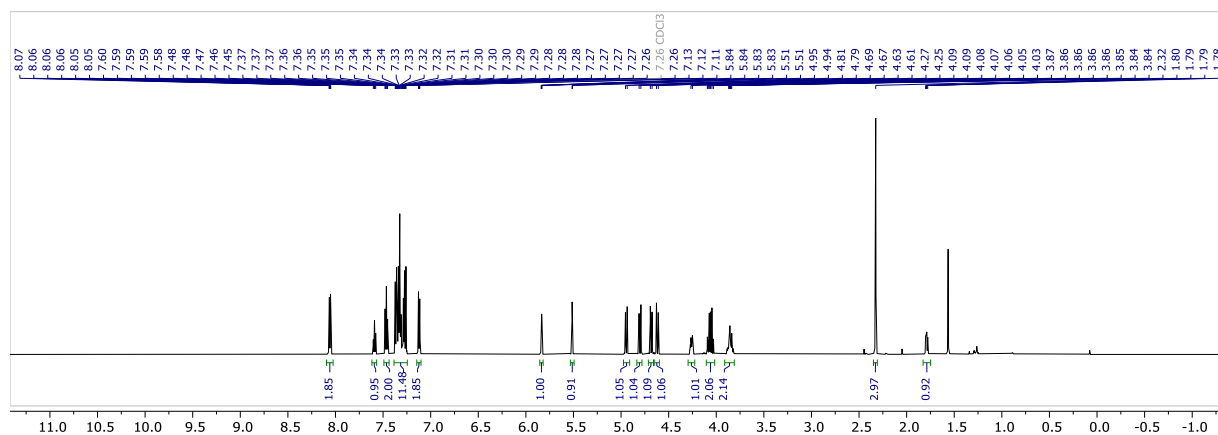
A solution of *p*-tolyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-6-*O*-(9-fluorenylmethoxycarbonyl)-1-thio- $\alpha$ -D-mannopyranoside (500 mg, 0.63 mmol, 1.0 equiv.) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (12 mL) was cooled to 0 °C and a solution of piperidine (4 mL of a 20% solution in anhydrous CH<sub>2</sub>Cl<sub>2</sub>) was added dropwise. The reaction mixture was stirred for 3 h at 0 °C, diluted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and washed with saturated aqueous citric acid (1 x 20 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 50 mL), the combined organic phase was washed with brine (50 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated in *vacuo* to give product **2** (310 mg, 0.54 mmol, 87%) as a colorless oil after purification by column chromatography (Hex:AcOEt 3:1).

$R_f$  = 0.25 (Hex: AcOEt 3:1).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):**  $\delta$  8.09 – 8.03 (m, 2H), 7.62 – 7.56 (m, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.39 – 7.23 (m, 12H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.84 (dd, *J* = 2.9, 1.8 Hz, 1H), 5.51 (d, *J* = 1.7 Hz, 1H), 4.94 (d, *J* = 10.9 Hz, 1H), 4.80 (d, *J* = 11.3 Hz, 1H), 4.68 (d, *J* = 10.9 Hz, 1H), 4.62 (d, *J* = 11.4 Hz, 1H), 4.26 (dt, *J* = 9.3, 3.4 Hz, 1H), 4.11 – 4.01 (m, 2H), 3.90 – 3.79 (m, 2H), 2.32 (s, 3H), 1.79 (dd, *J* = 7.9, 5.5 Hz, 1H) ppm.

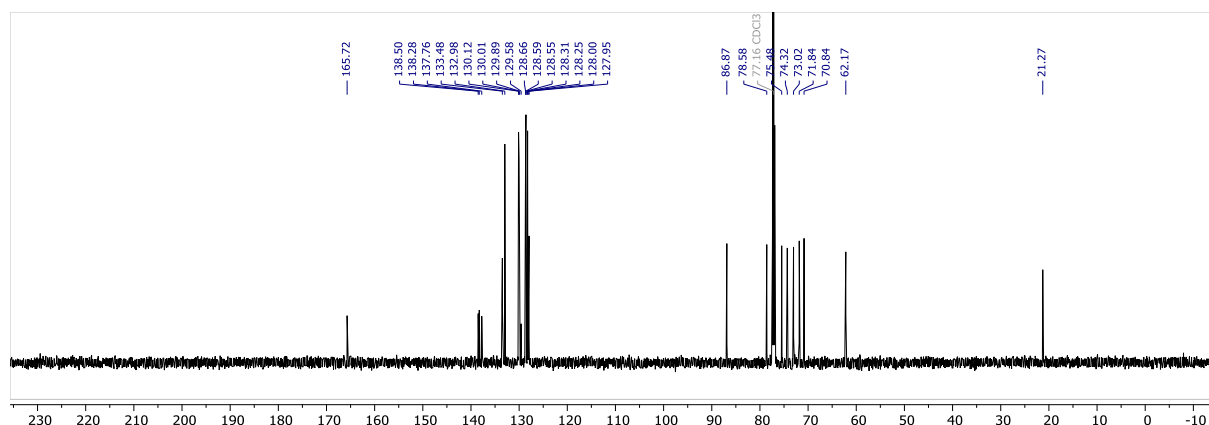
**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):**  $\delta$  165.7, 138.5, 138.2, 137.7, 133.4, 132.9, 130.1, 130.0, 129.8, 129.5, 128.6, 128.5, 128.5, 128.3, 128.2, 128.0, 127.9, 86.8, 78.5, 75.4, 74.3, 73.02, 71.84, 70.8, 62.1, 21.2 ppm.

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) of **2**:**

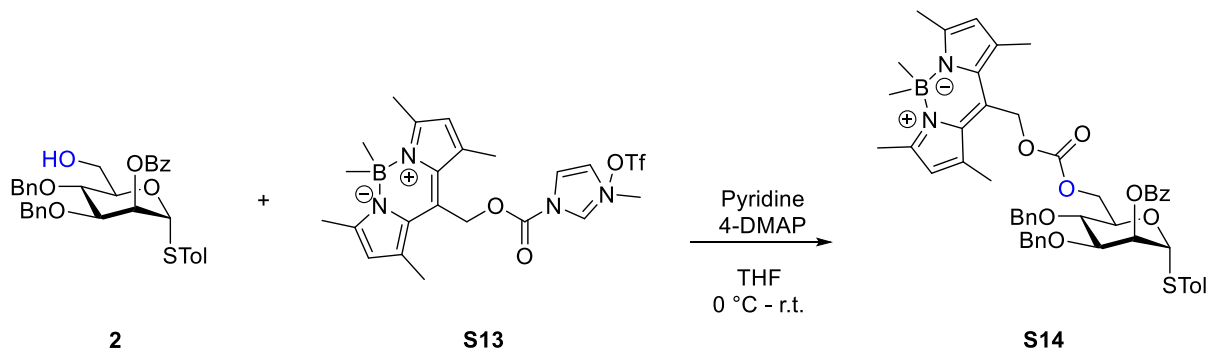




$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **2**:



**p**-Tolyl 2-O-benzoyl-3,4-di-O-benzyl-6-O-(8-(4,4'-dimethyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacenyl)methoxycarbonyl)-1-thio- $\alpha$ -D-mannopyranoside (**S14**)



To a solution of mannose **2** (40 mg, 0.07 mmol, 1.0 equiv.) and pyridine (57  $\mu\text{L}$ , 0.70 mmol, 10.0 equiv.) in anhydrous THF (5 mL) **S13** (41 mg, 0.08 mmol, 1.1 equiv.) was added in small portions at 0  $^{\circ}\text{C}$  followed by 4-DMAP (1 mg, 0.01 mmol, 0.1 equiv.). The reaction was warmed up to room temperature and was stirred overnight. The reaction mixture was diluted with ethyl acetate and washed with water and brine. The organic phase was dried over  $\text{Na}_2\text{SO}_4$ , filtered, concentrated and purified by flash column chromatography (Hex/EtOAc 9:1 to 3:1) to give compound **S14** (30 mg, 0.04 mmol, 49%) as a red foam.

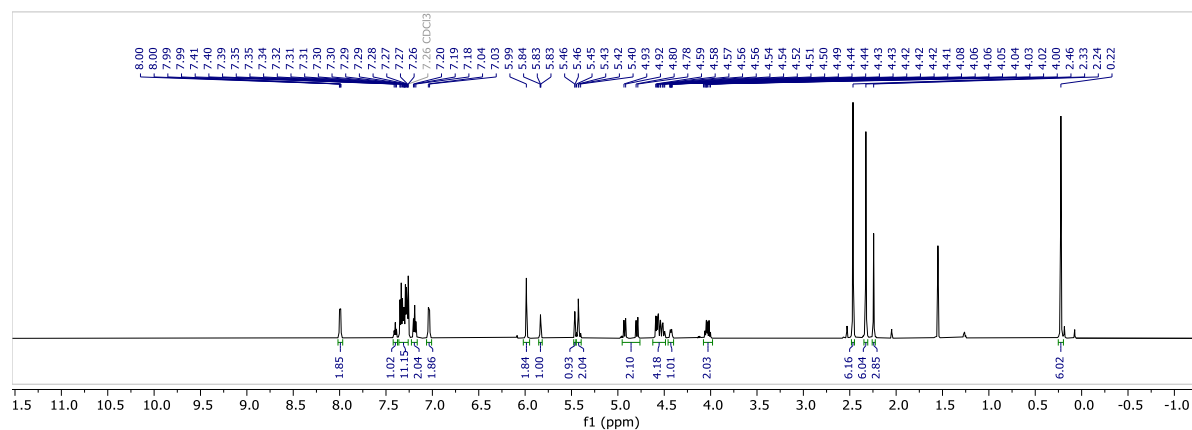
$R_f = 0.46$  (Hex: AcOEt 3:1).

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.99 (d,  $J = 6.6$  Hz, 2H), 7.40 (t,  $J = 7.4$  Hz, 1H), 7.36 – 7.25 (m, 11H), 7.19 (t,  $J = 7.7$  Hz, 2H), 7.04 (d,  $J = 7.9$  Hz, 2H), 5.99 (s, 2H, BODIPY-CH), 5.83 (t,  $J = 2.3$  Hz, 1H, H-2), 5.46 (d,  $J = 1.8$  Hz, 1H, H-1), 5.45 – 5.39 (m, 2H, BODIPY-CH<sub>2</sub>), 4.86 (dd,  $J = 78.7, 11.1$  Hz, 2H, Ph-CH<sub>2</sub>), 4.61 – 4.48 (m, 4H, Ph-CH<sub>2</sub>, H-6, H-6'), 4.43 (ddd,  $J = 9.4, 4.1, 2.3$  Hz, 1H, H-5), 4.08 – 3.99 (m, 2H, H-3, H-4), 2.46 (s, 6H, BODIPY-CH<sub>3</sub>), 2.33 (s, 6H, BODIPY-CH<sub>3</sub>), 2.24 (s, 3H, Tol-CH<sub>3</sub>), 0.22 (s, 6H, B(CH<sub>3</sub>)) ppm.

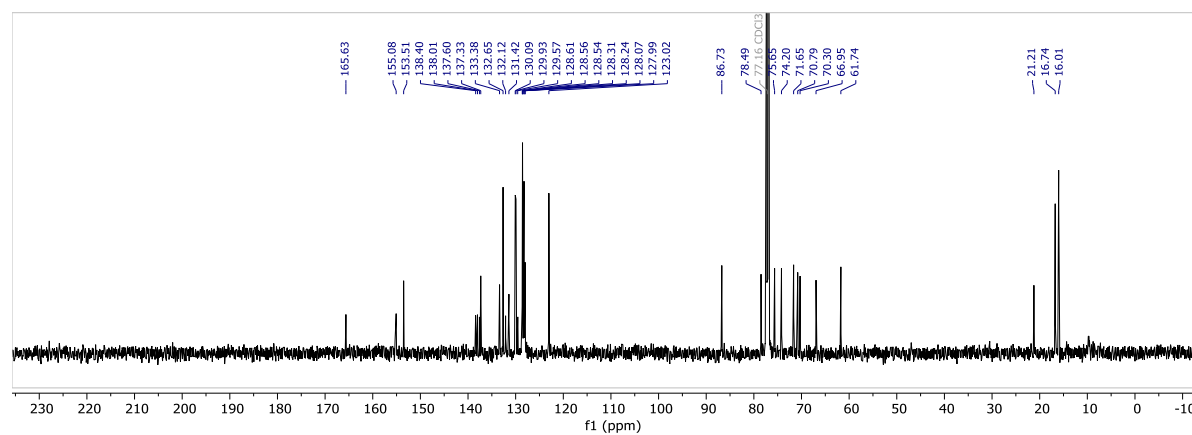
**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):** δ 165.6, 155.0, 153.5, 138.4, 138.0, 137.6, 137.3, 133.3, 132.6, 132.1, 131.4, 130.0, 129.9, 129.5, 128.6, 128.5, 128.5, 128.3, 128.2, 128.0, 127.9, 123.0, 86.7, 78.4, 75.6, 74.2, 71.6, 70.7, 70.3, 66.9, 61.7, 21.2, 16.7, 16.0 ppm.

**HRMS (QToF):** Calcd for C<sub>51</sub>H<sub>55</sub>BN<sub>2</sub>O<sub>8</sub>S [M + H]<sup>+</sup> 867.3845; found 867.3879.

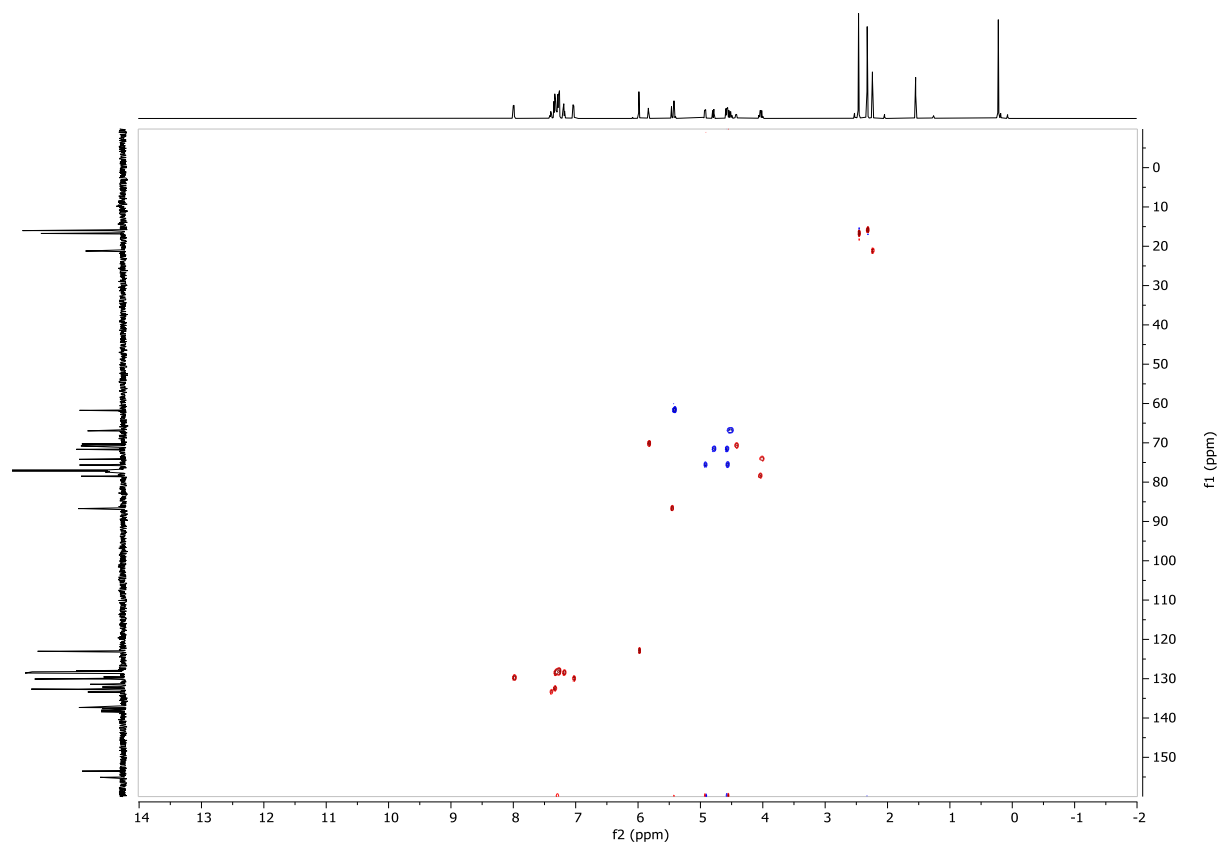
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) of S14:**



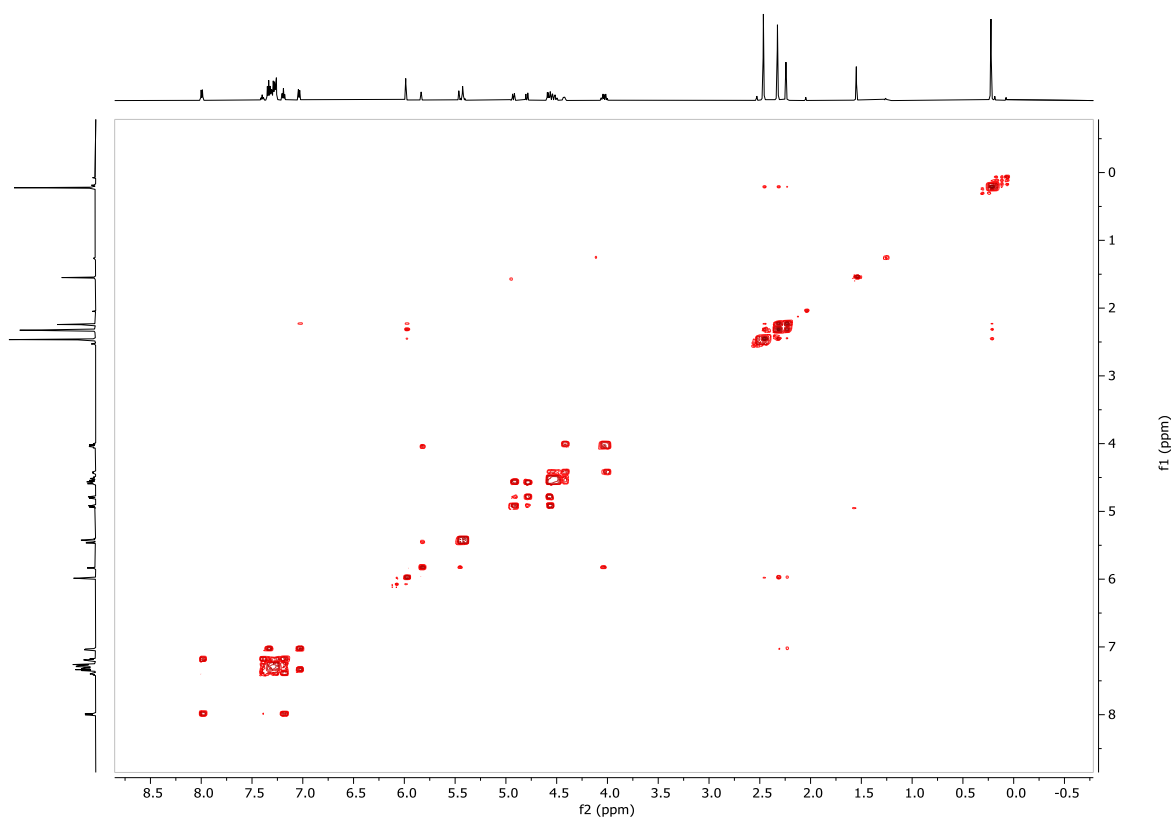
**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) of S14:**



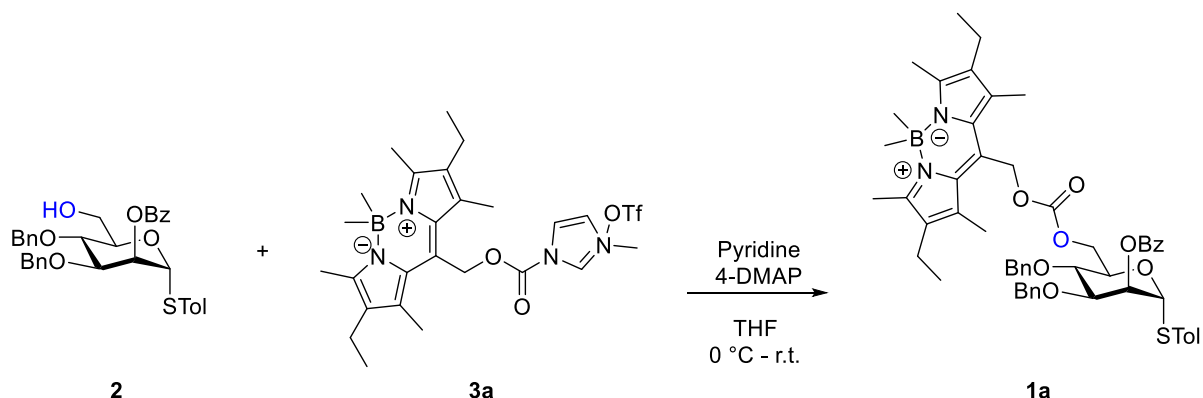
$^{13}\text{C}, ^1\text{H}$  HSQC of **S14**:



$^1\text{H}, ^1\text{H}$  COSY of **S14**:



**p-Tolyl 2-O-benzoyl-3,4-di-O-benzyl-6-O-(8-(2,6-diethyl-4,4'-dimethyl-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indaceny)methoxycarbonyl)-1-thio- $\alpha$ -D-mannopyranoside (1a)**



To a solution of mannose **2** (80 mg, 0.14 mmol, 2.0 equiv.) and pyridine (57  $\mu$ L, 0.70 mmol, 10.0 equiv.) in anhydrous THF (5 mL) **3a** (41 mg, 0.07 mmol, 1.0 equiv.) was added in small portions at 0 °C followed by 4-DMAP (1 mg, 0.01 mmol, 0.1 equiv.). The reaction was warmed up to room temperature and was stirred overnight. The reaction mixture was diluted with ethyl acetate and washed with water and brine. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated and purified by flash column chromatography (Hex/EtOAc 9:1 to 3:1) to give compound **1a** (40 mg, 0.04 mmol, 62%) as a red foam.

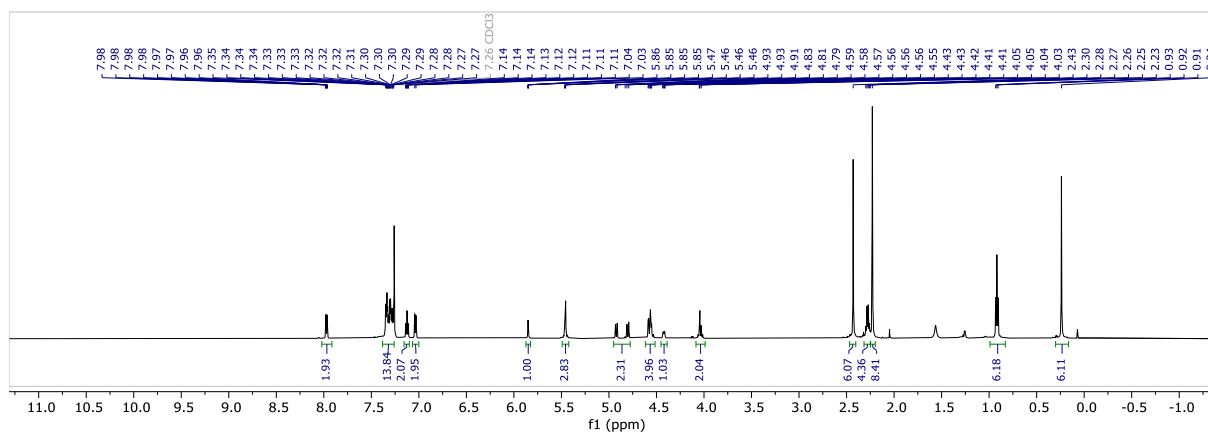
$R_f$  = 0.49 (Hex: AcOEt 3:1).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):**  $\delta$  7.97 (dt,  $J$  = 8.5, 1.1 Hz, 2H), 7.37 – 7.27 (m, 13H), 7.12 (tt,  $J$  = 7.3, 0.9 Hz, 2H), 7.04 (d,  $J$  = 7.9 Hz, 2H), 5.88 – 5.83 (m, 1H), 5.46 (dd,  $J$  = 4.2, 1.8 Hz, 3H), 4.86 (dd,  $J$  = 72.6, 11.0 Hz, 2H), 4.61 – 4.52 (m, 4H), 4.42 (dd,  $J$  = 7.6, 4.3 Hz, 1H), 4.08 – 4.01 (m, 2H), 2.43 (s, 6H), 2.28 (q,  $J$  = 7.6 Hz, 4H), 2.23 (s, 9H), 0.92 (t,  $J$  = 7.6 Hz, 6H), 0.24 (s, 6H) ppm.

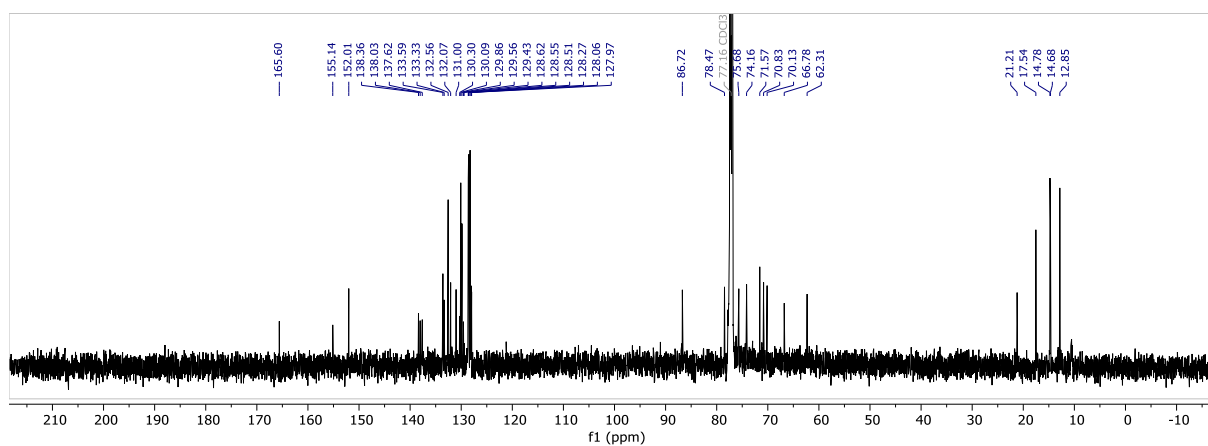
**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):**  $\delta$  165.6, 155.1, 152.0, 138.4, 138.0, 137.6, 133.6, 133.3, 132.6, 132.1, 131.0, 130.3, 130.1, 129.9, 129.6, 129.4, 128.6, 128.5, 128.5, 128.3, 128.1, 128.0, 86.7, 78.5, 75.7, 74.2, 71.6, 70.8, 70.1, 66.8, 62.3, 21.2, 17.5, 14.8, 14.7, 12.8 ppm.

**HRMS (QToF):** Calcd for C<sub>55</sub>H<sub>64</sub>BN<sub>2</sub>O<sub>8</sub>SNa [M + Na]<sup>+</sup> 945.4290; found 945.4369.

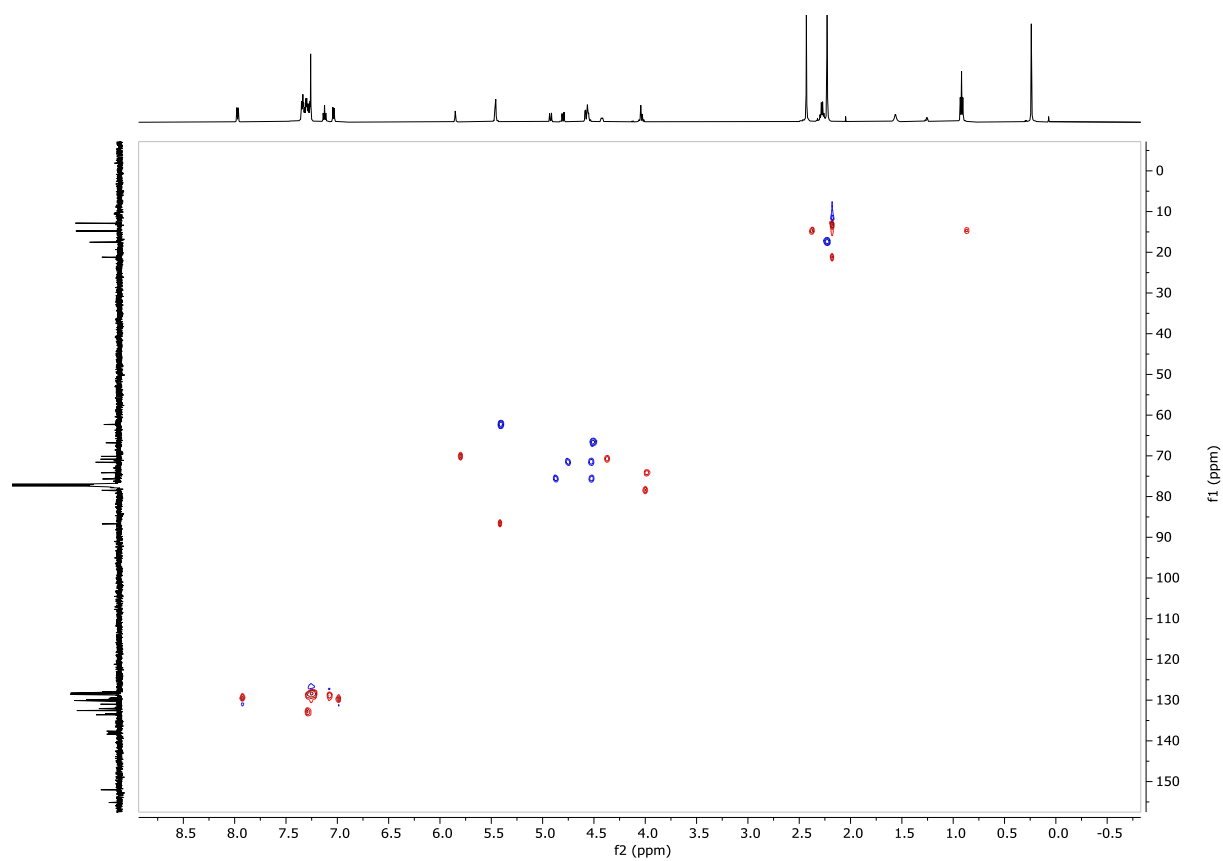
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) of **1a**:



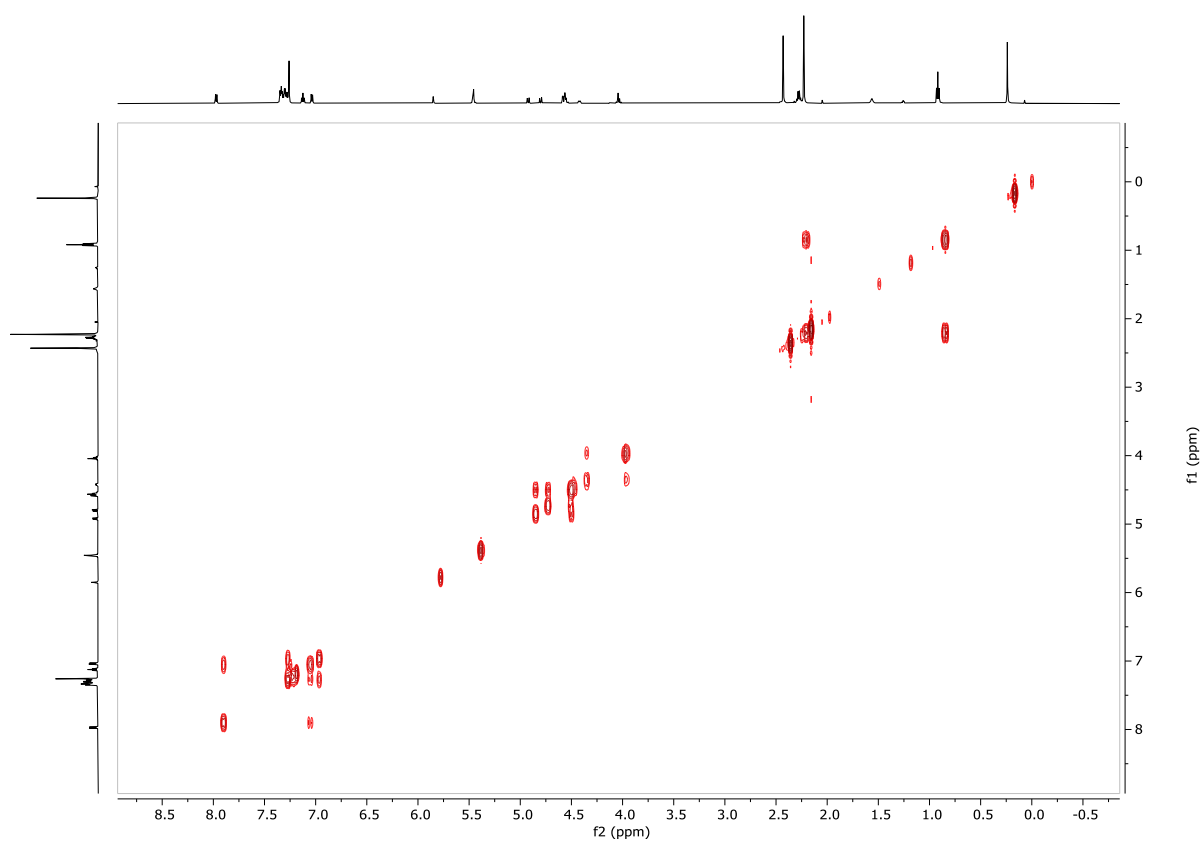
<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) of **1a**:



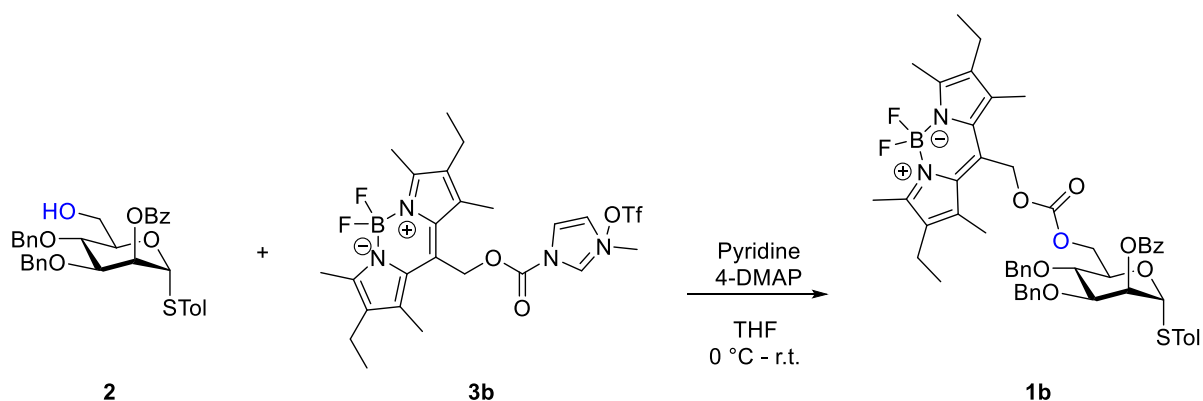
$^{13}\text{C}, ^1\text{H}$  HSQC of **1a**:



$^1\text{H}, ^1\text{H}$  COSY of **1a**:



***p*-Tolyl 2-O-benzoyl-3,4-di-O-benzyl-6-O-(8-(2,6-diethyl-4,4'-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacenyl)methoxycarbonyl)-1-thio- $\alpha$ -D-mannopyranoside (**1b**)**



To a solution of mannose **2** (80 mg, 0.14 mmol, 2.0 equiv.) and pyridine (57  $\mu$ L, 0.70 mmol, 10.0 equiv.) in anhydrous THF (5 mL) **3b** (41 mg, 0.07 mmol, 1.0 equiv.) was added in small portions at 0 °C followed by 4-DMAP (1 mg, 0.01 mmol, 0.1 equiv.). The reaction was warmed up to room temperature and was stirred overnight. The reaction mixture was diluted with ethyl acetate and washed with water and brine. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, concentrated and purified by flash column chromatography (Hex/EtOAc 9:1 to 3:1) to give compound **1b** (45 mg, 0.05 mmol, 69%) as a red foam.

$R_f$  = 0.48 (Hex: AcOEt 3:1).

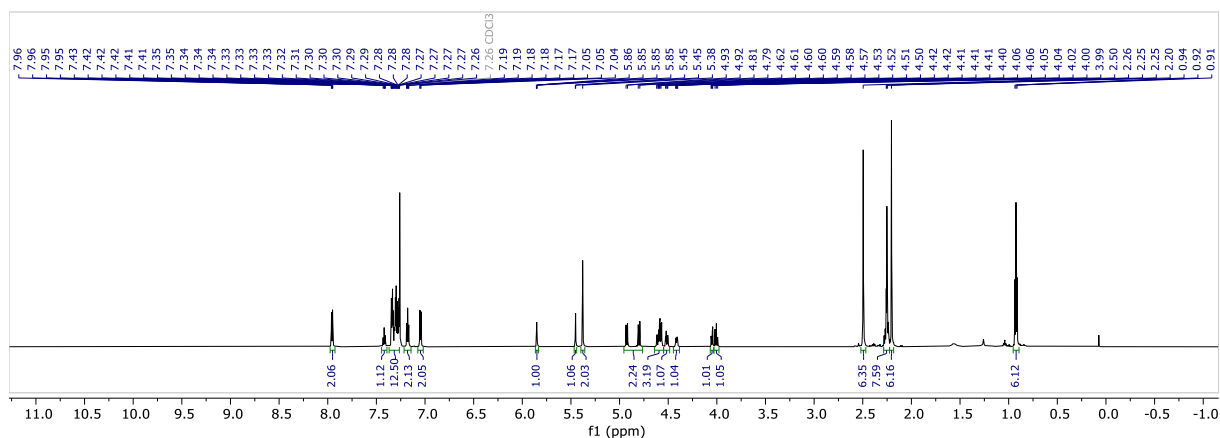
**<sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>):**  $\delta$  8.00 – 7.92 (m, 2H), 7.42 (tt,  $J$  = 7.4, 1.4 Hz, 1H), 7.36 – 7.26 (m, 12H), 7.21 – 7.15 (m, 2H), 7.07 – 7.03 (m, 2H), 5.87 – 5.84 (m, 1H), 5.45 (d,  $J$  = 2.0 Hz, 1H), 5.38 (s, 2H), 4.86 (dd,  $J$  = 88.1, 11.0 Hz, 2H), 4.64 – 4.57 (m, 3H), 4.52 (dd,  $J$  = 11.5, 3.9 Hz, 1H), 4.41 (ddd,  $J$  = 9.8, 4.0, 2.3 Hz, 1H), 4.05 (dd,  $J$  = 9.2, 2.8 Hz, 1H), 4.00 (t,  $J$  = 9.5 Hz, 1H), 2.50 (s, 6H), 2.30 – 2.23 (m, 7H), 2.20 (s, 6H), 0.92 (t,  $J$  = 7.6 Hz, 6H) ppm.

**<sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>):**  $\delta$  165.6, 155.4, 155.0, 138.4, 138.0, 137.6, 136.7, 133.8, 133.6, 132.5, 130.2, 130.1, 129.8, 129.3, 128.6, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 86.8, 78.5, 75.6, 74.1, 71.6, 70.9, 70.2, 66.9, 61.4, 21.2, 17.2, 14.7, 12.8, 12.7 ppm.

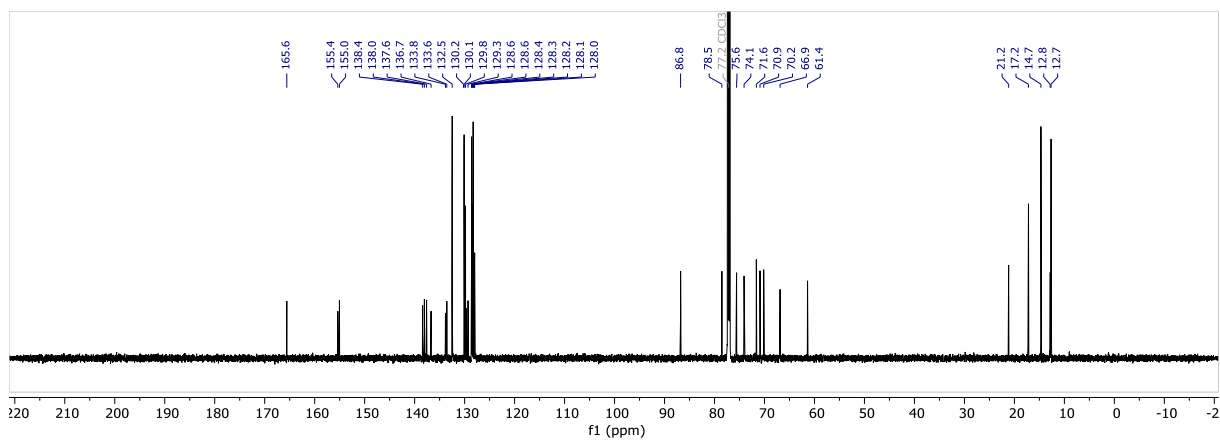
**<sup>19</sup>F NMR (659 MHz, CDCl<sub>3</sub>):**  $\delta$  -145.72 (dd,  $J$  = 65.6, 32.2 Hz) ppm.

**HRMS (QToF):** Calcd for C<sub>53</sub>H<sub>57</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>8</sub>SNa [M + Na]<sup>+</sup> 953.3789; found 953.3829.

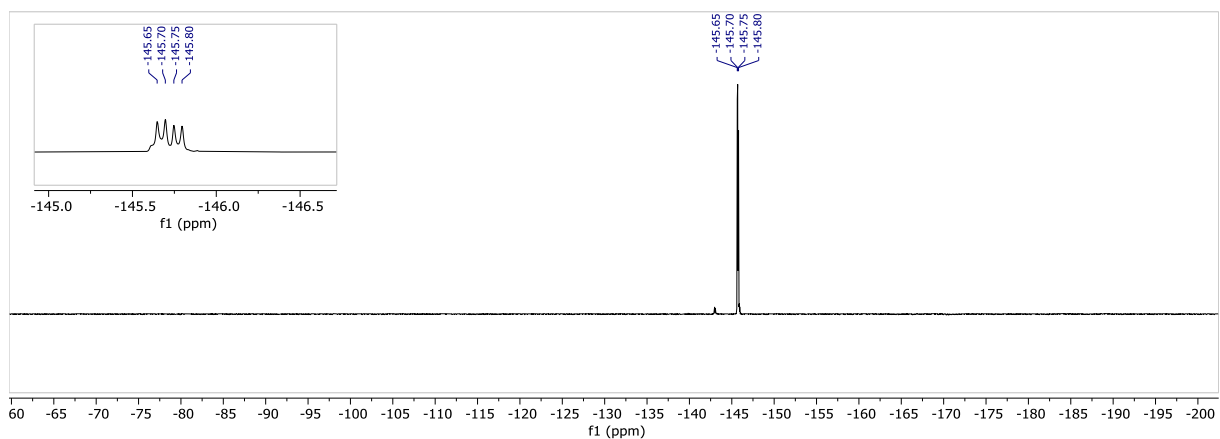
$^1\text{H}$  NMR (700 MHz,  $\text{CDCl}_3$ ) of **1b**:



$^{13}\text{C}$  NMR (176 MHz,  $\text{CDCl}_3$ ) of **1b**:

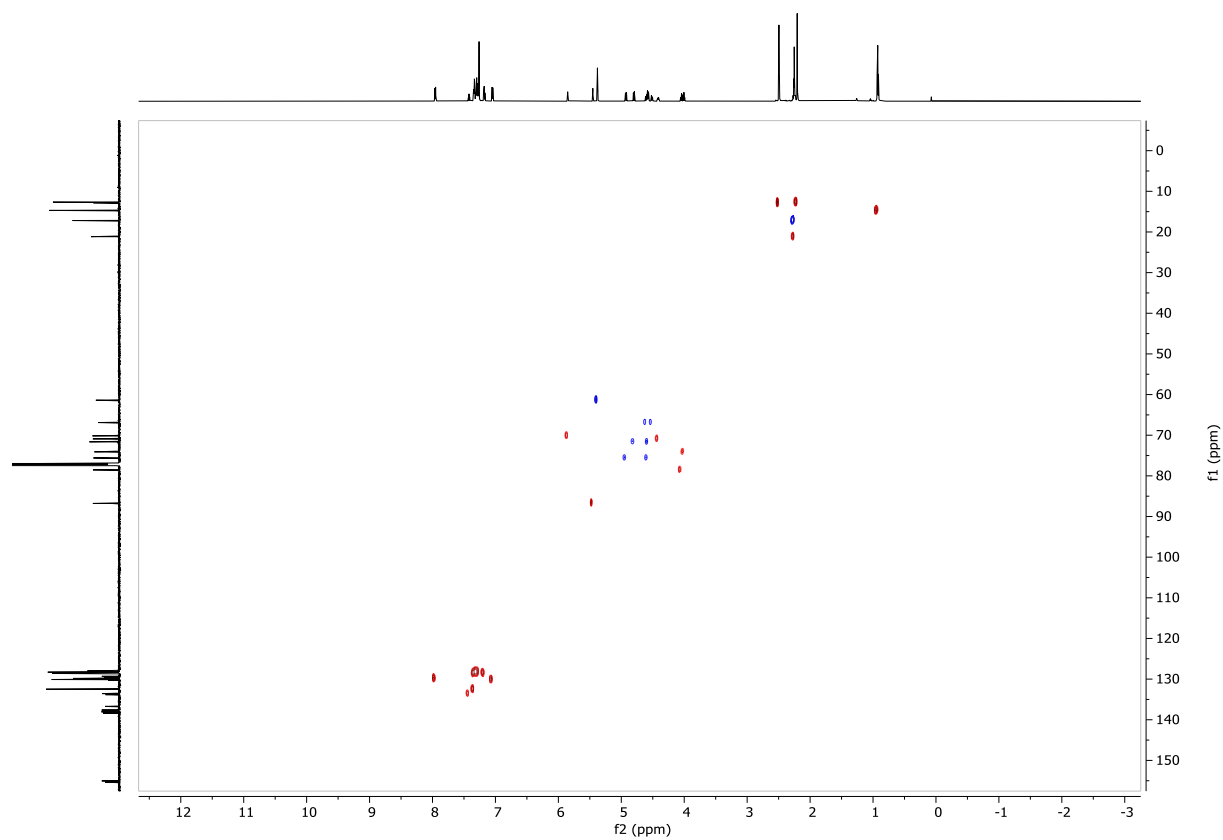


$^{19}\text{F}$  NMR (659 MHz,  $\text{CDCl}_3$ ) of **1b**:

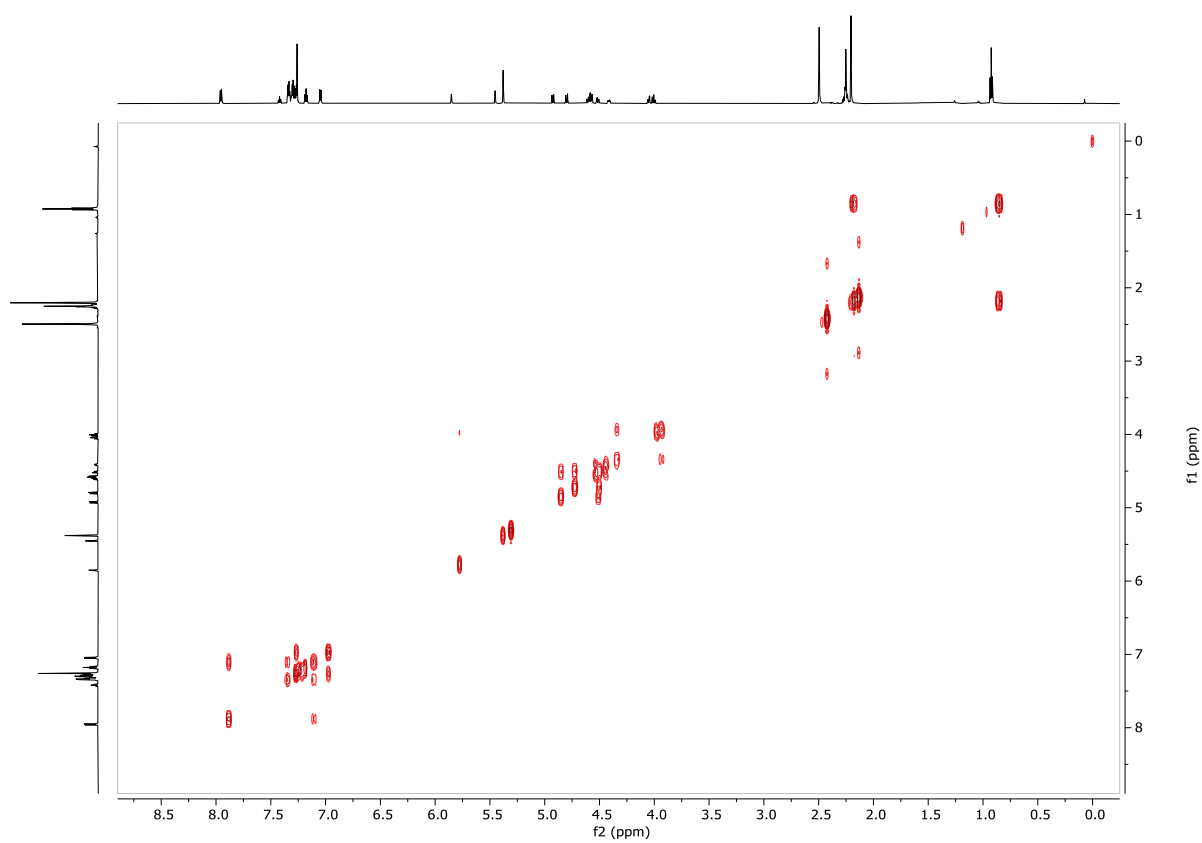




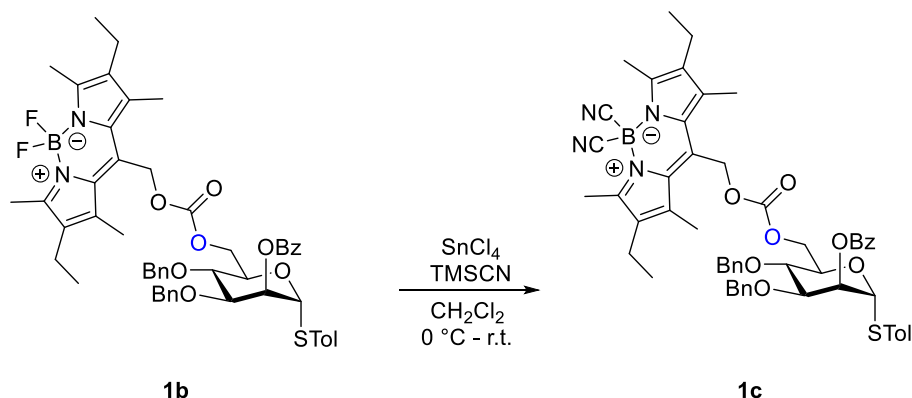
$^{13}\text{C}, ^1\text{H}$  HSQC of **1b**:



$^1\text{H}, ^1\text{H}$  COSY of **1b**:



***p*-Tolyl 2-*O*-benzoyl-3,4-di-*O*-benzyl-6-*O*-(8-(2,6-diethyl-4,4'-dicyano-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-*s*-indacenyl)methoxycarbonyl)-1-thio- $\alpha$ -D-mannopyranoside (**1c**)**



Tin tetrachloride (27  $\mu$ L, 1 M in  $\text{CH}_2\text{Cl}_2$ ) was added at 0  $^\circ\text{C}$  to a solution of **1b** (50 mg, 0.05 mmol, 1.0 equiv.) and trimethylsilyl cyanide (72  $\mu$ L, 0.54 mmol, 10.0 equiv.) in anhydrous  $\text{CH}_2\text{Cl}_2$  (2 mL). The reaction was stirred at room temperature for 2 h and was then quenched with water (1 mL). The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (3 x 20 mL) and washed with saturated aqueous  $\text{NaHCO}_3$  solution and water. The organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered, concentrated and the residue was purified by column chromatography (Hex:AcOEt 3:1) to obtain **1c** (49 mg, 0.05 mmol, 97%) as a red foam.

$R_f$  = 0.22 (Hex: AcOEt 3:1).

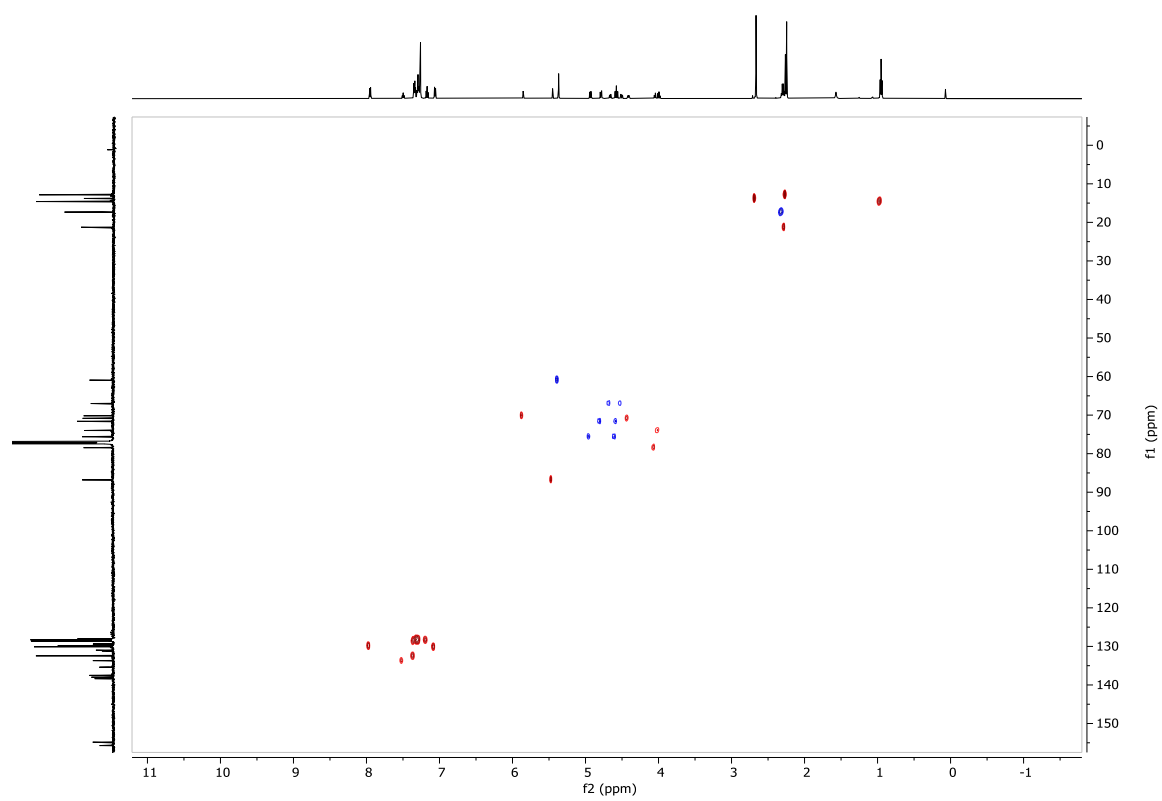
**$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):**  $\delta$  7.97 – 7.93 (m, 2H), 7.50 (tt,  $J$  = 7.5, 1.3 Hz, 1H), 7.38 – 7.32 (m, 4H), 7.32 – 7.26 (m, 8H), 7.17 (t,  $J$  = 7.7 Hz, 2H), 7.06 (d,  $J$  = 7.9 Hz, 2H), 5.85 (t,  $J$  = 2.4 Hz, 1H), 5.45 (d,  $J$  = 1.8 Hz, 1H), 5.37 (s, 2H), 4.93 (d,  $J$  = 10.8 Hz, 1H), 4.79 (d,  $J$  = 11.3 Hz, 1H), 4.66 (dd,  $J$  = 11.5, 2.3 Hz, 1H), 4.58 (t,  $J$  = 10.6 Hz, 2H), 4.51 (dd,  $J$  = 11.5, 3.7 Hz, 1H), 4.41 (dt,  $J$  = 10.0, 2.9 Hz, 1H), 4.05 (dd,  $J$  = 9.2, 2.8 Hz, 1H), 3.99 (t,  $J$  = 9.4 Hz, 1H), 2.66 (s, 6H), 2.30 (q,  $J$  = 7.6 Hz, 4H), 2.26 (s, 3H), 2.25 (s, 6H), 0.95 (t,  $J$  = 7.6 Hz, 6H) ppm.

**$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):**  $\delta$  165.5, 155.7, 154.8, 138.4, 138.2, 138.0, 137.5, 135.4, 133.7, 132.4, 131.2, 131.0, 130.1, 129.9, 129.6, 129.3, 128.6, 128.6, 128.3, 128.3, 128.2, 128.1, 128.0, 86.8, 78.4, 75.6, 74.0, 71.6, 70.8, 70.2, 67.0, 60.9, 21.3, 17.3, 14.6, 13.8, 12.8 ppm.

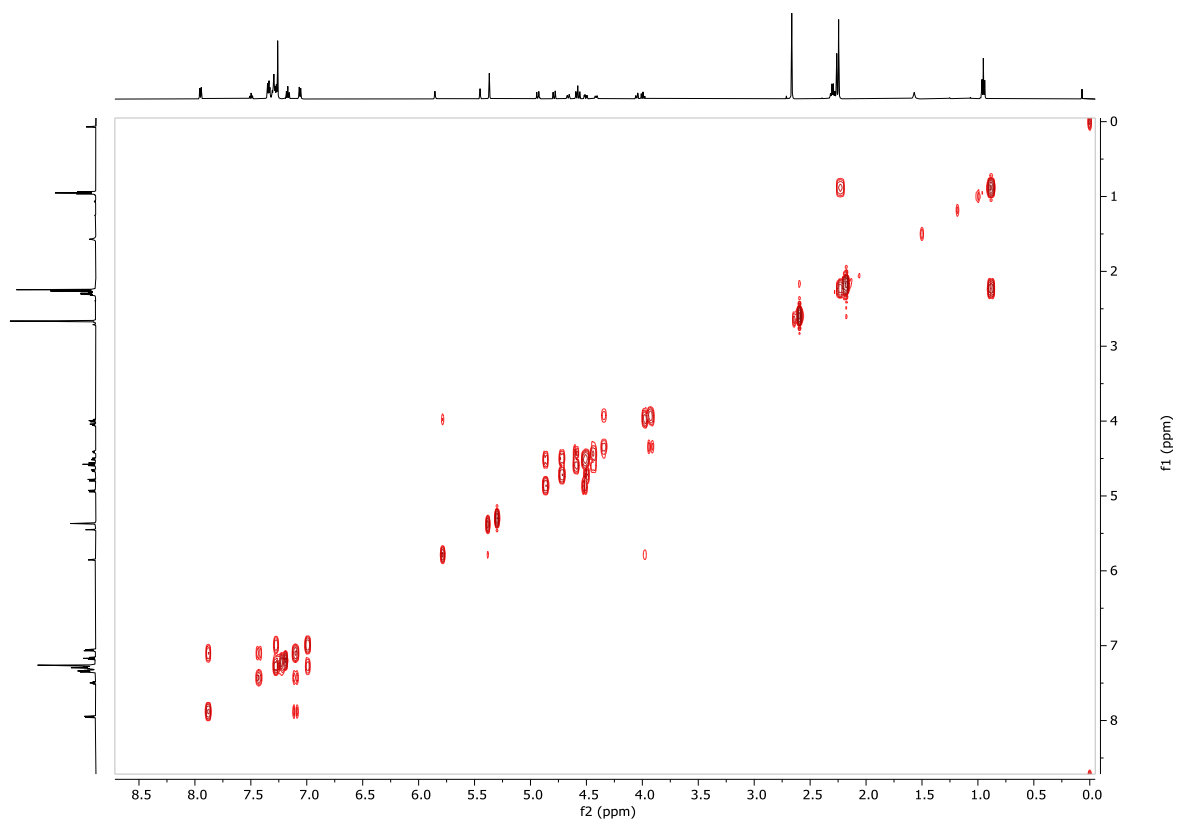
**HRMS (QToF):** Calcd for  $\text{C}_{55}\text{H}_{57}\text{BN}_4\text{O}_8\text{SNa}$  [ $\text{M} + \text{Na}$ ] $^+$  967.3882; found 967.3890.



$^{13}\text{C}, ^1\text{H}$  HSQC of **1c**:



$^1\text{H}, ^1\text{H}$  COSY of **1c**:



## 2.3 UV/Vis Spectra of 1a-c

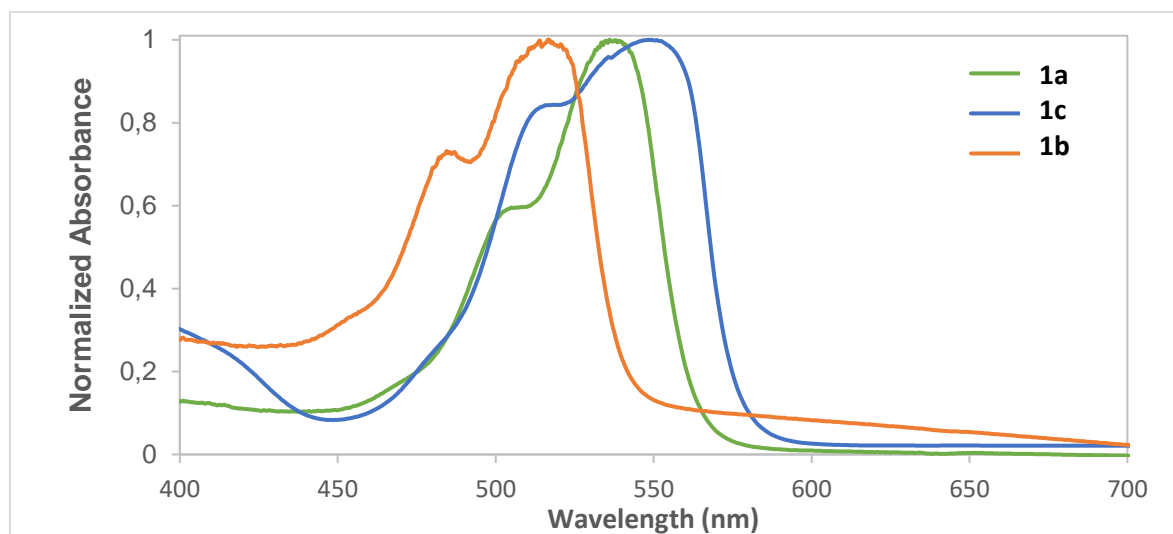
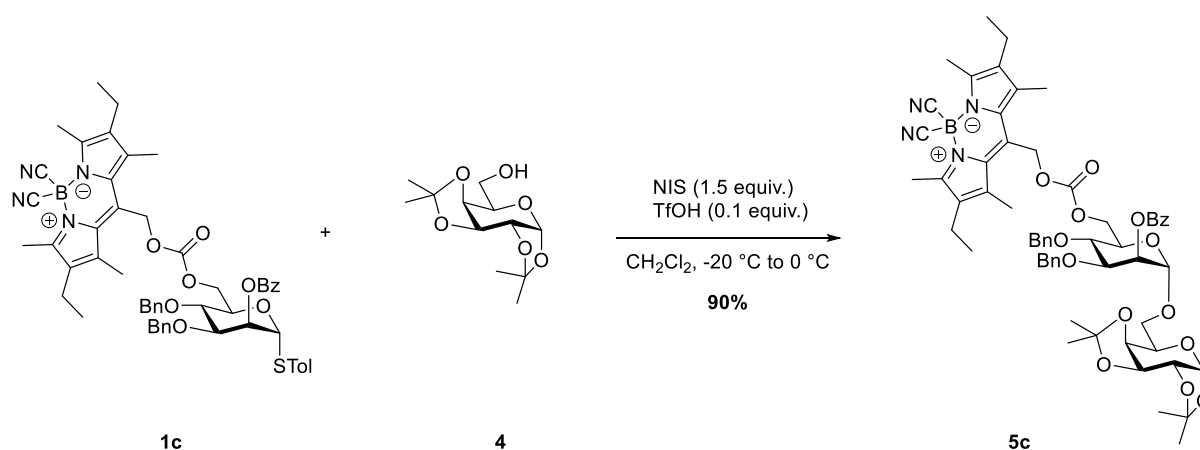


Figure S1. Normalized absorbance of 1a-c in MeOH/CHCl<sub>3</sub> (3:2).

## 3 Glycosylation Reactions

1,2:3,4-Bis-O-(1-methylethylidene)-6-O-[2-O-benzoyl-3,4-di-O-benzyl-6-O-{8-(2,6-diethyl-4,4'-dicyano-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacenyl)methoxycarbonyl}}- $\alpha$ -D-mannopyranosyl]- $\alpha$ -D-galactopyranoside (5c)



Donor **1c** (17.0 mg, 0.02 mmol, 1.0 equiv.) and **4** (4.7 mg, 0.02 mmol, 1.0 equiv.) were co-evaporated with anhydrous toluene (3 x 2 mL) and kept under high vacuum for two hours. Anhydrous CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added and the mixture was stirred over activated molecular sieves (3 Å-AW) for 30 minutes at room temperature. The solution was cooled to -20 °C and NIS (6.1 mg, 0.03 mmol, 1.5 equiv.) was added followed by TfOH (20  $\mu$ L of a 1% solution in CH<sub>2</sub>Cl<sub>2</sub>, 2  $\mu$ mol, 0.1 equiv.) and the mixture was stirred for three hours, while it was allowed to warm up to 0 °C. The reaction mixture was quenched with pyridine, diluted with CH<sub>2</sub>Cl<sub>2</sub>, filtered

and was then washed with 10% Na<sub>2</sub>SO<sub>3</sub> (10 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by column chromatography (Hex:AcOEt 3:1 to 1:1) to obtain **5c** (17.5 mg, 0.02 mmol, 90%) as a red foam.

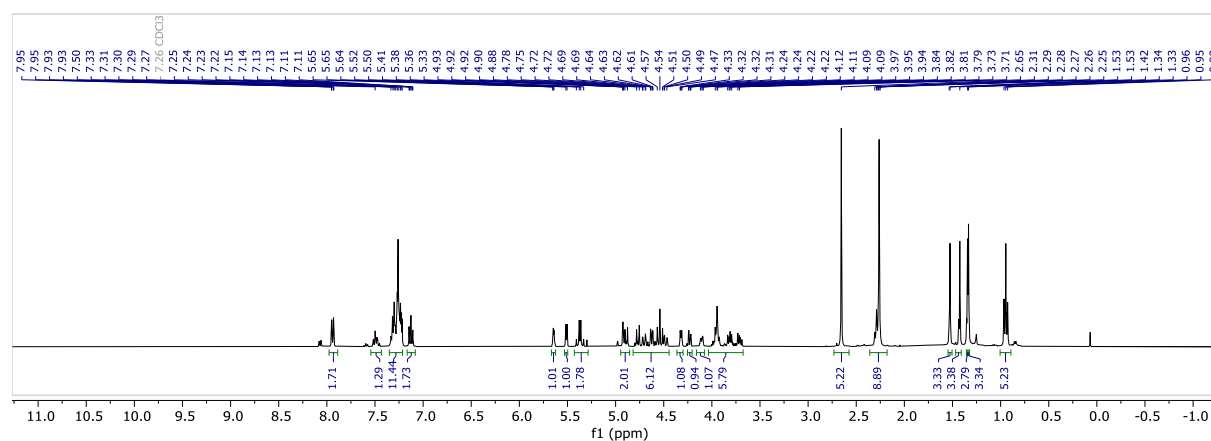
R<sub>f</sub> = 0.10 (Hex: AcOEt 3:1).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):** δ 7.94 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.50 (s, 1H), 7.38 – 7.19 (m, 10H), 7.17 – 7.08 (m, 2H), 5.68 – 5.61 (m, 1H), 5.51 (d, *J* = 5.0 Hz, 1H), 5.43 – 5.28 (m, 2H), 4.95 – 4.84 (m, 2H), 4.82 – 4.44 (m, 6H), 4.32 (dd, *J* = 5.0, 2.4 Hz, 1H), 4.23 (dd, *J* = 7.9, 1.9 Hz, 1H), 4.16 – 4.07 (m, 1H), 4.02 – 3.67 (m, 5H), 2.65 (s, 6H), 2.35 – 2.21 (m, 10H), 1.53 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H), 0.95 (t, *J* = 7.6 Hz, 6H) ppm.

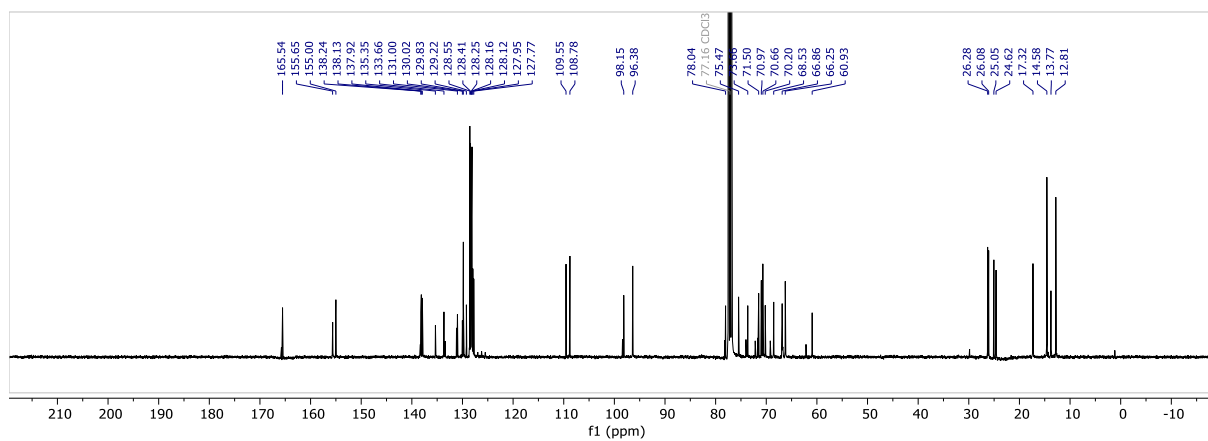
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):** δ 165.5, 155.7, 155.0, 138.2, 138.1, 137.9, 135.3, 133.7, 131.0, 130.0, 129.8, 129.2, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 109.5, 108.8, 98.1, 96.4, 78.0, 75.5, 73.7, 71.5, 71.0, 70.7, 70.2, 68.5, 66.9, 66.2, 60.9, 26.3, 26.1, 25.0, 24.6, 17.3, 14.6, 13.8, 12.8 ppm.

**HRMS (QToF):** Calcd for C<sub>60</sub>H<sub>69</sub>BN<sub>4</sub>O<sub>14</sub>Na [M + Na]<sup>+</sup> 1103.4796; found 1103.4791.

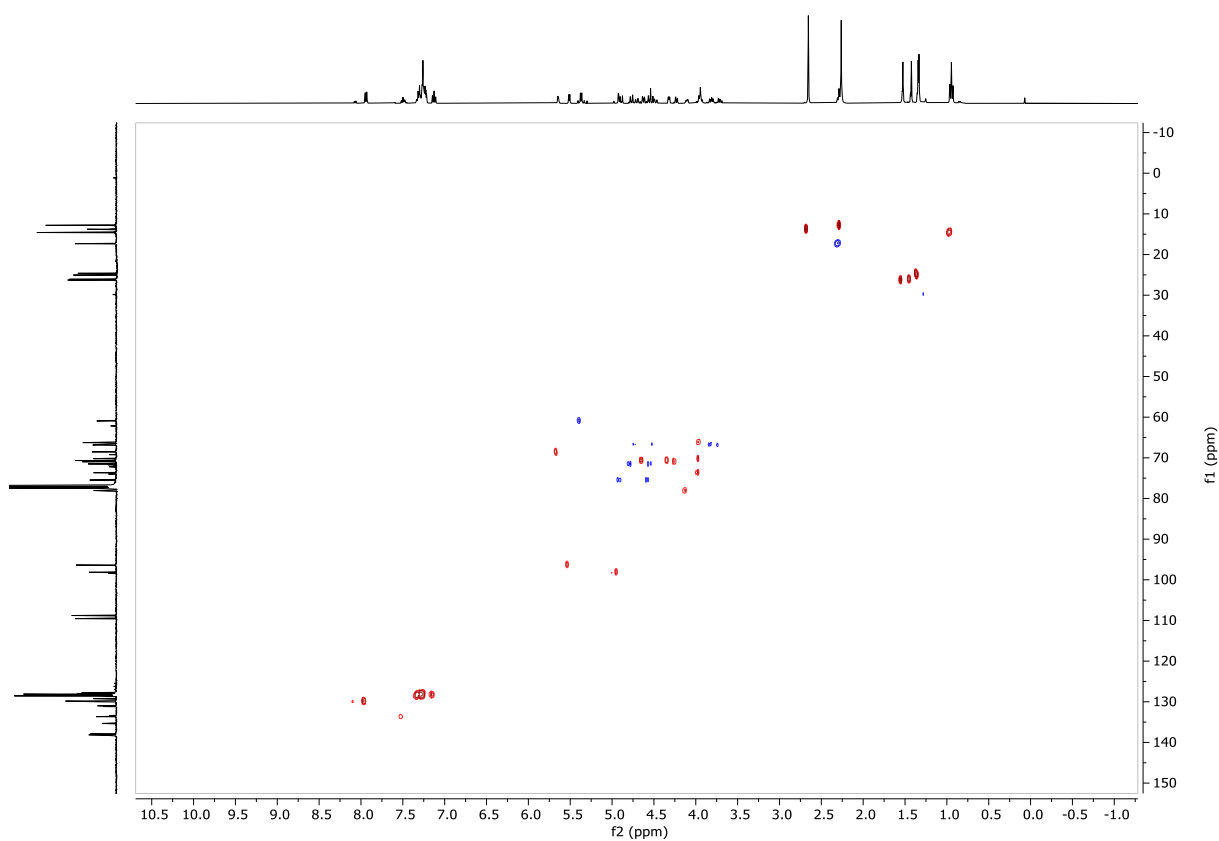
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of **5c**:**



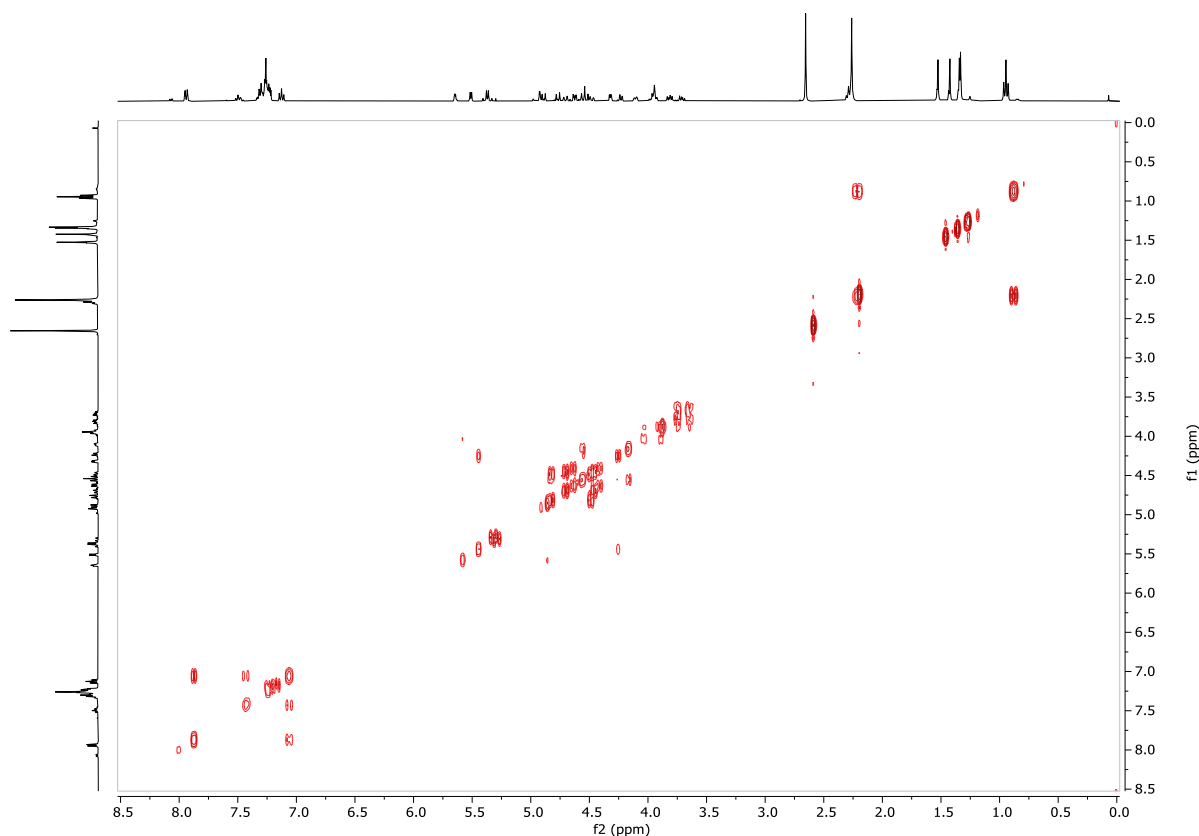
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **5c**:



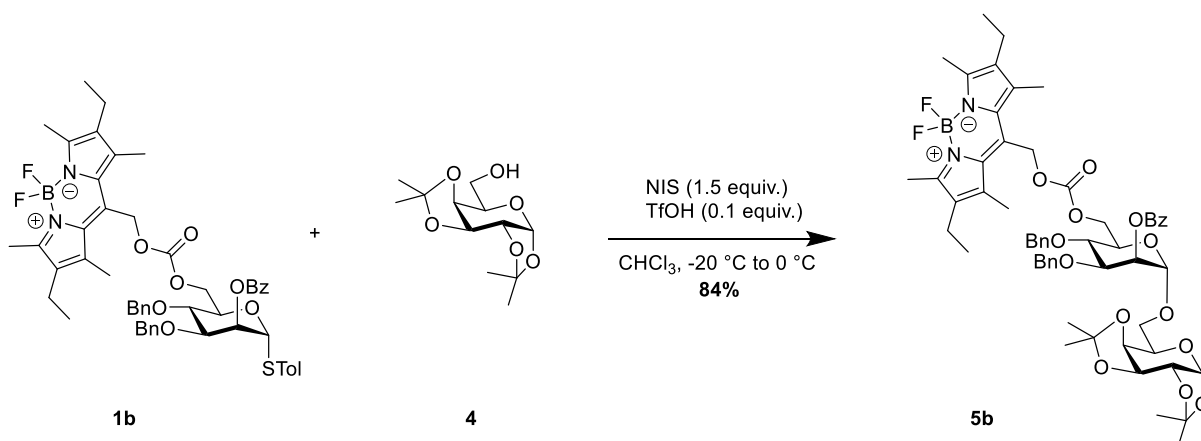
$^{13}\text{C}, ^1\text{H}$  HSQC of **5c**:



$^1\text{H}, ^1\text{H}$  COSY of **5c**:



**1,2:3,4-Bis-O-(1-methylethylidene)-6-O-[2-O-benzoyl-3,4-di-O-benzyl-6-O-(8-(2,6-diethyl-4,4'-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacenyl)methoxycarbonyl)}- $\alpha$ -D-mannopyranosyl]- $\alpha$ -D-galactopyranoside (**5b**)**



Donor **1b** (28.0 mg, 0.03 mmol, 1.0 equiv.) and **4** (8.6 mg, 0.03 mmol, 1.0 equiv.) were co-evaporated with anhydrous toluene (3 x 2 mL) and kept under high vacuum for two hours. Anhydrous  $\text{CH}_2\text{Cl}_2$  (3 mL) was added and the mixture was stirred over activated molecular sieves (3 Å-AW) for 30 minutes at room temperature. The solution was cooled to  $-20\text{ }^\circ\text{C}$  and NIS (10.2 mg, 0.05 mmol, 1.5 equiv.) was added followed by TfOH (27  $\mu\text{L}$  of a 1% solution in  $\text{CH}_2\text{Cl}_2$ , 3  $\mu\text{mol}$ , 0.1 equiv.) and the mixture was stirred for one hour, while it was allowed to



warm up to 0 °C. The reaction mixture was quenched with pyridine, diluted with CH<sub>2</sub>Cl<sub>2</sub>, filtered and was then washed with 10% Na<sub>2</sub>SO<sub>3</sub> (10 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by column chromatography (Hex:AcOEt 9:1 to 3:1) to obtain **5b** (27 mg, 0.02 mmol, 84%) as a red foam.

$R_f = 0.18$  (Hex: AcOEt 3:1).

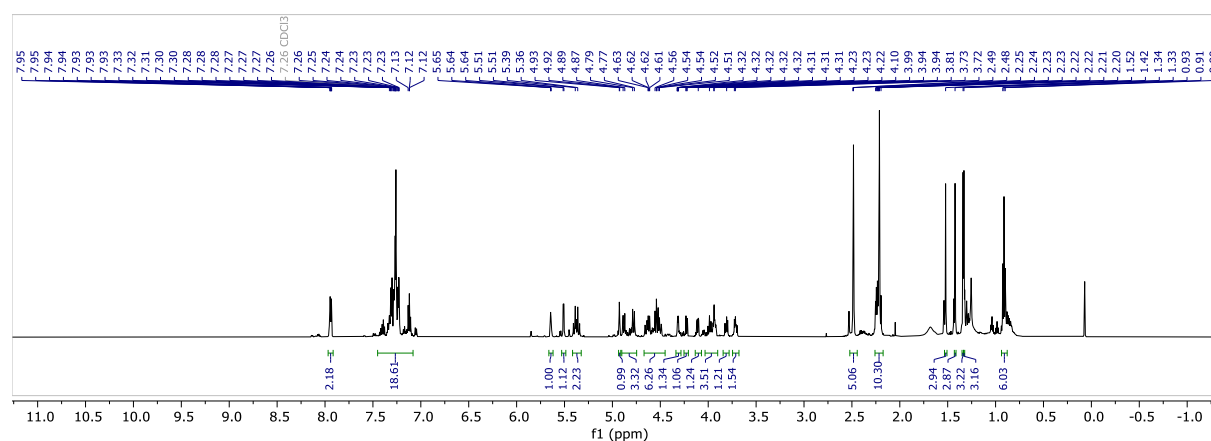
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):** δ 7.98 – 7.89 (m, 2H), 7.44 – 7.08 (m, 13H), 5.66 – 5.62 (m, 1H), 5.51 (d,  $J = 4.9$  Hz, 1H), 5.43 – 5.32 (m, 2H), 4.93 (d,  $J = 2.2$  Hz, 1H), 4.90 – 4.74 (m, 3H), 4.70 – 4.46 (m, 5H), 4.32 (ddd,  $J = 5.0, 2.5, 0.8$  Hz, 1H), 4.22 (dd,  $J = 7.9, 1.8$  Hz, 1H), 4.11 (dd,  $J = 9.4, 2.8$  Hz, 1H), 4.03 – 3.89 (m, 2H), 3.81 (dd,  $J = 10.4, 6.4$  Hz, 1H), 3.75 – 3.68 (m, 1H), 2.48 (s, 6H), 2.27 – 2.17 (m, 10H), 1.52 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H), 0.91 (t,  $J = 7.7$  Hz, 6H) ppm.

**<sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>):** δ 165.6, 155.3, 155.2, 138.2, 138.0, 136.7, 133.8, 133.5, 132.5, 129.8, 129.1, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 109.6, 108.8, 98.1, 96.4, 78.1, 75.5, 73.7, 71.5, 71.0, 70.7, 70.3, 68.4, 66.8, 66.6, 66.2, 61.4, 26.3, 26.1, 25.0, 24.6, 17.2, 14.7, 12.6 ppm.

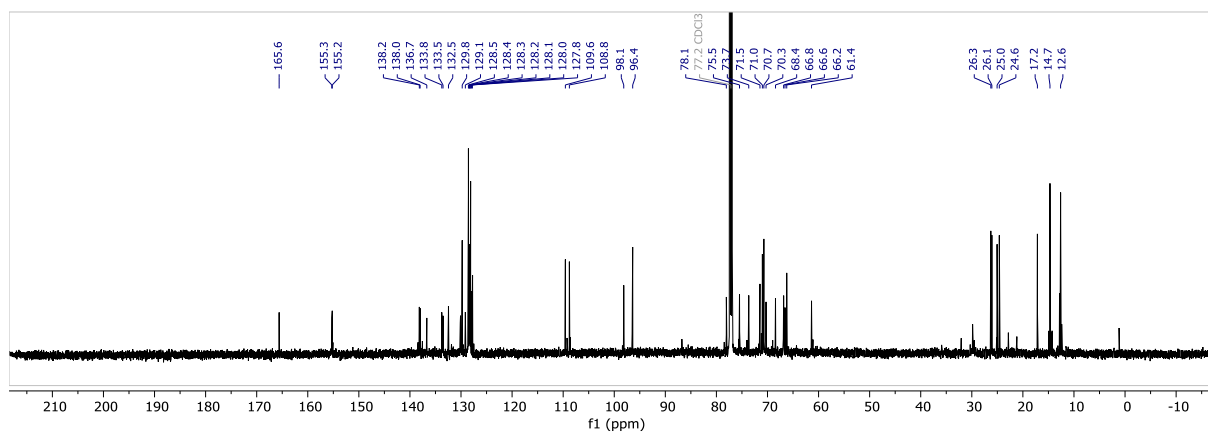
**<sup>19</sup>F NMR (564 MHz, CDCl<sub>3</sub>):** δ -145.71 (dd,  $J = 65.4, 31.1$  Hz) ppm.

**HRMS (QToF):** Calcd for C<sub>58</sub>H<sub>69</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>14</sub>Na [M + Na]<sup>+</sup> 1089.4702; found 1089.5118.

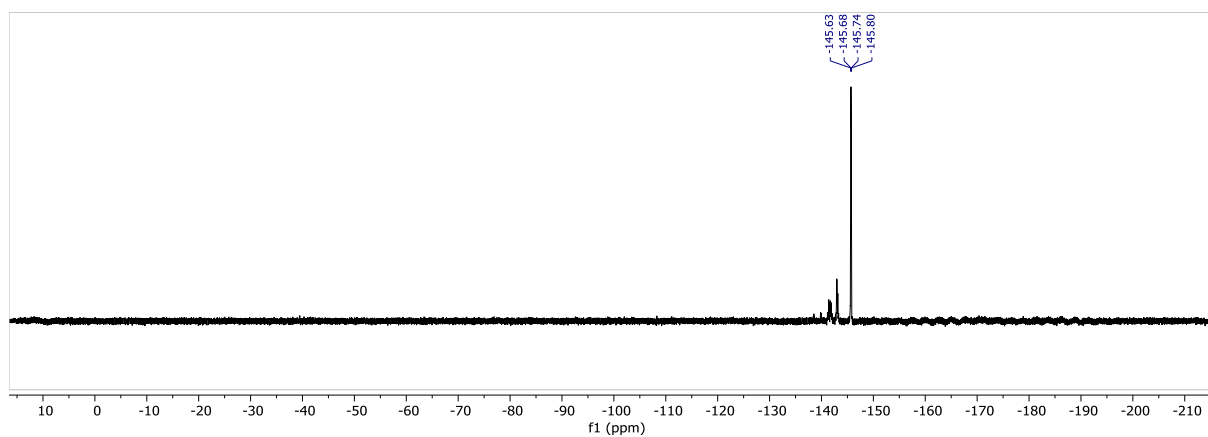
**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) of **5b**:**



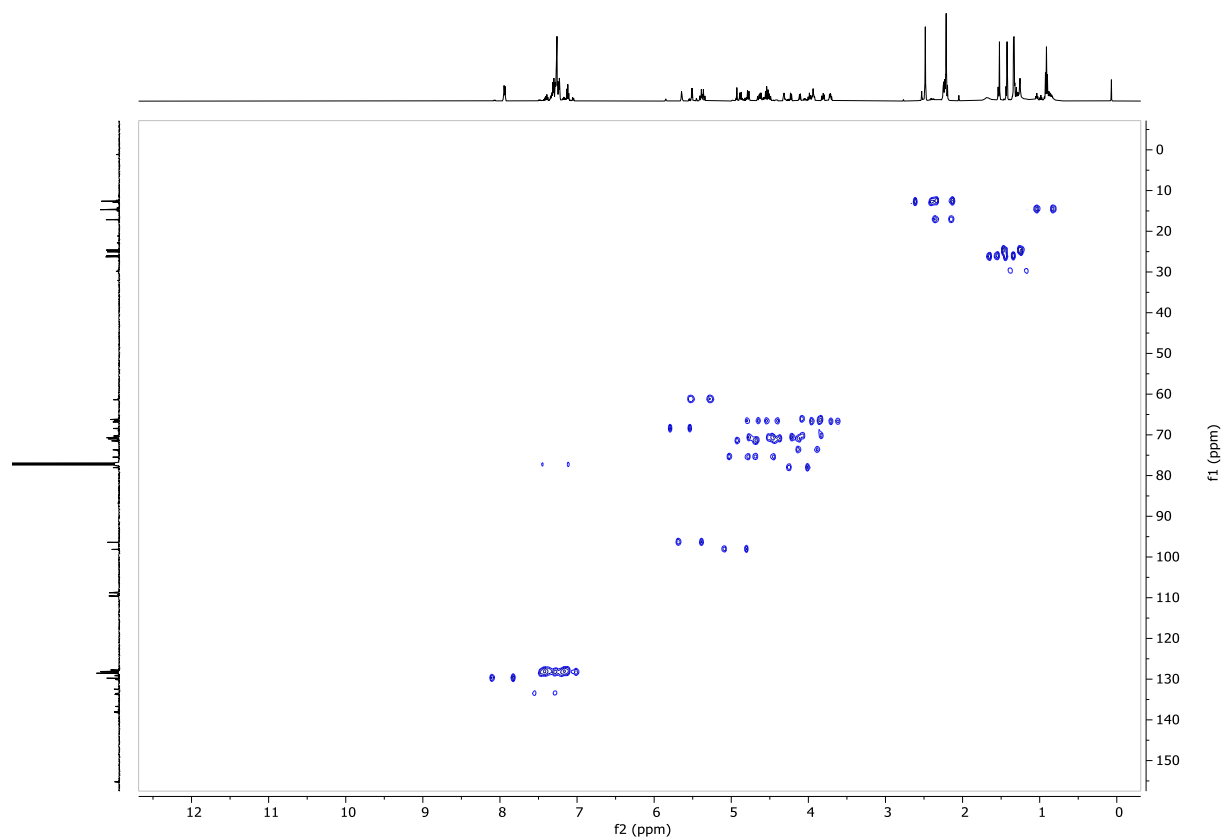
$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **5b**:



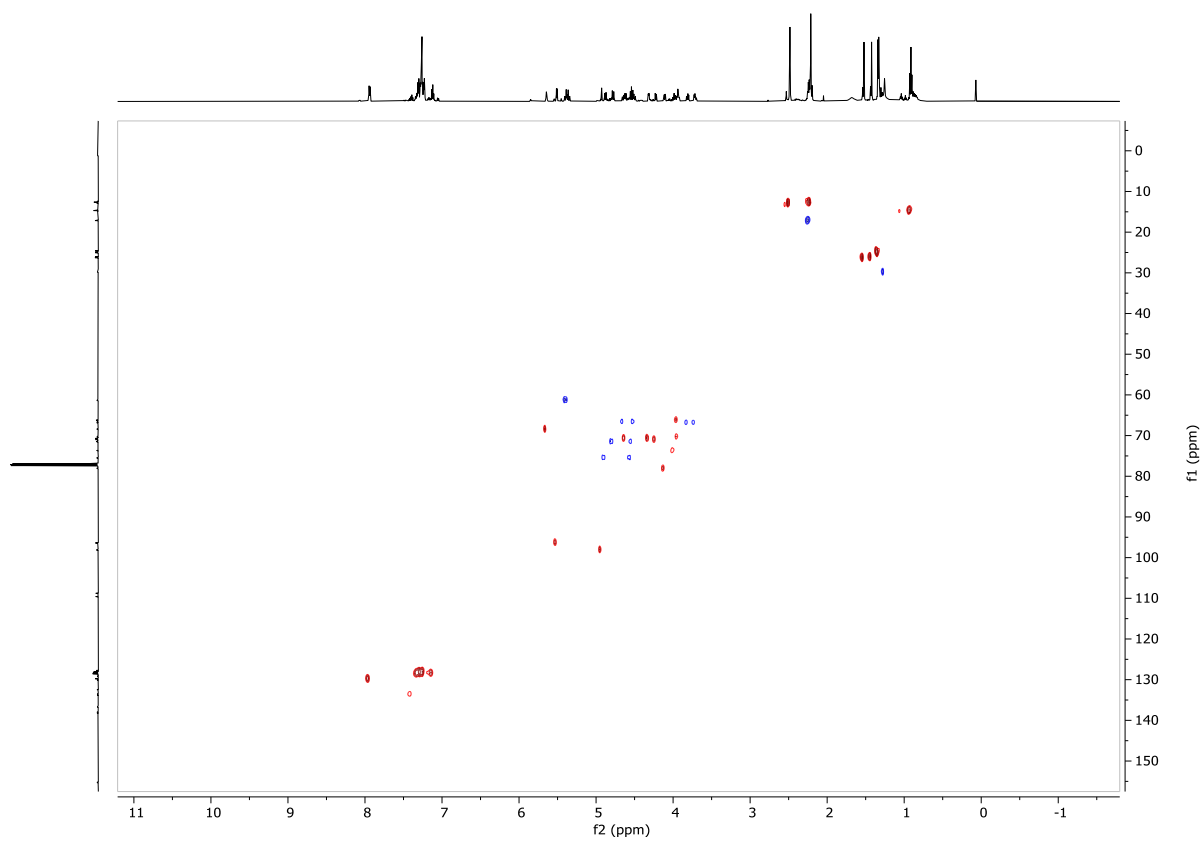
$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) of **5b**:



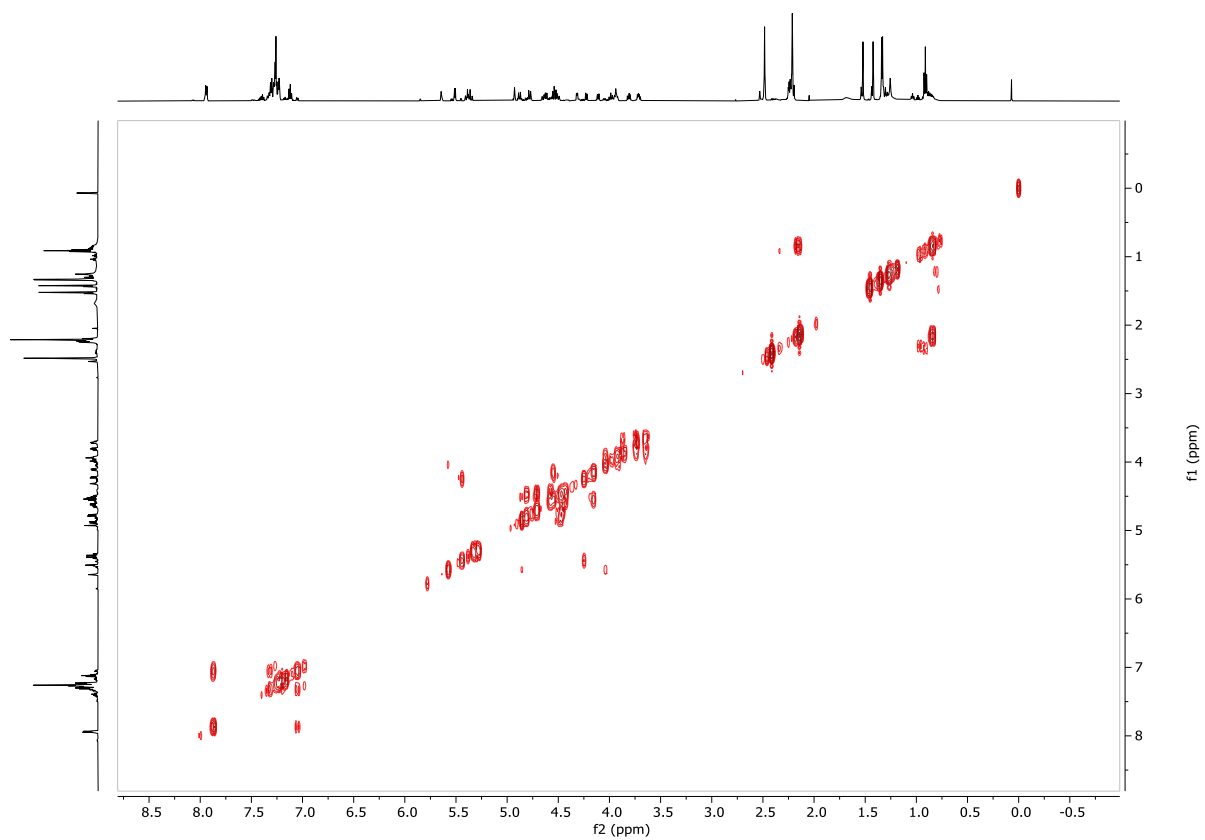
Coupled  $^{13}\text{C}, ^1\text{H}$  HSQC of **5b**:



$^{13}\text{C}, ^1\text{H}$  HSQC of **5b**:

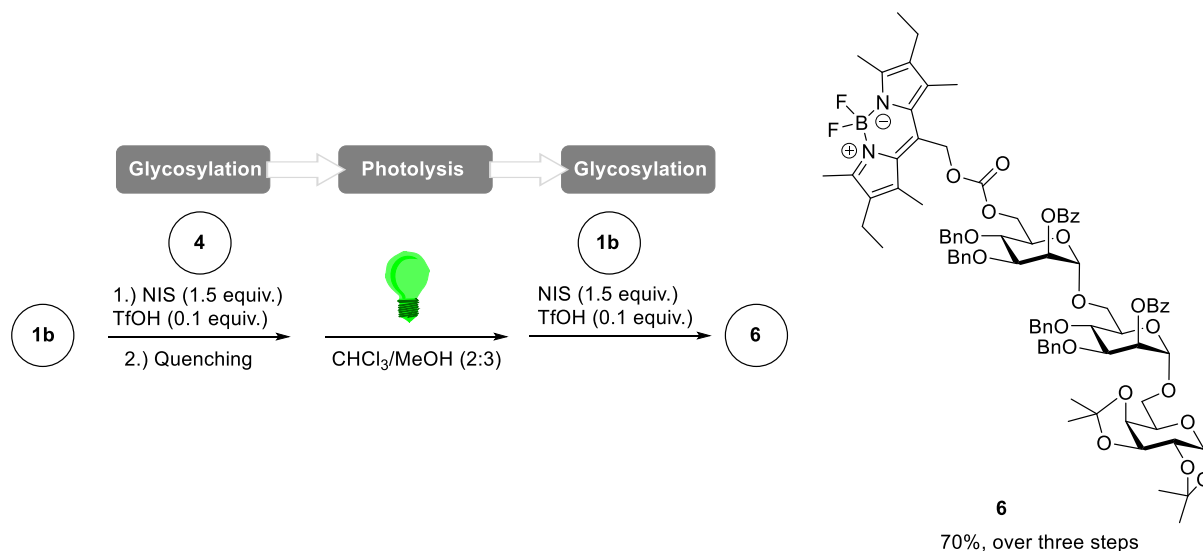


$^1\text{H}, ^1\text{H}$  COSY of **5b**:



## 4 Consecutive Glycan Assembly

**2-O-benzoyl-3,4-di-O-benzyl-6-O-(8-(2,6-diethyl-4,4'-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacenyl)methoxycarbonyl)- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 6)-2-O-benzoyl-3,4-di-O-benzyl-6-O- $\alpha$ -D-mannopyranosyl-(1 $\rightarrow$ 6)-1,2:3,4-bis-O-(1-methylethylidene)- $\alpha$ -D-galactopyranoside (6)**



Donor **1b** (28.0 mg, 0.03 mmol, 1.0 equiv.) and **4** (8.6 mg, 0.03 mmol, 1.0 equiv.) were co-evaporated with anhydrous toluene (3 x 2 mL) and kept under high vacuum for two hours. Anhydrous CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added and the solution was cooled to -20 °C. NIS (18.2 mg, 0.08 mmol, 1.5 equiv.) was added followed by TfOH (48  $\mu$ L of a 1% solution in CH<sub>2</sub>Cl<sub>2</sub>, 5  $\mu$ mol, 0.1 equiv.) and the mixture was stirred for one hour, while it was allowed to warm up to 0 °C. The reaction mixture was quenched with pyridine, filtered and volatiles were removed under reduced pressure. The residue was redissolved in 5 mL of CHCl<sub>3</sub>/MeOH (2:3) and was stirred for 3 h irradiated by green light from an LED lamp. Volatiles were removed under reduced pressure, donor **1b** (65 mg, 0.07 mmol, 1.3 equiv.) was added and the residue co-evaporated with anhydrous toluene (3 x 2 mL). Anhydrous CH<sub>2</sub>Cl<sub>2</sub> (4 mL) was added and the solution was cooled to -20 °C. NIS (18.2 mg, 0.08 mmol, 1.5 equiv.) was added followed by TfOH (48  $\mu$ L of a 1% solution in CH<sub>2</sub>Cl<sub>2</sub>, 5  $\mu$ mol, 0.1 equiv.) and the mixture was stirred for one hour, while it was allowed to warm up to 0 °C. The reaction mixture was quenched with pyridine, filtered and washed with 10% Na<sub>2</sub>SO<sub>3</sub> (10 mL). The aqueous phase was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 10 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. The residue was purified by column chromatography (Hex:AcOEt 9:1 to 3:1) to obtain **6** (57 mg, 0.04 mmol, 70%) as a red foam.

$R_f$  = 0.17 (Hex: AcOEt 3:1).

**<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):**  $\delta$  8.16 – 8.12 (m, 2H), 7.94 (dt,  $J$  = 8.4, 1.4 Hz, 2H), 7.52 – 7.47 (m, 3H), 7.40 – 7.01 (m, 23H), 5.78 (t,  $J$  = 2.5 Hz, 1H), 5.71 (dd,  $J$  = 3.3, 1.8 Hz, 1H), 5.51 (dd,

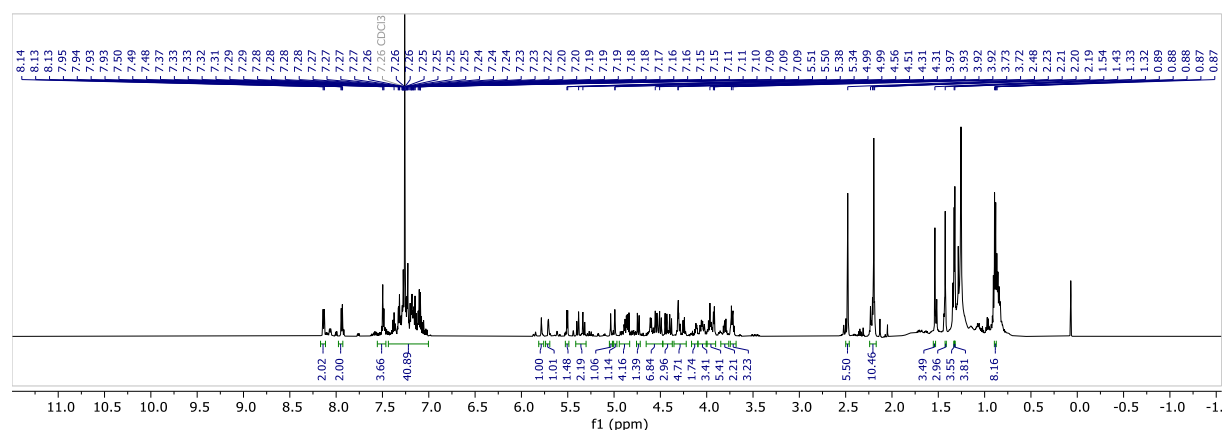
$J = 5.1, 1.9$  Hz, 1H), 5.42 – 5.31 (m, 2H), 5.04 (d,  $J = 2.1$  Hz, 1H), 4.99 (d,  $J = 1.8$  Hz, 1H), 4.91 – 4.83 (m, 3H), 4.74 (d,  $J = 11.4$  Hz, 1H), 4.65 – 4.49 (m, 4H), 4.41 (dd,  $J = 30.0, 11.4$  Hz, 2H), 4.35 – 4.23 (m, 3H), 4.11 (d,  $J = 5.6$  Hz, 1H), 4.09 – 4.02 (m, 2H), 4.01 – 3.91 (m, 3H), 3.84 – 3.78 (m, 2H), 3.72 (dt,  $J = 10.3, 5.7$  Hz, 3H), 2.48 (s, 6H), 2.20 (d,  $J = 8.4$  Hz, 10H), 1.54 (s, 3H), 1.43 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H), 0.91 – 0.85 (m, 6H) ppm.

**$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ):**  $\delta$  165.8, 165.4, 155.3, 155.2, 138.5, 138.3, 138.1, 137.7, 136.7, 133.8, 133.5, 133.5, 132.5, 130.1, 130.0, 129.8, 128.8, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 128.1, 127.8, 127.8, 127.6, 127.5, 109.6, 108.8, 98.4, 98.1, 96.4, 78.7, 77.8, 75.4, 75.2, 74.2, 73.5, 71.8, 71.0, 71.0, 70.7, 70.4, 69.0, 68.0, 66.6, 66.3, 66.1, 61.4, 32.1, 29.9, 26.3, 26.1, 25.0, 24.6, 22.8, 17.1, 14.7, 14.3, 12.8, 12.6 ppm.

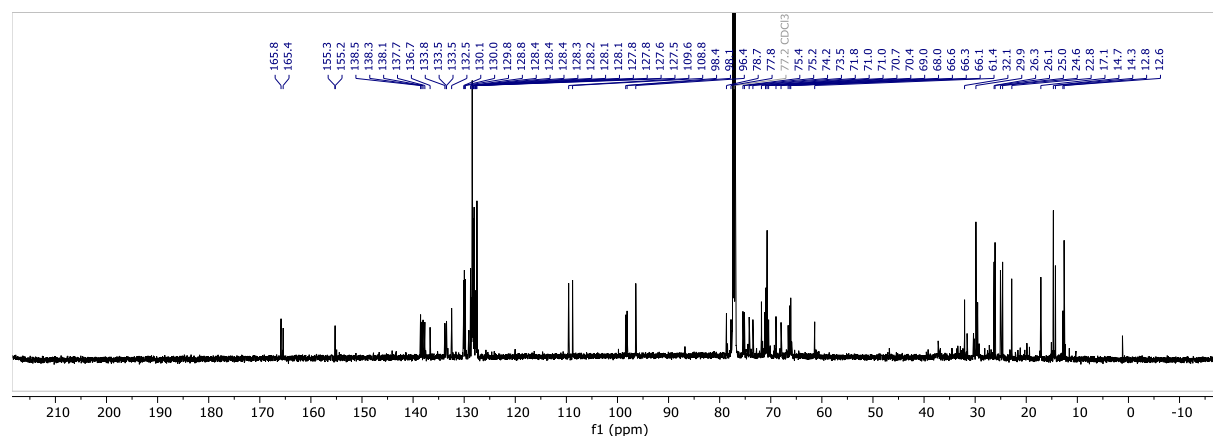
**$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ):**  $\delta$  -145.69 (dd,  $J = 65.6, 30.2$  Hz) ppm.

**HRMS (QToF):** Calcd for  $\text{C}_{85}\text{H}_{95}\text{BF}_2\text{N}_2\text{O}_{20}\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  1535.6432; found 1535.6710.

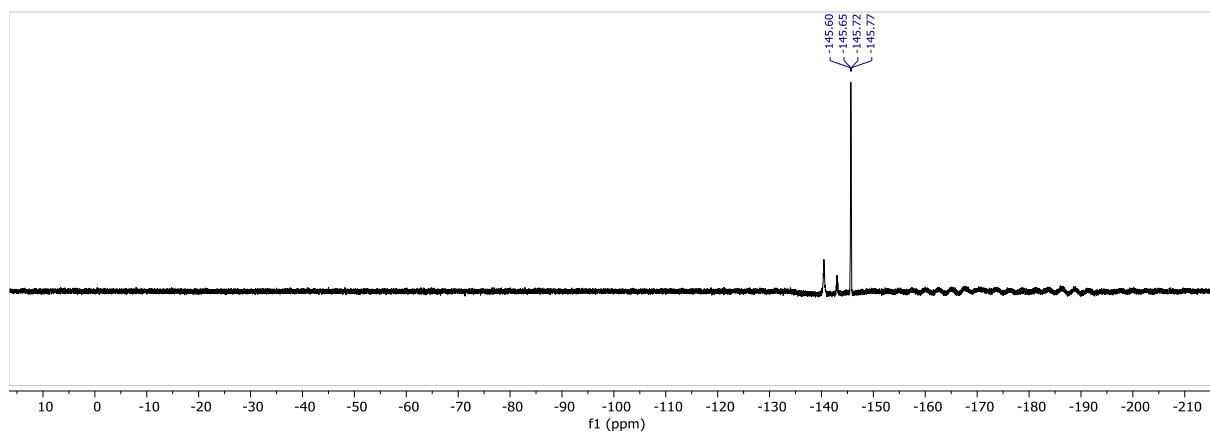
**$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ) of **6**:**



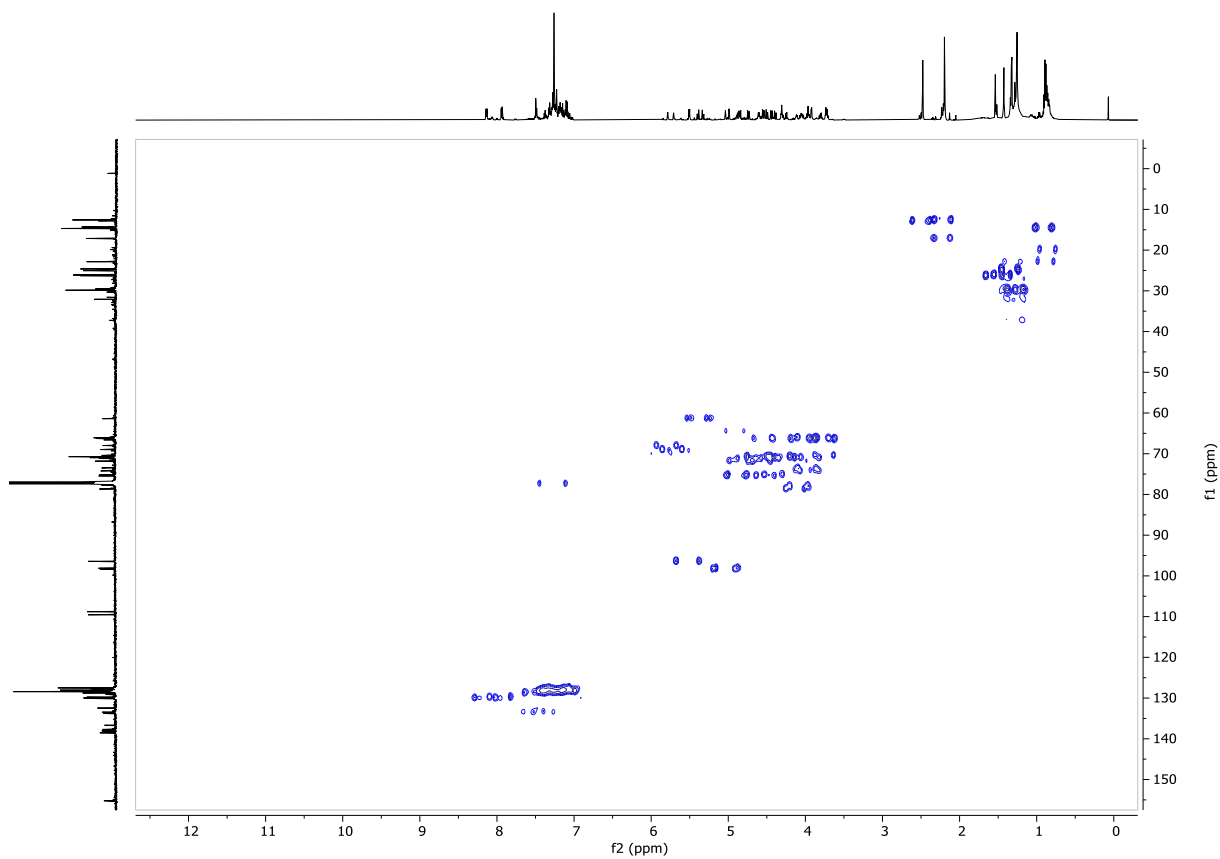
**$^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ ) of **6**:**



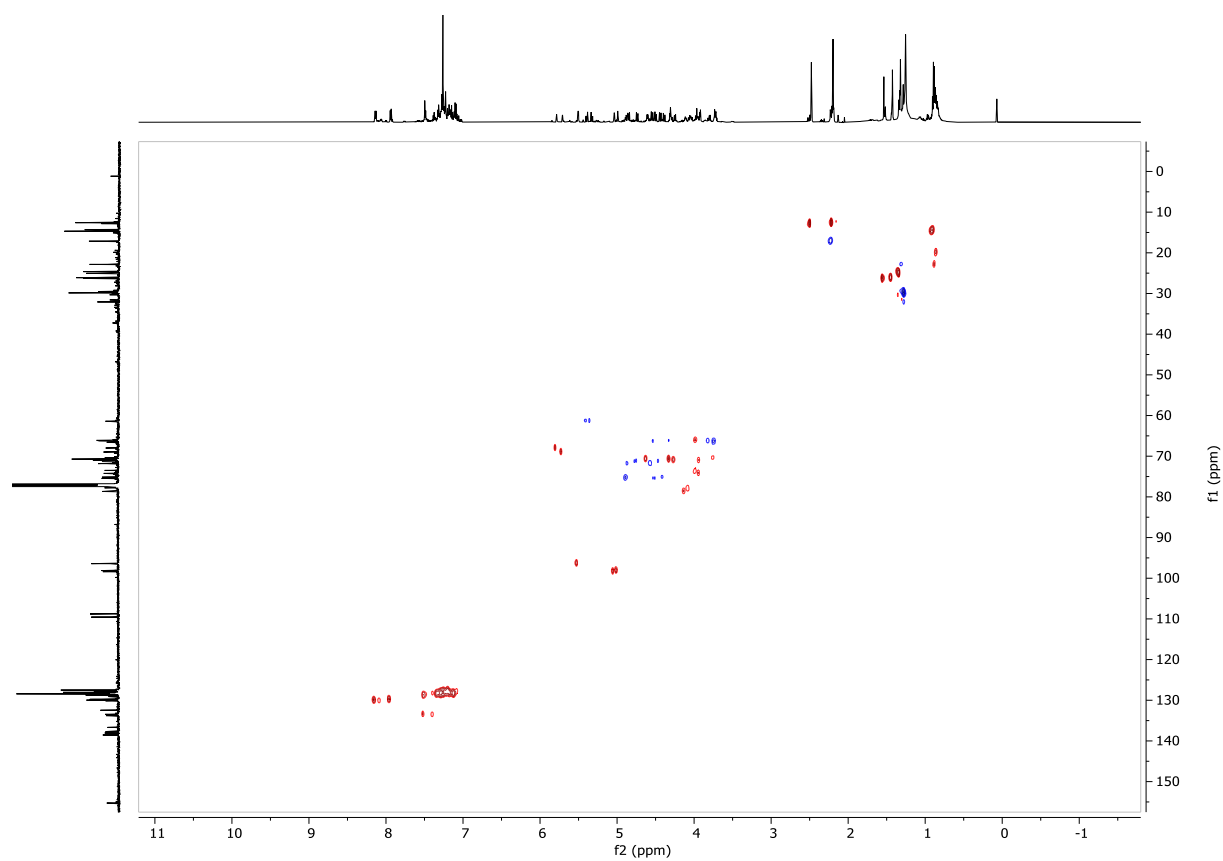
$^{19}\text{F}$  NMR (564 MHz,  $\text{CDCl}_3$ ) of **6**:



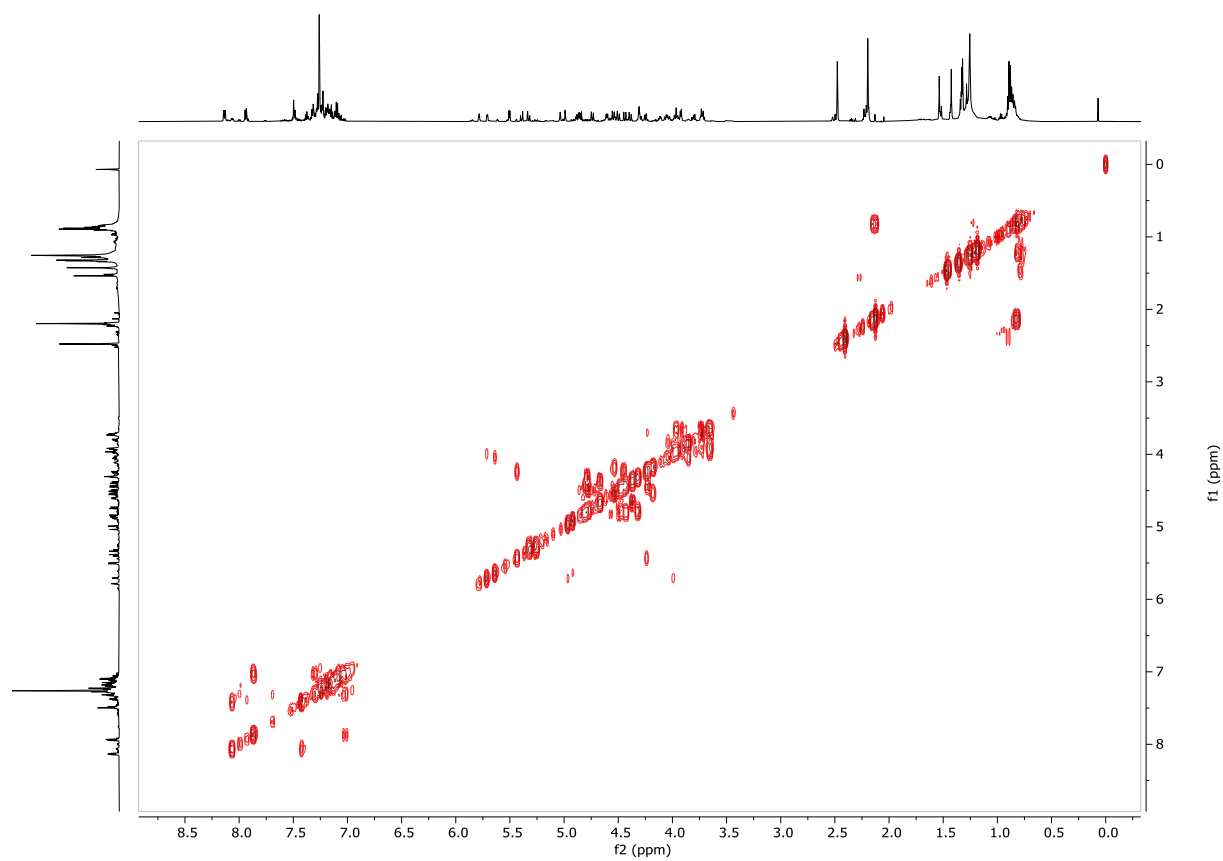
Coupled  $^{13}\text{C}$ ,  $^1\text{H}$  HSQC of **6**:



$^{13}\text{C}, ^1\text{H}$  HSQC of **6**:



$^1\text{H}, ^1\text{H}$  COSY of **6**:

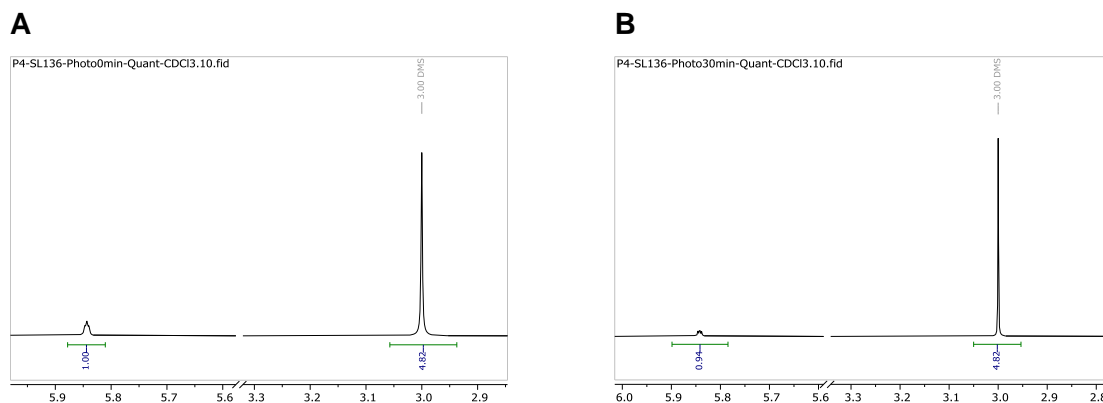




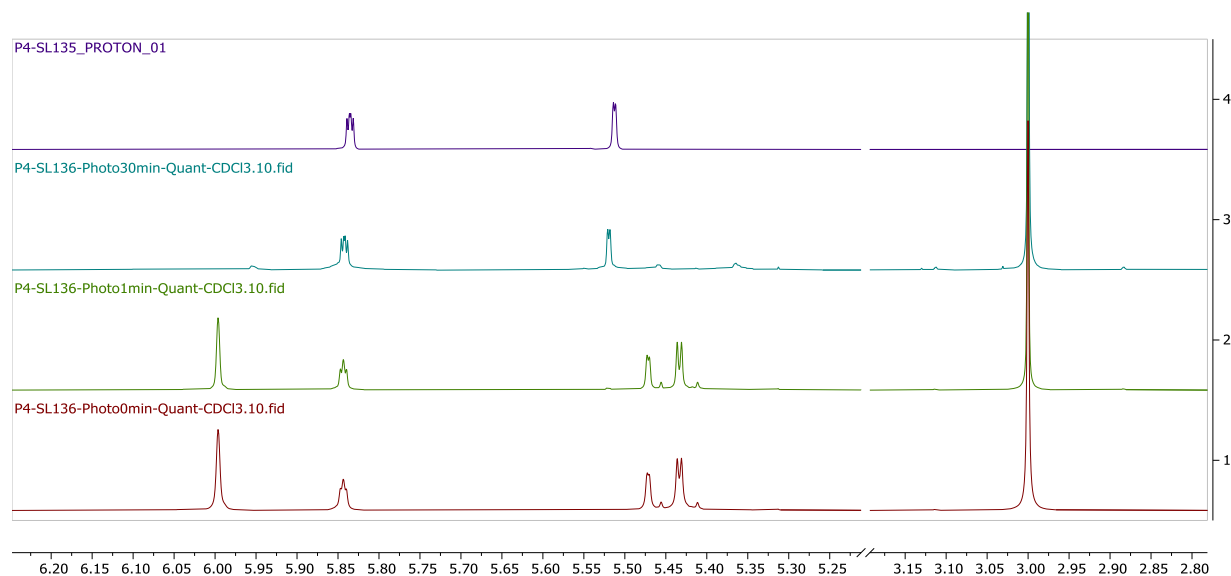
## 5 Quantitative Photo-De protections Followed by $^1\text{H}$ NMR

### 5.1 Photodeprotection of S14

#### Photodeprotection of S14 in $\text{CDCl}_3$ (500 W halogen lamp)

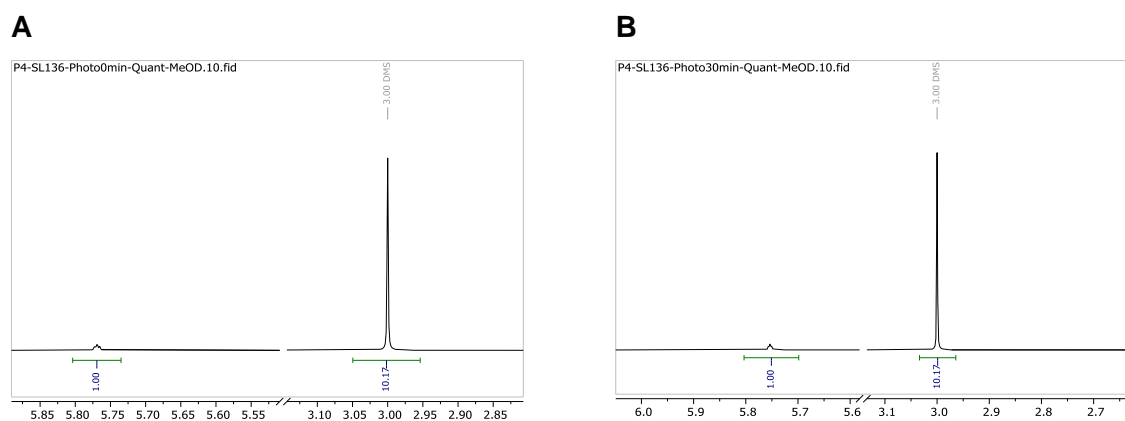


**Figure S2.** (A) Extract from  $^1\text{H}$ -NMR-spectrum in  $\text{CDCl}_3$  of **S14** before photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of **S14** (1H). (B) Extract from  $^1\text{H}$ -NMR-spectrum in  $\text{CDCl}_3$  of deprotected **S14** after 30 min photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of deprotected **S14** (1H) results in a yield of 94%.

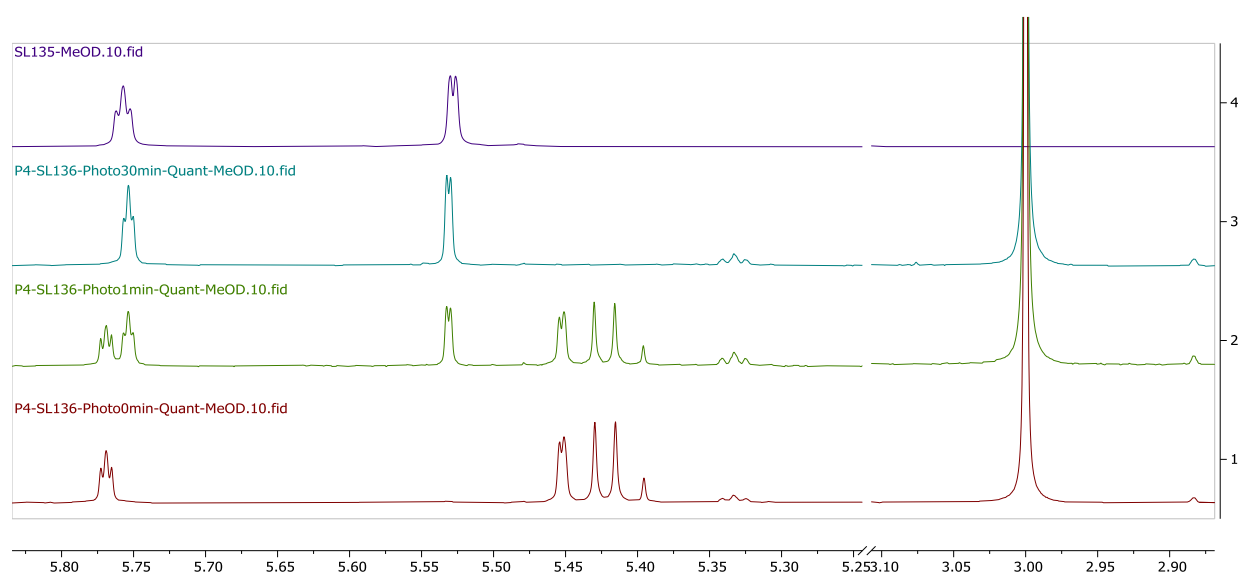


**Figure S3.** Zoom of stacked  $^1\text{H}$ -NMR-spectra in  $\text{CDCl}_3$  before (1), after 1 min (2) and 30 min (3) photodeprotection of **S14** and reference-spectrum of the deprotected sugar (4).

## Photodeprotection of S14 in MeOD (500 W halogen lamp)

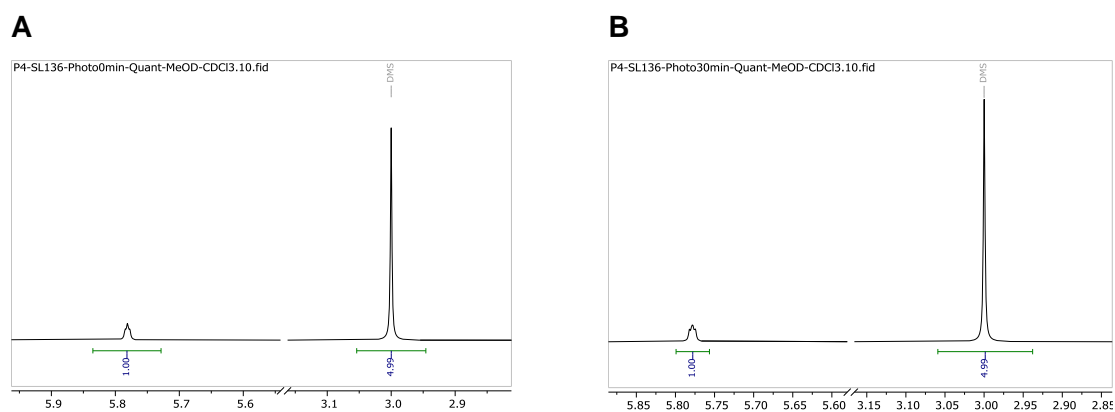


**Figure S4.** (A) Extract from <sup>1</sup>H-NMR-spectrum in MeOD of **S14** before photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of **S14** (1H). (B) Extract from <sup>1</sup>H-NMR-spectrum in MeOD of deprotected **S14** after 30 min photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of deprotected **S14** (1H) results in a yield of 100%.

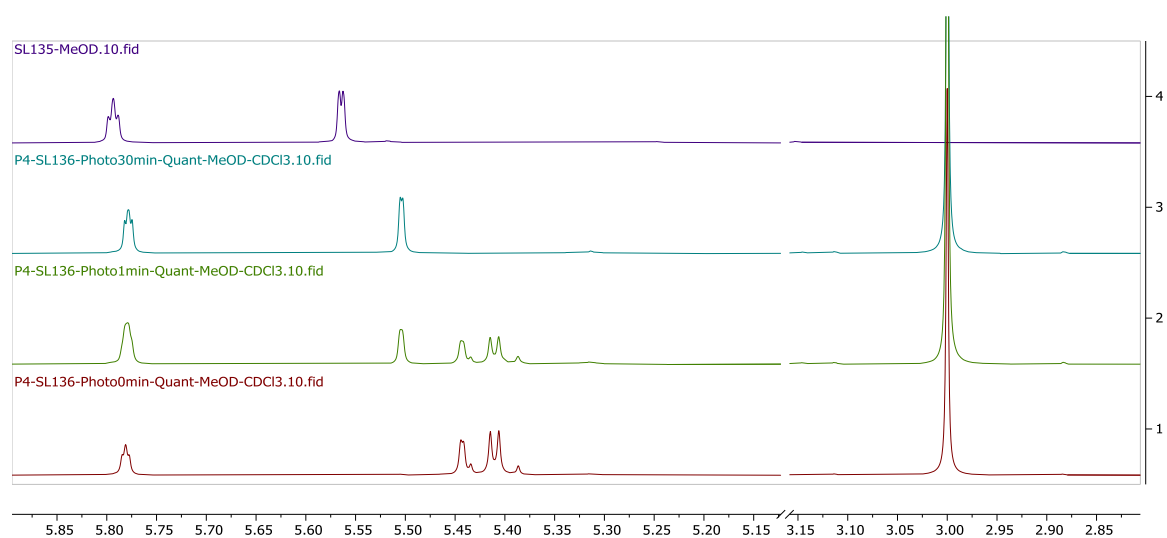


**Figure S5.** Zoom of stacked <sup>1</sup>H-NMR-spectra in MeOD before (1), after 1 min (2) and 30 min (3) photodeprotection of **S14** and reference-spectrum of the deprotected sugar (4).

## Photodeprotection of S14 in MeOD:CDCl<sub>3</sub> (1:2) (500 W halogen lamp)

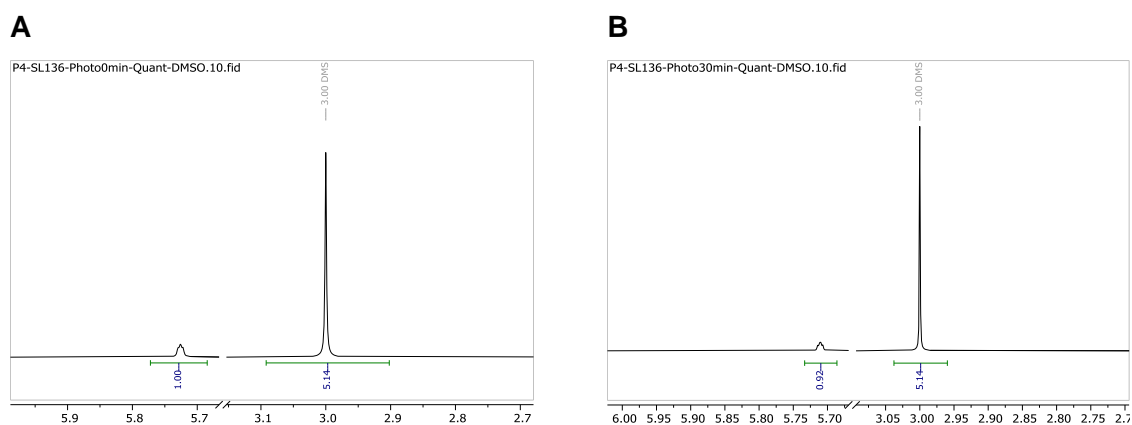


**Figure S6.** (A) Extract from <sup>1</sup>H-NMR-spectrum in MeOD:CDCl<sub>3</sub> (1:2) of **S14** before photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of **S14** (1H). (B) Extract from <sup>1</sup>H-NMR-spectrum in MeOD:CDCl<sub>3</sub> (1:2) of deprotected **S14** after 30 min photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of deprotected **S14** (1H) results in a yield of 100%.

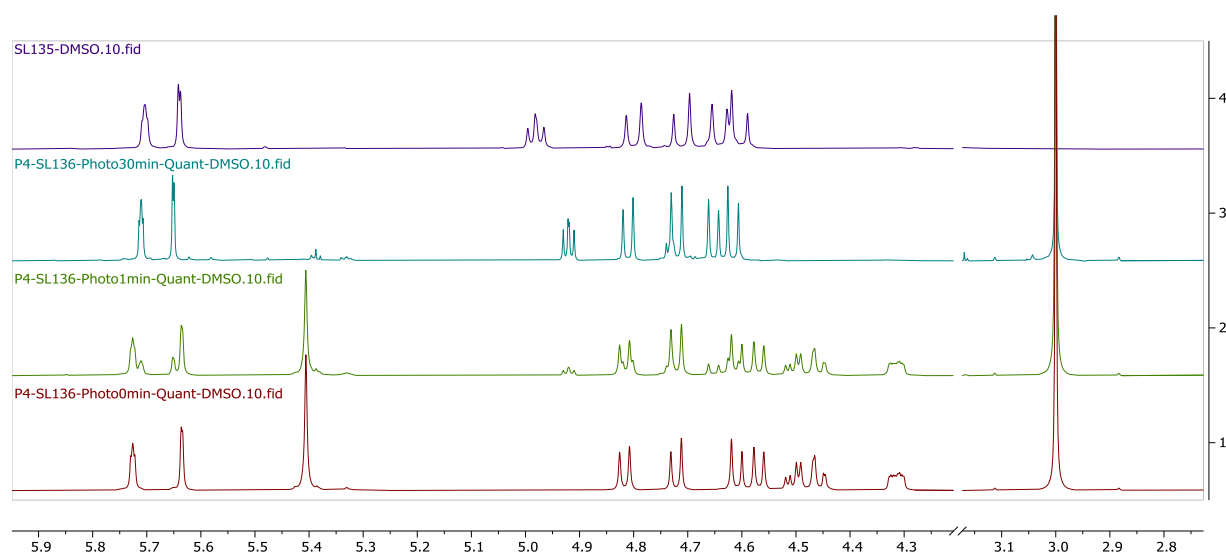


**Figure S7.** Zoom of stacked <sup>1</sup>H-NMR-spectra in MeOD:CDCl<sub>3</sub> (1:2) before (1), after 1 min (2) and 30 min (3) photodeprotection of **S14** and reference-spectrum of the deprotected sugar (4).

## Photodeprotection of S14 in DMSO (500 W halogen lamp)



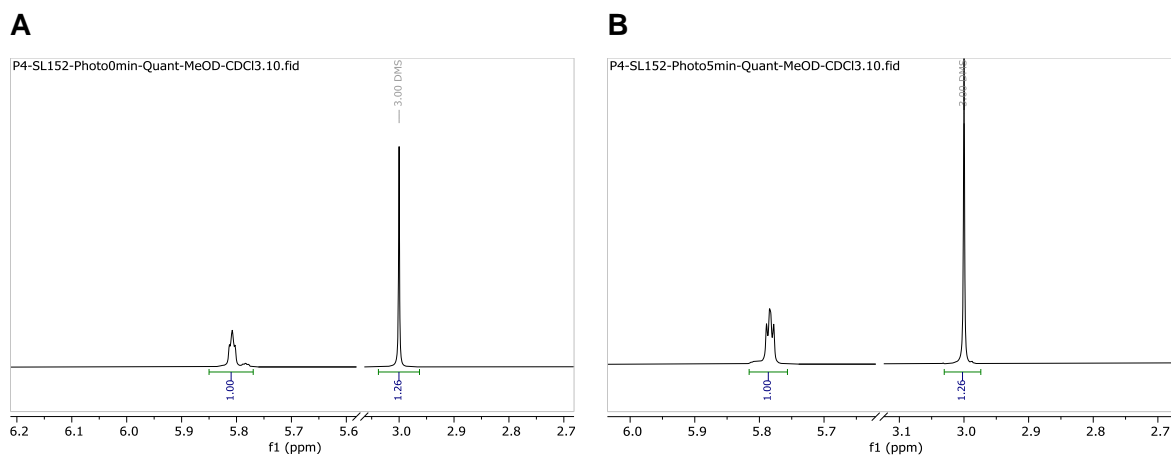
**Figure S8.** (A) Extract from <sup>1</sup>H-NMR-spectrum in DMSO of **S14** before photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of **S14** (1H). (B) Extract from <sup>1</sup>H-NMR-spectrum in DMSO of deprotected **S14** after 30 min photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of deprotected **S14** (1H) results in a yield of 92%.



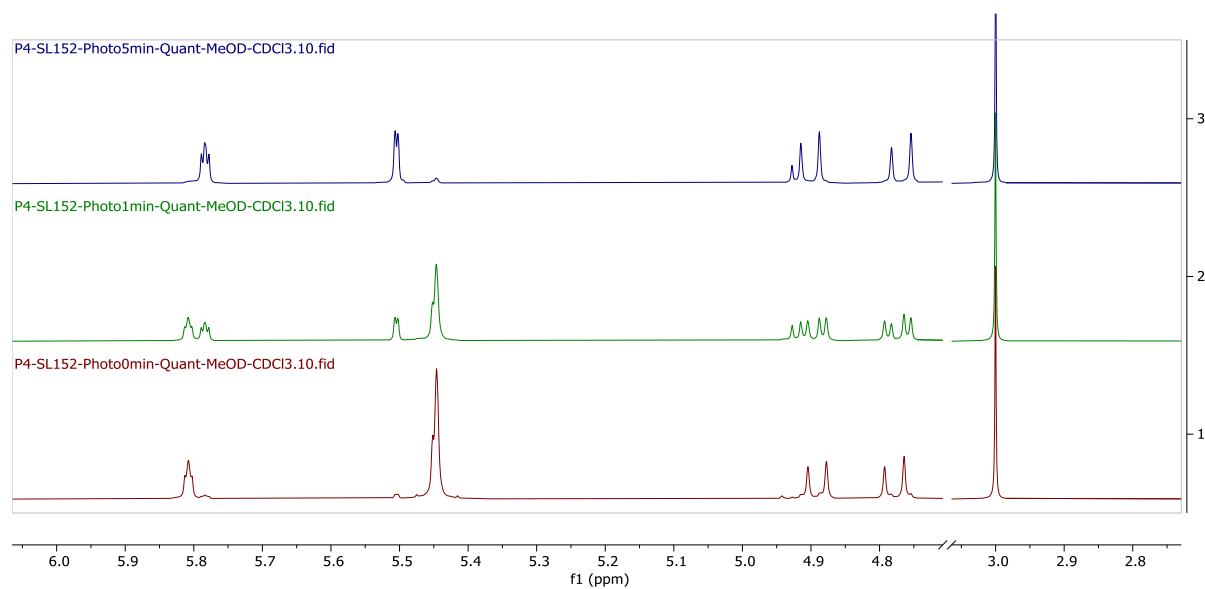
**Figure S9.** Zoom of stacked <sup>1</sup>H-NMR-spectra in DMSO before (1), after 1 min (2) and 30 min (3) photodeprotection of **S14** and reference-spectrum of the deprotected sugar (4).

## 5.2 Photodeprotection of 1a

### Photodeprotection of 1a in MeOD:CDCl<sub>3</sub> (1:2) (500 W halogen lamp)

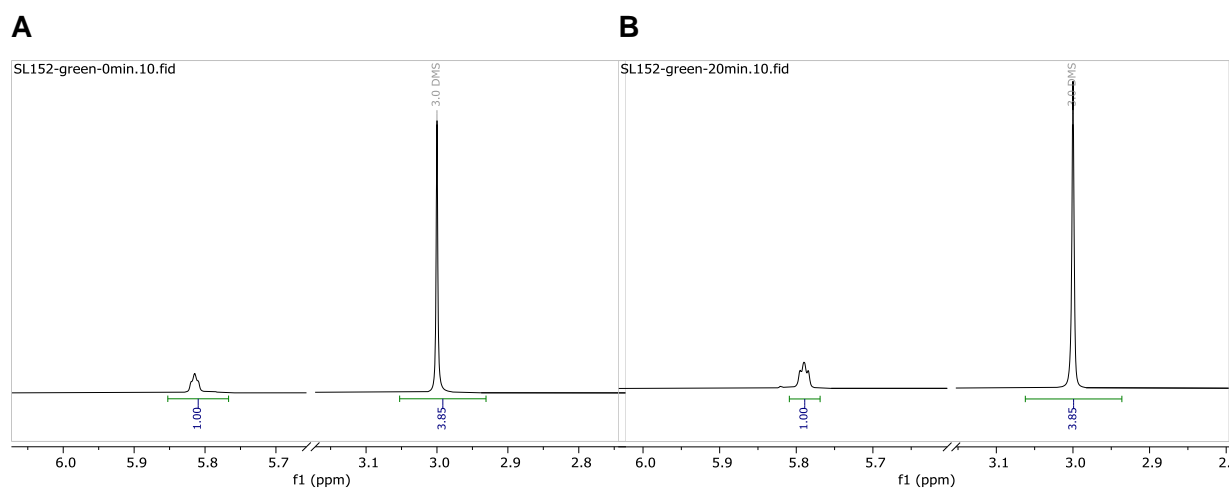


**Figure S10.** (A) Extract from <sup>1</sup>H-NMR-spectrum in MeOD:CDCl<sub>3</sub> (1:2) of **1a** before photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of **1a** (1H). (B) Extract from <sup>1</sup>H-NMR-spectrum in MeOD:CDCl<sub>3</sub> (1:2) of deprotected **1a** after 5 min photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of deprotected **1a** (1H) results in a yield of 100%.

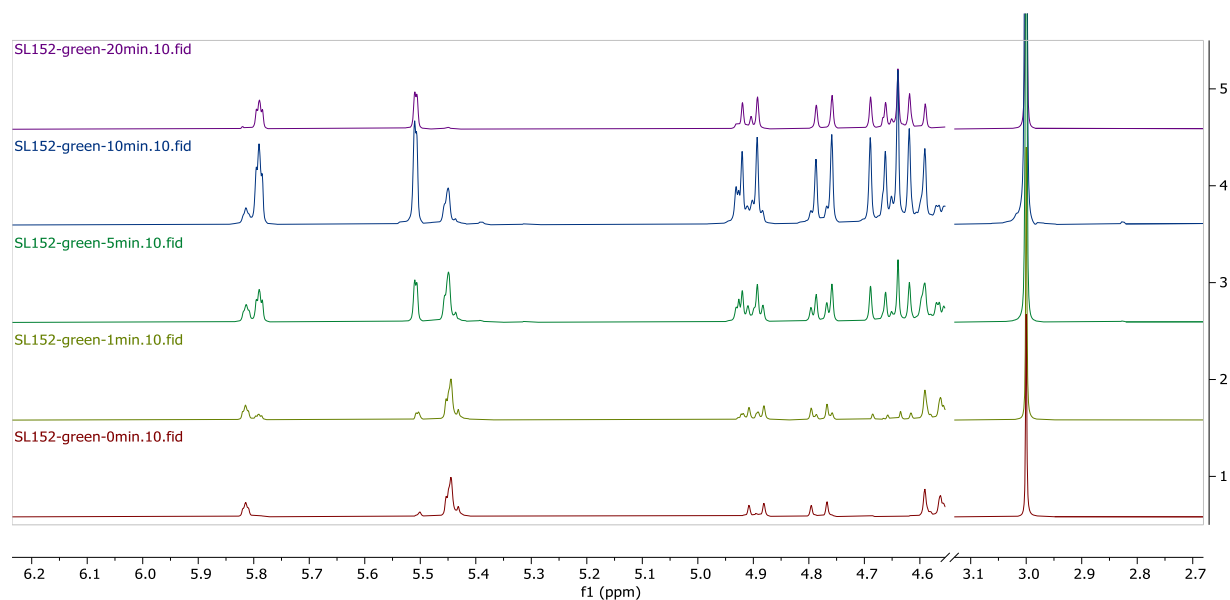


**Figure S11.** Zoom of stacked <sup>1</sup>H-NMR-spectra in MeOD:CDCl<sub>3</sub> (1:2) before (1), after 1 min (2) and 5 min (3) photodeprotection of **1a**.

## Photodeprotection of 1a in MeOD:CDCl<sub>3</sub> (1:2) (green LED lamp)



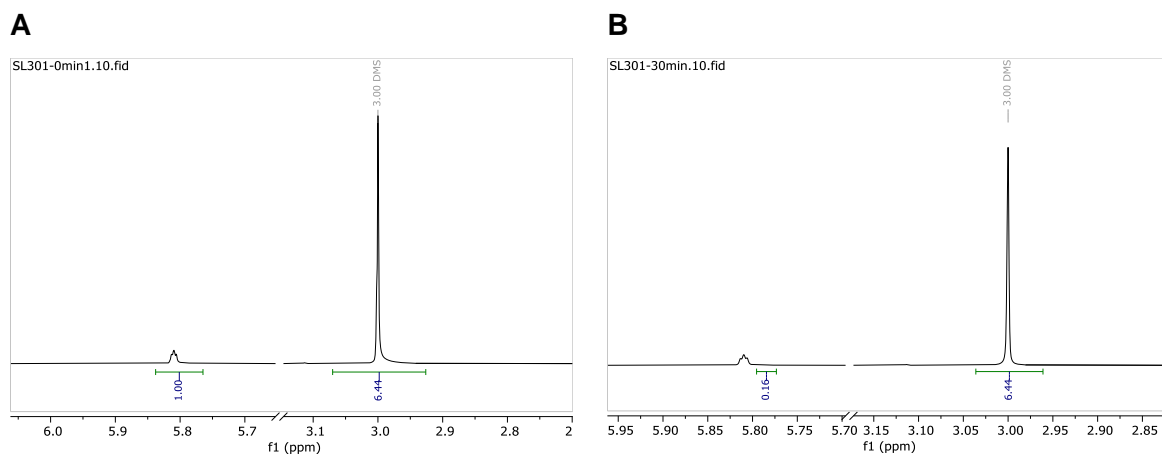
**Figure S12.** (A) Extract from <sup>1</sup>H-NMR-spectrum in MeOD:CDCl<sub>3</sub> (1:2) of **1a** before photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of **1a** (1H). (B) Extract from <sup>1</sup>H-NMR-spectrum in MeOD:CDCl<sub>3</sub> (1:2) of deprotected **1a** after 20 min photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of deprotected **1a** (1H) results in a yield of 100%.



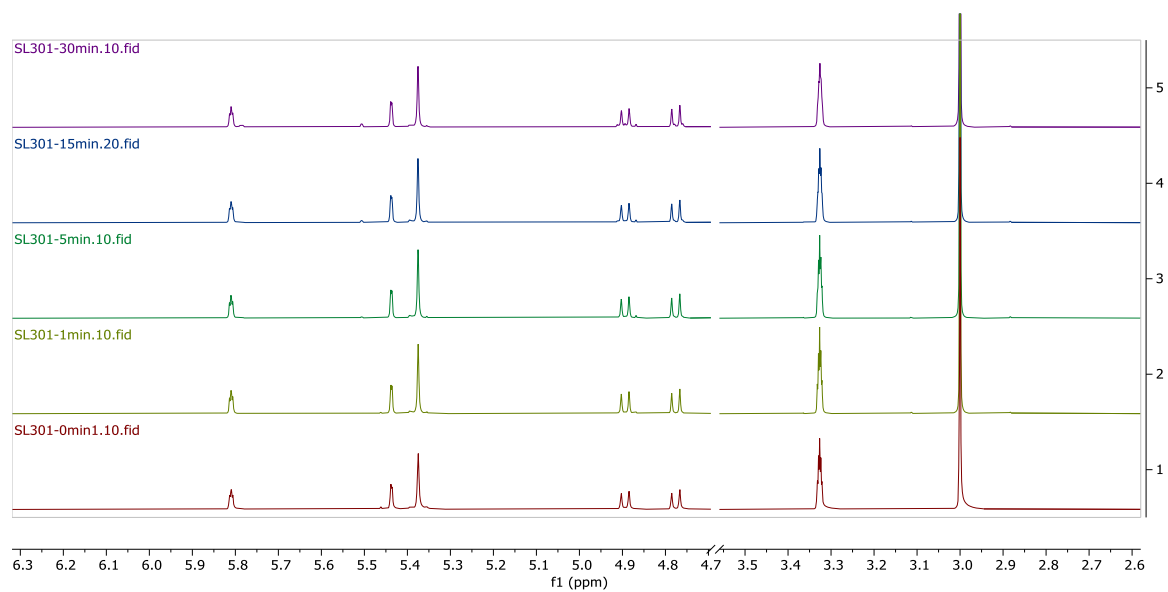
**Figure S13.** Zoom of stacked <sup>1</sup>H-NMR-spectra in MeOD:CDCl<sub>3</sub> (1:2) before (1), after 1 min (2), after 5 min (3), after 10 min (4) and 20 min (5) photodeprotection of **1a**.

### 5.3 Photodeprotection of 1b

#### Photodeprotection of 1b in MeOD:CDCl<sub>3</sub> (3:2) (500 W halogen lamp)

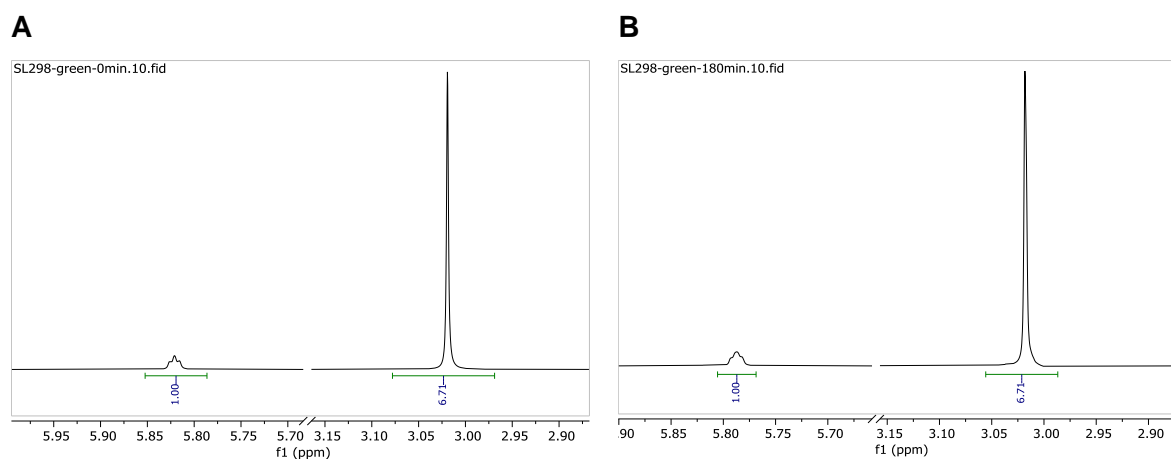


**Figure S14.** (A) Extract from <sup>1</sup>H-NMR-spectrum in MeOD:CDCl<sub>3</sub> (3:2) of **1b** before photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of **1b** (1H). (B) Extract from <sup>1</sup>H-NMR-spectrum in MeOD:CDCl<sub>3</sub> (1:2) of deprotected **1b** after 30 min photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of deprotected **1b** (1H) results in a yield of 16%.

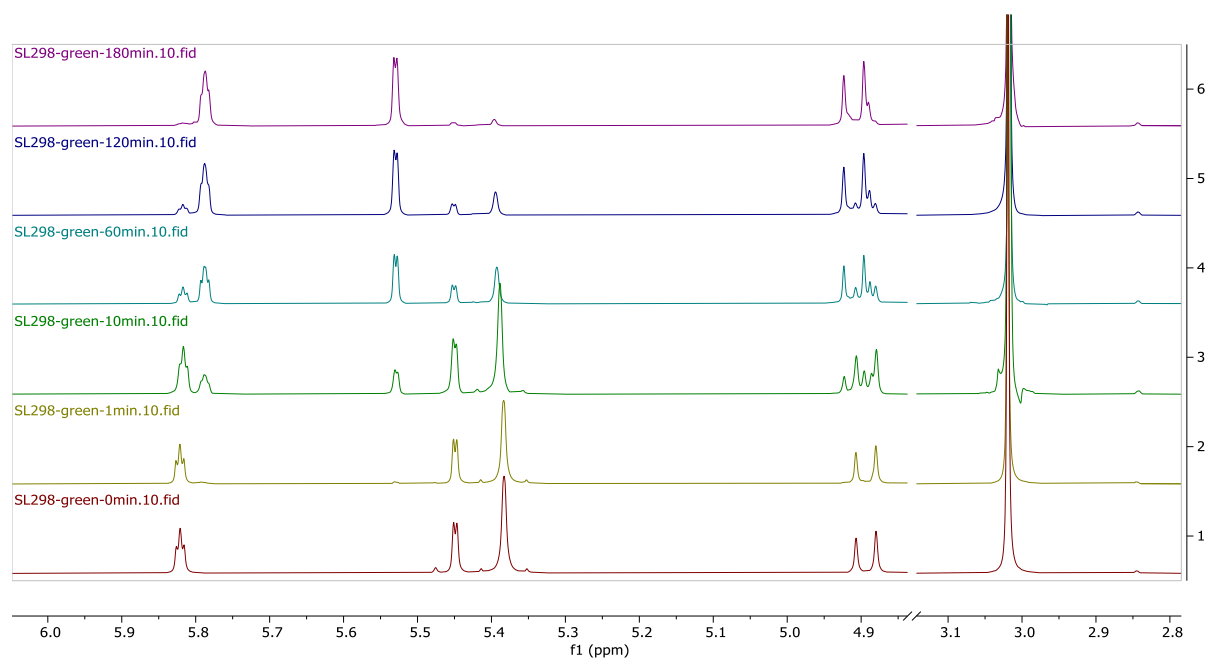


**Figure S15.** Zoom of stacked <sup>1</sup>H-NMR-spectra in MeOD:CDCl<sub>3</sub> (3:2) before (1), after 1 min (2), after 5 min (3), after 15 min (4) and after 30 min (5) photodeprotection of **1b**.

## Photodeprotection of **1b** in MeOD:CDCl<sub>3</sub> (3:2) (green LED lamp)



**Figure S16.** (A) Extract from <sup>1</sup>H-NMR-spectrum in MeOD:CDCl<sub>3</sub> (3:2) of **1b** before photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of **1b** (1H). (B) Extract from <sup>1</sup>H-NMR-spectrum in MeOD:CDCl<sub>3</sub> (1:2) of deprotected **1b** after 180 min photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of deprotected **1b** (1H) results in a yield of 100%.

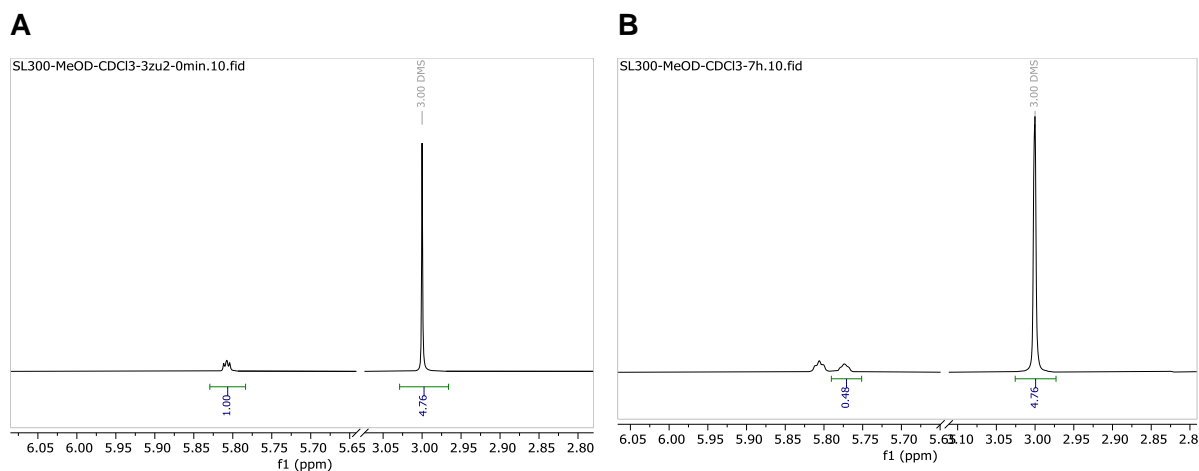


**Figure S17.** Zoom of stacked <sup>1</sup>H-NMR-spectra in MeOD:CDCl<sub>3</sub> (3:2) before (1), after 1 min (2), after 10 min (3), after 60 min (4), after 120 min (5) and after 180 min (6) photodeprotection of **1b**.

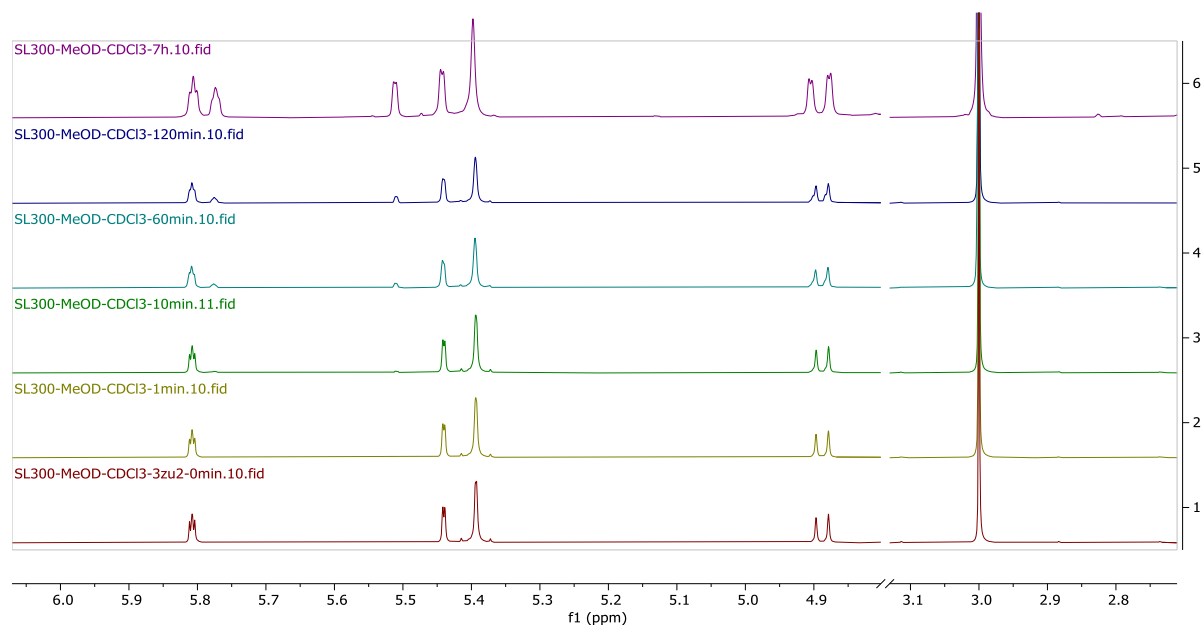


## 5.4 Photodeprotection of 1c

### Photodeprotection of 1c in MeOD:CDCl<sub>3</sub> (3:2) (500 W halogen lamp)

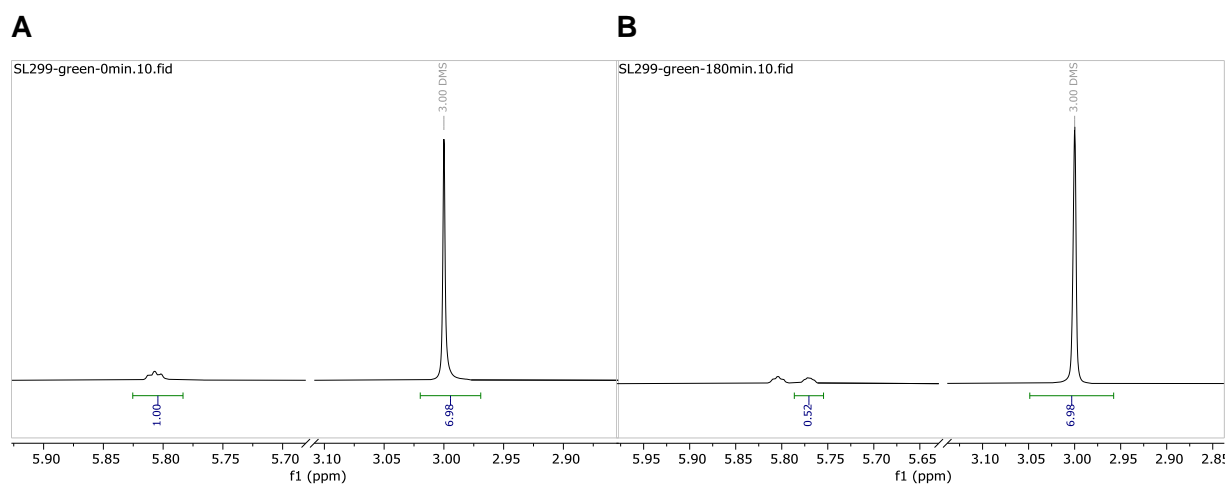


**Figure S18.** (A) Extract from <sup>1</sup>H-NMR-spectrum in MeOD:CDCl<sub>3</sub> (3:2) of **1c** before photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of **1c** (1H). (B) Extract from <sup>1</sup>H-NMR-spectrum in MeOD:CDCl<sub>3</sub> (1:2) of deprotected **1c** after 7 h photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of deprotected **1c** (1H) results in a yield of 48%.

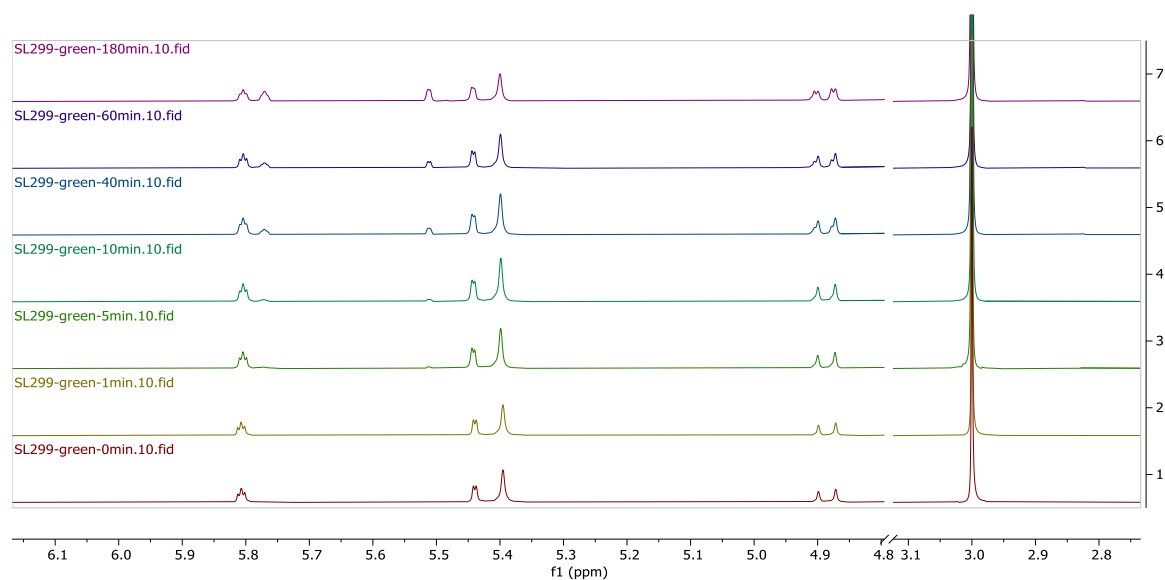


**Figure S19.** Zoom of stacked <sup>1</sup>H-NMR-spectra in MeOD:CDCl<sub>3</sub> (3:2) before (1), after 1 min (2), after 10 min (3), after 60 min (4), after 120 min (5) and after 7 h (6) photodeprotection of **1c**.

## Photodeprotection of **1c** in MeOD:CDCl<sub>3</sub> (3:2) (green LED lamp)



**Figure S20.** (A) Extract from <sup>1</sup>H-NMR-spectrum in MeOD:CDCl<sub>3</sub> (3:2) of **1c** before photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of **1c** (1H). (B) Extract from <sup>1</sup>H-NMR-spectrum in MeOD:CDCl<sub>3</sub> (1:2) of deprotected **1c** after 180 min photodeprotection for quantification. Dimethylsulfone DMS (6H) in relation to H-2 of deprotected **1c** (1H) results in a yield of 52%.



**Figure S21.** Zoom of stacked <sup>1</sup>H-NMR-spectra in MeOD:CDCl<sub>3</sub> (3:2) before (1), after 1 min (2), after 5 min (3), after 10 min (4), after 40 min (5), after 60 min (6) and after 180 min (7) photodeprotection of **1c**.

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