

Electronic Supplementary Information

Synthesis and Photophysical Properties of a Bichromophoric System Hosting a Disaccharide Spacer

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Phenyl 3,4-*O*-(1-methylethylidene)-6-*O*-[(1,1-dimethylethyl)diphenylsilyl]-2-*O*-2-propyn-1-yl-1-thio- β -D-galactopyranoside (2). To a solution of methyl 2,6-bis-*O*-(*tert*-butyldiphenylsilyl)- β -D-galactopyranoside (**1**) (1.5 g, 2.7 mmol) in dry DMF (14 mL) was added NaH (60% w/w in mineral oil, 0.16 g, 4.1 mmol) at 0°C. Then, propargyl bromide (0.8 mL, 6.8 mmol) was added slowly and the mixture was stirred at 0°C for 20' and maintained at rt for 3h. TLC (Exane/EtOAc 80:20) indicated the disappearance of the starting material. The reaction mixture was cooled to 0°C and MeOH (14 mL) was added. The solvents were removed under reduced pressure. The residue was suspended in water and extracted with ethyl acetate. The combined organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na₂SO₄, filtered and concentrated under reduced pressure, to give a brown oil which was purified by chromatography (eluants Exane/EtOAc 50:50) on silica gel. Compound **2** is a pale oil obtained from the reaction crude with 75% yield. *Rf*: 0.48 (Exane/EtOAc 80:20). ¹H NMR: δ 7.8-7.2 (m, 15H, ArH), 4.78 (d, ³*J*_{1,2} 9.8, 1H, H-1), 4.43 and 4.40 (split AB system, ²*J*_{gem} 15.6, ⁴*J* 2.5, 2H, 2-OCH₂C \equiv), 4.40 (dd, ³*J*_{3,4} 6.2, ³*J*_{4,5} 2.0, 1H, H-4), 4.28 (t, ³*J*_{2,3} 6.2, ³*J*_{3,4} 6.2, 1H, H-3), 4.20 (ddd, ³*J*_{4,5} 2.0, ³*J*_{5,6A} 5.6, ³*J*_{5,6B} 6.9, 1H, H-5), 3.94 and 3.91 (split AB system, ³*J*_{5,6A} 5.6, ³*J*_{5,6B} 6.9, ²*J*_{6A,6B} 10.4, 2H, H₂-6), 3.63 (dd, ³*J*_{1,2} 9.8, ³*J*_{2,3} 6.2, 1H, H-2), 2.94 (t, ⁴*J* 2.5, 1H, \equiv CH), 1.44 and 1.30 [two s, 6H, OC(CH₃)₂], 1.05 [s, 9H, SiC(CH₃)₃]. ¹³C NMR: δ 135.4, 134.6, 133.1, 133.0, 129.7, 129.6, 129.1, 128.7, 127.6, 127.3, and 126.6 (ArC), 109.4 [C(CH₃)₂], 85.0 (C-1), 79.5 (C \equiv CH), 79.2 (C-3), 77.0 (C-2), 76.5 (C-5), 75.2 (\equiv CH), 73.7 (C-4), 63.3 (C-6), 57.6 (2-OCH₂C \equiv), 27.2 and 25.5 [OC(CH₃)₂], 26.1 [SiC(CH₃)₃], 18.7 [SiC(CH₃)₃]. Anal. Calcd for C₃₀H₄₀O₅SSi: C, 69.35; H, 6.85. Found: C, 69.46; H, 6.86.

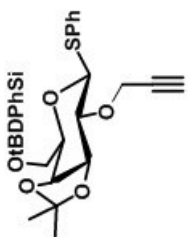
2-Propyn-1-yl 6-*O*-[(1,1-dimethylethyl)diphenylsilyl]- β -D-glucopyranoside (4). Propargyl β -D-glucopyranoside **3** (1.8 g, 8.25 mmol) was dissolved in dry DMF (6 mL) and imidazole (1.23 g, 18.15 mmol, 2.2 eq) was added. Then *tert*-butyldiphenylsilyl chloride (2.48 mL, 9.1 mmol, 1.1 eq) was added dropwise and the reaction was stirred for 5 h at room temperature, before being

concentrated in vacuo. The residue was dissolved in Et₂O (40 mL), washed with NH₄Cl sat and NaHCO₃ and water (20 mL). The aqueous layers were extracted with DCM (2 x 30 mL) and the combined organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure. Compound **4** is an oil obtained in quantitative yield *Rf*: 0.59. (CHCl₃/MeOH 90:10). ¹H NMR: δ 7.8-7.4 (m, 10H, ArH), 4.49 (d, ³J_{1,2} 7.8, 1H, H-1), 4.45 and 4.37 (split AB system, ²J_{gem} 15.7, ⁴J 2.4, 2H, 2-OCH₂C≡), 4.27, 4.21 and 4.17 (d, *J* 3.9, 3 x OH), 4.06 and 3.94 (split AB system ³J_{5,6A} 1.9, ³J_{5,6B} 5.4, ²J_{6A,6B} 10.8, 2H, H₂-6), 3.51-3.40 (m, 3H, H-3-5), 3.24 (ddd, *J*_{2,OH} 3.9 ³J_{2,1} 7.8, ³J_{2,3} 11.7, 1H, H-2), 2.98 (t, ⁴J 2.5, 1H, ≡CH), 1.05 [s, 9H, SiC(CH₃)₃]. ¹³C NMR: δ 137.3, 136.7, 136.2, 135.6, 134.6, 134.5, 134.3, 130.5, 130.0, 128.6 and 128.3 (ArC), 101.8 (C-1), 80.2 (C≡CH), 77.8, 76.0, 71.0, and 70.9 (C-2-5), 74.7 (≡CH), 64.4 (C-6), 55.7 (1-OCH₂C≡), 27.1 [SiC(CH₃)₃], 19.8 [SiC(CH₃)₃].

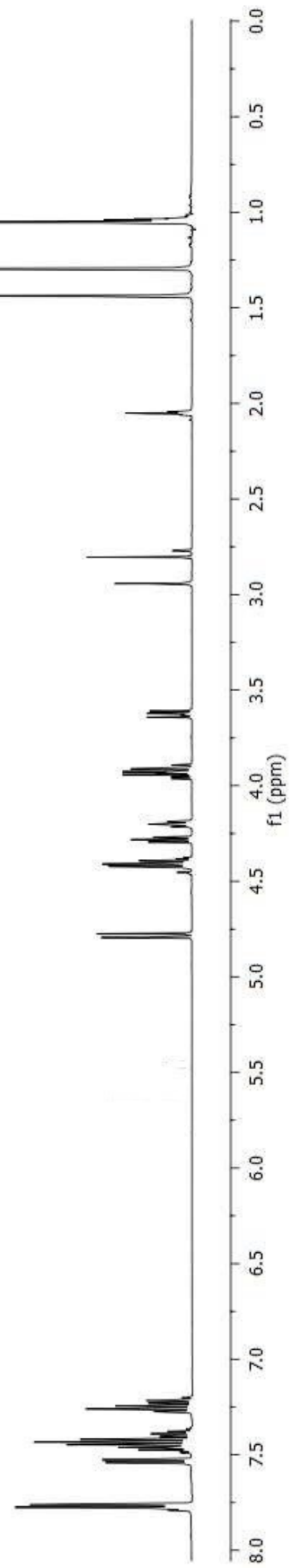
2-Propyn-1-yl 6-*O*-[(1,1-dimethylethyl)diphenylsilyl]-β-D-glucopyranoside 2,3,4-triacetate (5**).**

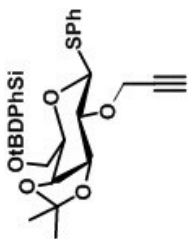
2-Propyn-1-yl β-D-glucopyranoside **4** (1.6 g, 3.5 mmol) was added to an excess of pyridine (3.5 mL) and the mixture was stirred at 0°C for 15', then, an excess of Ac₂O was added (3.5 mL) and the mixture was stirred for 12 h at room temperature. The crude was dissolved in EtOAc (40 mL) and washed three times with an aqueous solution of HCl 2N (20 mL). The organic layer was then washed with saturated NaCl solution (20 mL, twice), dried over MgSO₄, filtered and concentrated under reduced pressure to give a brown oil that was purified by chromatography (eluants Exane/EtOAc 80:20) on silica gel. Compound **5** is an oil obtained in 70% yield. *Rf*: 0.50 (Exane/EtOAc 80:20). ¹H NMR: δ 7.8-7.4 (m, 10H, ArH), 5.3-5.2 (m, 2H, H-1, H-6_A), 5.0-4.9 (m, 2H, H-3, H-6_B), 4.44 and 4.37 (split AB system, ²J_{gem} 15.8, ⁴J 1.8, 2H, 1-OCH₂C≡), 3.9-3.8 (m, 3H, H-2,4,5), 3.04 (t, ⁴J 1.8, 1H, ≡CH), 1.99 and 1.94 (two s, 9H, 3 x COCH₃), 1.05 [s, 9H, SiC(CH₃)₃]. ¹³C NMR: δ 169.3 and 168.6 (CO), 135.2, 133.1, 132.8, 129.6, 127.6, and 127.5 (ArC), 98.1 (C-1), 78.5 (C≡CH), 75.7 (≡CH), 74.0, 72.9, 71.0, 68.0 (C-2-5), and 62.0 (C-6), 55.2 (1-OCH₂C≡), 26.0 [SiC(CH₃)₃], 19.5 (COCH₃), 18.7 [SiC(CH₃)₃].

2-Propyn-1-yl β -D-glucopyranoside 2,3,6-triacetate (6). Propargyl β -D-glucopyranoside **5** (1.94 g, 3.9 mmol) was dissolved in aqueous TFA (95%, 14.08 mL). The mixture was stirred for 1h at room temperature. TLC (Hexane/EtOAc 40:60) indicated the disappearance of the starting material. Toluene (47.26 mL) was added to the reaction crude. The organic layer was dried over MgSO_4 , filtered and concentrated under reduced pressure to give a solid that was purified by chromatography (eluants Hexane/EtOAc 60:40) on silica gel. Compound **6** is a white solid obtained in 85% yield. M.p. 130-140°C. *Rf*: 0.48 (Hexane/EtOAc 40:60). ^1H NMR: δ 5.11 (t, $^3J_{2,3} = ^3J_{3,4}$ 9.0, 1H, H-3), 4.82 (d, $^3J_{1,2}$ 7.8, 1H, H-1), 4.79 (dd, $^3J_{1,2}$ 7.8, $^3J_{2,3}$ 9.0, 1H, H-2), 4.38 and 4.26 (split AB system, $^3J_{5,6A}$ 2.2, $^3J_{5,6B}$ 5.3, $^2J_{6A,6B}$ 12.1, 2H, H₂-6), 4.37 and 4.33 (split AB system, $^2J_{\text{gem}}$ 15.6, 4J 2.4, 2H, 1-OCH₂C \equiv), 3.72 (m, 1H, H-5), 3.66 (br t, $^3J_{3,4} = ^3J_{4,5}$ 9.0, 1H, H-4), 3.00 (t, 4J 2.4, 1H, $\equiv\text{CH}$), 2.03, 1.98, and 1.97 (three s, 9H, 3 x COCH₃). ^{13}C NMR: δ 171.6, 171.1, and 170.4 (CO), 99.9 (C-1), 80.3 ($\underline{\text{C}}\equiv\text{CH}$), 76.7 ($\equiv\text{CH}$), 77.1, 75.4, 72.9, 69.9 (C-2-5) and 64.2 (C-6), 57.0 (1-OCH₂C \equiv), 21.4 and 21.3 (COCH₃). Anal. Calcd for C₁₅H₂₀O₉: C, 52.32; H, 5.85. Found: C, 52.30; H, 5.84. From the same chromatography column **2-Propyn-1-yl β -D-glucopyranoside 2,3,4-triacetate (7)** was recovered as an oil in 10% yield. ^1H NMR (CDCl₃): δ 5.30 (t, $^3J_{2,3} = ^3J_{3,4}$ 9.0, 1H, H-3), 5.09-4.95 (m, 2H, H-2 and H-4), 4.81 (d, $^3J_{1,2}$ 7.8, 1H, H-1), 4.43-4.35 (m, 2H, and 1-OCH₂C \equiv), 3.80-3.52 (m, 3H, H₂-6, H-5), 2.48 (t, 4J 2.4, 1H, $\equiv\text{CH}$), 2.07 and 2.02 (three s, 9H, 3 x COCH₃). ^{13}C NMR (CDCl₃): δ 170.2, 170.1, and 169.4 (CO), 98.4 (C-1), 78.2 ($\underline{\text{C}}\equiv\text{CH}$), 76.6 ($\equiv\text{CH}$), 74.1, 72.6, 71.1, 68.6, and 61.2 (C-2-6), 56.1 (1-OCH₂C \equiv), 20.7 and 20.6 (COCH₃).

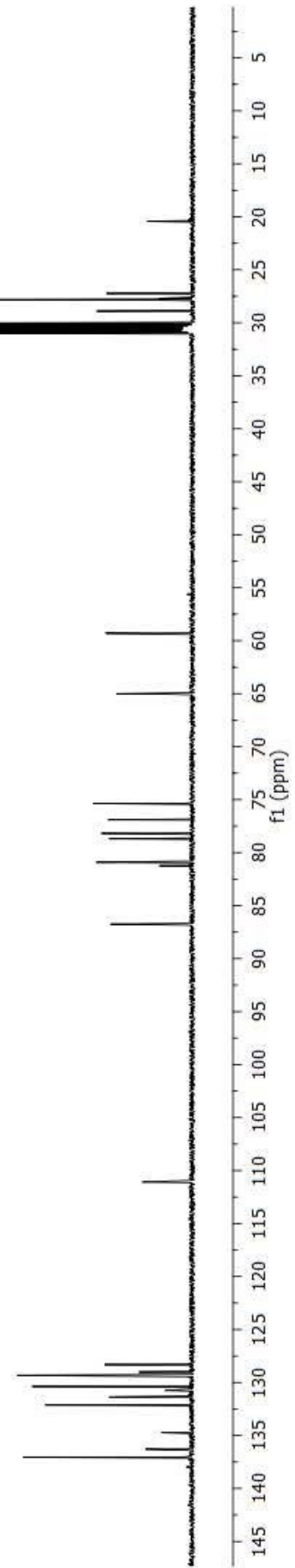


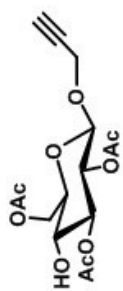
^1H NMR of Compound 2



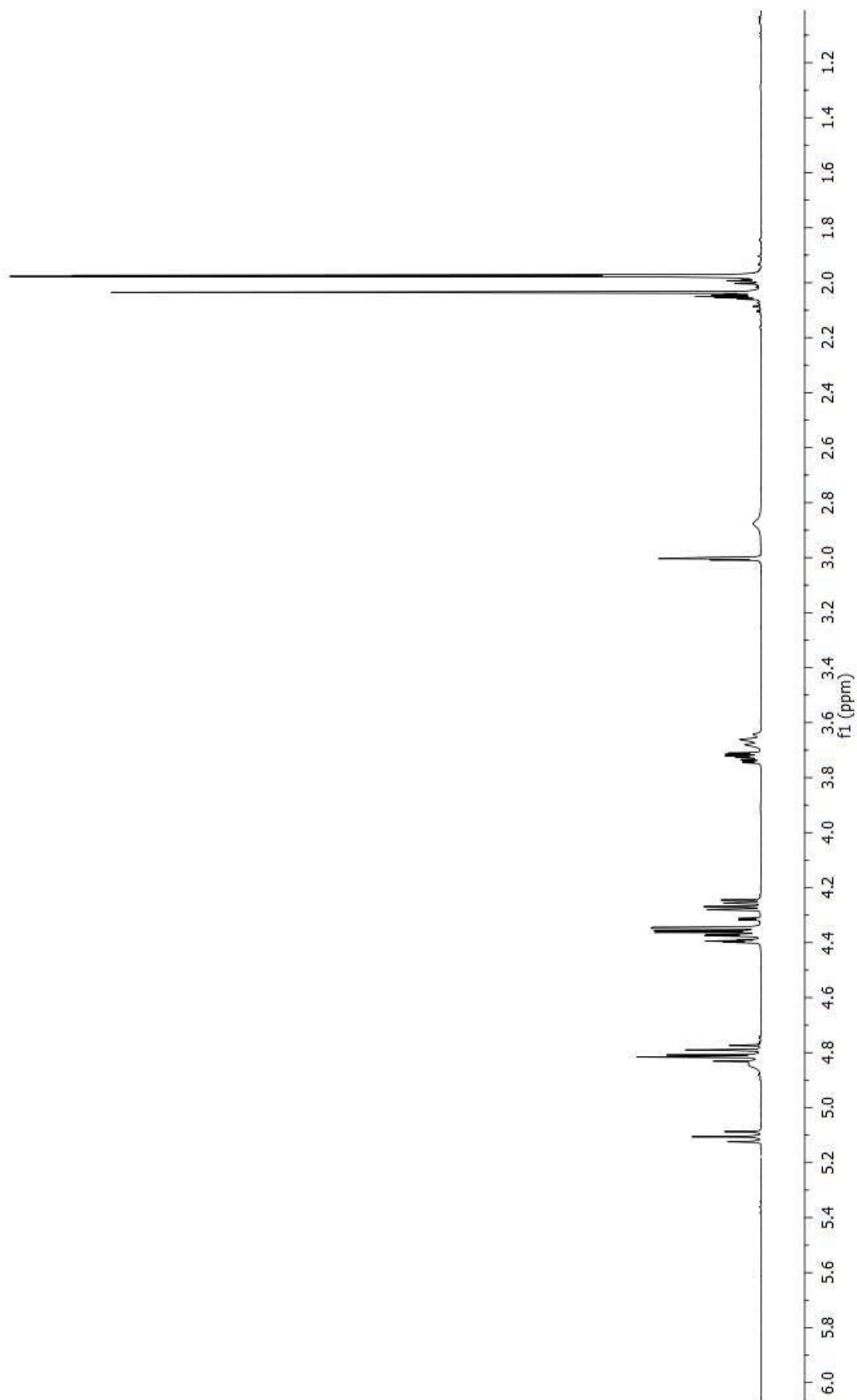


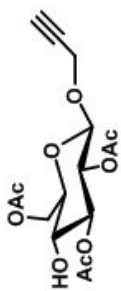
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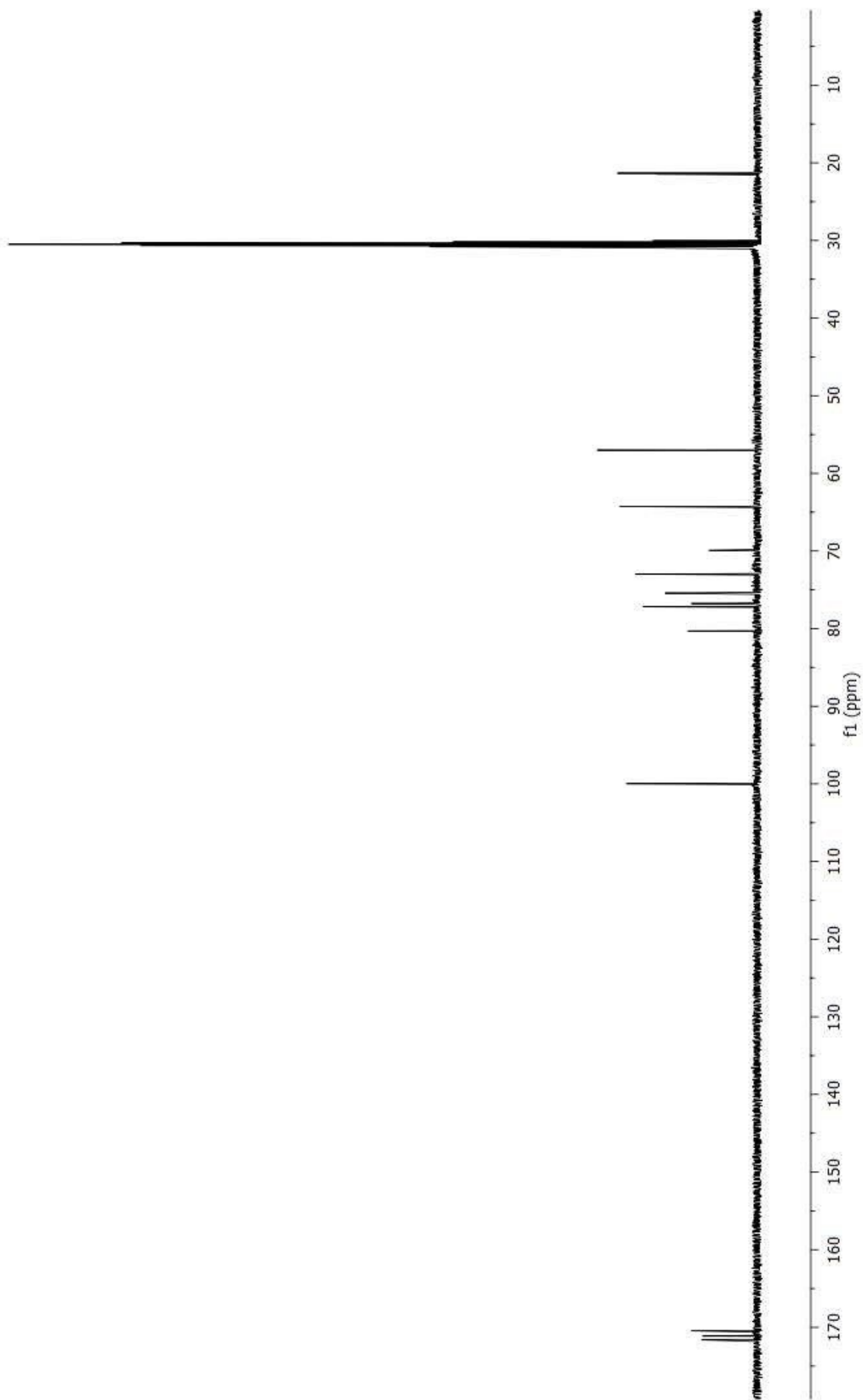


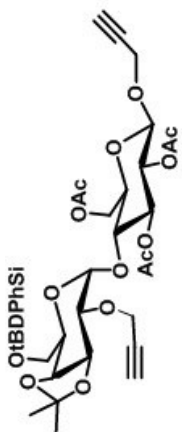
^1H NMR of Compound 6



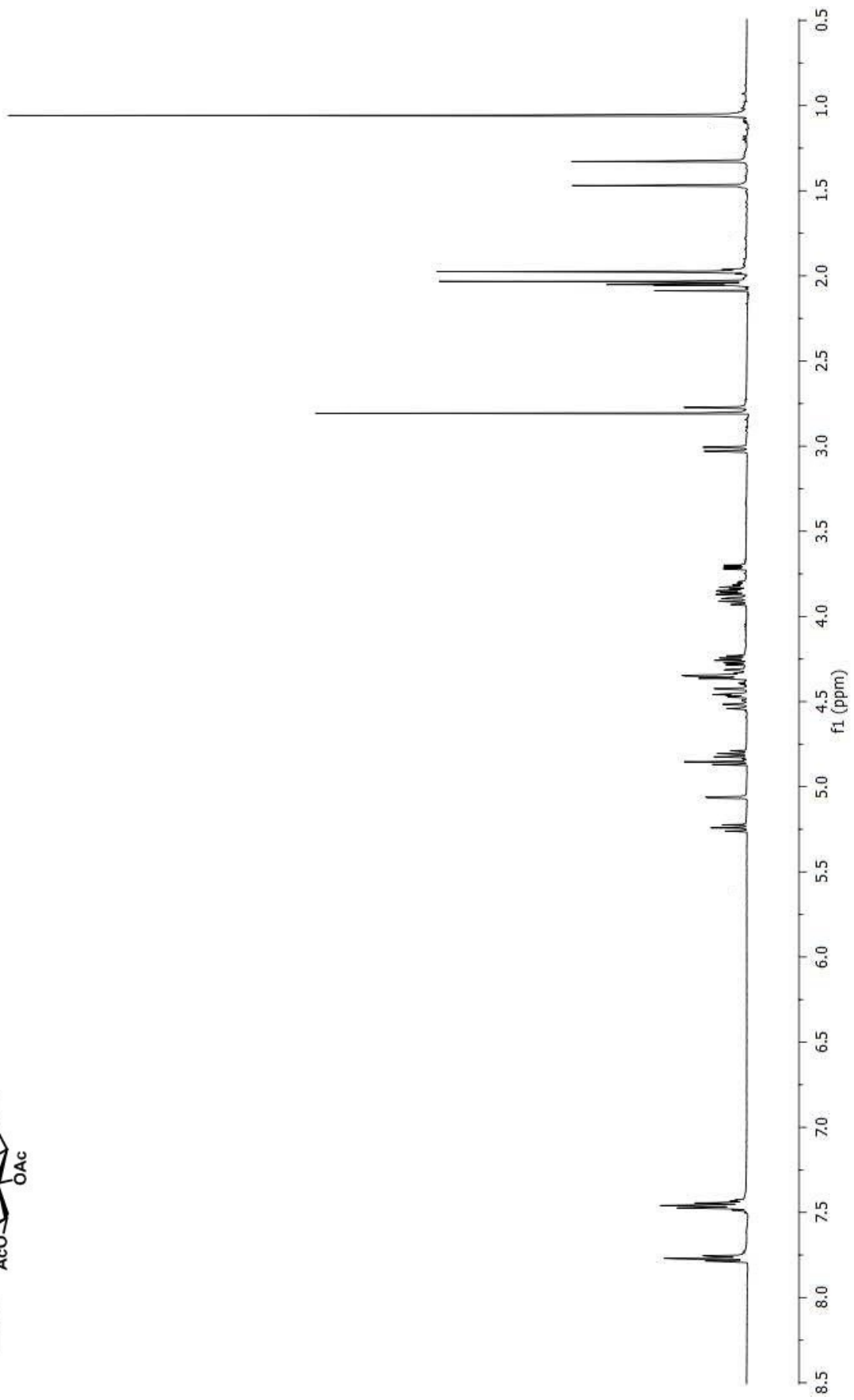


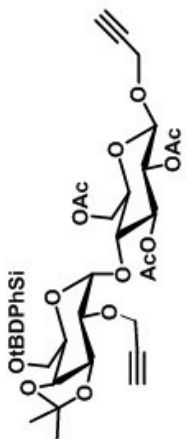
¹³C NMR of Compound 6



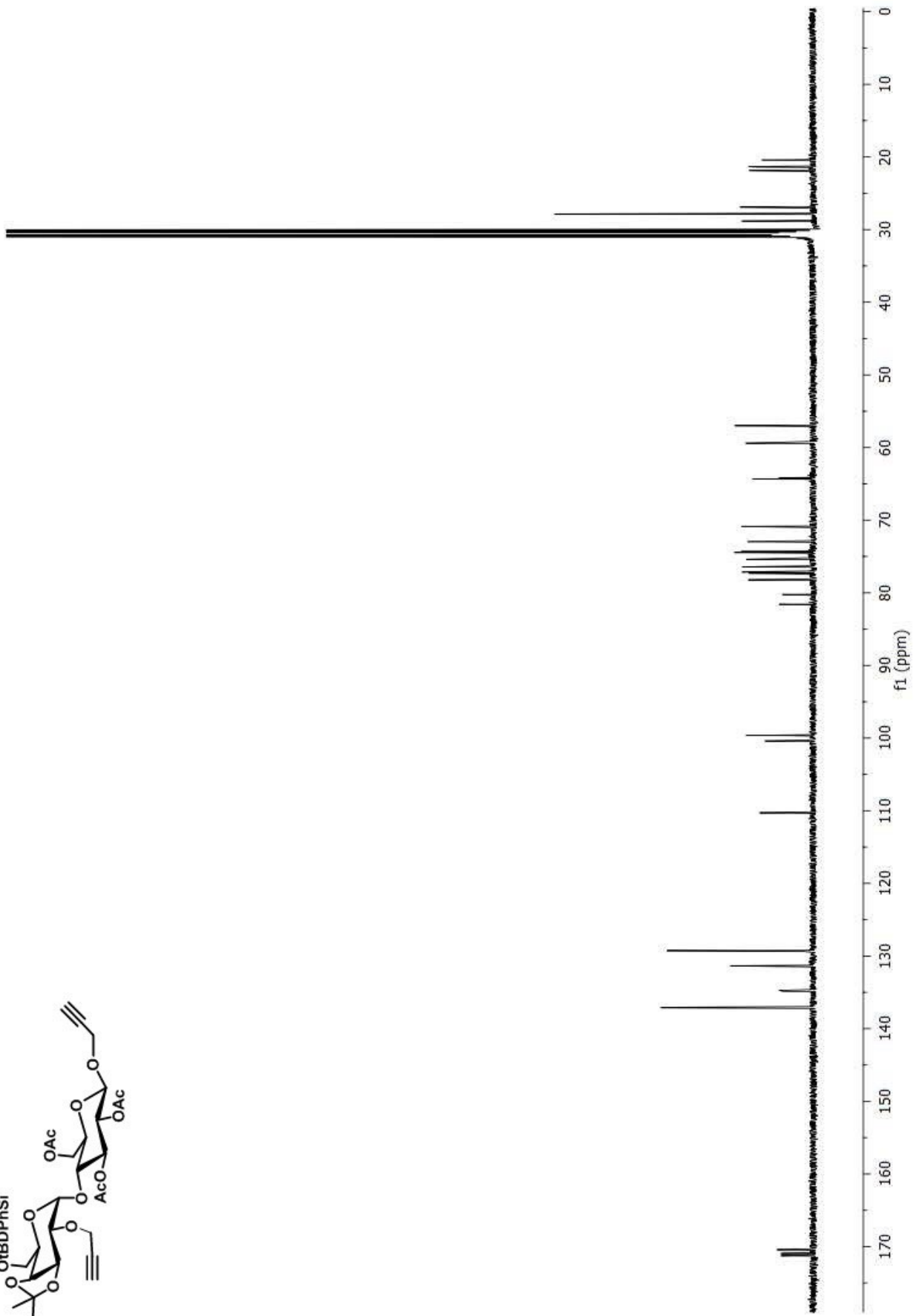


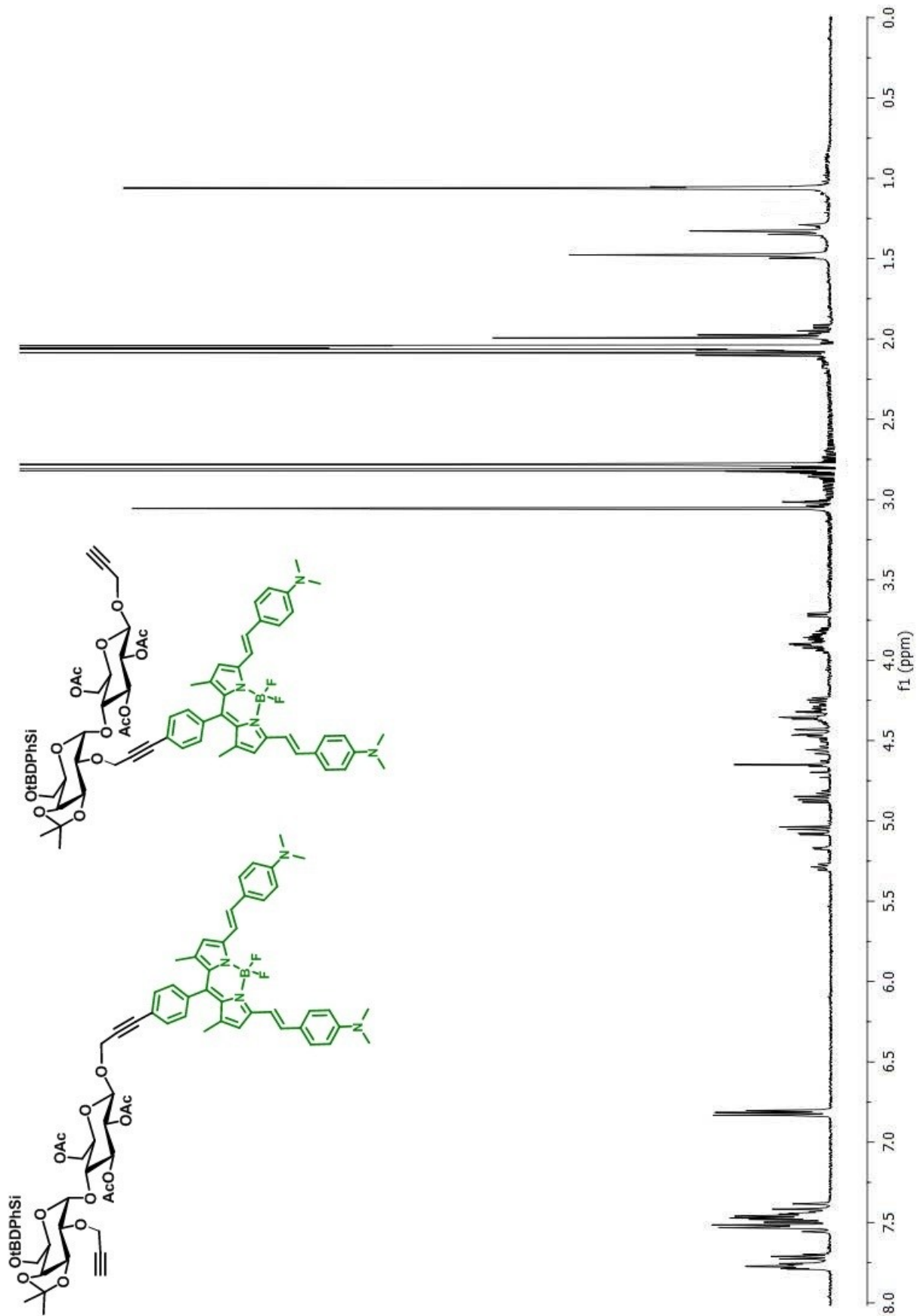
^1H NMR of Compound **8**



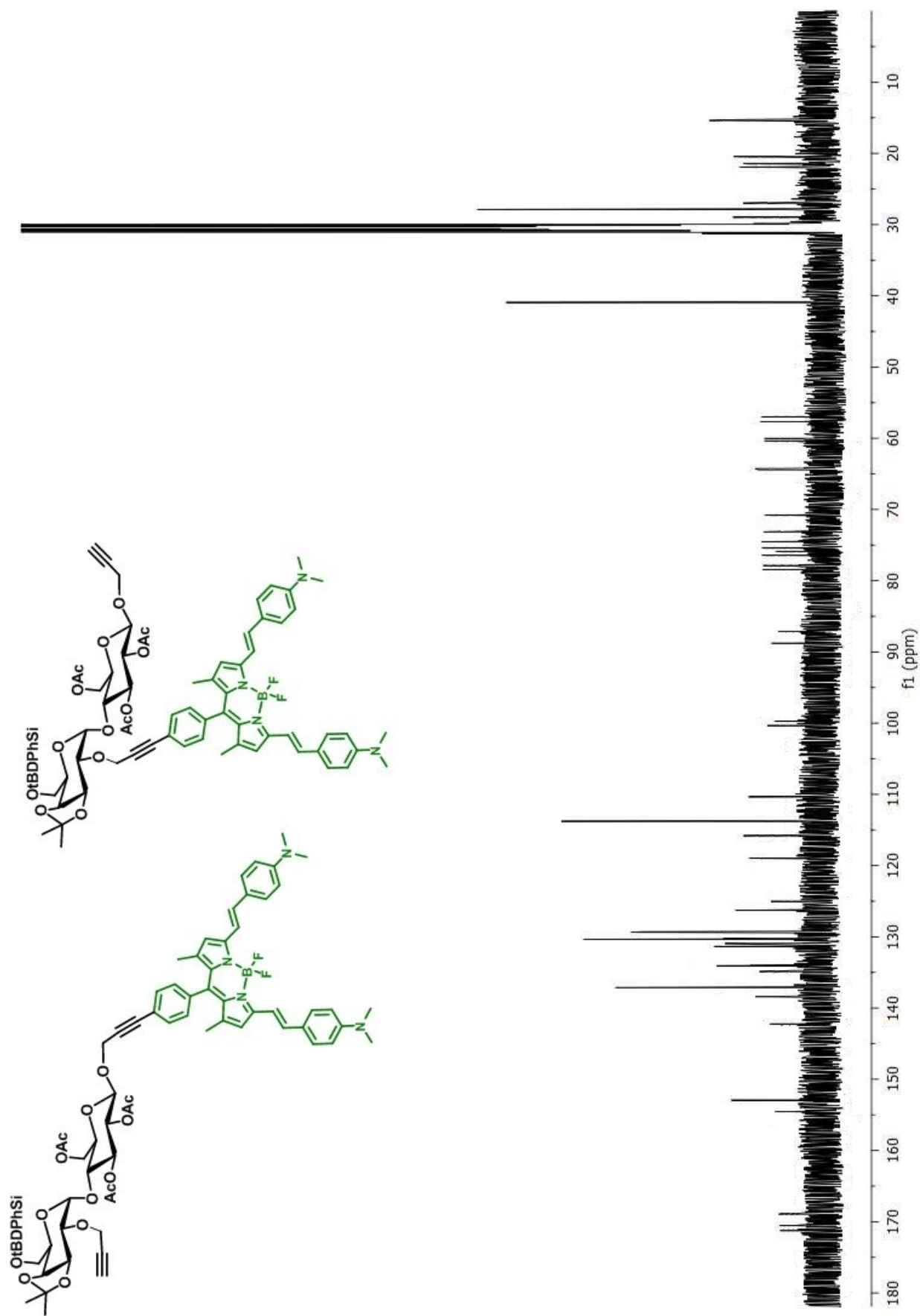


^{13}C NMR of Compound 8

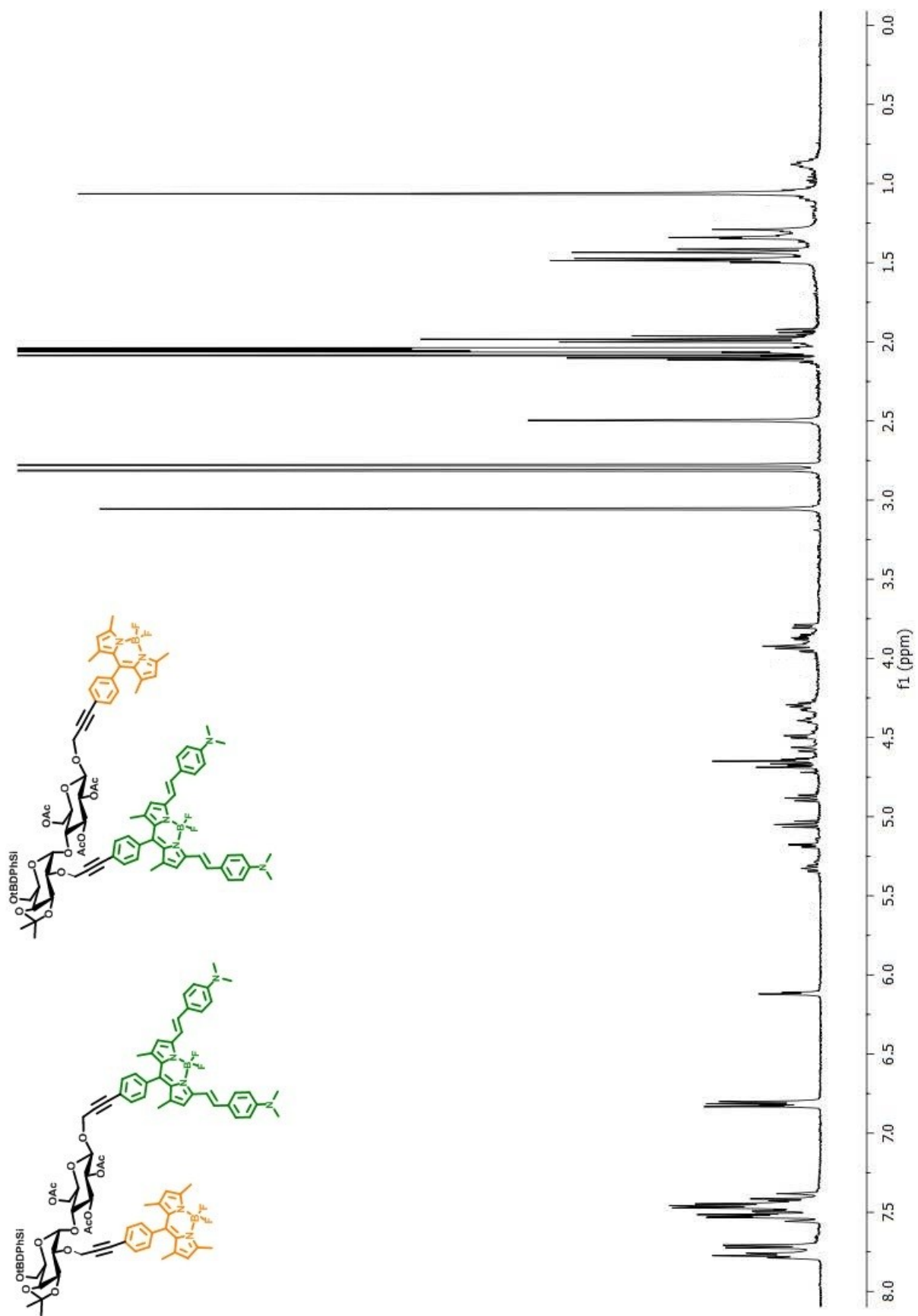




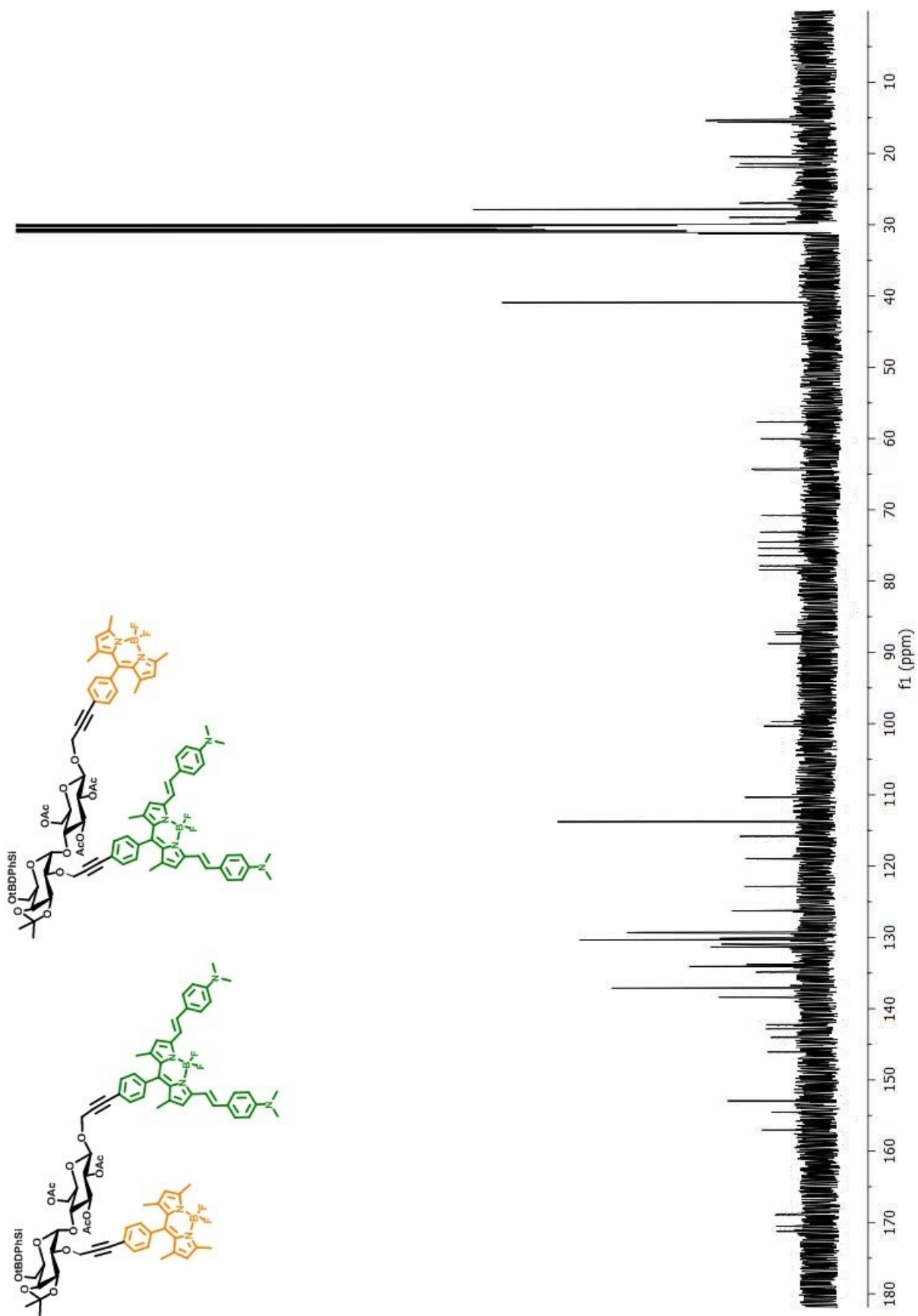
¹H NMR of Compound 10



¹³C NMR of Compound 10



¹H NMR of Compound 12



¹³C NMR of Compound 12