

Supporting information

Conformationally Switchable Glycosyl Donors

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Complexation studies of 1

Figure S1. ^1H -NMR spectrum of glycosyl donor **1** and glycosyl donor **1** with zinc(II) triflate (1 equiv.)

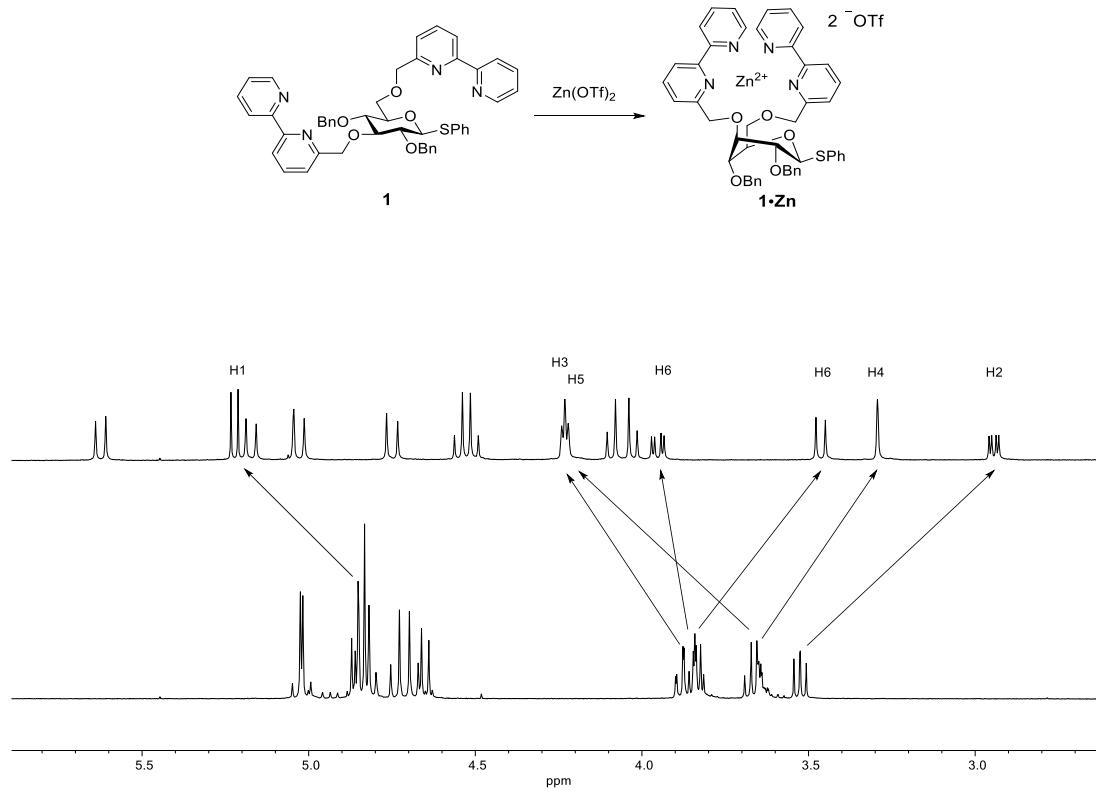


Table S1. J -couplings of glycosyl donor **1** and **1-Zn**.

Glycosyl donor	$\delta(\text{H}1)/J_{1-2}(\text{Hz})$	$\delta(\text{H}2)/J_{2-3}(\text{Hz})$	$\delta(\text{H}3)/J_{3-4}(\text{Hz})$	$\delta(\text{H}4)/J_{4-5}(\text{Hz})$	$\delta(\text{H}5)/J_{5-6}(\text{Hz})$
1	4.84/9.8	3.53/8.8	3.85/9.9	3.67/9.8	3.65/4.8, 1.7
1-Zn	5.22/10.6	2.94/4.1	4.23/ ≈ 0	3.29/ ≈ 0	4.23/ ≈ 0 , 4.9

Figure S2. ^1H -NMR titration of glycosyl donor **1 with zinc(II) triflate**

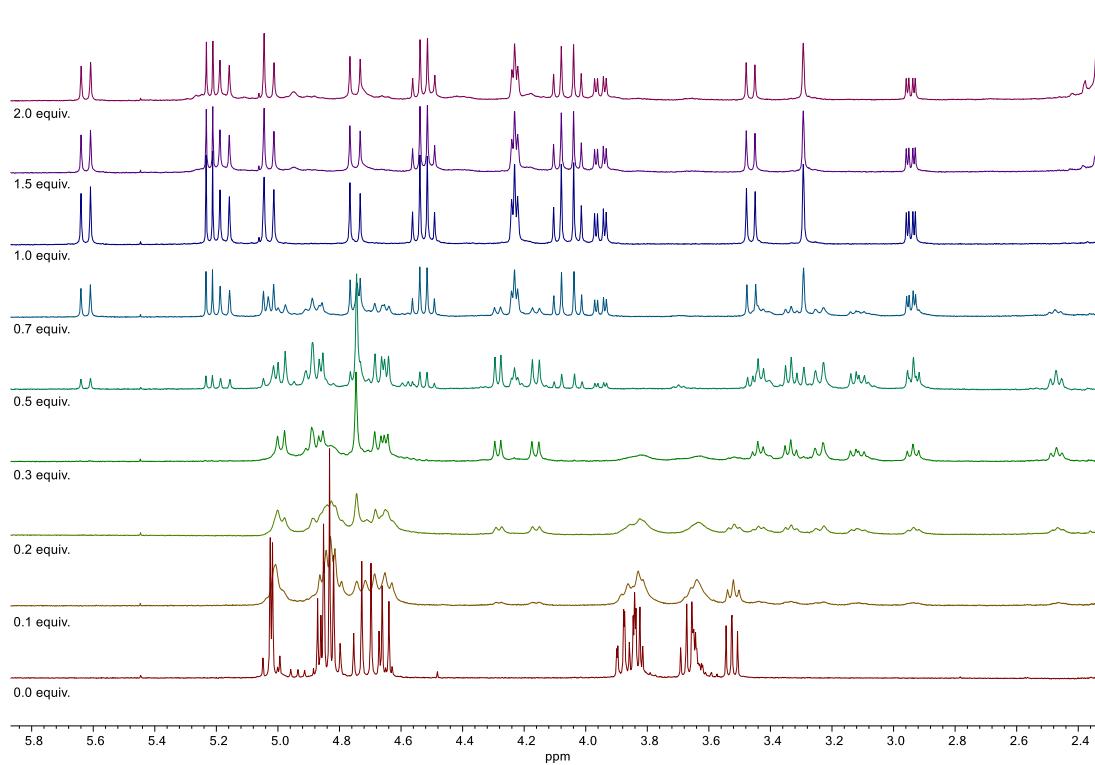


Figure S3. DOSY spectrum of glycosyl donor **1 in acetonitrile- d_3 :**

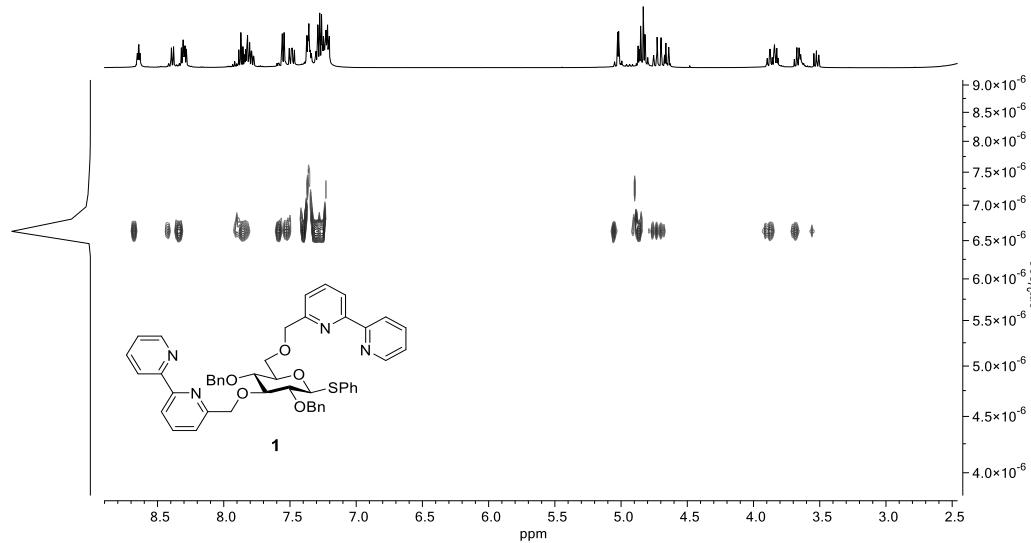


Figure S4. DOSY spectrum of glycosyl donor **1 + 0.5 equiv. Zn(OTf)₂ in acetonitrile-*d*₃:**

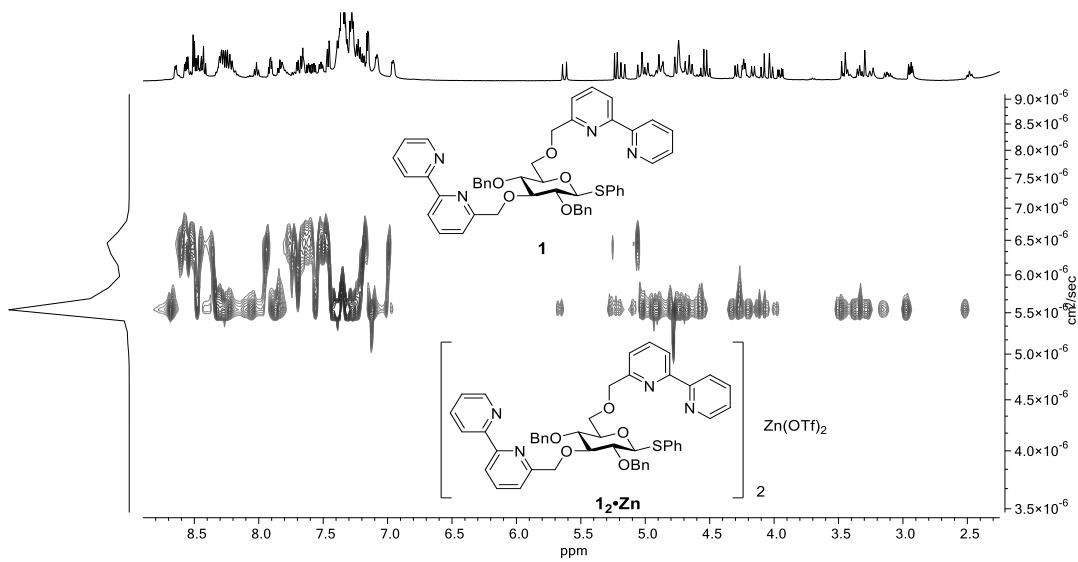
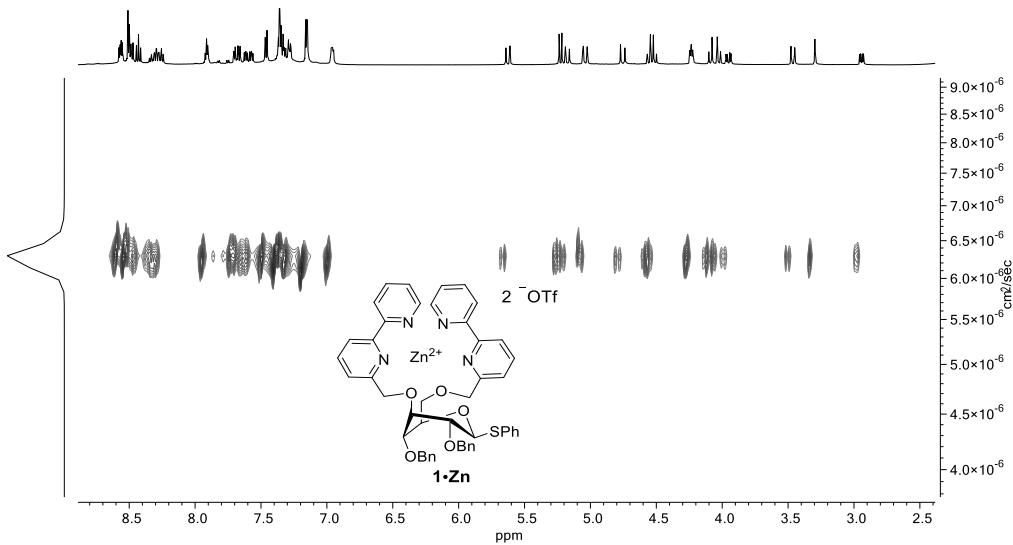


Figure S5. DOSY spectrum of glycosyl donor **1 + 1.0 equiv. Zn(OTf)₂ in acetonitrile-*d*₃:**



Complexation studies of 2

Figure S6. ^1H -NMR spectrum of glycosyl donor 2 and glycosyl donor 2 with zinc(II) triflate (1 equiv.)

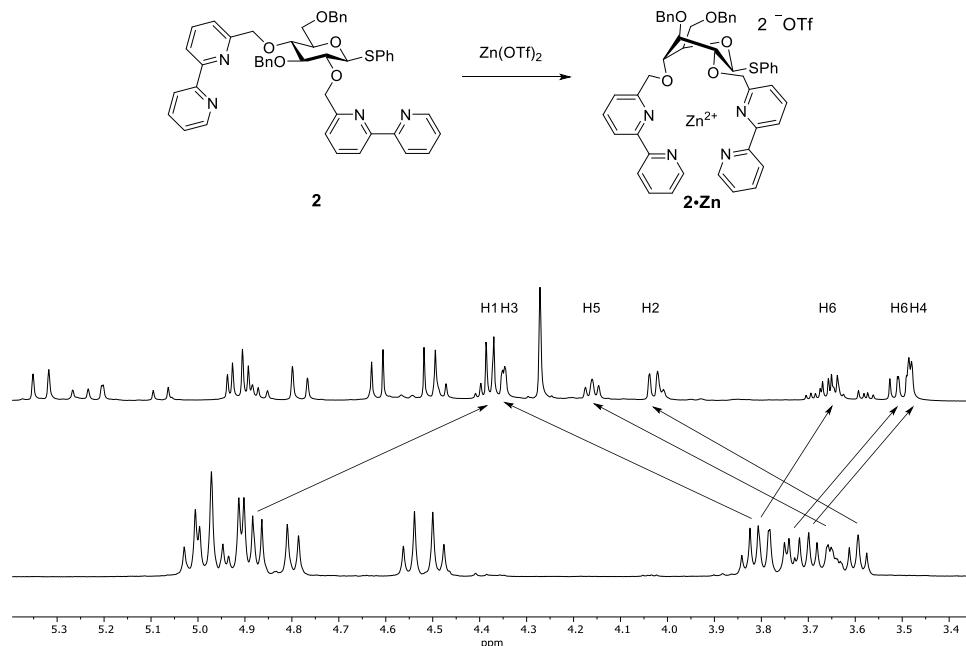
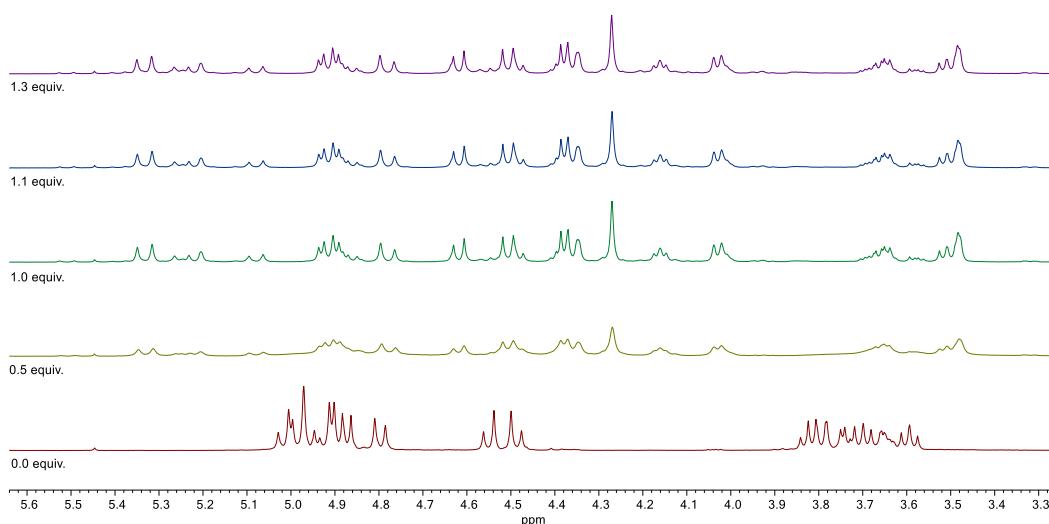


Table S2. J -couplings of glycosyl donor 2 and $2 \cdot \text{Zn}$.

Glycosyl donor	$\delta(\text{H1})/\text{J}_{1-2}(\text{Hz})$	$\delta(\text{H2})/\text{J}_{2-3}(\text{Hz})$	$\delta(\text{H3})/\text{J}_{3-4}(\text{Hz})$	$\delta(\text{H4})/\text{J}_{4-5}(\text{Hz})$	$\delta(\text{H5})/\text{J}_{5-6}(\text{Hz})$
2	4.87/9.8	3.59/8.7	3.82/9.3	3.70/9.7	3.65/1.8, 4.8
2-Zn	4.38/8.2	4.03/1.3	4.35/3.3	3.29/ ≈ 0	4.16/6.2, 8.1

Figure S7. ^1H -NMR titration of glycosyl donor 2 with zinc(II) triflate



Complexation studies of 18

Figure S8. ^1H -NMR spectrum of glycosyl donor **18** and glycosyl donor **18** with zinc(II) triflate (0.5 equiv.)

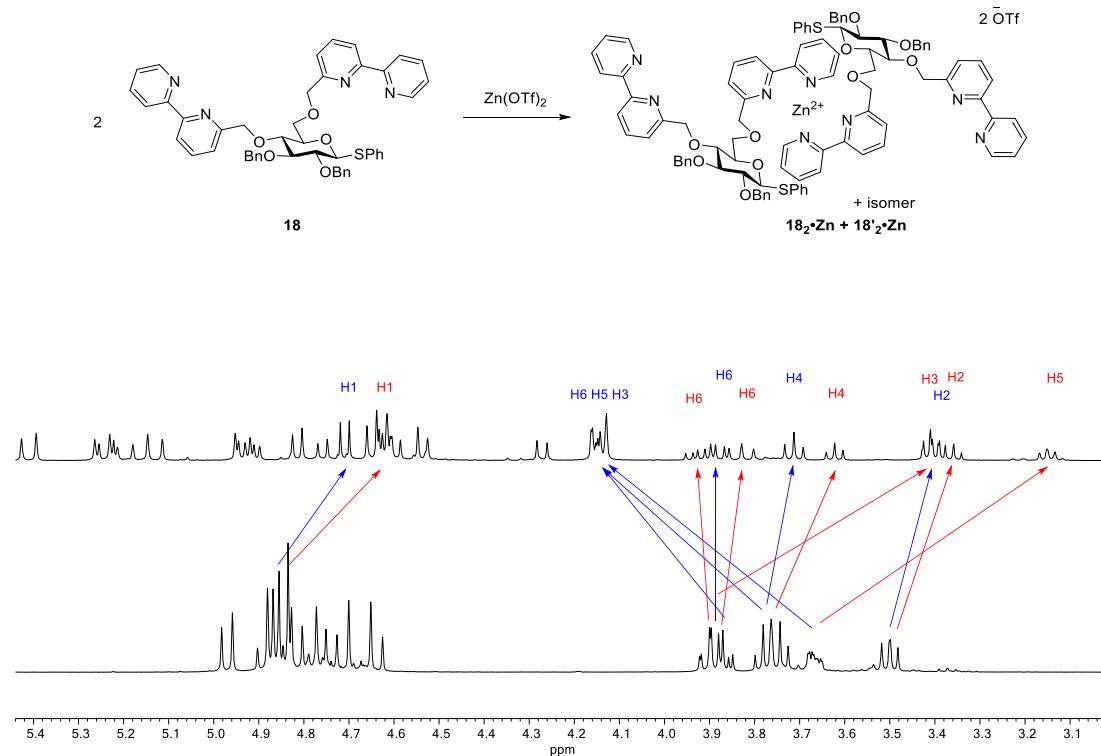


Table S3. J -couplings of glycosyl donor **18**, 18_2-Zn and $18'_2\text{-Zn}$.

Glycosyl donor	$\delta(\text{H}1)/J_{1-2}\text{(Hz)}$	$\delta(\text{H}2)/J_{2-3}\text{(Hz)}$	$\delta(\text{H}3)/J_{3-4}\text{(Hz)}$	$\delta(\text{H}4)/J_{4-5}\text{(Hz)}$	$\delta(\text{H}5)/J_{5-6}\text{(Hz)}$
18	4.85/9.8	3.50/8.6	3.78/9.1	3.74/9.1	3.67/4.6, 2.0
18₂-Zn	4.71/9.9	3.41/8.3	4.14/10.3	3.71/10.3	4.14/5.3, n/a
18'₂-Zn	4.62/n/a	3.36/8.7	3.40/8.6	3.62/9.3	3.15/8.0, n/a

Figure S9. ^1H -NMR titration of glycosyl donor **18** with zinc(II) triflate

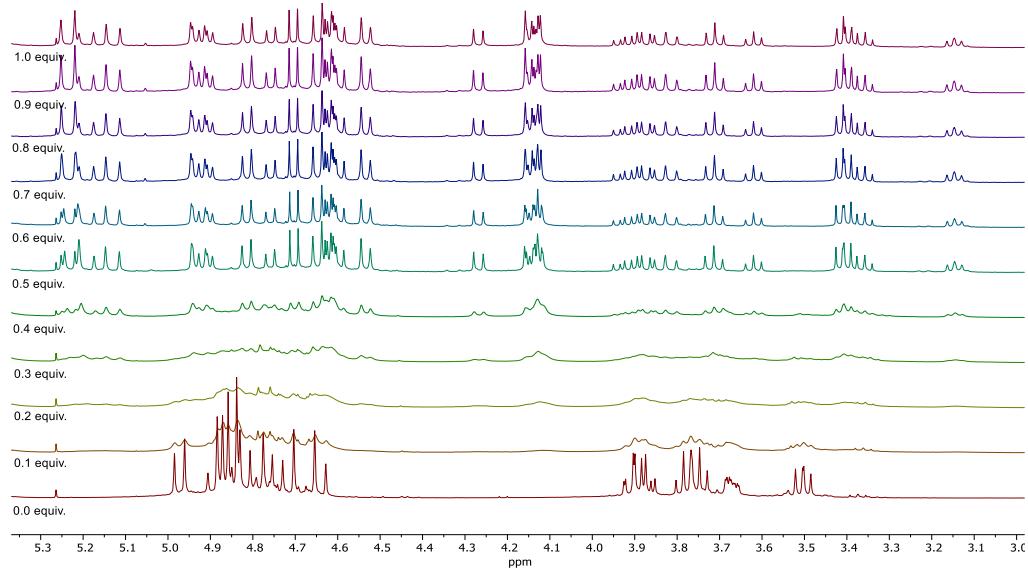


Figure S10. DOSY spectrum of glycosyl donor **18** in acetonitrile- d_3 :

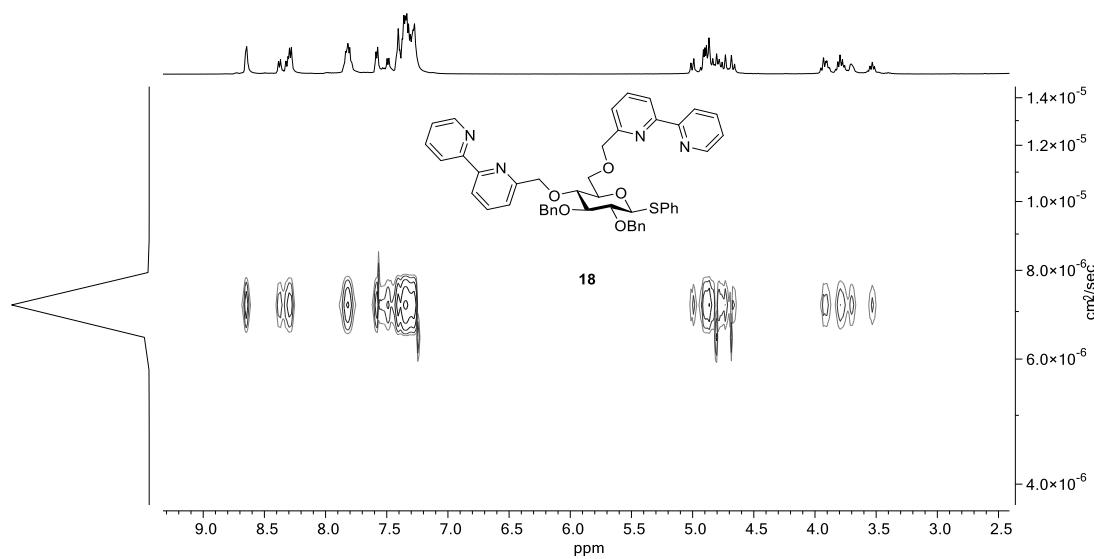
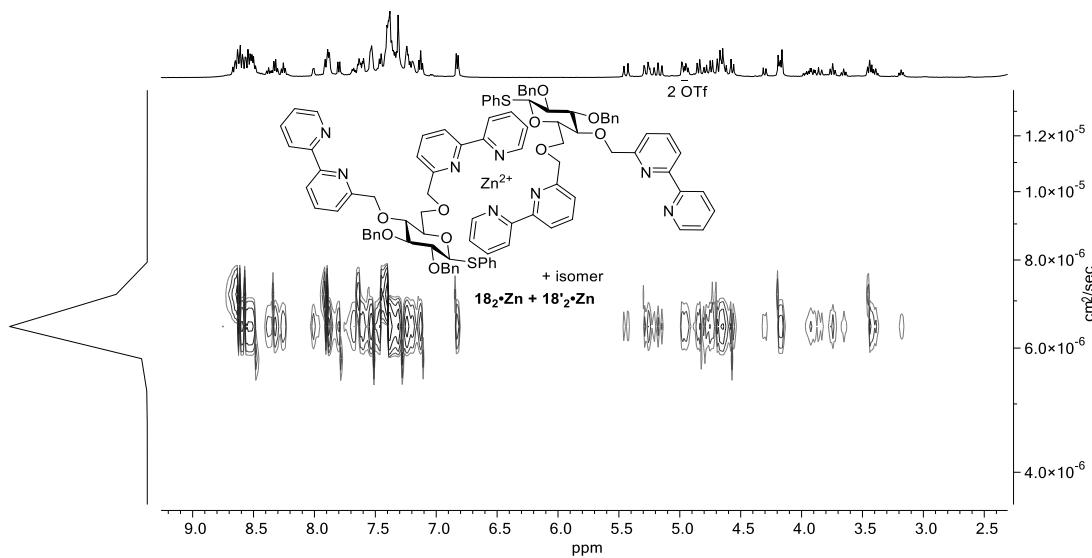
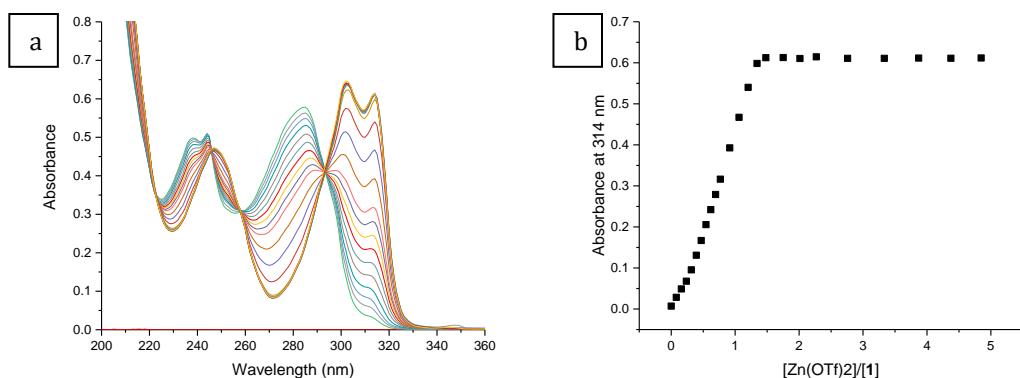


Figure S11. DOSY spectrum of glycosyl donor **18** + 0.5 equiv. Zn(OTf)₂ in acetonitrile-*d*₃:



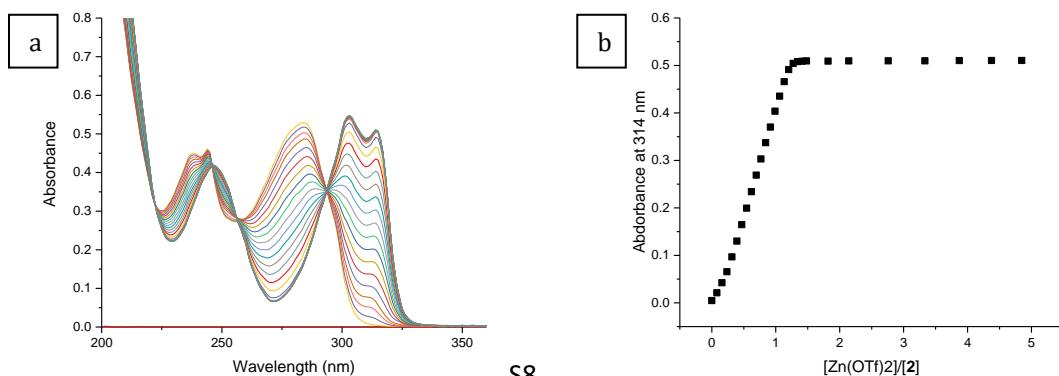
UV-Vis titration of 1

Figure S12. UV-Vis titration of glycosyl donor **1** with zinc(II) triflate (a), Plot of absorbance at 314 nm against the ratio of glycosyl donor **1** to Zn²⁺ ions (b).

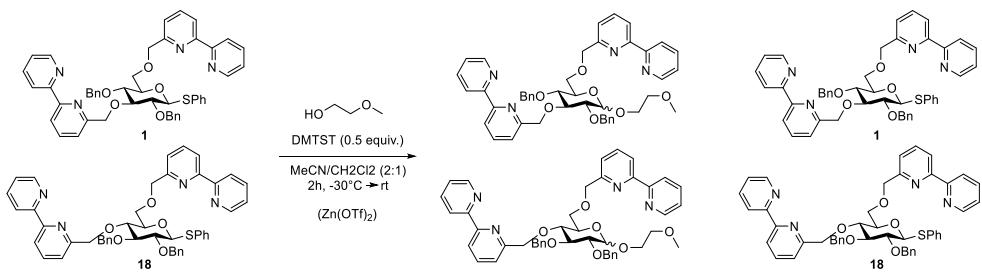


UV-Vis titration of 2

Figure S13. UV-Vis titration of glycosyl donor **2** with zinc(II) triflate (a), Plot of absorbance at 314 nm against the ratio of glycosyl donor **2** to Zn²⁺ ions (b).



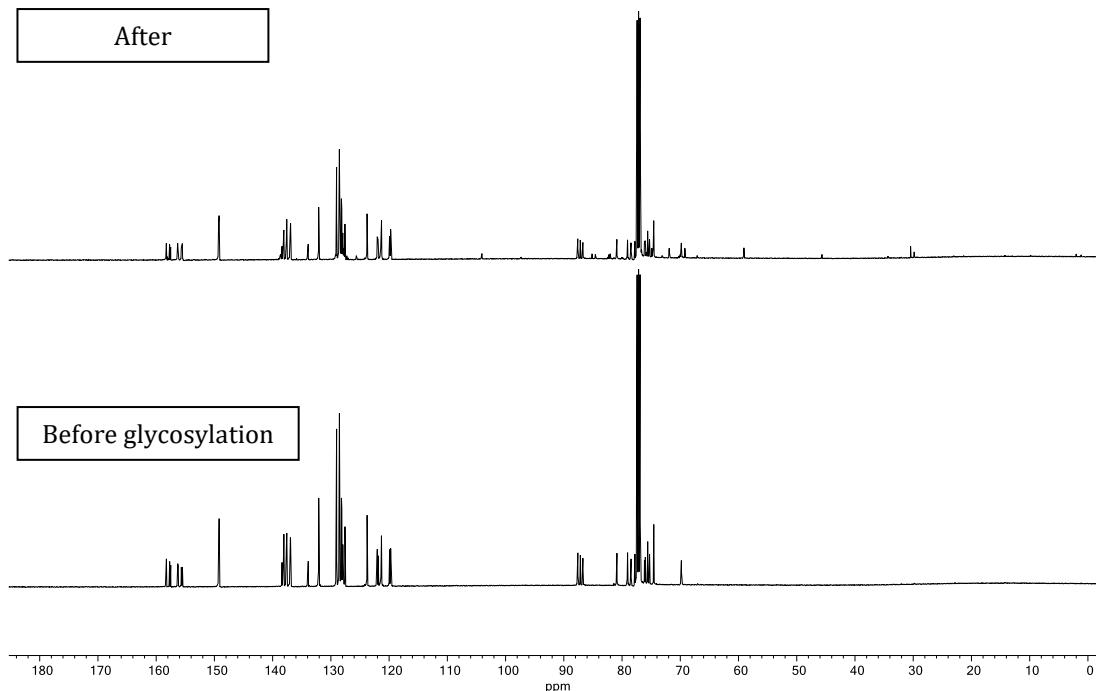
Competition experiments

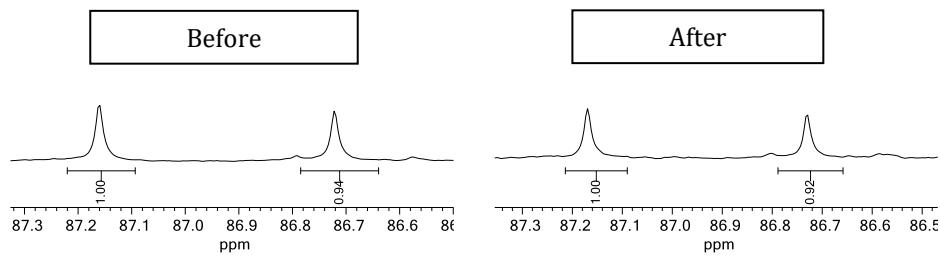


A mixture of glycosyl donor **1** (18 mg, 0.023 mmol, 1 equiv.) and glycosyl donor **18** (18 mg, 0.023 mmol, 1 equiv.) was dissolved in chloroform-*d* and a ^{13}C -NMR spectrum (126 MHz, 512 scans) was recorded. The glycosyl donor solution was then concentrated under reduced pressure and co evaporated several times with toluene and dried under reduced pressure on a Schlenk line for 1 h together with 3 Å molecular sieves. The glycosyl donor mixture was then dissolved in $\text{MeCN}/\text{CH}_2\text{Cl}_2$ (2:1) together with 2-methoxymethanol (8.7 mg, 0.011 mmol, 5 equiv.) and the resulting mixture cooled to -30°C . A solution of DMTST in CH_2Cl_2 (59 μL , 387 mM, 1 equiv.) was added after which the reaction mixture was allowed to reach rt. After 2 h, the reaction was stopped by addition of Et_3N , diluted with Et_2O , filtered and extracted several times with water and brine. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo* to afford the mixture of starting materials and glycosides.

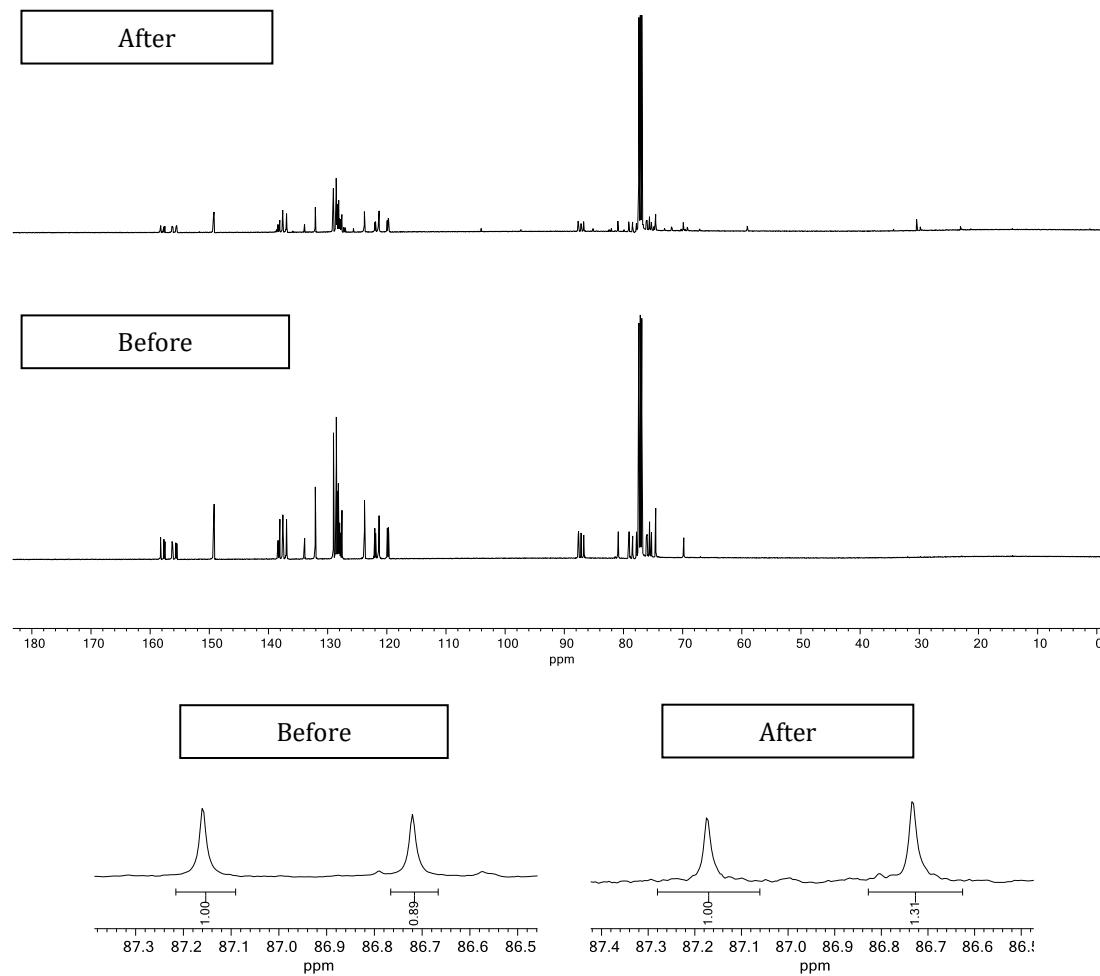
The experiment was repeated in the presence of 2 equiv. zinc(II) triflate added after the co evaporation with toluene.

^{13}C -NMR spectra of a 1:1 mixture of glycosyl donor **1** and **18** before and after a glycosylation *without* zinc(II) triflate:



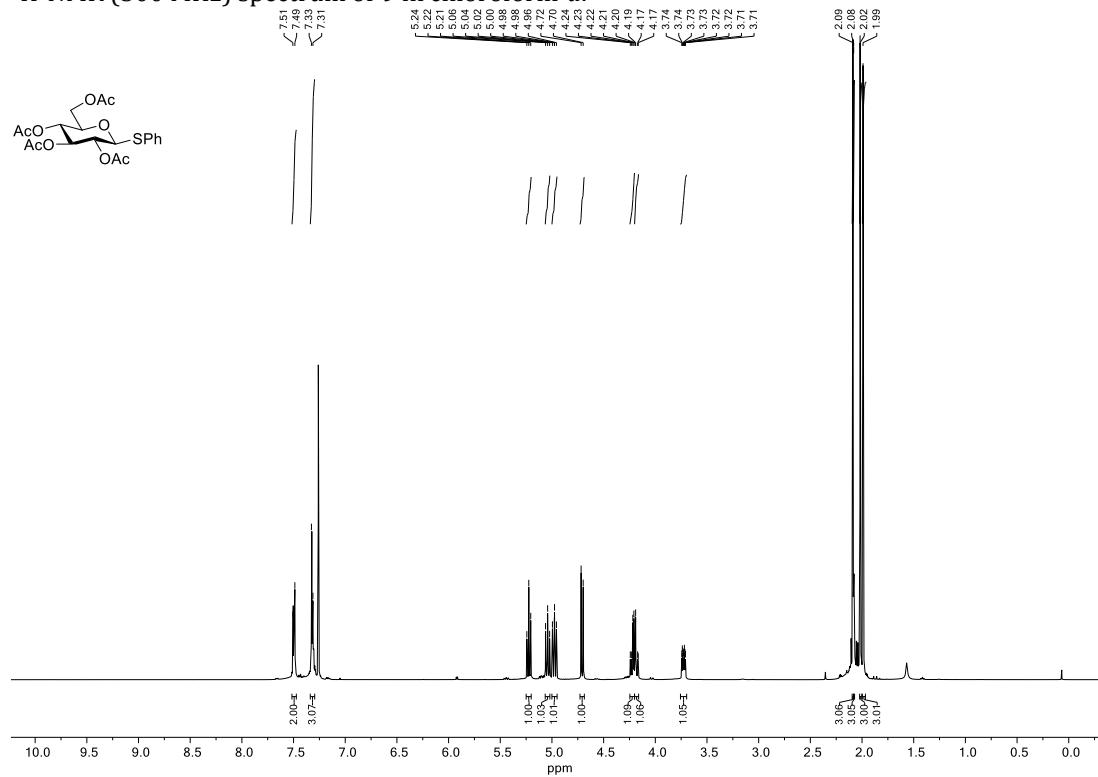


¹³C-NMR spectra of a 1:1 mixture of glycosyl donor **1** and **18** before and after a glycosylation with zinc(II) triflate:

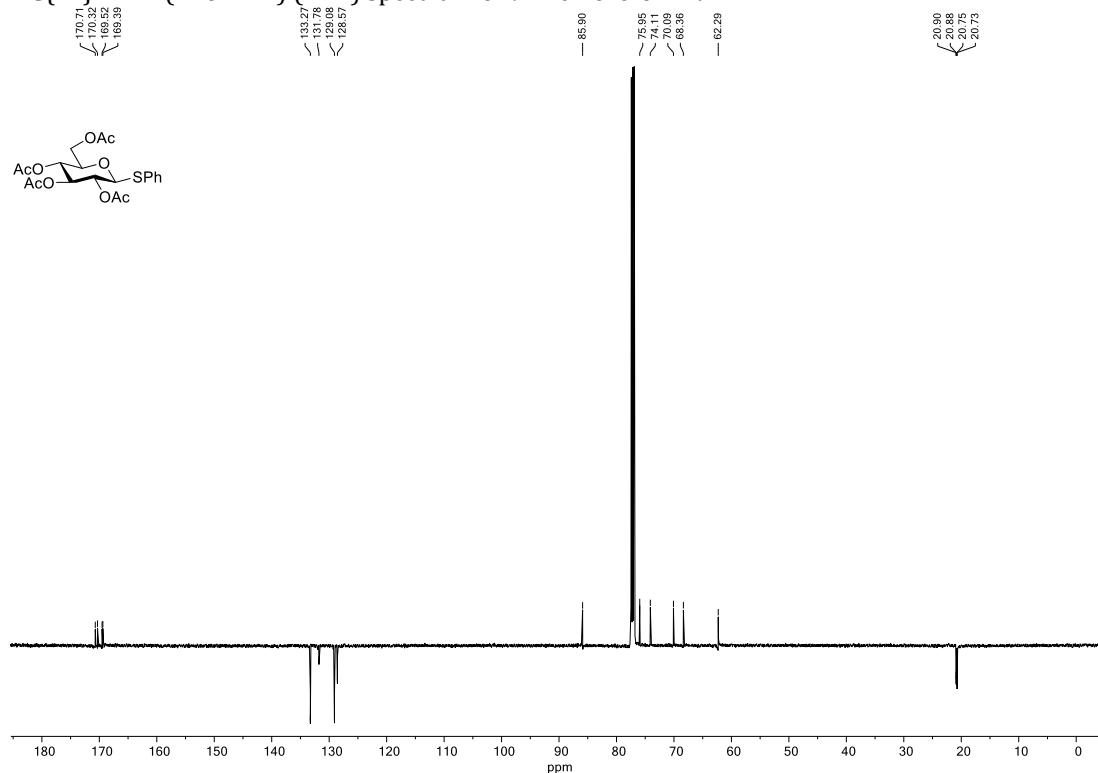


NMR Spectra

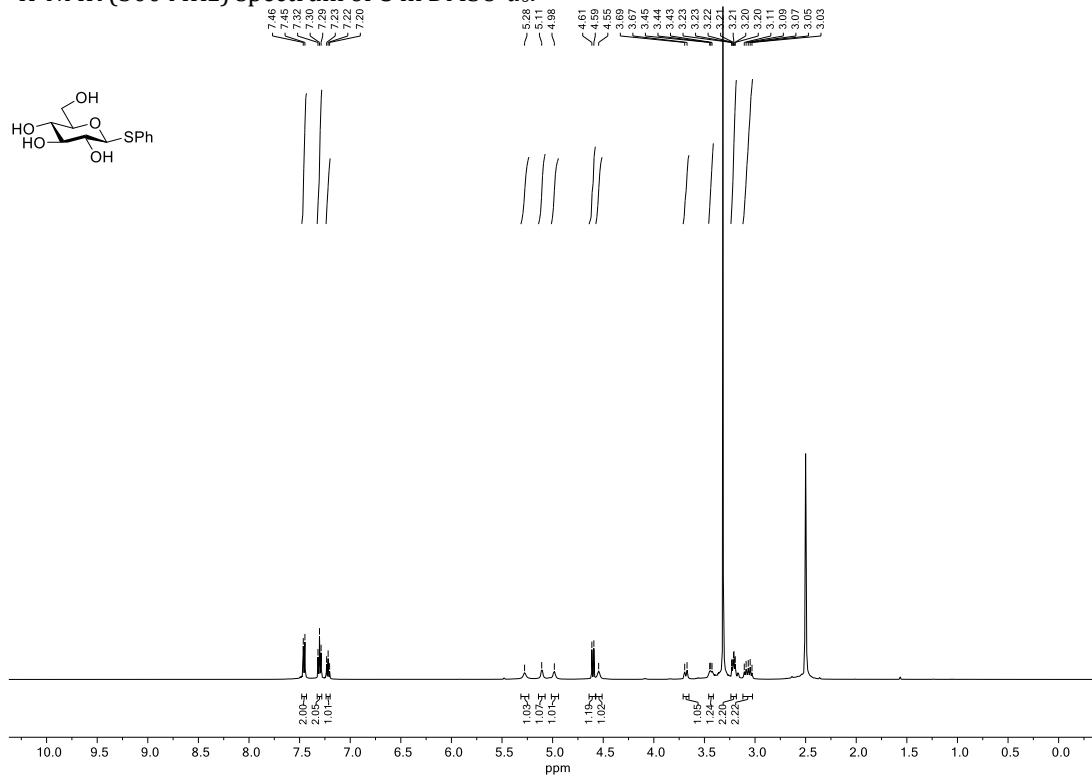
^1H -NMR (500 MHz) spectrum of **9** in chloroform-*d*.



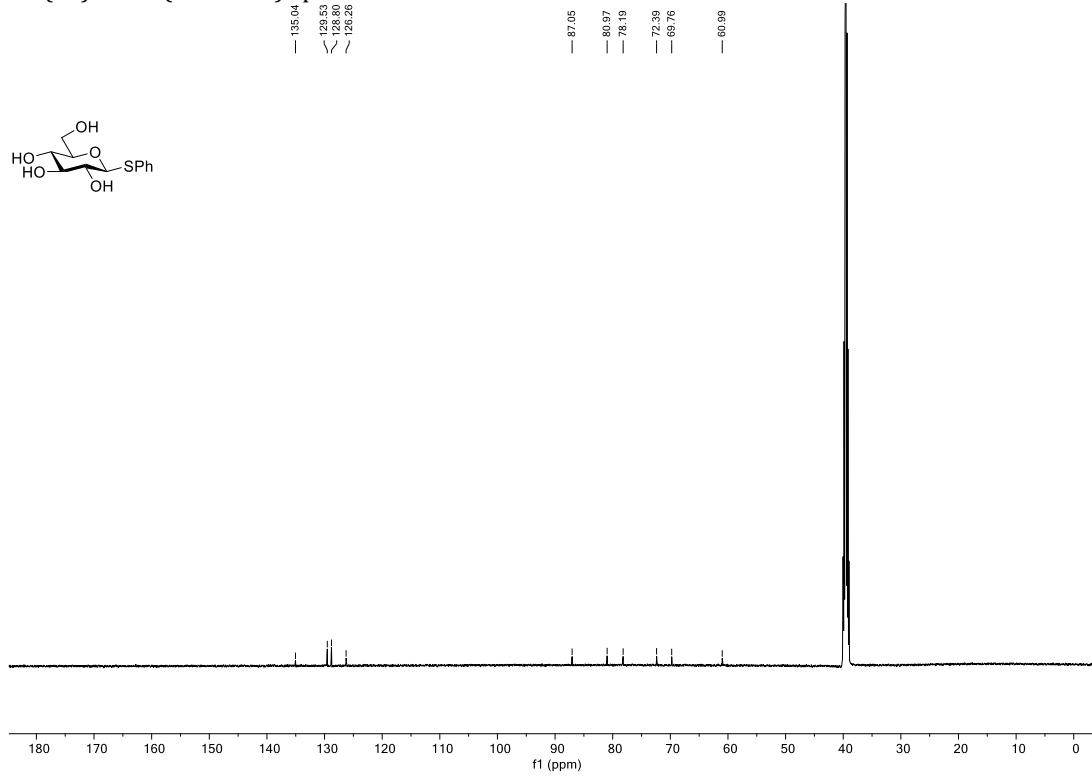
$^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz) (APT) spectrum of **9** in chloroform-*d*.



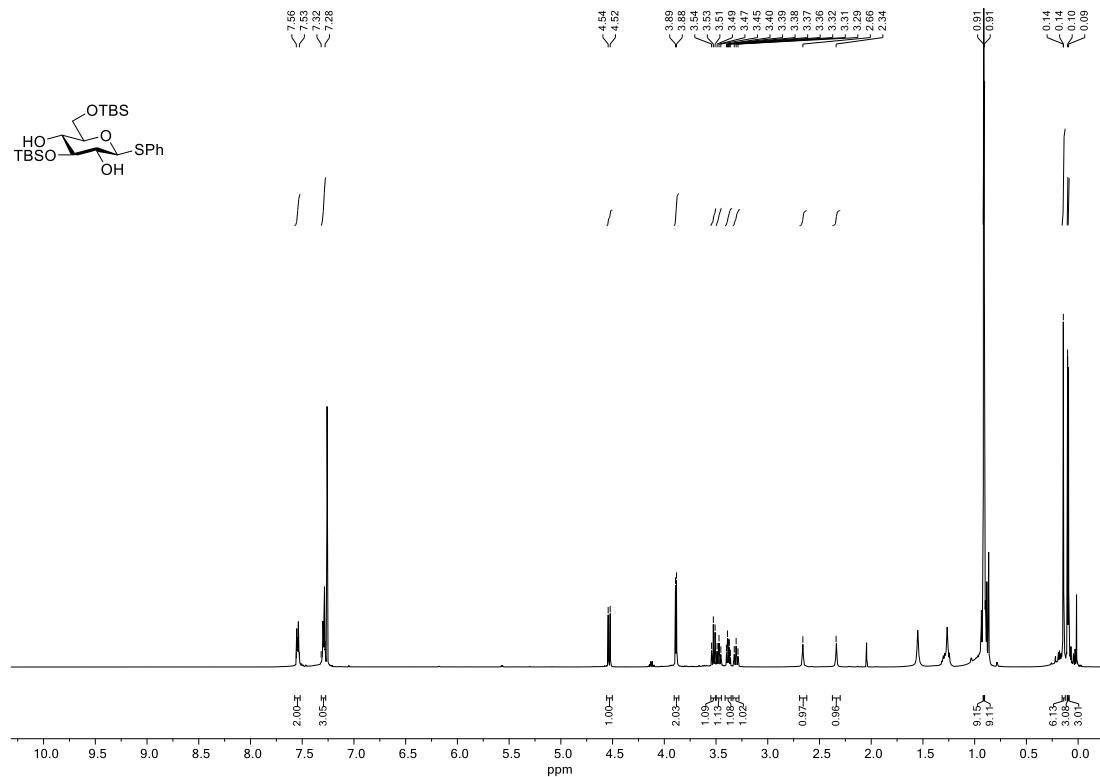
¹H-NMR (500 MHz) spectrum of **8** in DMSO-*d*₆.



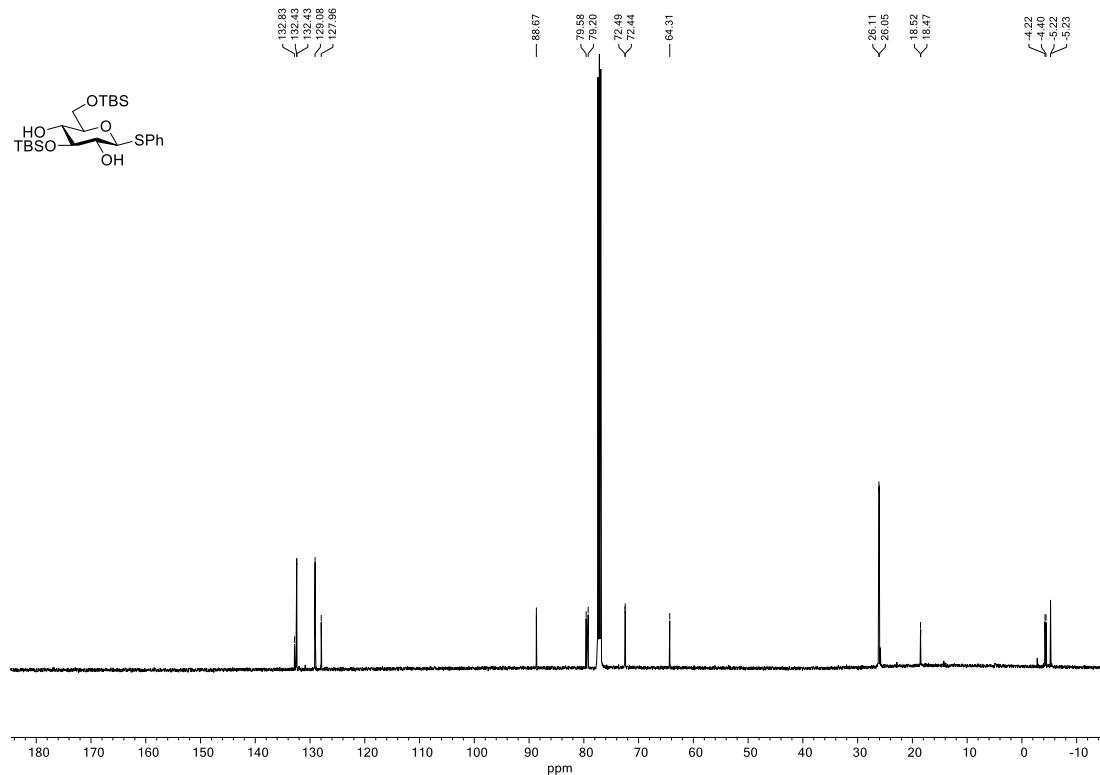
$^{13}\text{C}\{\text{H}\}$ -NMR (126 MHz) spectrum of **8** in $\text{DMSO}-d_6$.



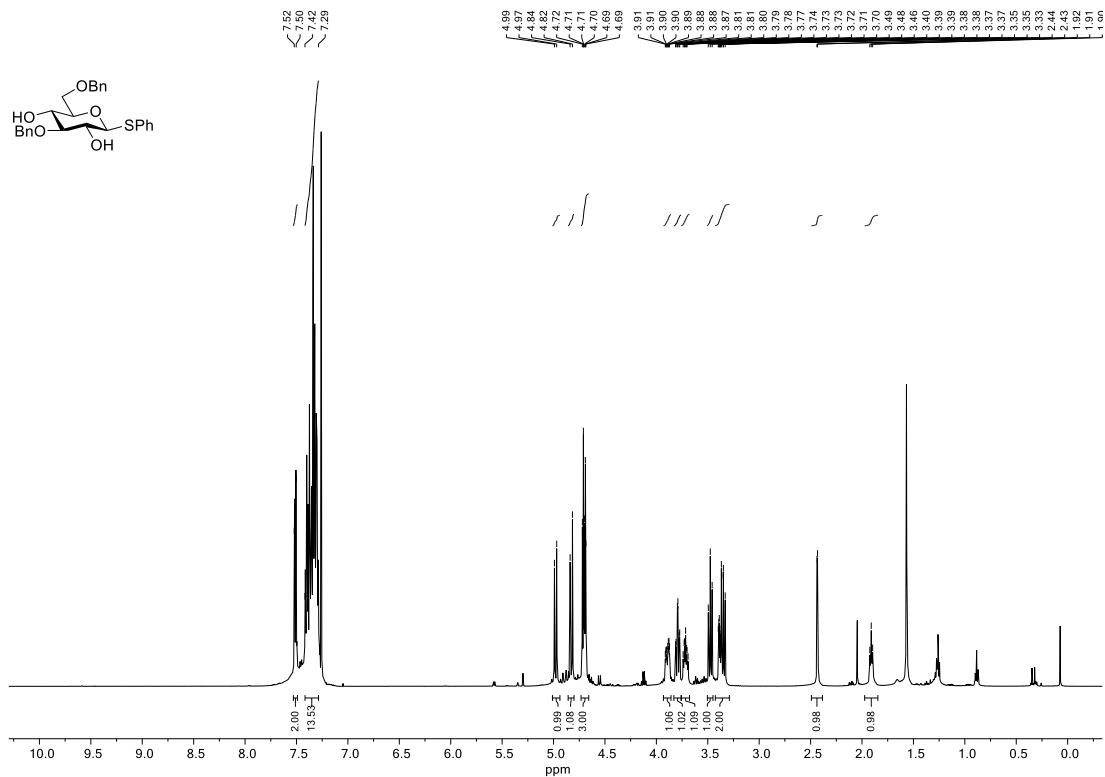
¹H-NMR (500 MHz) spectrum of **5** in chloroform-*d*.



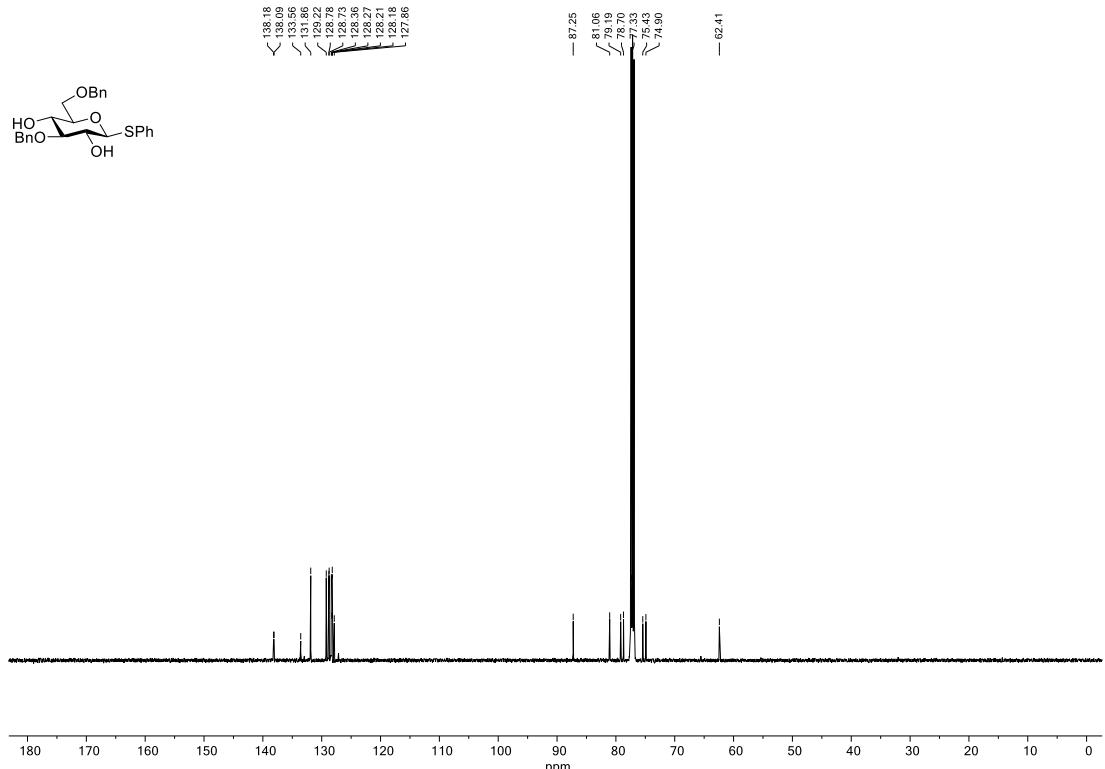
$^{13}\text{C}\{\text{H}\}$ -NMR (126 MHz) spectrum of **5** in chloroform-*d*.



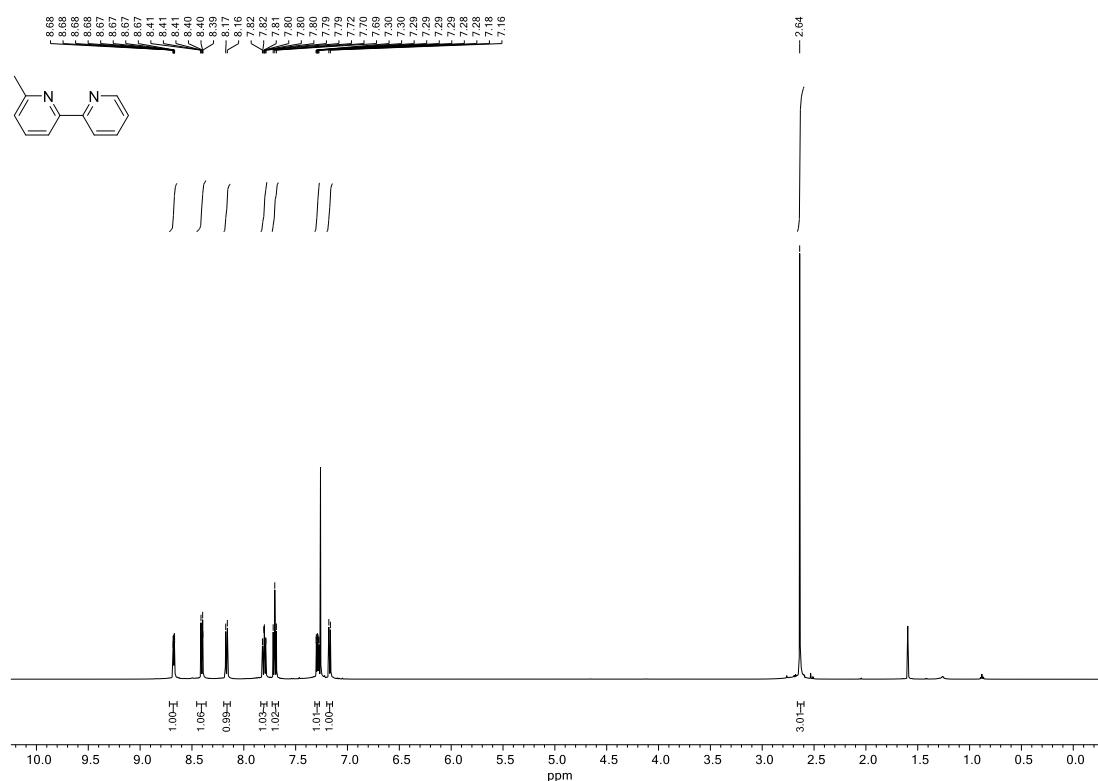
¹H-NMR (500 MHz) spectrum of **4** in chloroform-*d*.



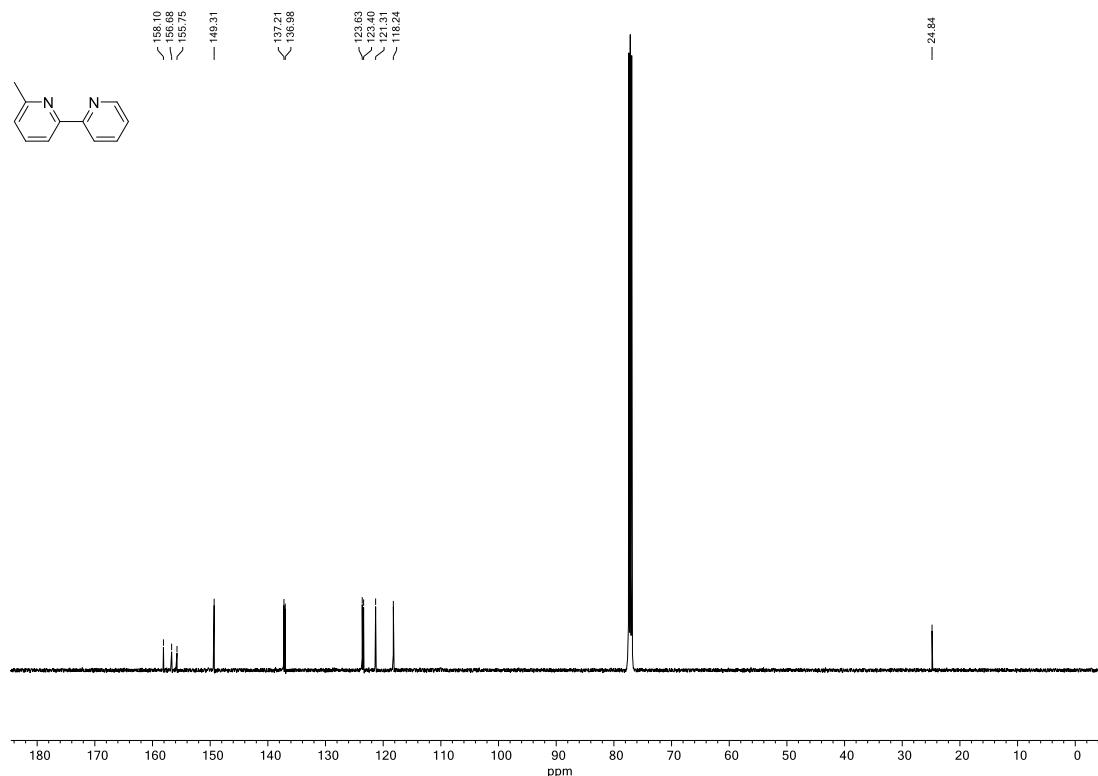
$^{13}\text{C}\{\text{H}\}$ -NMR (126 MHz) spectrum of **4** in chloroform-*d*.



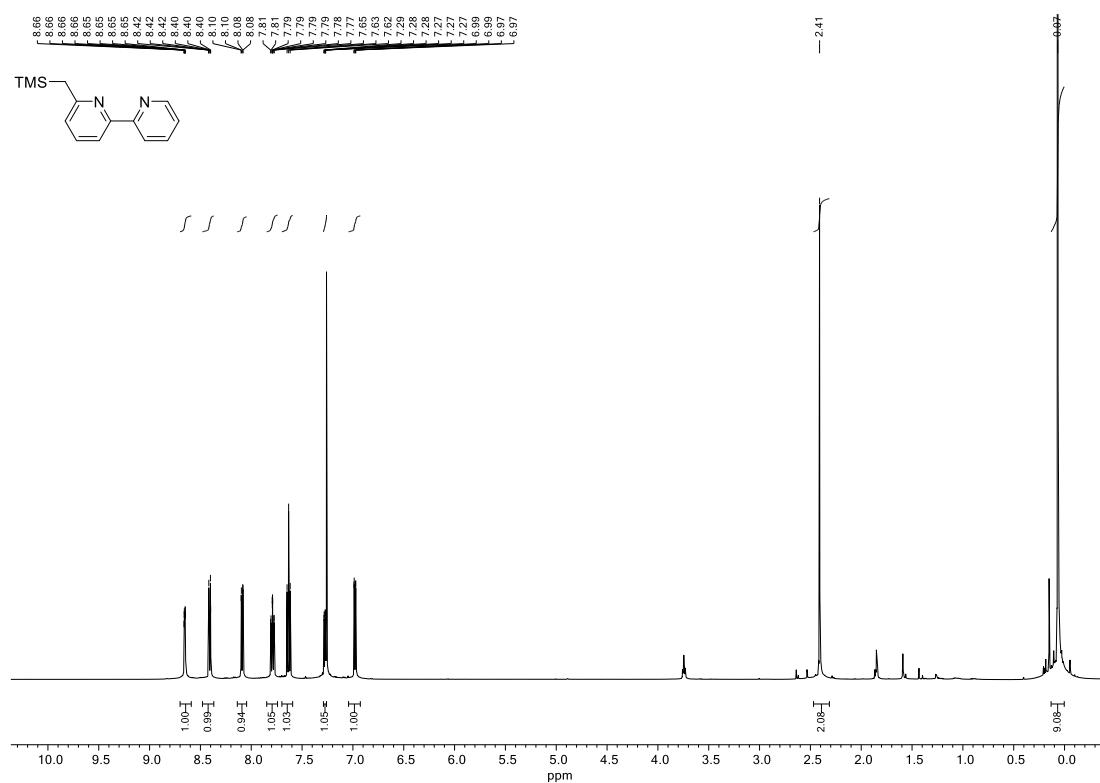
¹H-NMR (500 MHz) spectrum of **23** in chloroform-*d*.



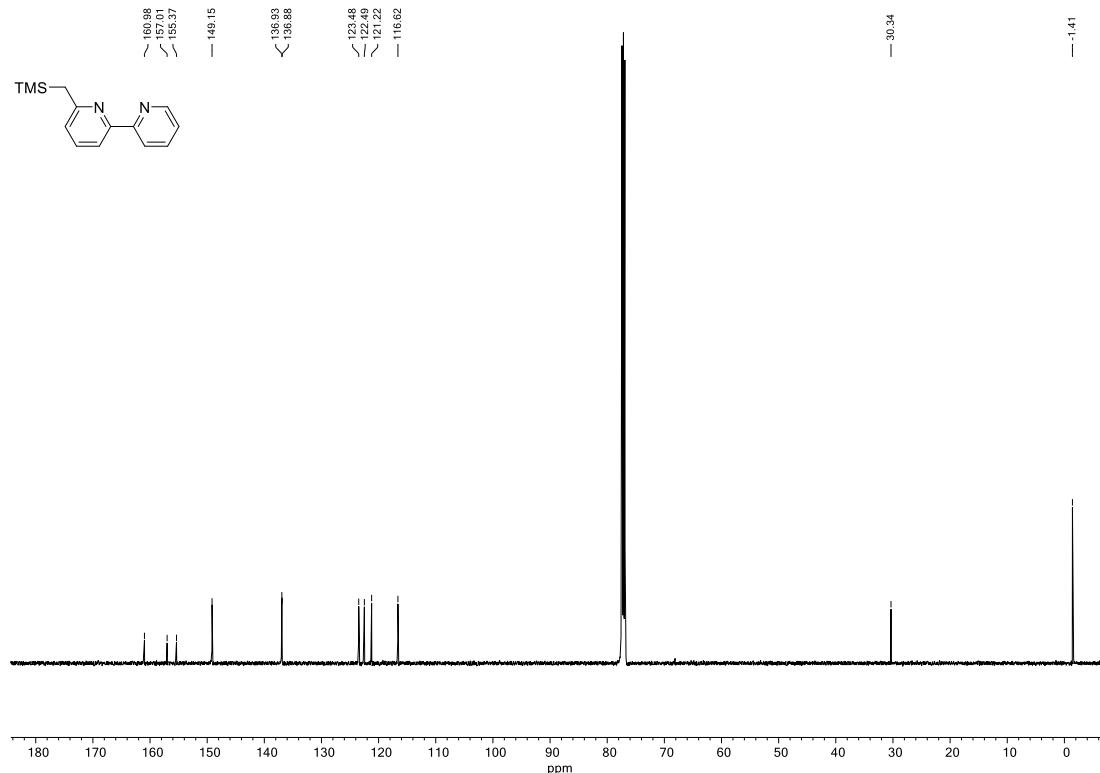
¹³C{¹H}-NMR (126 MHz) spectrum of **23** in chloroform-*d*.



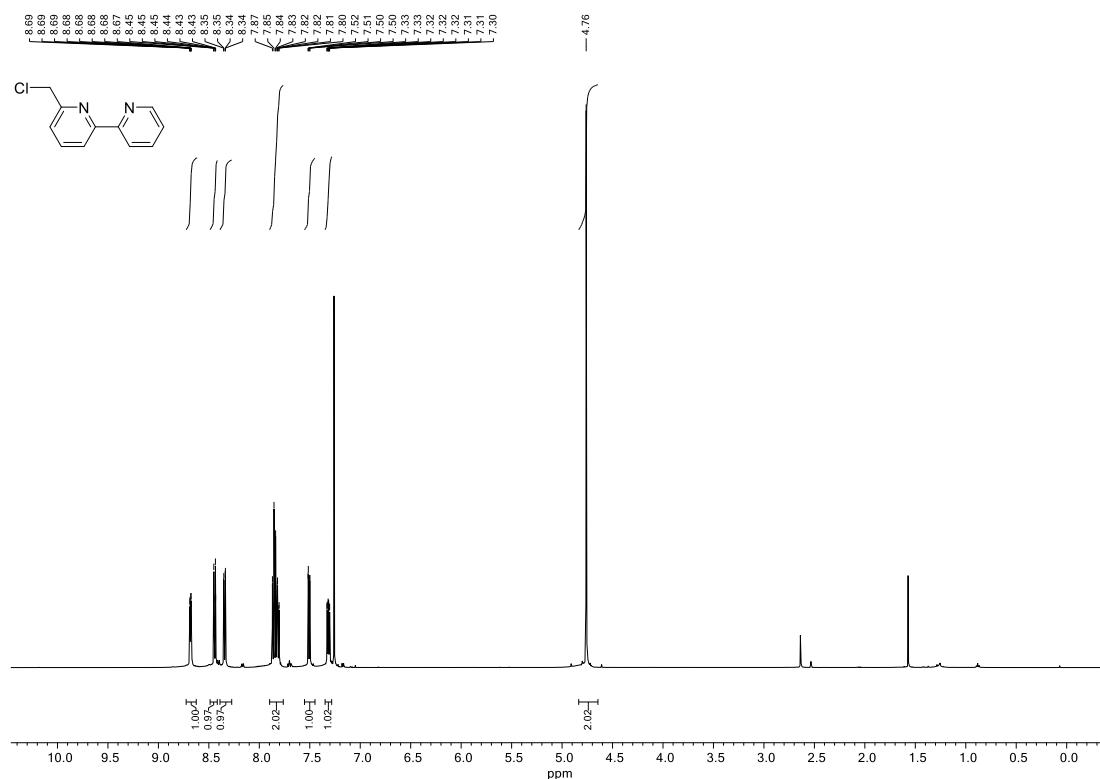
¹H-NMR (500 MHz) spectrum of **24** in chloroform-*d*.



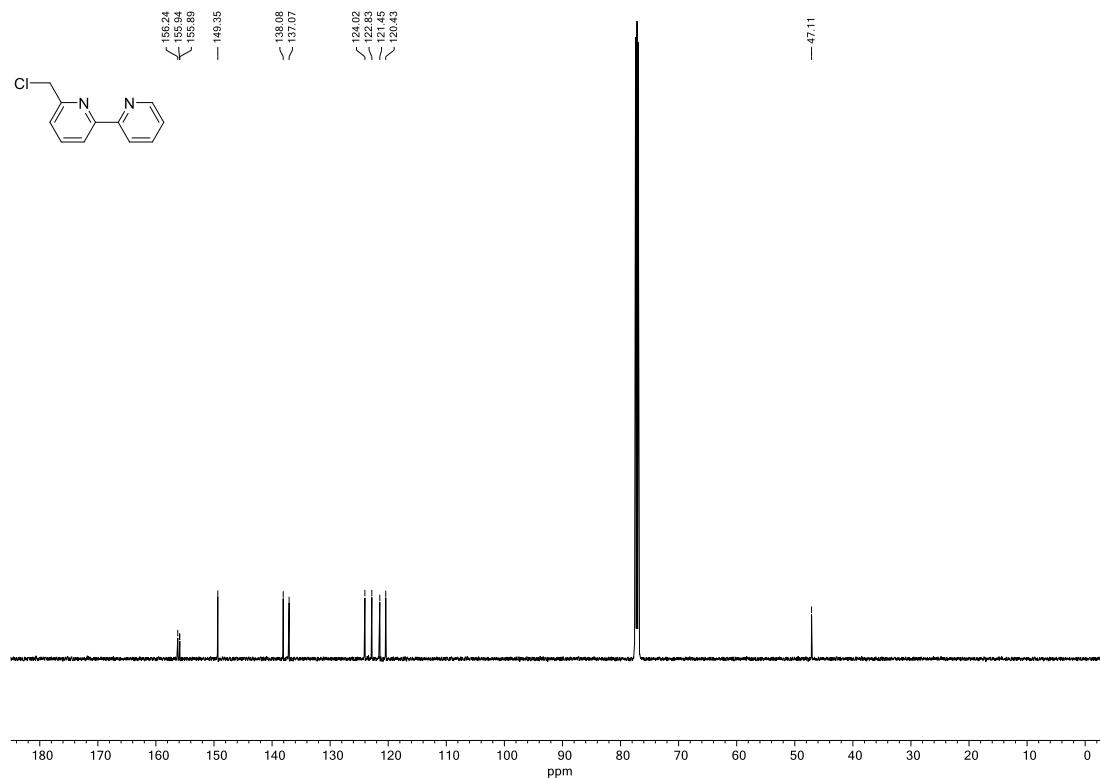
$^{13}\text{C}\{\text{H}\}$ -NMR (126 MHz) spectrum of **24** in chloroform-*d*.



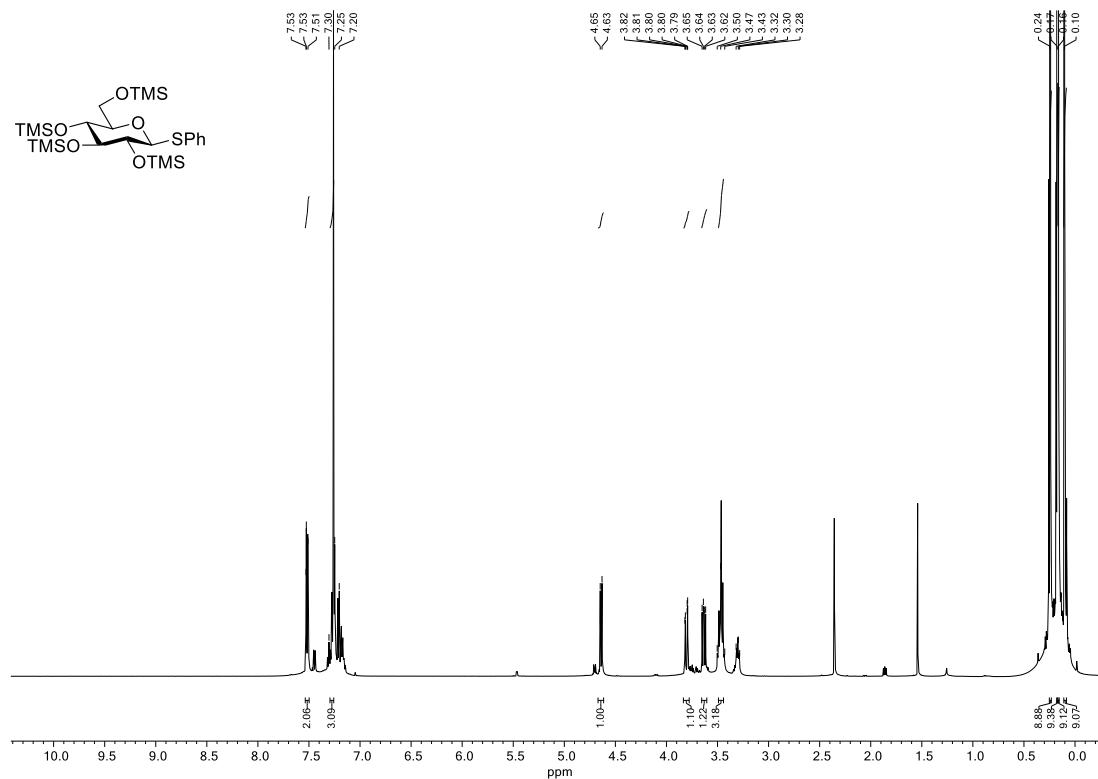
¹H-NMR (500 MHz) spectrum of **3** in chloroform-*d*.



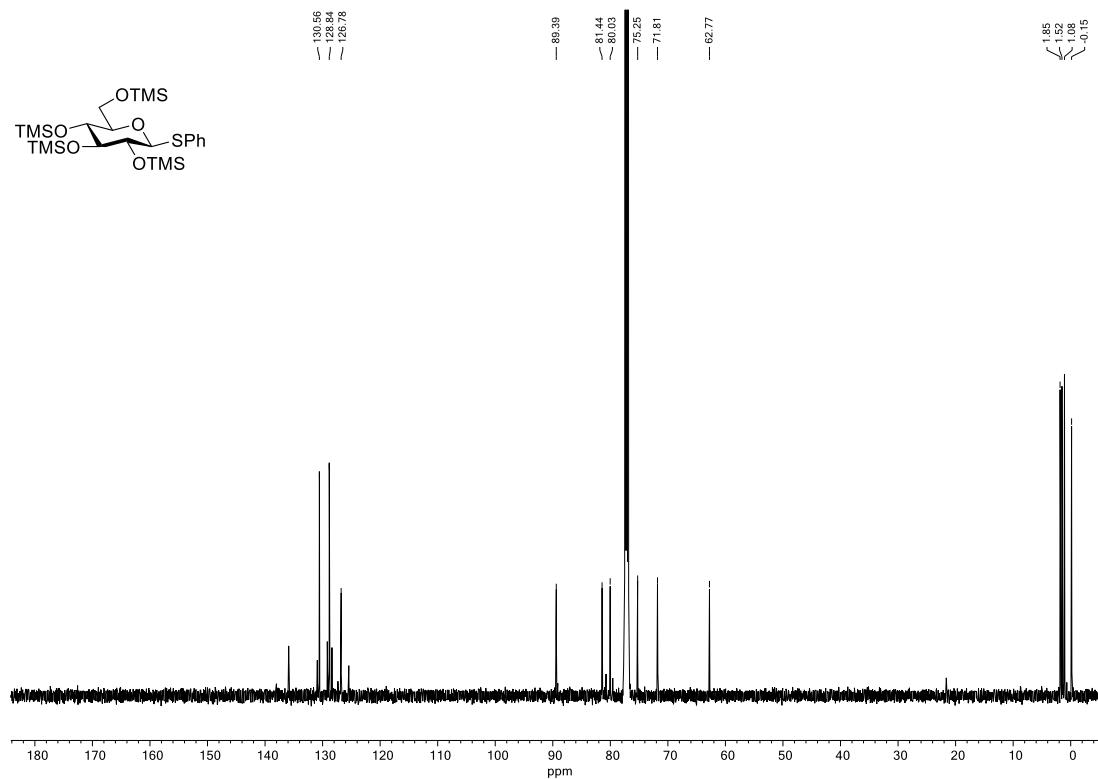
$^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz) spectrum of **3** in chloroform-*d*.



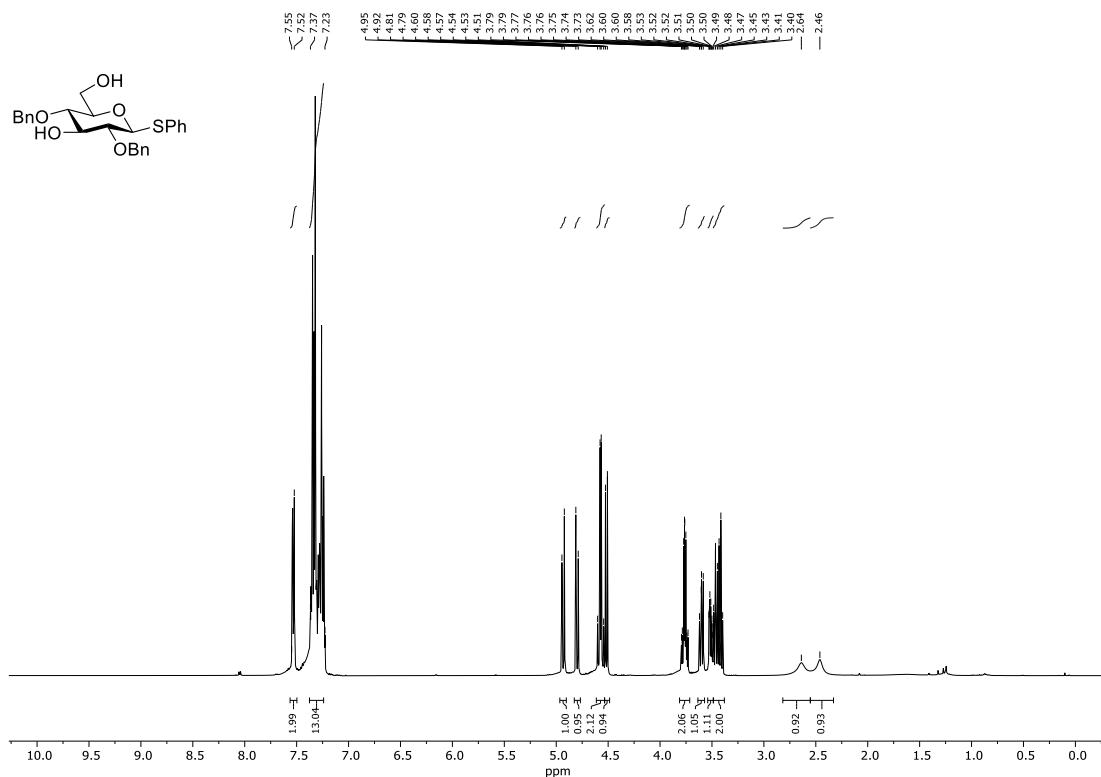
¹H-NMR (500 MHz) spectrum of **7** in chloroform-*d*.



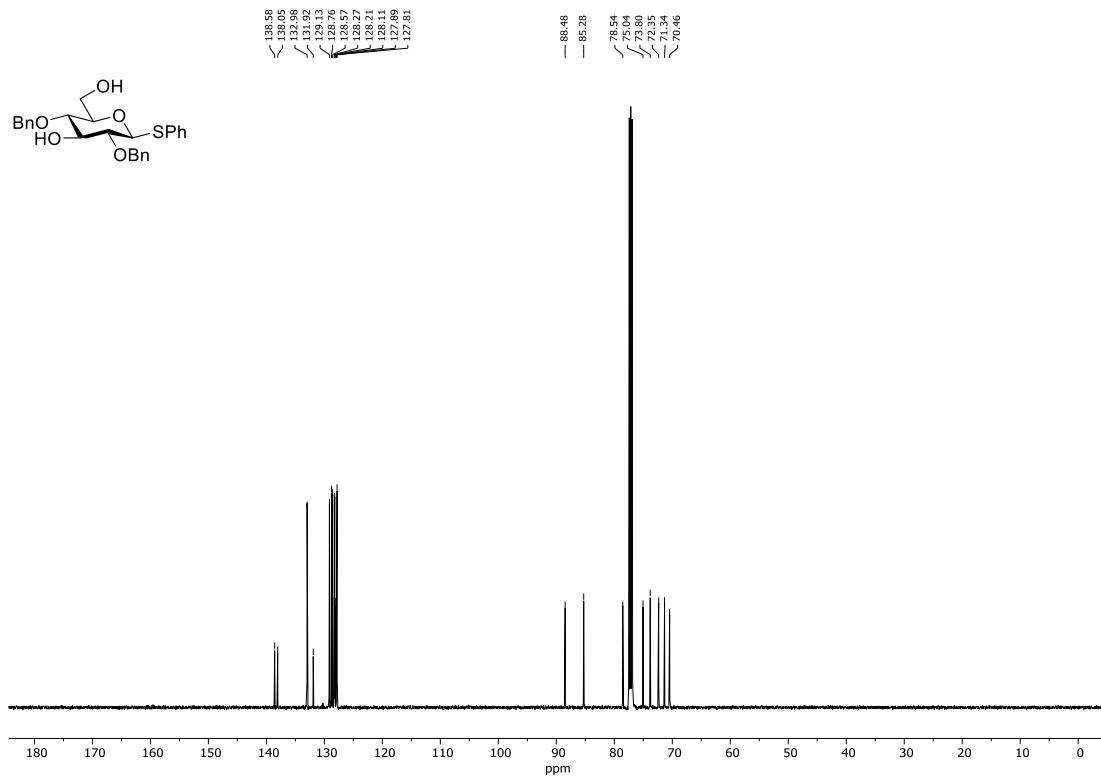
¹³C{¹H}-NMR (126 MHz) spectrum of **7** in chloroform-*d*.



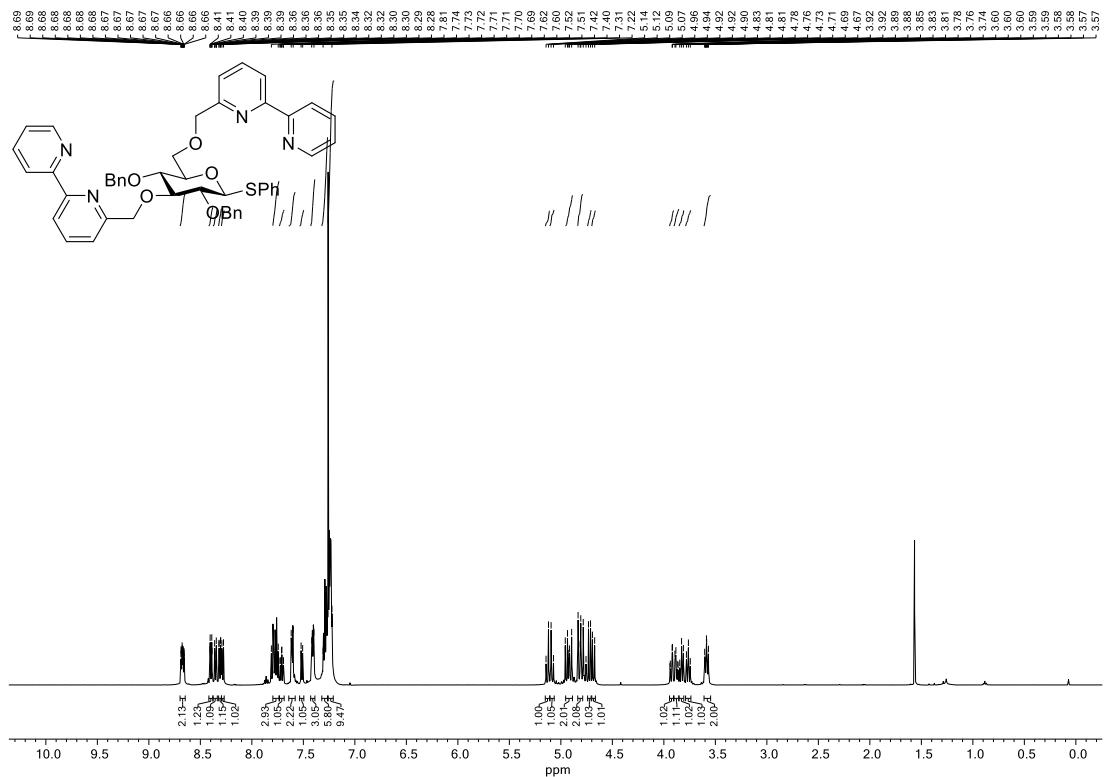
¹H-NMR (500 MHz) spectrum of **6** in chloroform-*d*.



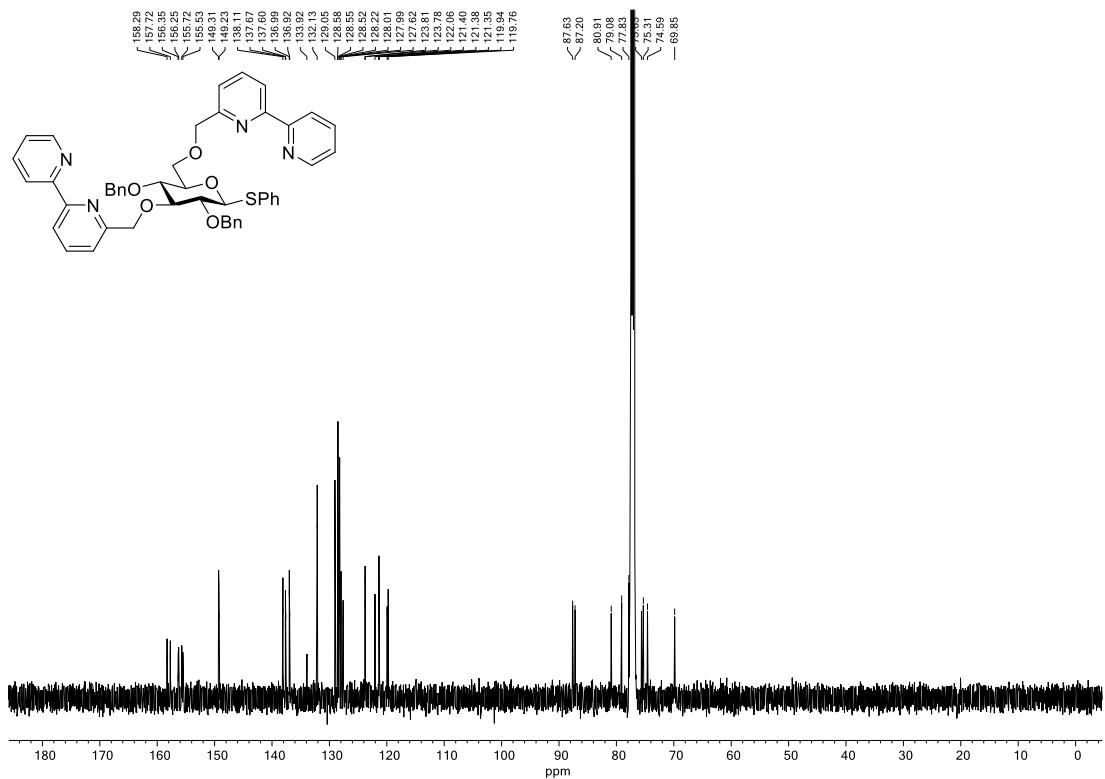
$^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz) spectrum of **6** in chloroform-*d*.



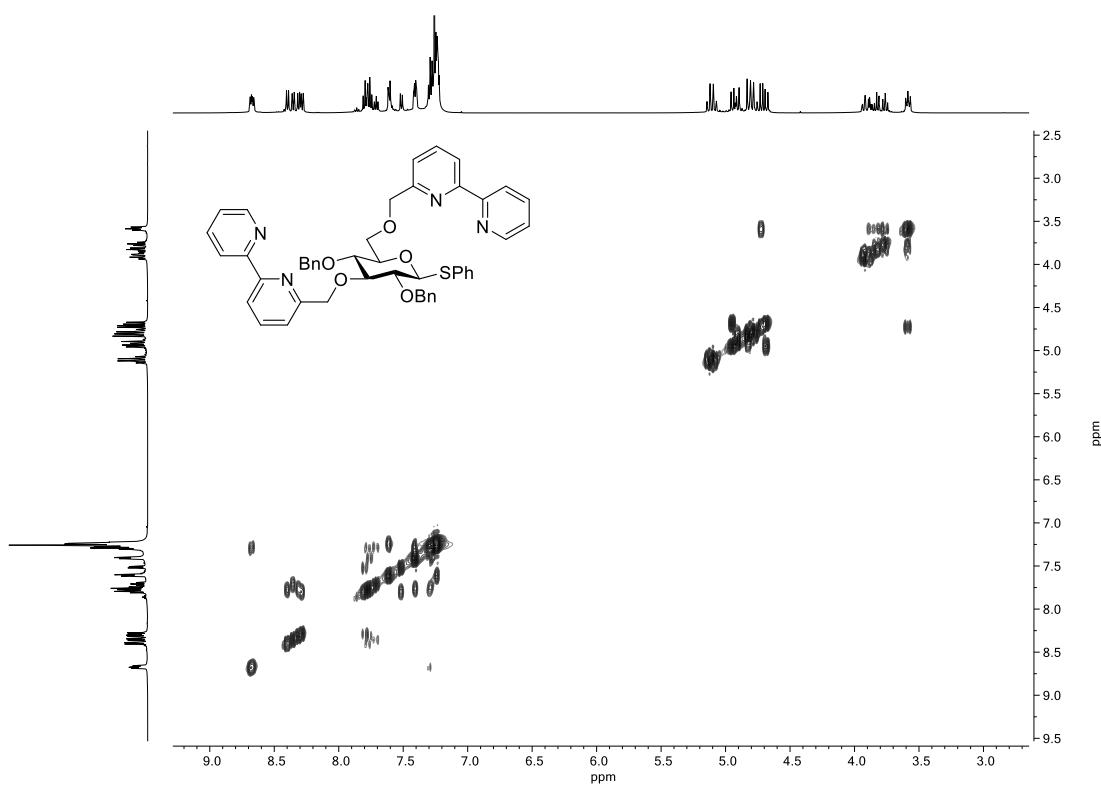
¹H-NMR (500 MHz) spectrum of **1** in chloroform-*d*.



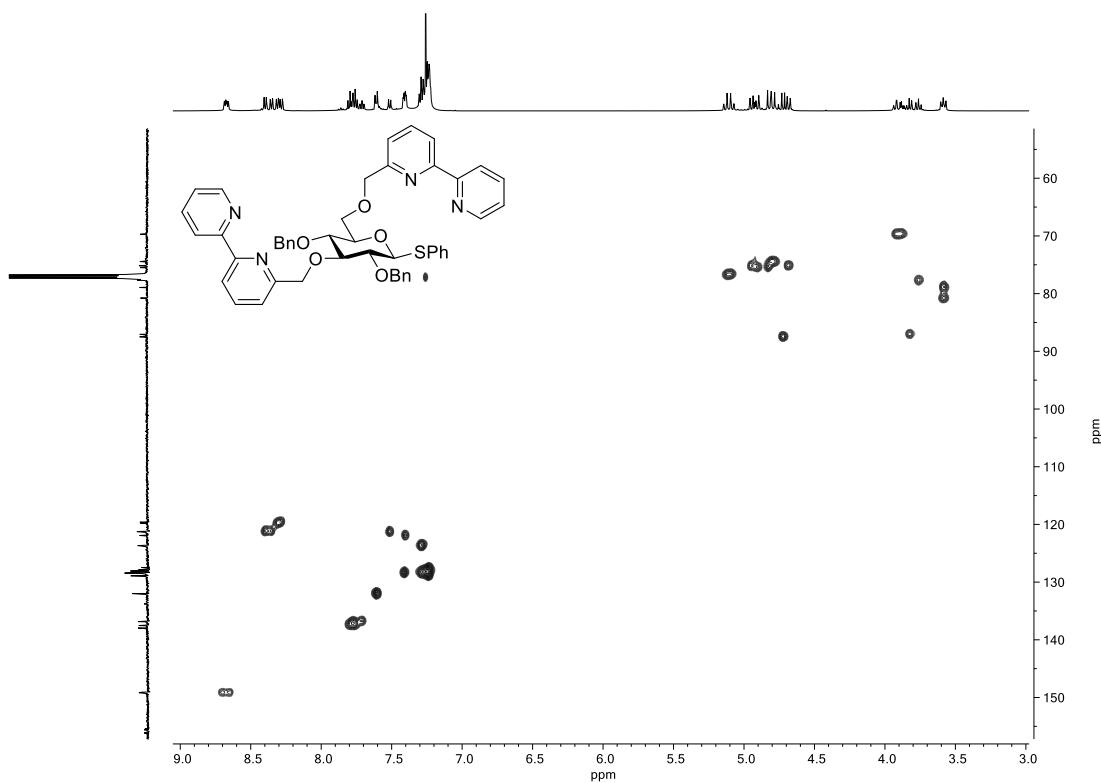
¹³C{¹H}-NMR (126 MHz) spectrum of **1** in chloroform-*d*.



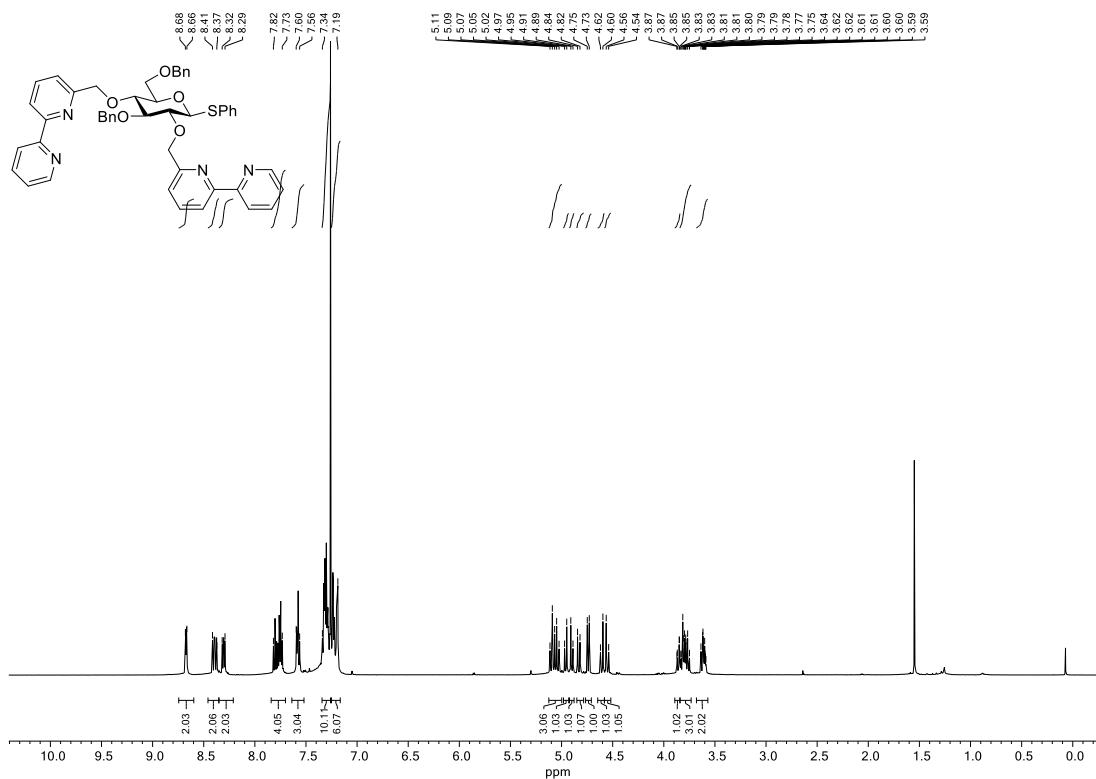
COSY spectrum of **1** in chloroform-*d*.



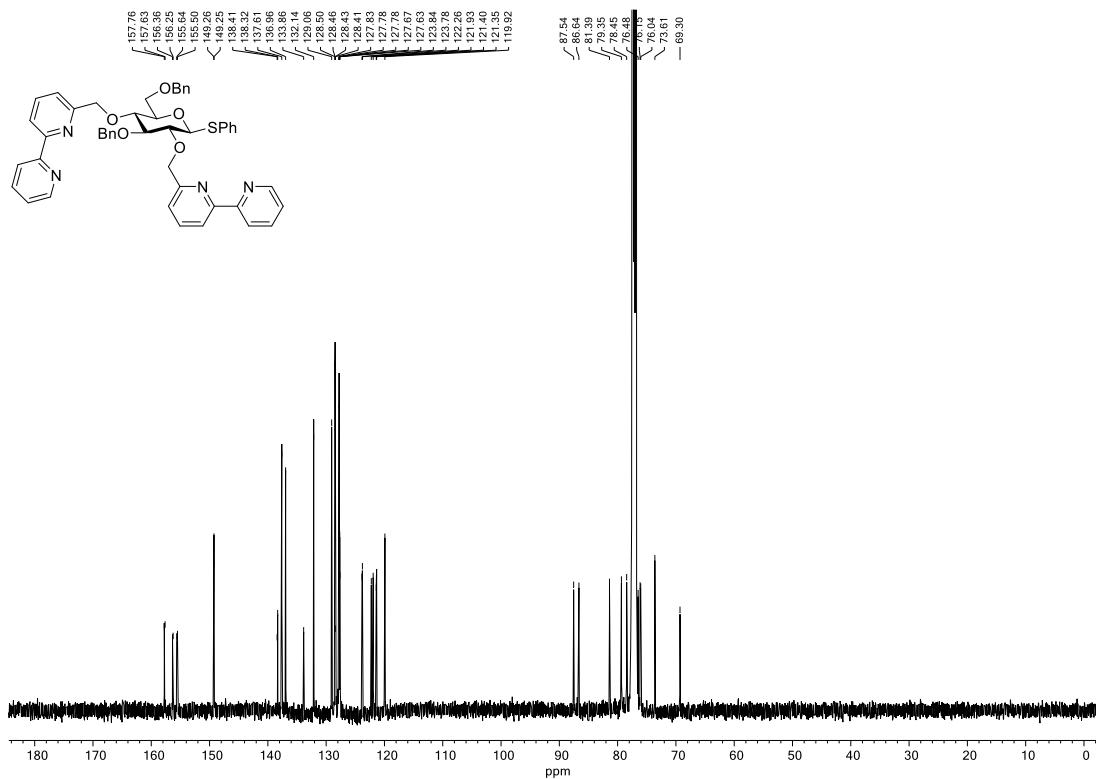
HSQC spectrum of **1** in chloroform-*d*.



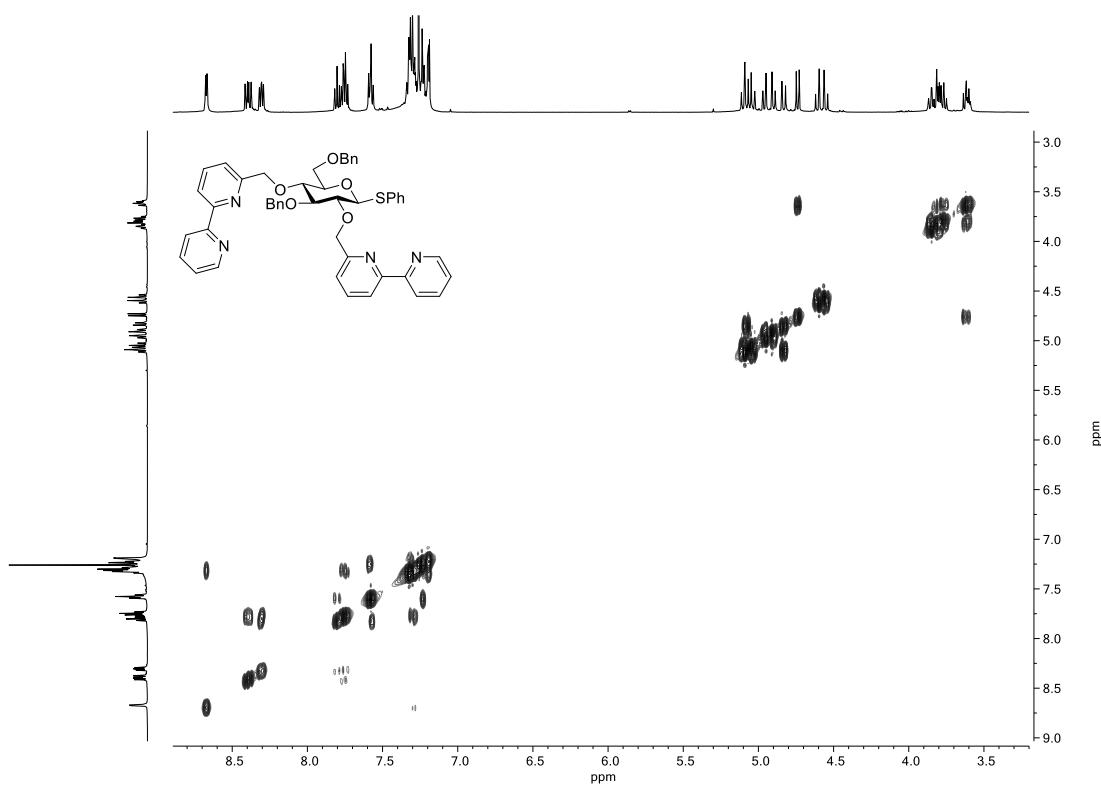
^1H -NMR (500 MHz) spectrum of **2** in chloroform-*d*.



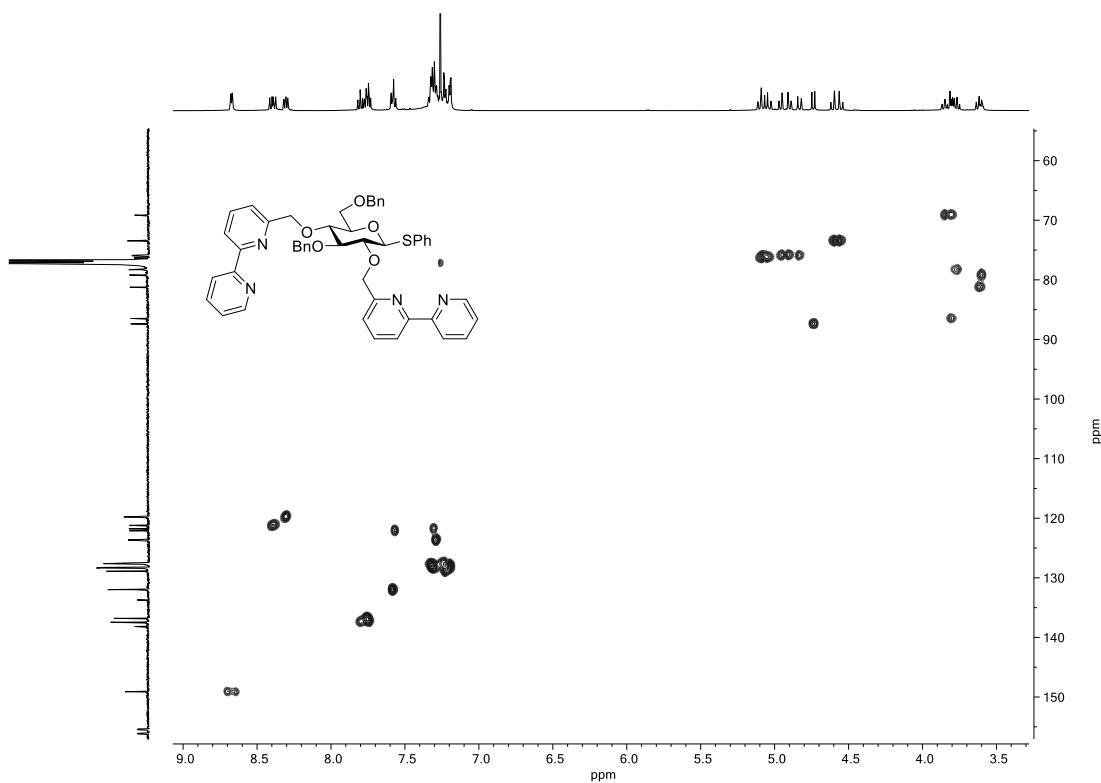
$^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz) spectrum of **2** in chloroform-*d*.



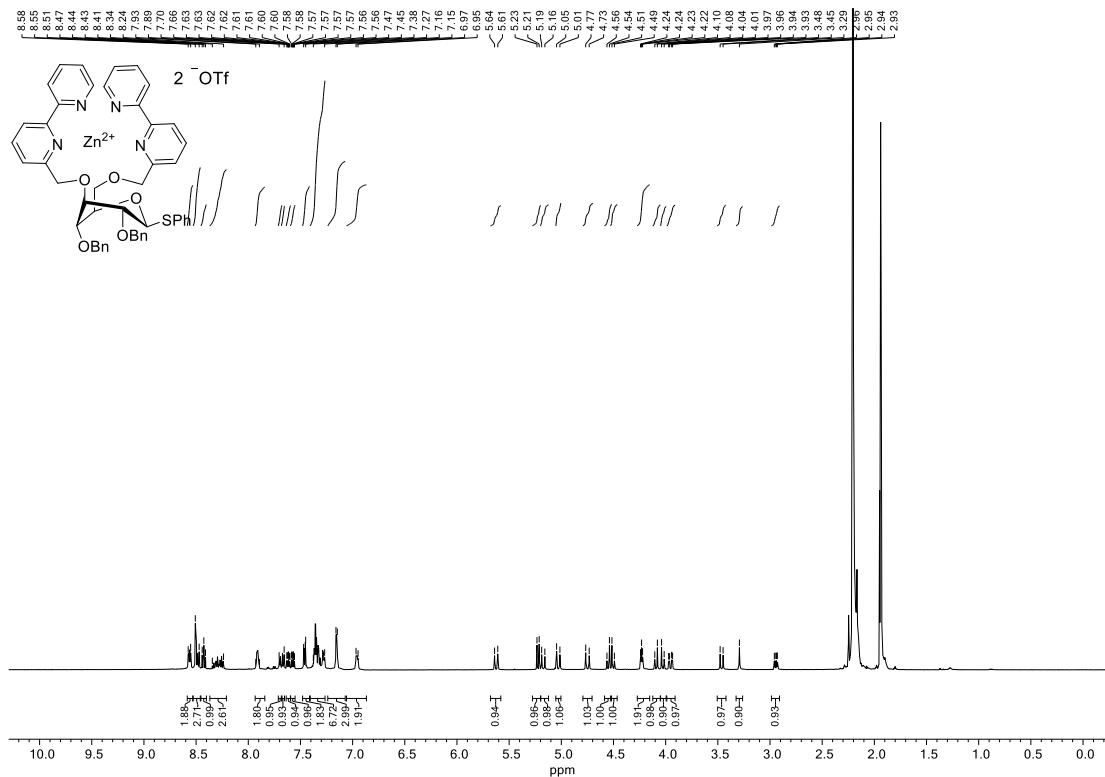
COSY spectrum of **2** in chloroform-*d*.



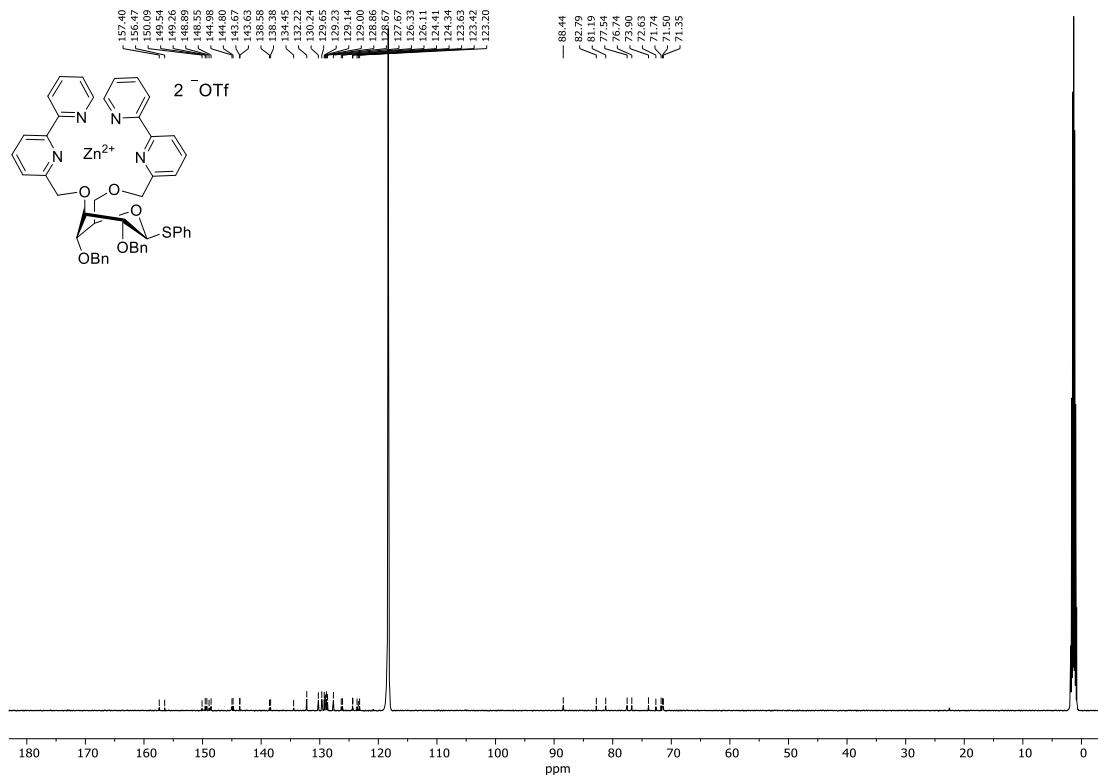
HSQC spectrum of **2** in chloroform-*d*.



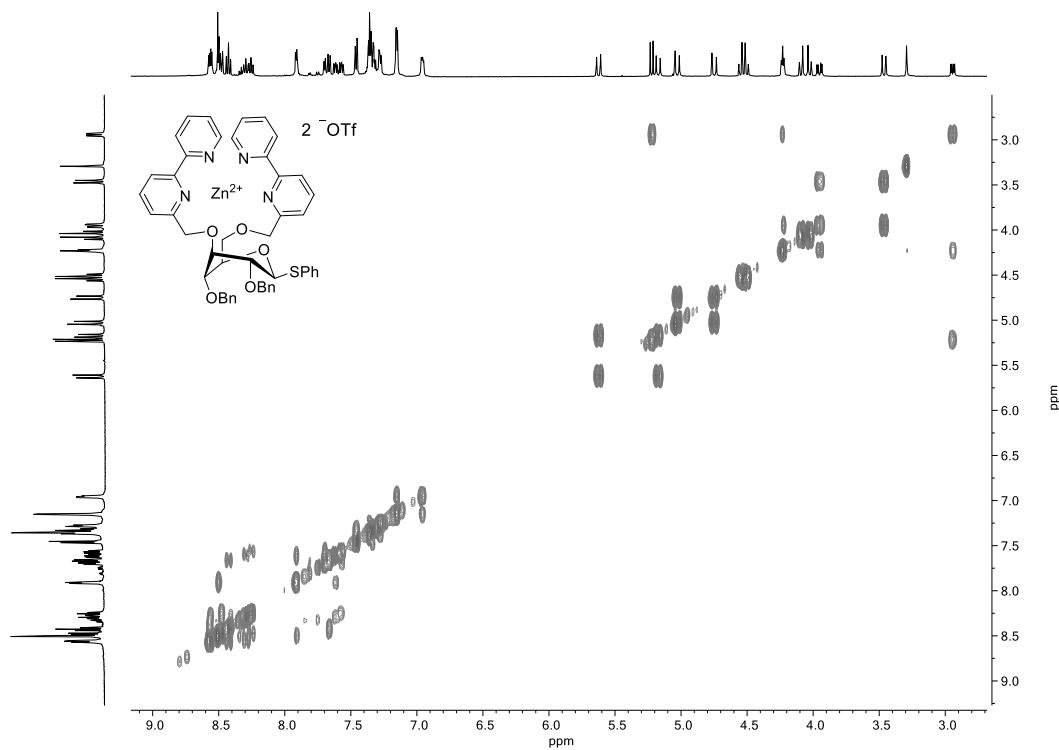
¹H-NMR (500 MHz) spectrum of **1•Zn** in acetonitrile-*d*₃.



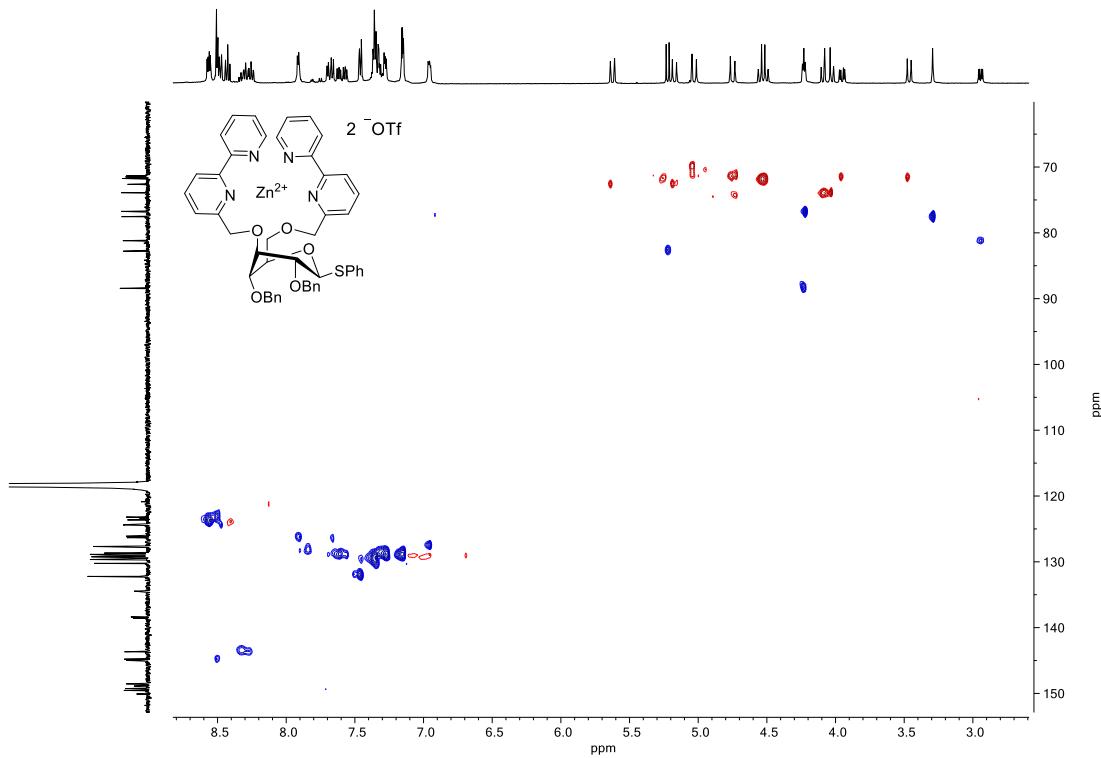
$^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz) spectrum of **1•Zn** in acetonitrile- d_3 .



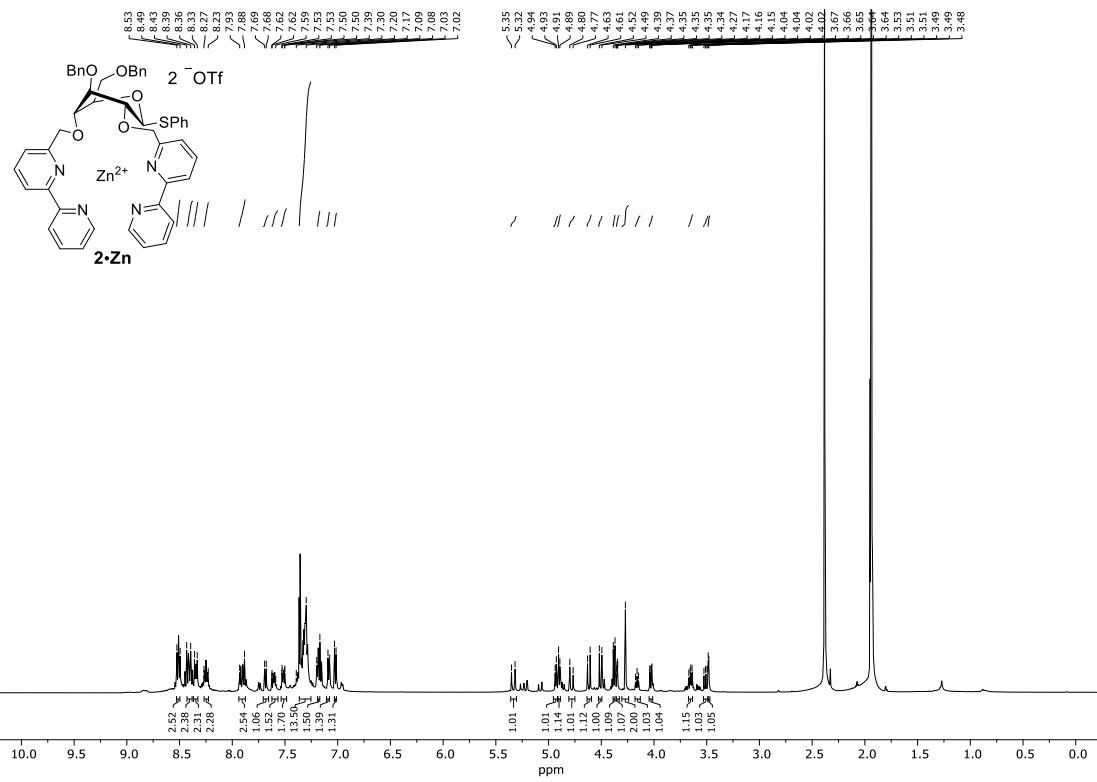
COSY spectrum of **1•Zn** in acetonitrile-*d*₃.



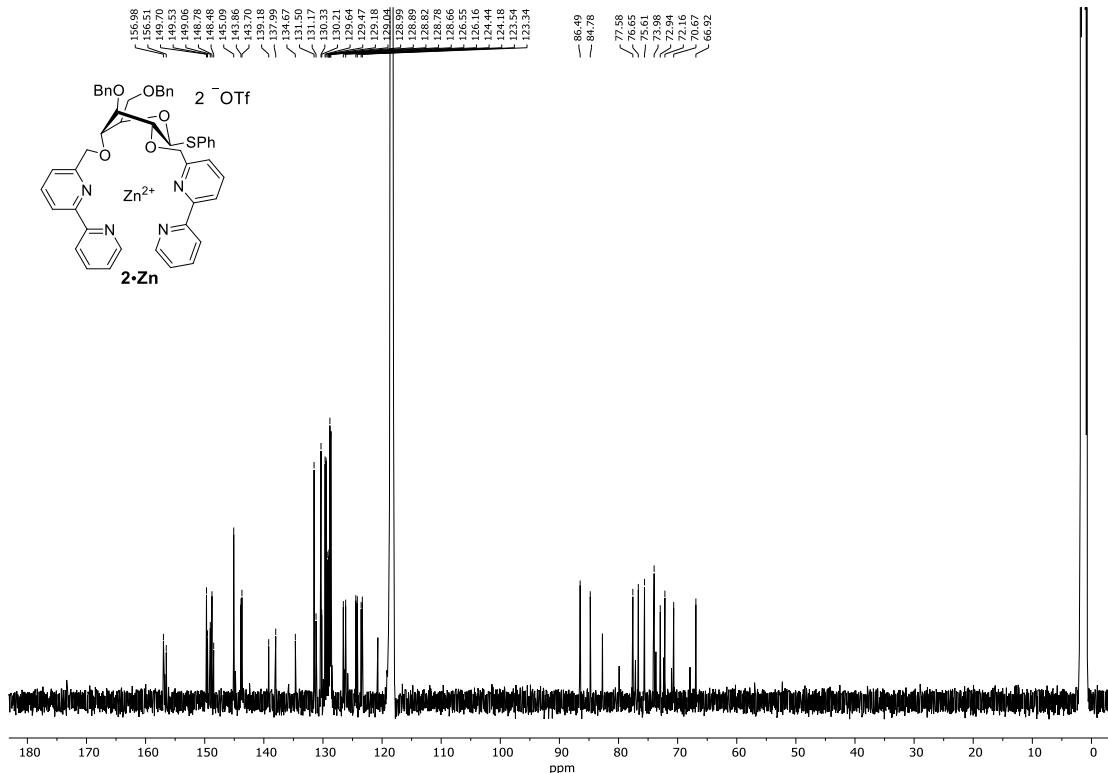
HSQC spectrum of **1•Zn** in acetonitrile-*d*₃.



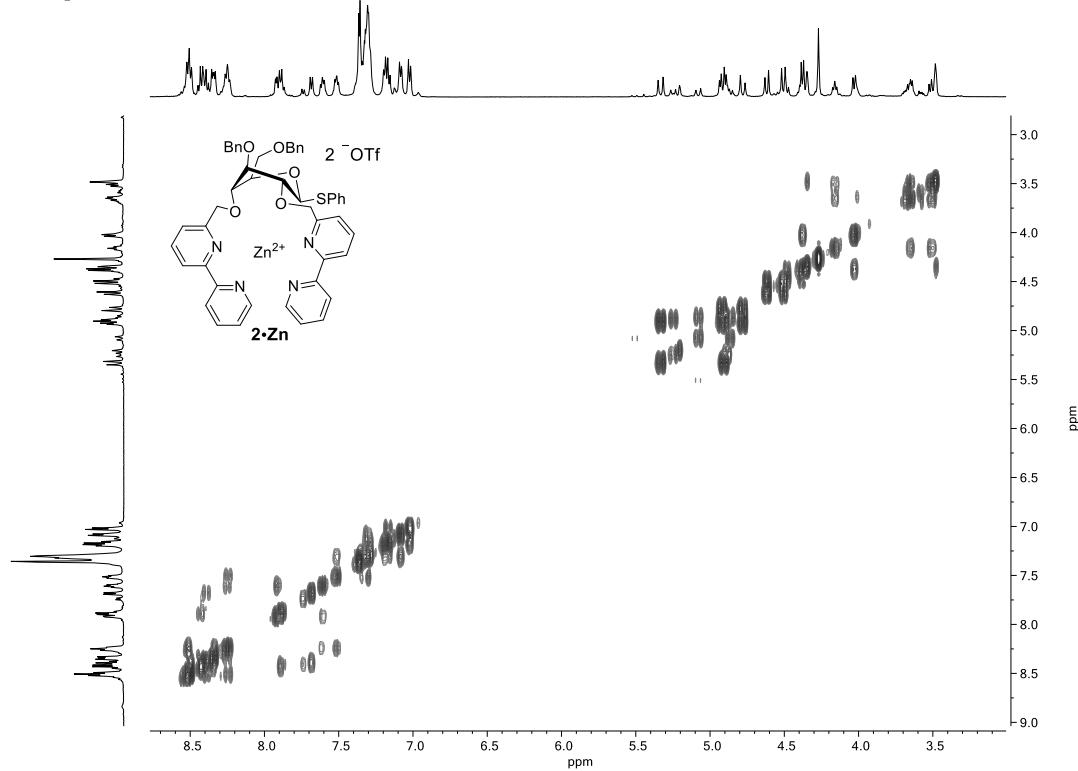
¹H-NMR (500 MHz) spectrum of **2•Zn** in acetonitrile-*d*₃.



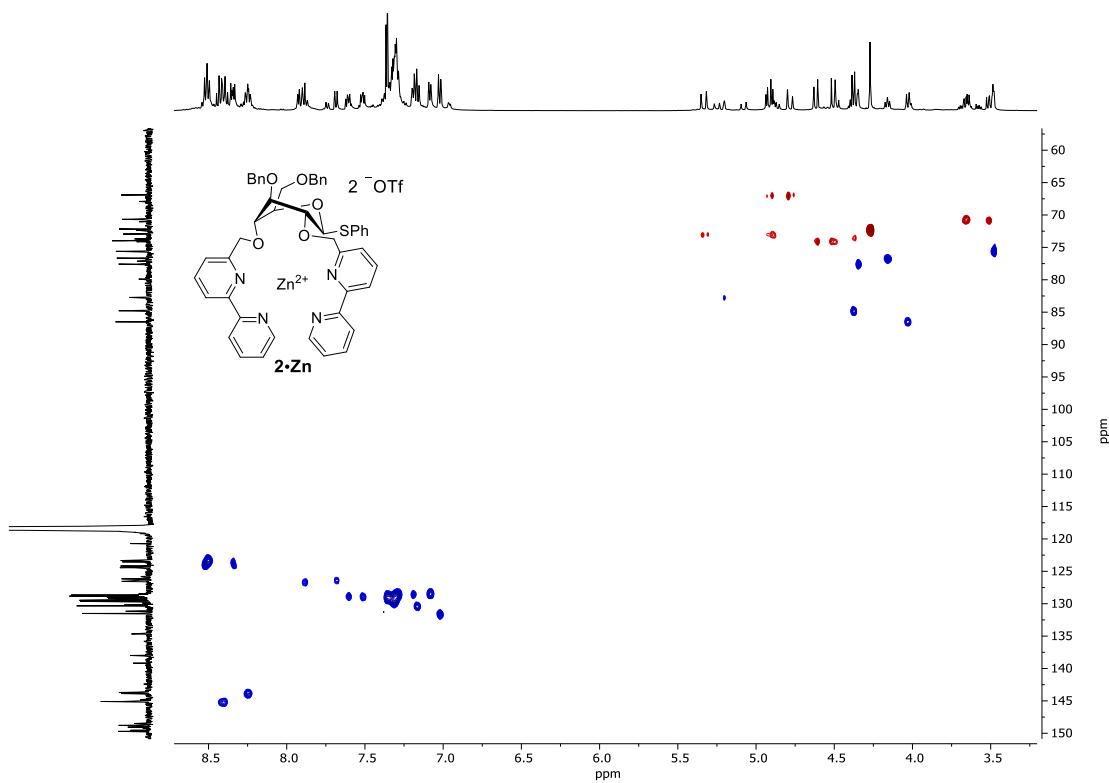
¹³C{¹H}-NMR (126 MHz) spectrum of **2•Zn** in acetonitrile-*d*₃.



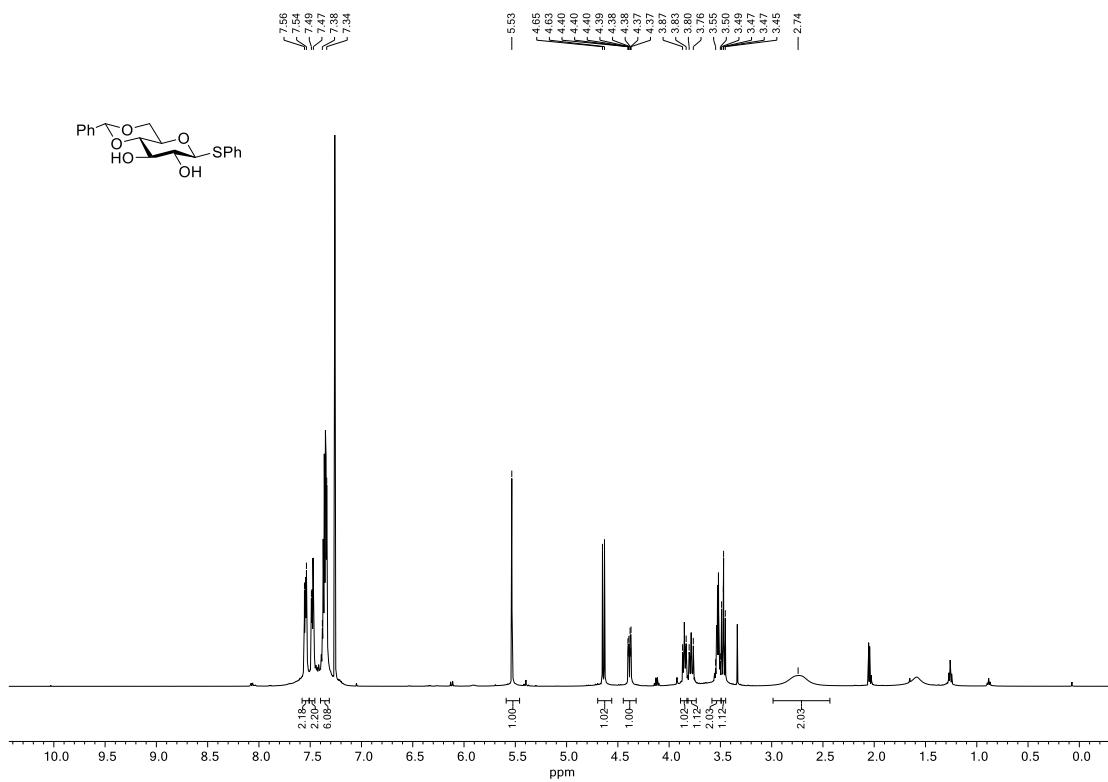
COSY spectrum of **2•Zn** in acetonitrile-*d*₃.



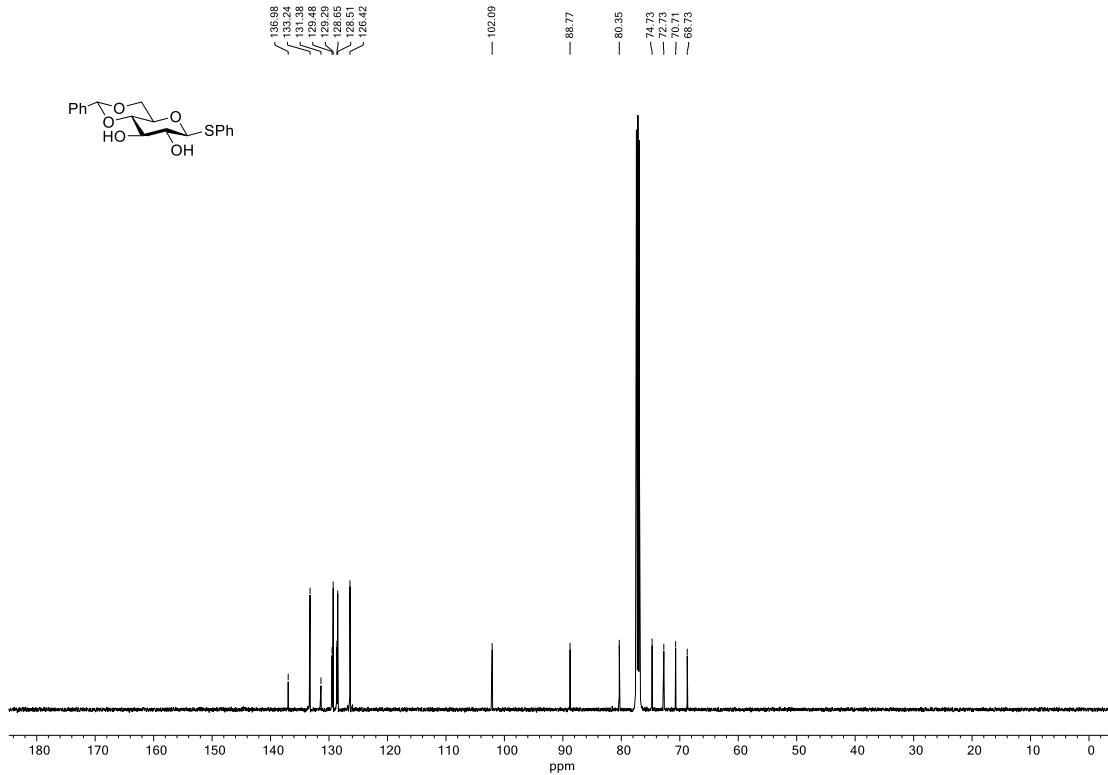
HSQC spectrum of **2•Zn** in acetonitrile-*d*₃.



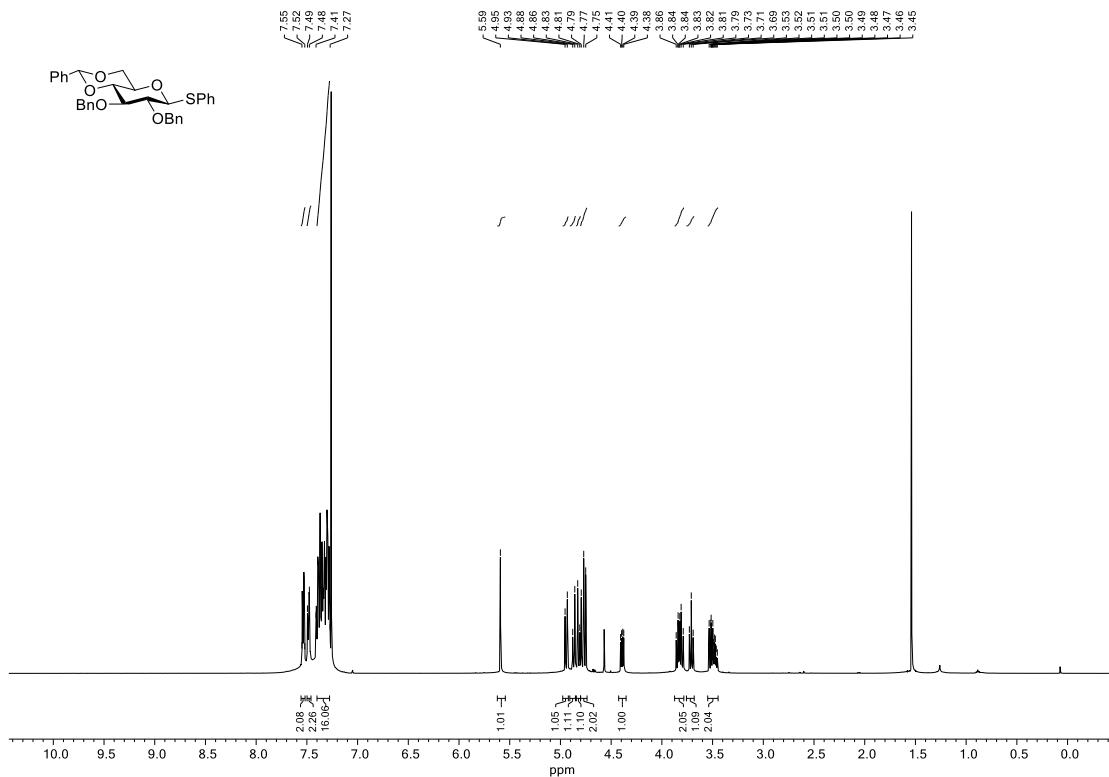
¹H-NMR (500 MHz) spectrum of **15** in chloroform-d.



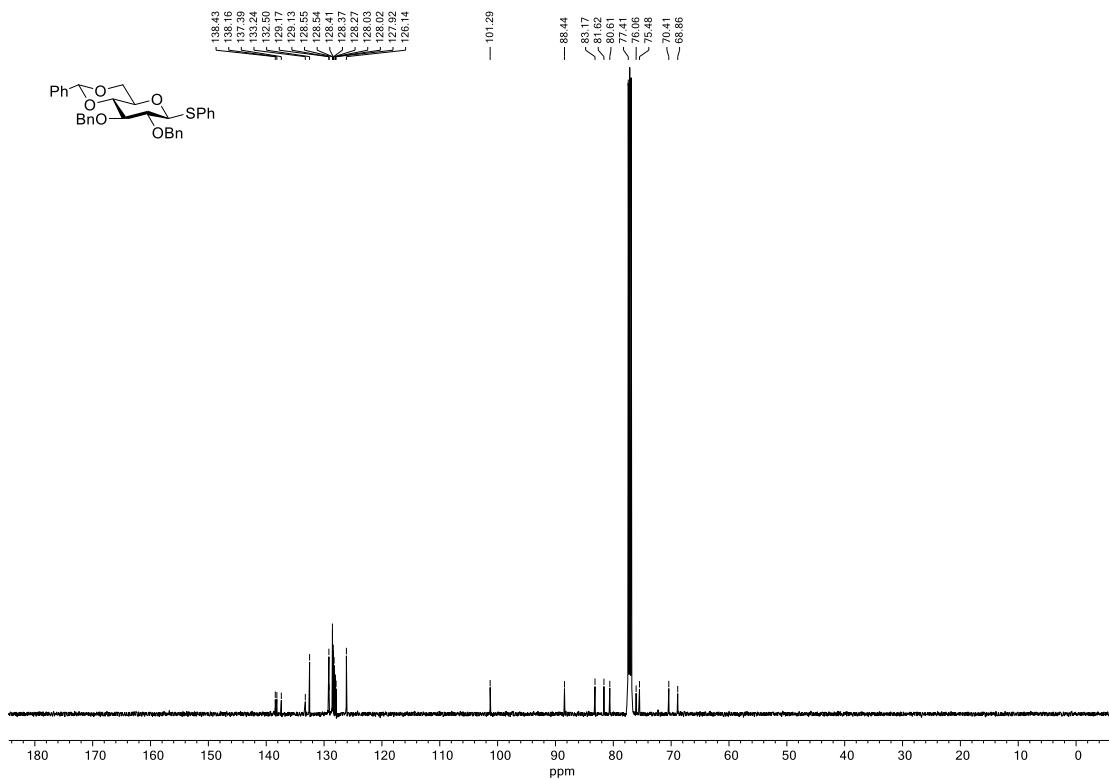
¹³C{¹H}-NMR (126 MHz) spectrum of **15** in chloroform-d.



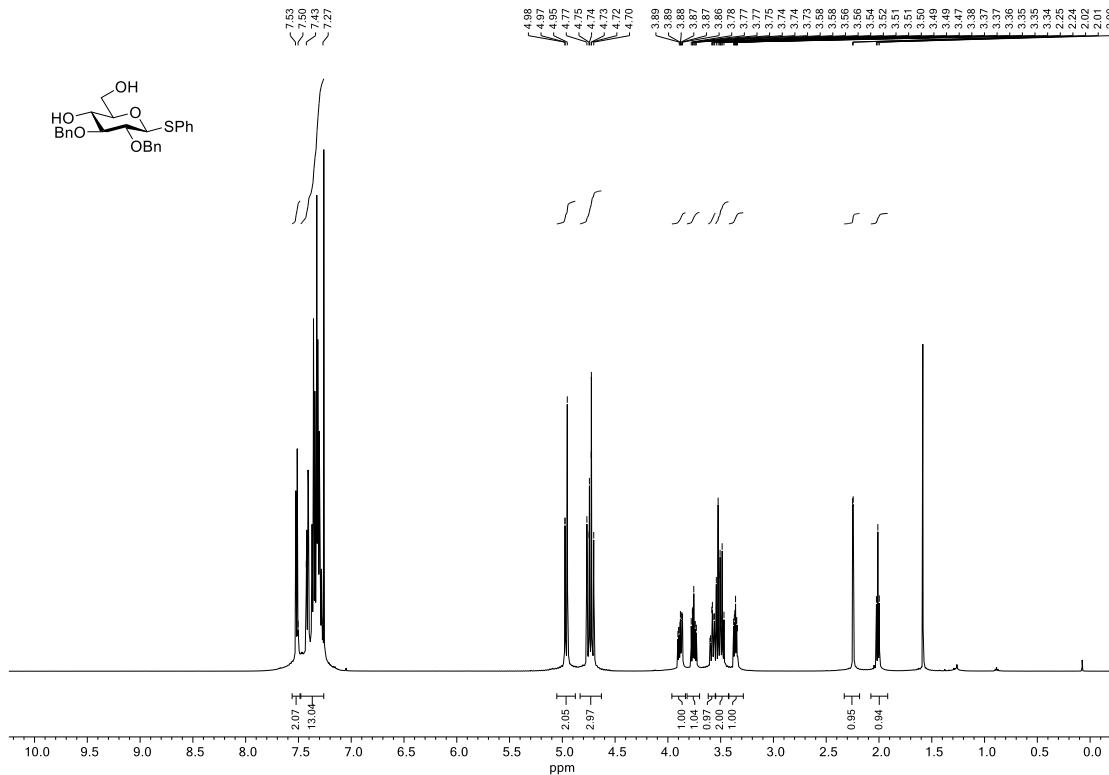
¹H-NMR (500 MHz) spectrum of **16** in chloroform-d.



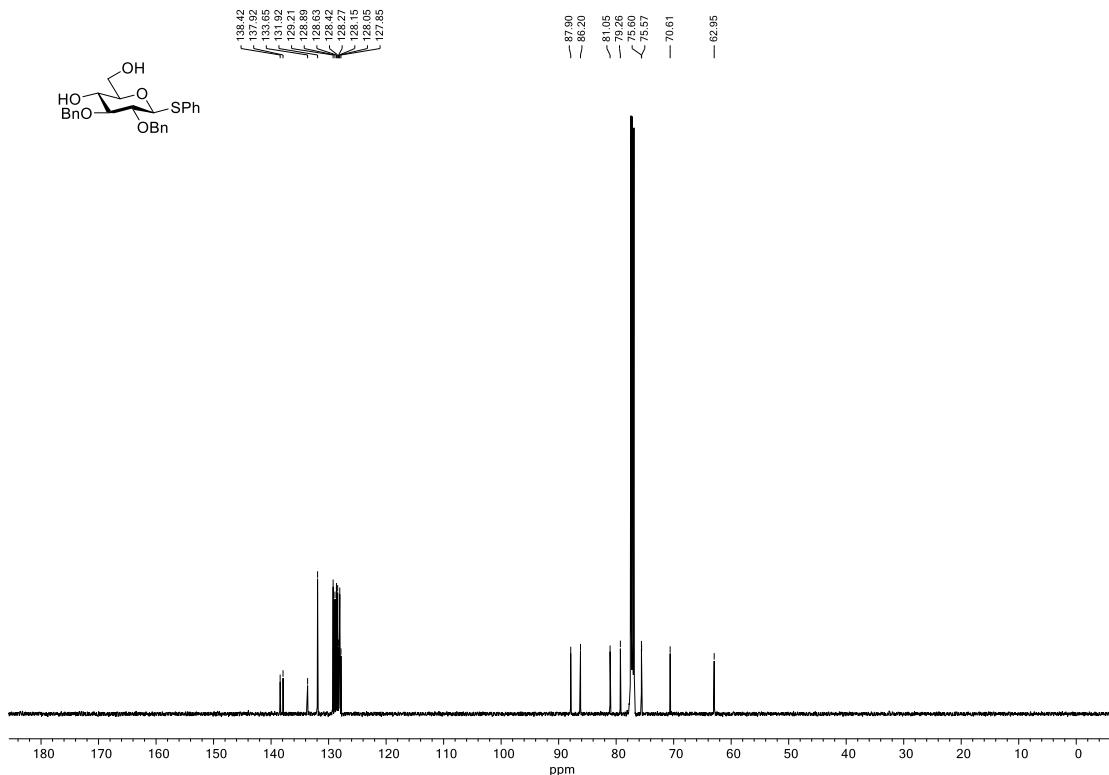
¹³C{¹H}-NMR (126 MHz) spectrum of **16** in chloroform-d.



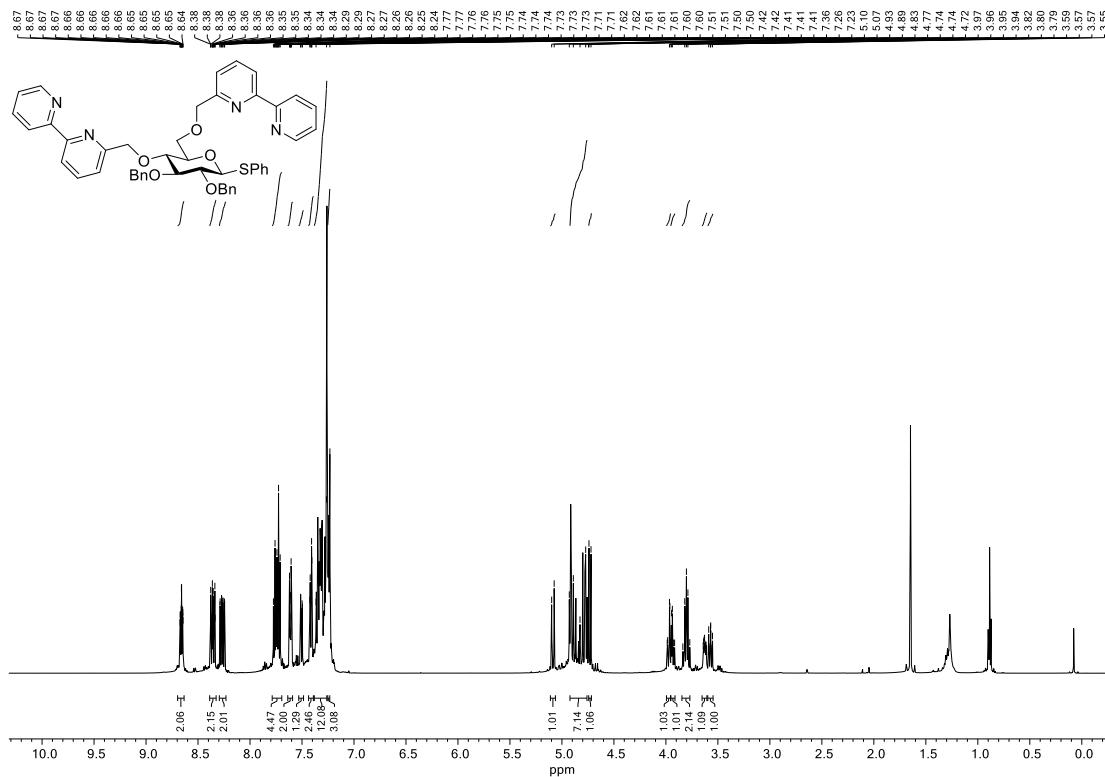
¹H-NMR (500 MHz) spectrum of **17** in chloroform-*d*.



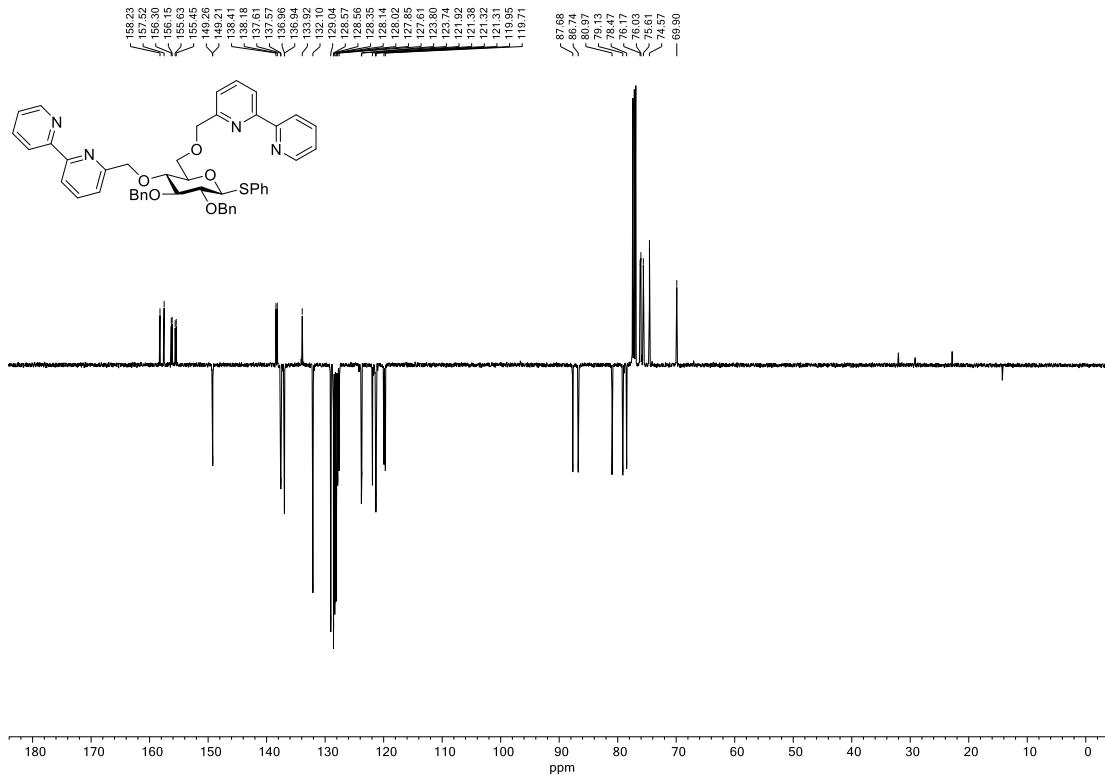
$^{13}\text{C}\{\text{H}\}$ -NMR (126 MHz) spectrum of **17** in chloroform-*d*.



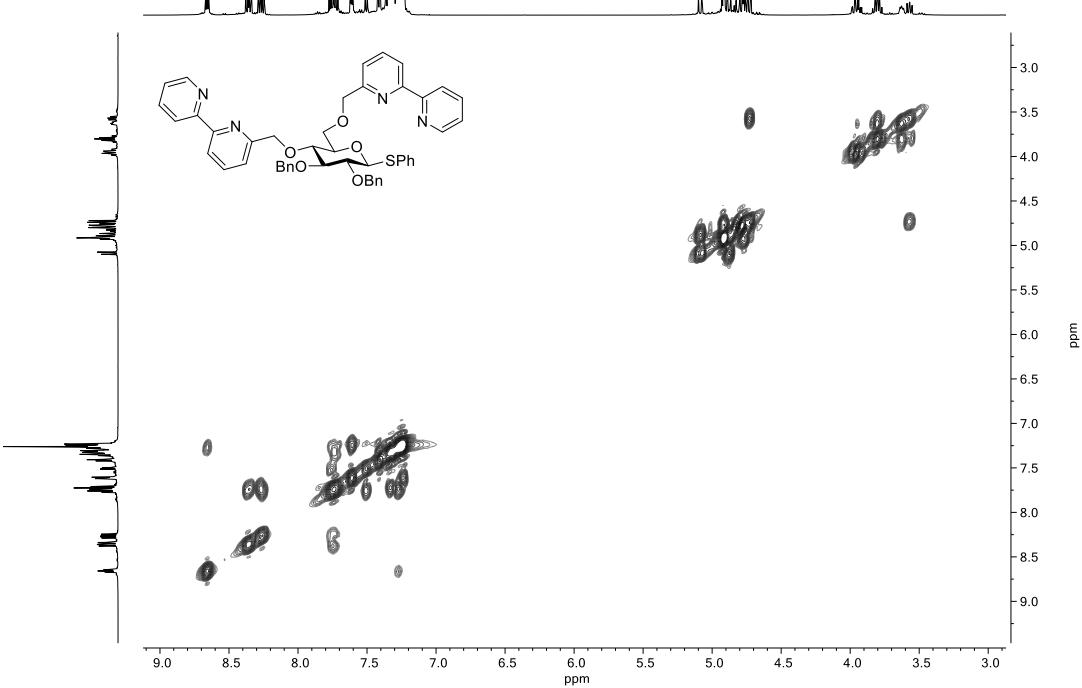
¹H-NMR (500 MHz) spectrum of **18** in chloroform-*d*.



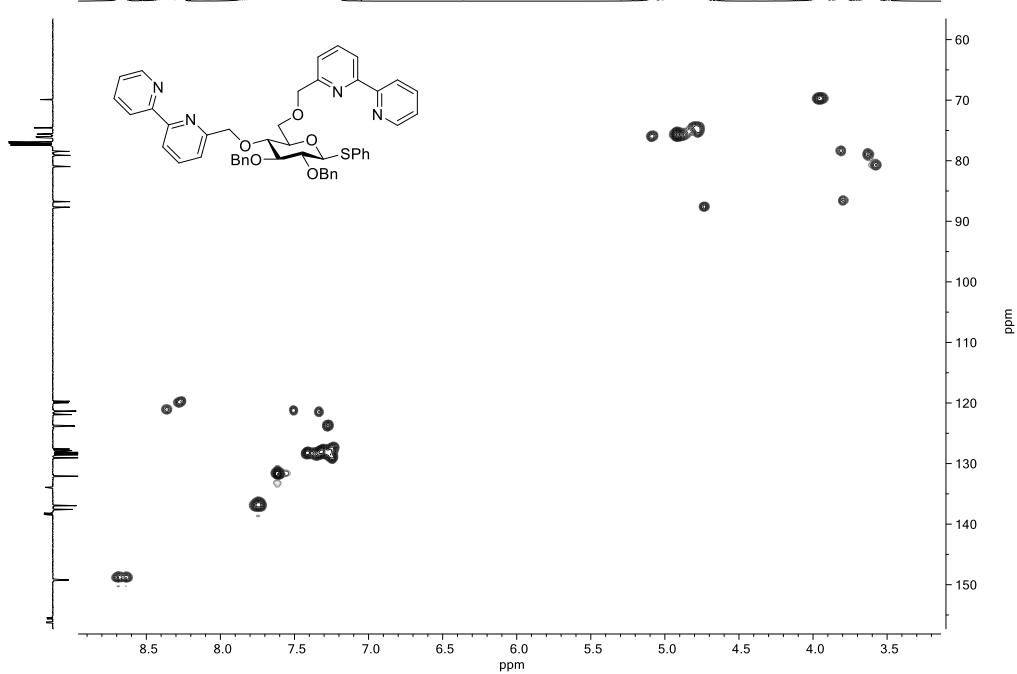
$^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz) (APT) spectrum of **18** in chloroform-*d*.



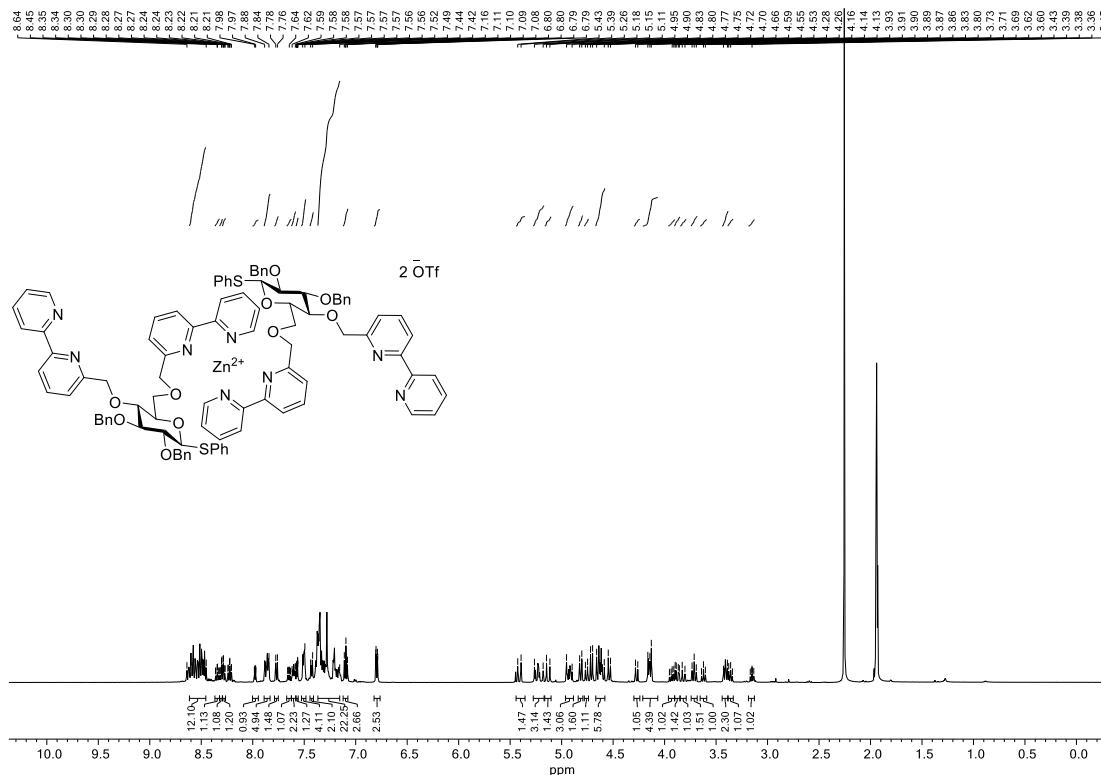
COSY spectrum of **18** in chloroform-*d*.



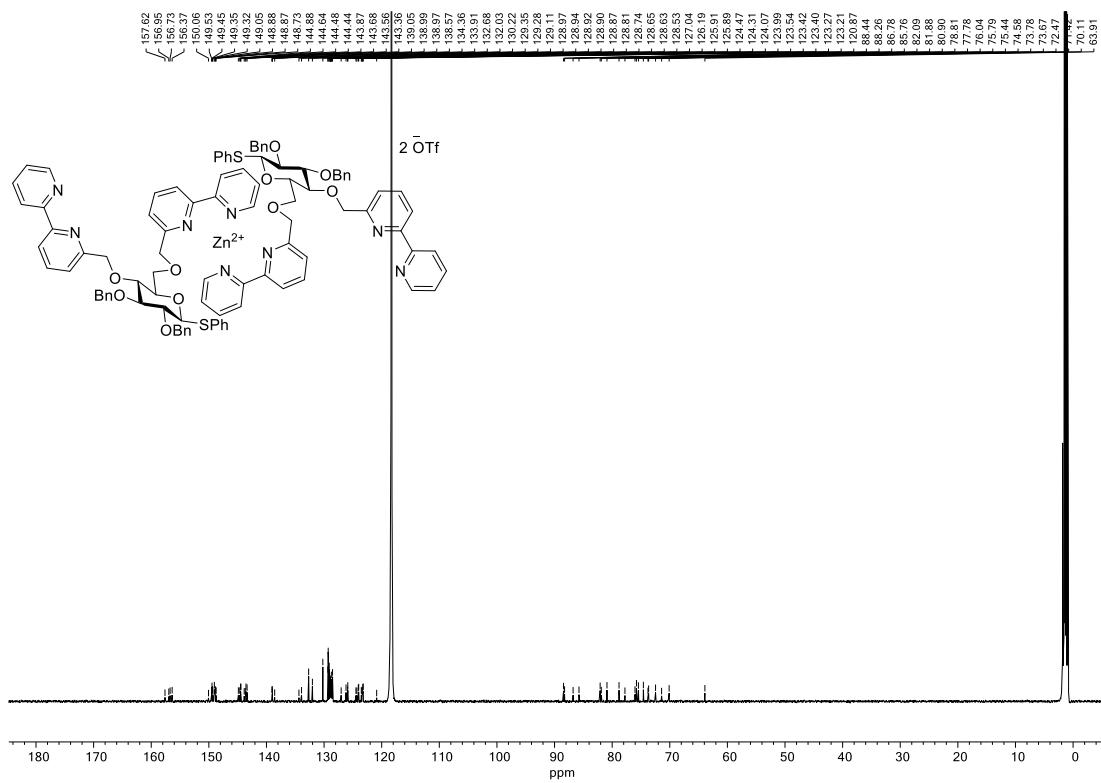
HSQC spectrum of **18** in chloroform-*d*.



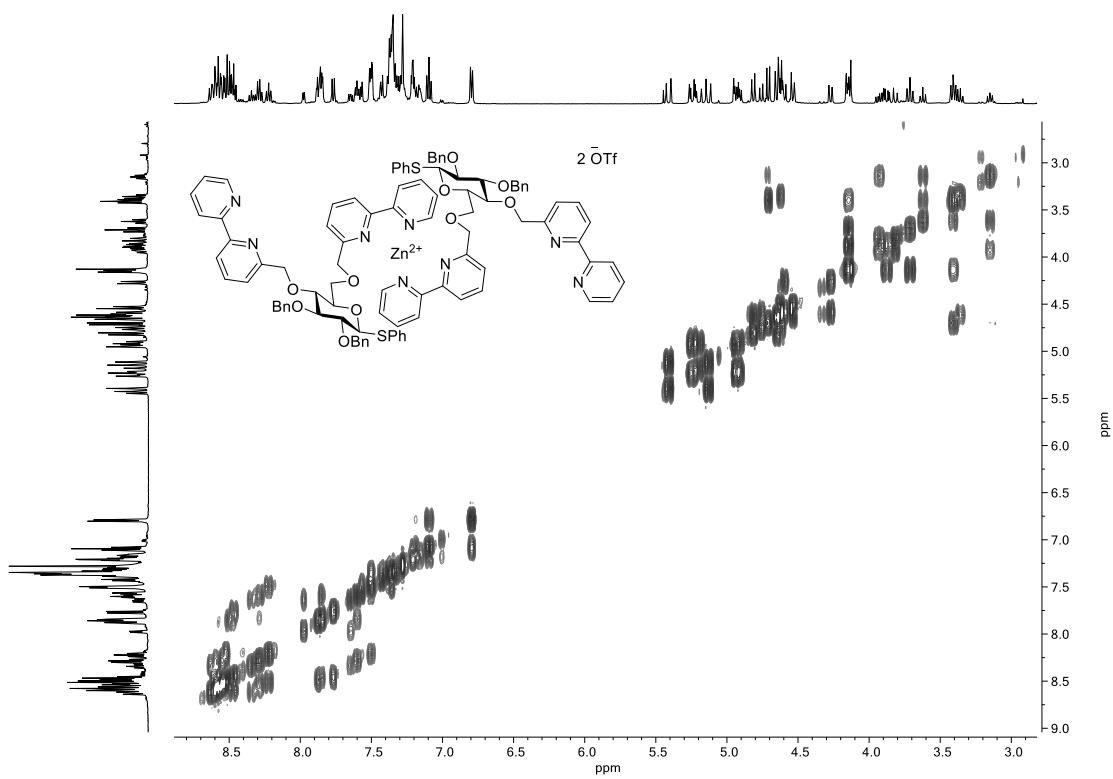
¹H-NMR (500 MHz) spectrum of **18₂•Zn** in acetonitrile-*d*₃.



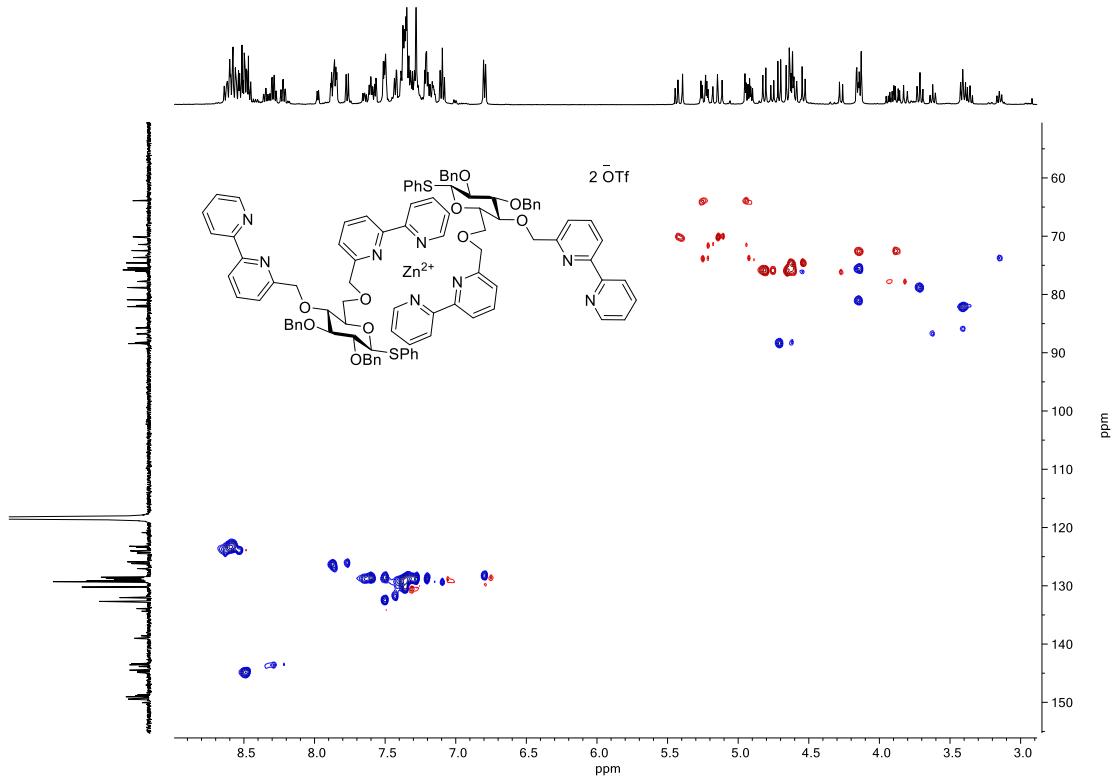
$^{13}\text{C}\{\text{H}\}$ -NMR (126 MHz) spectrum of **182**•**Zn** in acetonitrile-*d*₃.



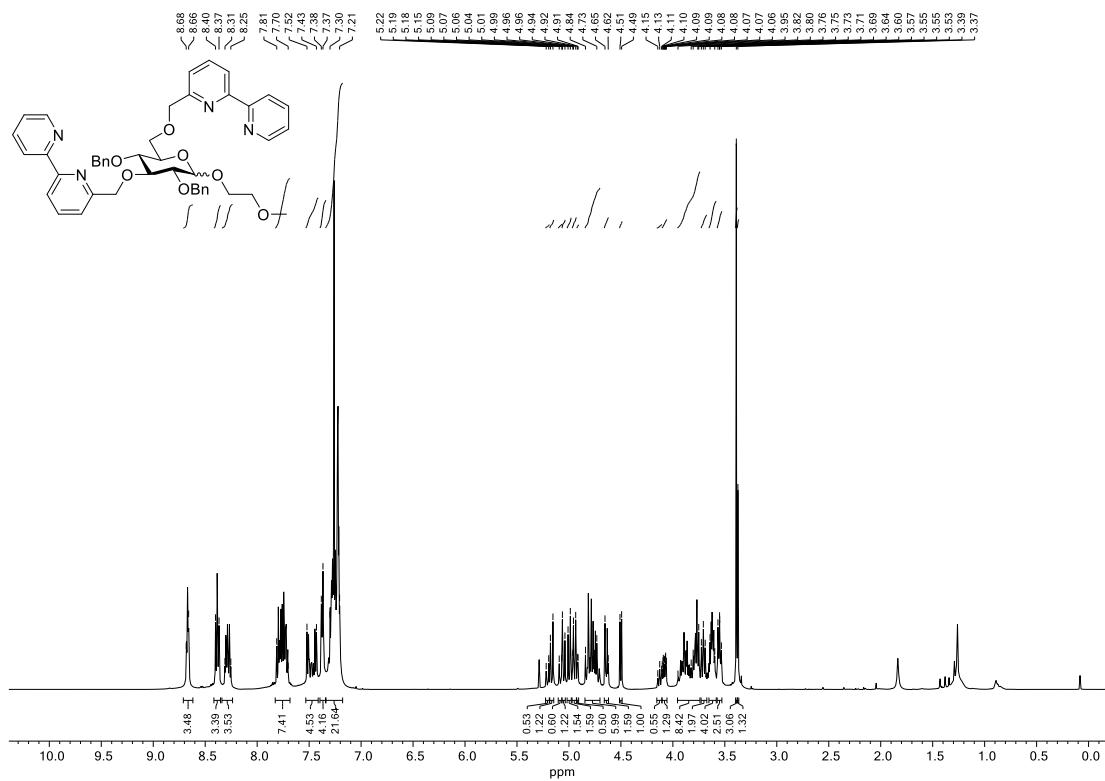
COSY spectrum of **18₂•Zn** in acetonitrile-*d*₃.



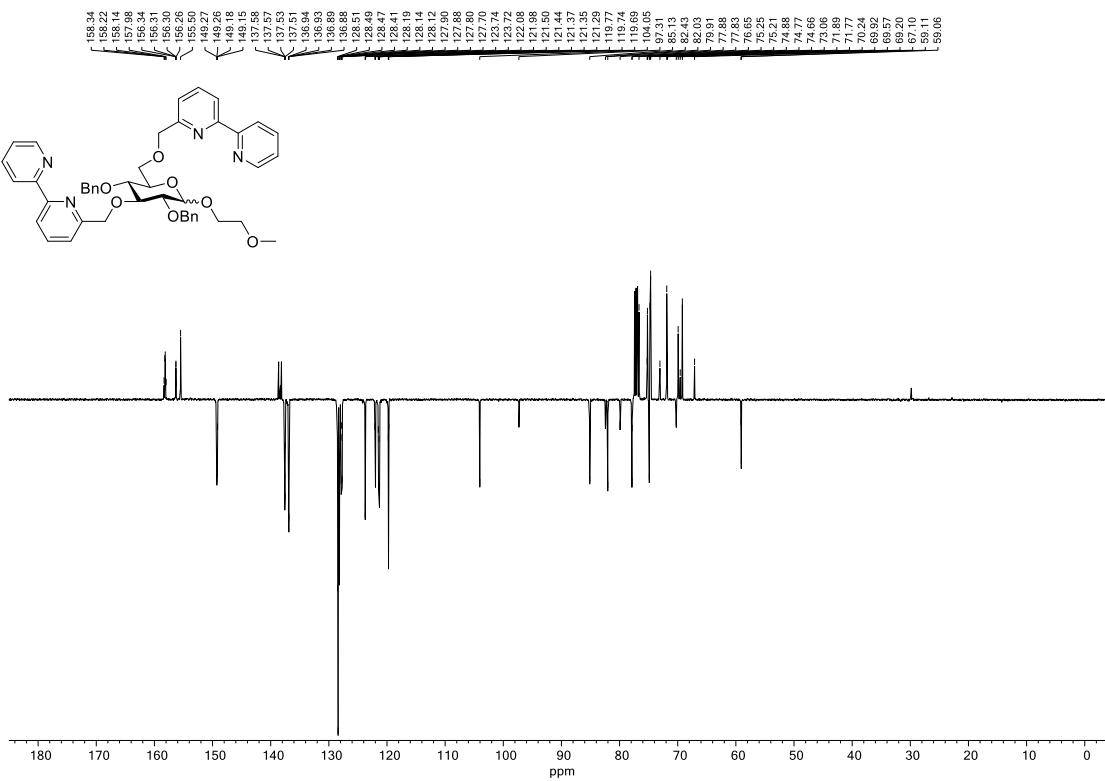
HSQC spectrum of **18₂•Zn** in acetonitrile-*d*₃.



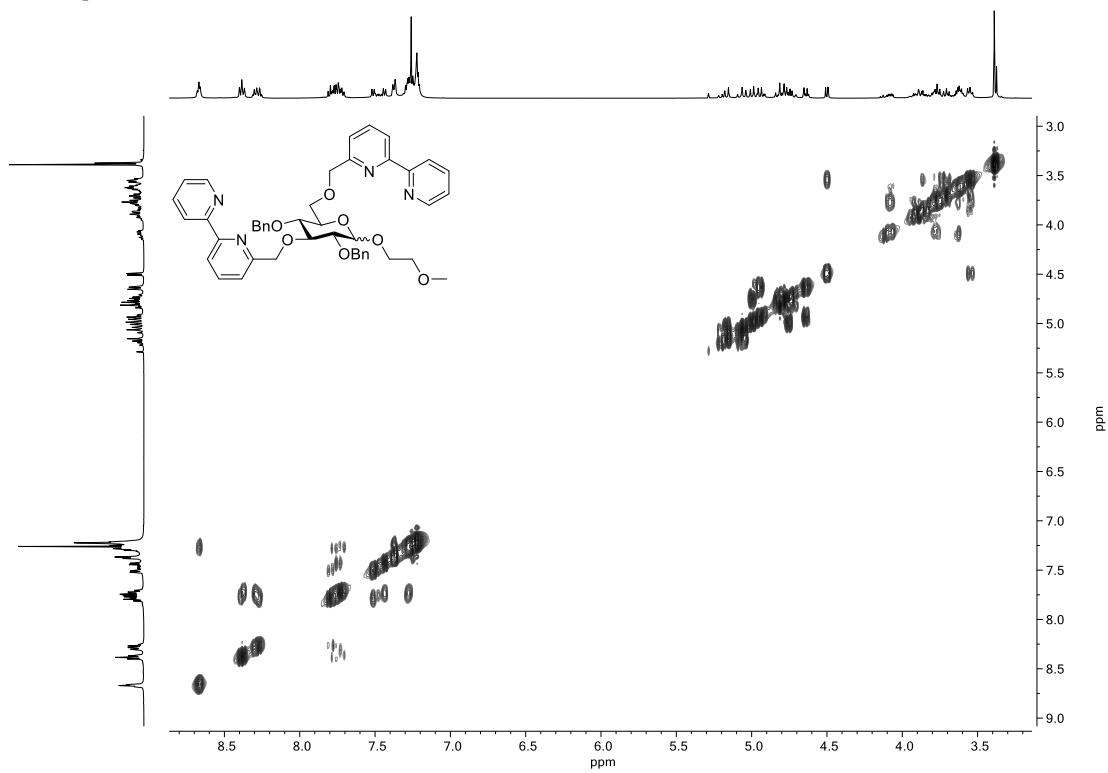
¹H-NMR (500 MHz) spectrum of **19** in chloroform-*d*.



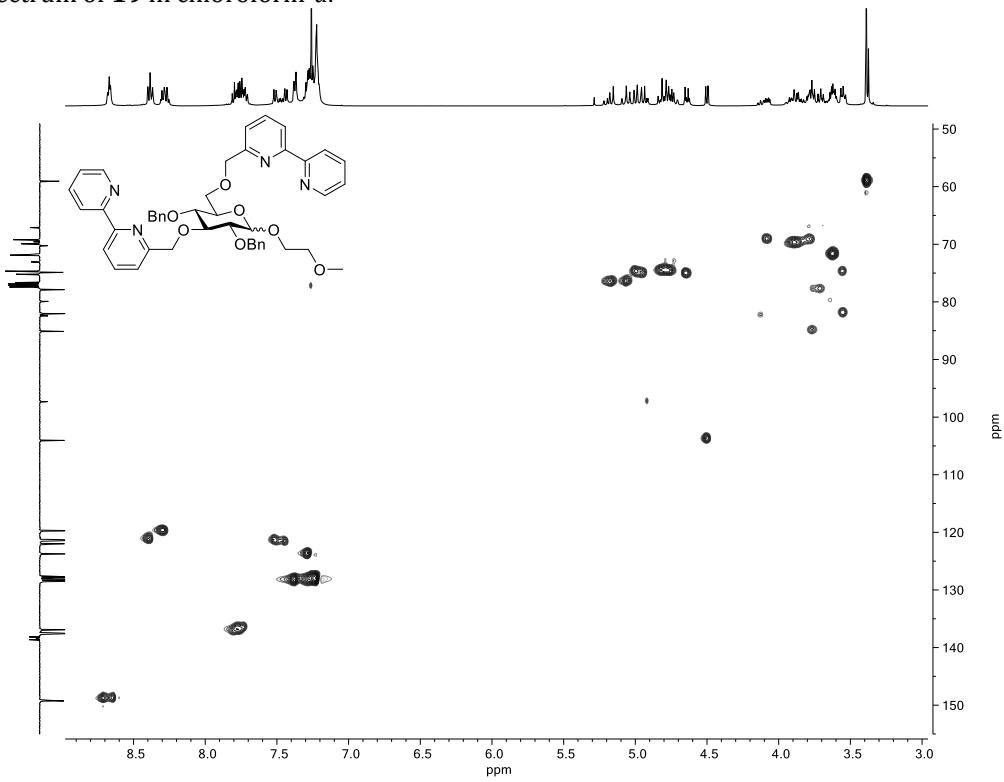
$^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz) (APT) spectrum of **19** in chloroform-*d*.



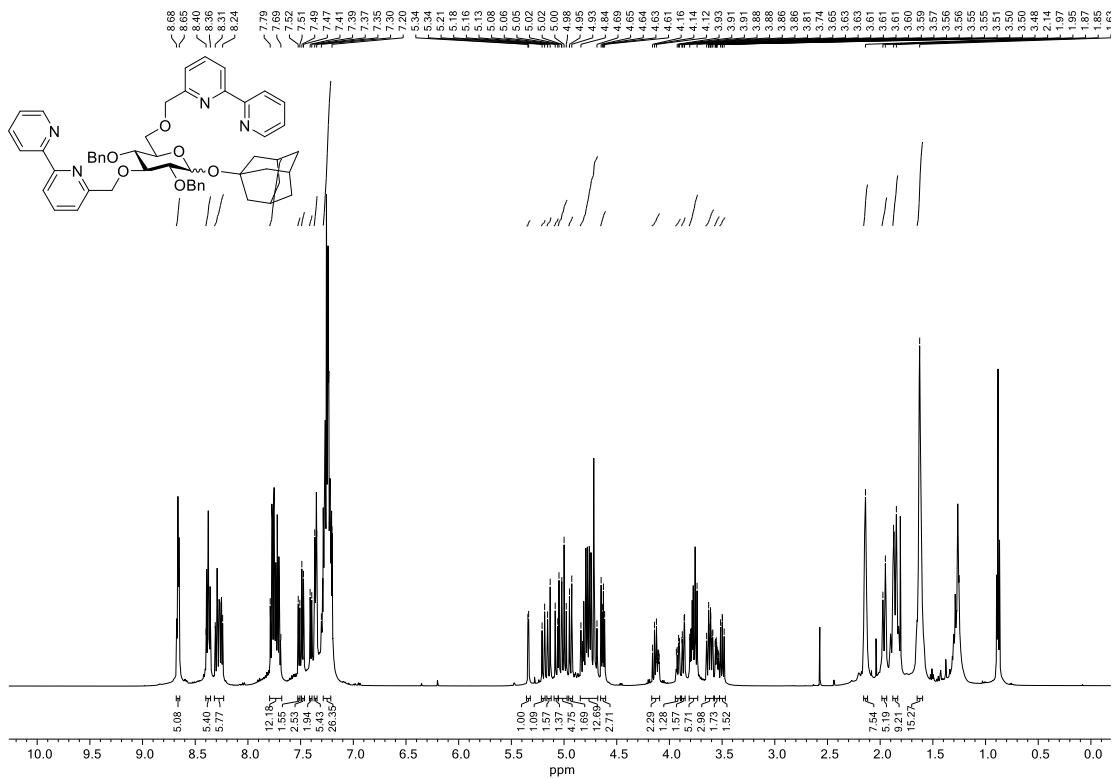
COSY spectrum of **19** in chloroform-*d*.



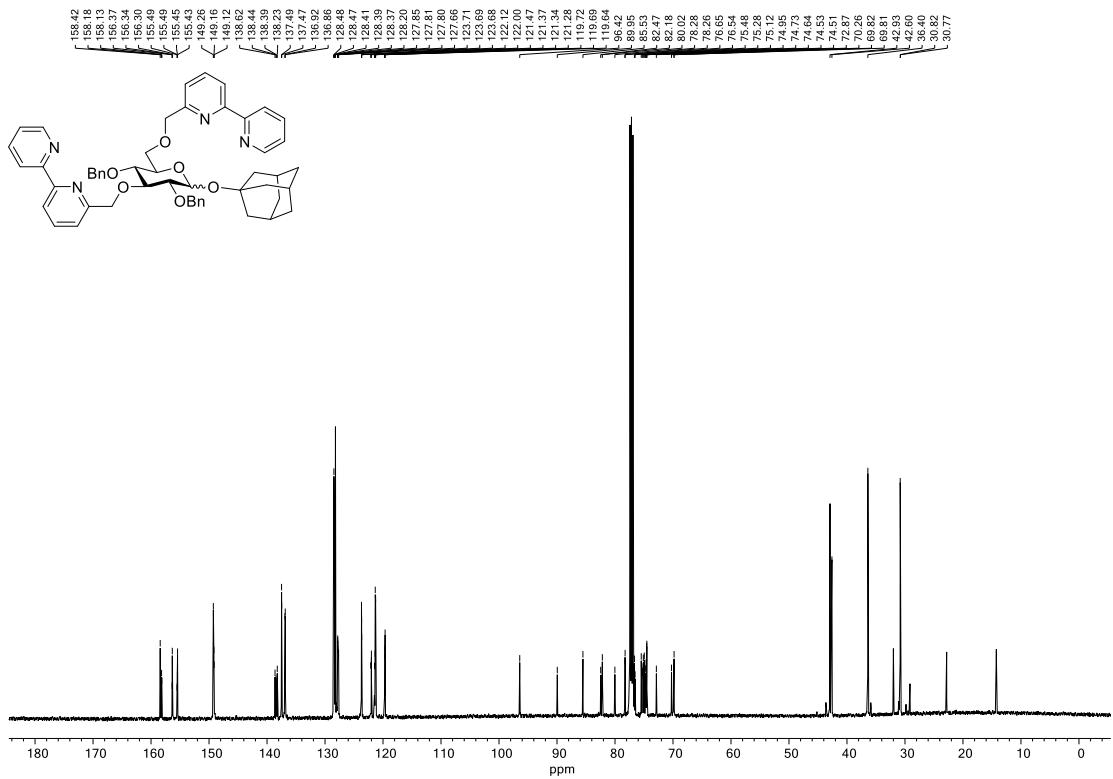
HSQC spectrum of **19** in chloroform-*d*.



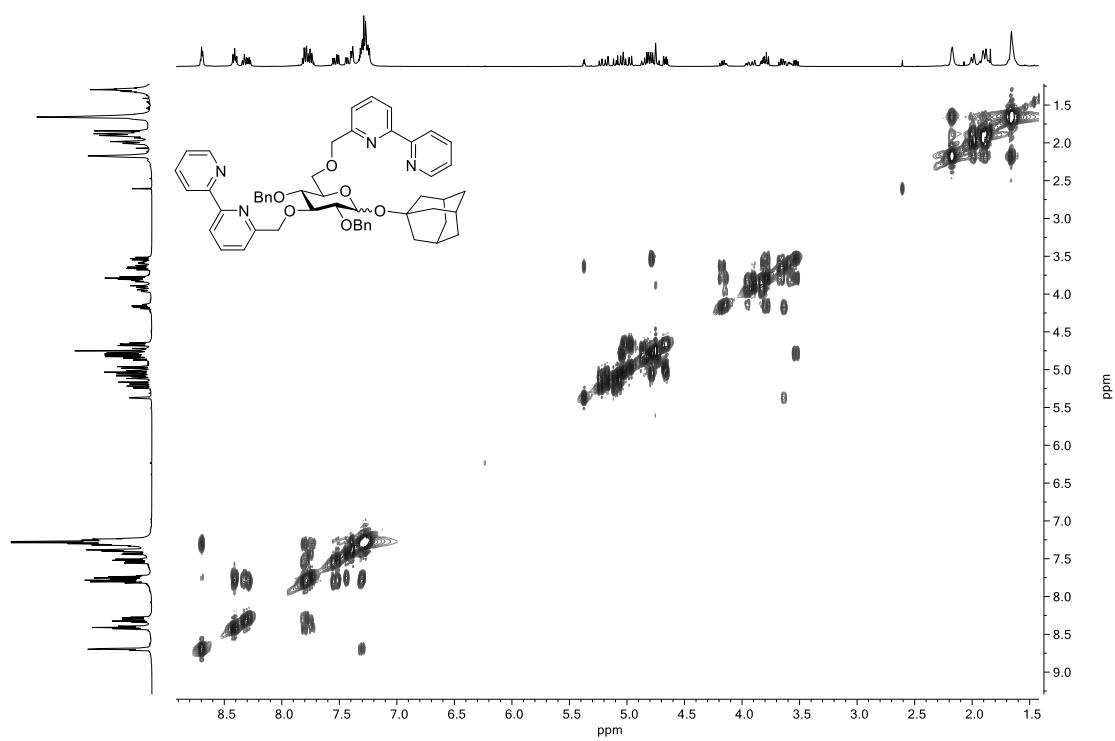
¹H-NMR (500 MHz) spectrum of **20** in chloroform-*d*.



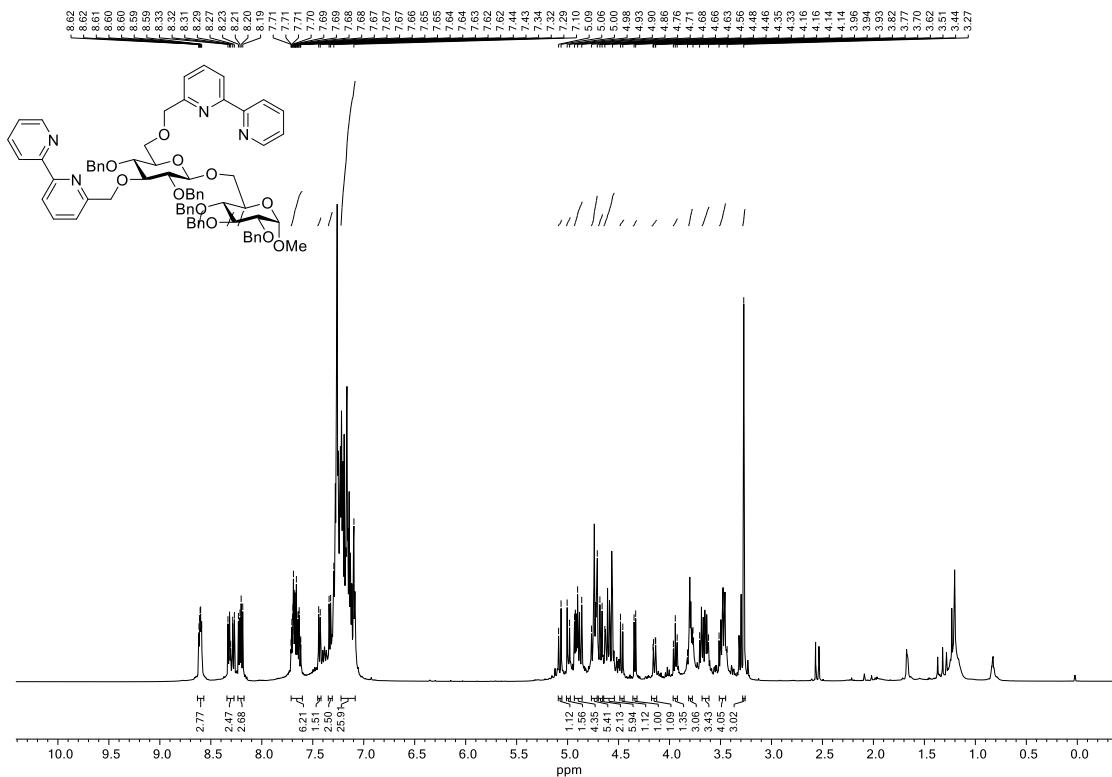
$^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz) spectrum of **20** in chloroform-*d*.



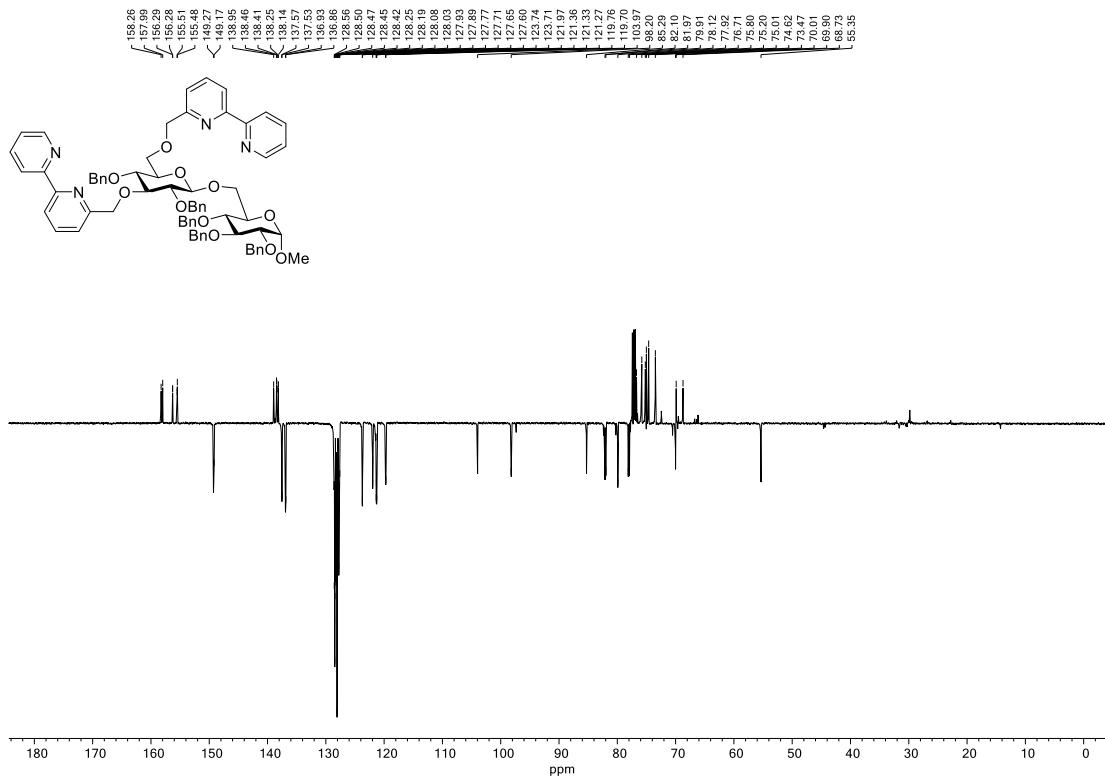
COSY spectrum of **20** in chloroform-*d*.



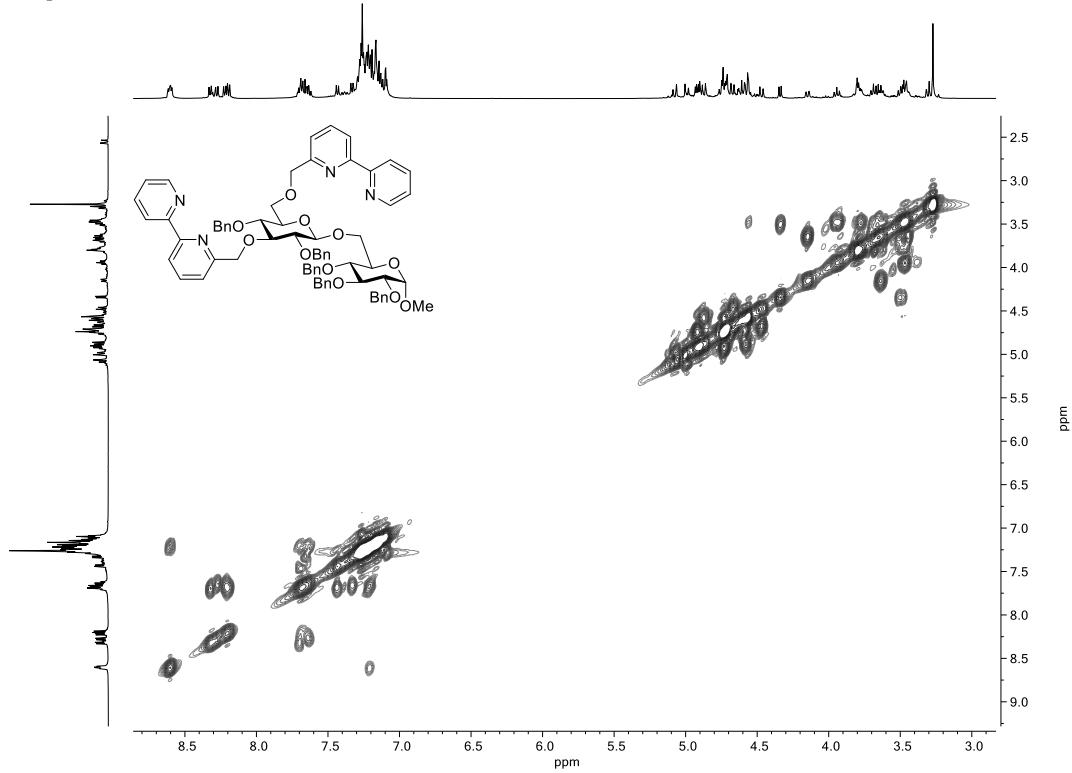
¹H-NMR (500 MHz) spectrum of **21** in chloroform-*d*.



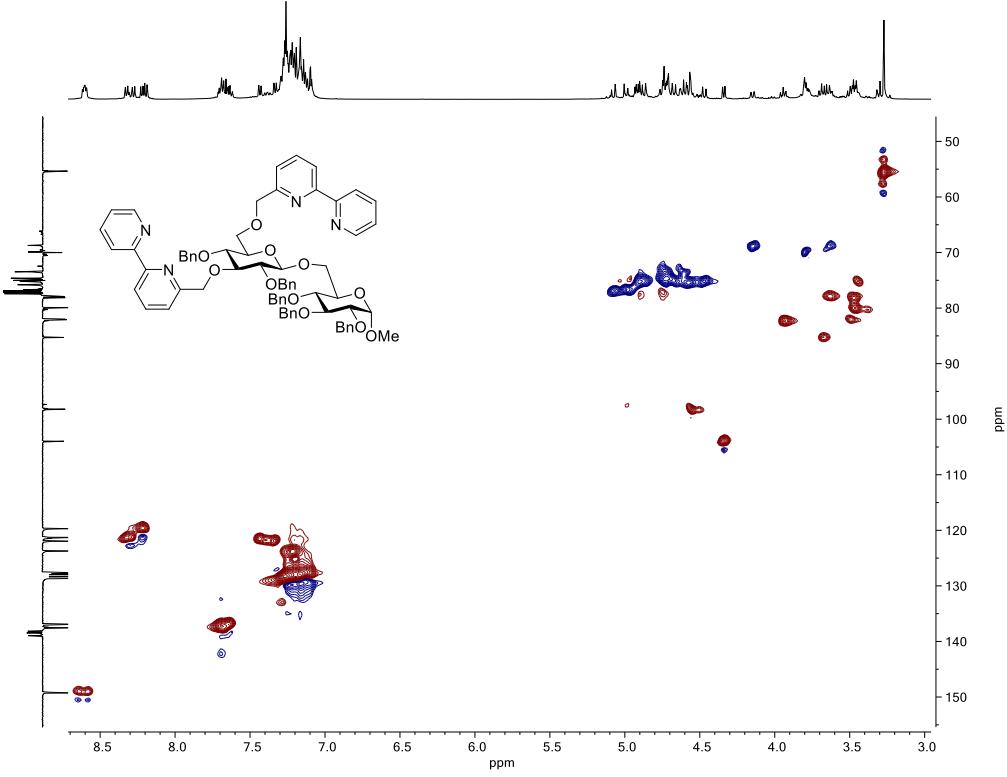
$^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz) (APT) spectrum of **21** in chloroform-*d*.



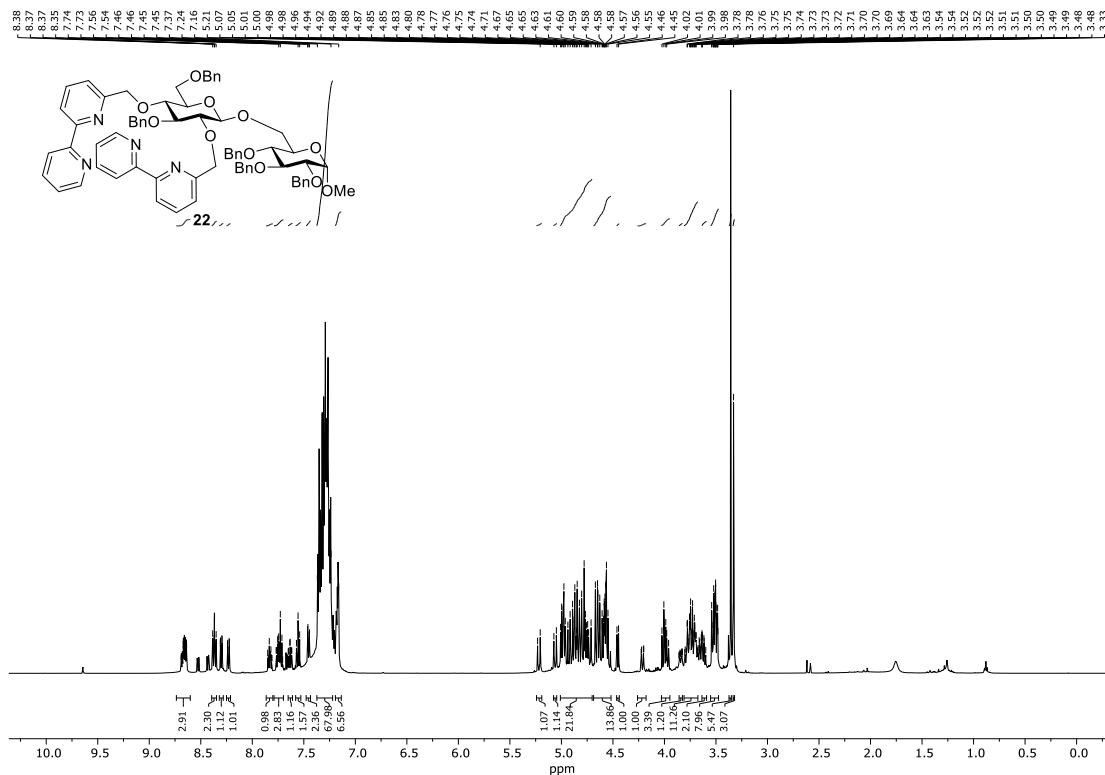
COSY spectrum of **21** in chloroform-*d*.



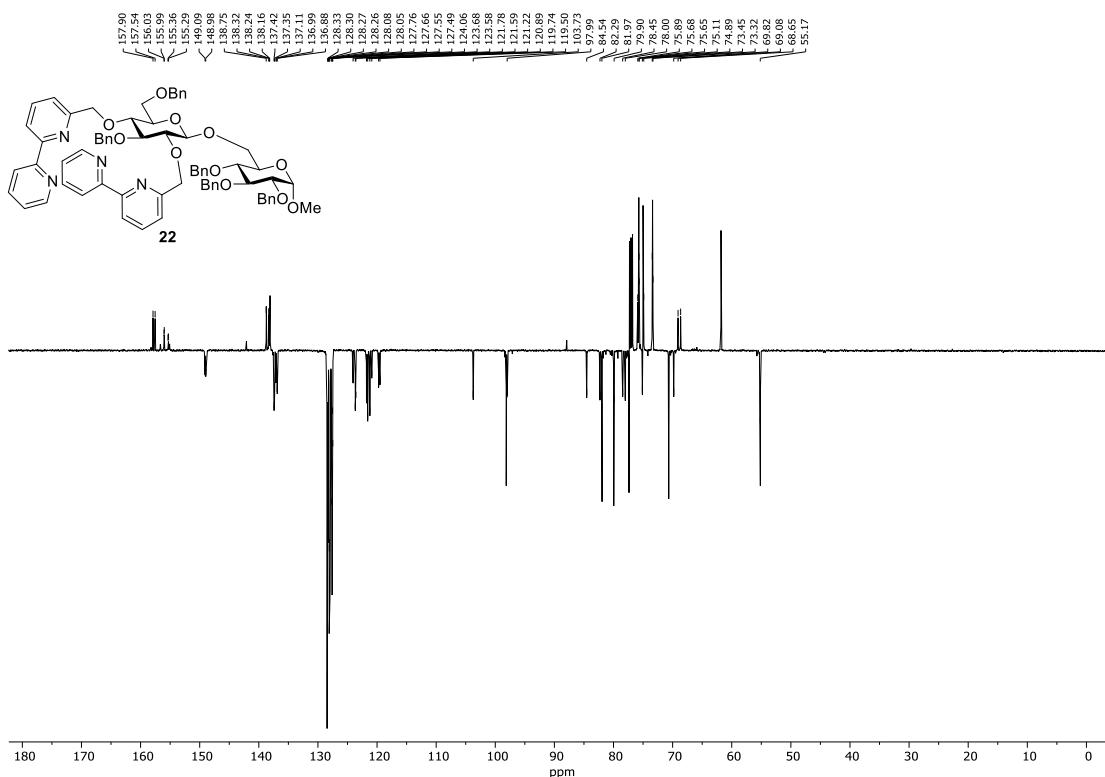
HSQC spectrum of **21** in chloroform-*d*.



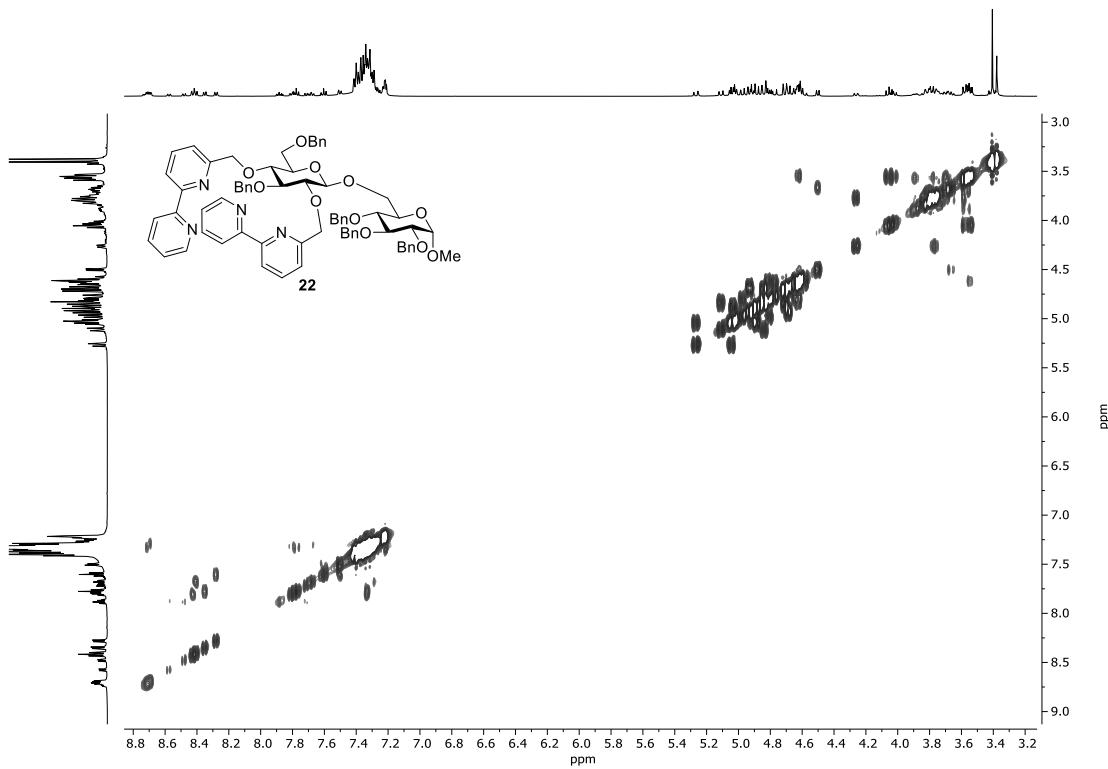
¹H-NMR (500 MHz) spectrum of **22** in chloroform-*d*.



$^{13}\text{C}\{\text{H}\}$ -NMR (126 MHz) (APT) spectrum of **22** in chloroform-*d*.



COSY spectrum of **22** in chloroform-*d*.



HSQC spectrum of **22** in chloroform-*d*.

