Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Neutral Glycoconjugated Amide-Based Calix[4]arenes: Complexation of Alkali Metal Cations in Water

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ELECTRONIC SUPPLEMENTARY INFORMATION

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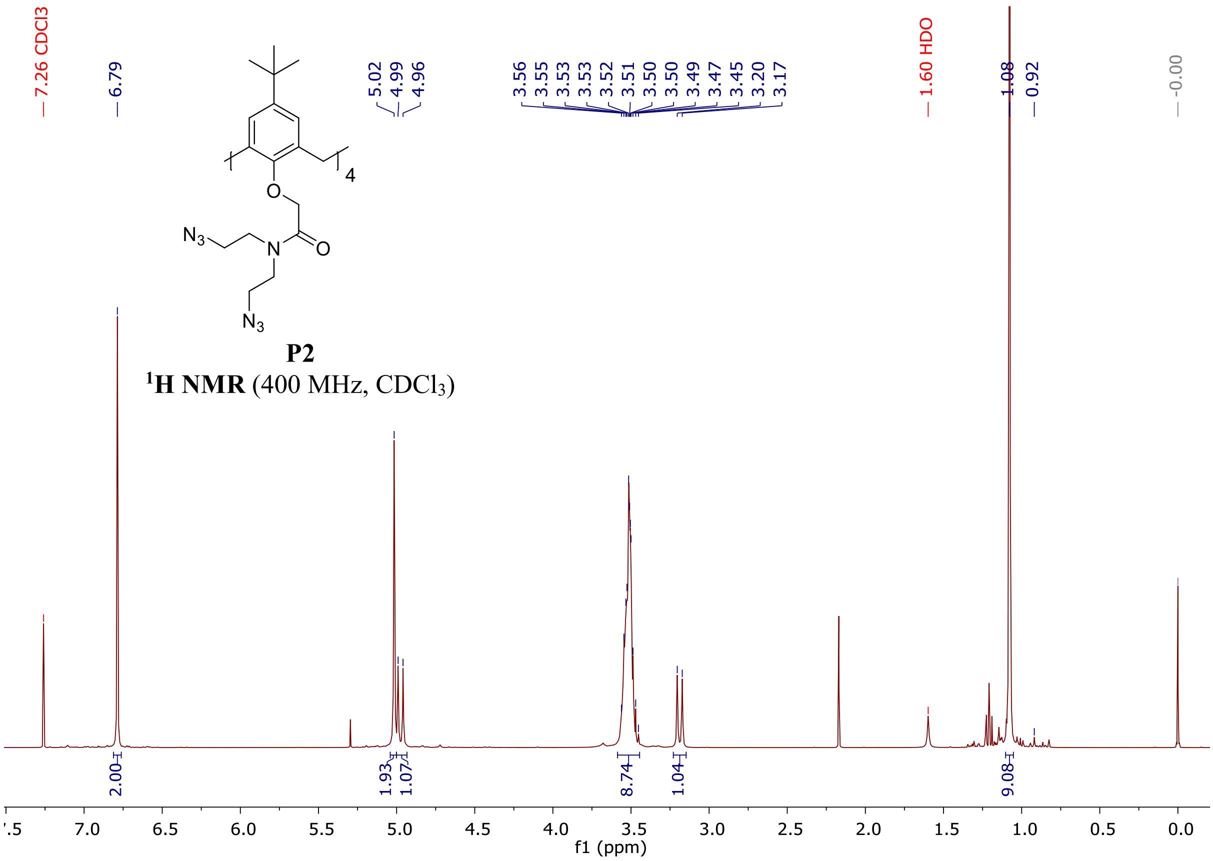
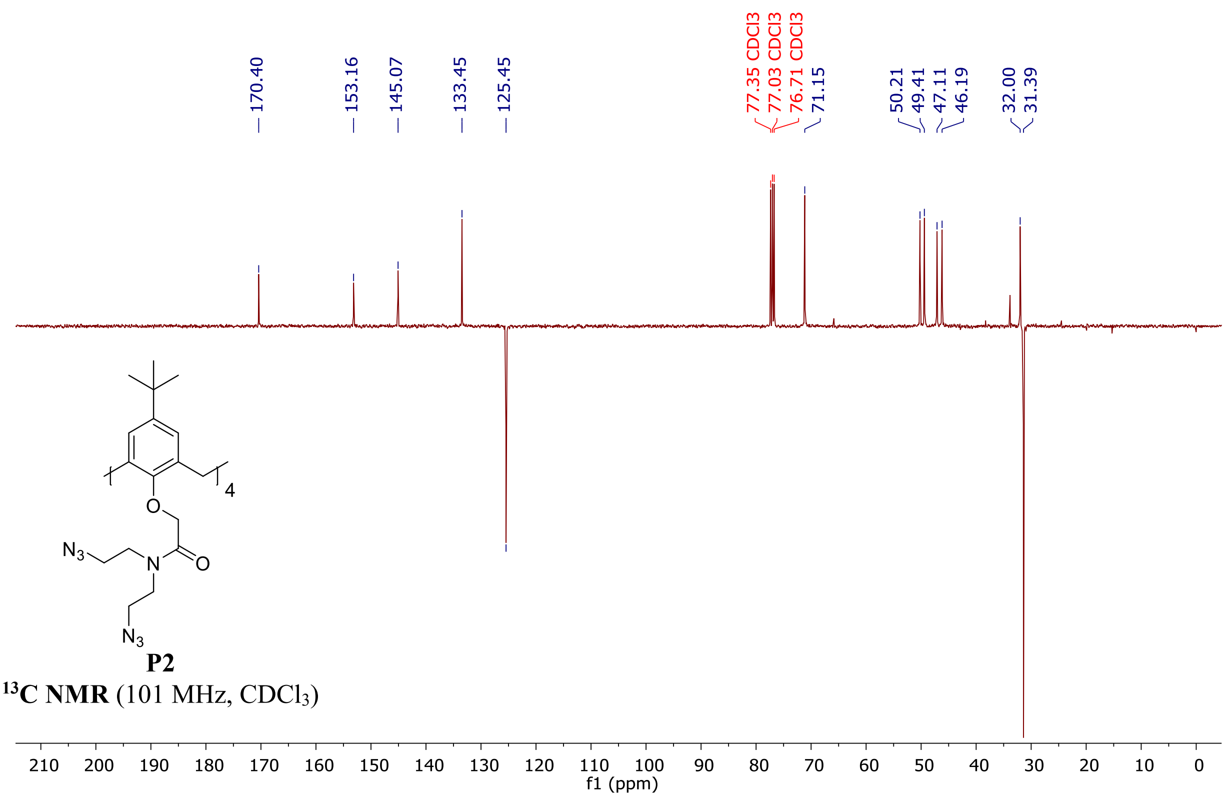
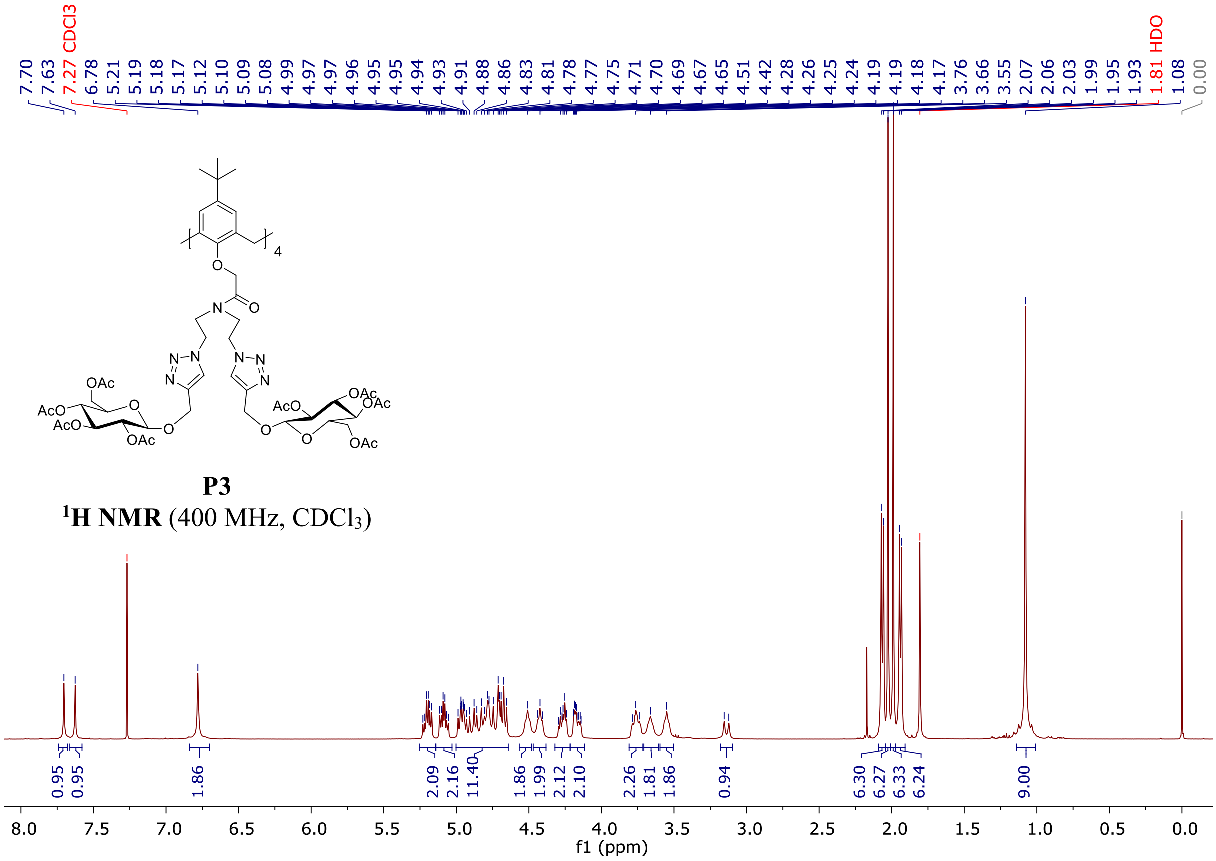
1. NMR Spectra of New Compounds

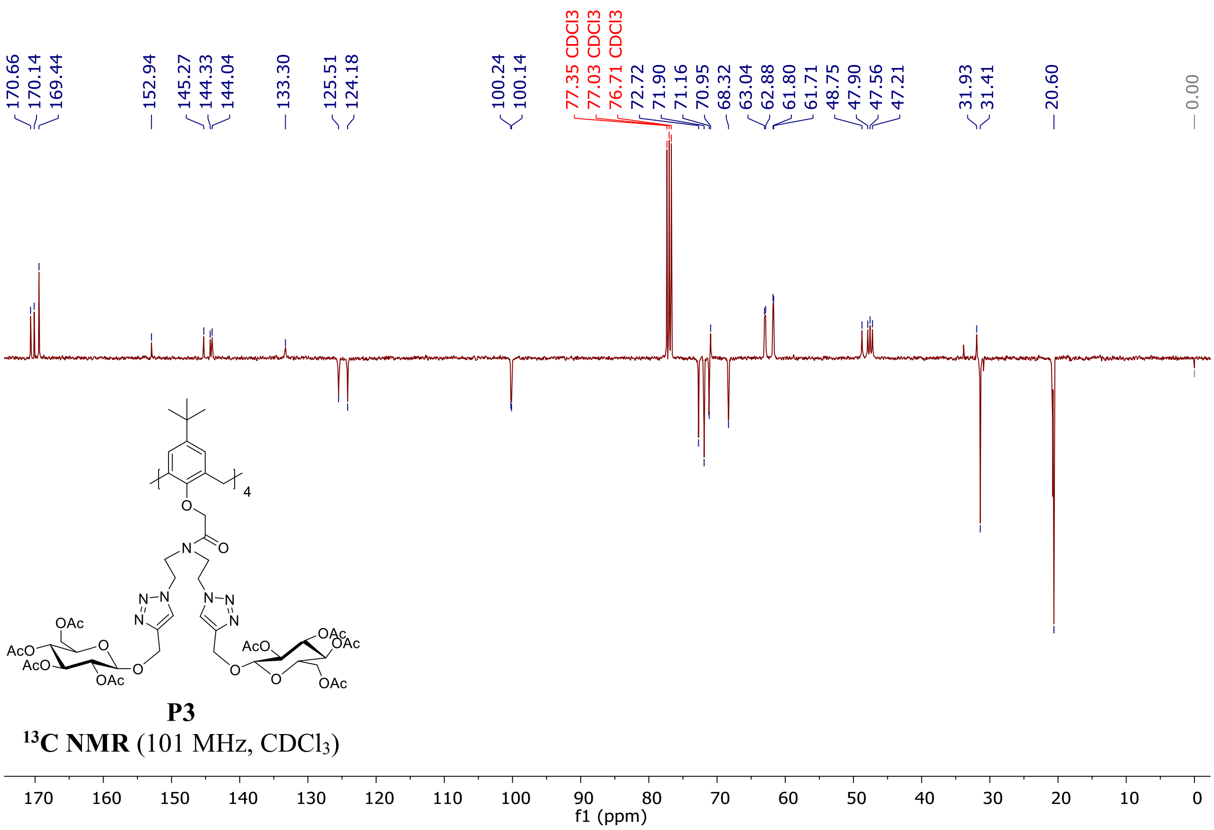






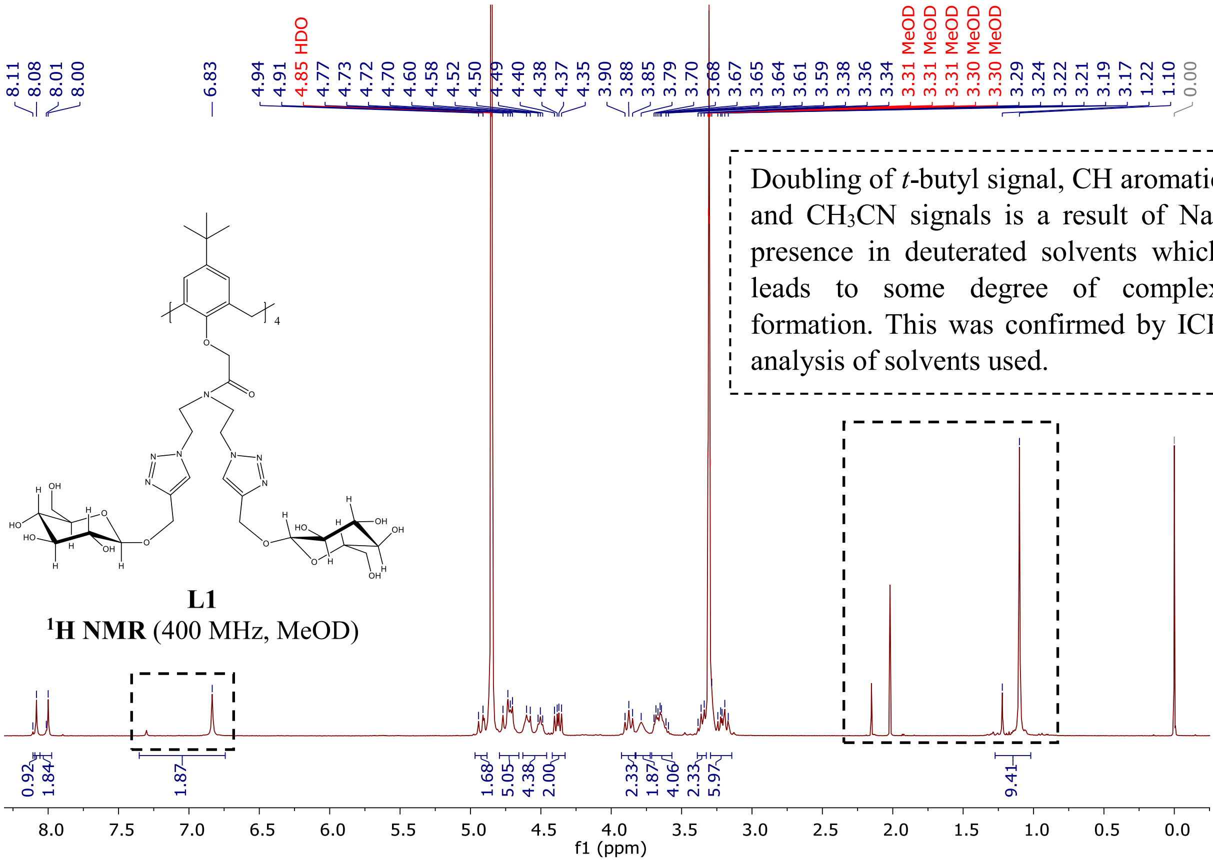
P3

^{1}H NMR (400 MHz, $CDCl_3$)



P3

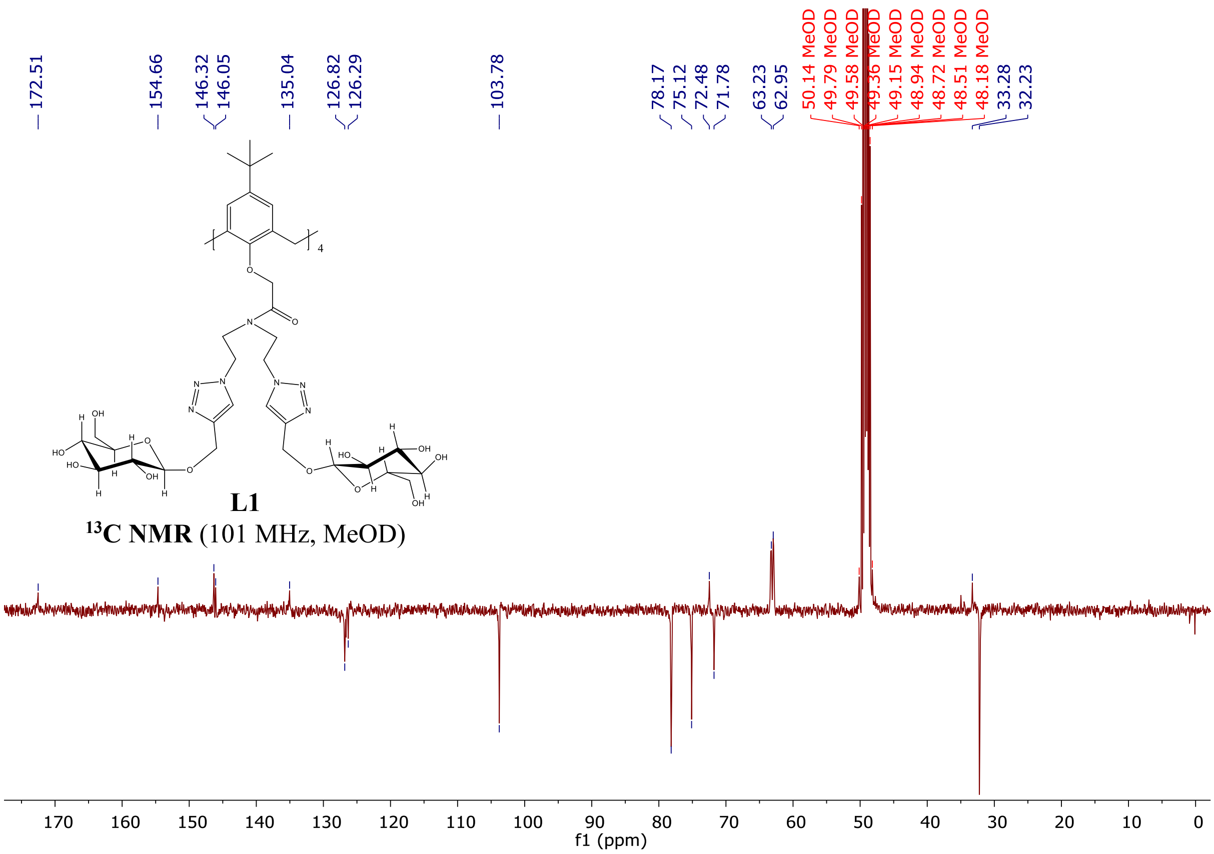
^{13}C NMR (101 MHz, $CDCl_3$)



L1

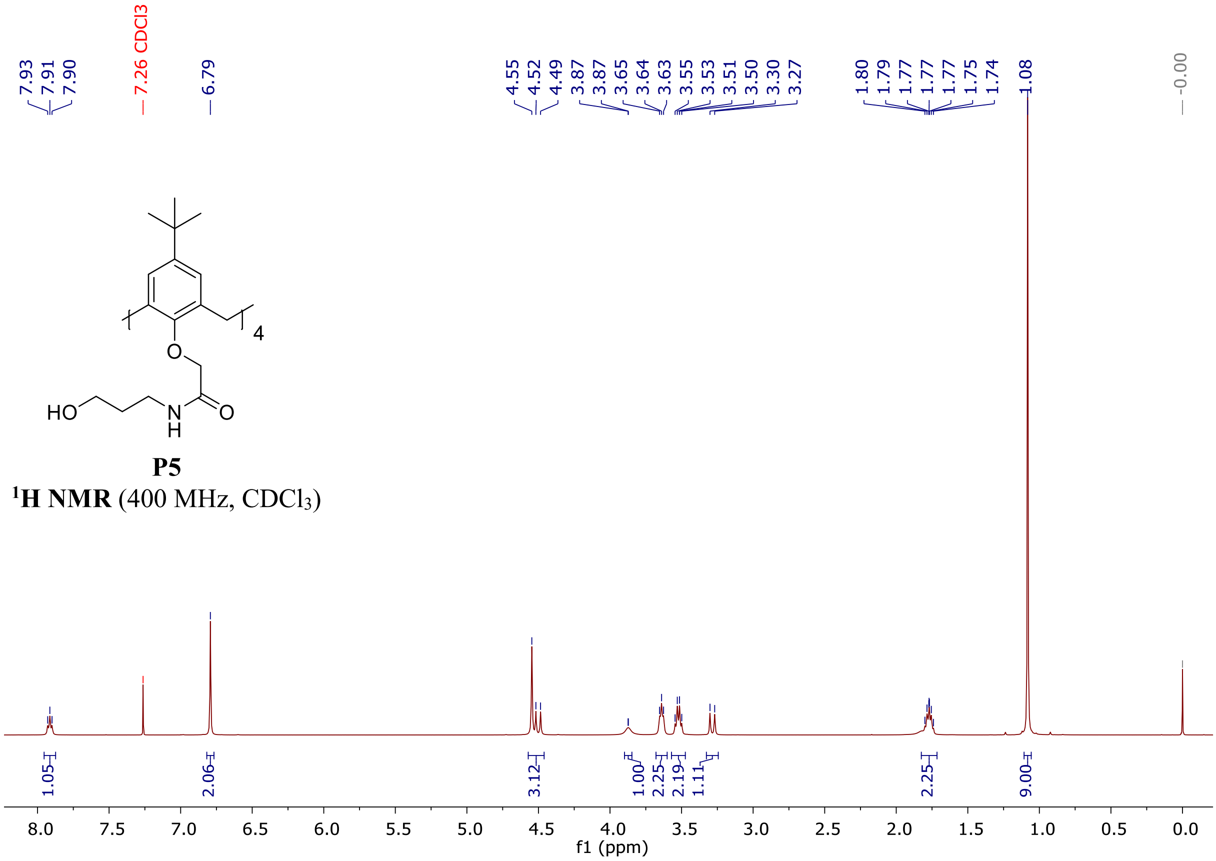
^{1}H NMR (400 MHz, MeOD)

Doubling of *t*-butyl signal, CH aromatic and CH_3CN signals is a result of Na^+ presence in deuterated solvents which leads to some degree of complex formation. This was confirmed by ICP analysis of solvents used.



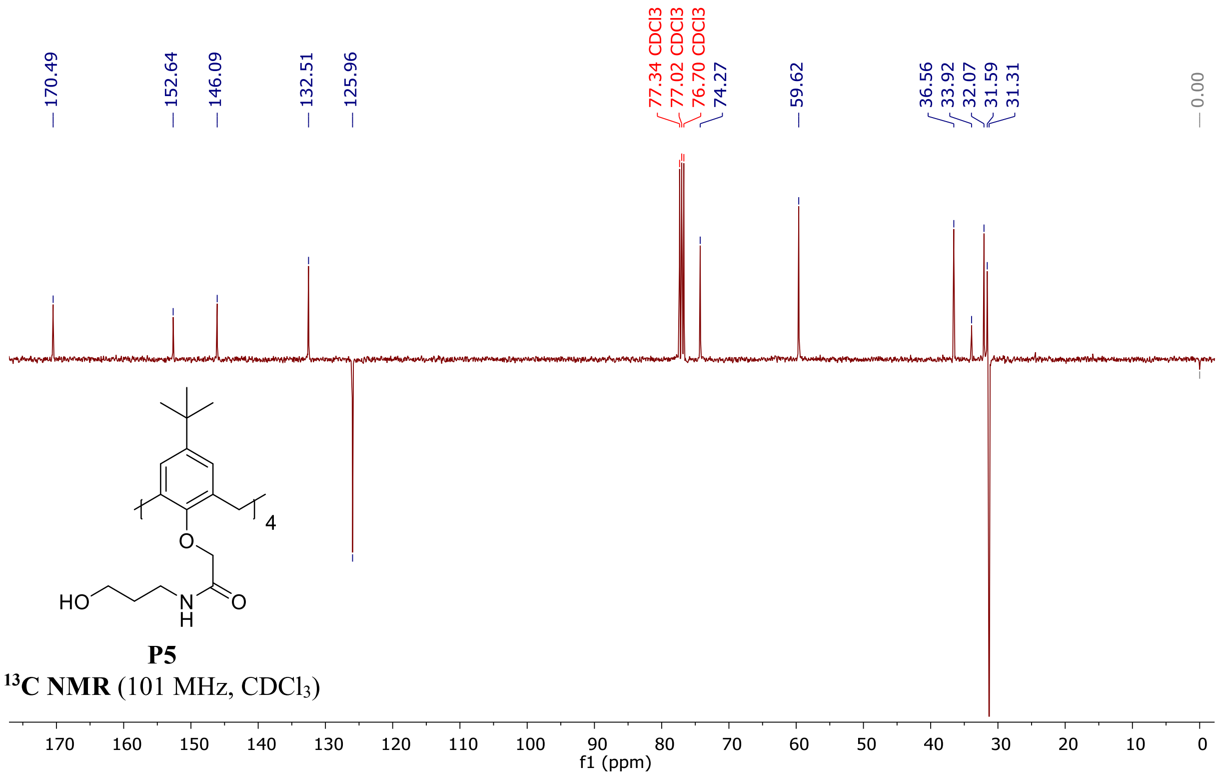
L1

^{13}C NMR (101 MHz, MeOD)



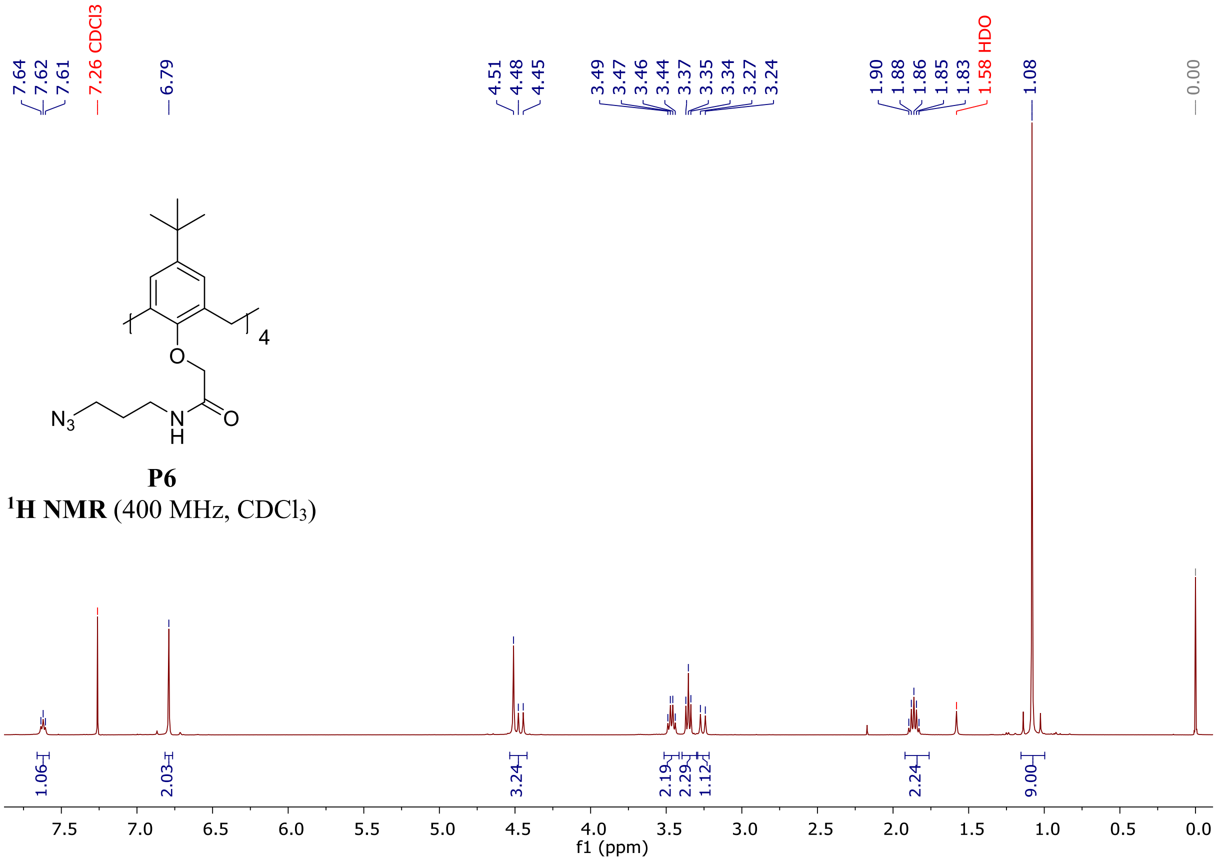
P5

^{1}H NMR (400 MHz, $CDCl_3$)



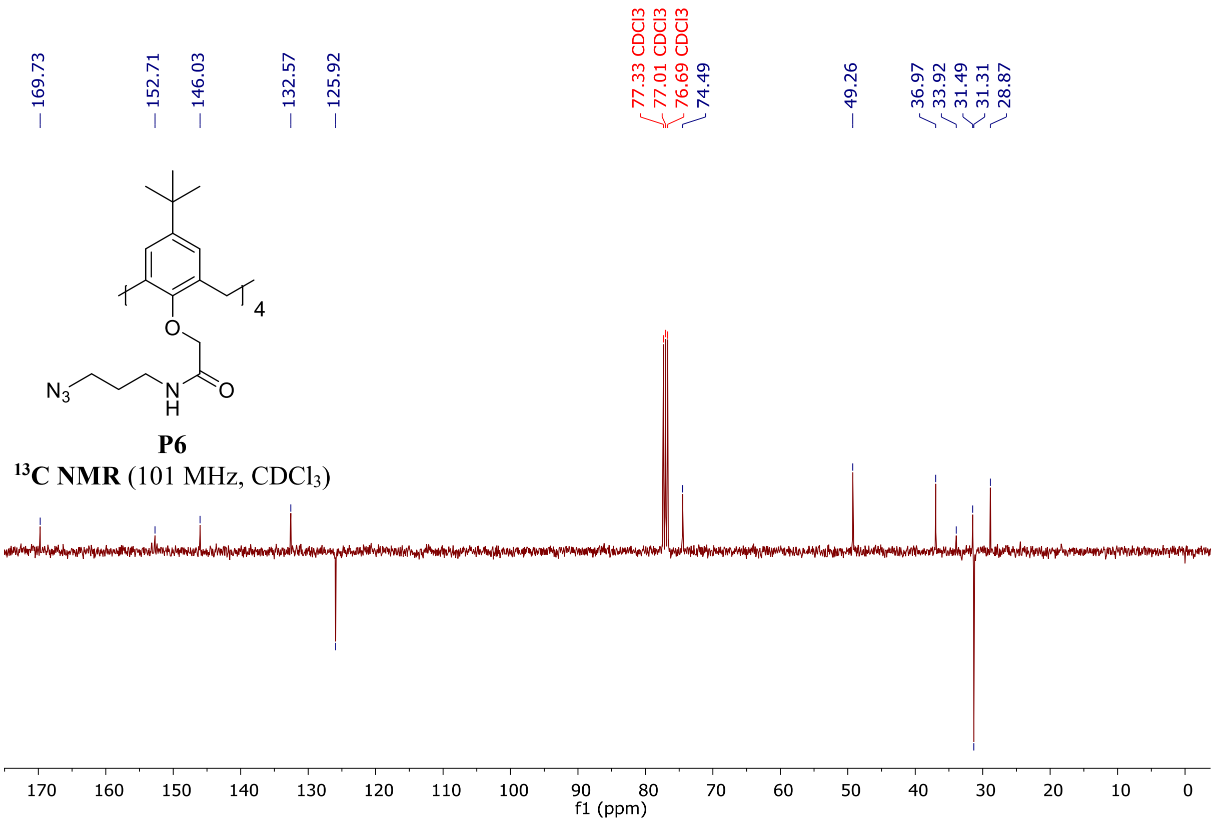
P5

^{13}C NMR (101 MHz, $CDCl_3$)



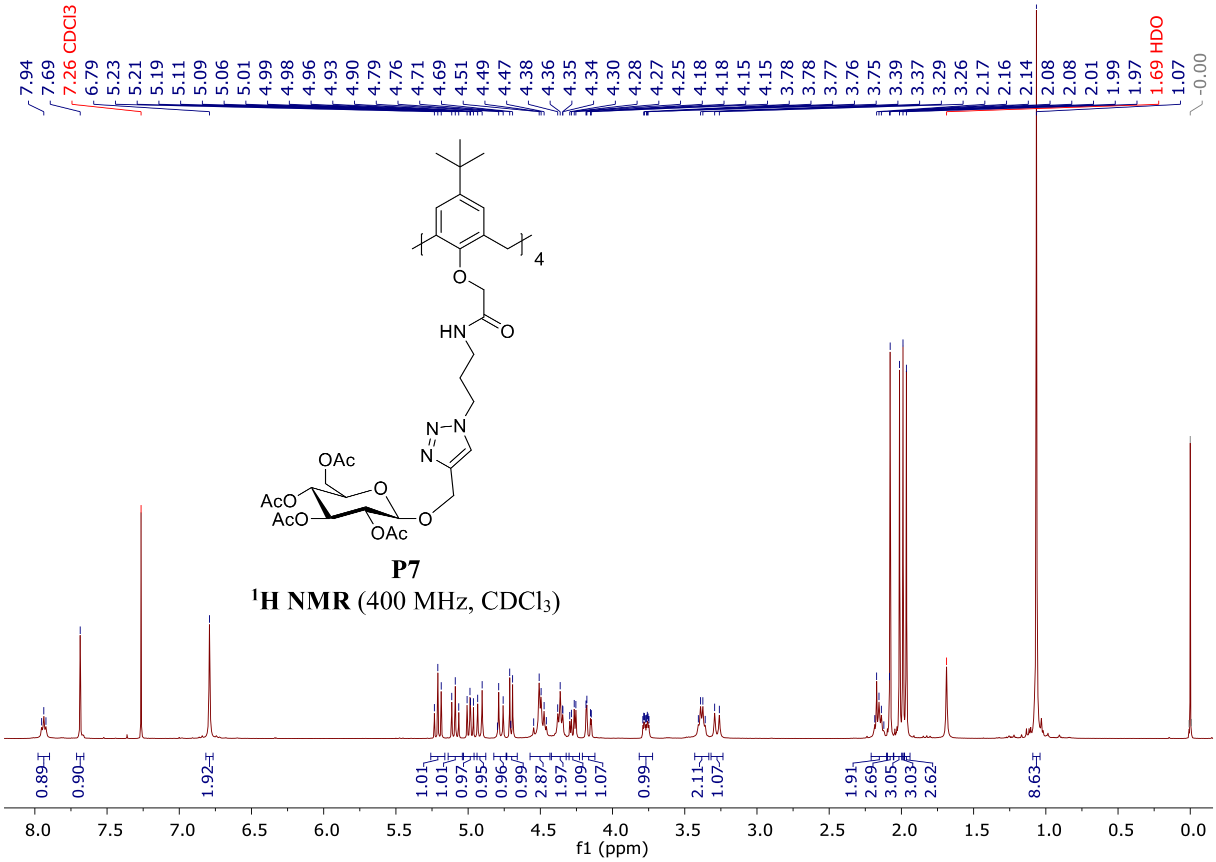
P6

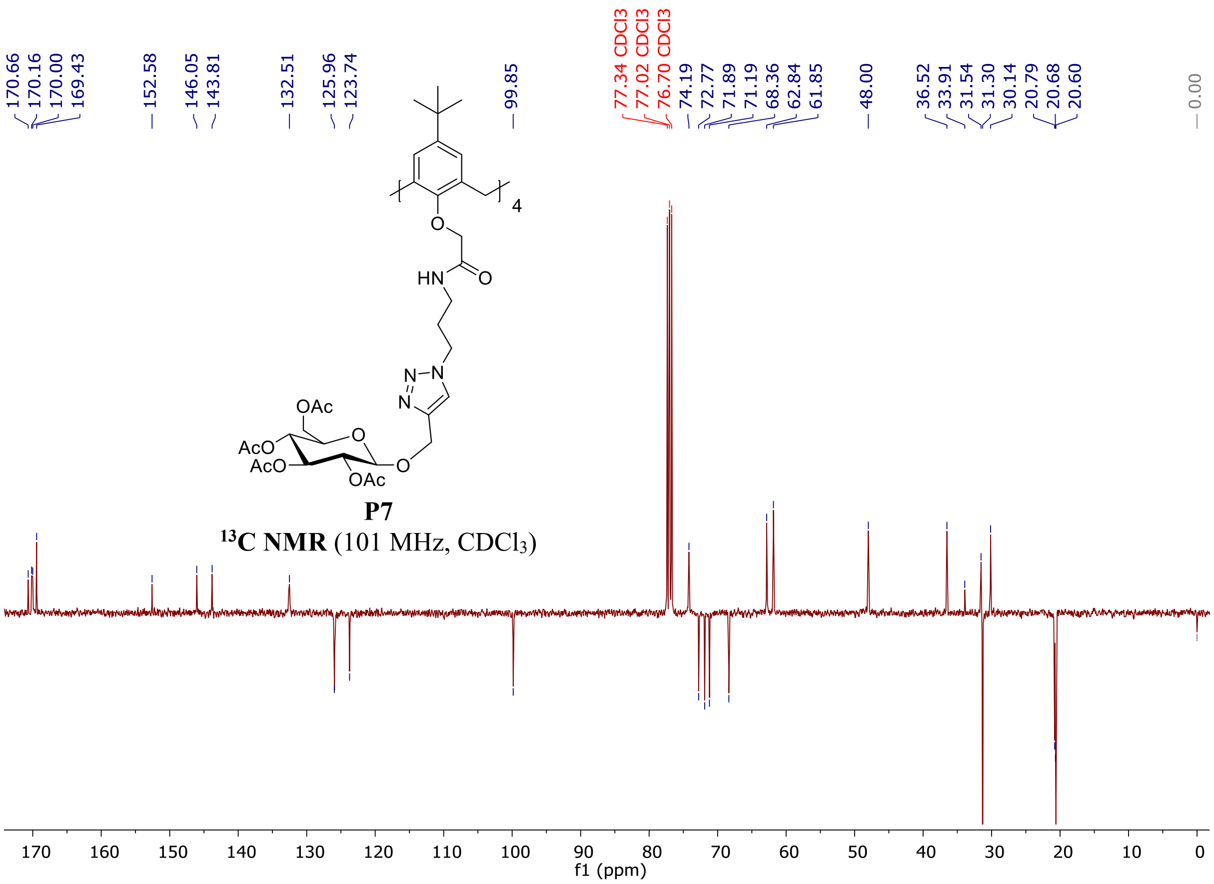
^{1}H NMR (400 MHz, $CDCl_3$)

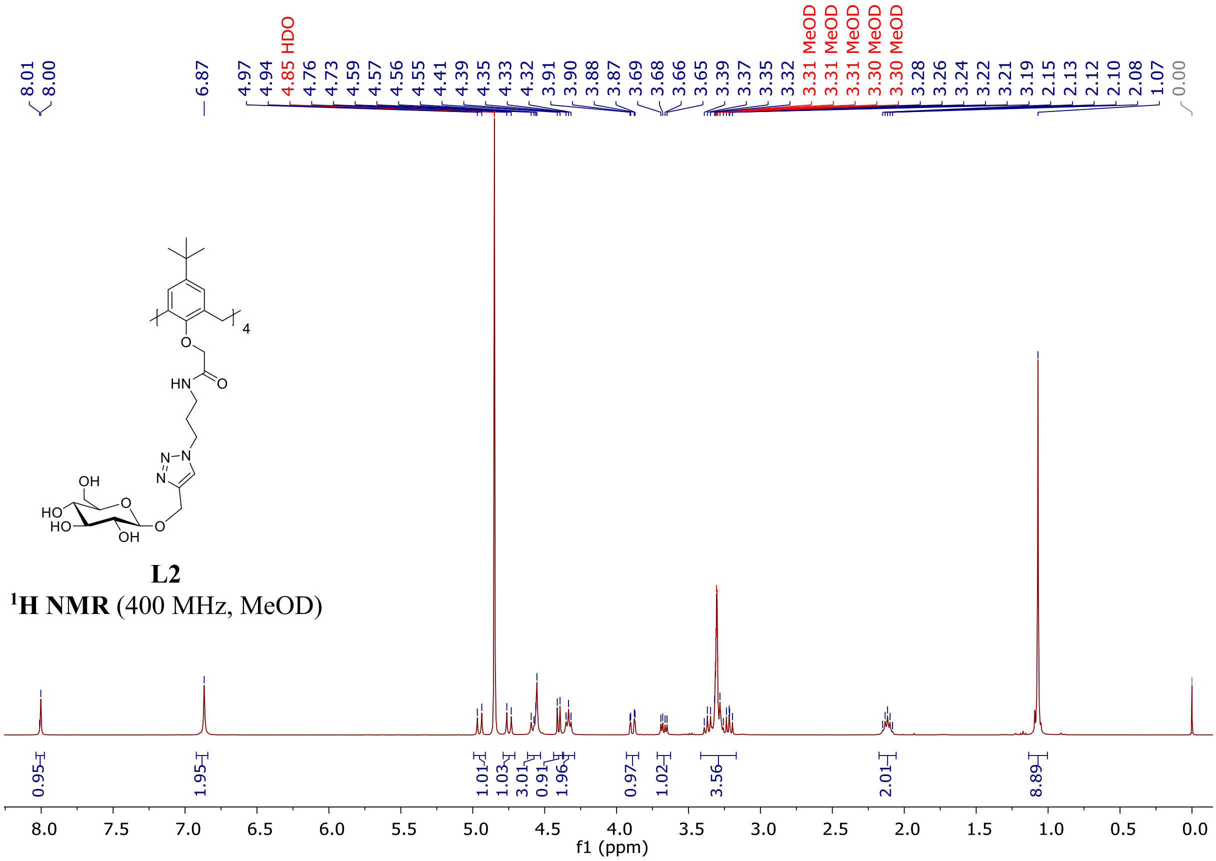


P6

^{13}C NMR (101 MHz, $CDCl_3$)

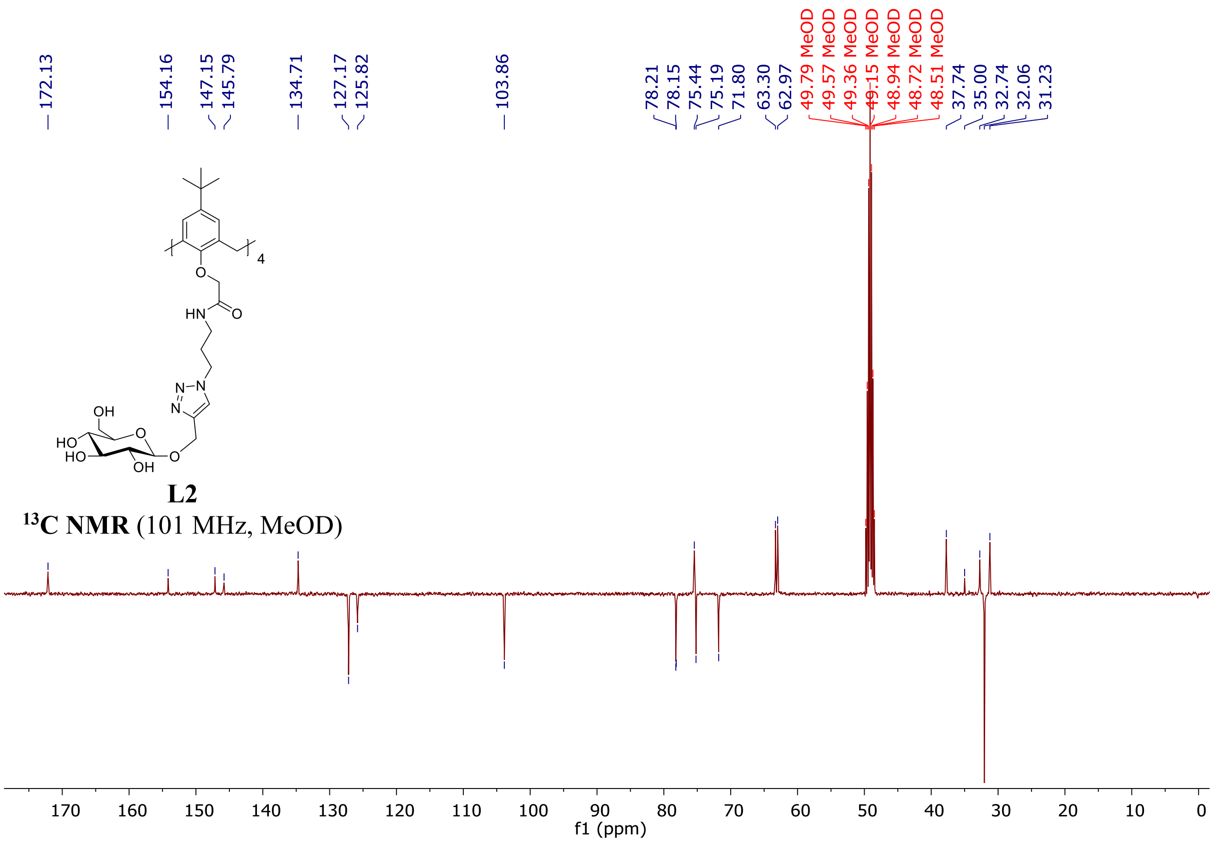

P7
1H NMR (400 MHz, CDCl3)
f1 (ppm)


P7
13C NMR (101 MHz, CDCl3)
f1 (ppm)



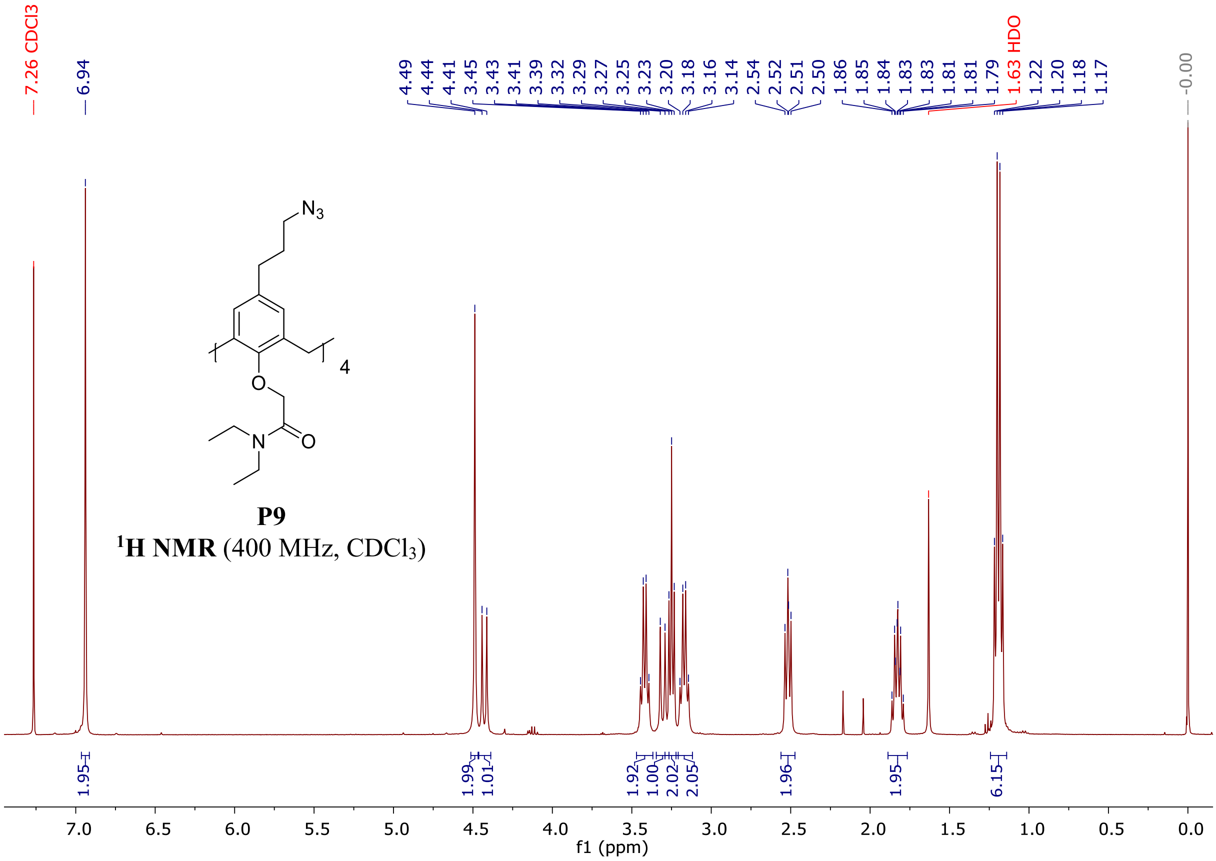
L2

^{1}H NMR (400 MHz, MeOD)



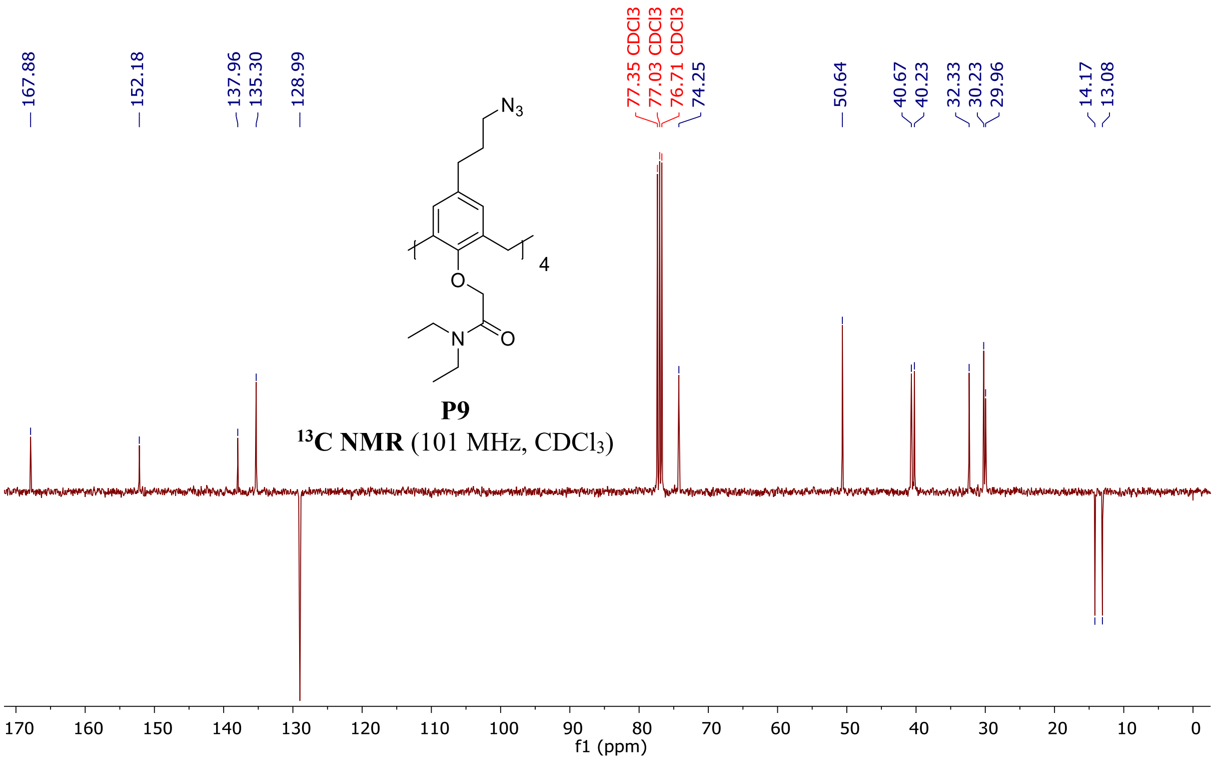
L2

^{13}C NMR (101 MHz, MeOD)



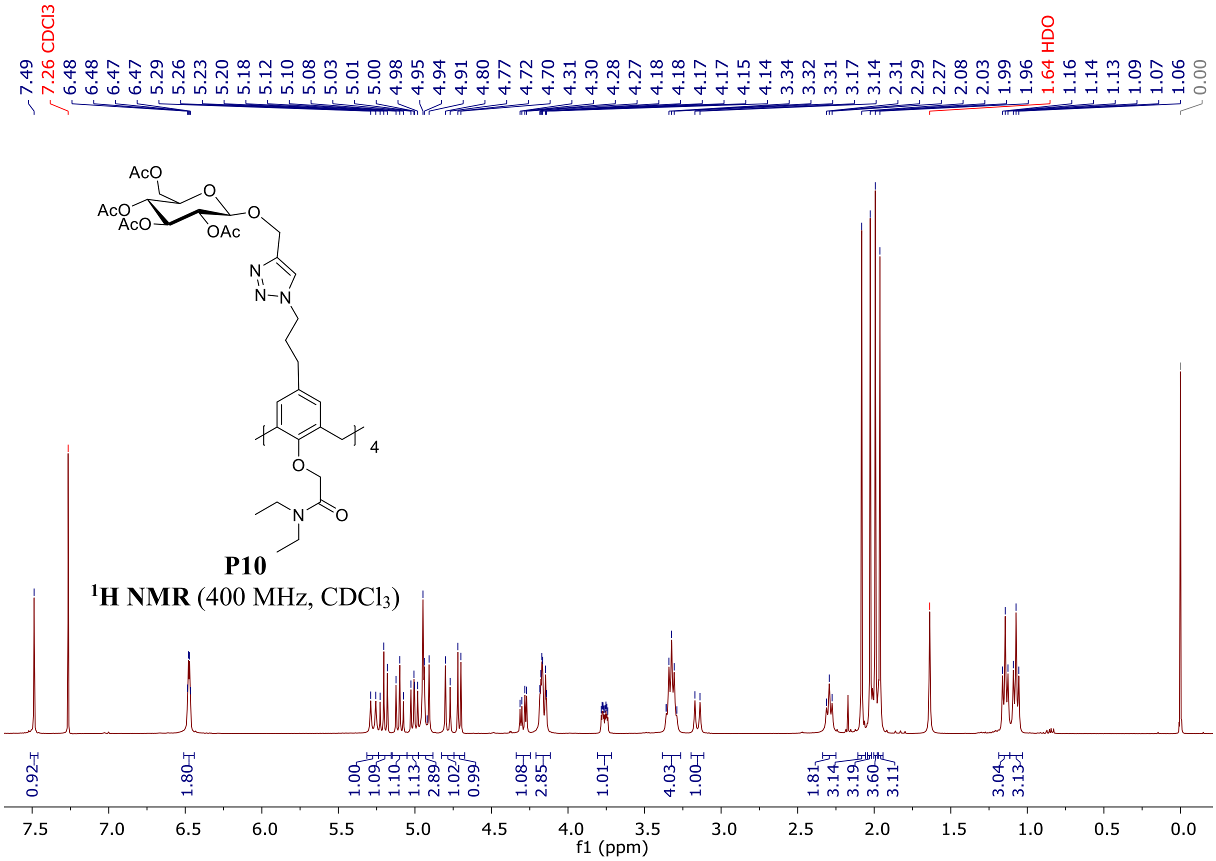
P9

[1]**H NMR** (400 MHz, $CDCl_3$)



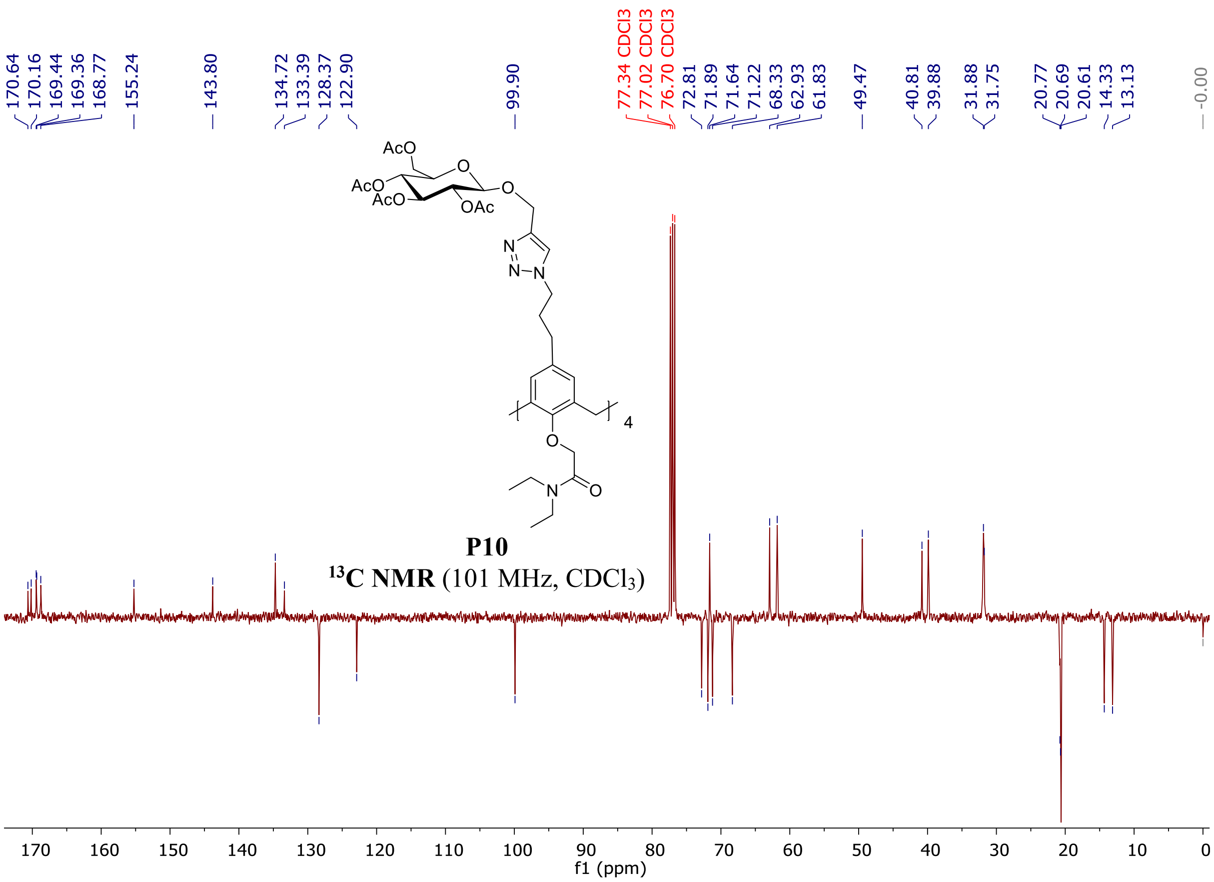
P9

[13]**C NMR** (101 MHz, $CDCl_3$)



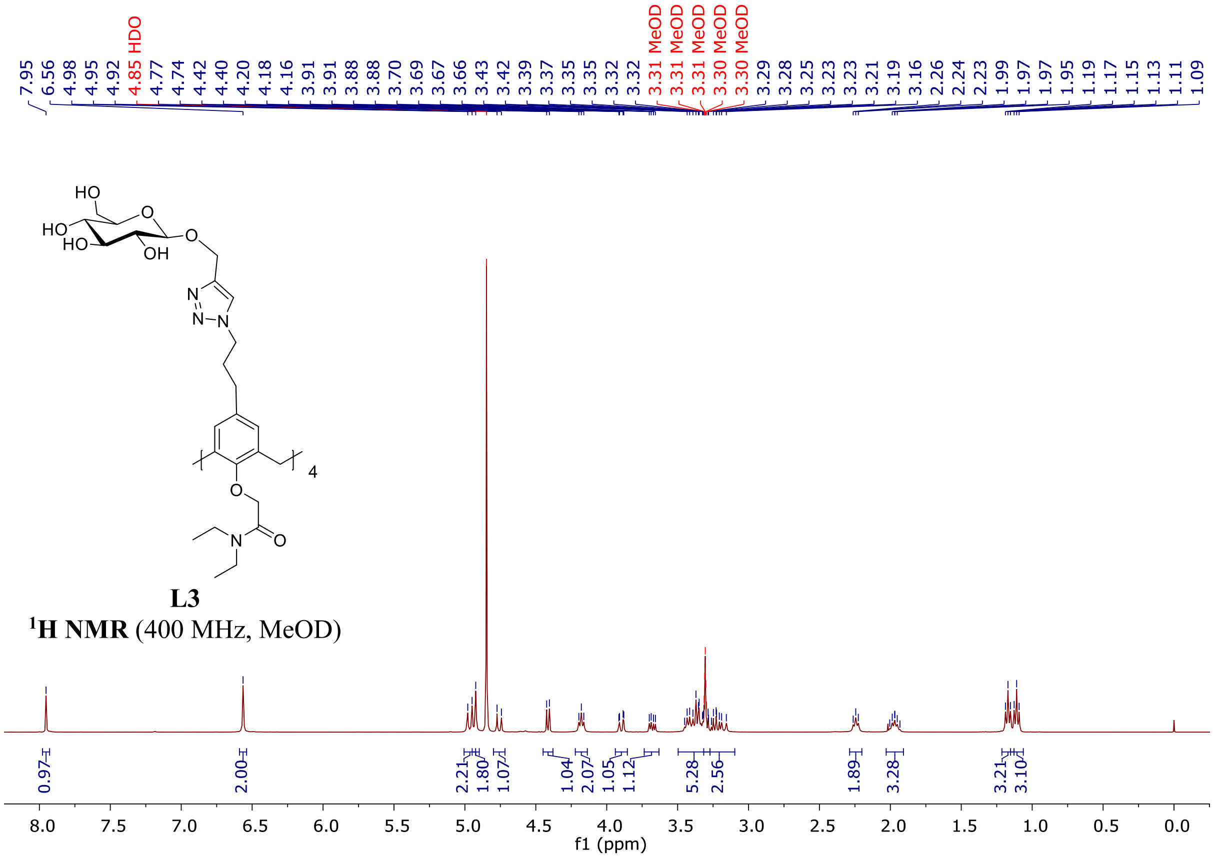
P10

[1]H NMR (400 MHz, $CDCl_3$)



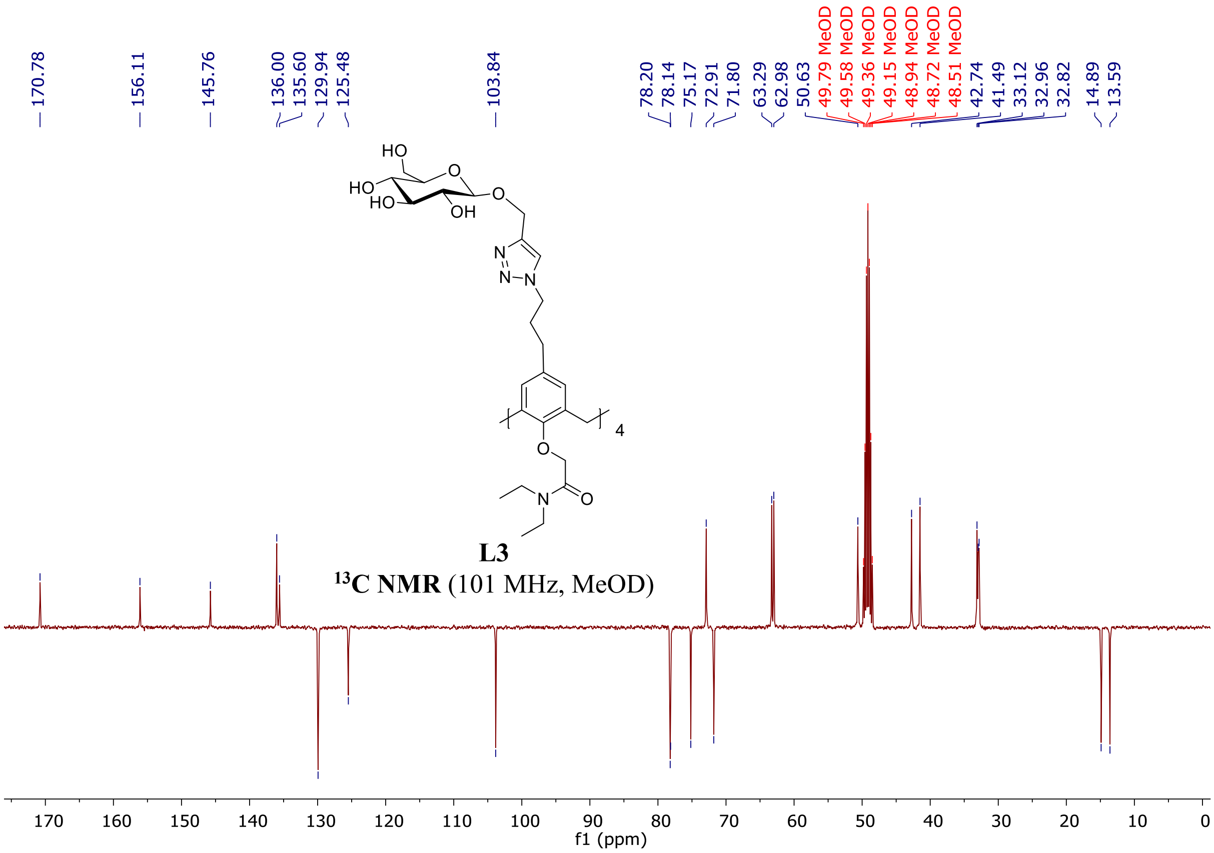
P10

[13]C NMR (101 MHz, $CDCl_3$)



L3

^{1}H NMR (400 MHz, MeOD)



L3

^{13}C NMR (101 MHz, MeOD)

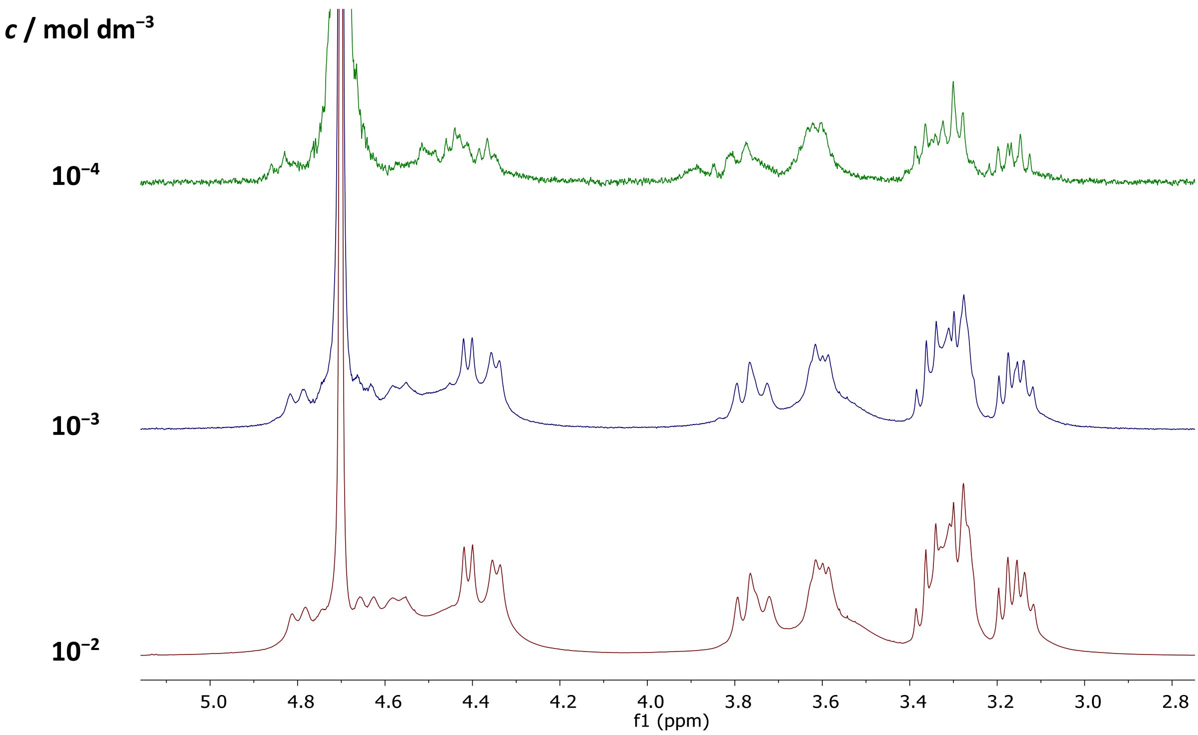


Figure S1. Concentration dependence of [1]H NMR spectra of **L1** in D_2O at 25 ºC.

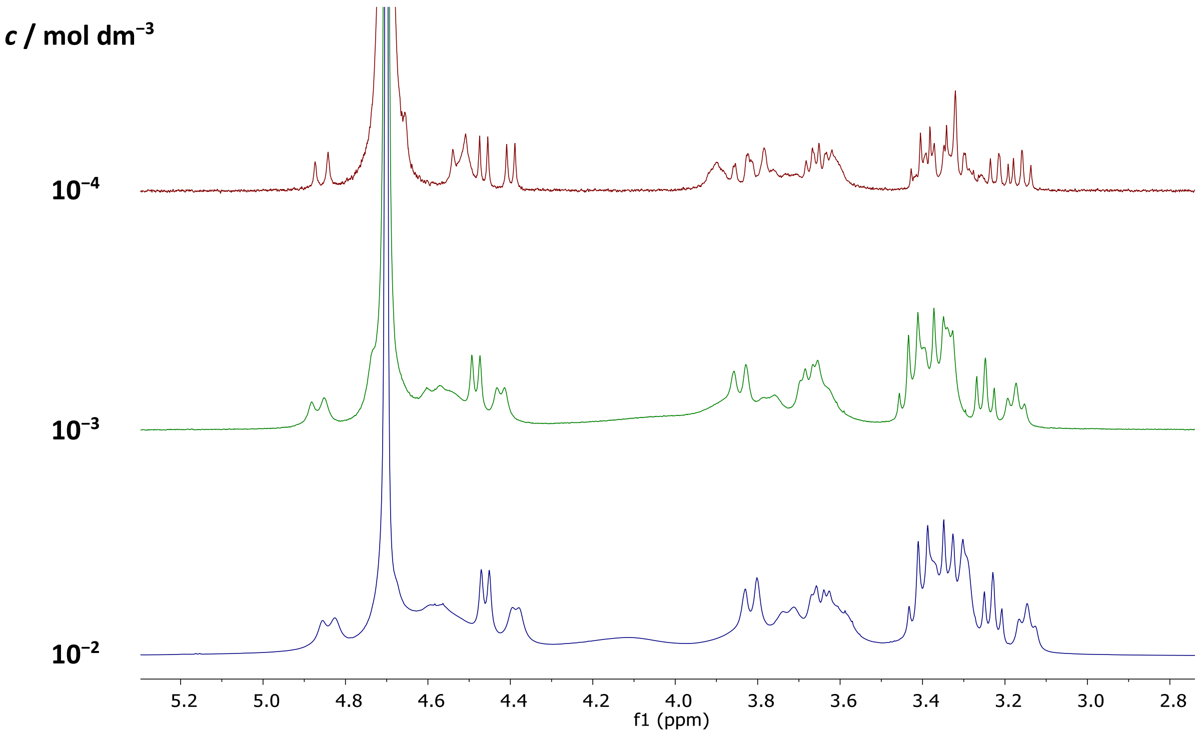


Figure S2. Concentration dependence of [1]H NMR spectra of Na**L1**$^+$ in D_2O at 25 ºC.

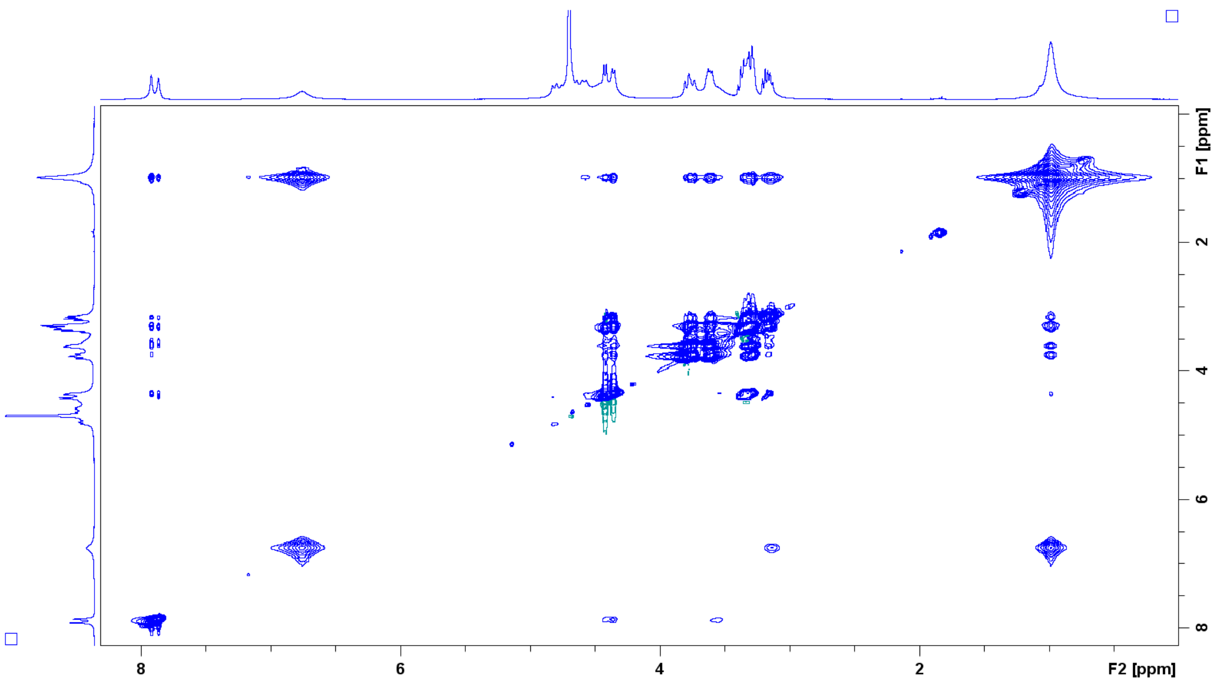


Figure S3. NOESY NMR spectrum of **L1** in D_2O at 25 ºC.

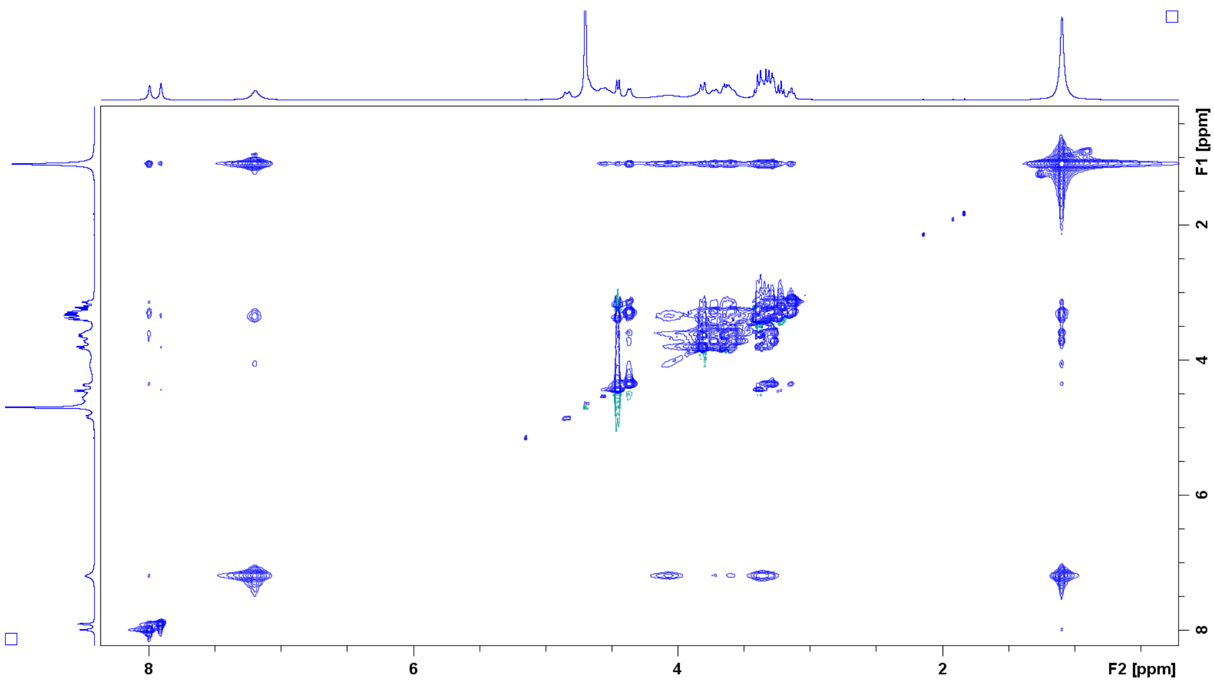


Figure S4. NOESY NMR spectrum of Na**L1**$^+$ in D_2O at 25 ºC.

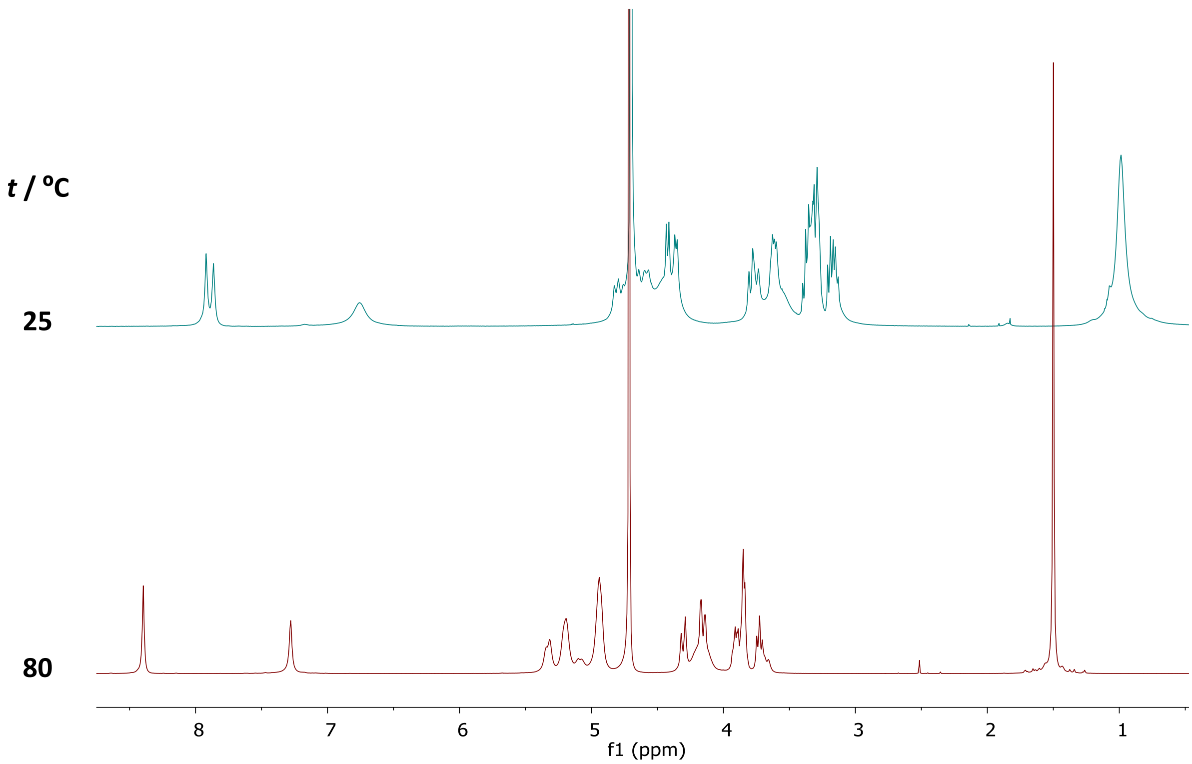


Figure S5. Temperature dependence of ^{1}H NMR spectra of **L1** in D_2O.

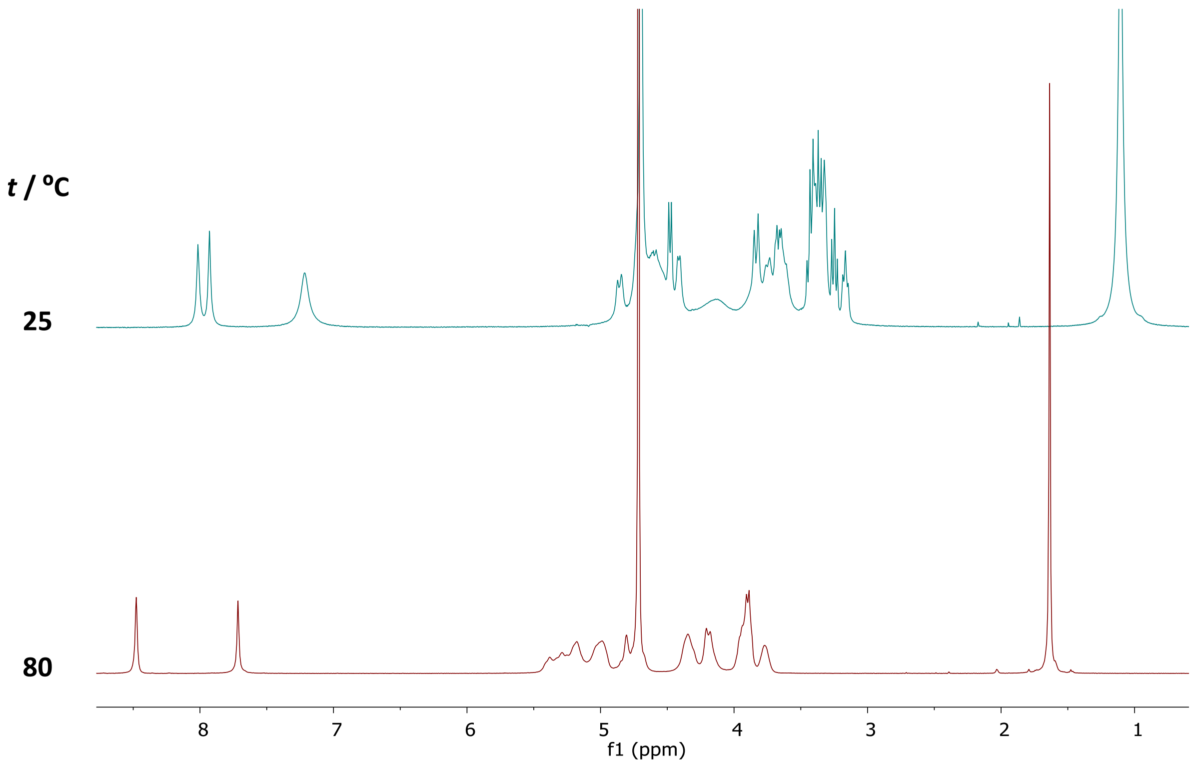


Figure S6. Temperature dependence of ^{1}H NMR spectra of Na**L1**$^{+}$ in D_2O.

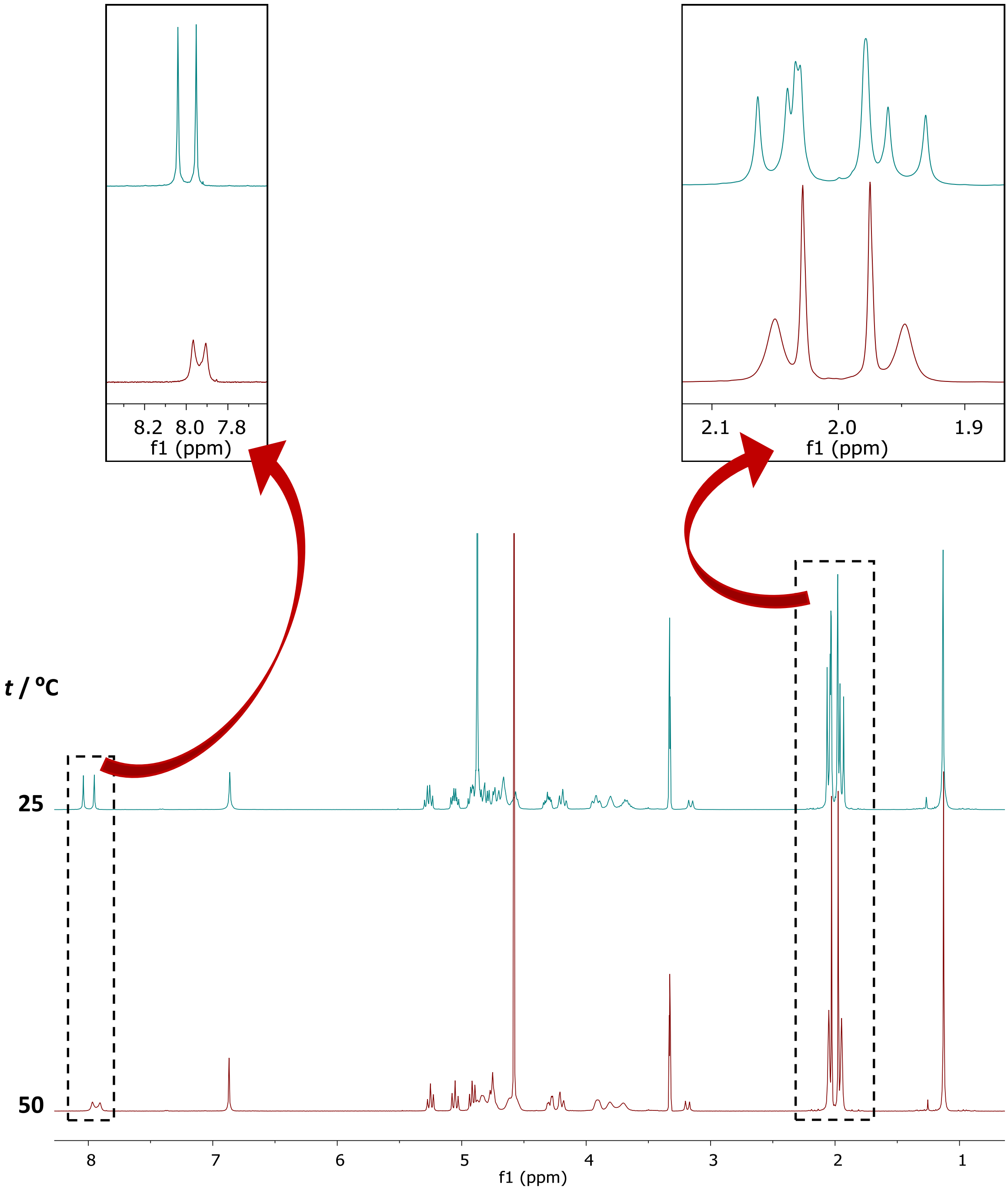


Figure S7. Temperature dependence ^{1}H NMR spectra of **P3** in MeOD.

2. Spectrophotometric Titration Data

L1

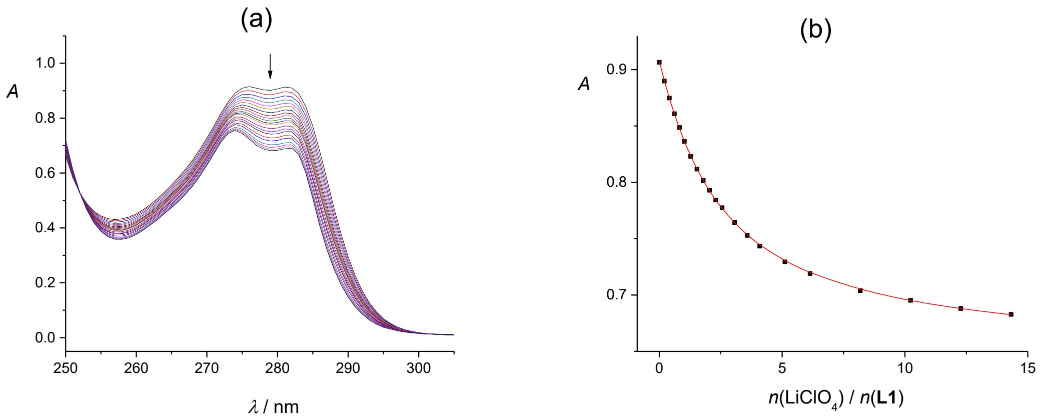


Figure S8. a) Spectrophotometric titration of **L1** ($c = 2.53 \times 10^{-4}$ mol dm^{-3}) with $LiClO_4$ ($c = 5.18 \times 10^{-3}$ mol dm^{-3}) in methanol at (25.0 ± 0.1) °C; $l = 1$ cm, $V_0 = 2.0$ ml. Spectra are corrected for dilution. b) Dependence of absorbance at 280 nm on $n(LiClO_4)$ / n(**L1**) molar ratio. ■ experimental, — calculated.

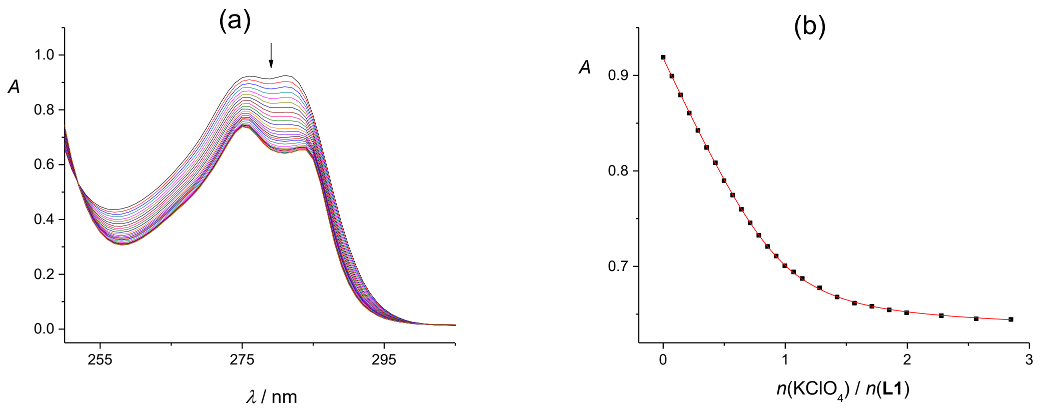


Figure S9. a) Spectrophotometric titration of **L1** ($c = 2.56 \times 10^{-4}$ mol dm^{-3}) with $KClO_4$ ($c = 1.46 \times 10^{-3}$ mol dm^{-3}) in methanol at (25.0 ± 0.1) °C; $l = 1$ cm, $V_0 = 2.0$ ml. Spectra are corrected for dilution. b) Dependence of absorbance at 280 nm on $n(KClO_4)$ / n(**L1**) molar ratio. ■ experimental, — calculated.

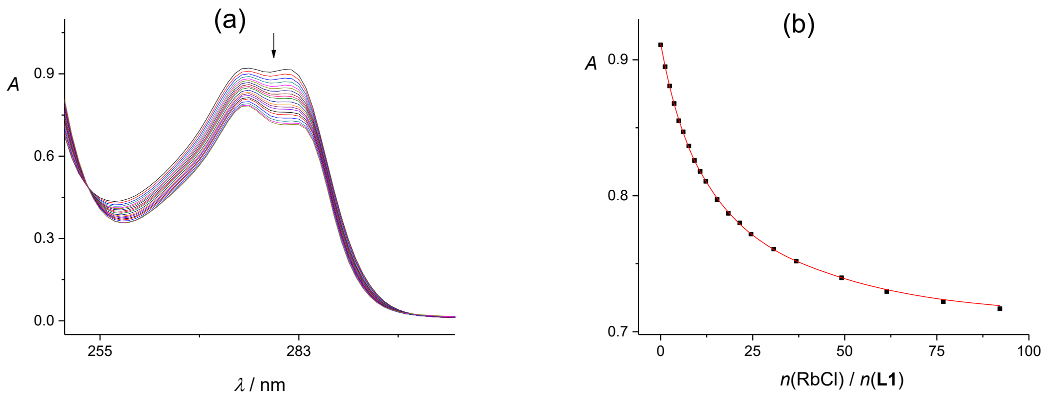


Figure S10. a) Spectrophotometric titration of **L1** ($c = 2.52 \times 10^{-4}$ mol dm^{-3}) with RbCl ($c = 3.10 \times 10^{-2}$ mol dm^{-3}) in methanol at (25.0 ± 0.1) °C; $l = 1$ cm, $V_0 = 2.0$ ml. Spectra are corrected for dilution. b) Dependence of absorbance at 280 nm on n(RbCl) / n(**L1**) molar ratio. ■ experimental, — calculated.

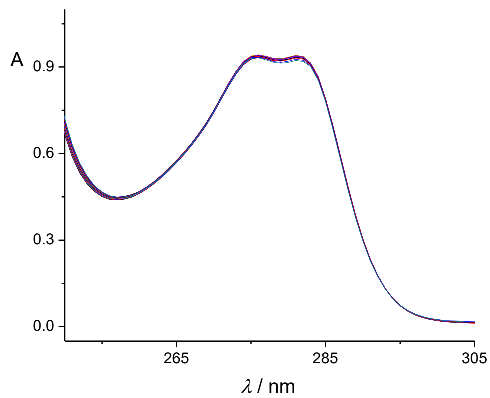


Figure S11. a) Spectrophotometric titration of **L1** ($c = 2.52 \times 10^{-4}$ mol dm^{-3}) with CsCl ($c = 7.78 \times 10^{-2}$ mol dm^{-3}) in methanol at (25.0 ± 0.1) °C; $l = 1$ cm, $V_0 = 2.0$ ml. Spectra are corrected for dilution. The n(CsCl) / n(**L1**) molar ratio at the end of titration is 216.

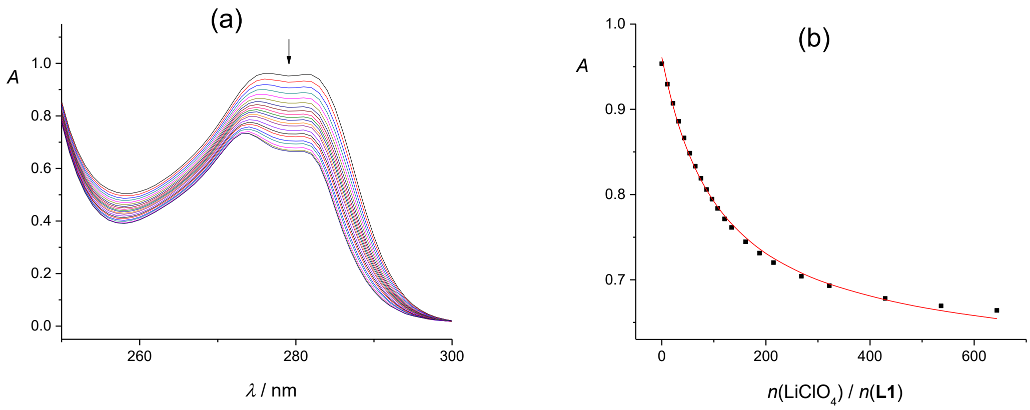


Figure S12. a) Spectrophotometric titration of **L1** ($c = 2.80 \times 10^{-4}$ mol dm^{-3}) with $LiClO_4$ ($c = 3.00 \times 10^{-1}$ mol dm^{-3}) in water at (25.0 ± 0.1) °C; $l = 1$ cm, $V_0 = 2.0$ ml. Spectra are corrected for dilution. b) Dependence of absorbance at 280 nm on $n(LiClO_4)$ / n(**L1**) molar ratio. ■ experimental, — calculated.

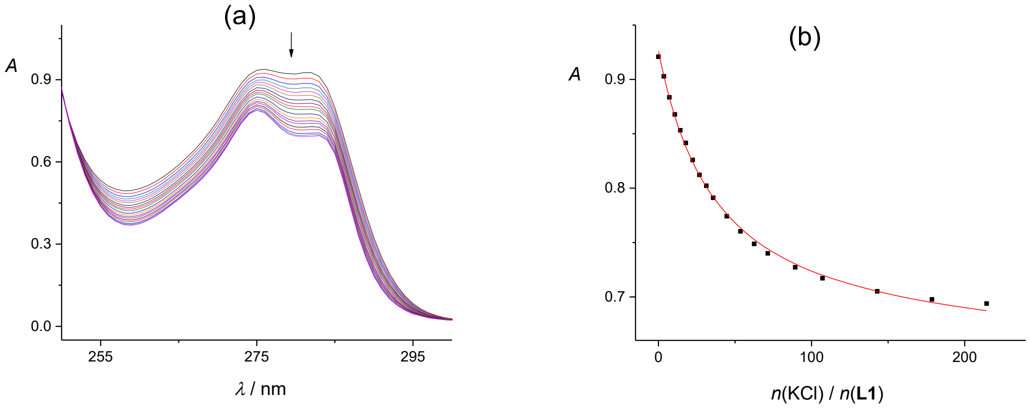


Figure S13. a) Spectrophotometric titration of **L1** ($c = 2.80 \times 10^{-4}$ mol dm^{-3}) with KCl ($c = 1.00 \times 10^{-1}$ mol dm^{-3}) in water at (25.0 ± 0.1) °C; $l = 1$ cm, $V_0 = 2.0$ ml. Spectra are corrected for dilution. b) Dependence of absorbance at 280 nm on n(KCl) / n(**L1**) molar ratio. ■ experimental, — calculated.

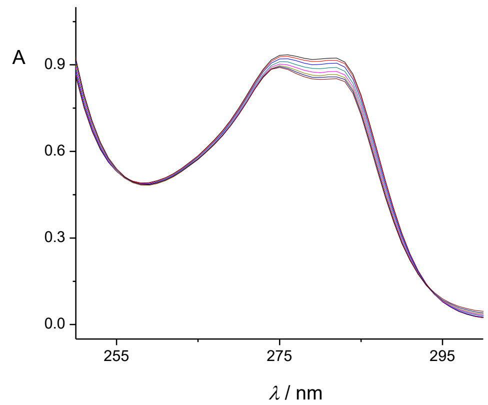


Figure S14. a) Spectrophotometric titration of **L1** ($c = 2.81 \times 10^{-4}$ mol dm^{-3}) with RbCl ($c = 5.00 \times 10^{-1}$ mol dm^{-3}) in water at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.0 ml. Spectra are corrected for dilution. The n(RbCl) / n(**L1**) molar ratio at the end of titration is 1332.

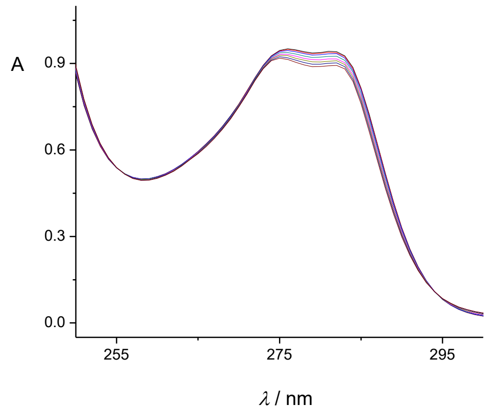


Figure S15. a) Spectrophotometric titration of **L1** ($c = 2.81 \times 10^{-4}$ mol dm^{-3}) with CsCl ($c = 5.00 \times 10^{-1}$ mol dm^{-3}) in water at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.0 ml. Spectra are corrected for dilution. The n(CsCl) / n(**L1**) molar ratio at the end of titration is 1330.

L2

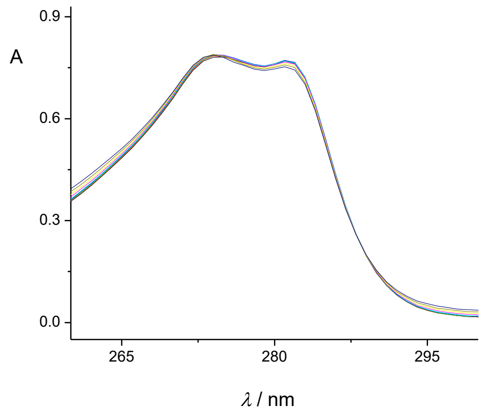


Figure S16. a) Spectrophotometric titration of **L2** ($c = 3.04 \times 10^{-4}$ mol dm^{-3}) with $LiClO_4$ ($c = 1.00$ mol dm^{-3}) in methanol at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.0 ml. Spectra are corrected for dilution. The $n(LiClO_4)$ / n(**L2**) molar ratio at the end of titration is 2467.

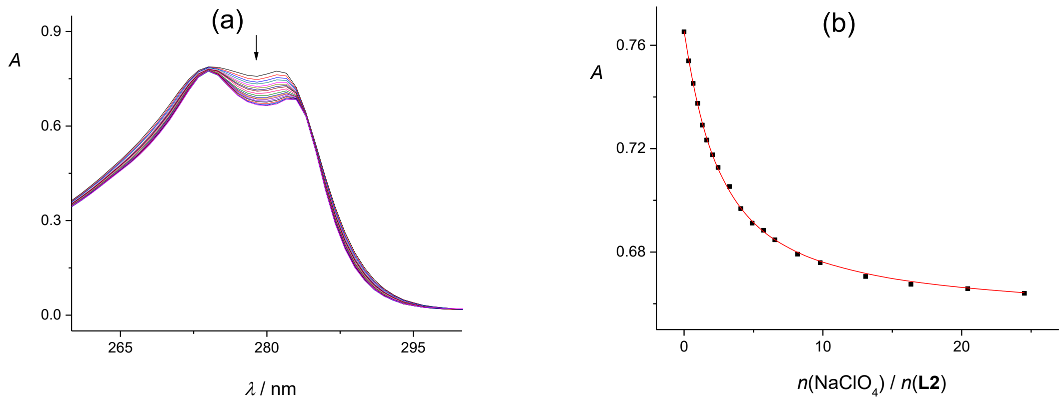


Figure S17. a) Spectrophotometric titration of **L2** ($c = 3.04 \times 10^{-4}$ mol dm^{-3}) with $NaClO_4$ ($c = 9.94 \times 10^{-3}$ mol dm^{-3}) in methanol at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.0 ml. Spectra are corrected for dilution. b) Dependence of absorbance at 280 nm on $n(NaClO_4)$ / n(**L2**) molar ratio. ■ experimental, — calculated.

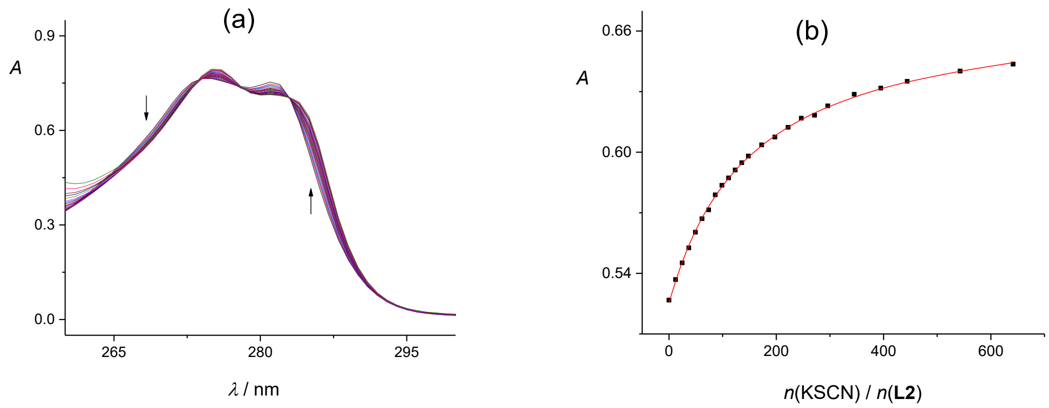


Figure S18. a) Spectrophotometric titration of **L2** ($c = 3.04 \times 10^{-4}$ mol dm^{-3}) with KSCN ($c = 3.00 \times 10^{-1}$ mol dm^{-3}) in methanol at (25.0 ± 0.1) °C; $l = 1$ cm, $V_0 = 2.0$ ml. Spectra are corrected for dilution and the absorption of KSCN. b) Dependence of absorbance at 285 nm on n(KSCN) / n(**L2**) molar ratio. ■ experimental, — calculated.

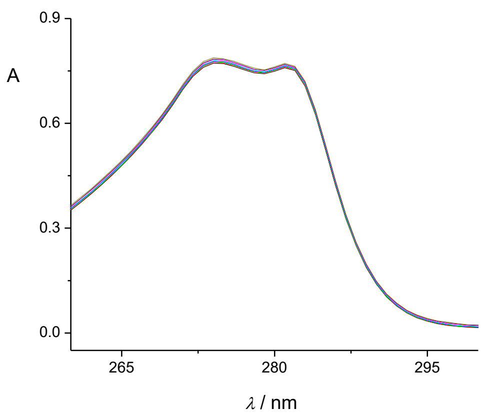


Figure S19. a) Spectrophotometric titration of **L2** ($c = 3.03 \times 10^{-4}$ mol dm^{-3}) with RbCl ($c = 3.05 \times 10^{-2}$ mol dm^{-3}) in methanol at (25.0 ± 0.1) °C; $l = 1$ cm, $V_0 = 2.0$ ml. Spectra are corrected for dilution. The n(RbCl) / n(**L2**) molar ratio at the end of titration is 75.

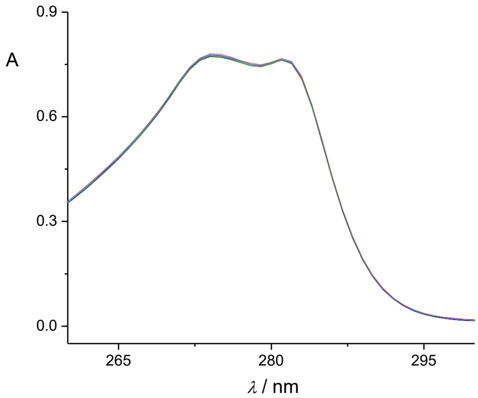


Figure S20. a) Spectrophotometric titration of **L2** ($c = 3.03 \times 10^{-4}$ mol dm^{-3}) with CsCl ($c = 7.78 \times 10^{-2}$ mol dm^{-3}) in methanol at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.0 ml. Spectra are corrected for dilution. The n(CsCl) / n(**L2**) molar ratio at the end of titration is 160.

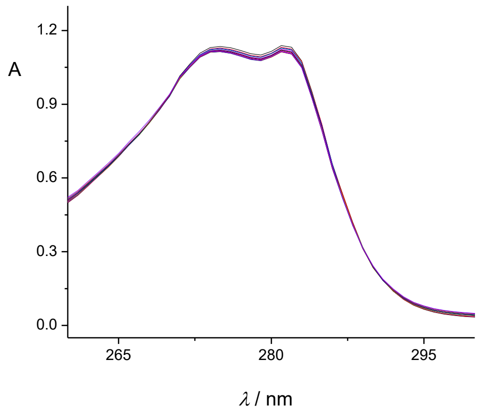


Figure S21. a) Spectrophotometric titration of **L2** ($c = 3.96 \times 10^{-4}$ mol dm^{-3}) with $LiClO_4$ (c = 1.00 mol dm^{-3}) in water at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.2 ml. Spectra are corrected for dilution. The $n(LiClO_4)$ / n(**L2**) molar ratio at the end of titration is 1152.

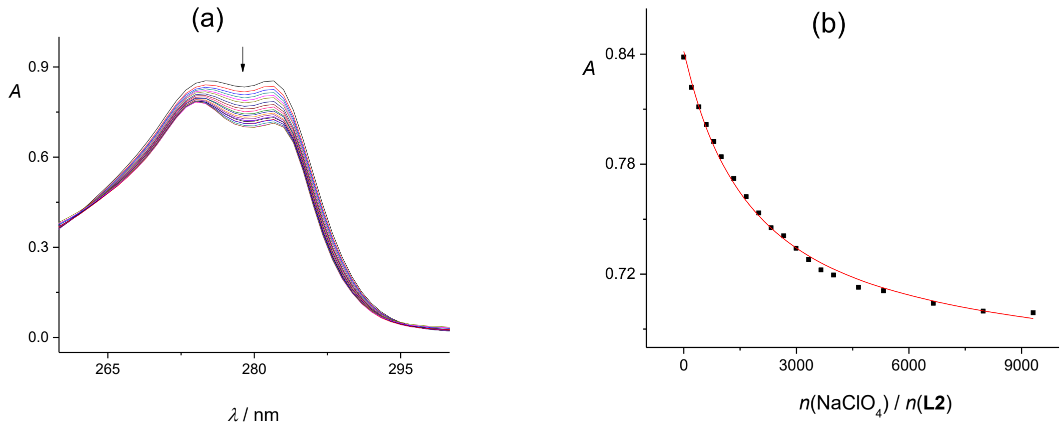


Figure S22. a) Spectrophotometric titration of **L2** (c = 3.03 × 10^{-4} mol dm^{-3}) with $NaClO_4$ (c = 4.03 mol dm^{-3}) in water at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.0 ml. Spectra are corrected for dilution. b) Dependence of absorbance at 280 nm on $n(NaClO_4)$ / n(**L2**) molar ratio. ■ experimental, — calculated.

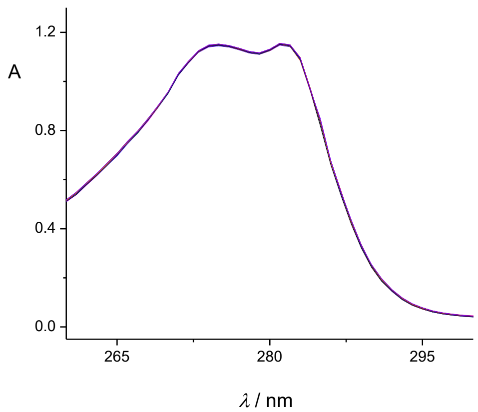


Figure S23. a) Spectrophotometric titration of **L2** (c = 3.96 × 10^{-4} mol dm^{-3}) with KCl (c = 1.00 mol dm^{-3}) in water at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.2 ml. Spectra are corrected for dilution. The n(KCl) / n(**L2**) molar ratio at the end of titration is 1148.

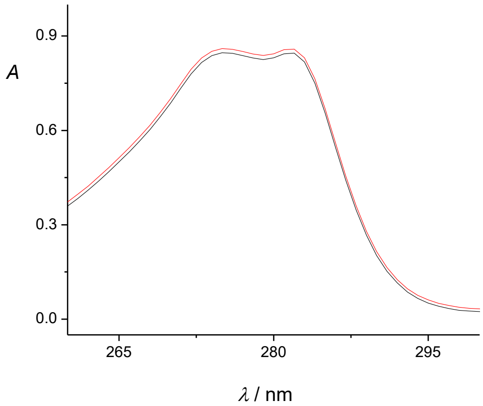


Figure S24. a) Spectrophotometric titration of **L2** (c = 2.99 × 10^{-4} mol dm^{-3}) with RbCl (c = 1.67 × 10^{-1} mol dm^{-3}) in water at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.0 ml. Spectra are corrected for dilution. The n(RbCl) / n(**L2**) molar ratio upon addition of titrant is 418.

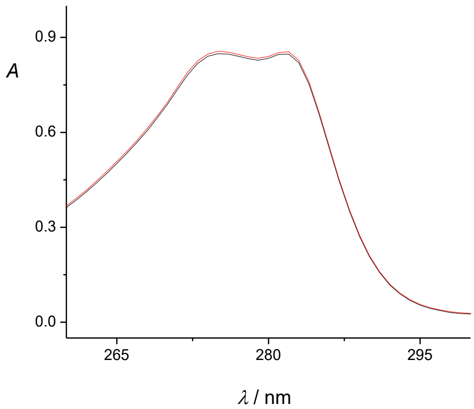


Figure S25. a) Spectrophotometric titration of **L2** (c = 2.99 × 10^{-4} mol dm^{-3}) with CsCl (c = 1.67 × 10^{-1} mol dm^{-3}) in water at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.0 ml. Spectra are corrected for dilution. The n(CsCl) / n(**L2**) molar ratio upon addition of titrant is 418.

L3

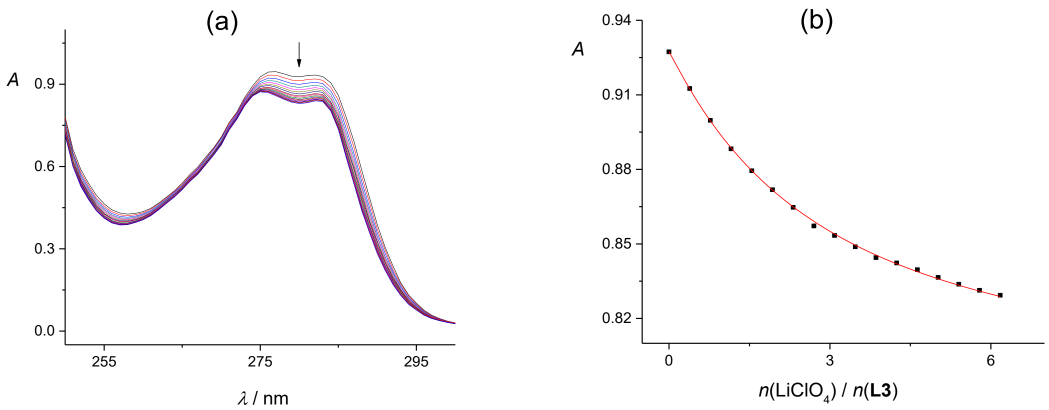


Figure S26. a) Spectrophotometric titration of **L3** (c = 2.48 × 10^{-4} mol dm^{-3}) with $LiClO_4$ (c = 3.01 × 10^{-3} mol dm^{-3}) in methanol at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.2 ml. Spectra are corrected for dilution. b) Dependence of absorbance at 280 nm on $n(LiClO_4)$ / n(**L3**) molar ratio. ■ experimental, — calculated.

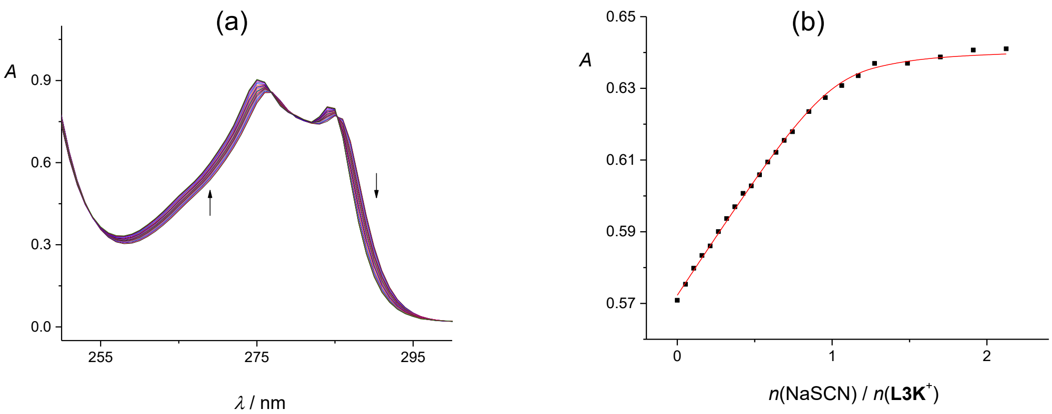


Figure S27. a) Spectrophotometric titration of K**L3**$^+$ (c = 2.40 × 10^{-4} mol dm^{-3}) with NaSCN (c = 1.02 × 10^{-3} mol dm^{-3}) in methanol at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.0 ml. Spectra are corrected for dilution. b) Dependence of absorbance at 270 nm on n(NaSCN) / n(K**L3**$^+$) molar ratio. ■ experimental, — calculated.

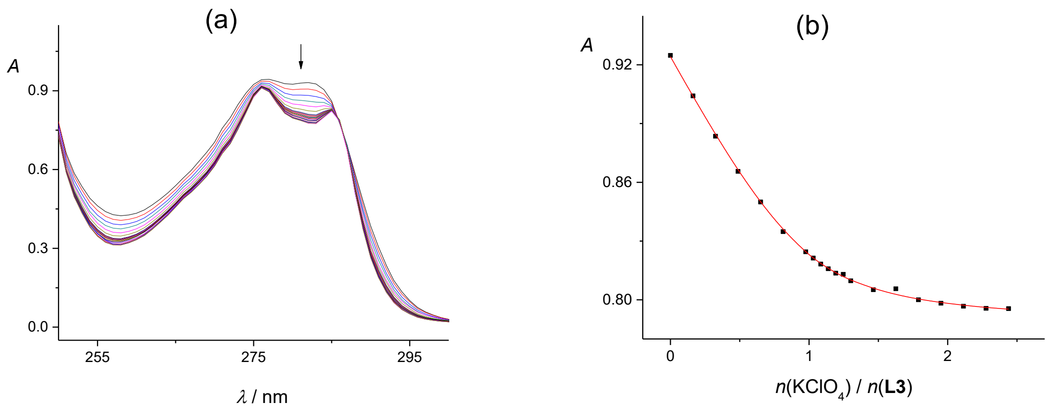


Figure S28. a) Spectrophotometric titration of **L3** (c = 2.48 × 10^{-4} mol dm^{-3}) with $KClO_4$ (c = 2.96 × 10^{-3} mol dm^{-3}) in methanol at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.2 ml. Spectra are corrected for dilution. b) Dependence of absorbance at 280 nm on $n(KClO_4)$ / n(**L3**) molar ratio. ■ experimental, — calculated.

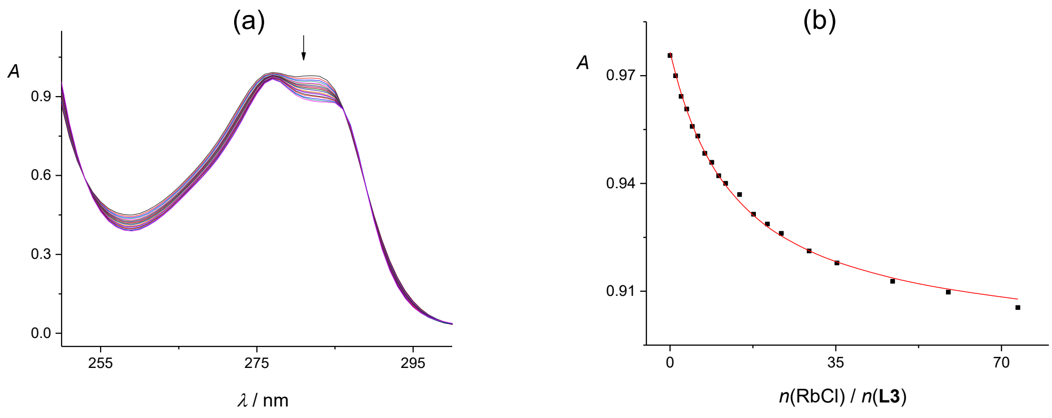


Figure S29. a) Spectrophotometric titration of **L3** (c = 2.60 × 10^{-4} mol dm^{-3}) with RbCl (c = 3.05 × 10^{-2} mol dm^{-3}) in methanol at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.0 ml. Spectra are corrected for dilution. b) Dependence of absorbance at 280 nm on n(RbCl) / n(**L3**) molar ratio. ■ experimental, — calculated.

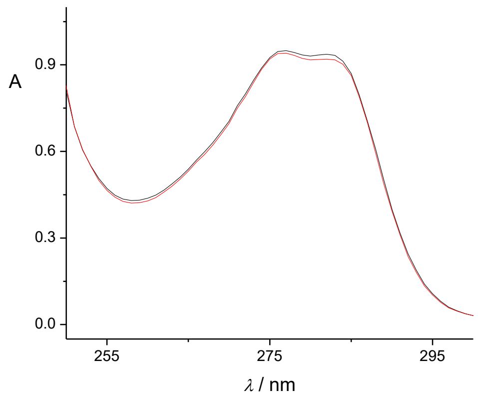


Figure S30. a) Spectrophotometric titration of **L3** ($c = 2.48 \times 10^{-4}$ mol dm^{-3}) with CsCl ($c = 7.10 \times 10^{-2}$ mol dm^{-3}) in methanol at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.4 ml. Spectrum is corrected for dilution. The n(CsCl) / n(**L3**) molar ratio upon addition of titrant is 119.

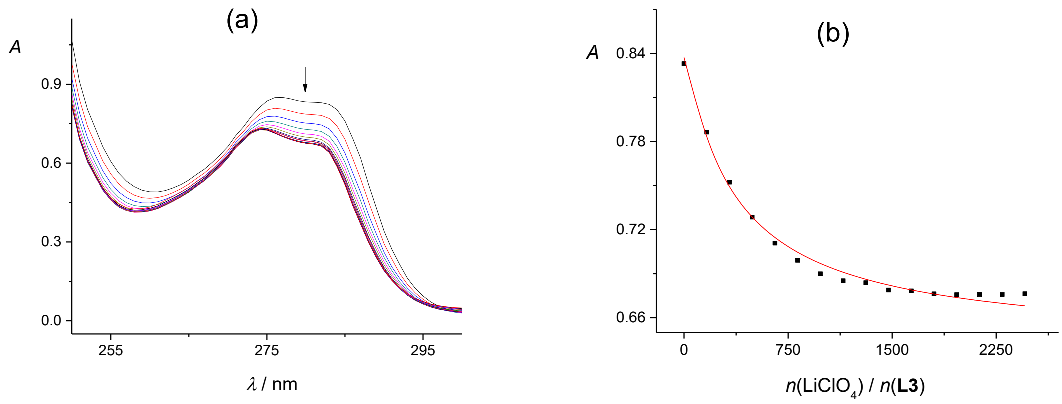


Figure S31. a) Spectrophotometric titration of **L3** ($c = 2.66 \times 10^{-4}$ mol dm^{-3}) with $LiClO_4$ (c = 1.60 mol dm^{-3}) in water at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.2 ml. Spectra are corrected for dilution. b) Dependence of absorbance at 280 nm on $n(LiClO_4)$ / n(**L3**) molar ratio. ■ experimental, — calculated.

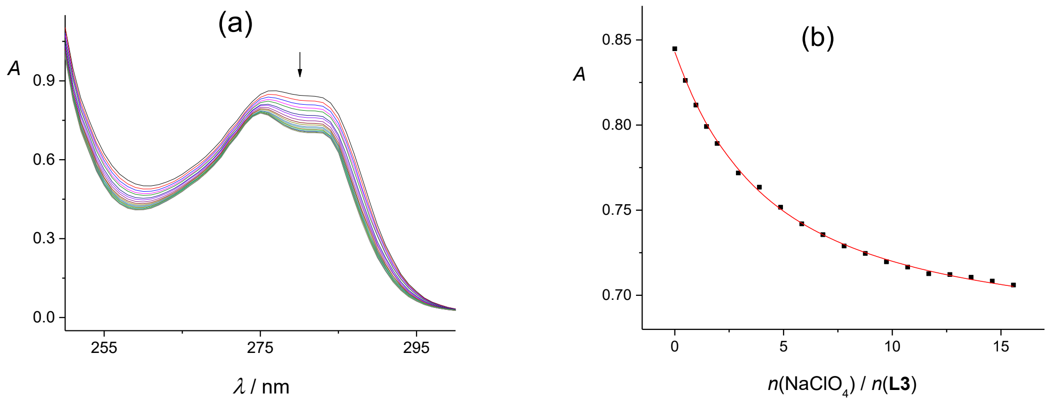


Figure S32. a) Spectrophotometric titration of **L3** (c = 2.80 × 10^{-4} mol dm^{-3}) with $NaClO_4$ (c = 3.00 × 10^{-2} mol dm^{-3}) in water at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.2 ml. Spectra are corrected for dilution. b) Dependence of absorbance at 280 nm on $n(NaClO_4)$ / n(**L3**) molar ratio. ■ experimental, — calculated.

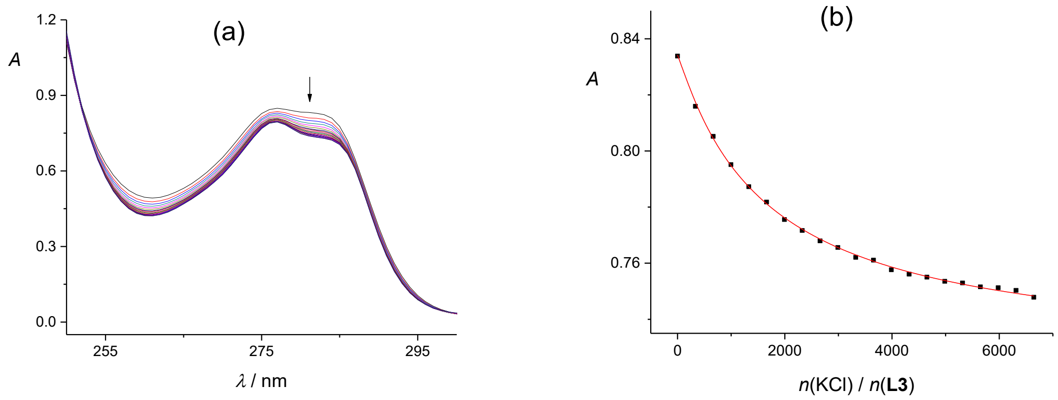


Figure S33. a) Spectrophotometric titration of **L3** (c = 2.71 × 10^{-4} mol dm^{-3}) with KCl (c = 3.00 mol dm^{-3}) in water at (25.0 ± 0.1) °C; l = 1 cm, V_0 = 2.0 ml. Spectra are corrected for dilution. b) Dependence of absorbance at 280 nm on n(KCl) / n(**L3**) molar ratio. ■ experimental, — calculated.

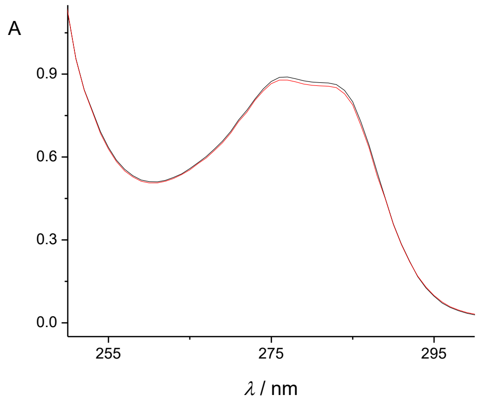


Figure S34. a) Spectrophotometric titration of **L3** ($c = 2.80 \times 10^{-4}$ mol dm^{-3}) with RbCl ($c = 3.00$ mol dm^{-3}) in water at (25.0 ± 0.1) °C; $l = 1$ cm, $V_0 = 2.2$ ml. Spectrum is corrected for dilution. The n(RbCl) / n(**L3**) molar ratio upon addition of titrant is 5357.

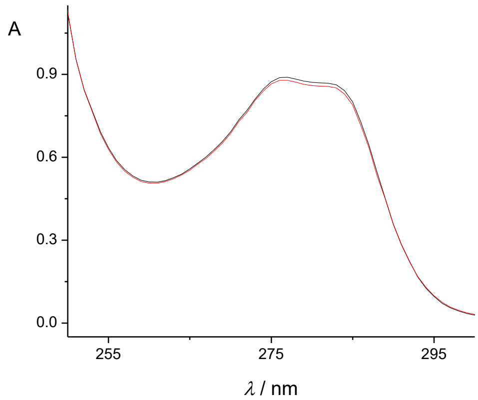


Figure S35. a) Spectrophotometric titration of **L3** ($c = 2.80 \times 10^{-4}$ mol dm^{-3}) with CsCl ($c = 2.64 \times 10^{-1}$ mol dm^{-}) in water at (25.0 ± 0.1) °C; $l = 1$ cm, $V_0 = 2.5$ ml. Spectrum is corrected for dilution. The n(CsCl) / n(**L3**) molar ratio upon addition of titrant is 943.

3. Microcalorimetric Titration Data

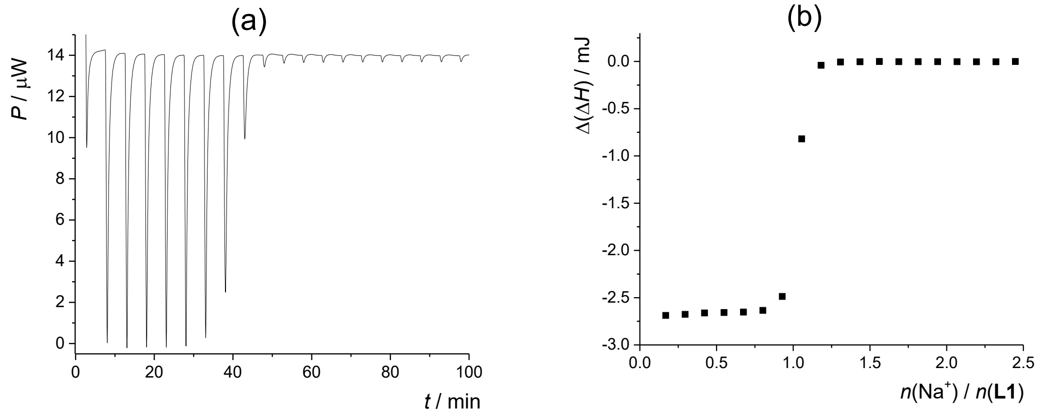


Figure S36. Microcalorimetric titration of **L1** ($c = 2.51 \times 10^{-4}$ mol dm^{-3}) with $NaClO_4$ ($c = 3.00 \times 10^{-3}$ mol dm^{-3}) in methanol at 25. 0 °C; V = 1.4182 ml. b) Dependence of successive enthalpy changes on $n(NaClO_4)$ / n(**L1**) molar ratio. The values have been corrected for titrant dilution enthalpy.

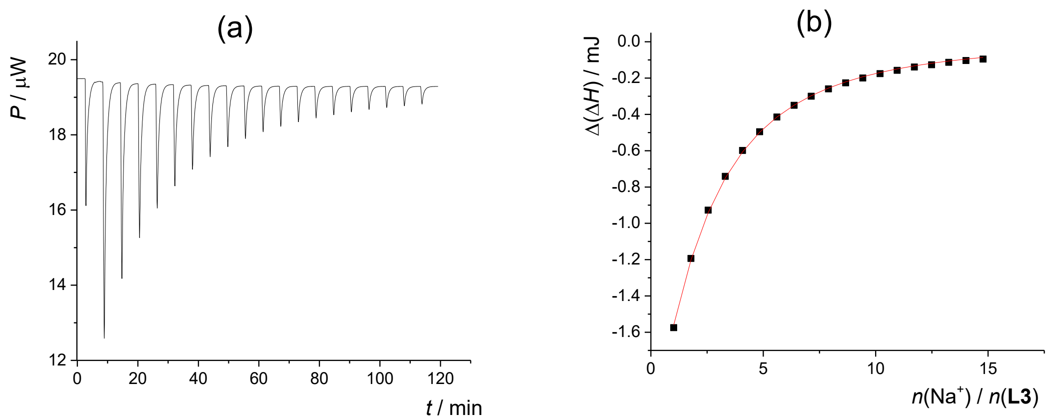


Figure S37. Microcalorimetric titration of **L3** ($c = 2.85 \times 10^{-4}$ mol dm^{-3}) with $NaClO_4$ ($c = 2.06 \times 10^{-2}$ mol dm^{-3}) in water at 25. 0 °C; V = 1.4182 ml. b) Dependence of successive enthalpy changes on $n(NaClO_4)$ / n(**L3**) molar ratio. The values have been corrected for titrant dilution enthalpy. ■- experimental, – calculated.

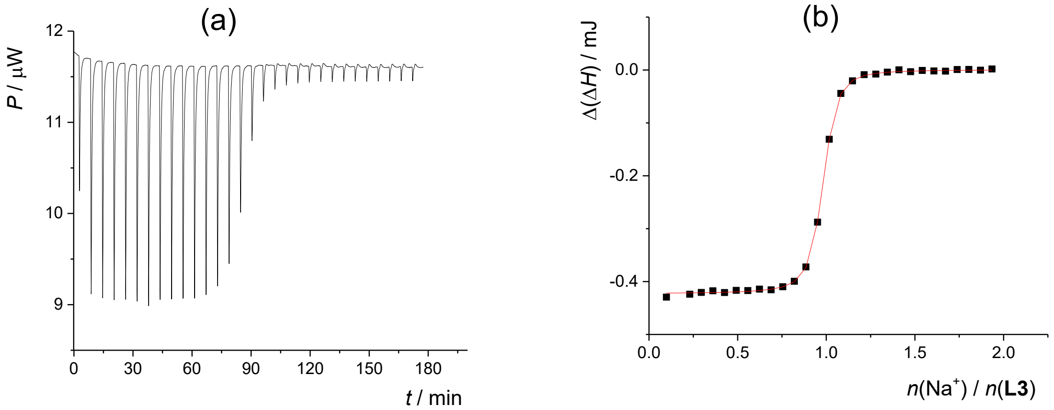


Figure S38. Microcalorimetric titration of **L3** ($c = 1.21 \times 10^{-4}$ mol dm^{-3}) with $NaClO_4$ ($c = 1.12 \times 10^{-3}$ mol dm^{-3}) in methanol at 25. 0 °C; $V = 1.4182$ ml. b) Dependence of successive enthalpy changes on $n(NaClO_4)$ / n(**L3**) molar ratio. The values have been corrected for titrant dilution enthalpy. ■- experimental, – calculated.

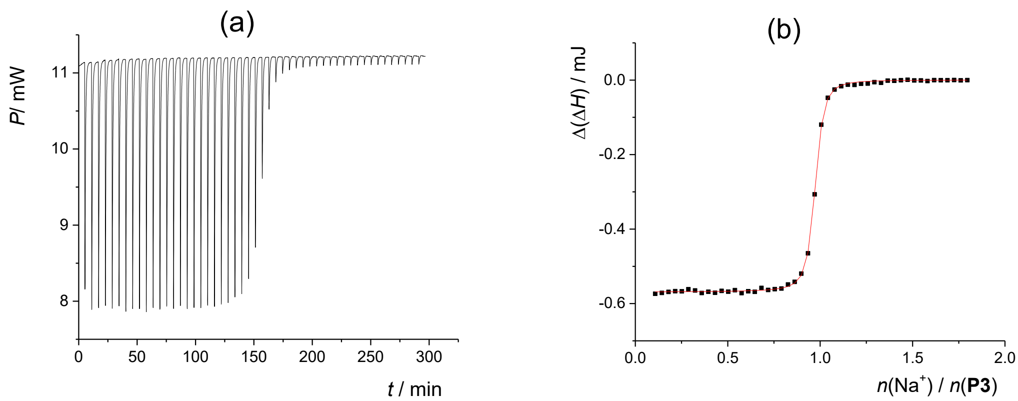


Figure S39. Microcalorimetric titration of **P3** ($c = 1.83 \times 10^{-4}$ mol dm^{-3}) with $NaClO_4$ ($c = 1.87 \times 10^{-3}$ mol dm^{-3}) in methanol at 25. 0 °C; $V = 1.4182$ ml. b) Dependence of successive enthalpy changes on $n(NaClO_4)$ / n(**P3**) molar ratio. The values have been corrected for titrant dilution enthalpy. ■ experimental, – calculated.

Table S1. Thermodynamic parameters for complexation of sodium cation with **L1** in water at 25 °C obtained microcalorimetrically by using different sodium salts.[a]

Salt used	log *K*	$\Delta_r G°$/ kJ mol^{-1}	$\Delta_r H°$/ kJ mol^{-1}	$\Delta_r S°$/ J K^{-1} mol^{-1}
$NaClO_4$	4.95(2)	–28.23(9)	–58.6(8)	–102(3)
NaCl	4.891(2)	–27.92(1)	–59.62(2)	–106(1)
NaBr	4.916(5)	–28.06(3)	–57.2(2)	–97.5(4)
NaI	4.872(9)	–27.81(5)	–56.2(2)	–95.3(9)
NaSCN	4.897(4)	–27.95(2)	–55.8(2)	–93.3(8)

[a] uncertainties of the last digit are given in parentheses as standard errors of the mean (N = 3)