Supporting Information

Triptycene Walled Glycoluril Trimer: Synthesis and Recognition Properties

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General experimental

Starting materials were purchased from commercial suppliers and used without further purification or were prepared by literature procedures. Melting points were measured on a Meltemp apparatus in open capillary tubes and are uncorrected. IR spectra were recorded on a JASCO FT/IR 4100 spectrometer and are reported in cm^{-1}. NMR spectra were measured on Bruker spectrometers operating at 400 or 600 MHz for ^{1}H and 100 or 125 MHz for ^{13}C using D_2O, or DMSO-d_6 as solvents. Chemical shifts (δ) are referenced relative to the residual resonances for HOD (4.80 ppm) and DMSO-d_6 (2.50 ppm for ^{1}H, 39.51 ppm for ^{13}C). Mass spectrometry was performed using a JEOL AccuTOF electrospray instrument (ESI). ITC data was collected on a Malvern Microcal PEAQ-ITC instrument and analyzed using the software provided by the vendor.

^{1}H and ^{13}C NMR spectra of host 1

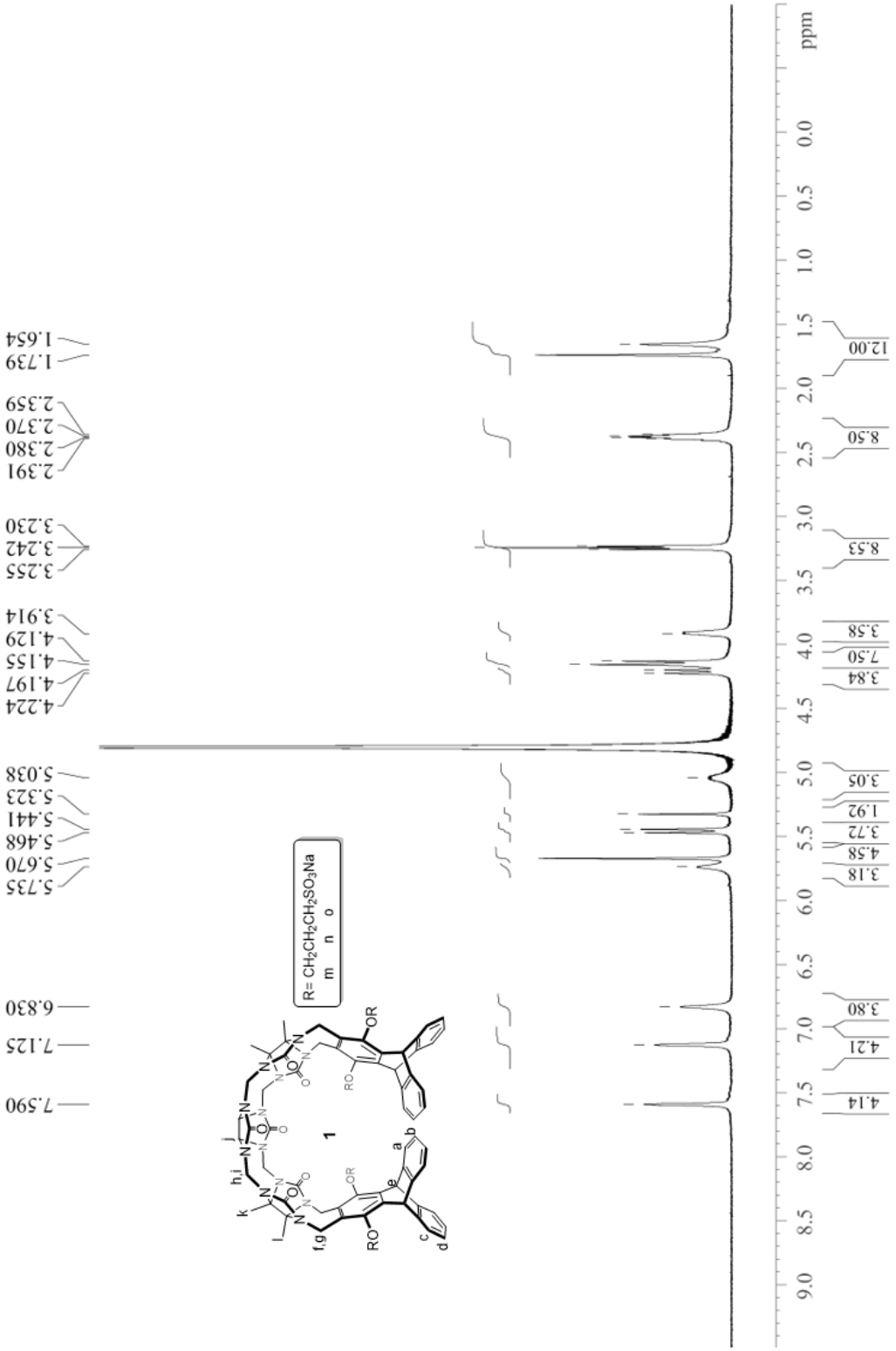

Figure S1. ^{1}H NMR spectrum (D_2O, 20 mM sodium phosphate, pD 7.4, 600 MHz, RT) recorded for **1.**

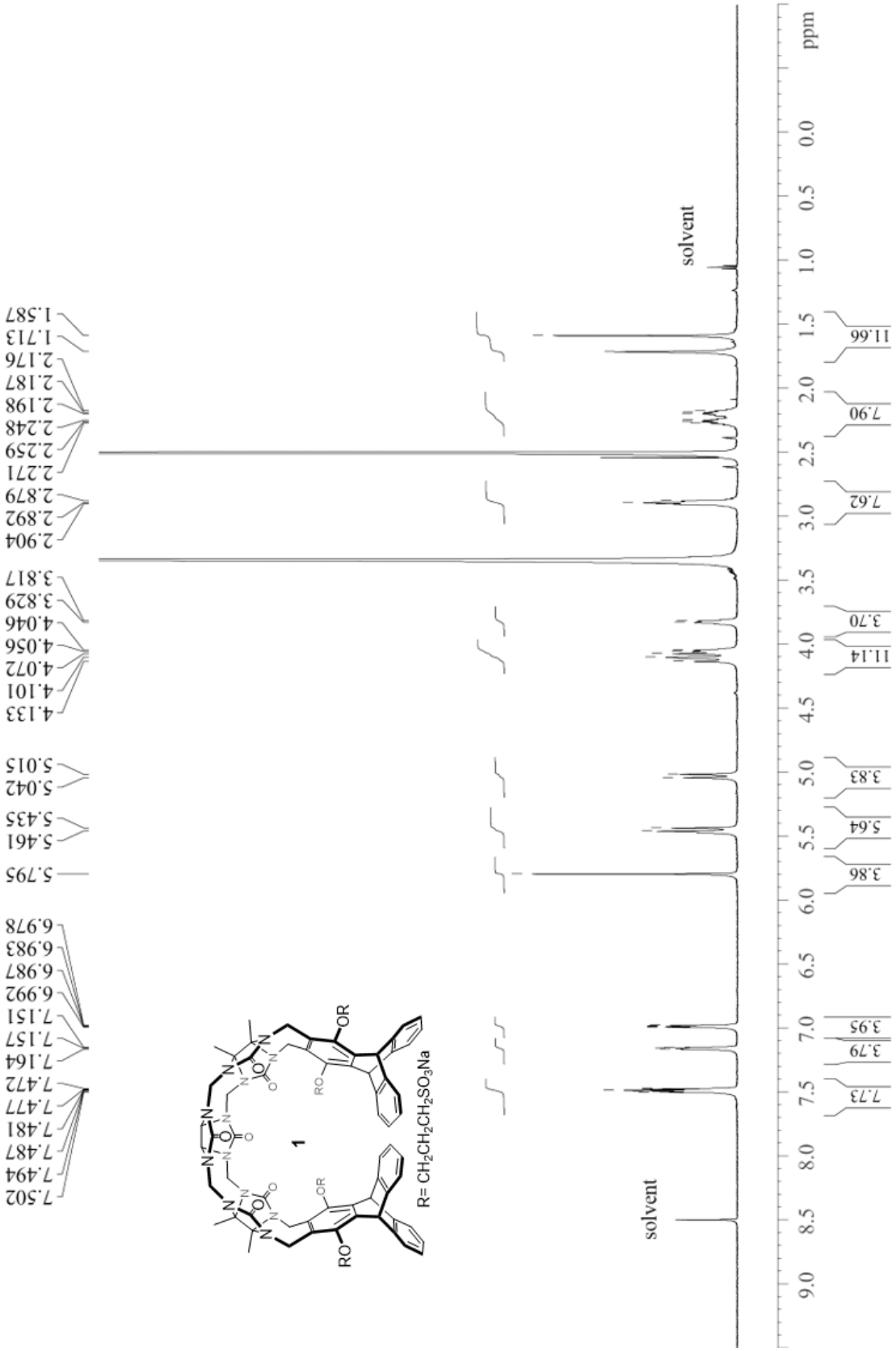

Figure S2. ^{1}H NMR spectrum (DMSO-d_6, 600 MHz, RT) recorded for **1**.

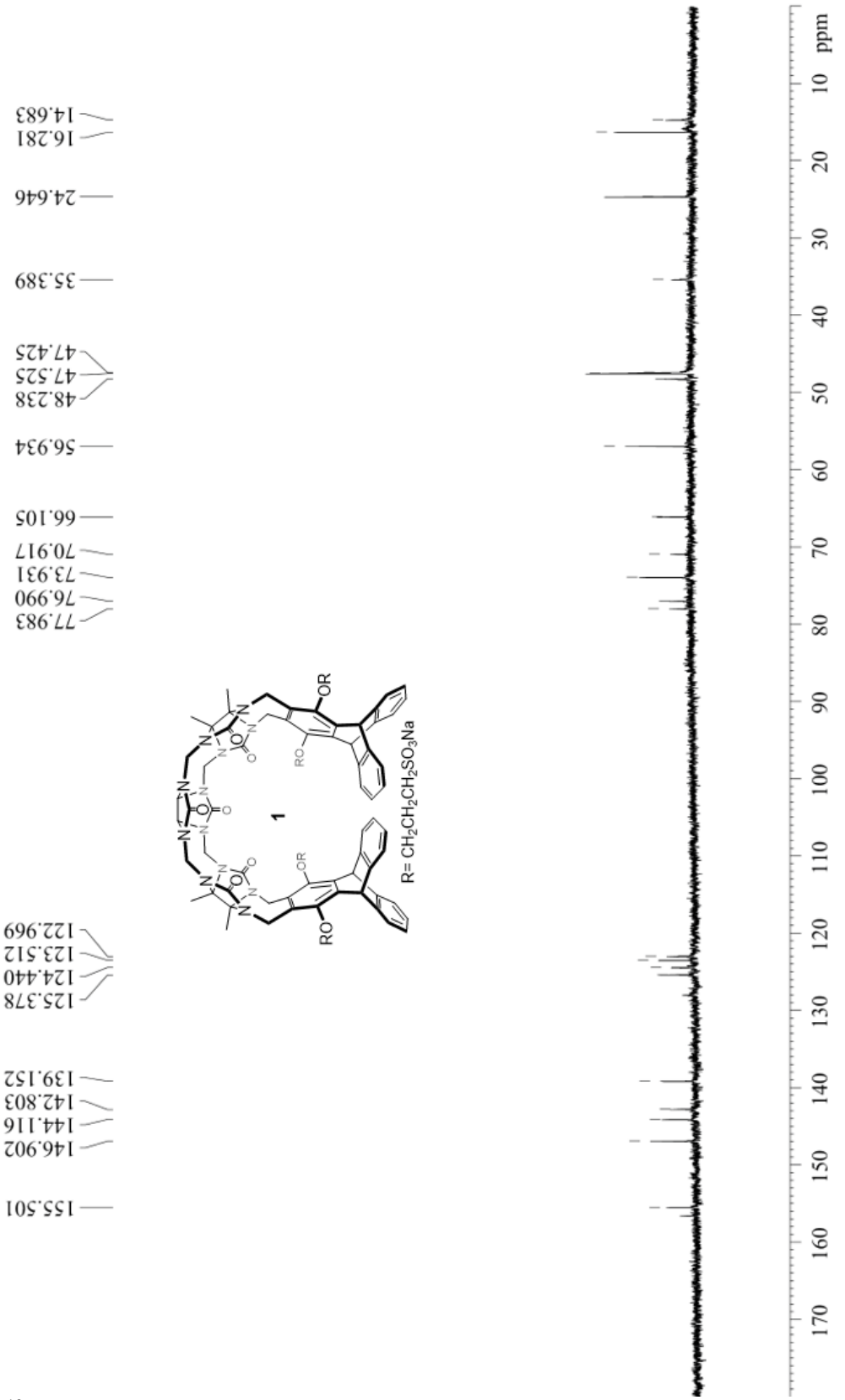

Figure S3. ^{13}C NMR spectrum (D_2O, 600 MHz, RT, 1,4-dioxane as internal reference) recorded for **1**.

^{1}H NMR Dilution Experiments Performed for host 1

Self-association Binding Model implemented in Scientist™
// Micromath Scientist Model File
// self-association model for NMR
IndVars: concTot
DepVars: Deltaobs
Params: K_a, Deltasat, Deltazero
K_a = concBound/(concFree*concFree)
concTot=concFree + concBound/2
Deltaobs = Deltazero + (Deltasat - Deltazero) * (1/2*concBound/concTot)
//Constraints
0 < K_a
0 < concFree < concTot
0 < concBound < concTot
***

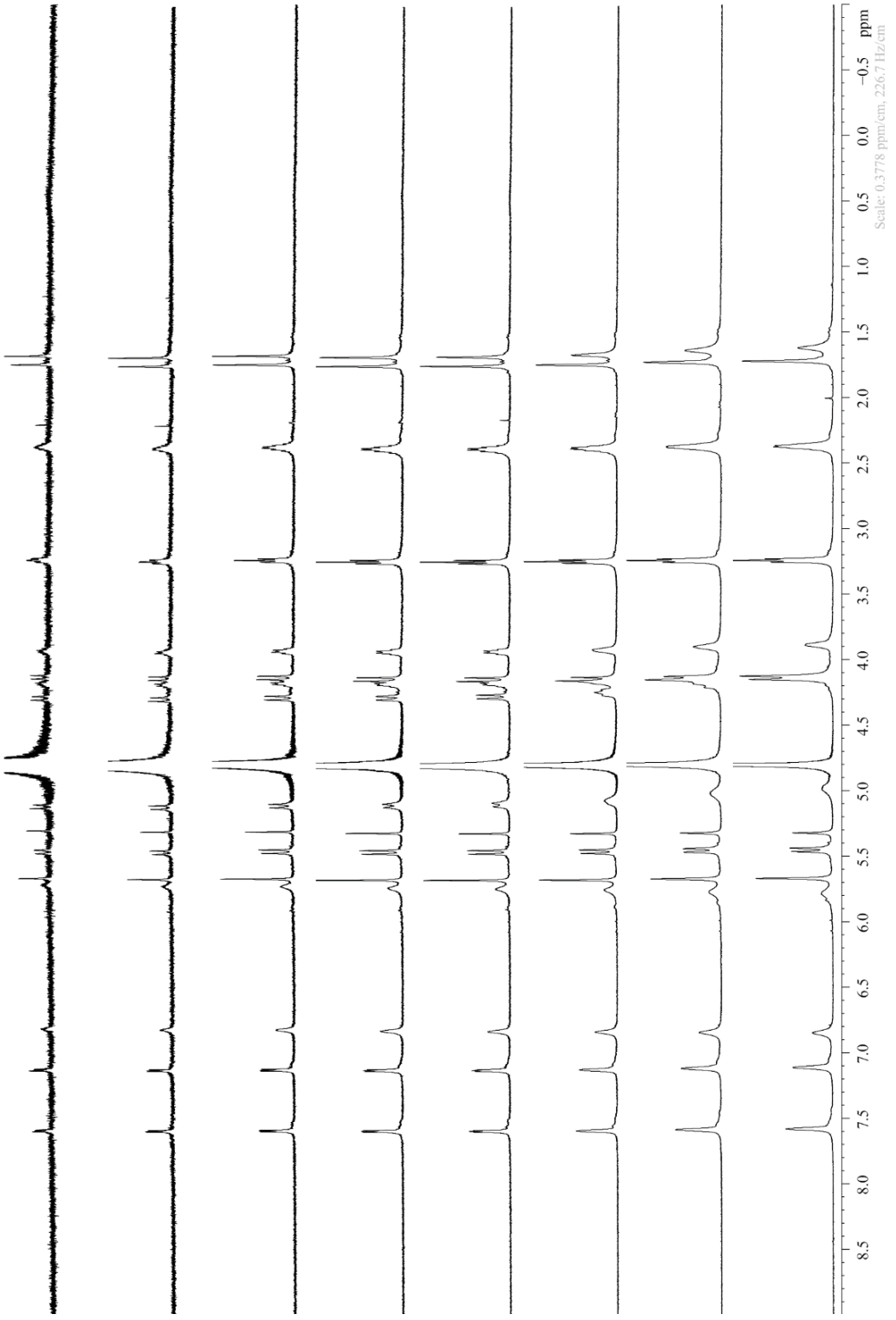

Figure S4. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for the dilution of host **1** (3 - 0.05 mM). Host **1** weakly self-associates in water (K_s = 480 ± 81 M^{-1}).

^{1}H NMR spectra of guests (4-26) with host 1

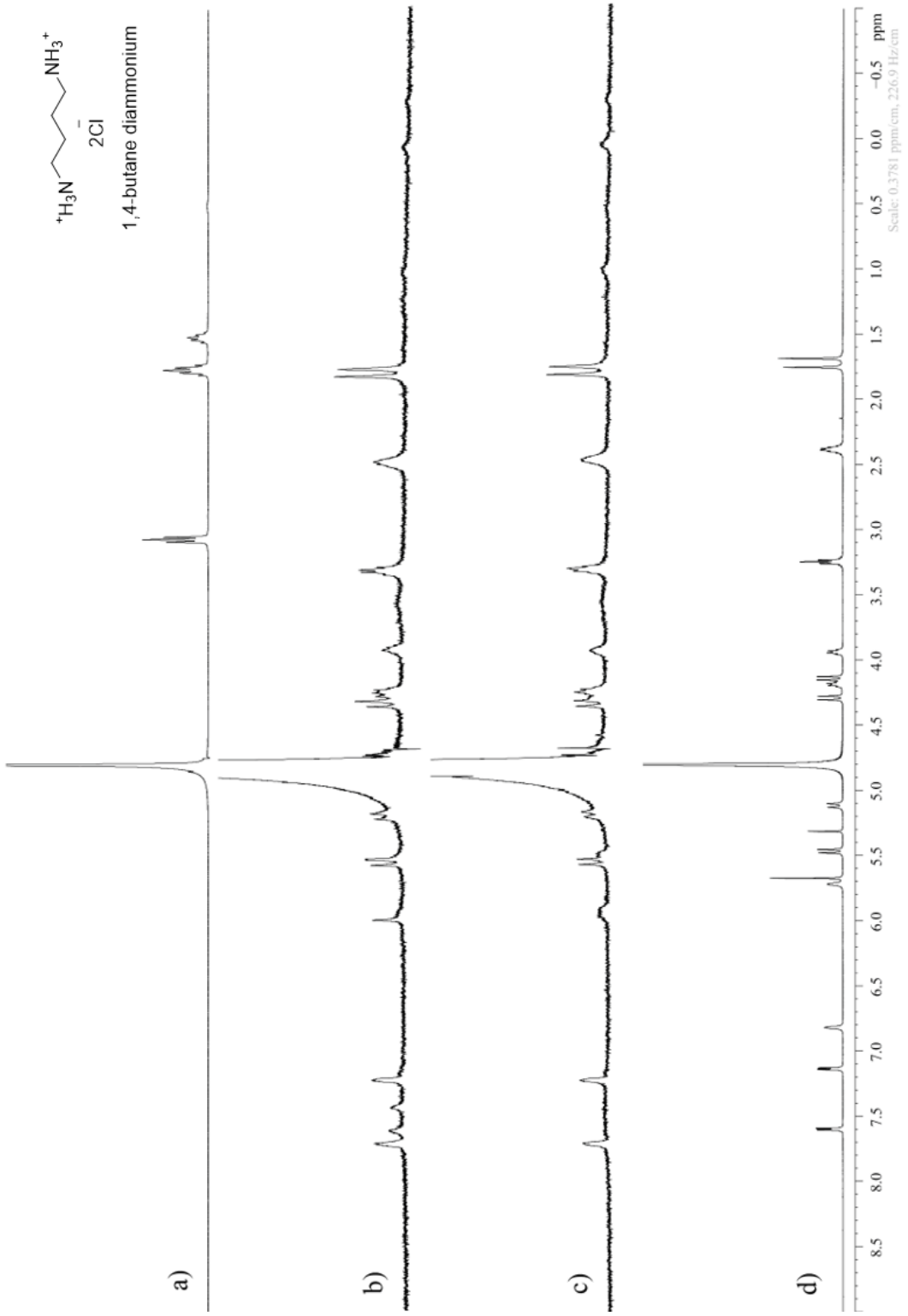

Figure S5. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 400 MHz, RT) for: a) **4** (5 mM), b) a mixture of **1** (125 μM) and **4** (250 μM), c) a mixture of **1** (125 μM) and **4** (125 μM), d) **1** (250 μM).

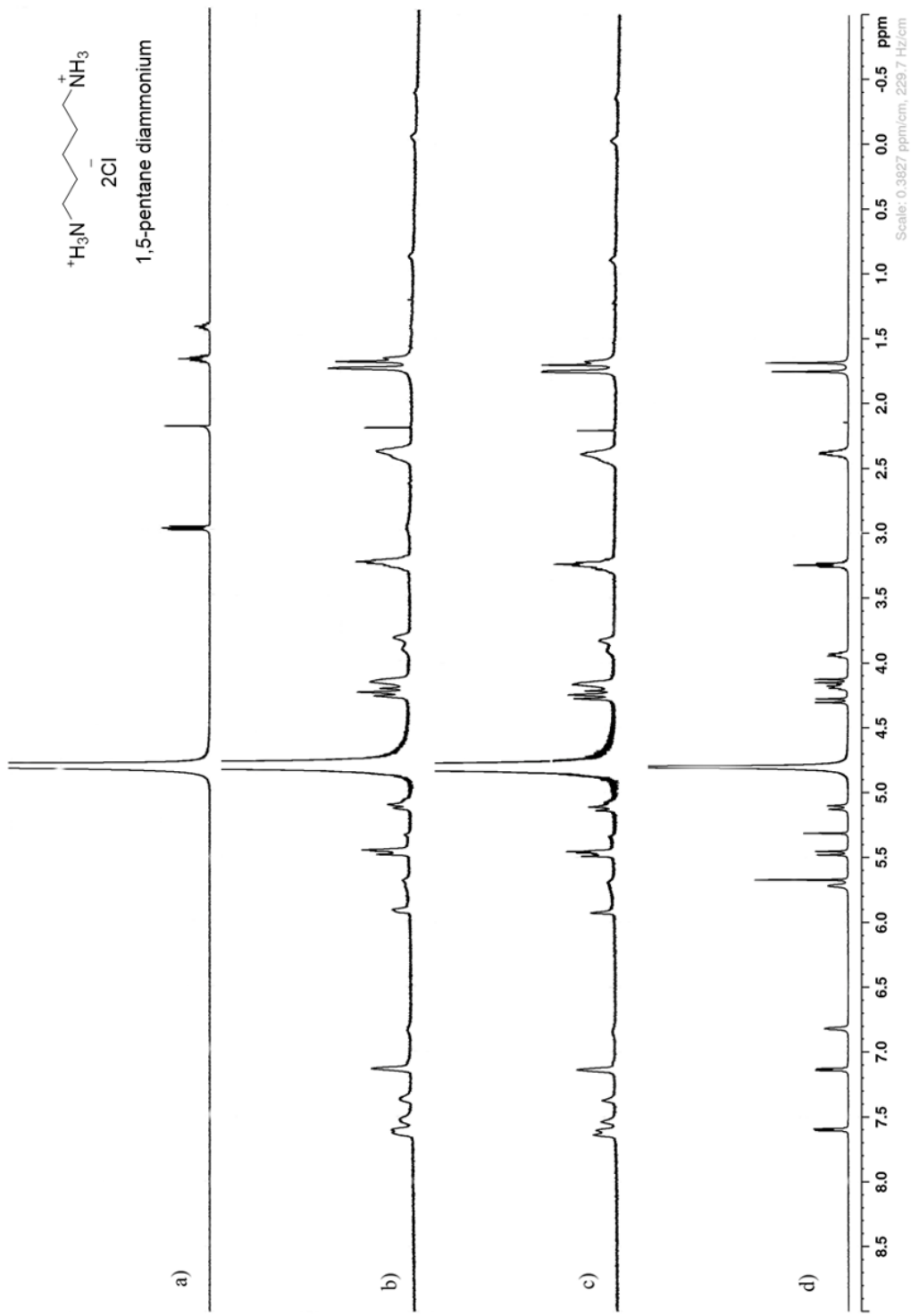

Figure S6. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **5** (5 mM), b) a mixture of **1** (250 μM) and **5** (500 μM), c) a mixture of **1** (250 μM) and **5** (250 μM), d) **1** (250 μM).

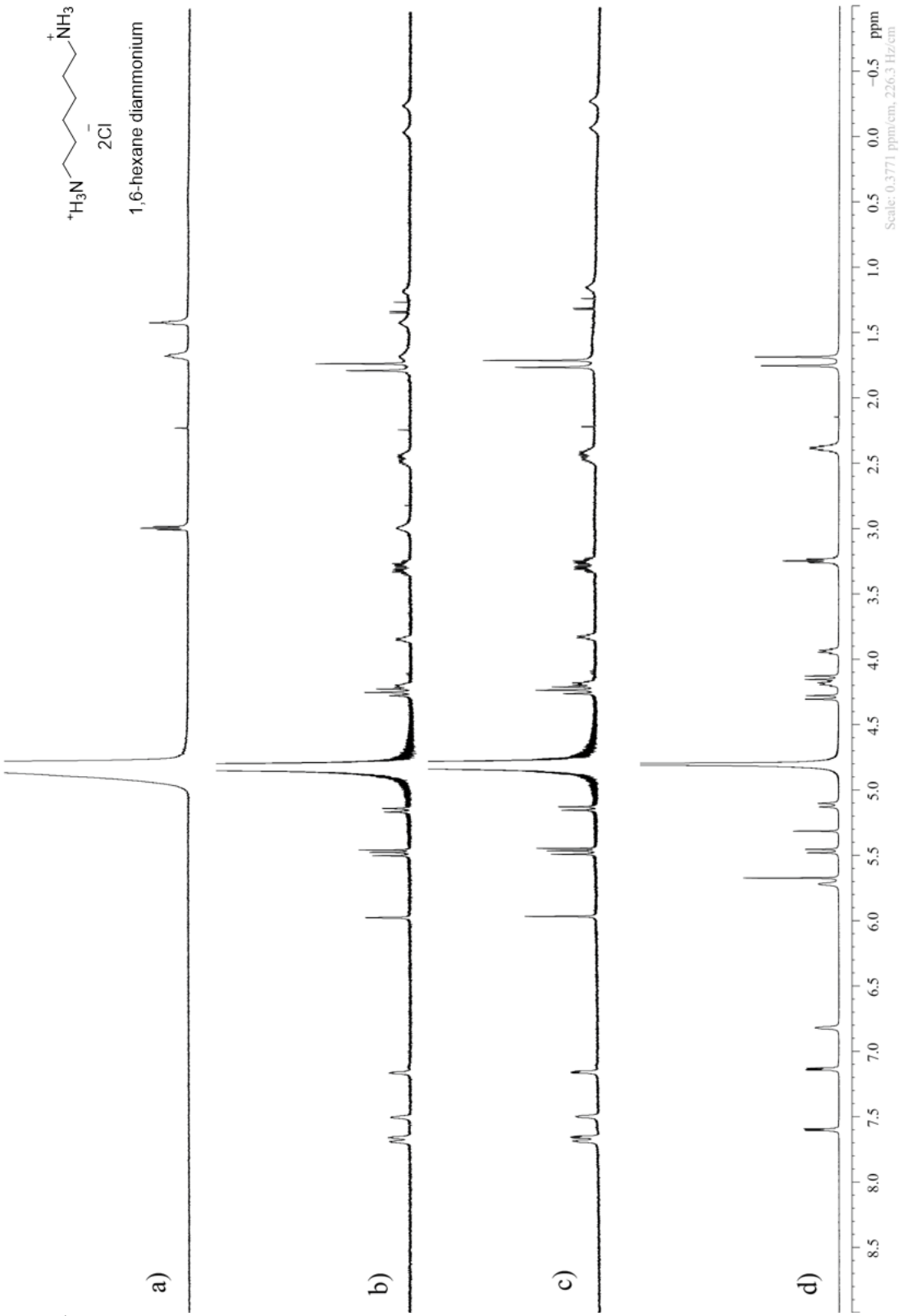

Figure S7. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **6** (5 mM), b) a mixture of **1** (250 μM) and **6** (500 μM), c) a mixture of **1** (250 μM) and **6** (250 μM), d) **1** (250 μM).

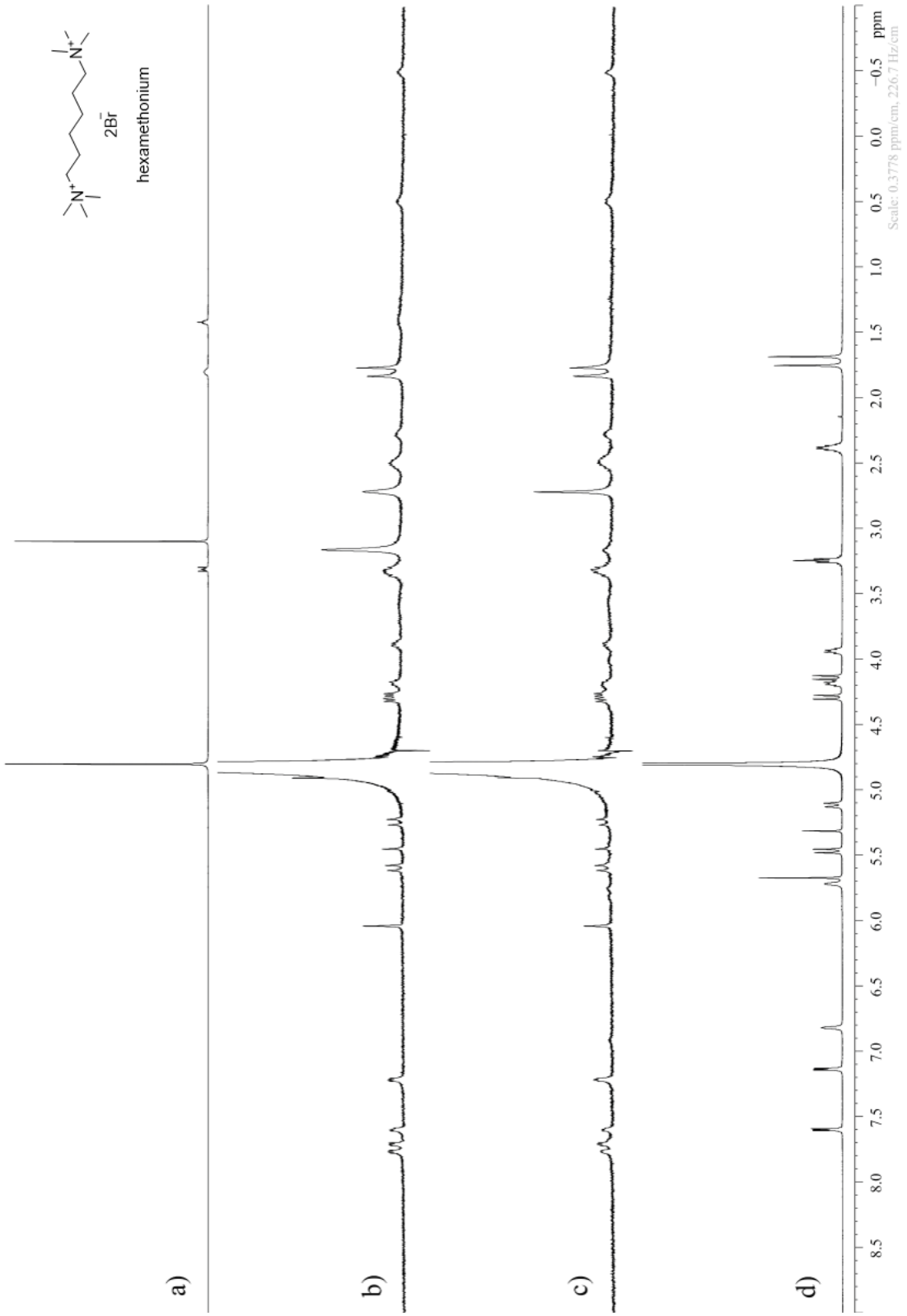

Figure S8. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **6DQ•2Br**$^{-}$ (6 mM), b) a mixture of **1** (250 μM) and **6DQ•2Br**$^{-}$ (500 μM), c) a mixture of **1** (250 μM) and **6DQ•2Br**$^{-}$ (250 μM), d) **1** (250 μM).

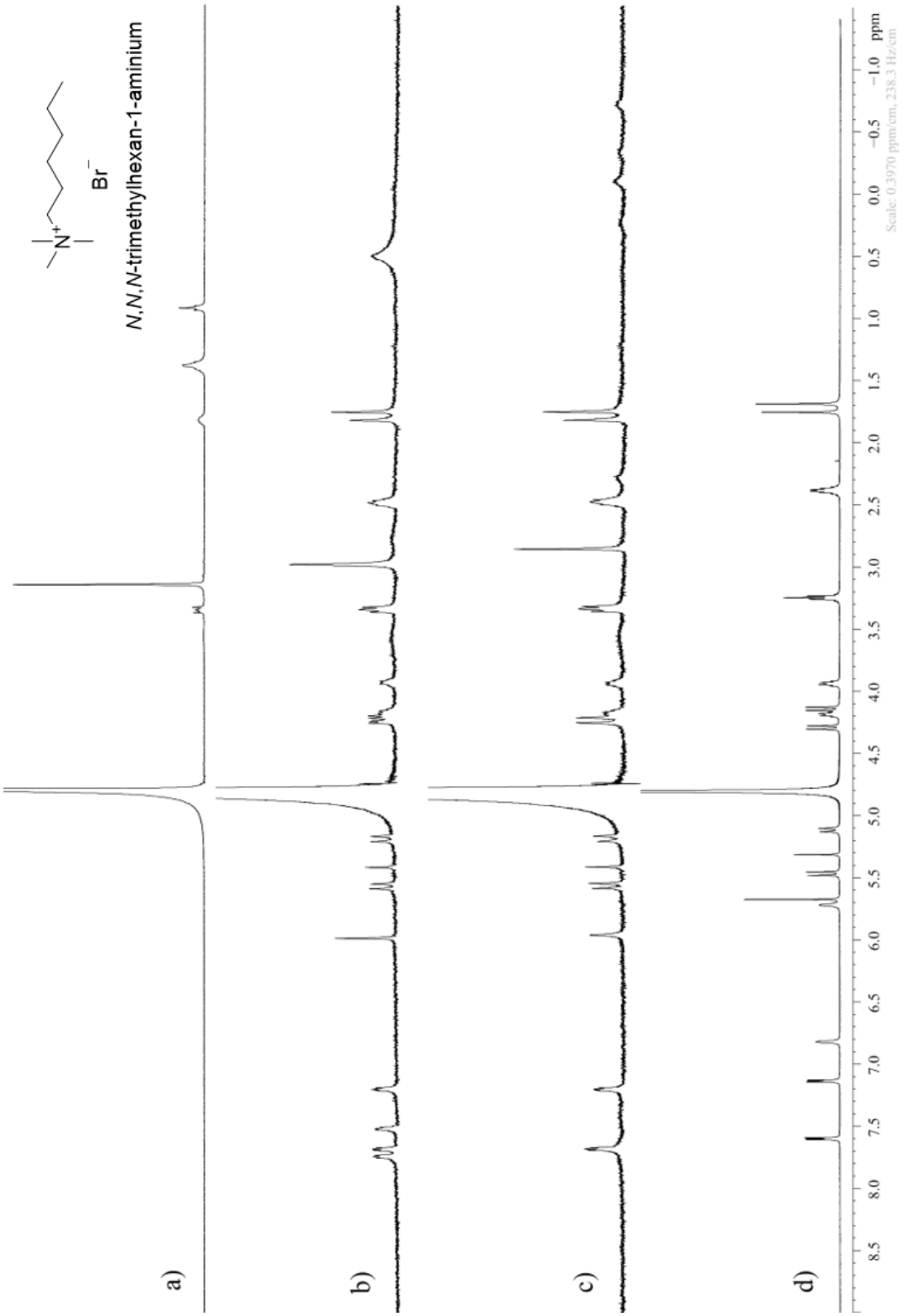

Figure S9. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 400 MHz, RT) for: a) **6Q•Br**$^{-}$ (4 mM), b) a mixture of **1** (125 μM) and **6Q•Br**$^{-}$ (250 μM), c) a mixture of **1** (125 μM) and **6Q•Br**$^{-}$ (125 μM), d) **1** (250 μM).

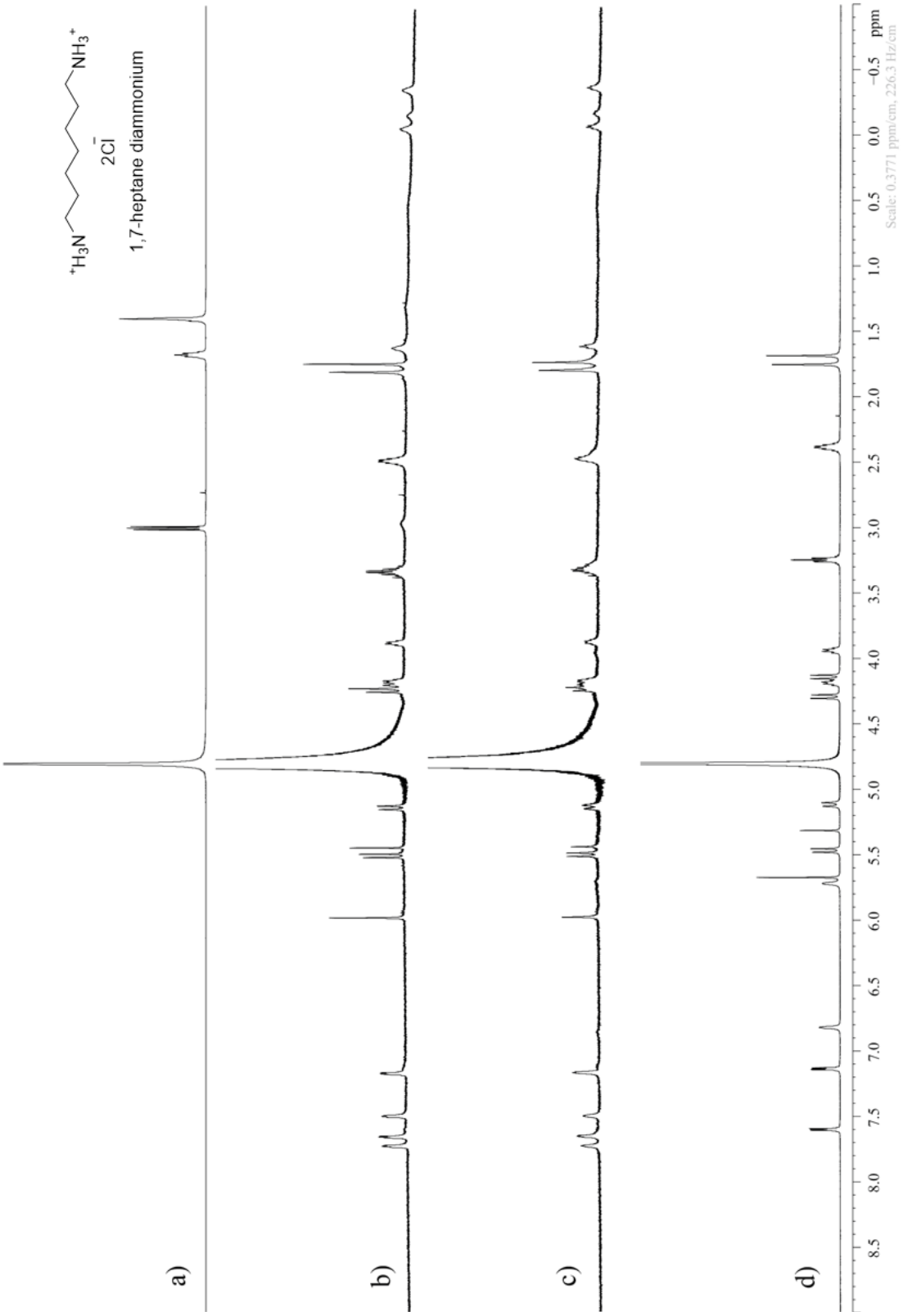

Figure S10. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **7** (2 mM), b) a mixture of **1** (125 μM) and **7** (250 μM), c) a mixture of **1** (125 μM) and **7** (125 μM), d) **1** (250 μM).

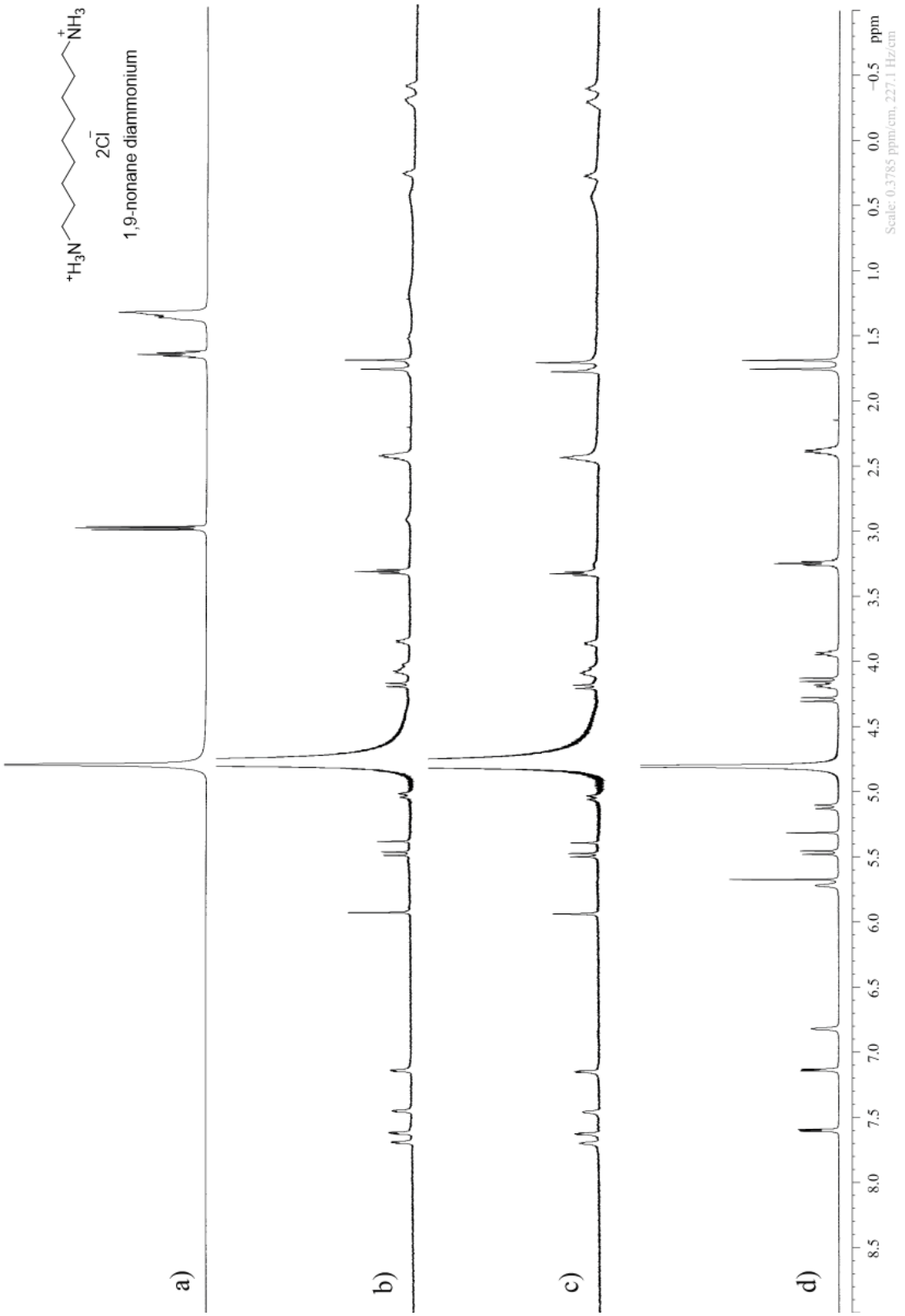

Figure S11. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **9** (2 mM), b) a mixture of **1** (125 μM) and **9** (250 μM), c) a mixture of **1** (125 μM) and **9** (125 μM), d) **1** (250 μM).

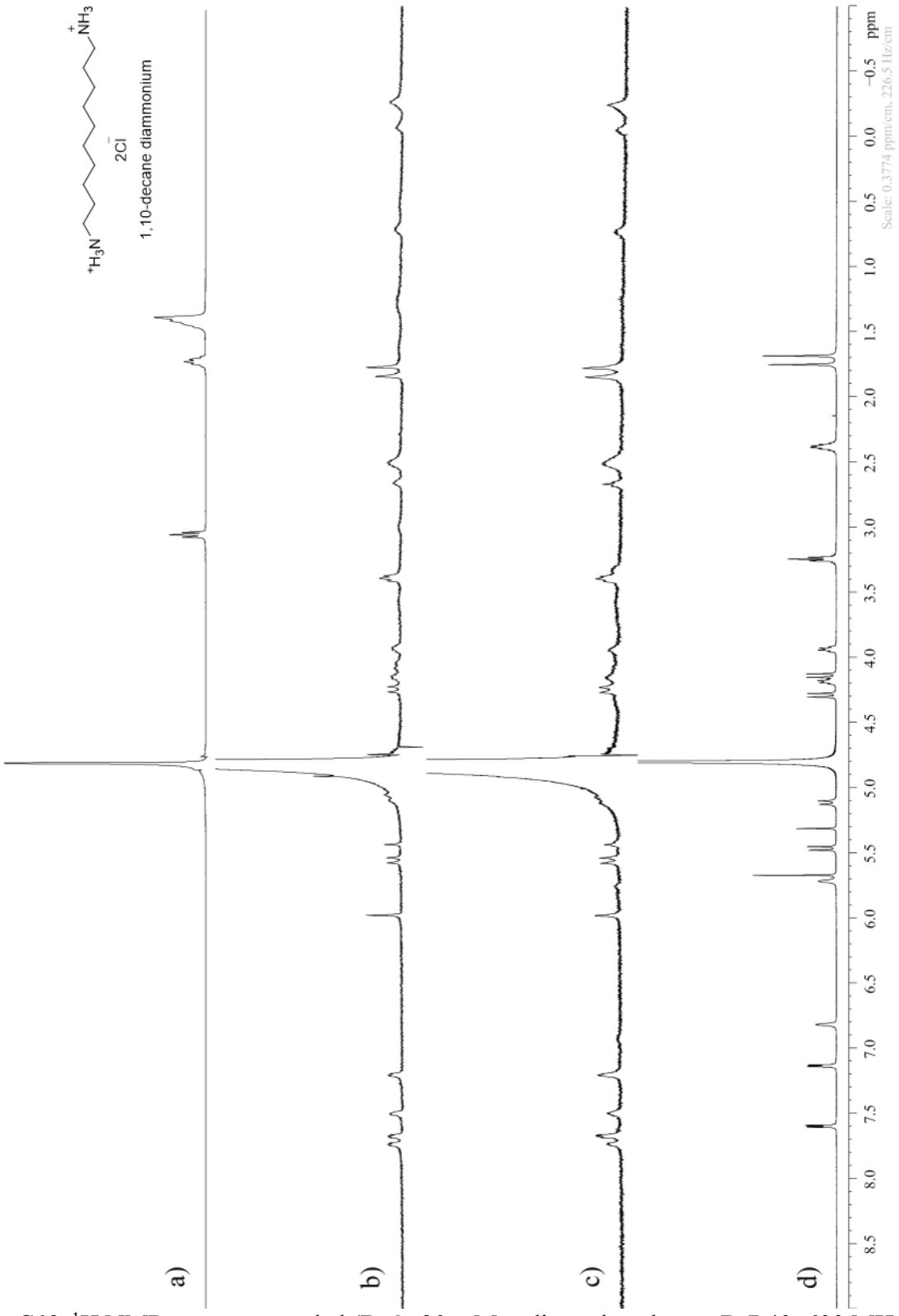

Figure S12. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **10** (2 mM), b) a mixture of **1** (125 μM) and **10** (250 μM), c) a mixture of **1** (125 μM) and **10** (125 μM), d) **1** (250 μM).

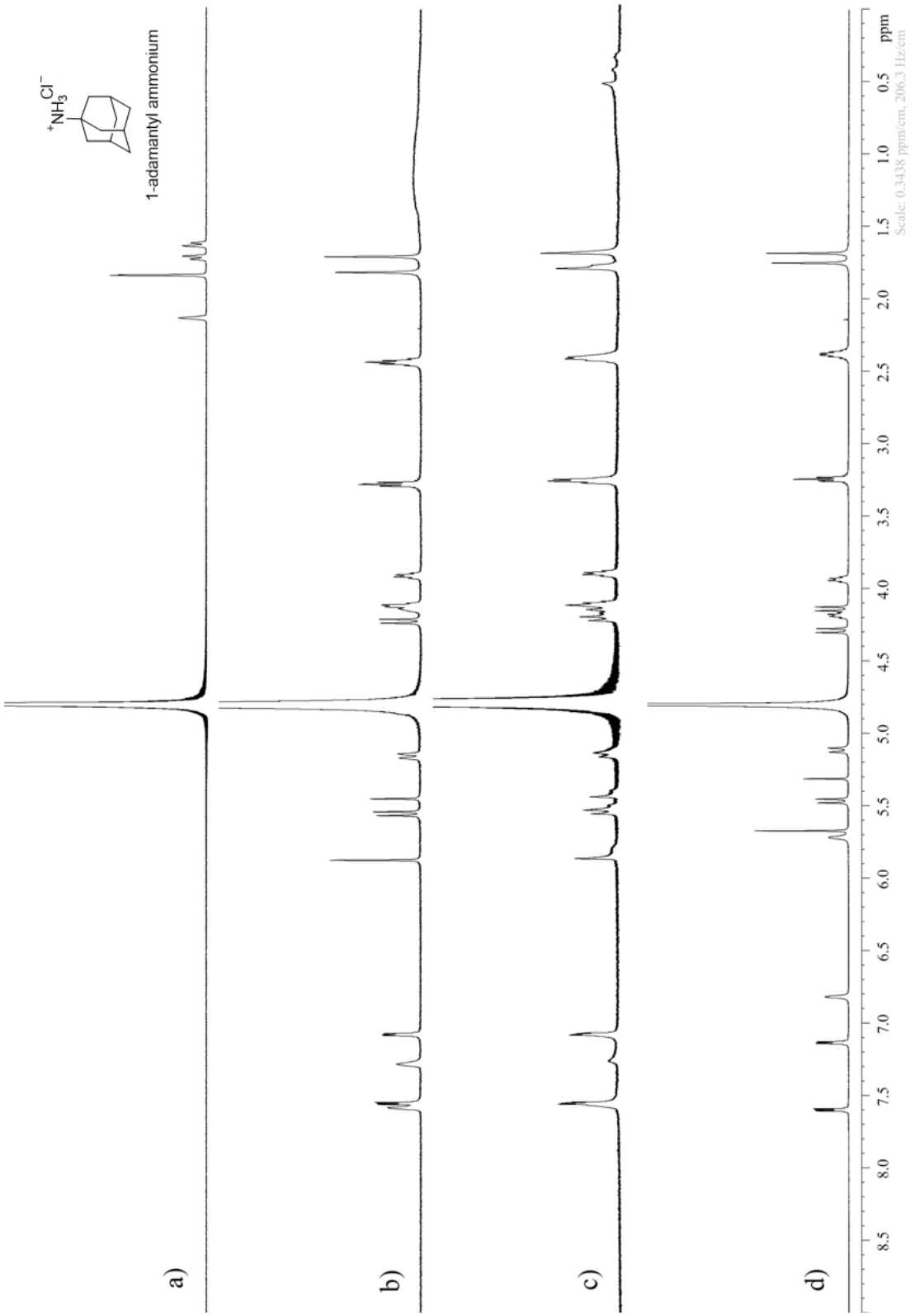

Figure S13. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **11** (5 mM), b) a mixture of **1** (250 μM) and **11** (500 μM), c) a mixture of **1** (250 μM) and **11** (250 μM), d) **1** (250 μM).

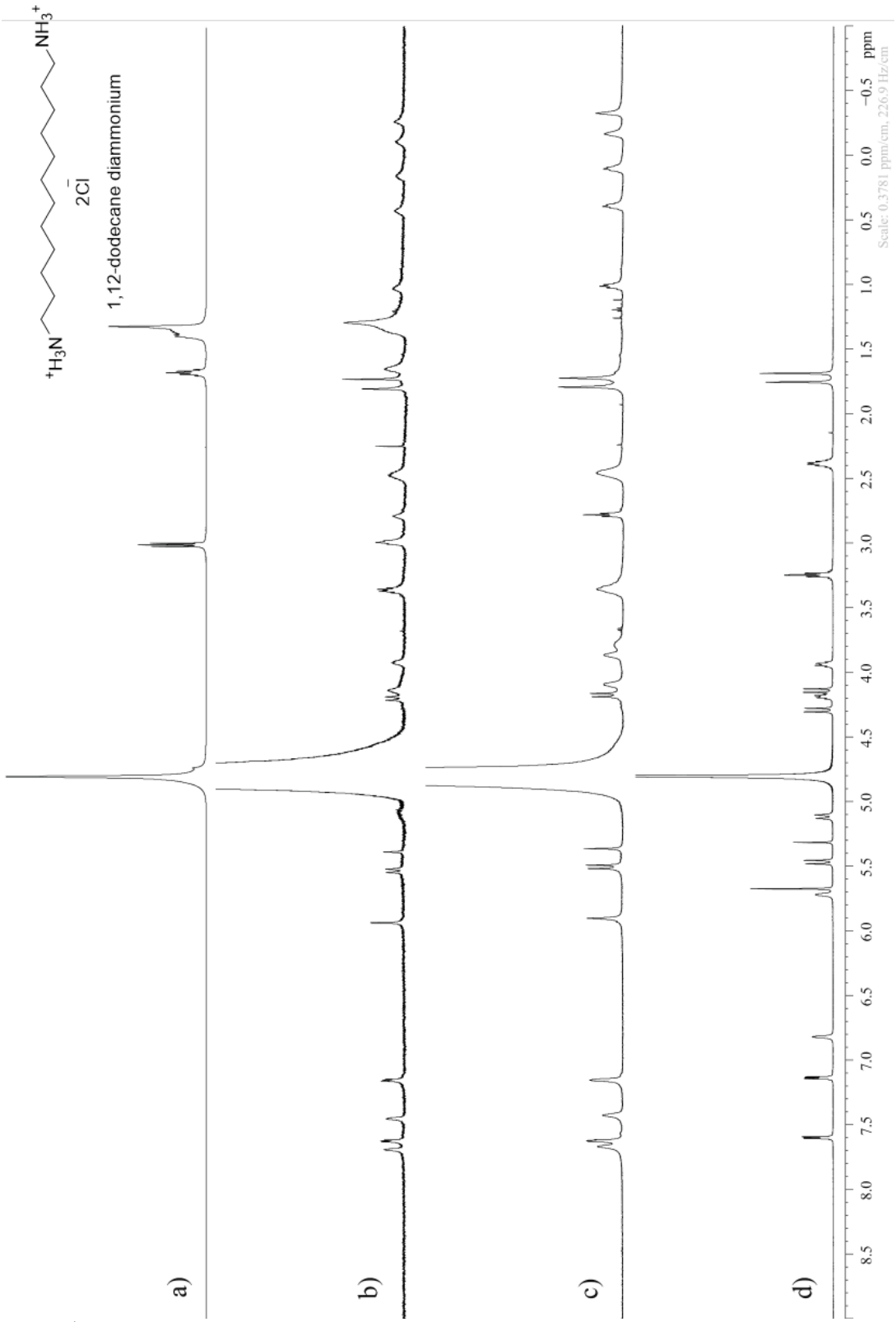

Figure S14. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 400 MHz, RT) for: a) **12** (2 mM), b) a mixture of **1** (125 µM) and **12** (250 µM), c) a mixture of **1** (125 µM) and **12** (125 µM), d) **1** (250 µM).

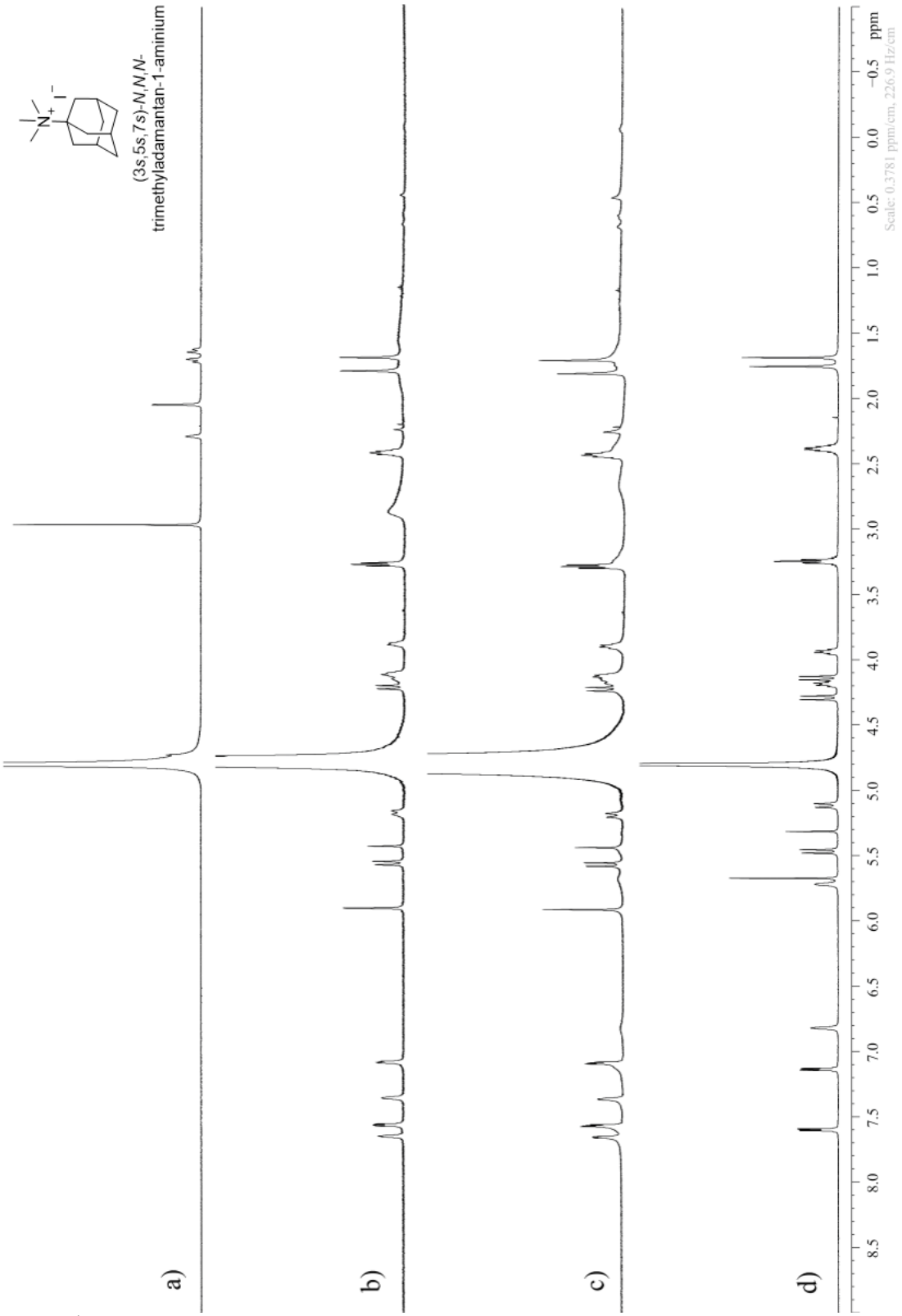

Figure S15. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **13** (2 mM), b) a mixture of **1** (125 μM) and **13** (250 μM), c) a mixture of **1** (125 μM) and **13** (125 μM), d) **1** (250 μM).

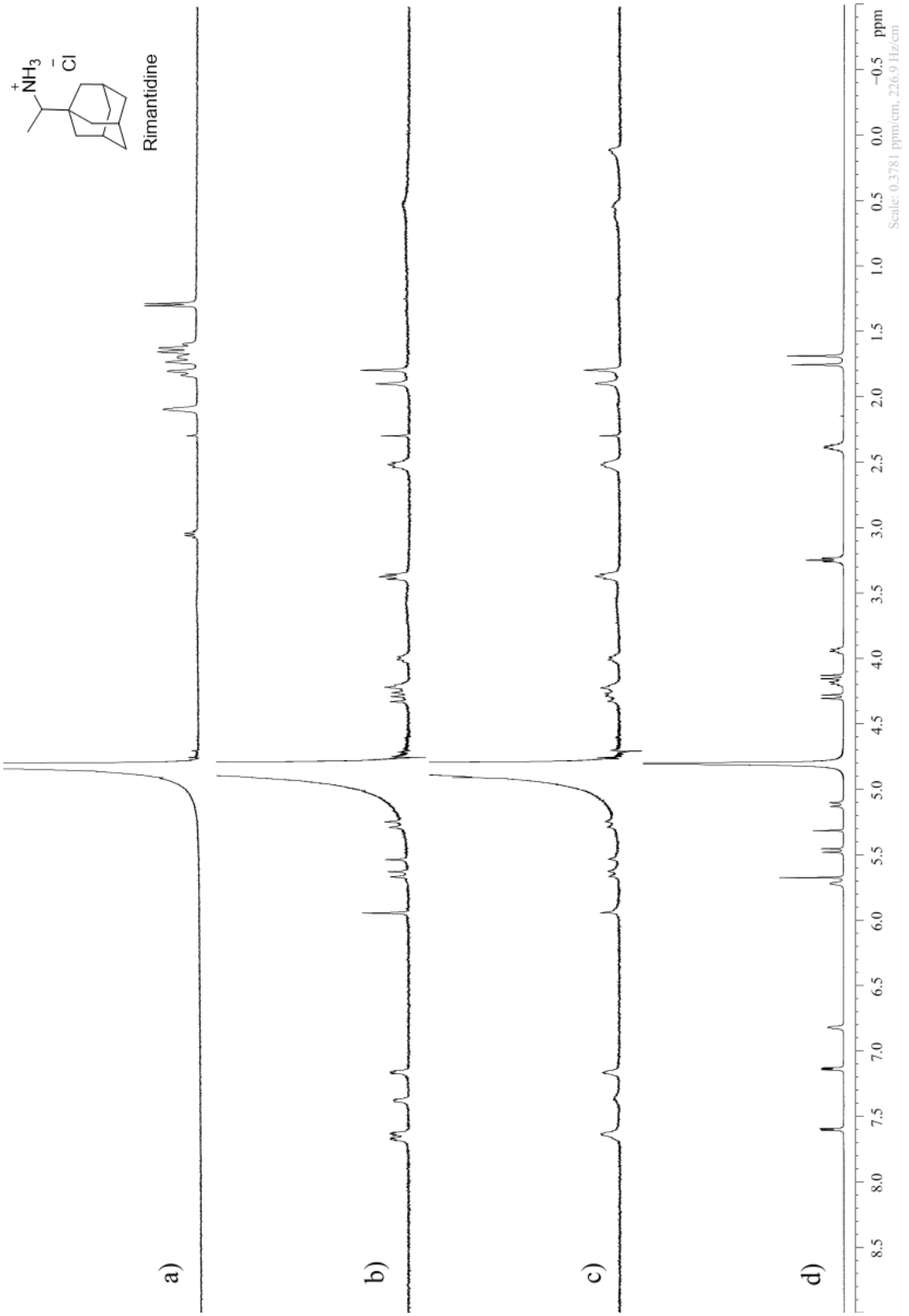

Figure S16. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **14** (4 mM), b) a mixture of **1** (125 μM) and **14** (250 μM), c) a mixture of **1** (125 μM) and **14** (125 μM), d) **1** (250 μM).

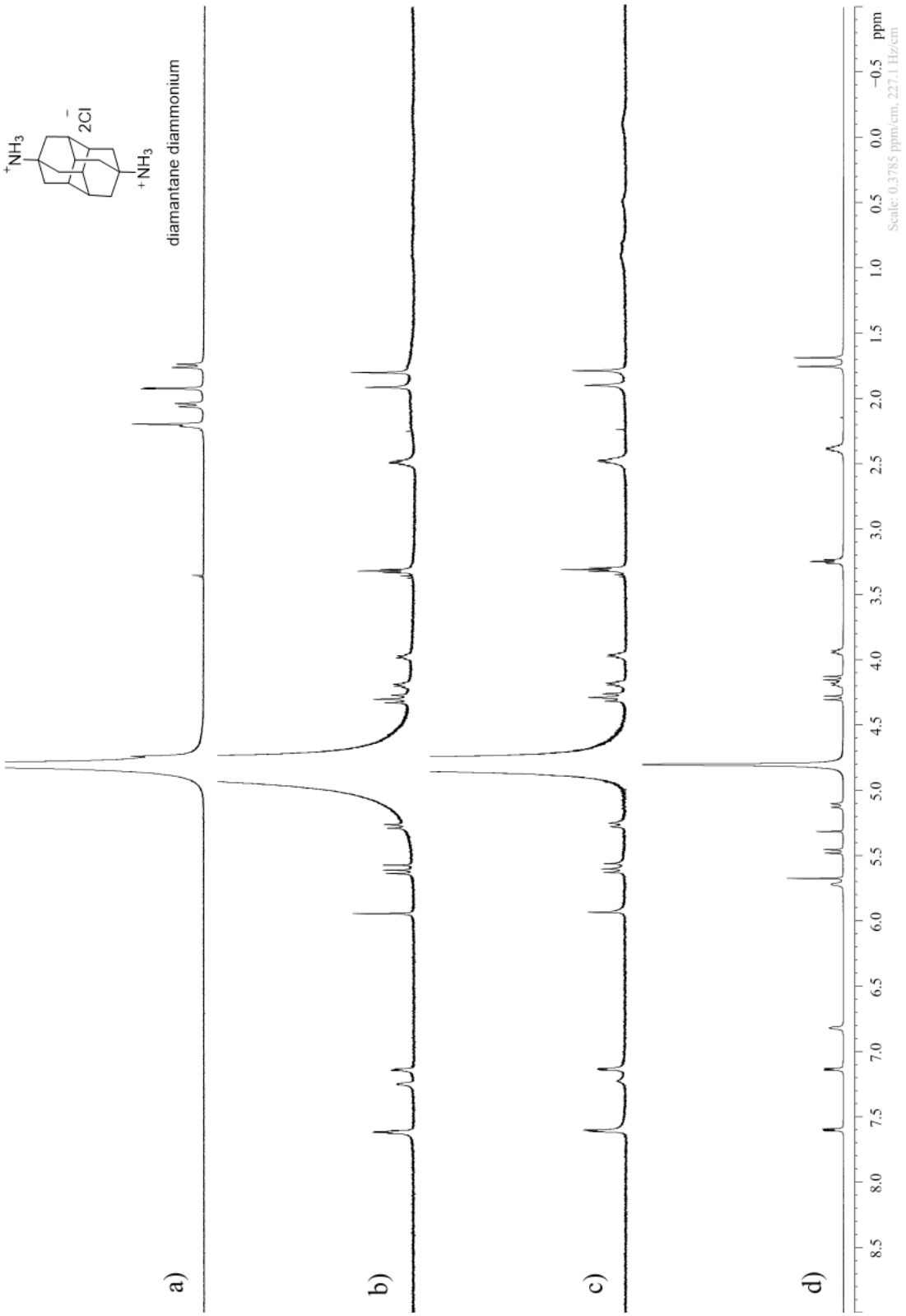

Figure S17. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **15** (4 mM), b) a mixture of **1** (250 μM) and **15** (500 μM), c) a mixture of **1** (250 μM) and **15** (250 μM), d) **1** (250 μM).

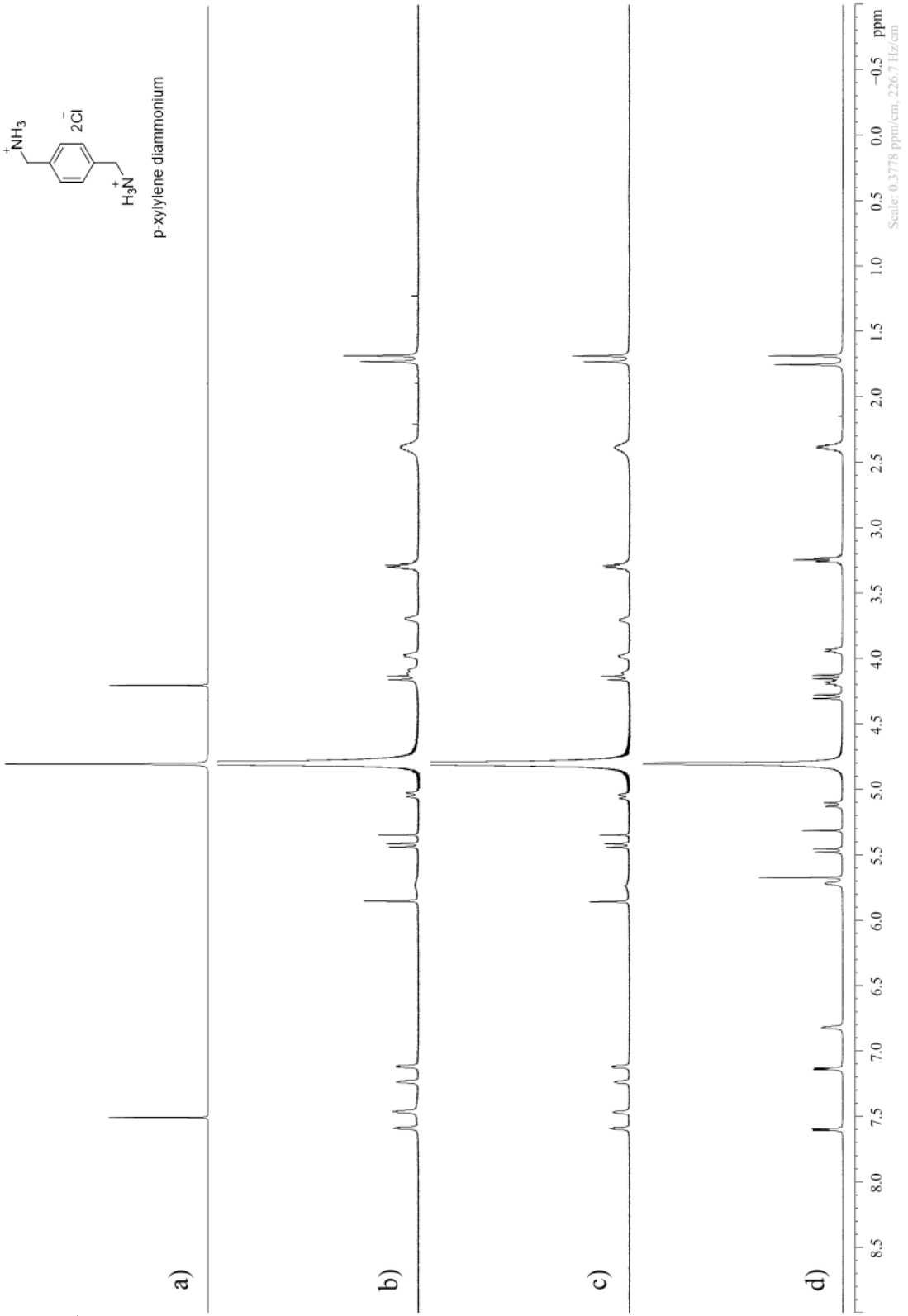

Figure S18. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **16** (4 mM), b) a mixture of **1** (250 μM) and **16** (500 μM), c) a mixture of **1** (250 μM) and **16** (250 μM), d) **1** (250 μM).

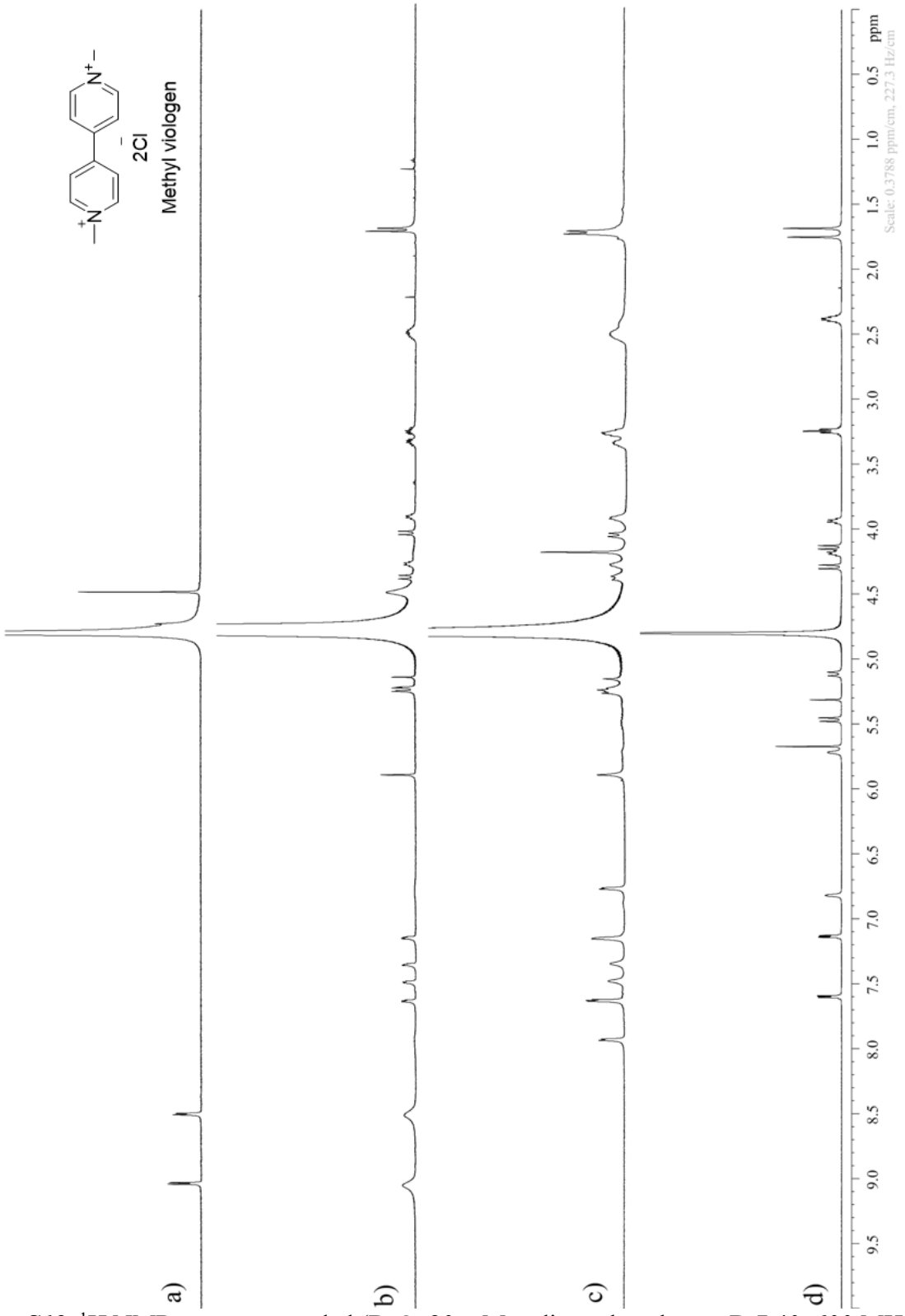

Figure S19. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **17** (2 mM), b) a mixture of **1** (250 μM) and **17** (500 μM), c) a mixture of **1** (250 μM) and **17** (250 μM), d) **1** (250 μM).

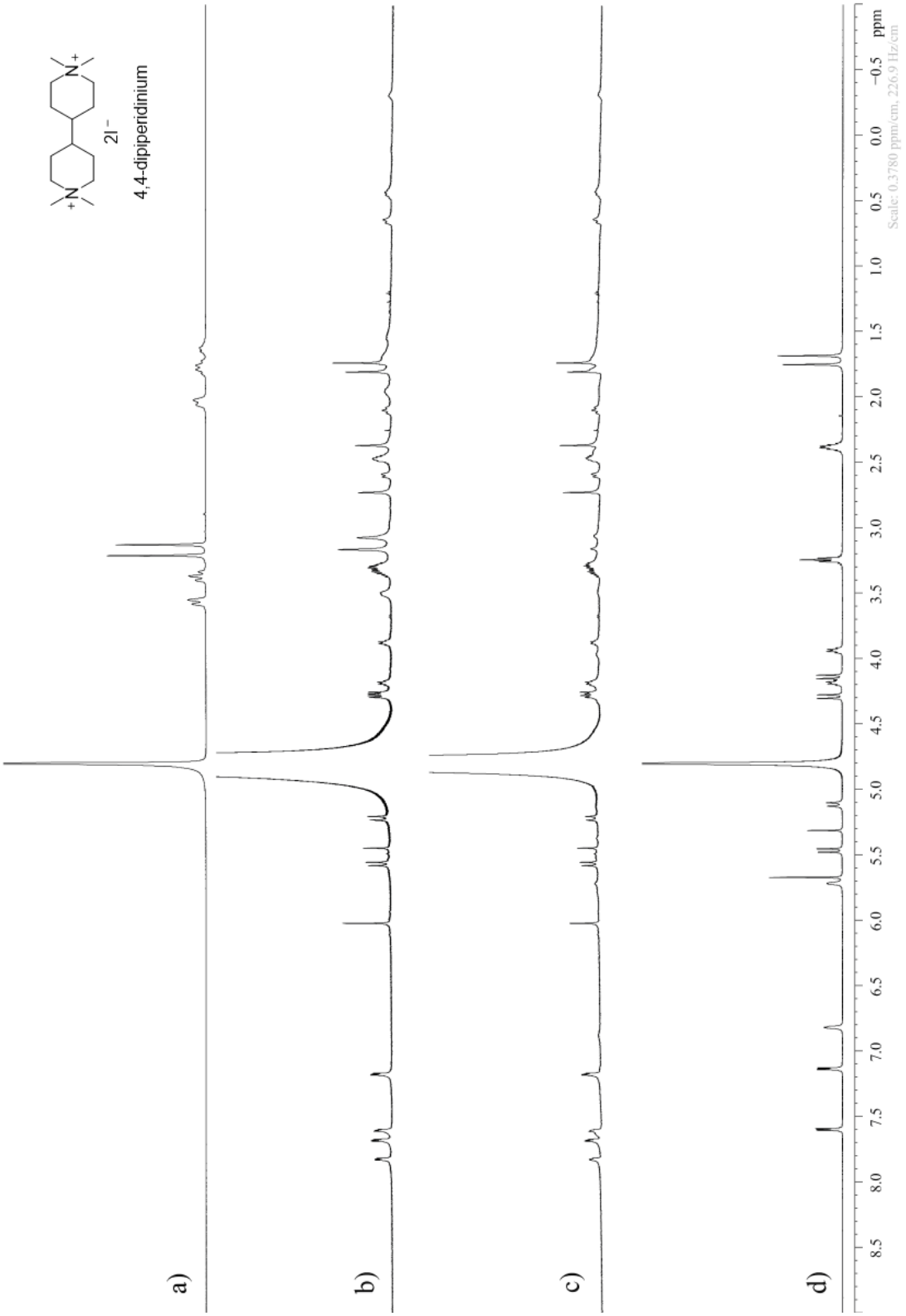

Figure S20. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **18** (1 mM), b) a mixture of **1** (125 μM) and **18** (250 μM), c) a mixture of **1** (125 μM) and **18** (125 μM), d) **1** (250 μM).

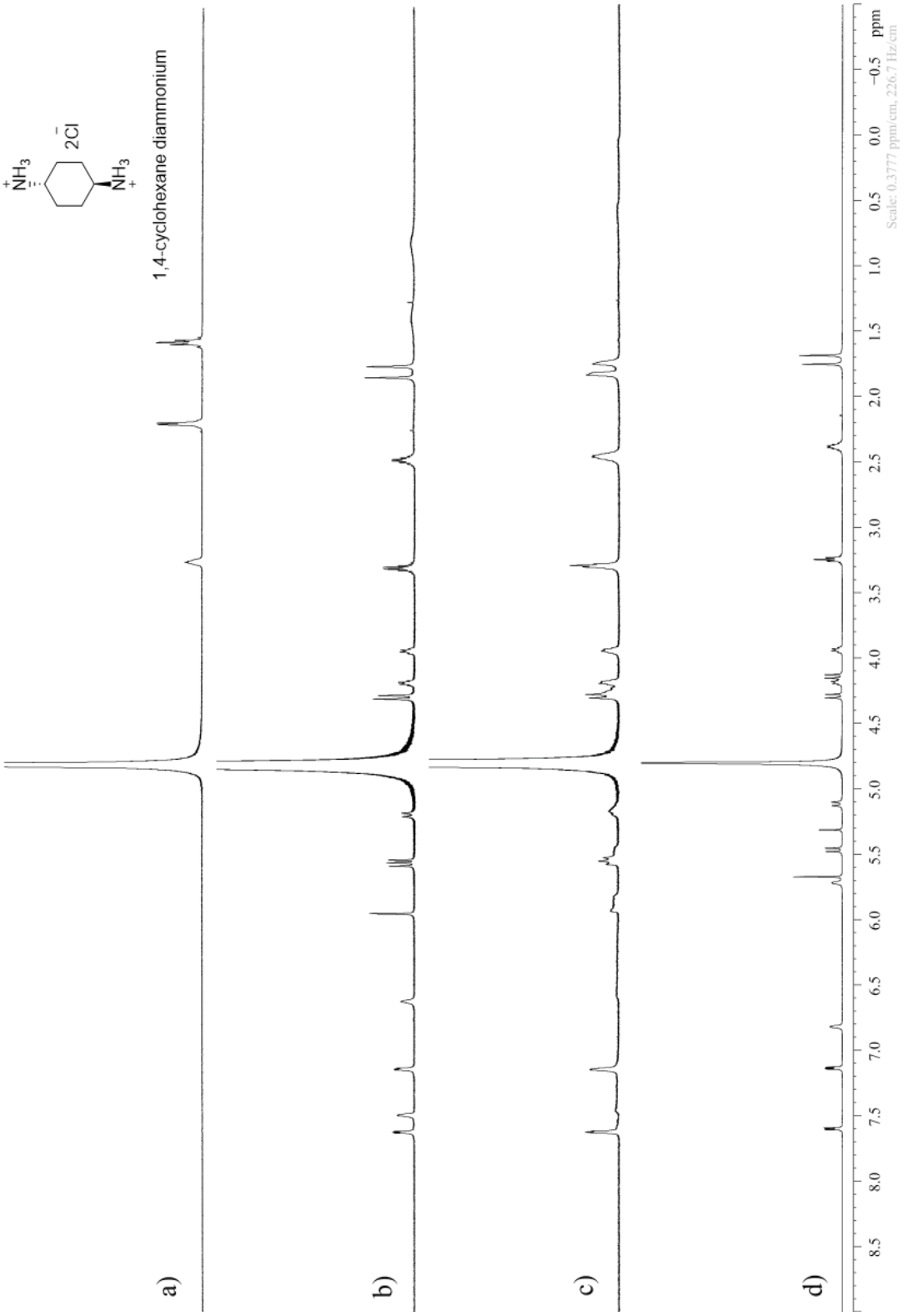

Figure S21. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **19** (4 mM), b) a mixture of **1** (250 μM) and **19** (500 μM), c) a mixture of **1** (250 μM) and **19** (250 μM), d) **1** (250 μM).

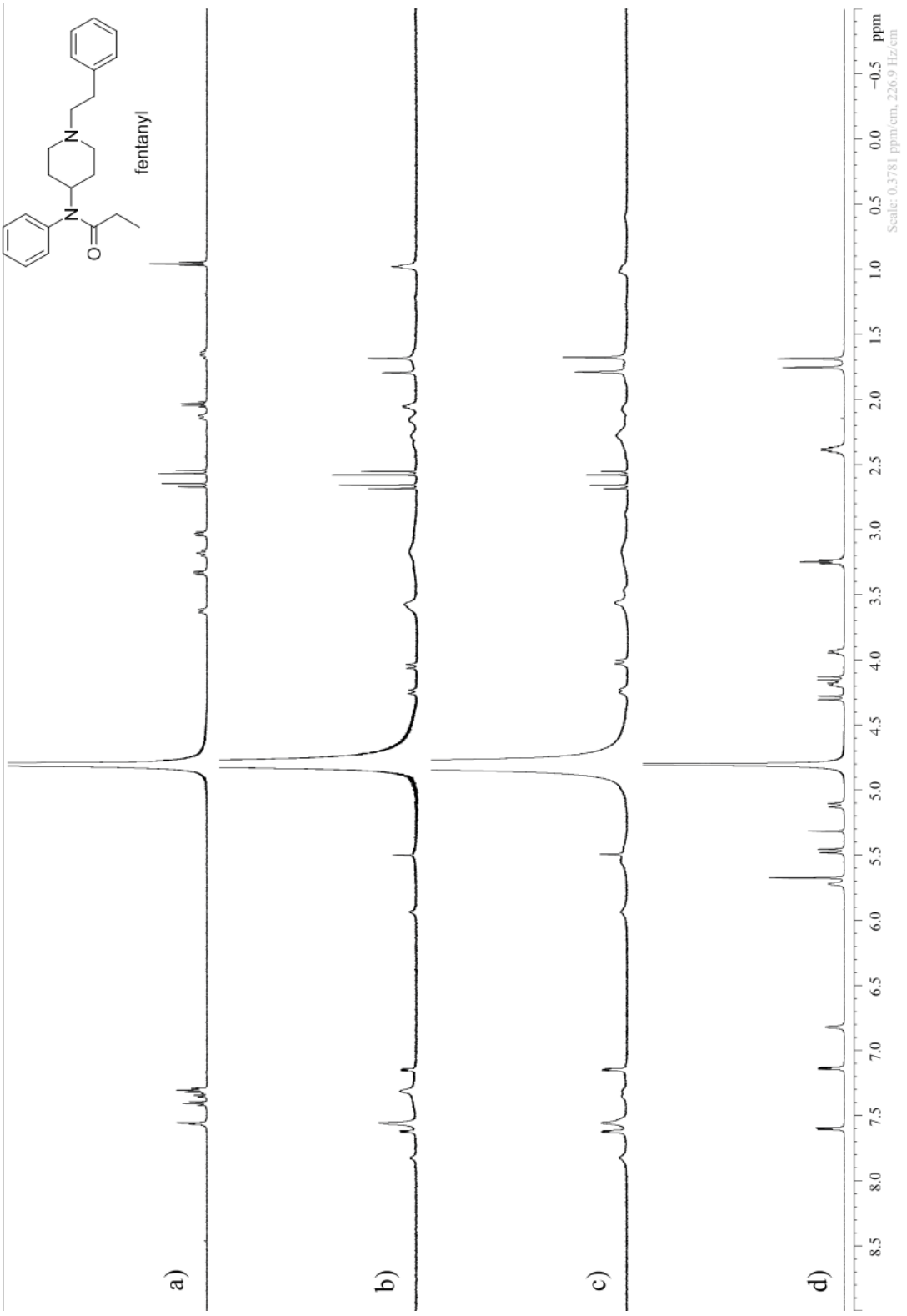

Figure S22. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **20** (250 μM), b) a mixture of **1** (125 μM) and **20** (250 μM), c) a mixture of **1** (125 μM) and **20** (125 μM), d) **1** (250 μM).

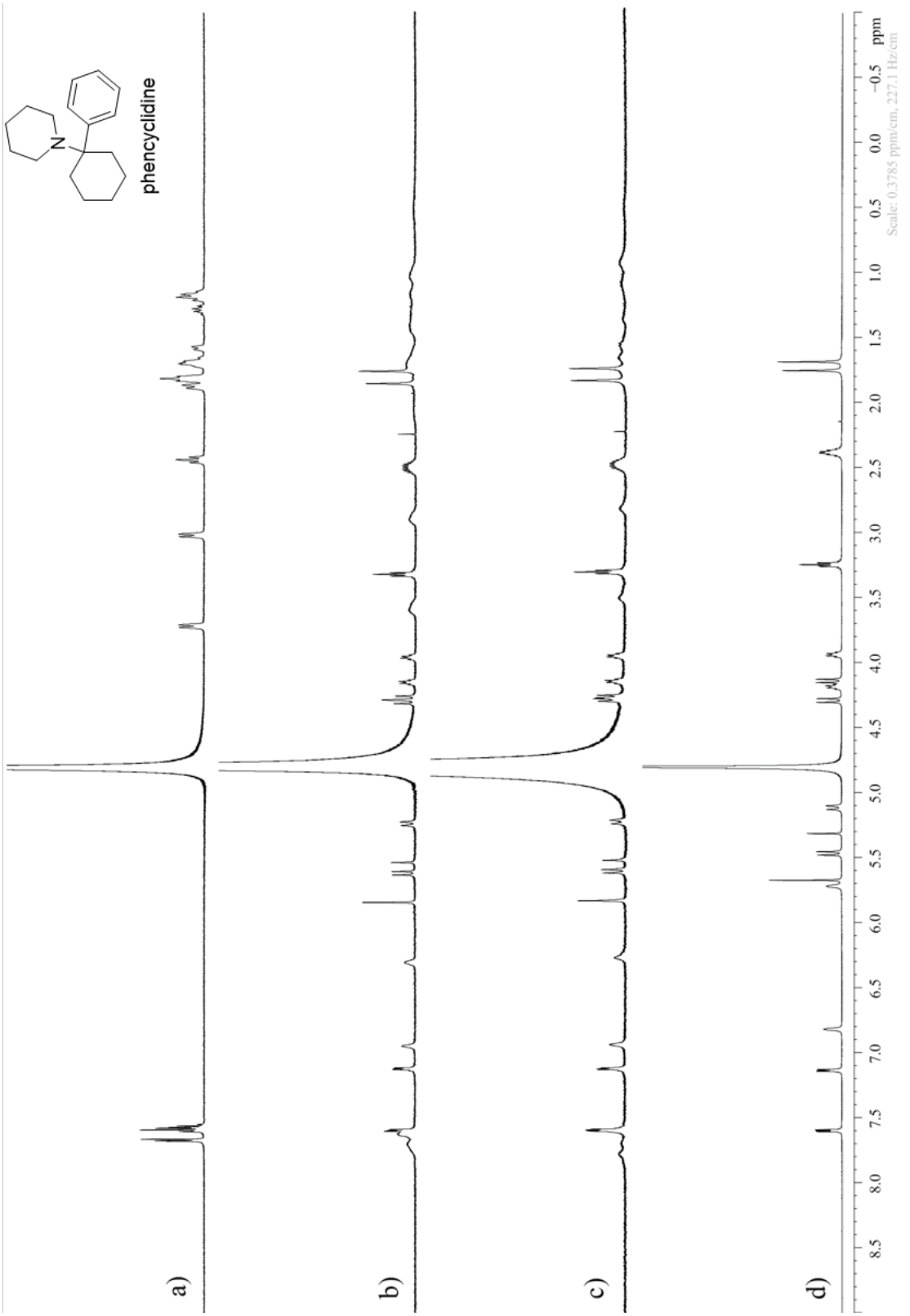

Figure S23. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **21** (1 mM), b) a mixture of **1** (125 μM) and **21** (250 μM), c) a mixture of **1** (125 μM) and **21** (125 μM), d) **1** (250 μM).

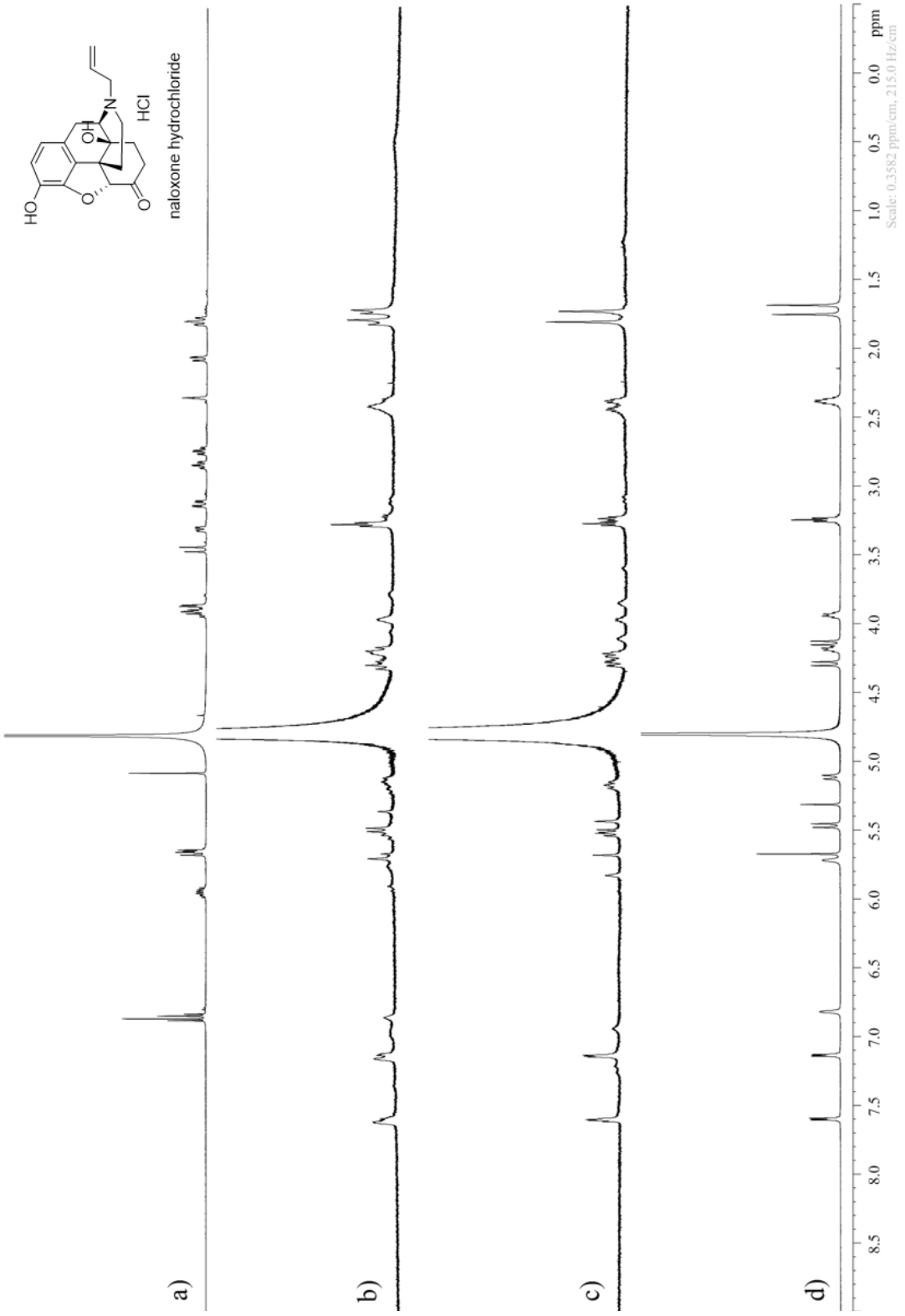

Figure S24. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **22** (2 mM), b) a mixture of **1** (125 μM) and **22** (250 μM), c) a mixture of **1** (125 μM) and **22** (125 μM), d) **1** (250 μM).

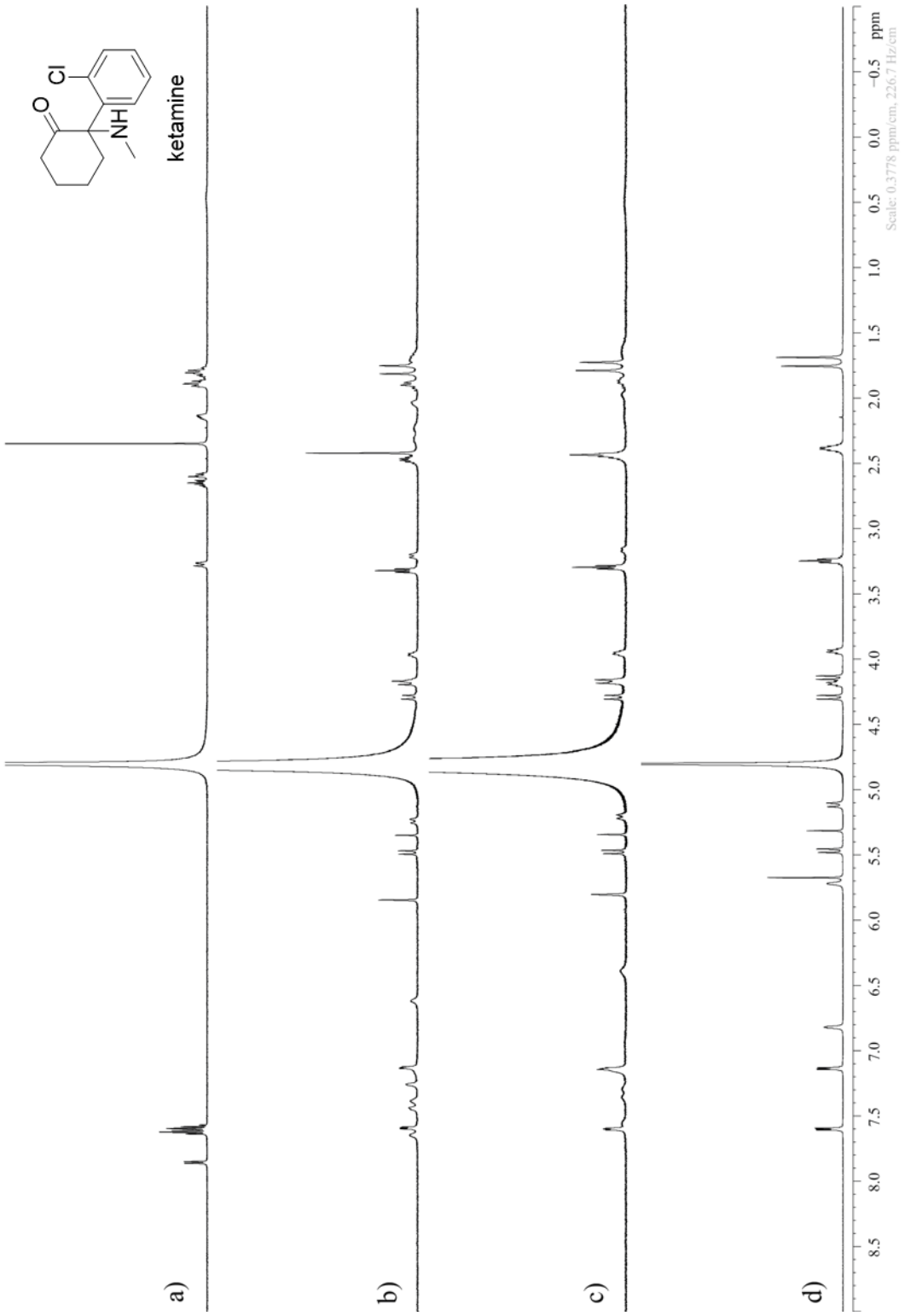

Figure S25. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **23** (250 μM), b) a mixture of **1** (125 μM) and **23** (250 μM), c) a mixture of **1** (125 μM) and **23** (125 μM), d) **1** (250 μM).

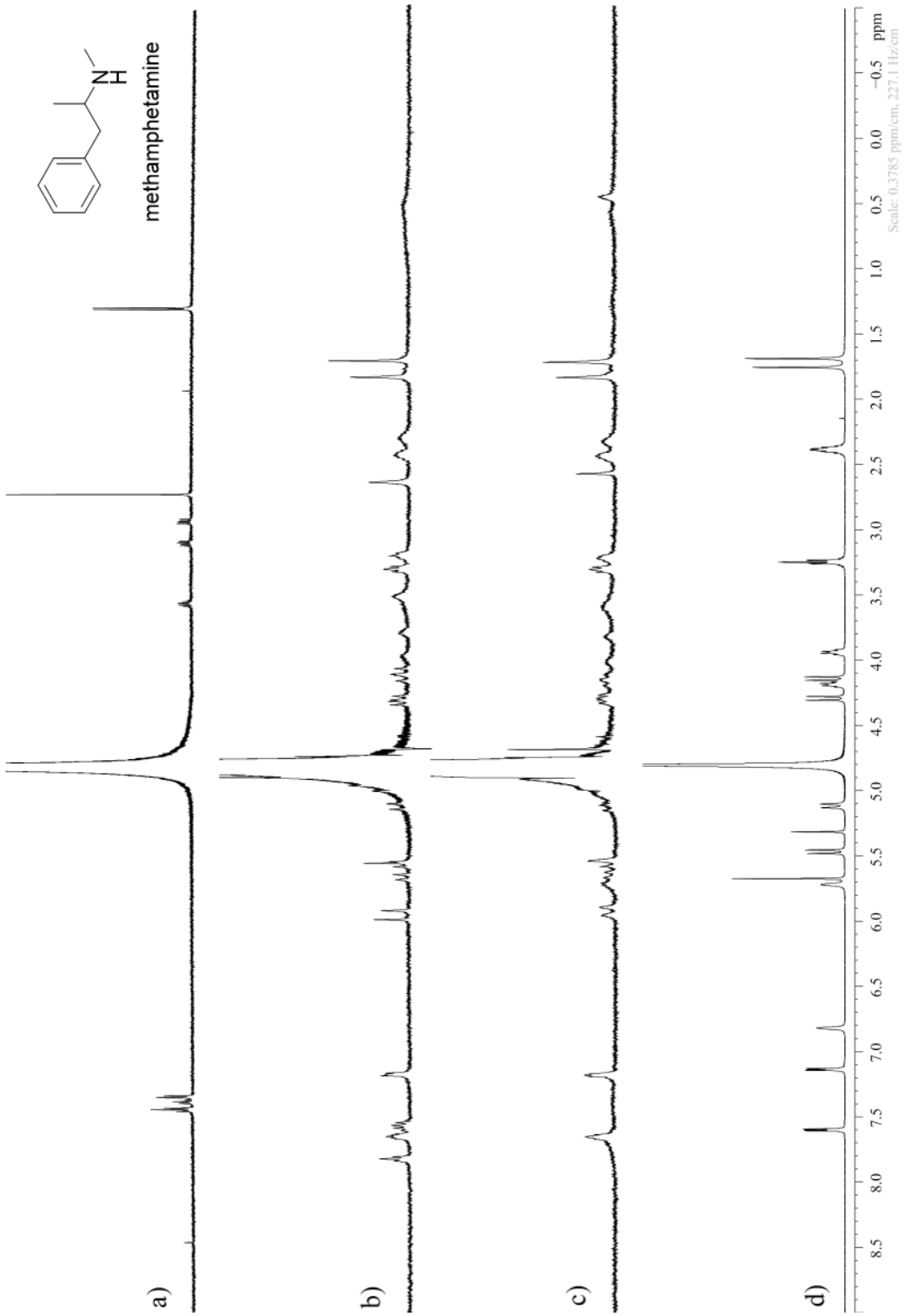

Figure S26. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 400 MHz, RT) for: a) **24** (250 μM), b) a mixture of **1** (125 μM) and **24** (250 μM), c) a mixture of **1** (125 μM) and **24** (125 μM), d) **1** (250 μM).

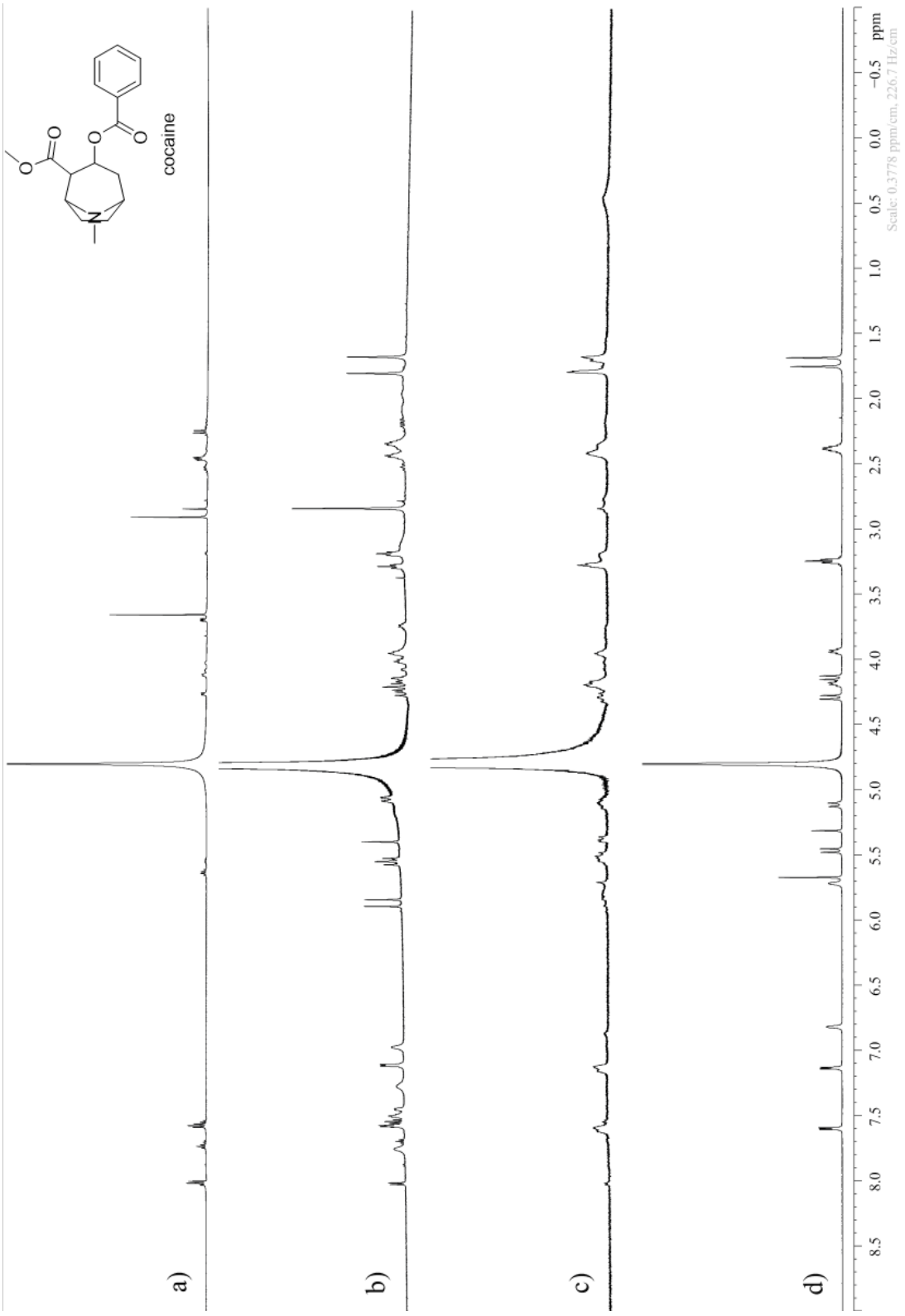

Figure S27. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **25** (1 mM), b) a mixture of **1** (125 μM) and **25** (250 μM), c) a mixture of **1** (125 μM) and **25** (125 μM), d) **1** (250 μM).

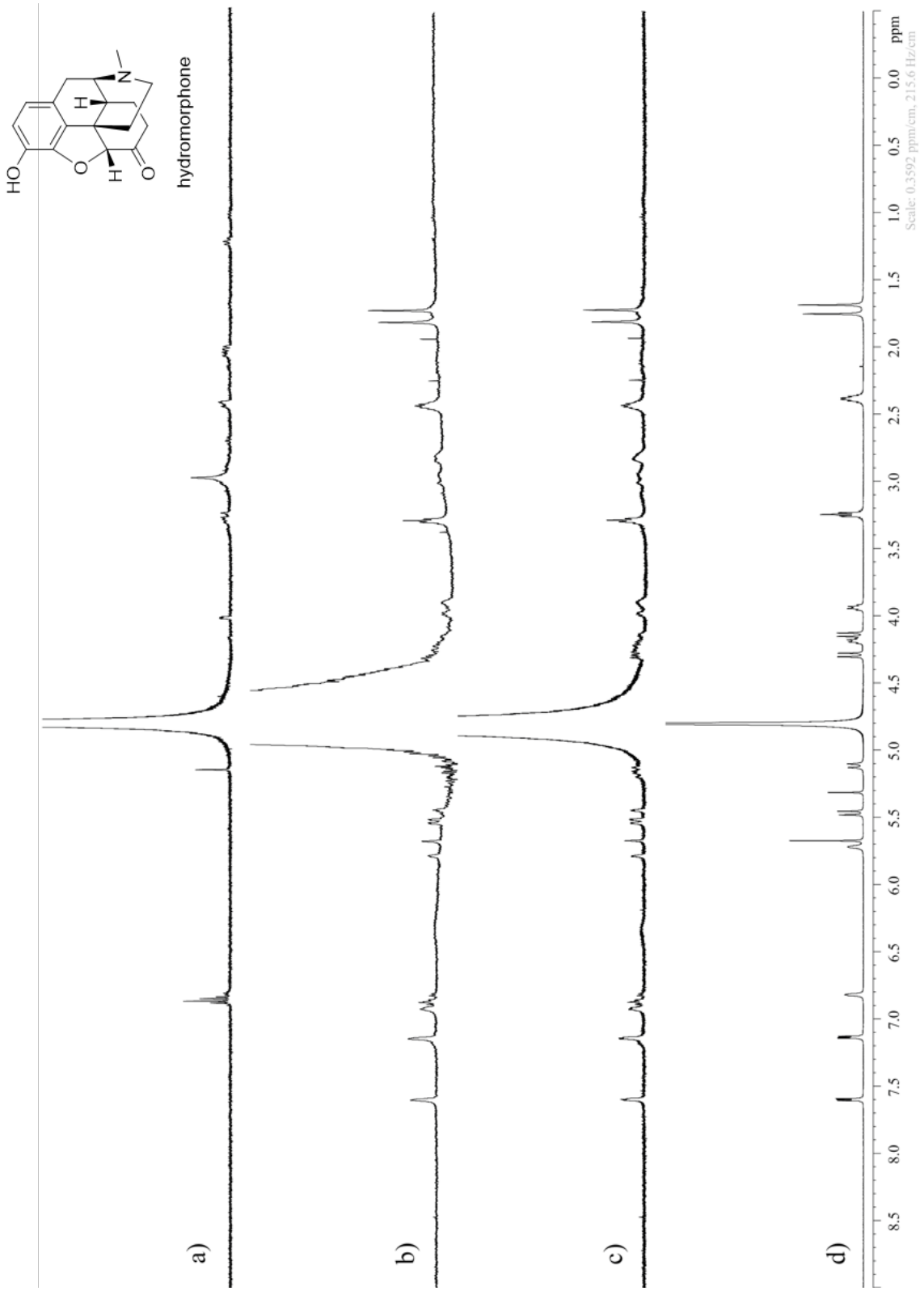

Figure S28. ^{1}H NMR spectra recorded (D_2O, 20 mM sodium phosphate, pD 7.40, 600 MHz, RT) for: a) **26** (250 mM), b) a mixture of **1** (62.5 μM) and **26** (125 μM), c) a mixture of **1** (125 μM) and **26** (125 μM), d) **1** (250 μM).

Isotherm of guests (4-26) with host 1

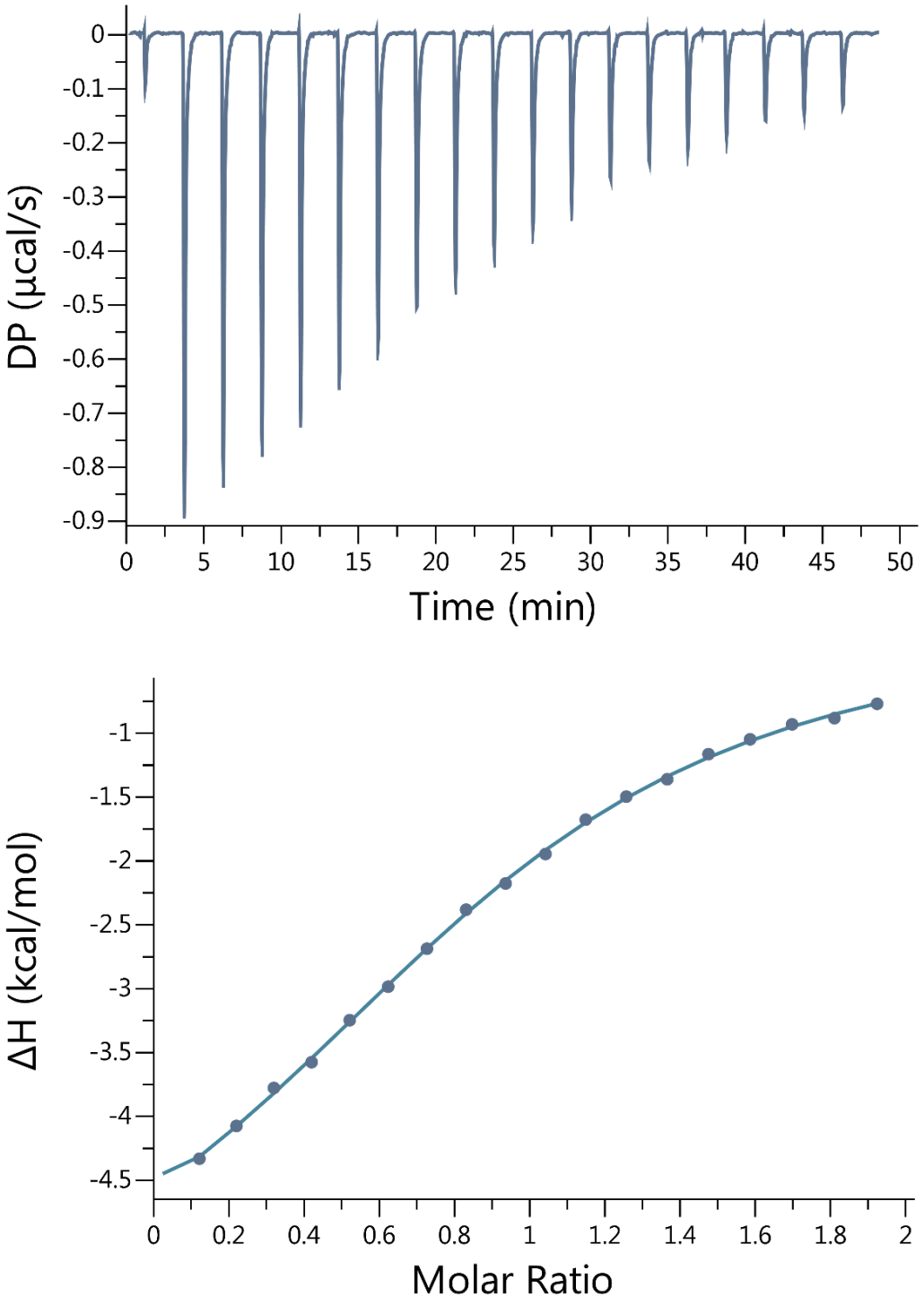

Figure S29. Isothermal Titration Calorimetry (ITC) curve obtained when a solution of **1** (100 µM) in the cell was titrated with **4** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 2.92 \times 10^4\ M^{-1}$ and $\Delta H = -6.03 \pm 0.260$ kcal•mol^{-1}

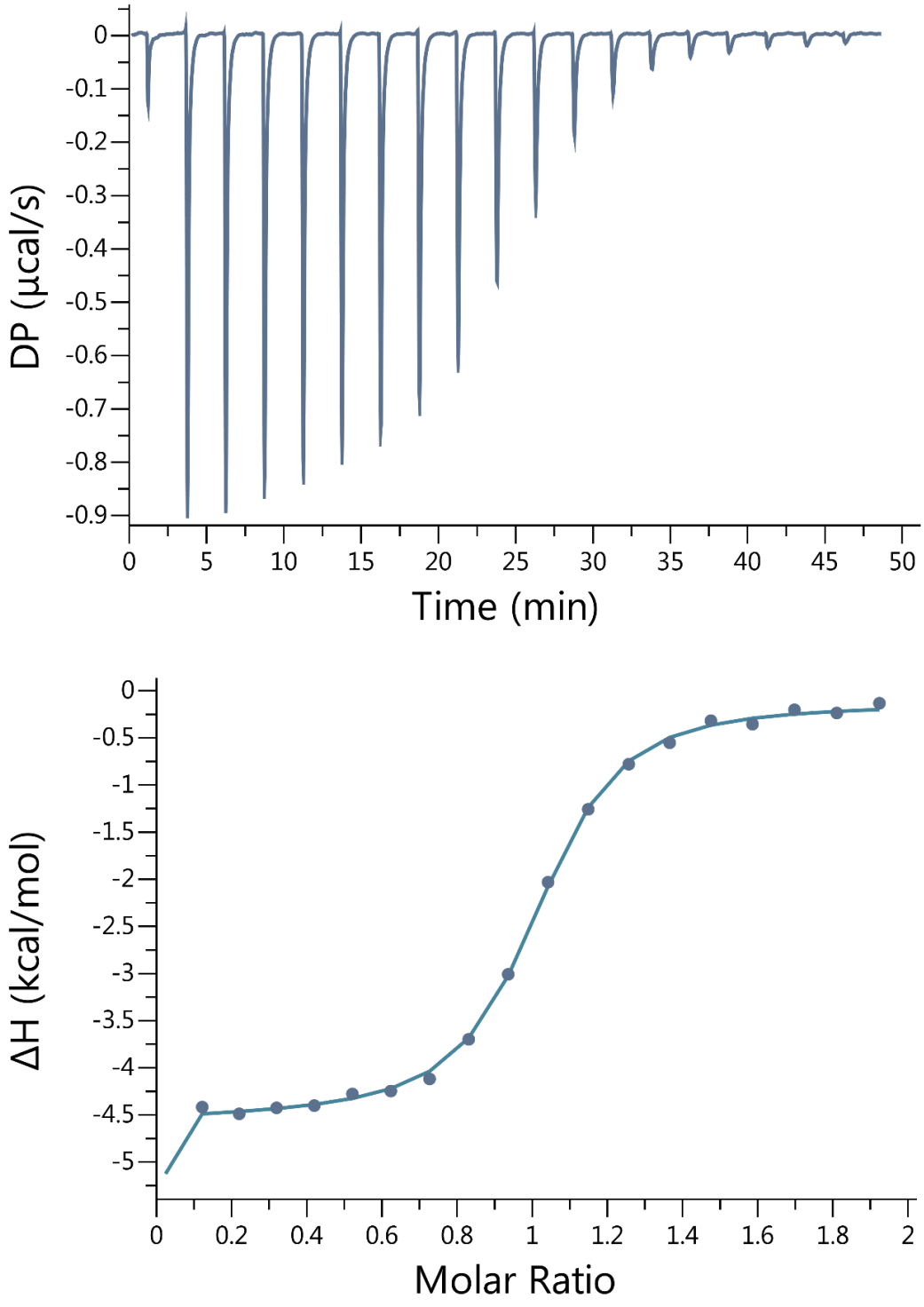

Figure S30. Isothermal Titration Calorimetry (ITC) curve obtained through competition binding studies. A solution of **1** (100 µM) and **19** (500 µM) in the cell was titrated with **6** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 2.30 \times 10^7$ M^{-1} and H = -10.8 ± 0.044 kcal•mol^{-1}.

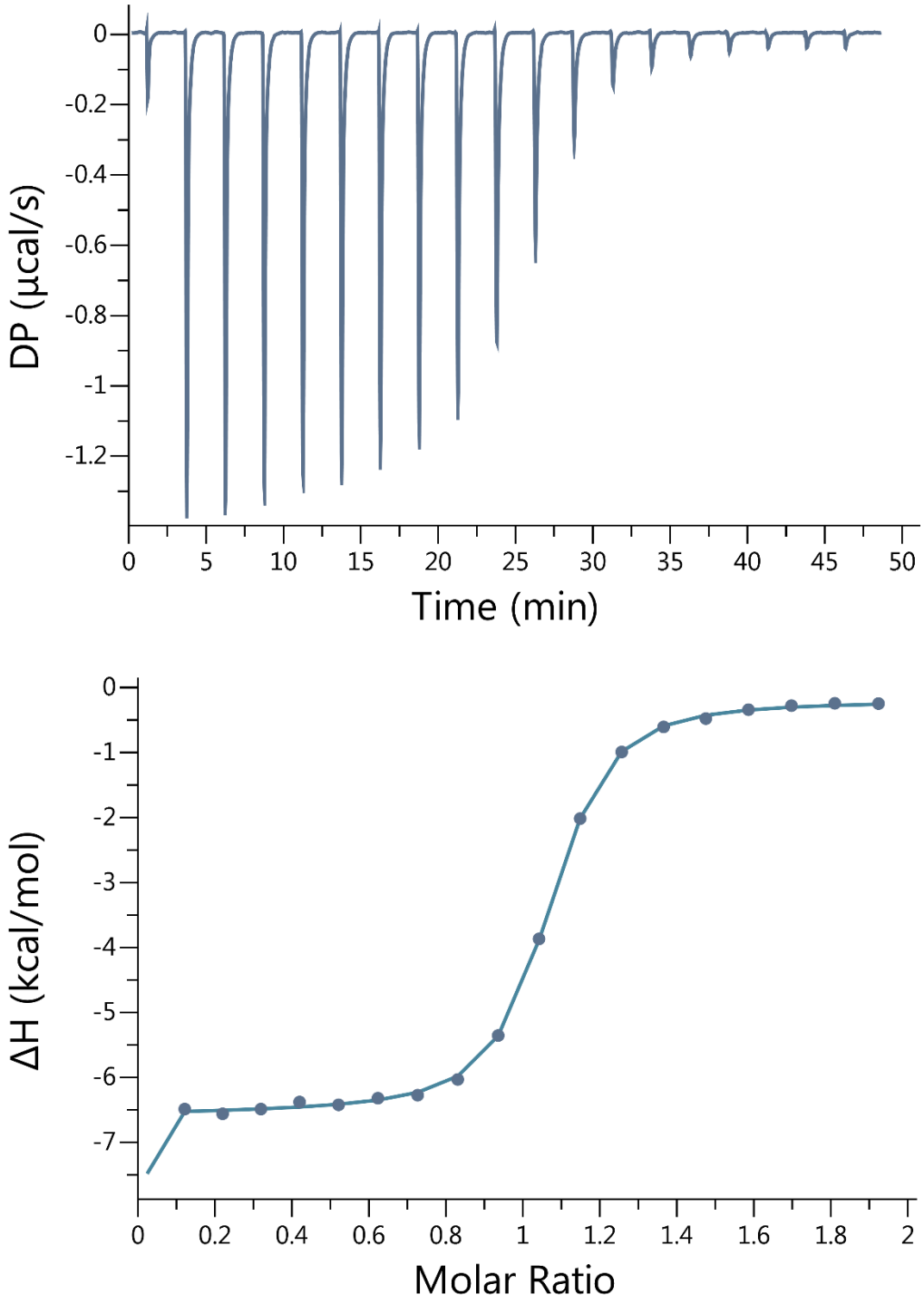

Figure S31. Isothermal Titration Calorimetry (ITC) curve obtained through competition binding studies. A solution of **1** (100 µM) and **19** (500 µM) in the cell was titrated with **6DQ** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 5.00 \times 10^7$ M^{-1} and $\Delta H = -12.7 \pm 0.028$ kcal•mol^{-1}

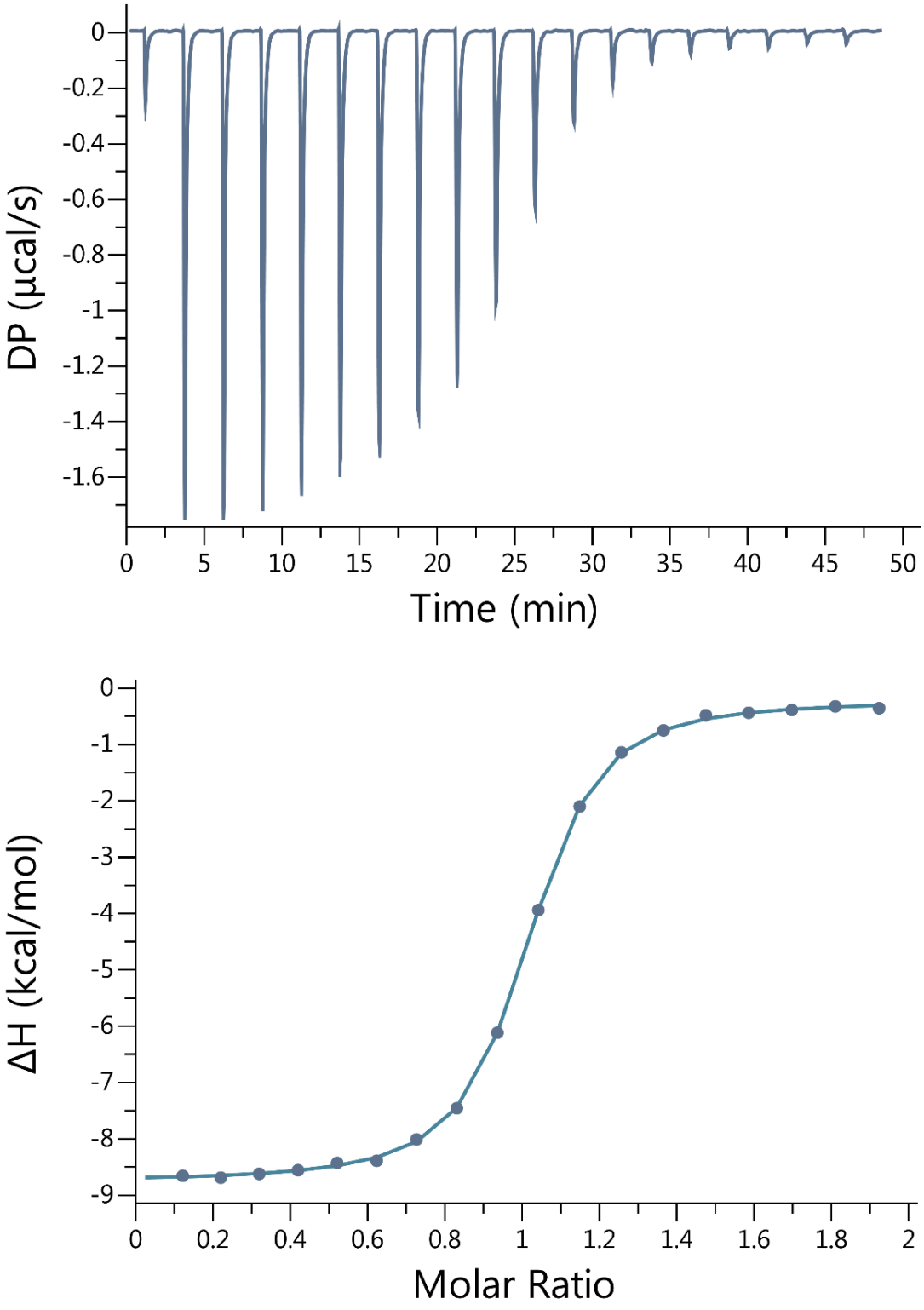

Figure S32. Isothermal Titration Calorimetry (ITC) curve obtained when a solution of **1** (100 µM) in the cell was titrated with **6Q** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 1.20 \times 10^6\ M^{-1}$ and $\Delta H = -8.54 \pm 0.027$ kcal•mol^{-1}.

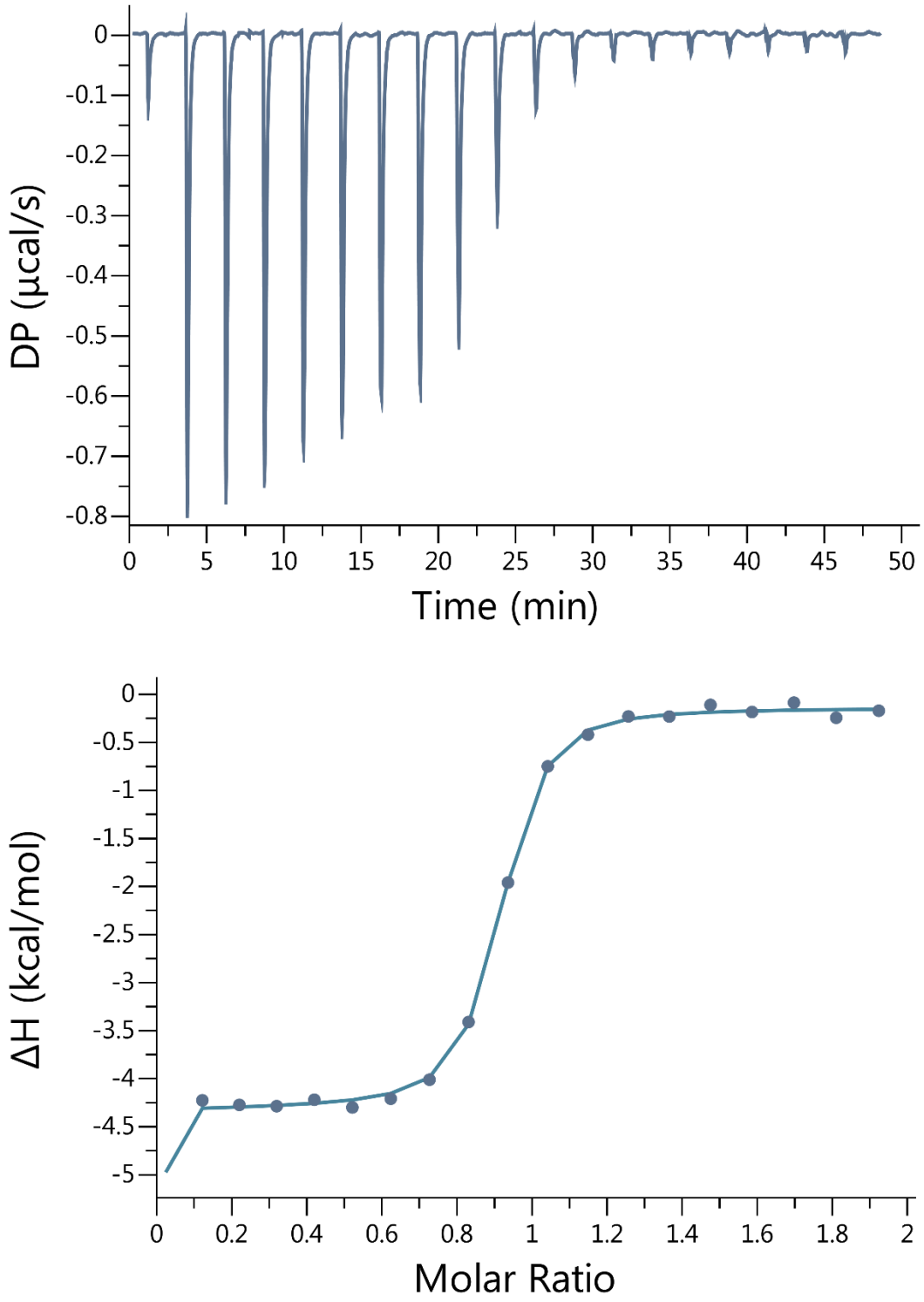

Figure S33. Isothermal Titration Calorimetry (ITC) curve obtained through competition binding studies. A solution of **1** (100 µM) and **19** (500 µM) in the cell was titrated with **7** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 7.24 \times 10^7$ M^{-1} and $\Delta H = -10.1 \pm 0.036$ kcal•mol^{-1}.

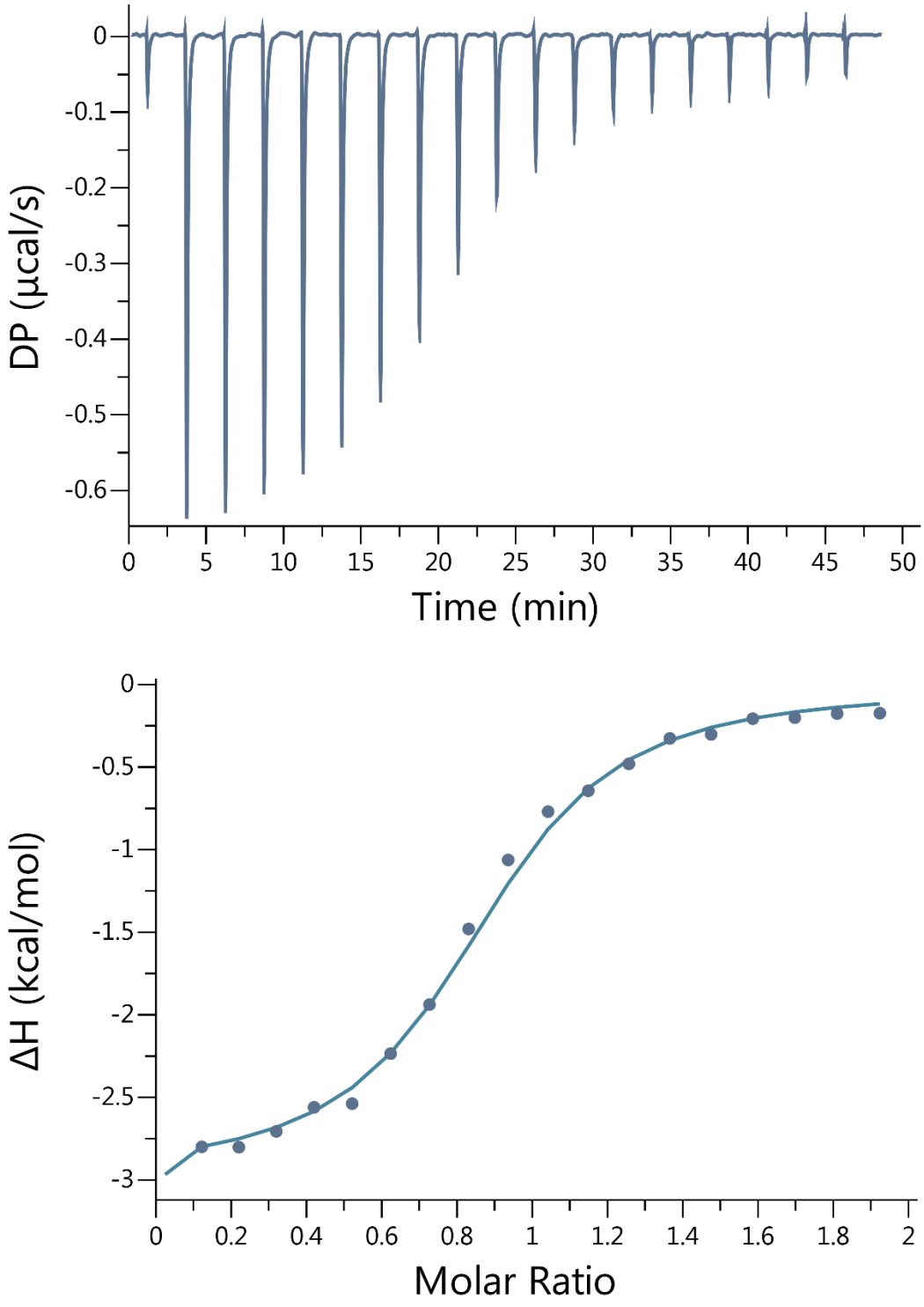

Figure S34. Isothermal Titration Calorimetry (ITC) curve obtained through competition binding studies. A solution of **1** (100 µM) and **5** (500 µM) in the cell was titrated with **8** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 1.41 \times 10^8\ M^{-1}$ and $\Delta H = -11.5 \pm 0.094$ kcal•mol^{-1}.

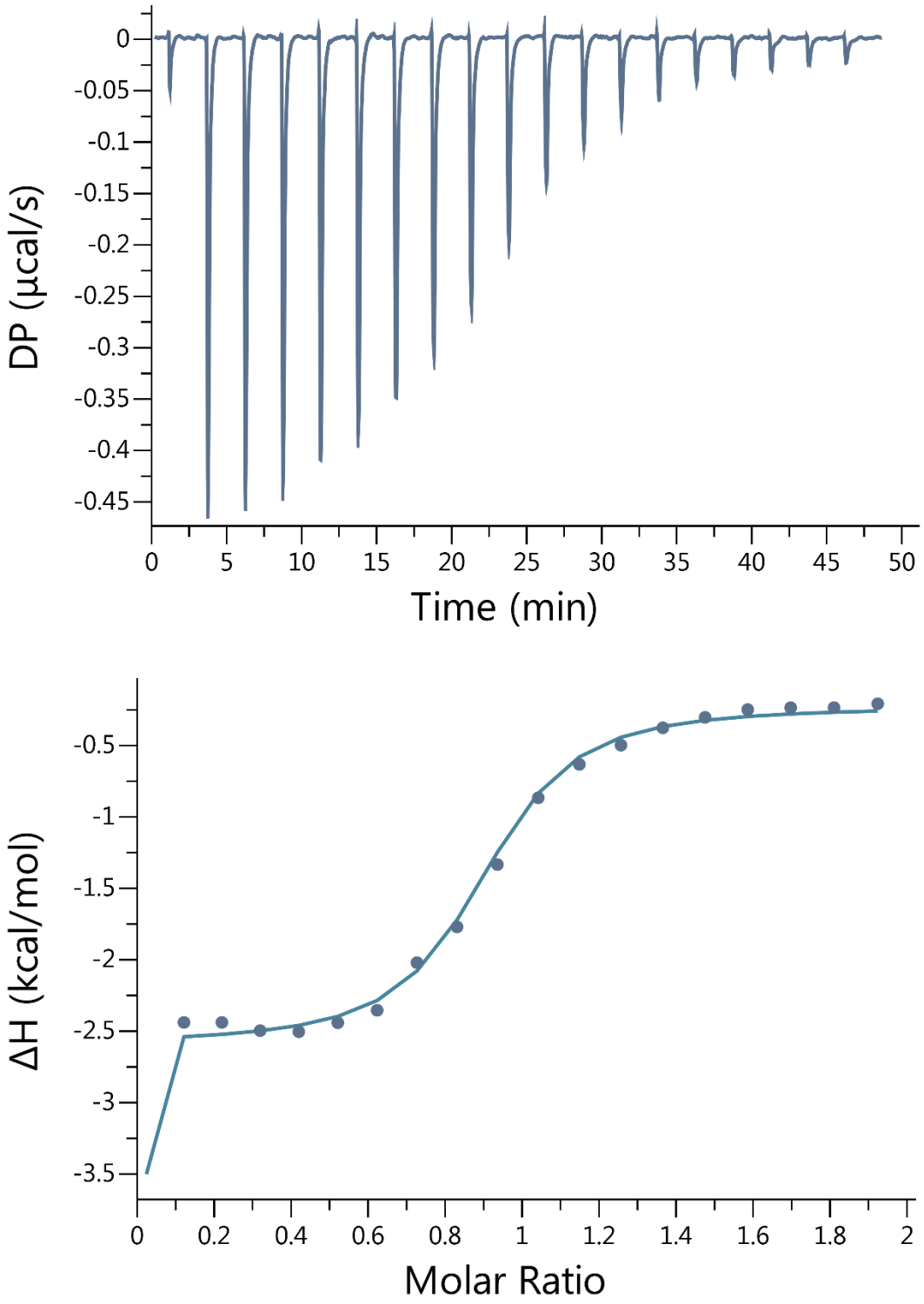

Figure S35. Isothermal Titration Calorimetry (ITC) curve obtained through competition binding studies. A solution of **1** (100 µM) and **5** (500 µM) in the cell was titrated with **9** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 2.42 \times 10^8$ M^{-1} and $\Delta H = -11.4 \pm 0.062$ kcal•mol^{-1}.

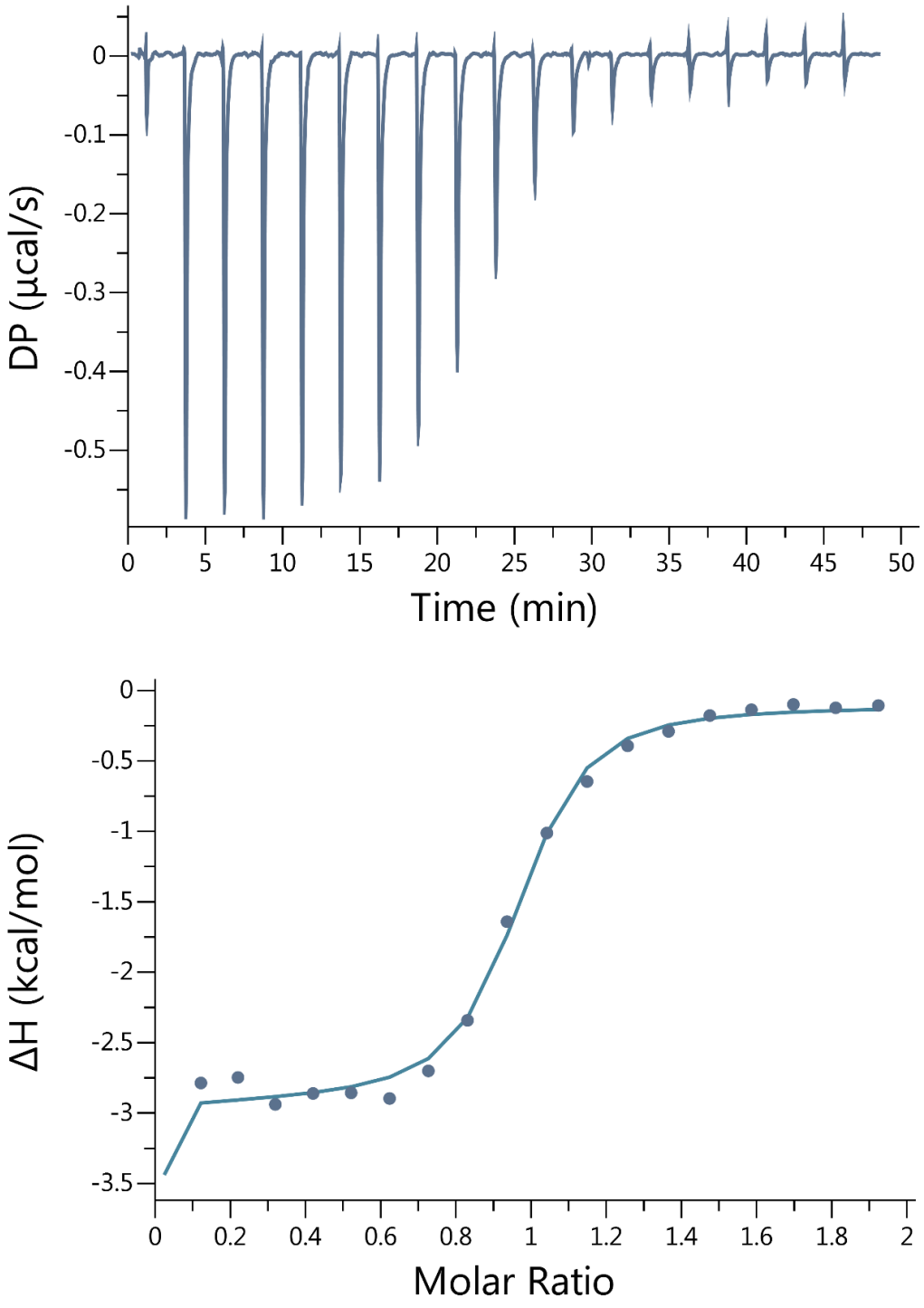

Figure S36. Isothermal Titration Calorimetry (ITC) curve obtained through competition binding studies. A solution of **1** (100 µM) and **5** (200 µM) in the cell was titrated with **10** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 2.81 \times 10^8$ M^{-1} and $\Delta H = -11.3 \pm 0.068$ kcal•mol^{-1}.

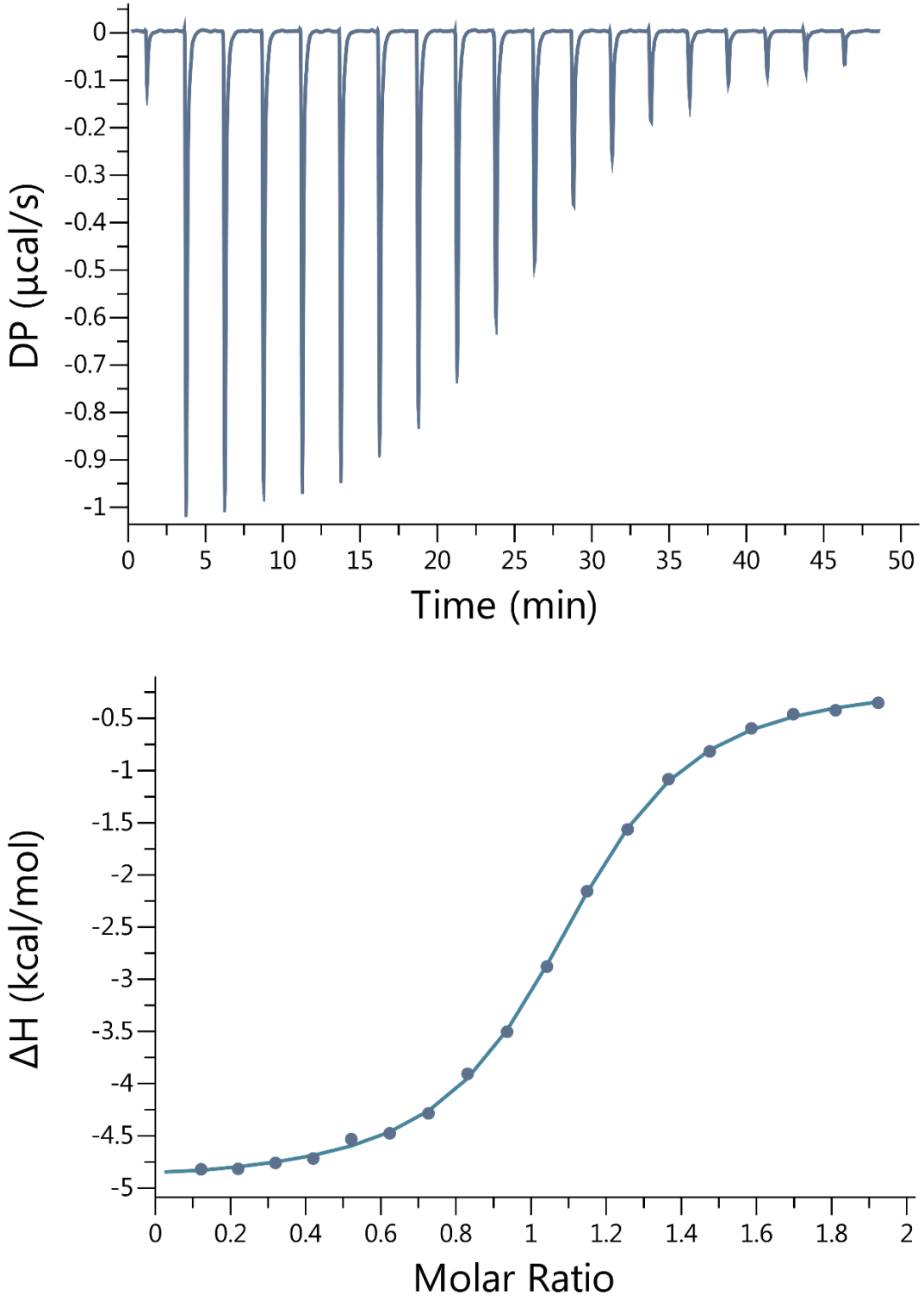

Figure S37. Isothermal Titration Calorimetry (ITC) curve obtained when a solution of **1** (100 µM) in the cell was titrated with **11** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 3.57 \times 10^5$ M^{-1} and $\Delta H = -4.83 \pm 0.036$ kcal•mol^{-1}.

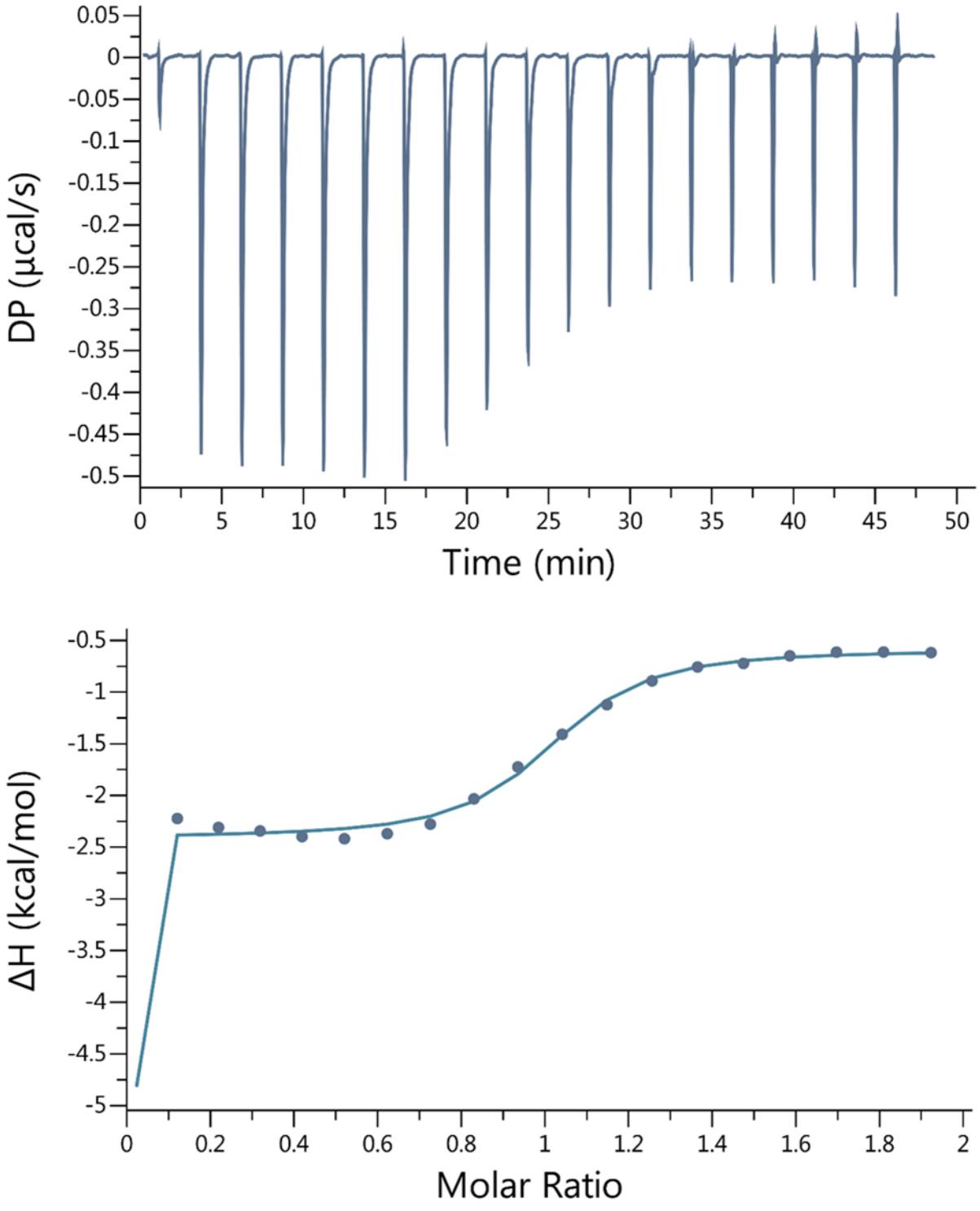

Figure S38. Isothermal Titration Calorimetry (ITC) curve obtained through competition binding studies. A solution of **1** (100 µM) and **5** (500 µM) in the cell was titrated with **12** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 4.55 \times 10^8$ M^{-1} and $\Delta H = -10.4 \pm 0.064$ kcal•mol^{-1}.

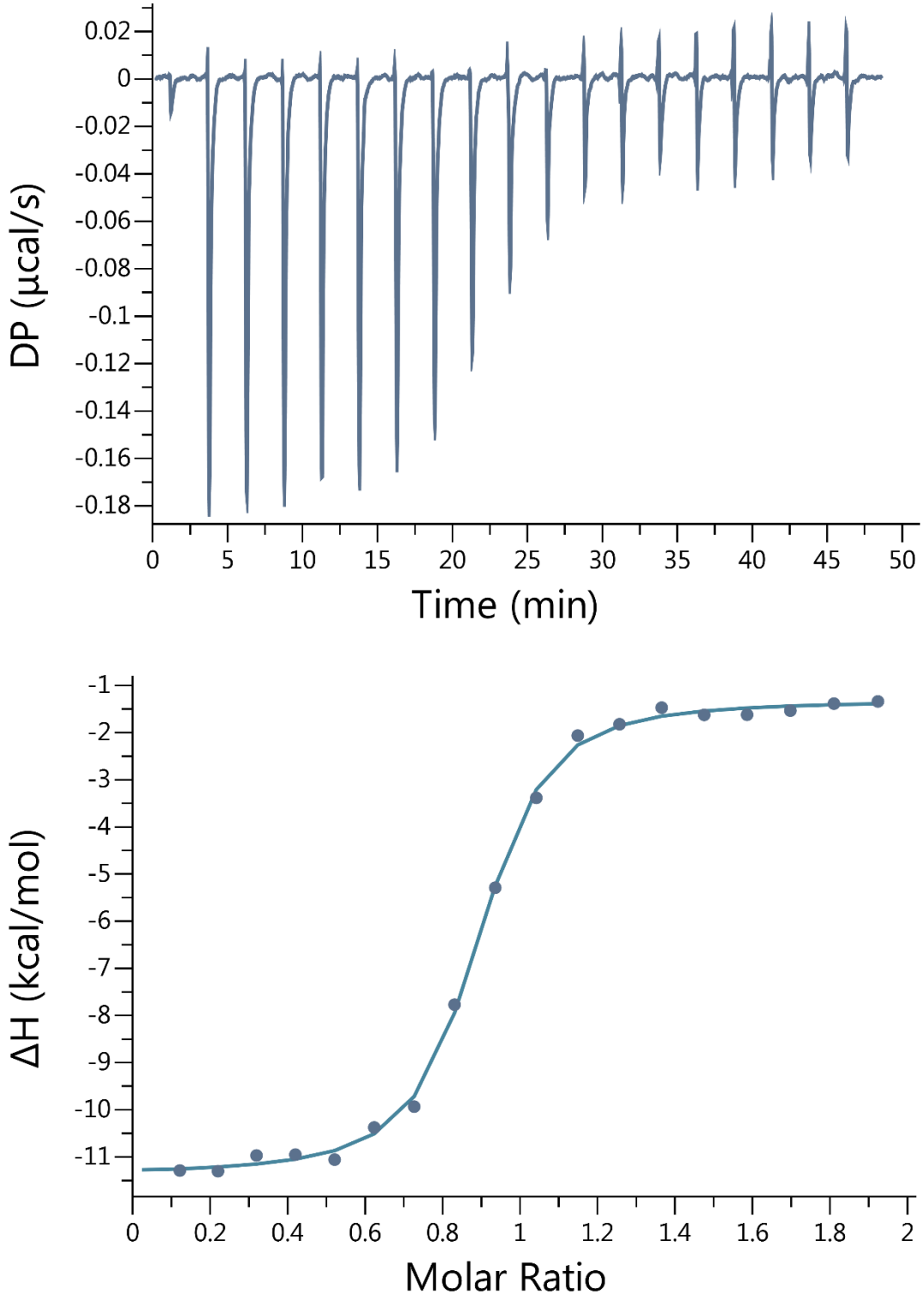

Figure S39. Isothermal Titration Calorimetry (ITC) curve obtained when a solution of **1** (10.0 µM) in the cell was titrated with **13** (100 µM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 1.13 \times 10^7$ M^{-1} and $\Delta H = -10.1 \pm 0.119$ kcal•mol^{-1}.

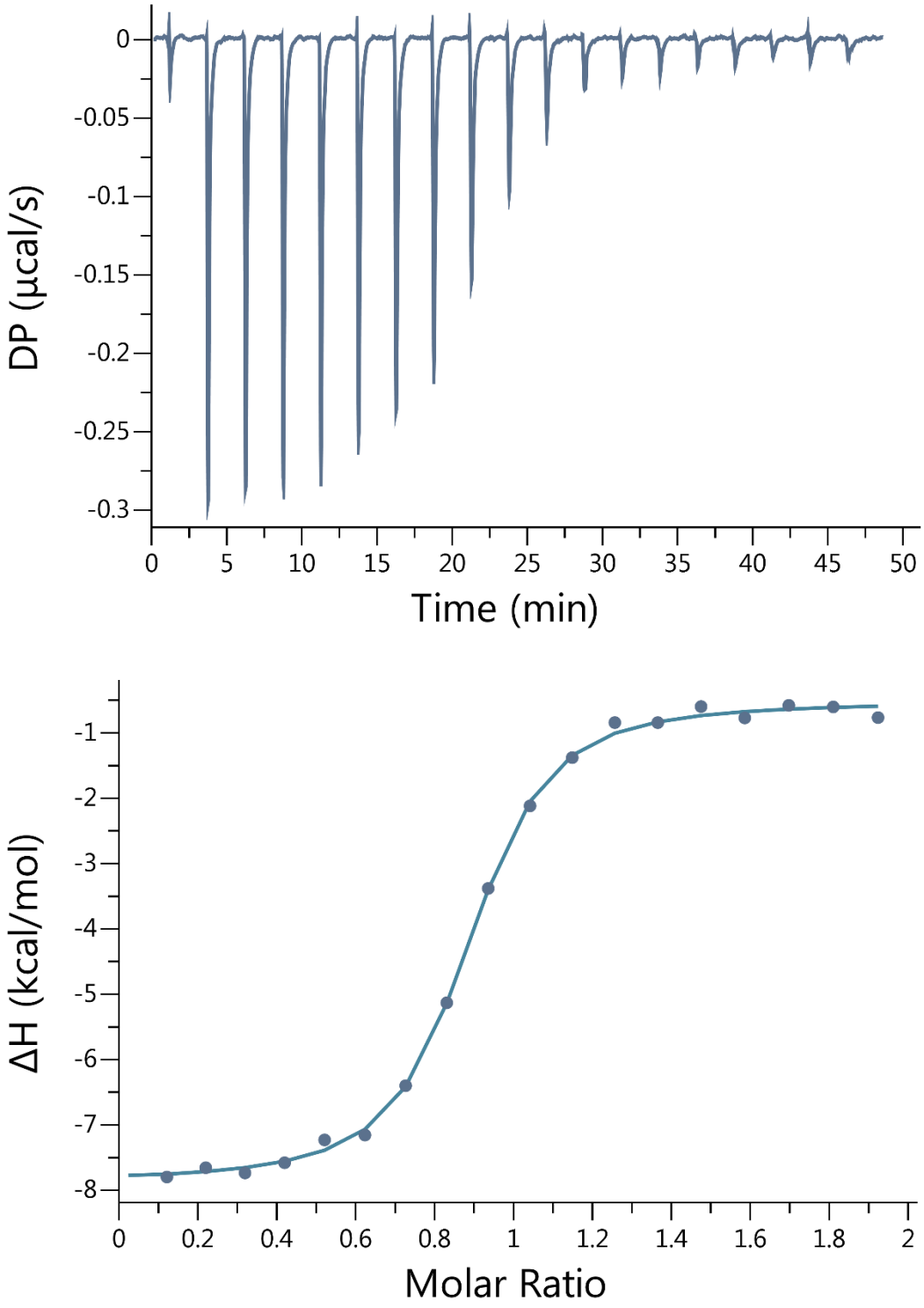

Figure S40. Isothermal Titration Calorimetry (ITC) curve obtained when a solution of **1** (20.0 µM) in the cell was titrated with **14** (200 µM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 4.08 \times 10^6$ M^{-1} and $\Delta H = -7.41 \pm 0.084$ kcal•mol^{-1}.

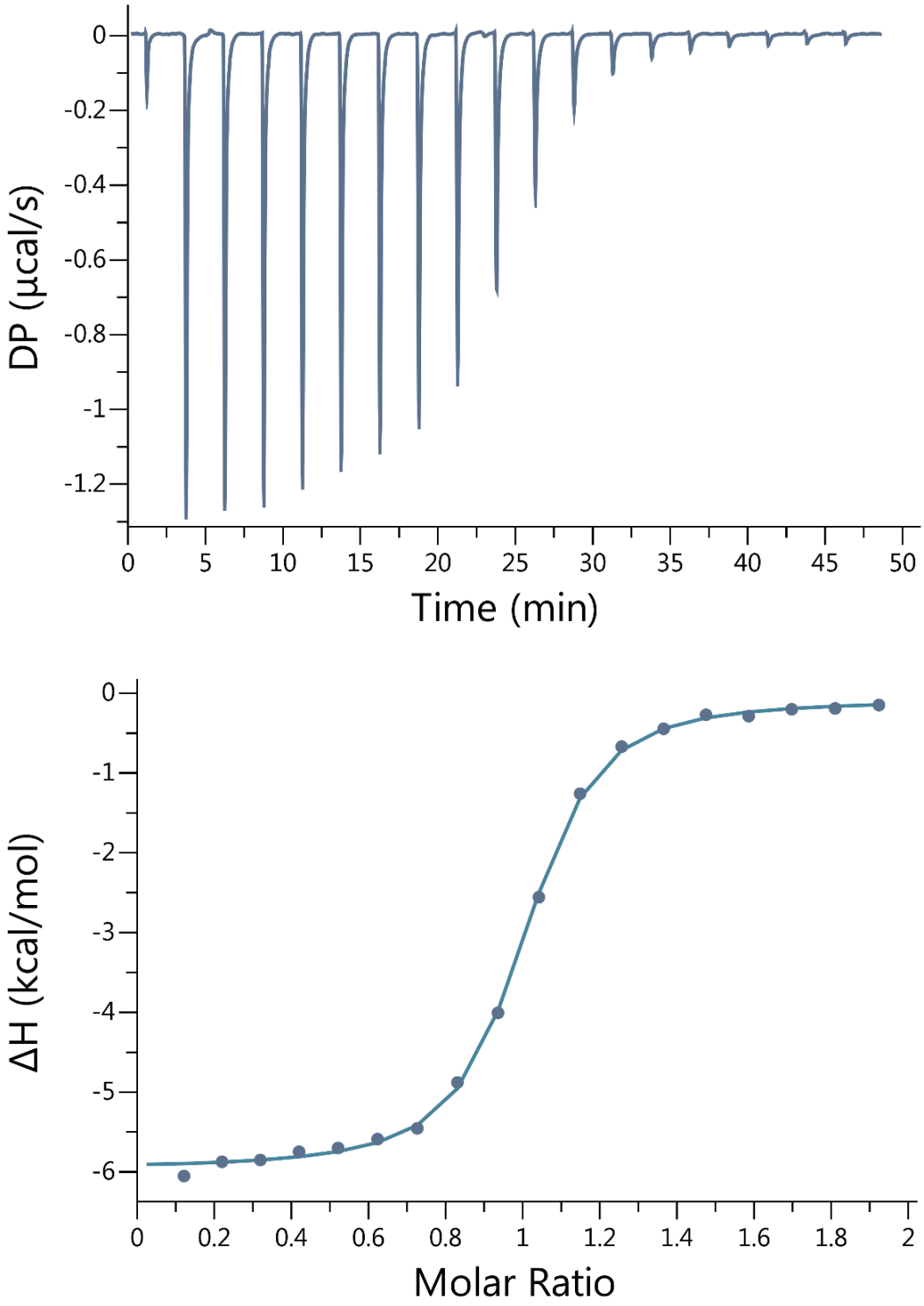

Figure S41. Isothermal Titration Calorimetry (ITC) curve obtained when a solution of **1** (100 µM) in the cell was titrated with **15** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 1.11 \times 10^6\ M^{-1}$ and $\Delta H = -5.88 \pm 0.049$ kcal•mol^{-1}.

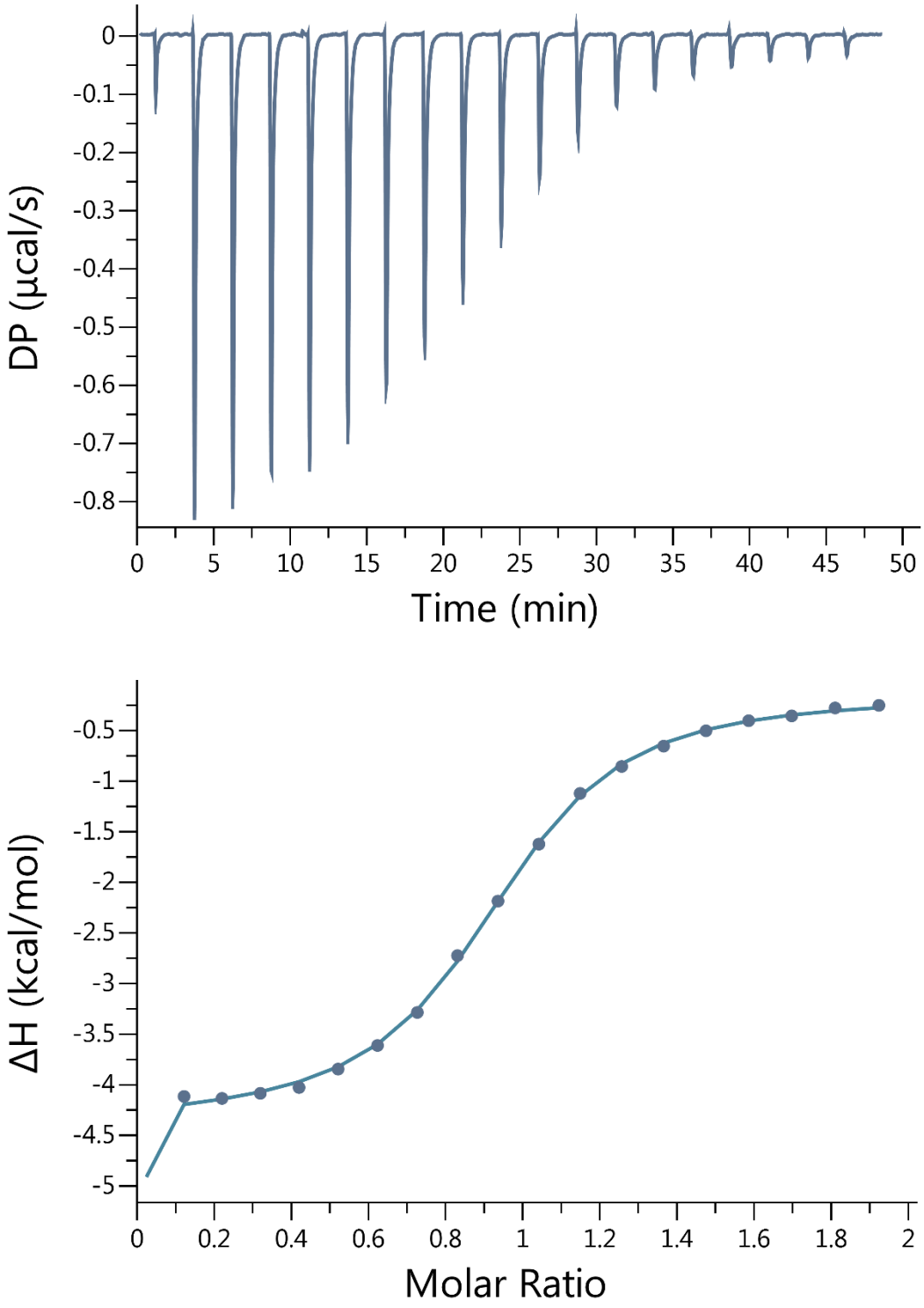

Figure S42. Isothermal Titration Calorimetry (ITC) curve obtained through competition binding studies. A solution of **1** (100 µM) and **19** (500 µM) in the cell was titrated with **16** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 8.77 \times 10^6$ M^{-1} and $\Delta H = -10.5 \pm 0.044$ kcal•mol^{-1}.

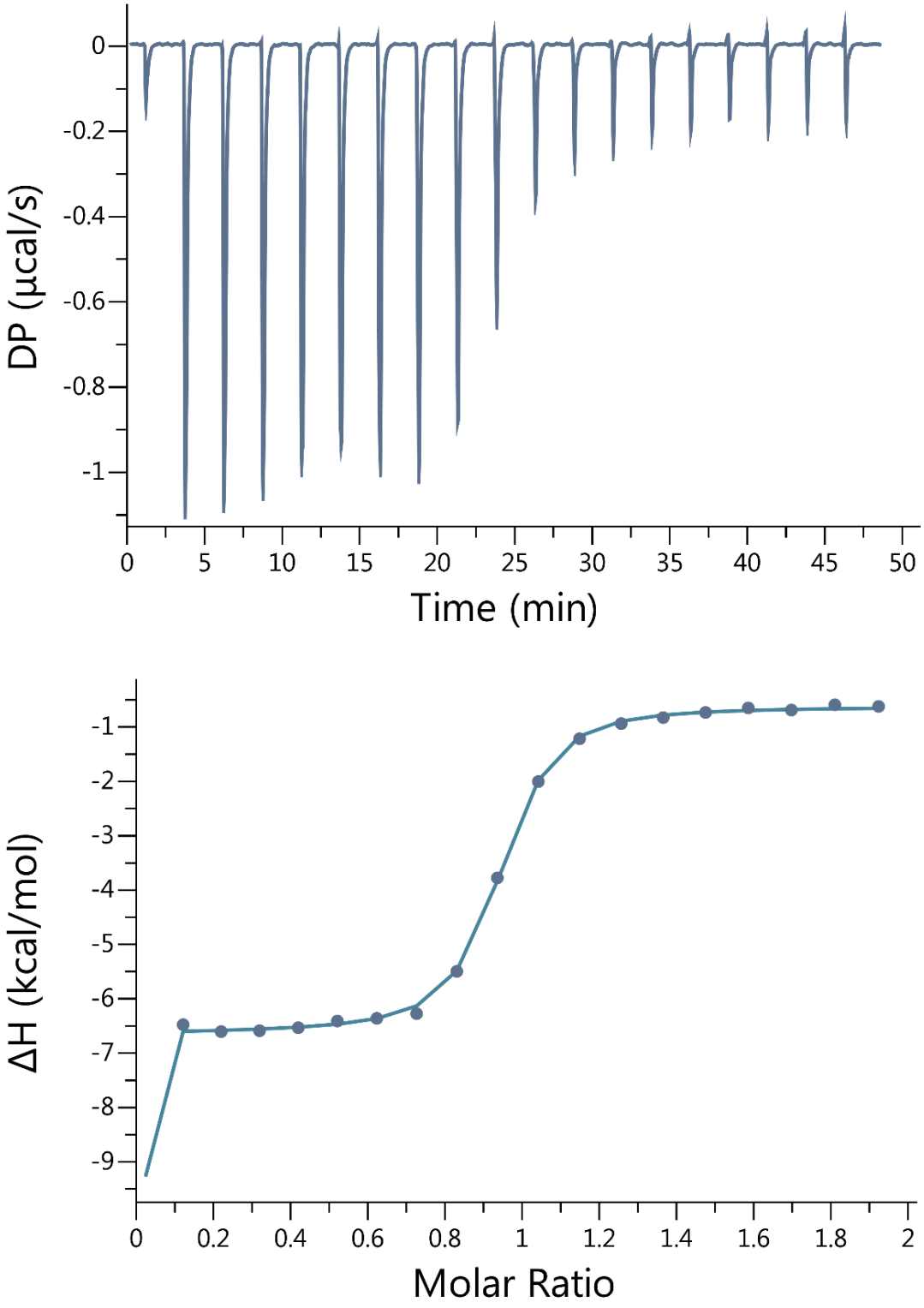

Figure S43. Isothermal Titration Calorimetry (ITC) curve obtained through competition binding studies. A solution of **1** (100 µM) and **19** (500 µM) in the cell was titrated with **17** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 5.81 \times 10^7$ M^{-1} and $\Delta H = -12.4 \pm 0.045$ kcal•mol^{-1}.

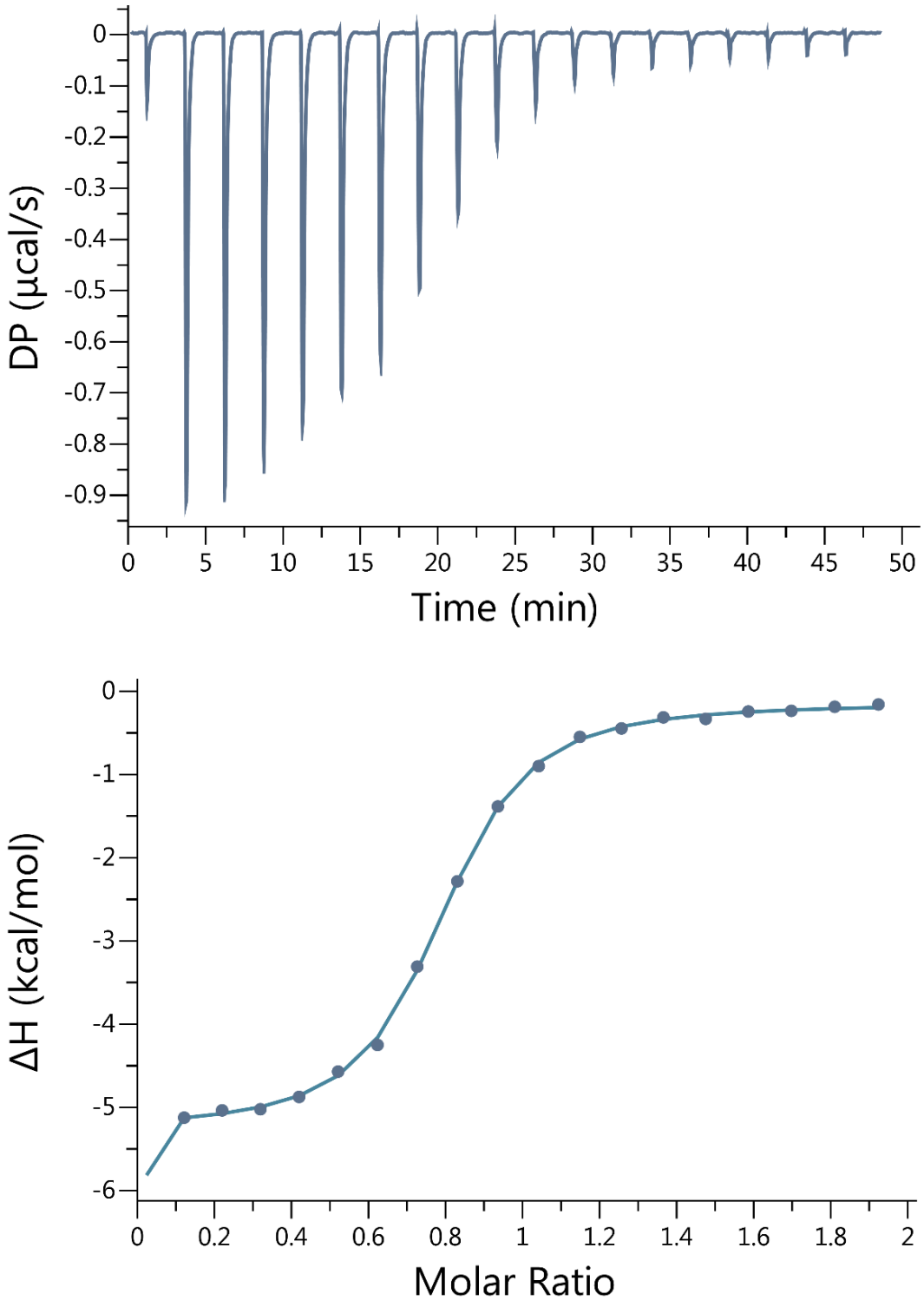

Figure S44. Isothermal Titration Calorimetry (ITC) curve obtained through competition binding studies. A solution of **1** (100 µM) and **5** (500 µM) in the cell was titrated with **18** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 3.57 \times 10^8$ M^{-1} and $\Delta H = -13.7 \pm 0.039$ kcal•mol^{-1}.

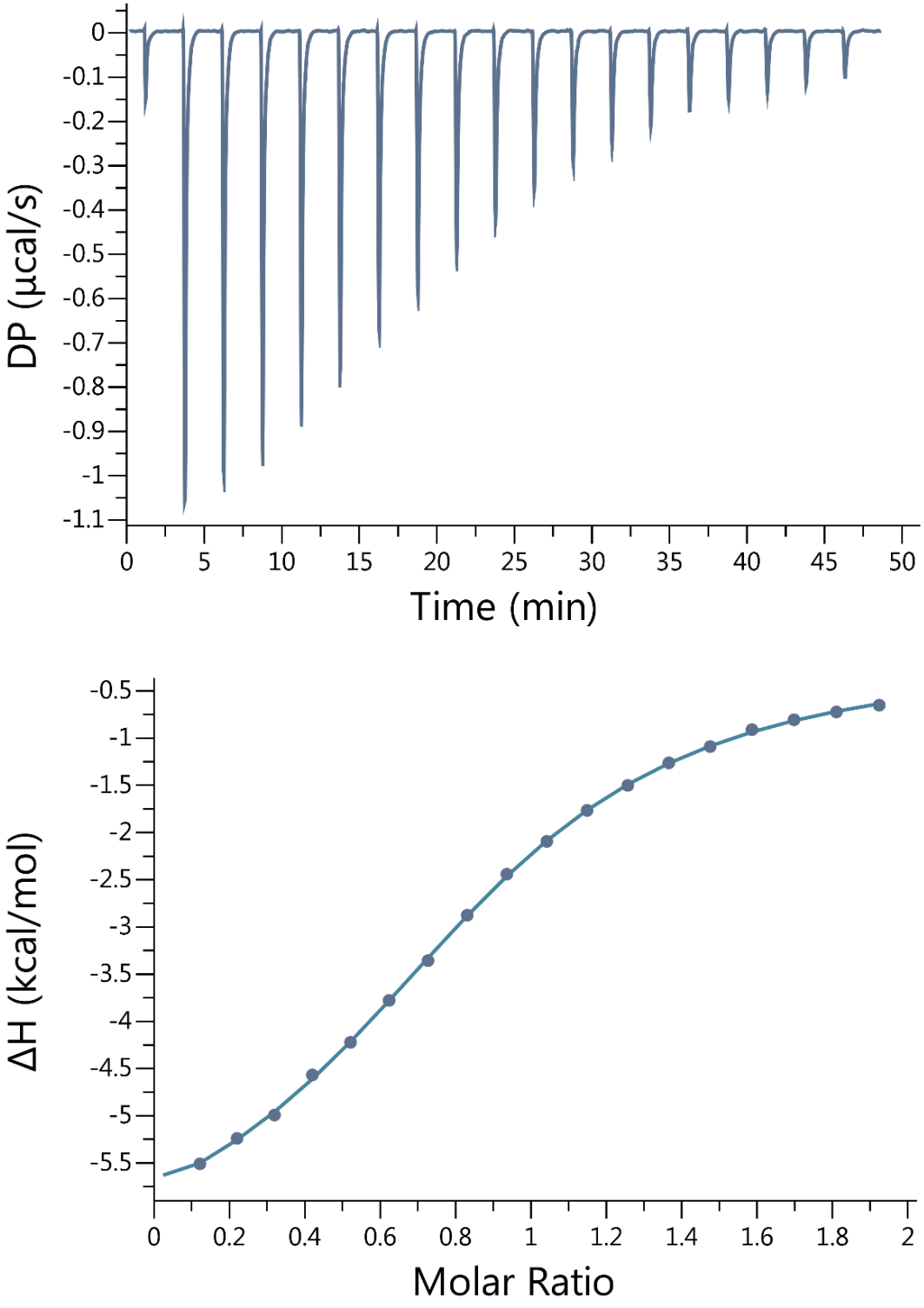

Figure S45. Isothermal Titration Calorimetry (ITC) curve obtained when a solution of **1** (100 µM) in the cell was titrated with **19** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 5.95 \times 10^4\ M^{-1}$ and $\Delta H = -6.61 \pm 0.088$ kcal•mol^{-1}.

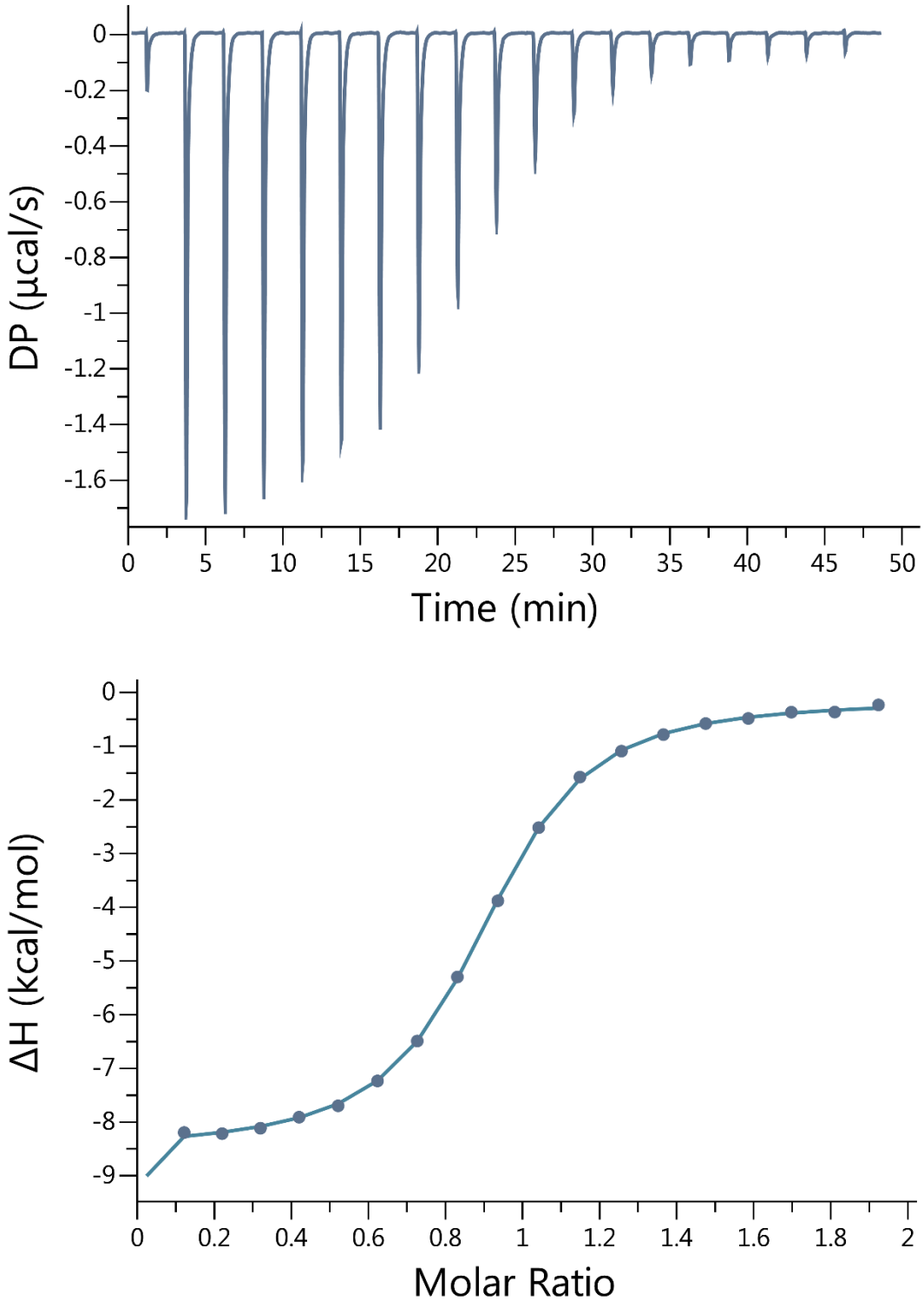

Figure S46. Isothermal Titration Calorimetry (ITC) curve obtained through competition binding studies. A solution of **1** (100 µM) and **19** (500 µM) in the cell was titrated with **20** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 1.32 \times 10^7$ M^{-1} and $\Delta H = -14.7 \pm 0.036$ kcal•mol^{-1}.

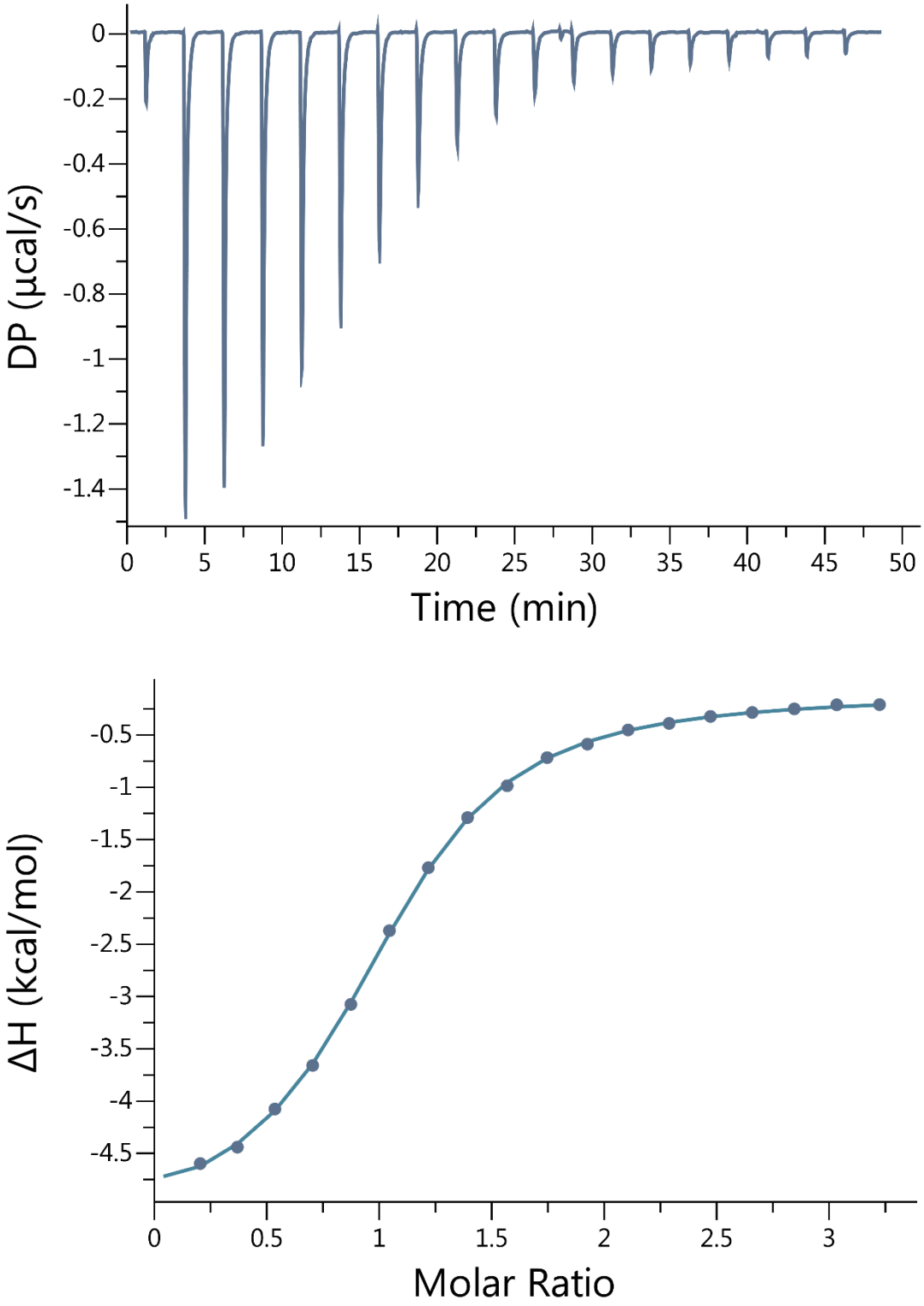

Figure S47. Isothermal Titration Calorimetry (ITC) curve obtained when a solution of **1** (100 µM) in the cell was titrated with **21** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 9.80 \times 10^4$ M^{-1} and $\Delta H = -5.09 \pm 0.042$ kcal•mol^{-1}.

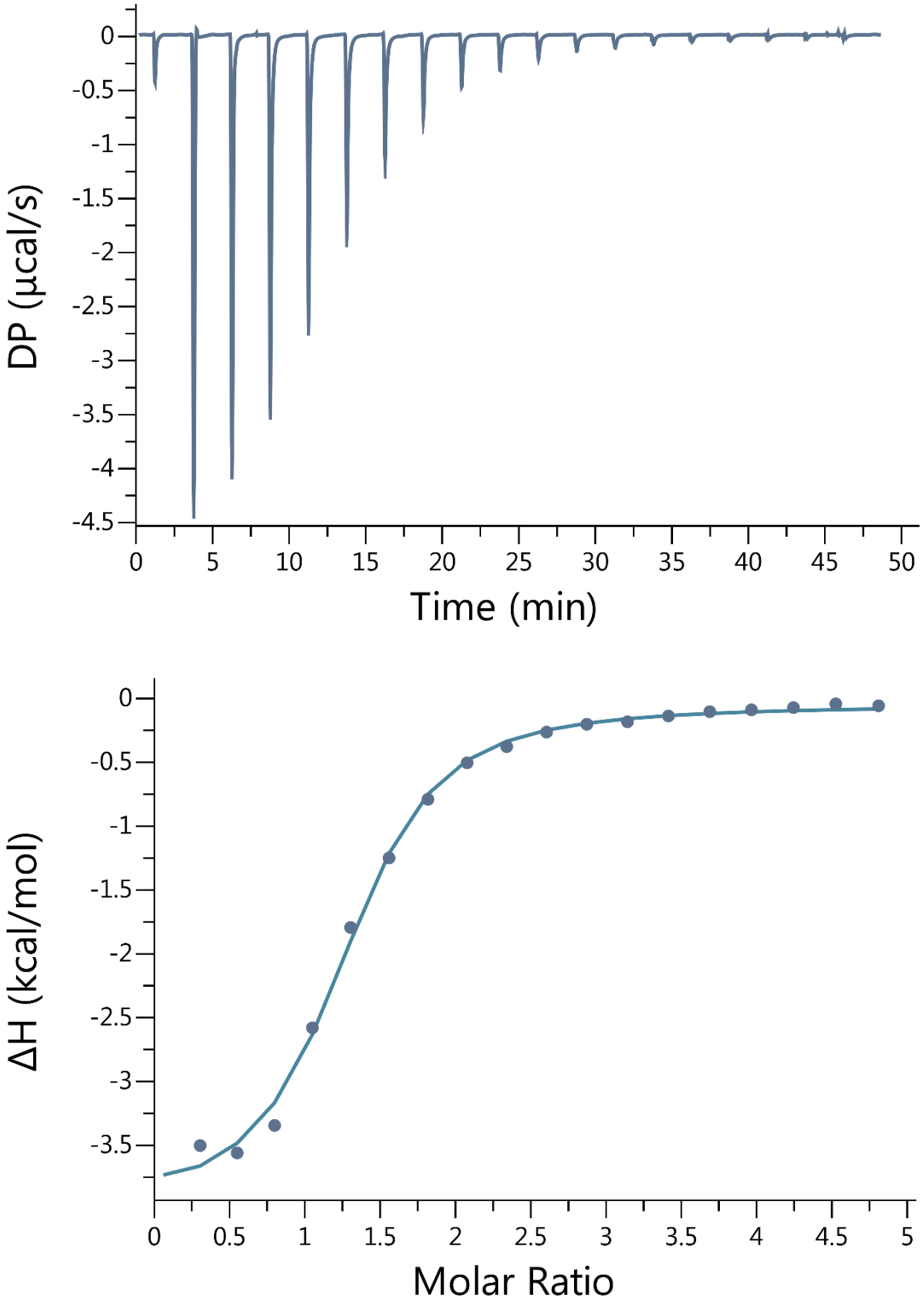

Figure S48. Isothermal Titration Calorimetry (ITC) curve obtained when a solution of **1** (200 µM) in the cell was titrated with **22** (5.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 5.61 \times 10^4\ M^{-1}$ and $\Delta H = -3.98 \pm 0.094$ kcal•mol^{-1}.

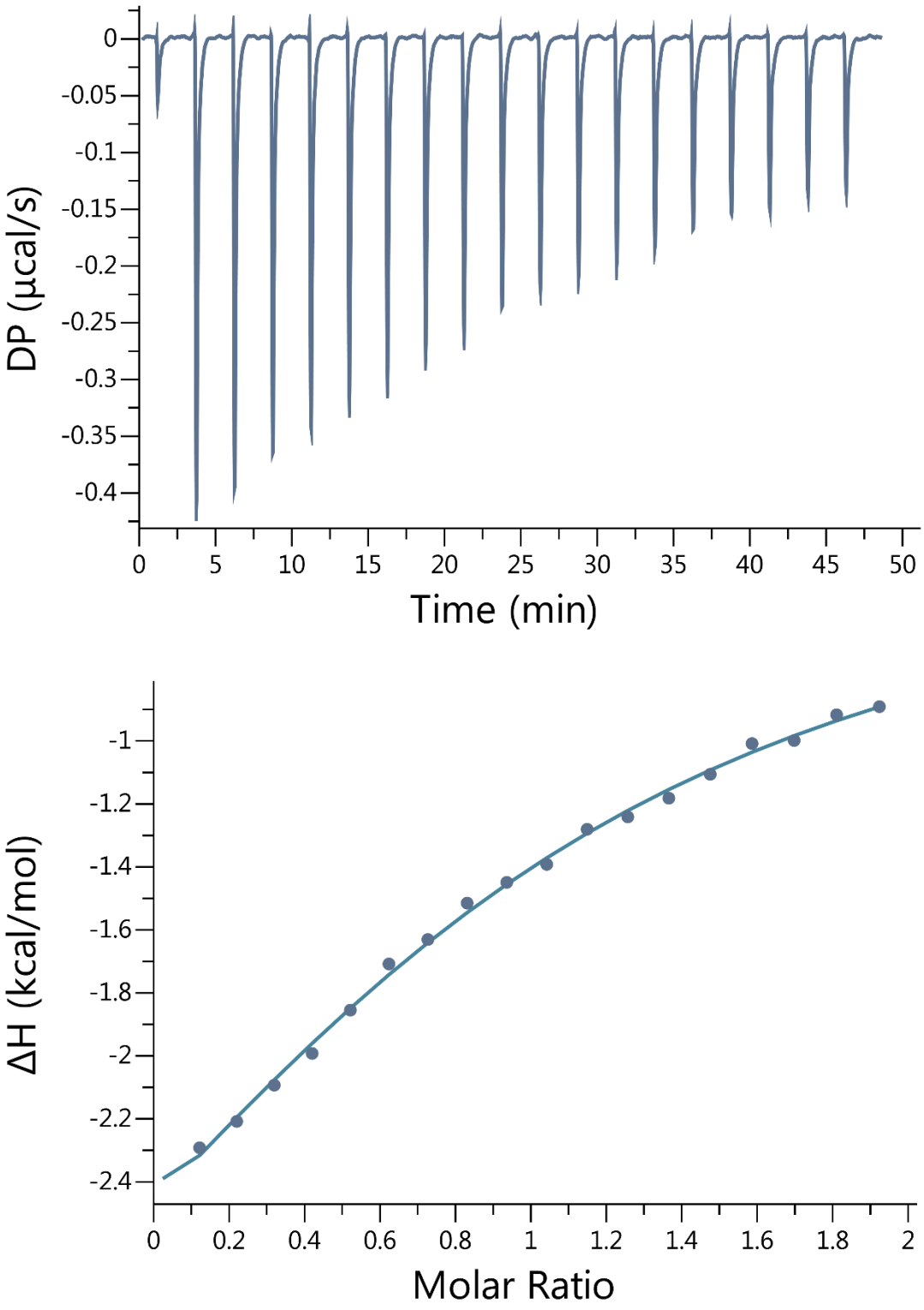

Figure S49. Isothermal Titration Calorimetry (ITC) curve obtained when a solution of **1** (100 µM) in the cell was titrated with **23** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 8.47 \times 10^3\ M^{-1}$ and $\Delta H = -4.95 \pm 2.30$ kcal•mol^{-1}.

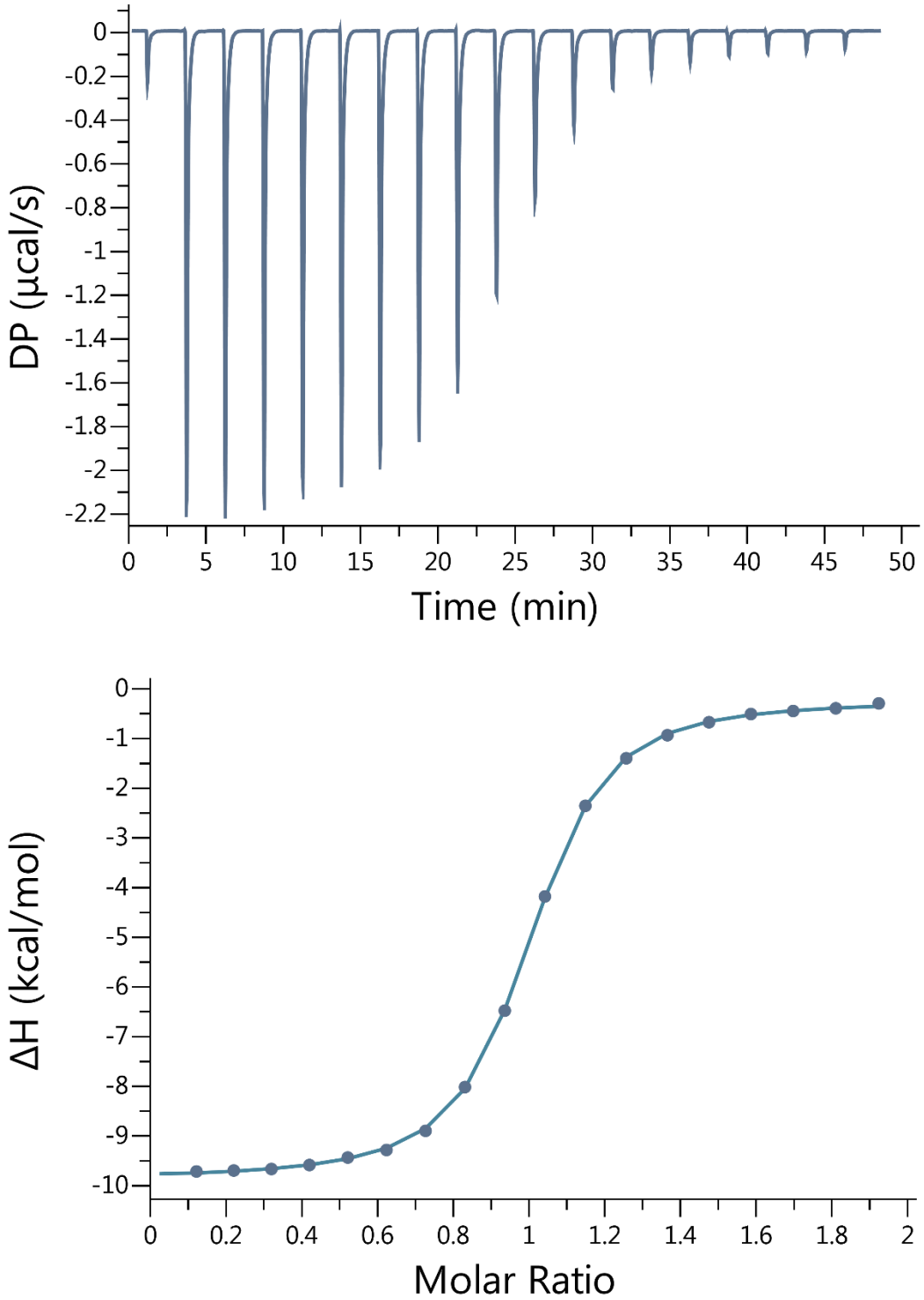

Figure S50. Isothermal Titration Calorimetry (ITC) curve obtained when a solution of **1** (100 µM) in the cell was titrated with **24** (1.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 9.43 \times 10^5\ M^{-1}$ and $\Delta H = -9.63 \pm 0.025$ kcal•mol^{-1}.

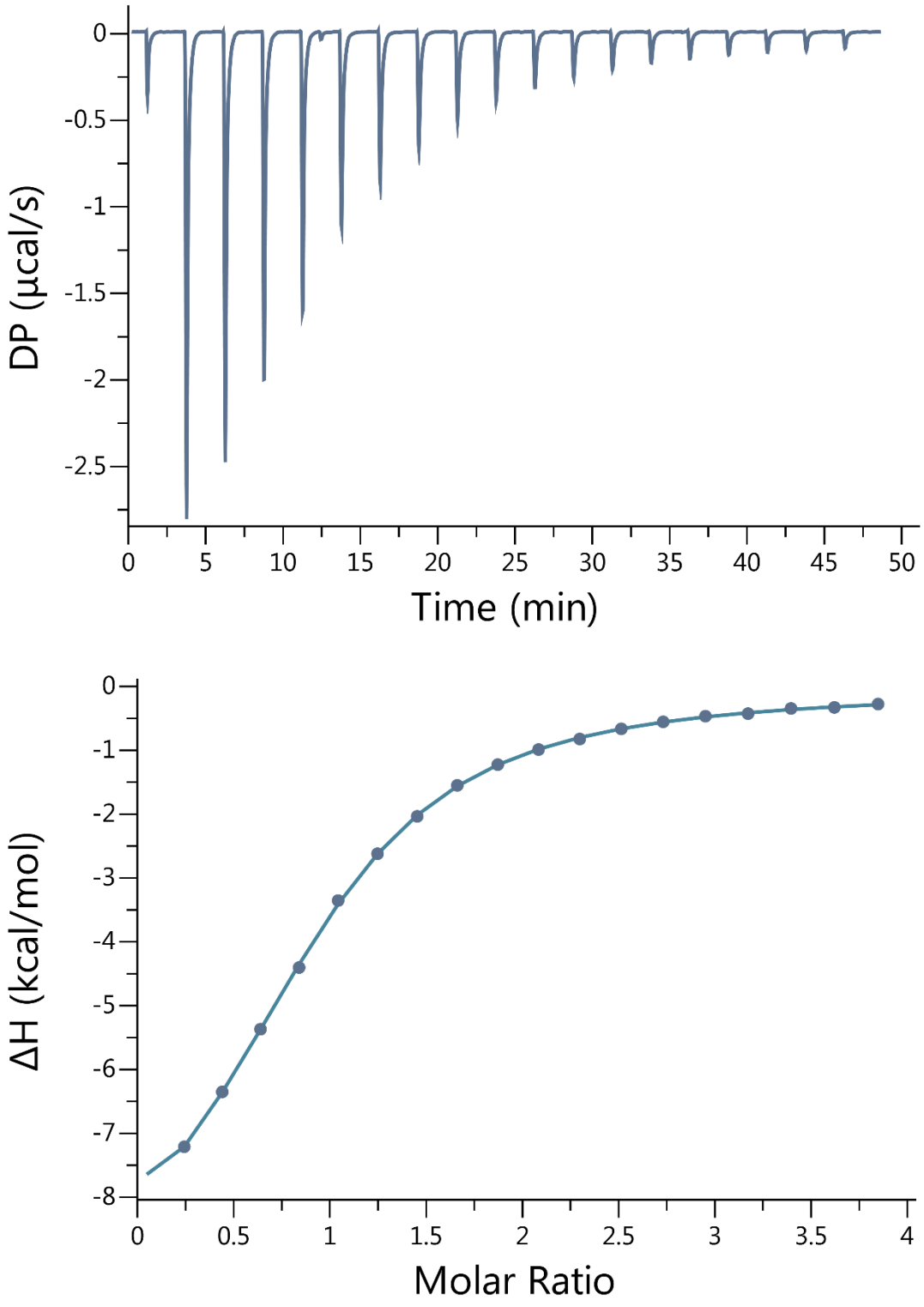

Figure S51. Isothermal Titration Calorimetry (ITC) curve obtained when a solution of **1** (100 µM) in the cell was titrated with **25** (2.00 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 3.70 \times 10^4\ M^{-1}$ and $\Delta H = -9.99 \pm 0.129$ kcal•mol^{-1}.

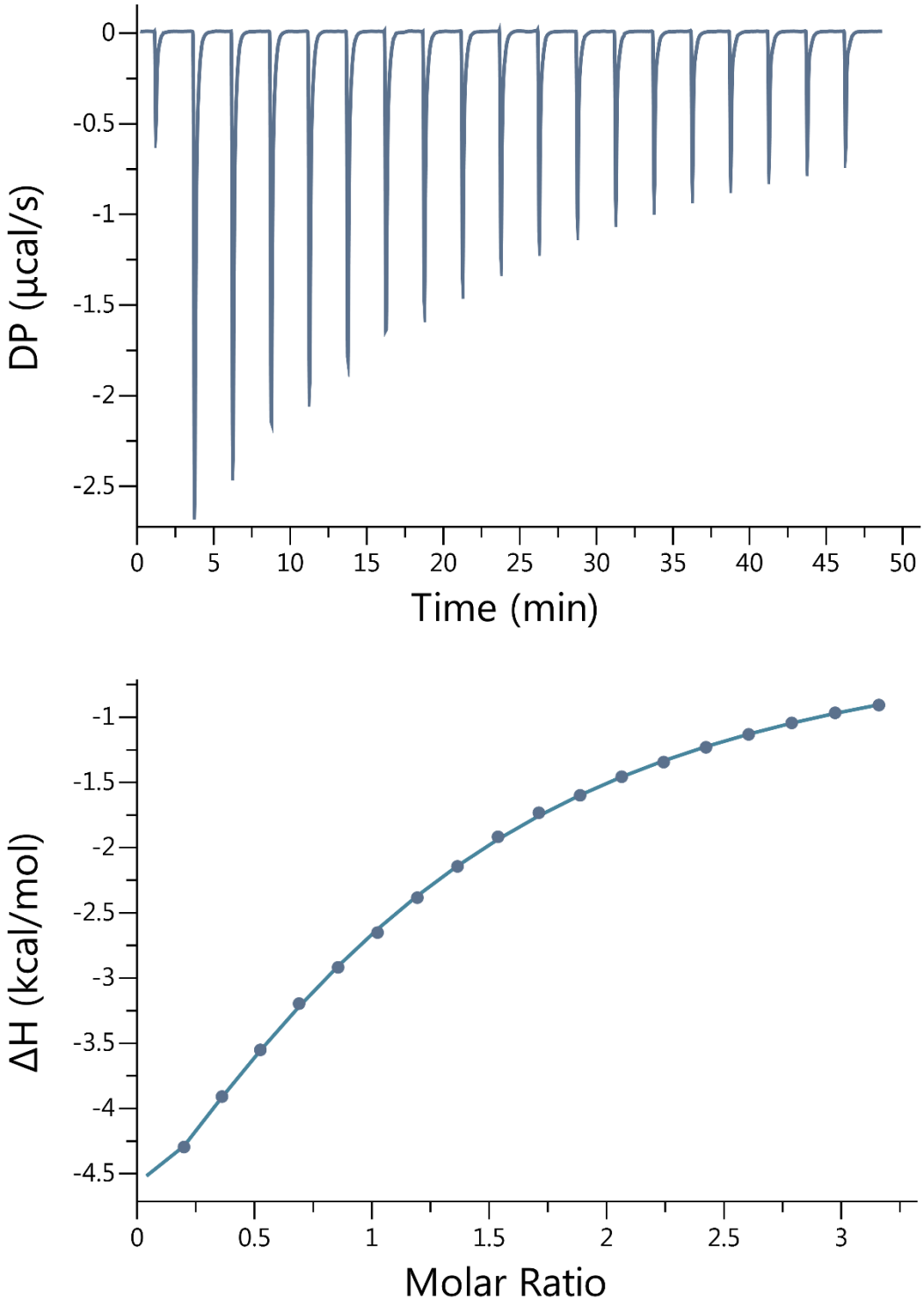

Figure S52. Isothermal Titration Calorimetry (ITC) curve obtained when a solution of **1** (200 µM) in the cell was titrated with **26** (2.40 mM) in the syringe at 298.0 K in 20 mM sodium phosphate buffered water at pH 7.4. $K_a = 4.67 \times 10^3$ M^{-1} and $\Delta H = -8.92 \pm 0.445$ kcal•mol^{-1}.

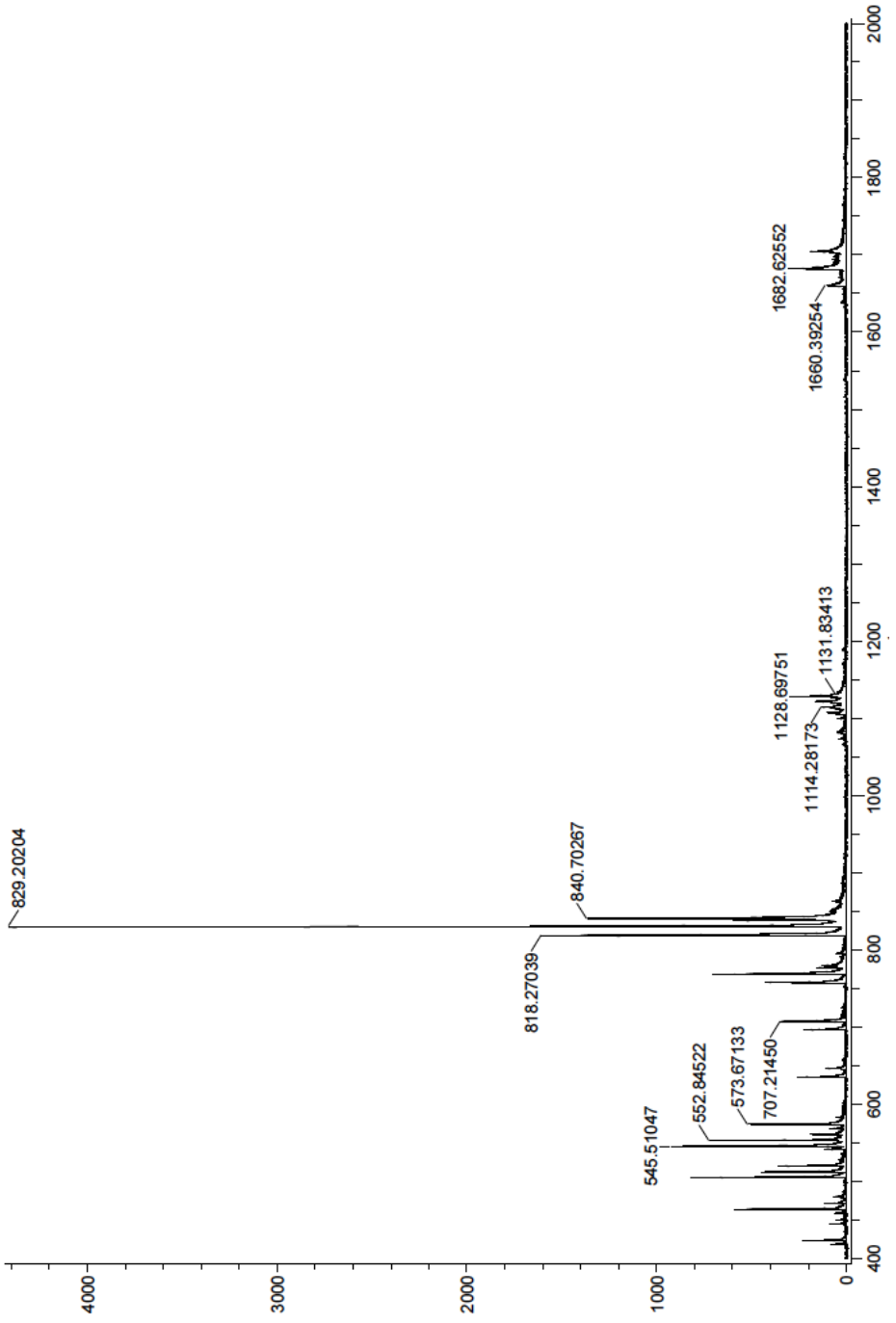

Figure S53. Electrospray mass spectrum for **1** recorded in the negative ion mode. The peak at 829.20204 corresponds to the $[M + 1H - 3Na]^{2-}$ ion.