

# **Isothermal Calorimetric Titrations on Charge-Assisted Halogen Bonds: Role of Entropy, Counterions, Solvent, and Temperature**

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## **Supporting Information**

### **Contents:**

- I) Syntheses and Experimental Data
- II) Experimental Setup and ITC-Measurements
- III) X-Ray Structural Analysis

## I) Syntheses and Experimental Data

### A) General Information

#### A.1) Chemicals

Chemicals were obtained from *ABCR*, *Acros Organics*, *Alfa Aesar*, *Merck*, *Sigma-Aldrich* or *VWR*. Commercially available reagents and starting materials were, unless mentioned otherwise, used without further purification. Solvents which were to be used in moisture-sensitive experiments were taken from a solvent drying system by *M. Braun* (type: *MB SPS-800*) and stored under an argon atmosphere. Other solvents were used after single distillation.

For reactions including oxygen- or moisture-sensitive reagents, glassware was baked out under high-vacuum conditions and procedures carried out under an argon atmosphere. Reagents were injected via a septum or added under argon counterflow.

#### A.2) Appliances and Materials

Isothermal titration calorimetry (ITC) experiments were performed on a *MicroCal VP-ITC* device.

Thin layer chromatography (TLC) was performed on plates from *Merck* (silica gel 60,  $F_{254}$ ). Detection of the substances was obtained by fluorescence detection under UV light (wavelength  $\lambda = 254$  nm). The corresponding  $R_f$  values and solvents used as eluents are listed in the experimental part. Column chromatographies were performed with silica gel (grain size 0.04-0.063 cm, *Merck*, *Si60*) at approximately 1.5 atm (hand pump). The used eluent relations are listed with the respective experiments.

Nuclear magnetic resonance spectra (NMR-spectra) were obtained on instruments of the type *AV-250* (for  $^1\text{H}$ -spectra), *AV-360* (for  $^1\text{H}$ - and  $^{13}\text{C}$ -spectra), *AV-500* (for  $^1\text{H}$ -spectra) or *AV-500c* (for  $^1\text{H}$ - and  $^{13}\text{C}$ -spectra) from *Bruker*. Chemical shifts ( $\delta$ ) are given as parts per million (ppm) and refer to the shift of the hydrogen or carbon atoms in the solvents used ( $\text{CDCl}_3$ ,  $\text{CD}_3\text{CN}$ ). The following abbreviations were

used for the assignment of the signals and their multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). The given coupling constants  $J$  are listed as the average of the experimental findings.

Mass spectrometry spectra (MS-spectra) were obtained by using electrospray ionization (ESI). Assigned  $m/z$ -relations are listed in ascending order. ESI-spectra were measured on a *Finnigan LCQ classic* or a *500-MS LC Ion Trap Mass Spectrometer* by *Varian*. EI-spectra were measured on a *MAT 8200* by *Finnigan*.

Infrared-spectra (IR-spectra) were measured on a *JASCO IR-4100* spectrometer directly from the substance via attenuated total reflectance (ATR-IR). The signals are labelled with the following abbreviations: vs (very strong), s (strong), m (medium), w (weak), vw (very weak).

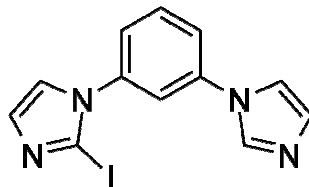
UV-spectra (UV/Vis-spectra) were measured on a *Lambda 35* spectrometer from *Perkin Elmer Instruments*.

## B) Syntheses

The synthesis of the following compounds has been described previously<sup>[1-1]</sup>: *m*-II-1<sup>Me</sup>/OTf, *p*-II-1<sup>Me</sup>/OTf, *m*-HH-1<sup>Me</sup>/OTf, *p*-HH-1<sup>Me</sup>/OTf, *m*-II-2, and *p*-II-2.

<sup>[1-1]</sup> Walter, S. M.; Kniep, F.; Herdtweck, E.; Huber, S. M.; *Angew. Chem. Int. Ed.* **2011**, *50*, 7181

### B.1) Synthesis of 1-(3-(Imidazol-1-yl)phenyl)-2-iodo-imidazole



Under an argon atmosphere, 0.30 g of 1,3-bis(imidazol-1-yl)benzene (1.43 mmol, 1.0 equiv.) were dissolved in 20 mL of THF and cooled to -78 °C. Over the course of 90 min, 0.69 mL of 2.5M *n*-BuLi (1.71 mmol, 1.2 equiv.) were added dropwise and the mixture was stirred for 90 min at -78 °C. Subsequently, 0.31 g of iodine (1.86 mmol, 1.3 equiv.) in 5 mL of THF were added slowly and the mixture was warmed up to room temperature over several hours. After stirring for 20 h, the solvent was evaporated. The residue was dissolved in 50 mL of CH<sub>2</sub>Cl<sub>2</sub> and was washed with H<sub>2</sub>O (50 mL) and a saturated solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (40 mL). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated. After column chromatography (eluent: ethyl acetate, *R<sub>f</sub>* = 0.09) 0.067 g (0.2 mmol, 14%) of the product were obtained as a pale yellow solid.

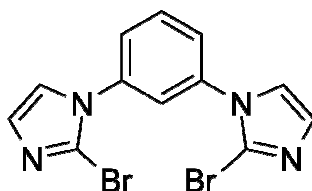
<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): 7.24-7.26 (m, 1H), 7.26-7.28 (m, 1H), 7.33-7.37 (m, 1H), 7.37-7.41 (m, 1H), 7.42-7.46 (m, 1H), 7.53-7.58 (m, 1H), 7.61-7.69 (m, 1H), 7.92-7.99 (s, 1H)

<sup>13</sup>C-NMR (500 MHz, CDCl<sub>3</sub>): 90.0, 118.2, 119.9, 121.9, 124.8, 125.7, 131.1, 131.2, 133.5, 135.6, 138.2, 139.8

Elemental analysis:	<i>calc.</i> :	C: 42.88	H: 2.70	N: 16.67
	<i>found</i> :	C: 43.21	H: 2.83	N: 16.36

ESI-MS: 169 [(M + 2H<sup>+</sup>)<sup>2+</sup>], 337 [(M + H<sup>+</sup>)<sup>+</sup>]

## B.2) Synthesis of 1,3-Bis(2-bromo-imidazol-1-yl)benzene



The compound was prepared according to a slightly modified published procedure.<sup>[1-2]</sup> Under an argon atmosphere, 0.10 g of 1,3-bis(imidazol-1-yl)benzene (0.48 mmol, 1.0 equiv.) were dissolved in 15 mL of THF and cooled to -78 °C. Over the course of 1 h, 0.45 mL of 2.5M *n*-BuLi (1.09 mmol, 2.3 equiv.) were added dropwise. Subsequently, 0.32 g of tetrabromo methane (0.95 mmol, 2.0 equiv.) were added and the mixture was stirred for 75 min at -78 °C. The reaction was stopped with an aqueous solution of NH<sub>4</sub>Cl, extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL), washed with a saturated solution of NaCl and dried over Na<sub>2</sub>SO<sub>4</sub>. After evaporation of the solvent and subsequent column chromatography (eluent: ethyl acetate, R<sub>f</sub> = 0.57), 0.12 g of product (0.33 mmol, 69%) were obtained as a pale yellow solid.

<sup>[1-2]</sup> Boga, C., Vecchio, E. D., Forlani, L., Todesco, P. E., *Journal of Organometallic Chemistry* **2000**, 601, 233-236.

<sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>): 7.18 (d, <sup>3</sup>J = 1.5 Hz, 2H), 7.21 (d, <sup>3</sup>J = 1.5 Hz, 2H), 7.46 (t, <sup>3</sup>J = 2.1 Hz, 1H), 7.50-7.53 (m, 2H), 7.63-7.70 (m, 1H)

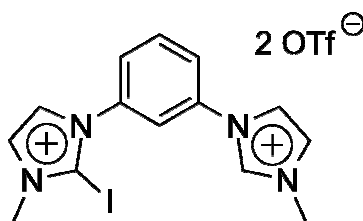
<sup>13</sup>C-NMR (500 MHz, CDCl<sub>3</sub>): 119.4, 123.7, 124.2, 126.7, 130.6, 131.0, 138.0

Elemental analysis:	<i>calc.</i> :	C: 39.16	H: 2.19	N: 15.22
	<i>found</i> :	C: 39.22	H: 2.34	N: 14.68

IR: 3100 (m), 3029 (vw), 2359 (vw), 2334 (vw), 1746 (vw), 1698 (vw), 1603 (m), 1483 (s), 1469 (s), 1440 (vs), 1382 (m), 1320 (m), 1272 (vs), 1253 (m), 1171 (w), 1123 (m), 999 (w), 971 (m), 913 (m), 870 (m), 803 (m), 760 (vs), 688 (s), 664 (w)

EI-MS: 368 [M]

**B.3) Synthesis of 2-Iodo-3-methyl-1-(3-(3-methyl-imidazolium-1-yl)phenyl)-imidazolium-bis(trifluoromethane sulfonate) [*m*-HI-1<sup>Me</sup>/OTf]**



Under an argon atmosphere, 0.04 g of 1-(3-(imidazol-1-yl)phenyl)-2-iodo-imidazole (0.12 mmol, 1.0 equiv.) were dissolved in 10 mL of CH<sub>2</sub>Cl<sub>2</sub>. Subsequently, 0.08 mg of methyl trifluoromethane sulfonate (0.50 mmol, 4.2 equiv.) were added dropwise and the yellow solution was stirred for 72 h at room temperature. The resulting liquid was separated from the solvent and stirred in 5 mL of Et<sub>2</sub>O for 24 h. After filtration, the residue was washed with several times with Et<sub>2</sub>O and dried in high vacuo, yielding 0.04 g (0.06 mmol, 51%) of the product as a slightly yellow solid.

<sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>CN): 3.93 (s, 3H), 3.96 (s, 3H), 7.57-7.62 (m, 1H), 7.69-7.75 (m, 1H), 7.75-7.78 (m, 1H), 7.78-7.83 (m, 3H), 7.89-7.93 (m, 2H), 9.02 (s, 1H)

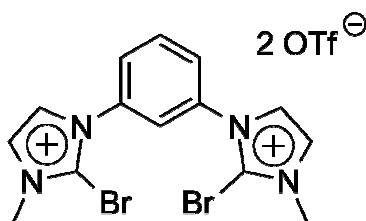
<sup>13</sup>C-NMR (500 MHz, CD<sub>3</sub>CN): 37.3, 40.8, 102.3, 122.0 (q, <sup>1</sup>J = 320.6 Hz), 122.3, 122.6, 125.7, 126.2, 127.5, 128.0, 129.6, 133.0, 136.7(1), 136.7(3), 138.7

Elemental analysis:	<i>calc.</i> :	C: 28.93	H: 2.28	N: 8.43	S: 9.65
	<i>found</i> :	C: 29.28	H: 2.44	N: 8.51	S: 9.78

IR: 3112 (vw), 2354 (vw), 1615 (w), 1581 (w), 1562 (w), 1557 (w), 1508 (w), 1277 (vs), 1250 (vs), 1224 (s), 1157 (vs), 1030 (vs), 870 (m), 805 (m), 770 (m), 687 (m)

ESI-MS: 183 [(M)<sup>2+</sup>], 365 [(M - H<sup>+</sup>)<sup>+</sup>], 389 [(M + Na)<sup>+</sup>], 515 [(M - OTf)<sup>+</sup>], 1178 [(2M + 3OTf)<sup>+</sup>], 1842 [(3M + 5OTf)<sup>+</sup>]

**B.4) Synthesis of 1,3-Bis(2-bromo-3-methyl-imidazolium)phenyl-bis(trifluoromethane sulfonate)**  
**[*m*-BrBr-1<sup>Me</sup>/OTf]**



Under an argon atmosphere, 0.10 g of 1,3-bis(2-bromo-imidazol-1-yl)benzene (0.27 mmol, 1.0 equiv.) were dissolved in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>. Subsequently, 0.11 mL of methyl trifluoromethane sulfonate (1.14 mmol, 4.2 equiv.) were added dropwise and the yellow solution was stirred at room temperature for 24 h. After filtration, the residue was washed with Et<sub>2</sub>O (2 x 20 mL). The resulting solid was filtered off and recrystallized from CH<sub>3</sub>CN with Et<sub>2</sub>O, yielding 0.09 g (0.13 mmol, 48%) of the product as a colorless solid.

<sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>CN): 3.91 (s, 6H), 7.73-7.76 (m, 3H), 7.78 (d, <sup>3</sup>J = 2.3 Hz, 2H), 7.81-7.83 (m, 1H), 7.83-7.86 (m, 1H), 7.91-7.97 (m, 1H)

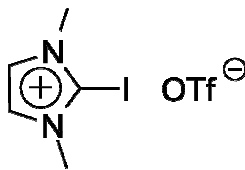
<sup>13</sup>C-NMR (500 MHz, CD<sub>3</sub>CN): 38.4, 122.0 (q, |<sup>1</sup>J| = 320.6 Hz), 124.8, 125.6, 126.0, 126.7, 130.2, 133.1, 136.6

Elemental analysis:	<i>calc.</i> :	C: 27.60	H: 2.03	N: 8.05	S: 9.21
	<i>found</i> :	C: 28.13	H: 2.14	N: 8.27	S: 9.23

IR: 3112 (w), 2349 (vw), 2170 (vw), 1973 (vw), 1610 (m), 1581 (w), 1519 (s), 1451 (w), 1422 (w), 1335 (vw), 1263 (vs), 1225 (s), 1157 (vs), 1032 (vs), 901 (w), 804 (m), 775 (m), 756 (m), 688 (m), 669 (w)

ESI-MS: 199 [(M)<sup>2+</sup>], 336 [(M-CH<sub>3</sub>)<sup>+</sup>], 385 [(M-H)<sup>+</sup>], 1243 [(2M + 3OTf)<sup>+</sup>]

**B.5) Synthesis of 2-Iodo-1,3-dimethyl-imidazolium [3]**



Under an argon atmosphere, 0.25 g of 2-iodo-1-methyl-1*H*-imidazole (1.20 mmol, 1.0 equiv.) were dissolved in 5 mL of CH<sub>2</sub>Cl<sub>2</sub>. 0.52 mL methyl trifluoromethane sulfonate (4.80 mmol, 4.0 equiv.) were added dropwise and the solution was stirred at room temperature for 24 h. The resulting precipitate was filtered off and recrystallized from CH<sub>3</sub>CN with Et<sub>2</sub>O. The precipitate was filtered off, washed with CH<sub>2</sub>Cl<sub>2</sub> dried under high vacuo, yielding 0.31 g (0.83 mmol, 69%) of the product as a white solid.

<sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>CN): 3.78 (s, 6H), 7.57 (s, 2H)

<sup>13</sup>C-NMR (500 MHz, CD<sub>3</sub>CN): 40.3, 99.9, 122.1, 127.2

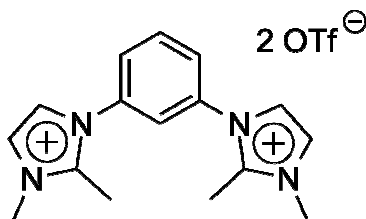
Elemental analysis:	<i>calc.</i> :	C: 19.37	H: 2.17	N: 7.53	S: 8.62
	<i>found</i> :	C: 19.54	H: 2.20	N: 7.46	S: 8.51

IR: 3156 (w), 3127 (w), 2949 (w), 2528 (vs), 2158 (vs), 2030 (vs), 1976 (vs), 1739 (w), 1616 (w), 1507 (w)

ESI-MS: 223 [(M-OTf)<sup>+</sup>]



**B.6)** Synthesis of 1,3-Bis(2-methyl-3-methyl-imidazolium)phenyl-bis(trifluoromethane sulfonate)  
[*m*-MeMe-1<sup>Me</sup>/OTf]



Under an argon atmosphere, 0.020 g of 1,3-bis(2-methyl-imidazol-1-yl)benzene (0.084 mmol, 1.0 equiv.) were dissolved in 4 mL of CH<sub>2</sub>Cl<sub>2</sub>. Subsequently, 0.04 mL of methyl trifluoromethane sulfonate (0.370 mmol, 4.4 equiv.) were added dropwise and the yellow solution was stirred at room temperature for 24 h. After filtration, the residue was washed with Et<sub>2</sub>O (2 x 5 mL). The resulting solid was filtered off and recrystallized from CH<sub>3</sub>CN with Et<sub>2</sub>O, yielding 0.030 g (0.053 mmol, 63%) of the product as a colorless solid.

<sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>CN): 2.50 (s, 6H), 3.82 (s, 6H), 7.43-7.54 (m, 4H), 7.57-7.62 (m, 1H), 7.70-7.75 (m, 2H), 7.85-7.92 (m, 1H)

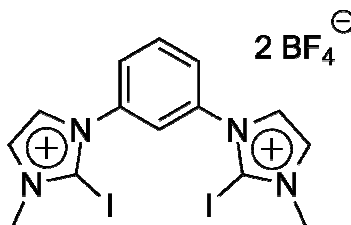
<sup>13</sup>C-NMR (500 MHz, CD<sub>3</sub>CN): 11.0, 36.1, 122.0 (q, <sup>1</sup>J = 320.6 Hz), 122.9, 123.9, 125.1, 129.4, 132.9, 136.8, 146.7

Elemental analysis:	<i>calc.</i> :	C: 38.16	H: 3.56	N: 9.89	S: 11.32
	<i>found</i> :	C: 36.68	H: 3.41	N: 9.46	S: 11.39

IR: 3136 (w), 2354 (vw), 1605 (w), 1586 (vw), 1528 (m), 1504 (vw), 1446 (w), 1412 (w), 1254 (vs), 1220 (vs), 1152 (vs), 1022 (vs), 886 (w), 756 (m), 688 (m), 664 (w)

ESI-MS: 134 [(M)<sup>2+</sup>], 267 [(M-H)<sup>+</sup>], 417 [(M + OTf)<sup>+</sup>], 982 [(2M + 3OTf)<sup>+</sup>], 1549 [(3M + 5OTf)<sup>+</sup>]

**B.7) Synthesis of 1,3-Bis(2-iodo-3-methyl-imidazolium)phenyl-bis(tetrafluoro borate) [*m*-II-1<sup>Me</sup>/BF<sub>4</sub>]**



Under an argon atmosphere, 0.14 g of trimethyloxonium tetrafluoro borate (0.95 mmol, 2.9 equiv.) were suspended in 25 mL of CH<sub>2</sub>Cl<sub>2</sub>. Subsequently, 0.15 g of 1,3-bis(2-iodo-imidazol-1-yl)benzene (0.33 mmol, 1.0 equiv.) were added and the suspension was stirred at room temperature for 4 d. After removal of the solvent, the resulting solid was recrystallized from CH<sub>3</sub>CN with Et<sub>2</sub>O, yielding 0.10 g (0.15 mmol, 45%) of the product as a colorless solid.

<sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>CN): 3.92 (s, 6H), 7.61-7.65 (m, 1H), 7.76-7.83 (m, 6H), 7.90-7.97 (m, 1H)

<sup>13</sup>C-NMR (500 MHz, CD<sub>3</sub>CN): 40.8, 102.0, 126.6, 127.5, 128.1, 130.8, 133.0, 138.5

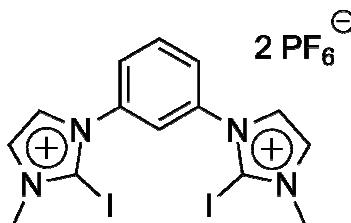
Elemental analysis: *calc.*: C: 25.26 H: 2.12 N: 8.42

*found*: C: 24.45 H: 2.16 N: 8.29

IR: 3131 (vw), 1601 (w), 1572 (w), 1495 (m), 1456 (w), 1413 (w), 1326 (vw), 1282 (vw), 1229 (w), 1061 (vs), 1017 (vs), 809 (v), 761 (m), 688 (m), 664 (w)

ESI-MS: 246 [(M)<sup>2+</sup>], 477 [(M - CH<sub>3</sub>)<sup>+</sup>], 491[(M - H)<sup>+</sup>], 579 [(M + BF<sub>4</sub>)<sup>+</sup>]

**B.8)** Synthesis of 1,3-Bis(2-iodo-3-methyl-imidazolium)phenyl-bis(hexafluoro phosphate)  
[*m*-II-1<sup>Me</sup>/PF<sub>6</sub>]



50.0 mg (0.06 mmol, 1.0 equiv.) of *m*-II-1<sup>Me</sup>/Otf were dissolved in 1 mL of methanol. Subsequently, 24.0 mg (0.14 mmol, 2.2 equiv.) of NaPF<sub>6</sub> were added. The solution was stirred at room temperature for 4 h. The precipitate was filtered off, washed with 0.5 mL of methanol and 1 mL of Et<sub>2</sub>O and dried under high vacuo. The product was isolated as 30.1 mg (0.04 mmol, 64%) of a white solid.

<sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>CN): 3.91 (s, 6H), 7.62 (t, <sup>3</sup>*J* = 2.1 Hz, 1H), 7.76-7.82 (m, 6H), 7.91-7.96 (m, 1H)

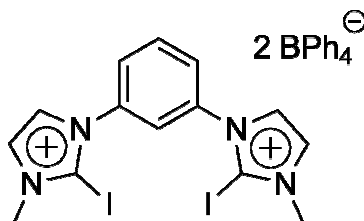
<sup>13</sup>C-NMR (500 MHz, CD<sub>3</sub>CN): 40.8, 102.0, 126.5, 127.5, 128.1, 130.8, 133.0, 138.5

Elemental analysis: *calc.*: C: 21.50 H: 1.80 N: 7.16  
*found*: C: 21.66 H: 1.81 N: 7.11

IR: 3174 (vw), 3150 (vw), 2359 (vw), 1611 (w), 1572 (w), 1501 (w), 1485 (w), 1415 (w), 1276 (w), 1227 (w), 1140 (w), 1092 (w), 869 (m), 825 (vs), 801 (vs), 779 (m), 758 (s), 696 (s), 664 (m)

ESI-MS: 246 [(M)<sup>2+</sup>], 637 [(M + PF<sub>6</sub>)<sup>+</sup>], 1419 [(2M + 3PF<sub>6</sub>)<sup>+</sup>]

**B.9) Synthesis of 1,3-Bis(2-iodo-3-methyl-imidazolium)phenyl-bis(tetraphenyl borate)**  
 $[m\text{-II-1}^{\text{Me}}/\text{BPh}_4]$



0.20 g (0.25 mmol, 1.0 equiv.) of  $m\text{-II-1}^{\text{Me}}/\text{Otf}$  were dissolved in 1 mL of methanol. Subsequently, 0.17 mg (0.50 mmol, 2.0 equiv.) of  $\text{NaBPh}_4$  were added. The solution was stirred at room temperature for 40 h. The precipitate was filtered off, washed with 1 mL of methanol and 5 mL of  $\text{Et}_2\text{O}$  and dried under high vacuo. The product was isolated as 0.26 g (0.23 mmol, 90%) of a white solid.

$^1\text{H-NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ): 3.91 (s, 6H), 6.83-6.89 (m, 8 H), 7.01 (t,  $^3J = 7.4$  Hz, 16 H), 7.23-7.34 (m, 16 H), 7.59 (t,  $^3J = 2.1$  Hz, 1H), 7.72 (d,  $^3J = 7.2$  Hz, 2 H), 7.74 (d,  $^3J = 7.2$  Hz, 2H), 7.77 (d,  $^3J = 2.1$  Hz, 1H), 7.79 (d,  $^3J = 2.1$  Hz, 1H), 7.90-7.96 (m, 1H)

$^{13}\text{C-NMR}$  (500 MHz,  $\text{CD}_3\text{CN}$ ):\* 40.7, 102.4, 122.7, 126.5 (q,  $|^2J_{\text{CB}}| = 2.8$  Hz), 127.4, 128.0, 130.8, 133.0, 136.6 (q,  $|^3J_{\text{CB}}| = 1.4$  Hz), 138.4, 164.7 (q,  $|^1J_{\text{CB}}| = 49.3$  Hz)

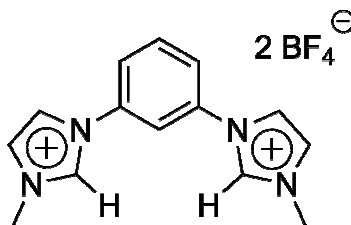
\* one signal of the cationic component is suspected to be covered by a phenyl signal

Elemental analysis: *calc.*: C: 65.87 H: 4.81 N: 4.96  
*found*: C: 65.53 H: 4.81 N: 4.81

IR: 3054 (vw), 3001 (vw), 2977 (vw), 2365 (w), 1476 (m), 1223 (w), 1106 (w), 841 (w), 734 (vs), 704 (vs), 668 (m)

ESI-MS: 246  $[(\text{M})^{2+}]$ , 811  $[(\text{M} + \text{BPh}_4)^+]$

**B.10)** Synthesis of 1,3-Bis(3-methyl-imidazolium)phenyl-bis(tetrafluoro borate) [*m*-HH-1<sup>Me</sup>/BF<sub>4</sub>]



0.20 g (0.37 mmol, 1.0 equiv.) of *m*-HH-1<sup>Me</sup>/Otf were dissolved in 3.5 mL of methanol. Subsequently, 0.09 g (0.80 mmol, 2.2 equiv.) of NaBF<sub>4</sub> were added. The solution was stirred at room temperature for 2.5 h. The precipitate was filtered off, washed with 5 mL of methanol and 5 mL of Et<sub>2</sub>O and dried under high vacuo. The product was isolated as 0.04 g (0.10 mmol, 27%) of a white solid.

<sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>CN): 3.97 (s, 6H), 7.60 (t, <sup>3</sup>*J* = 1.8 Hz, 2H), 7.79-7.91 (m, 6H), 8.99 (s, 2H)

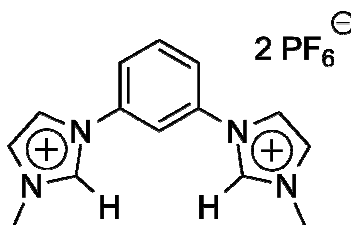
<sup>13</sup>C-NMR (500 MHz, CD<sub>3</sub>CN): 37.3, 118.0, 122.5, 124.9, 125.7, 133.3, 136.7, 136.9

Elemental analysis: *calc.*: C: 40.62 H: 3.90 N: 13.54  
*found*: C: 40.79 H: 4.04 N: 13.52

IR: 3143 (vw), 1617 (m), 1583 (m), 1545 (m), 1512 (w), 1473 (w), 1425 (w), 1354 (w), 1286 (w), 1220 (m), 1200 (w), 1052 (vs), 1018 (vs), 847 (s), 789 (w), 755 (s), 679 (m)

ESI-MS: 239 [(M - H<sup>+</sup>)<sup>+</sup>], 327 [(M + BF<sub>4</sub><sup>-</sup>)<sup>+</sup>], 741 [(2M + 3 BF<sub>4</sub><sup>-</sup>)<sup>+</sup>], 1154 [(3M + 5 BF<sub>4</sub><sup>-</sup>)<sup>+</sup>], 1568 [(4M + 7 BF<sub>4</sub><sup>-</sup>)<sup>+</sup>], 1982 [(5M + 9 BF<sub>4</sub><sup>-</sup>)<sup>+</sup>]

**B.11)** Synthesis of 1,3-Bis(3-methyl-imidazolium)phenyl-bis(hexafluoro phosphate) [*m*-HH-1<sup>Me</sup>/PF<sub>6</sub>]



0.29 g (0.54 mmol, 1.0 equiv.) of *m*-HH-1<sup>Me</sup>/Otf were dissolved in 5 mL of methanol. Subsequently, 0.20 g (1.18 mmol, 2.2 equiv.) of NaPF<sub>6</sub> were added. The solution was stirred at room temperature for 2.5 h. The precipitate was filtered off, washed with 5 mL of methanol and 5 mL of Et<sub>2</sub>O and dried under high vacuo. The product was isolated as 0.18 g (0.35 mmol, 64%) of a white solid.

<sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>CN): 3.97 (s, 6H), 7.59 (t, <sup>3</sup>*J* = 1.9 Hz, 2H), 7.77-7.93 (m, 6H), 8.91 (s, 2H)

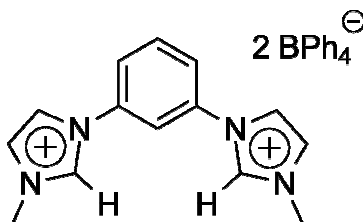
<sup>13</sup>C-NMR (500 MHz, CD<sub>3</sub>CN): 37.4, 118.1, 122.6, 125.0, 125.8, 133.3, 136.5, 136.9

Elemental analysis: *calc.*: C: 31.71 H: 3.04 N: 10.57  
*found*: C: 31.20 H: 3.11 N: 10.31

IR: 3179 (vw), 3126 (vw), 2195 (vw), 1987 (vw), 1620 (w), 1591 (w), 1557 (m), 1495 (w), 1466 (w), 1417 (w), 1364 (w), 1268 (vw), 1244 (w), 1196 (m), 1114 (w), 1070 (w), 818 (vs), 746 (m), 679 (w)

ESI-MS: 239 [(M - H)<sup>+</sup>], 385 [(M + PF<sub>6</sub>)<sup>+</sup>], 915 [(2M + 3 PF<sub>6</sub>)<sup>+</sup>], 1445 [(3M + 5 PF<sub>6</sub>)<sup>+</sup>], 1976 [(4M + 7PF<sub>6</sub>)<sup>+</sup>]

**B.12)** Synthesis of 1,3-Bis(3-methyl-imidazolium)phenyl-bis(tetraphenyl borate) [*m*-HH-1<sup>Me</sup>/BPh<sub>4</sub>]



0.13 g (0.29 mmol, 1.0 equiv.) of *m*-HH-1<sup>Me</sup>/Otf were dissolved in 5 mL of methanol. Subsequently, 0.20 g (0.58 mmol, 2.0 equiv.) of NaBPh<sub>4</sub> were added. The solution was stirred at room temperature for 18 h. The precipitate was filtered off, washed with 5 mL of methanol and 5 mL of Et<sub>2</sub>O and dried under high vacuo. The product was isolated as 0.26 g (0.23 mmol, 90%) of a white solid.

<sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>CN): 3.87 (s, 6H), 6.80-6.87 (m, 8H), 6.98 (t, <sup>3</sup>*J* = 7.4 Hz, 16H), 7.20-7.33 (m, 16H), 7.50 (t, <sup>3</sup>*J* = 1.9 Hz, 2H), 7.64 (t, <sup>3</sup>*J* = 2.2 Hz, 1H), 7.67-7.73 (m, 4H), 7.81-7.87 (m, 1H), 8.59 (s, 2H)

<sup>13</sup>C-NMR (500 MHz, CD<sub>3</sub>CN):\* 37.4, 122.6, 122.7, 125.2, 125.7, 126.6 (q, |<sup>2</sup>*J*<sub>CB</sub>| = 2.7 Hz), 133.3, 136.4, 136.6 (q, |<sup>3</sup>*J*<sub>CB</sub>| = 1.3 Hz), 136.7, 164.7 (q, |<sup>1</sup>*J*<sub>CB</sub>| = 49.3 Hz)

\* one signal of the cationic component is suspected to be covered by a phenyl signal

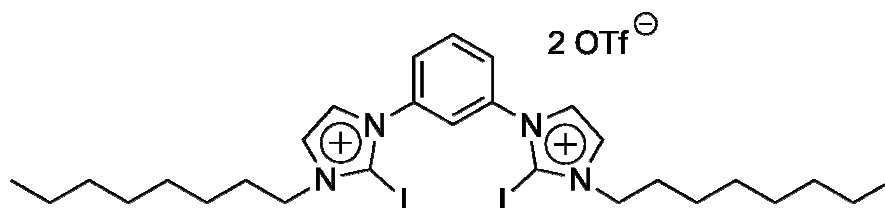
Elemental analysis: *calc.*: C: 84.74 H: 6.42 N: 6.38

*found*: C: 84.03 H: 6.38 N: 6.34

IR: 3054 (w), 2991 (vw), 1591 (w), 1543 (m), 1480 (m), 1432 (m), 1258 (w), 1225 (vw), 1176 (m), 1147 (w), 1070 (w), 1037 (w), 876 (vw), 843 (w), 795 (w), 737 (s), 708 (vs), 684 (m)

ESI-MS: 239 [(M - H<sup>+</sup>)<sup>+</sup>], 559 [(M + BPh<sub>4</sub><sup>-</sup>)<sup>+</sup>], 1437 [(2M + 3 BPh<sub>4</sub><sup>-</sup>)<sup>+</sup>]

**B.13) Synthesis of 1,3-Bis(2-iodo-3-octyl-imidazolium)phenyl-bis(tetrafluoromethane sulfonate) [*m*-II-1<sup>Oct</sup>/OTf]**



Under an argon atmosphere, 0.12 g of *m*-II-2 (0.27 mmol, 1.0 equiv.) were suspended in 15 mL of CH<sub>2</sub>Cl<sub>2</sub>. Subsequently, 0.29 g of octyl trifluoromethane sulfonate (1.10 mmol, 4.1 equiv.) were added and the suspension was stirred at room temperature for 18 h. After removal of the solvent, the resulting solid was recrystallized from CH<sub>3</sub>CN with Et<sub>2</sub>O, yielding 0.19 g (0.19 mmol, 70%) of the product as a colorless solid.

<sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>CN): 3.97 (t, <sup>3</sup>*J* = 6.8 Hz, 6H), 1.24-1.48 (m, 20H), 1.84-1.92 (m, 4H), 4.23 (t, <sup>3</sup>*J* = 7.5 Hz, 4H), 7.72 (t, <sup>3</sup>*J* = 2.1 Hz, 1H), 7.79-7.86 (m, 6H), 7.91-7.96 (m, 1H)

<sup>13</sup>C-NMR (500 MHz, CD<sub>3</sub>CN): 14.3, 23.3, 26.7, 29.6, 29.7, 30.1, 32.4, 54.0, 101.4, 121.9 (q, <sup>1</sup>*J* = 320.6 Hz), 126.9(6), 127.0(3), 127.8, 130.9, 132.9, 138.4

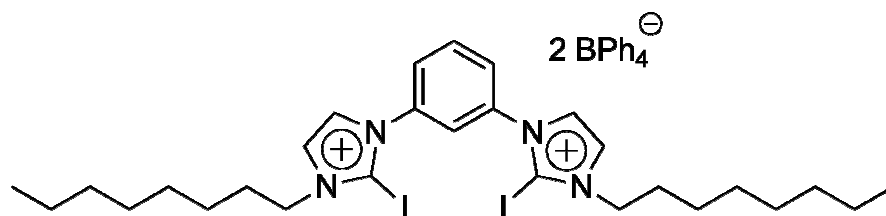
Elemental analysis:	<i>calc.</i> :	C: 36.52	H: 4.29	N: 5.68	S: 6.50
	<i>found</i> :	C: 36.45	H: 4.25	N: 5.77	S: 6.25

IR: 3145 (vw), 2924 (m), 2861 (w), 1615 (vw), 1552 (vw), 1504 (m), 1471 (w), 1442 (w), 1278 (s), 1258 (s), 1220 (vs), 1167 (s), 1022 (vs), 876 (vw), 804 (w), 751 (m), 688 (w)

ESI-MS: 344 [(M)<sup>2+</sup>], 711 [(M+Na)<sup>+</sup>], 837 [(M + OTf)<sup>+</sup>], 1823 [(3M + 5OTf)<sup>+</sup>]



**B.14)** Synthesis of 1,3-Bis(3-octyl-imidazolium)phenyl-bis(tetrafluoromethane sulfonate)  
[*m*-II-1<sup>Oct</sup>/BPh<sub>4</sub>]



0.04 g (0.04 mmol, 1.0 equiv.) of *m*-II-1<sup>Oct</sup>/Otf were dissolved in 0.5 mL of methanol. Subsequently, 0.03 g (0.09 mmol, 2.5 equiv.) of NaBPh<sub>4</sub> were added. The solution was stirred at room temperature for 4 h. The precipitate was filtered off, washed with 2 mL of methanol and dried under high vacuo. The resulting solid was recrystallized from CH<sub>3</sub>CN with Et<sub>2</sub>O, yielding the product as 27.5 mg (0.02 mmol, 52%) of a white solid.

<sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>CN): 0.86-1.00 (m, 6H), 1.20-1.56 (m, 20H), 1.85-1.95 (m, 4H), 4.20 (t, <sup>3</sup>*J* = 7.5 Hz, 4H), 6.83-6.90 (m, 8H), 7.01 (t, <sup>3</sup>*J* = 7.4 Hz, 16H), 7.26-7.33 (m, 16H), 7.57 (t, <sup>3</sup>*J* = 2.1 Hz, 1H), 7.67 (d, <sup>3</sup>*J* = 2.2 Hz, 2H), 7.73 (d, <sup>3</sup>*J* = 2.2 Hz, 2H), 7.77 (d, <sup>3</sup>*J* = 2.0 Hz, 1H), 7.79 (d, <sup>3</sup>*J* = 2.1 Hz, 1H), 7.89-7.94 (m, 1H)

<sup>13</sup>C-NMR (500 MHz, CD<sub>3</sub>CN): 14.3, 23.3, 26.7, 29.6, 29.7, 30.1, 32.4, 54.1, 100.8, 122.7, 126.6 (q, |<sup>2</sup>*J*<sub>CB</sub>| = 2.7 Hz), 126.7, 127.0, 127.8, 130.9, 132.9, 136.6 (q, |<sup>3</sup>*J*<sub>CB</sub>| = 1.3 Hz), 138.3, 164.7 (q, |<sup>1</sup>*J*<sub>CB</sub>| = 49.3 Hz)

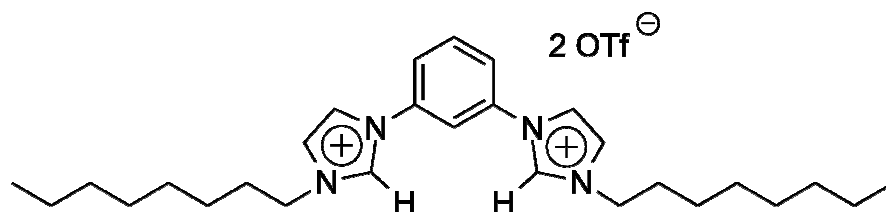
Elemental analysis: *calc.*: C: 68.79 H: 6.23 N: 4.22

*found*: C: 64.25 H: 6.00 N: 4.29

IR: 3054 (w), 2924 (w), 2856 (w), 1578 (w), 1479 (m), 1426 (m), 1132 (m), 843 (m), 799 (m), 747 (s), 733 (s), 703 (vs), 690 (s)

ESI-MS: 344 [(M)<sup>2+</sup>], 1007 [(M + BPh<sub>4</sub>)<sup>+</sup>]

**B.15) Synthesis of 1,3-Bis(2-iodo-3-octyl-imidazolium)phenyl-bis(tetraphenyl borate)**  
**[*m*-HH-1<sup>Oct</sup>/OTf]**



Under an argon atmosphere, 0.05 g of 1,3-bis(imidazol-1-yl)benzene (0.24 mmol, 1.0 equiv.) were suspended in 20 mL of CH<sub>2</sub>Cl<sub>2</sub>. Subsequently, 0.27 g of octyl trifluoromethane sulfonate (1.01 mmol, 4.2 equiv.) were added and the suspension was stirred at room temperature for 18 h. After removal of the solvent, the resulting solid was recrystallized from CH<sub>3</sub>CN with Et<sub>2</sub>O, yielding 0.13 g (0.18 mmol, 74%) of the product as a colorless solid.

<sup>1</sup>H-NMR (500 MHz, CD<sub>3</sub>CN): 0.85-0.92 (m, 6H), 1.23-1.44 (m, 20H), 1.90-1.93 (m, 4H), 4.26 (t, <sup>3</sup>*J* = 7.4 Hz, 4H), 7.64 (t, <sup>3</sup>*J* = 1.9 Hz, 2H), 7.81-7.93 (m, 5H), 7.98 (t, <sup>3</sup>*J* = 2.2 Hz, 1H), 9.17 (s, 2H)

<sup>13</sup>C-NMR (500 MHz, CD<sub>3</sub>CN): 14.3, 23.3, 26.7, 29.5, 29.7, 30.4, 32.4, 51.2, 117.9, 122.0 (q, <sup>1</sup>*J* = 320.6 Hz), 122.6, 124.5, 124.6, 133.2, 136.0, 137.0

Elemental analysis:	<i>calc.</i> :	C: 49.04	H: 6.04	N: 7.62	S: 8.73
	<i>found</i> :	C: 49.05	H: 6.39	N: 7.61	S: 8.74

IR: 3145 (vw), 3107 (vw), 3063 (vw), 2926 (vw), 2861 (vw), 2360 (w), 1614 (w), 1576 (w), 1556 (w), 1500 (vw), 1461 (vw), 1379 (vw), 1251 (vs), 1225 (m), 1163 (s), 1081 (w), 1031 (s), 874 (w), 791 (m), 758 (w), 682 (m)

ESI-MS: 218 [(M)<sup>2+</sup>], 435 [(M - H)<sup>+</sup>], 585 [(M + OTf)<sup>+</sup>], 1319 [(2M + 3OTf)<sup>+</sup>]

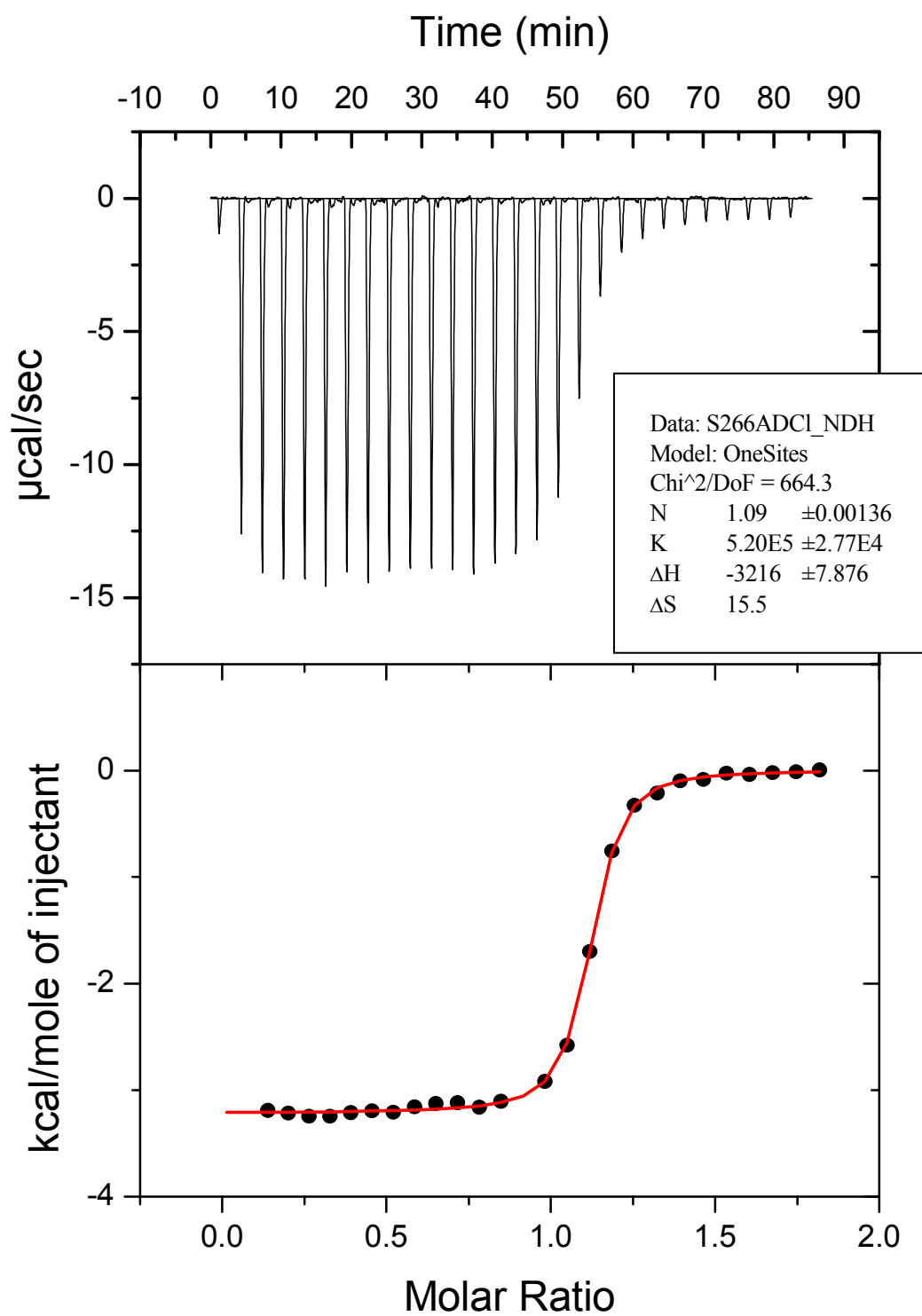
## II) Experimental Setup and ITC-Measurements

All solvents used were purchased dry and stored over molecular sieves. Prior to use, solvents were degassed under reduced pressure. Synthesized compounds used in the measurements were dried under high vacuo prior to use. The experiments were performed in an air-conditioned laboratory (room-temperature 20-22 °C). The following table shows the concentration of the guest (X<sup>-</sup>) and host (XB-donor) solutions used in the experiments from Table 1 and the experimental setup.

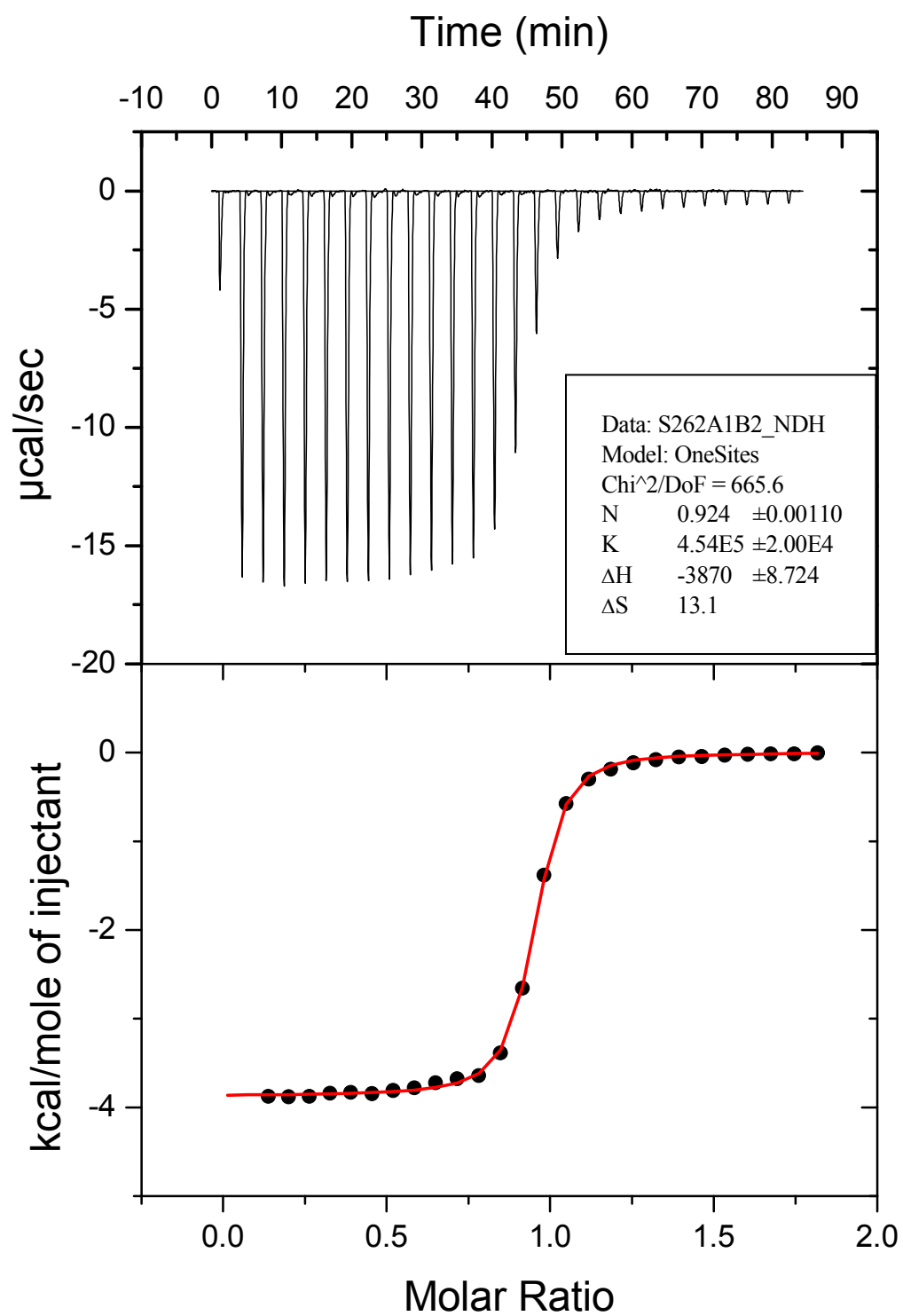
	#	XB-Donor	X <sup>-</sup>	T [°C]	Solvent	Setup	c [Syringe]	c [Cell]
<i>m</i> vs. <i>p</i>	1	<i>m</i> -II-1 <sup>Me</sup> /OTf	Cl <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	2	<i>m</i> -II-1 <sup>Me</sup> /OTf	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	3	<i>m</i> -II-1 <sup>Me</sup> /OTf	I <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	4	<i>p</i> -II-1 <sup>Me</sup> /OTf	Cl <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	0.5 mM
	5	<i>p</i> -II-1 <sup>Me</sup> /OTf	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	0.5 mM
	6	<i>p</i> -II-1 <sup>Me</sup> /OTf	I <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	0.5 mM
References	7	<i>m</i> -BrBr-1 <sup>Me</sup> /OTf	Cl <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	55.7 mM	5.0 mM
	8	<i>m</i> -BrBr-1 <sup>Me</sup> /OTf	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	50.0 mM	5.0 mM
	9	<i>m</i> -BrBr-1 <sup>Me</sup> /OTf	I <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	50.0 mM	5.0 mM
	10	<i>m</i> -HH-1 <sup>Me</sup> /OTf	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	11	<i>p</i> -HH-1 <sup>Me</sup> /OTf	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	12	<i>m</i> -MeMe-1 <sup>Me</sup> /OTf	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	13	<i>m</i> -HI-1 <sup>Me</sup> /OTf	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	14	3	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Host-into-Guest	7.62 mM	0.7 mM
	15	<i>m</i> -II-2	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	16	4	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	30.0 mM	3.3 mM
Temperature	17	<i>m</i> -II-1 <sup>Me</sup> /OTf	Br <sup>-</sup>	10	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	18	<i>m</i> -II-1 <sup>Me</sup> /OTf	Br <sup>-</sup>	20	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	19	<i>m</i> -II-1 <sup>Me</sup> /OTf	Br <sup>-</sup>	40	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	20	<i>m</i> -II-1 <sup>Me</sup> /OTf	Br <sup>-</sup>	50	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	21	<i>m</i> -II-1 <sup>Me</sup> /BPh <sub>4</sub>	Br <sup>-</sup>	10	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	22	<i>m</i> -II-1 <sup>Me</sup> /BPh <sub>4</sub>	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	23	<i>m</i> -II-1 <sup>Me</sup> /BPh <sub>4</sub>	Br <sup>-</sup>	50	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
H-Analogues	24	<i>m</i> -HH-1 <sup>Me</sup> /BF <sub>4</sub>	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	25	<i>m</i> -HH-1 <sup>Me</sup> /PF <sub>6</sub>	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	26	<i>m</i> -HH-1 <sup>Me</sup> /BPh <sub>4</sub>	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	27	<i>m</i> -HH-1 <sup>Oct</sup> /OTf	Br <sup>-</sup>	23	CH <sub>2</sub> Cl <sub>2</sub>	Guest-into-Host	10.0 mM	1.0 mM
	28	<i>m</i> -HH-1 <sup>Oct</sup> /OTf	Br <sup>-</sup>	30	THF	Guest-into-Host	10.0 mM	1.0 mM
Anions	29	<i>m</i> -II-1 <sup>Me</sup> /BF <sub>4</sub>	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	30	<i>m</i> -II-1 <sup>Me</sup> /PF <sub>6</sub>	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	31	<i>m</i> -II-1 <sup>Oct</sup> /OTf	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
	32	<i>m</i> -II-1 <sup>Oct</sup> /BPh <sub>4</sub>	Br <sup>-</sup>	30	CH <sub>3</sub> CN	Guest-into-Host	10.0 mM	1.0 mM
Solvents	33	<i>m</i> -II-1 <sup>Me</sup> /OTf	Br <sup>-</sup>	30	Acetone	Guest-into-Host	10.0 mM	1.0 mM
	34	<i>m</i> -II-1 <sup>Me</sup> /OTf	Br <sup>-</sup>	30	H <sub>2</sub> O/MeOH (1/9)	Guest-into-Host	10.0 mM	1.0 mM
	35	<i>m</i> -II-1 <sup>Me</sup> /OTf	Br <sup>-</sup>	30	Ethanol	Guest-into-Host	10.0 mM	1.0 mM
	36	<i>m</i> -II-1 <sup>Me</sup> /OTf	Br <sup>-</sup>	30	DMSO	Guest-into-Host	10.0 mM	1.0 mM
	37	<i>m</i> -II-1 <sup>Oct</sup> /OTf	Br <sup>-</sup>	30	THF	Guest-into-Host	10.0 mM	1.0 mM
	38	<i>m</i> -II-1 <sup>Oct</sup> /OTf	Br <sup>-</sup>	23	CH <sub>2</sub> Cl <sub>2</sub>	Guest-into-Host	10.0 mM	1.0 mM
	39	<i>m</i> -II-1 <sup>Oct</sup> /OTf	Cl <sup>-</sup>	23	CH <sub>2</sub> Cl <sub>2</sub>	Guest-into-Host	10.0 mM	1.0 mM
	40	<i>m</i> -II-1 <sup>Oct</sup> /OTf	I <sup>-</sup>	23	CH <sub>2</sub> Cl <sub>2</sub>	Guest-into-Host	10.0 mM	1.0 mM
	41	<i>m</i> -II-1 <sup>Oct</sup> /OTf	Br <sup>-</sup>	30	Acetone	Guest-into-Host	10.0 mM	1.0 mM
	42	<i>m</i> -II-1 <sup>Oct</sup> /OTf	Cl <sup>-</sup>	30	Acetone	Guest-into-Host	10.0 mM	1.0 mM
	43	<i>m</i> -II-1 <sup>Oct</sup> /OTf	I <sup>-</sup>	30	Acetone	Guest-into-Host	10.0 mM	1.0 mM

The plots on the following pages show data gathered in the ITC experiments. The legend included shows the following thermodynamic properties:

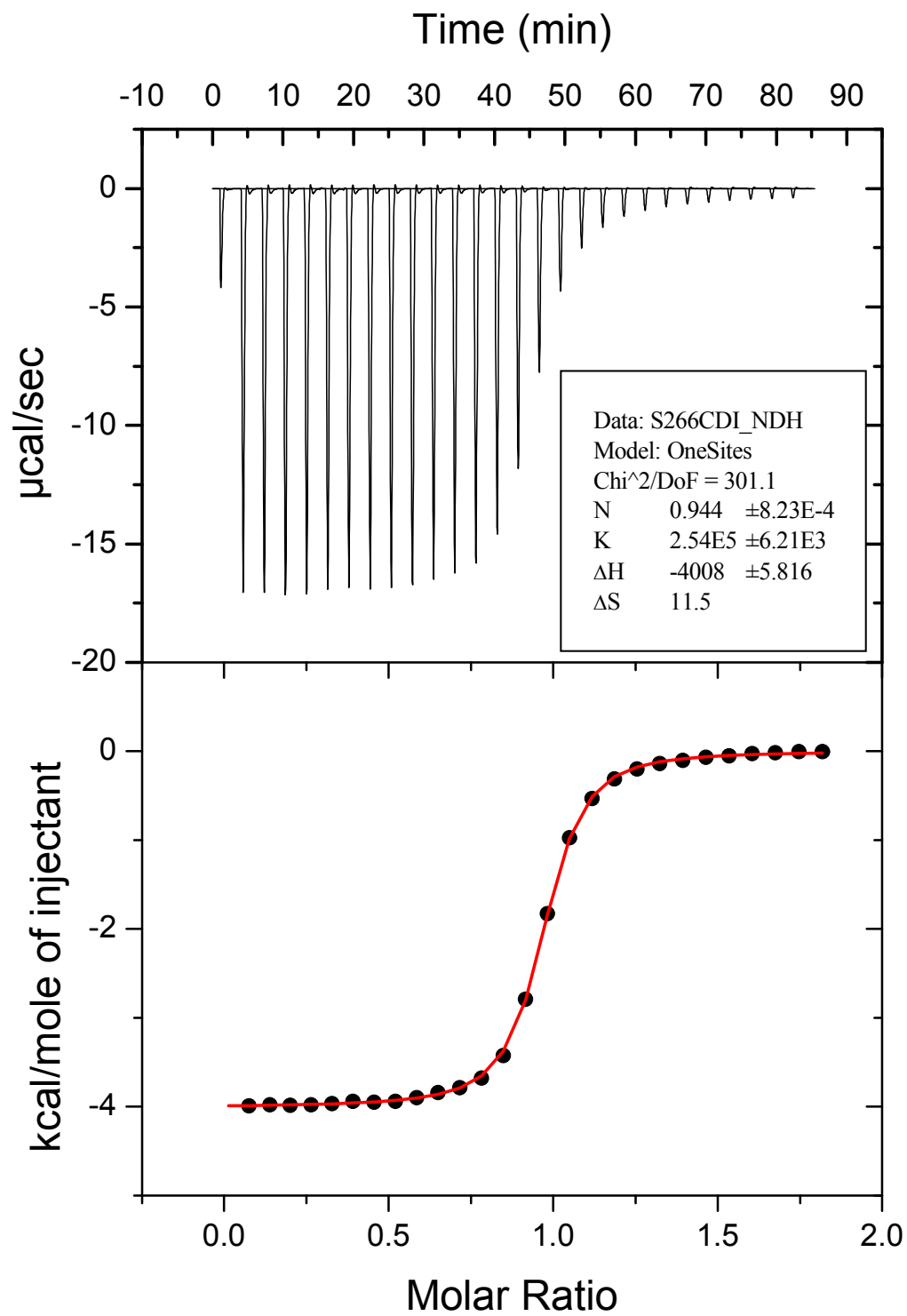
Data: S262A1B2_NDH			
Model: OneSites			
Chi^2/DoF = 665.6			
Molarity	N	0.924	±0.00110
Binding constant	K	4.54E5	±2.00E4
Enthalpy	ΔH	-3870	±8.724
Entropy	ΔS	13.1	



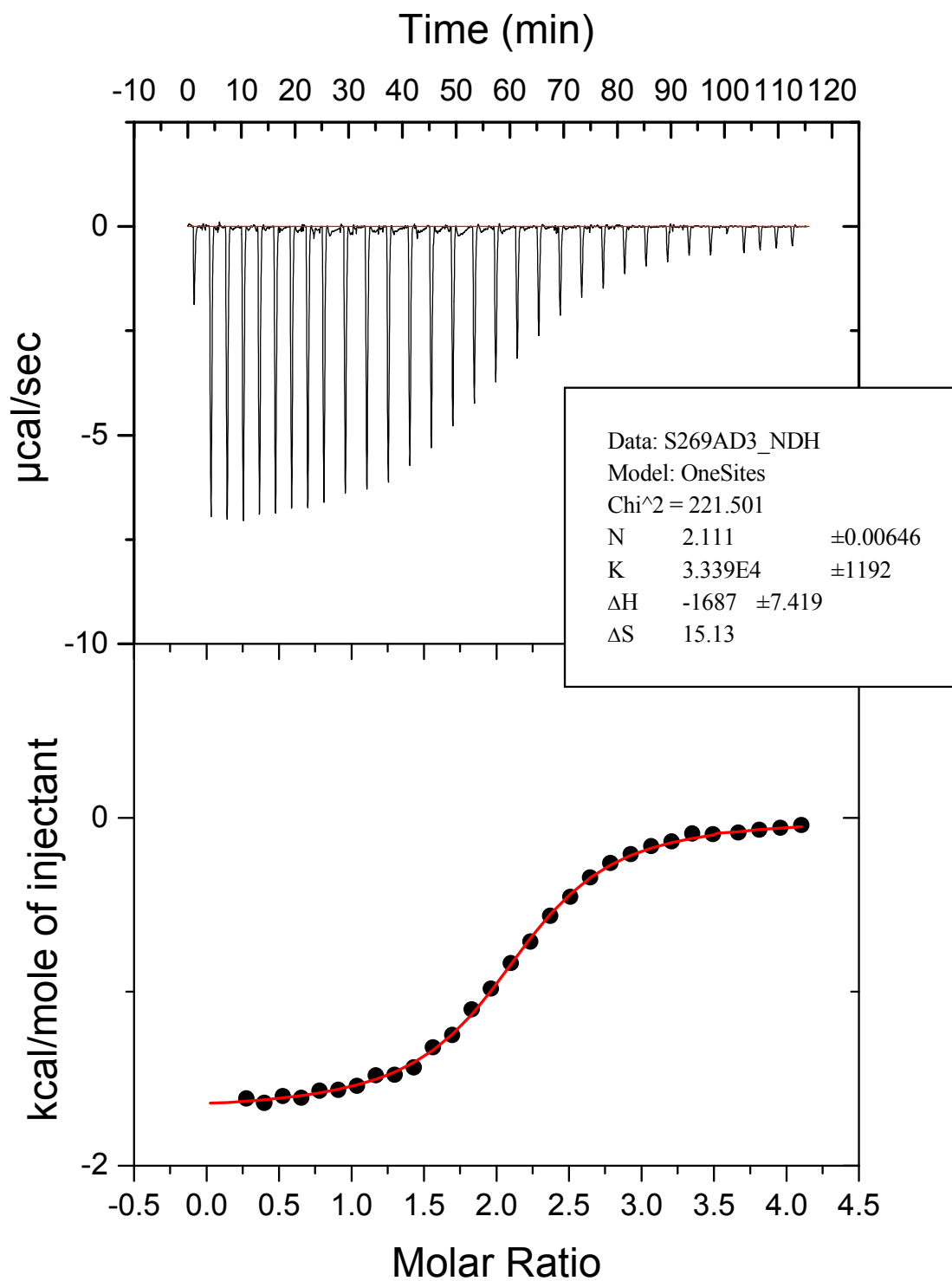
$\text{NBu}_4\text{Cl}$  to  $m\text{-II-1}^{\text{Me}}/\text{OTf}$  in  $\text{CH}_3\text{CN}$ ,  $30^\circ\text{C}$  (see Table 1, entry 1)



NBu<sub>4</sub>Br to *m*-II-1<sup>Me</sup>/OTf in CH<sub>3</sub>CN, 30 °C (see Table 1, entry 2)

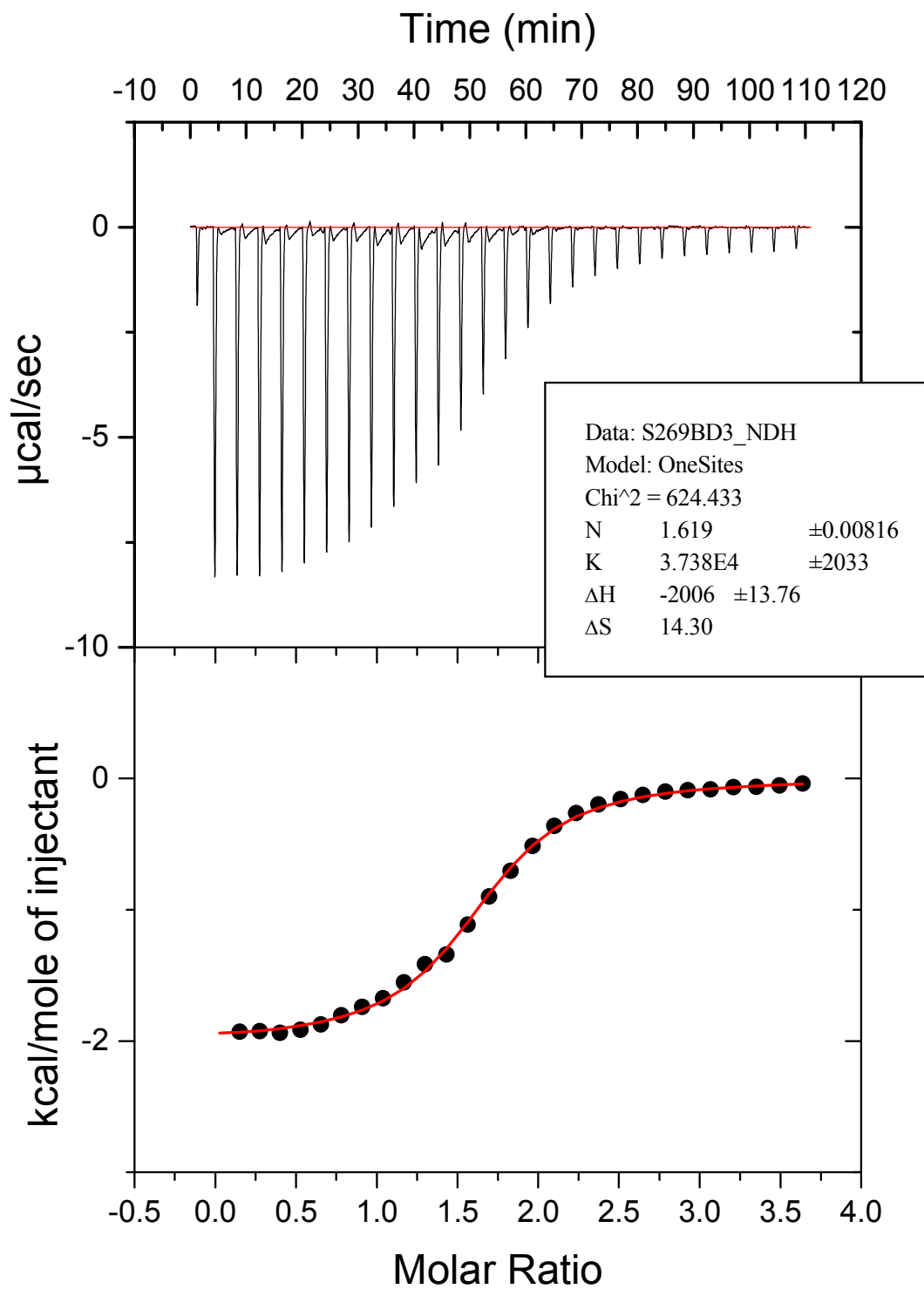


NBu<sub>4</sub>I to *m*-**II-1**<sup>Me</sup>/OTf in CH<sub>3</sub>CN, 30 °C (see Table 1, entry 3)

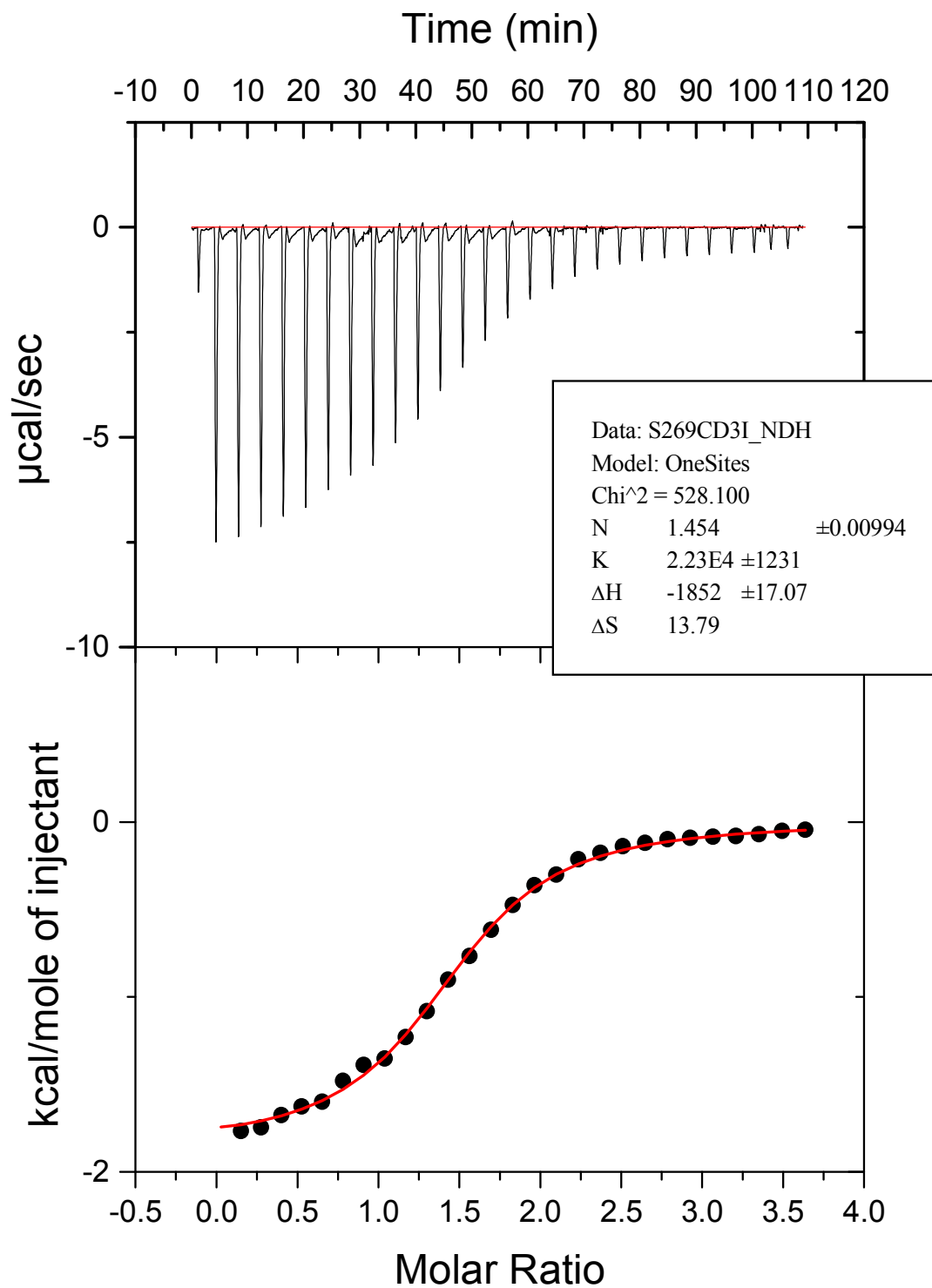


NBu<sub>4</sub>Cl to *p*-II-1<sup>Me</sup>/OTf in CH<sub>3</sub>CN, 30 °C (see Table 1, entry 4)

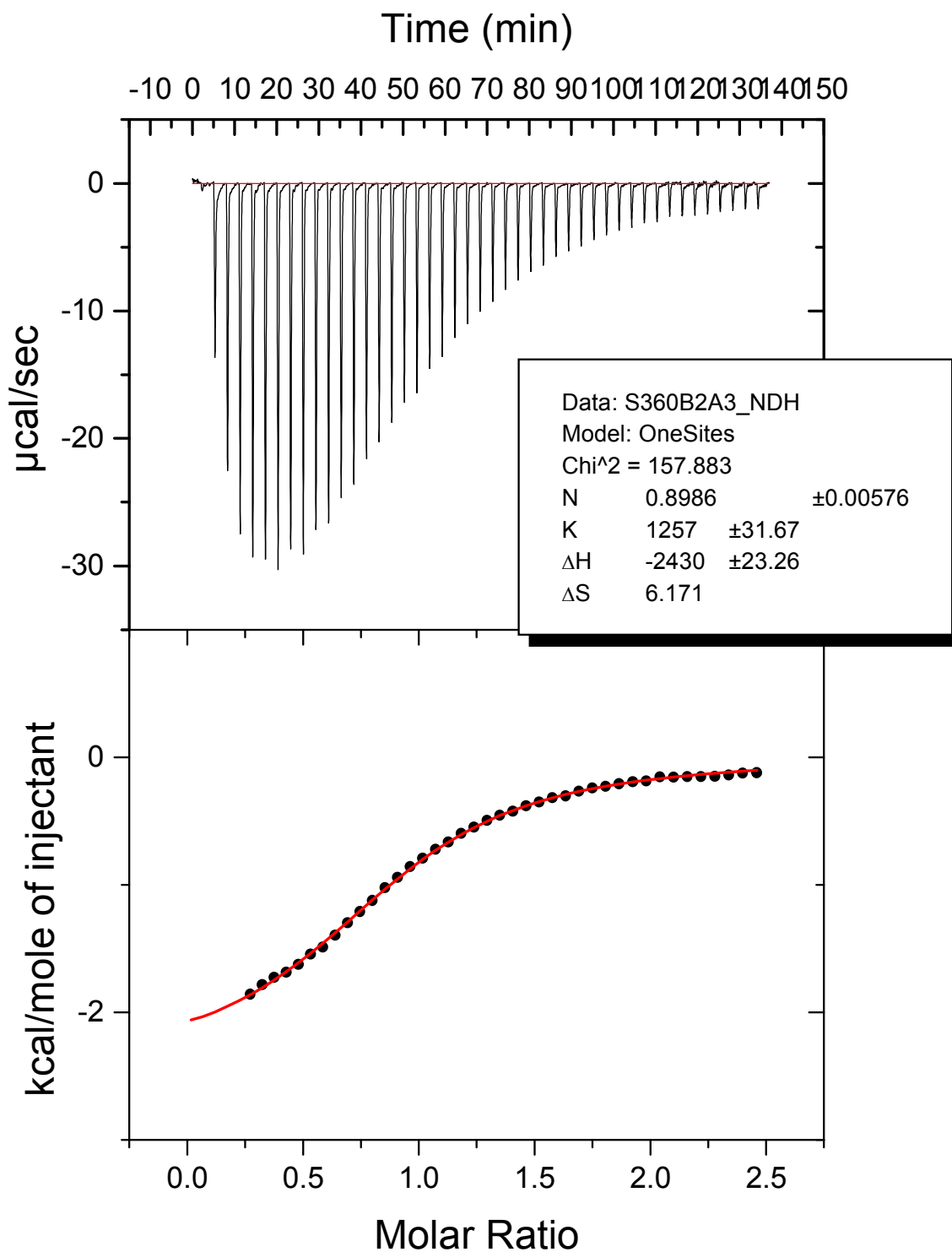




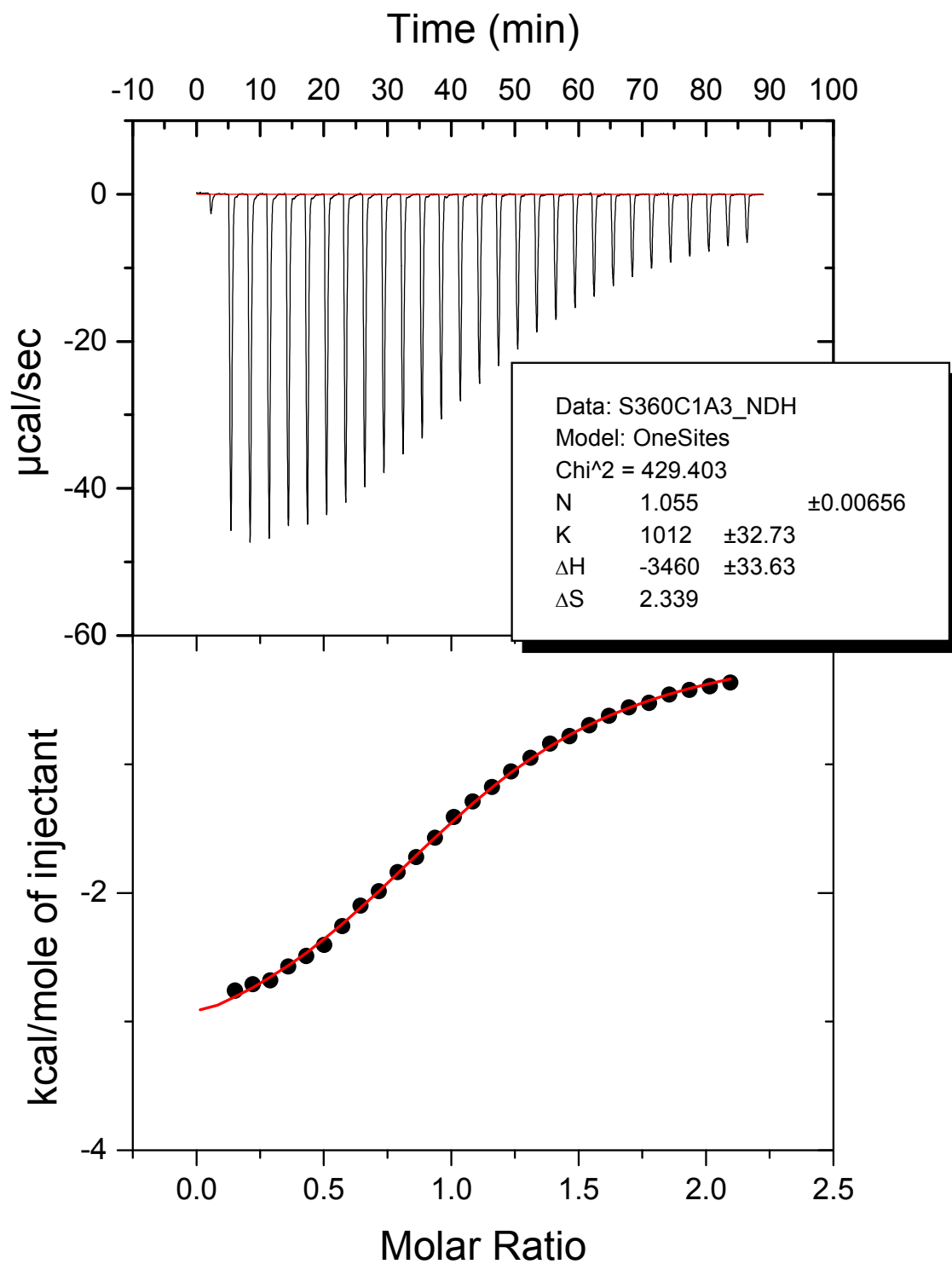
NBu<sub>4</sub>Br to *p*-**II**-1<sup>Me</sup>/OTf in CH<sub>3</sub>CN, 30 °C (see Table 1, entry 5)



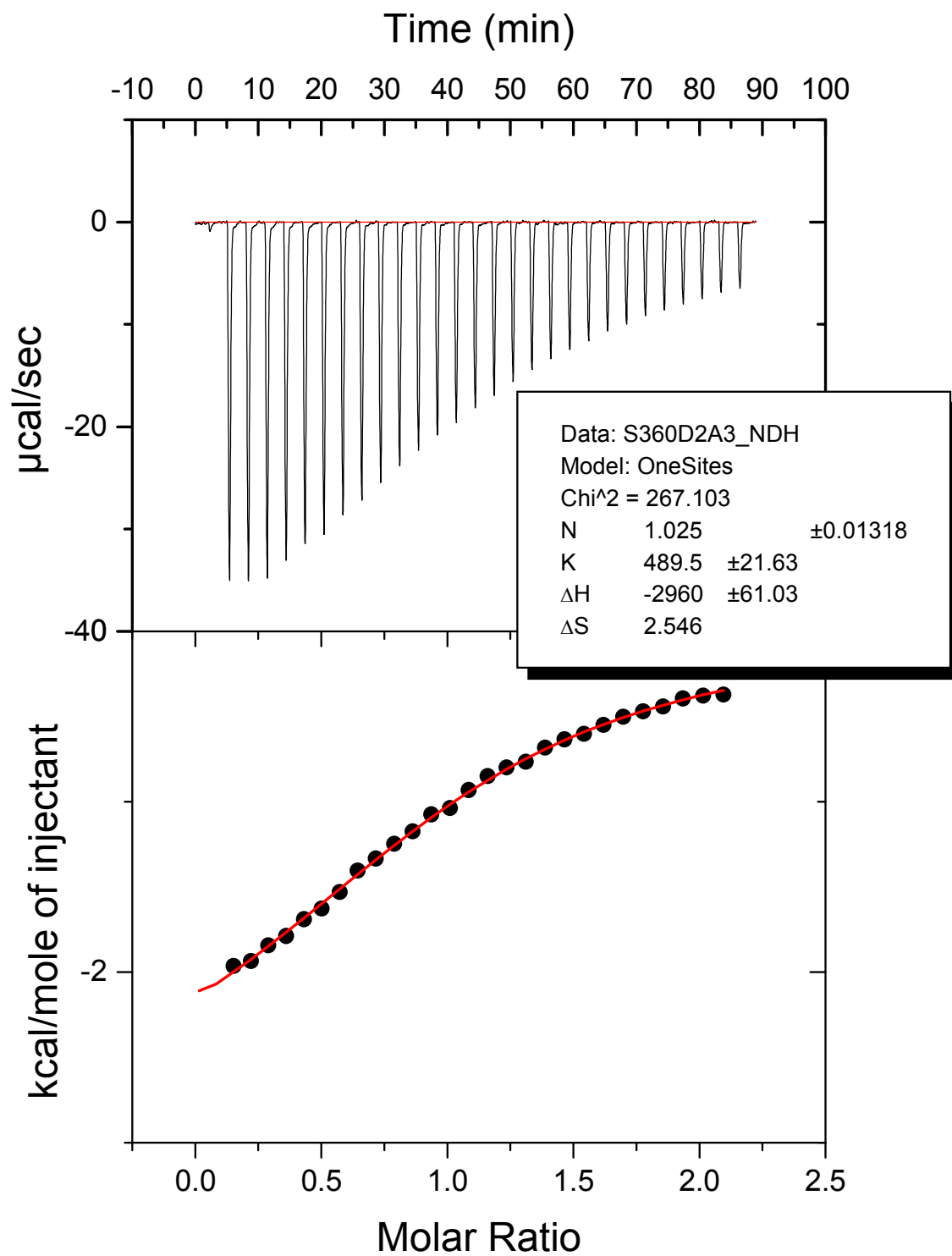
NBu<sub>4</sub>I to *p*-II-1<sup>Me</sup>/OTf in CH<sub>3</sub>CN, 30 °C (*see Table 1, entry 6*)



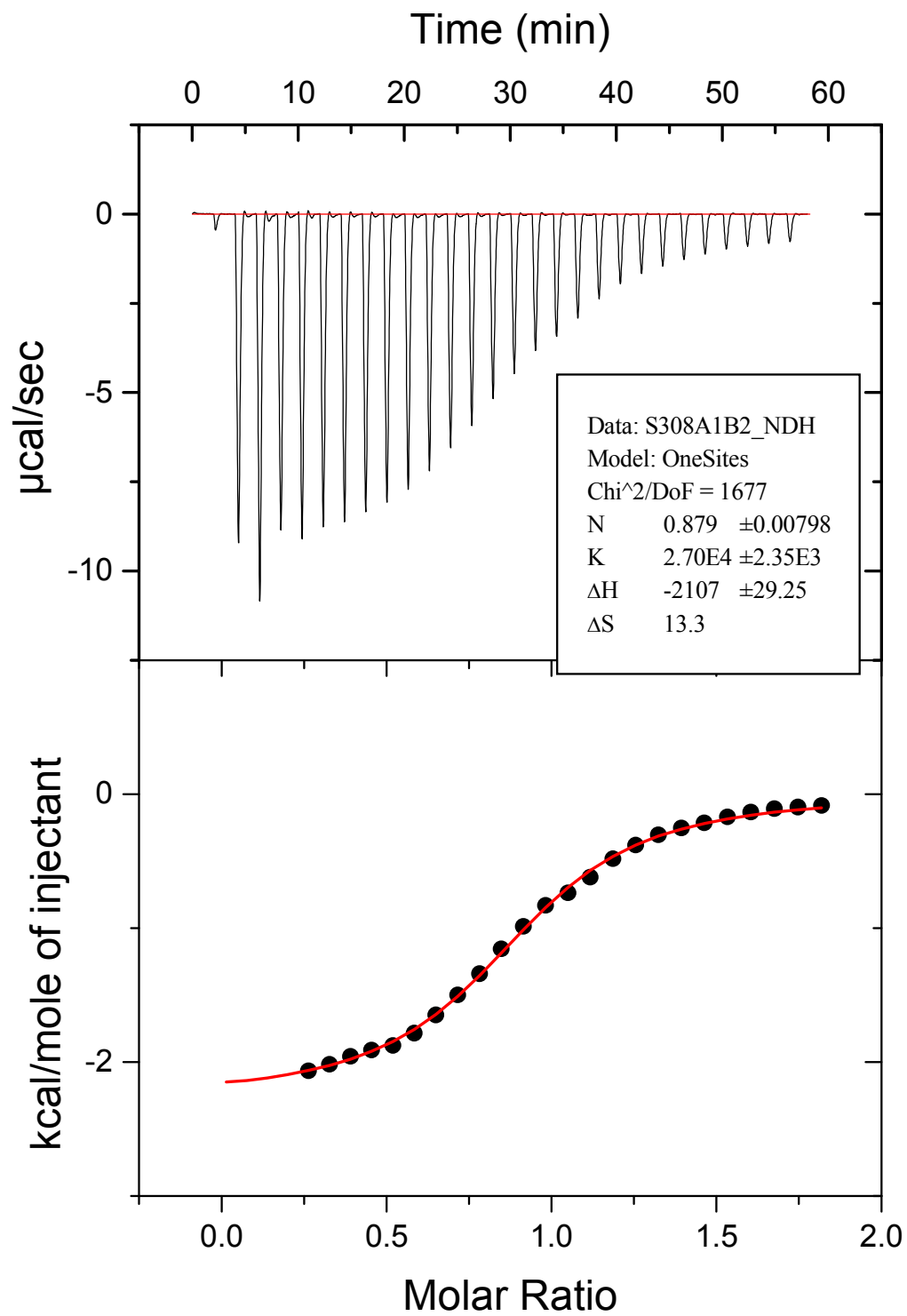
NBu<sub>4</sub>Cl to *m*-BrBr-1<sup>Me</sup>/OTf in CH<sub>3</sub>CN, 30 °C (see Table 1, entry 7)



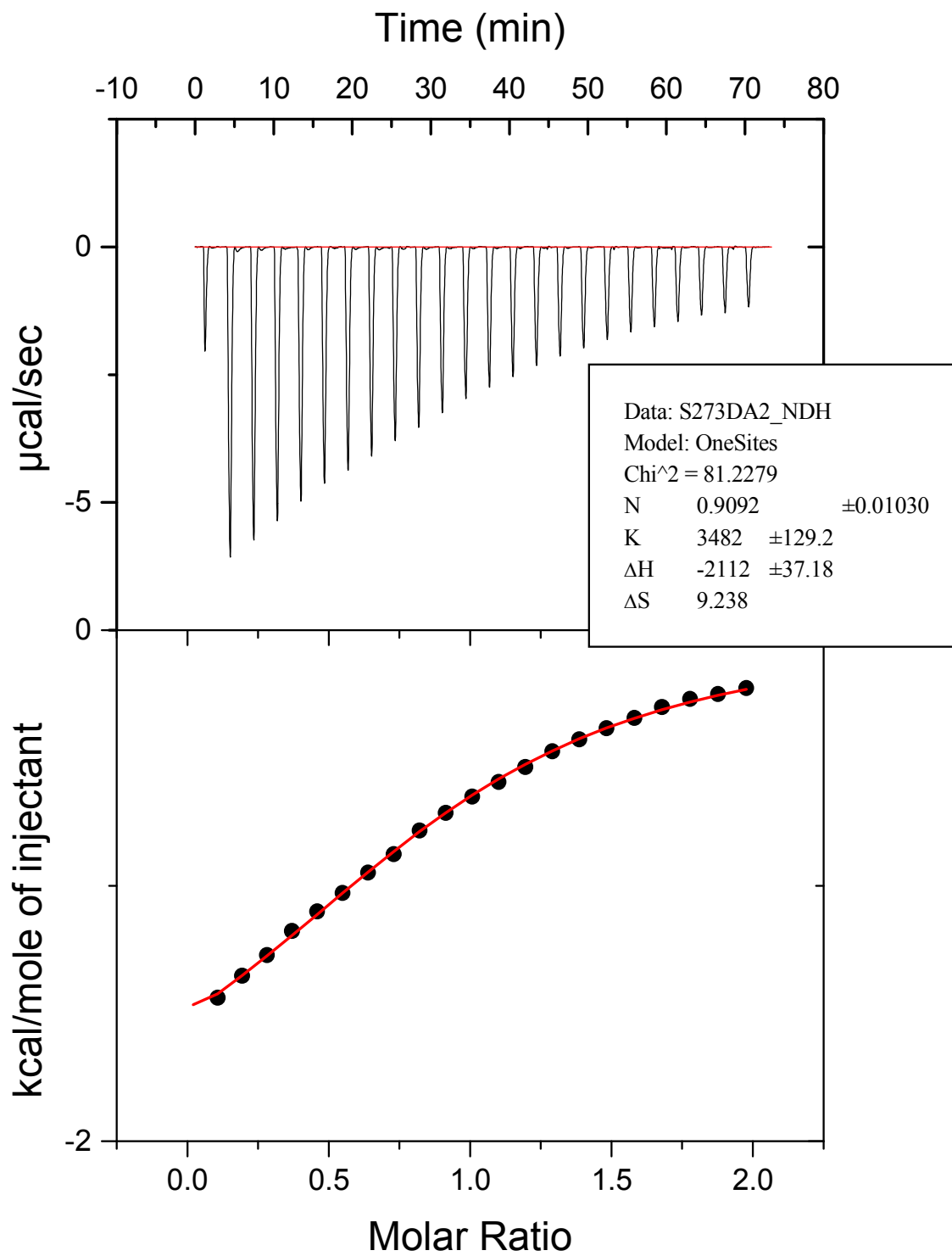
$\text{NBu}_4\text{Br}$  to *m*-**BrBr-1**<sup>Me</sup>/OTf in  $\text{CH}_3\text{CN}$ , 30 °C (see Table 1, entry 8)



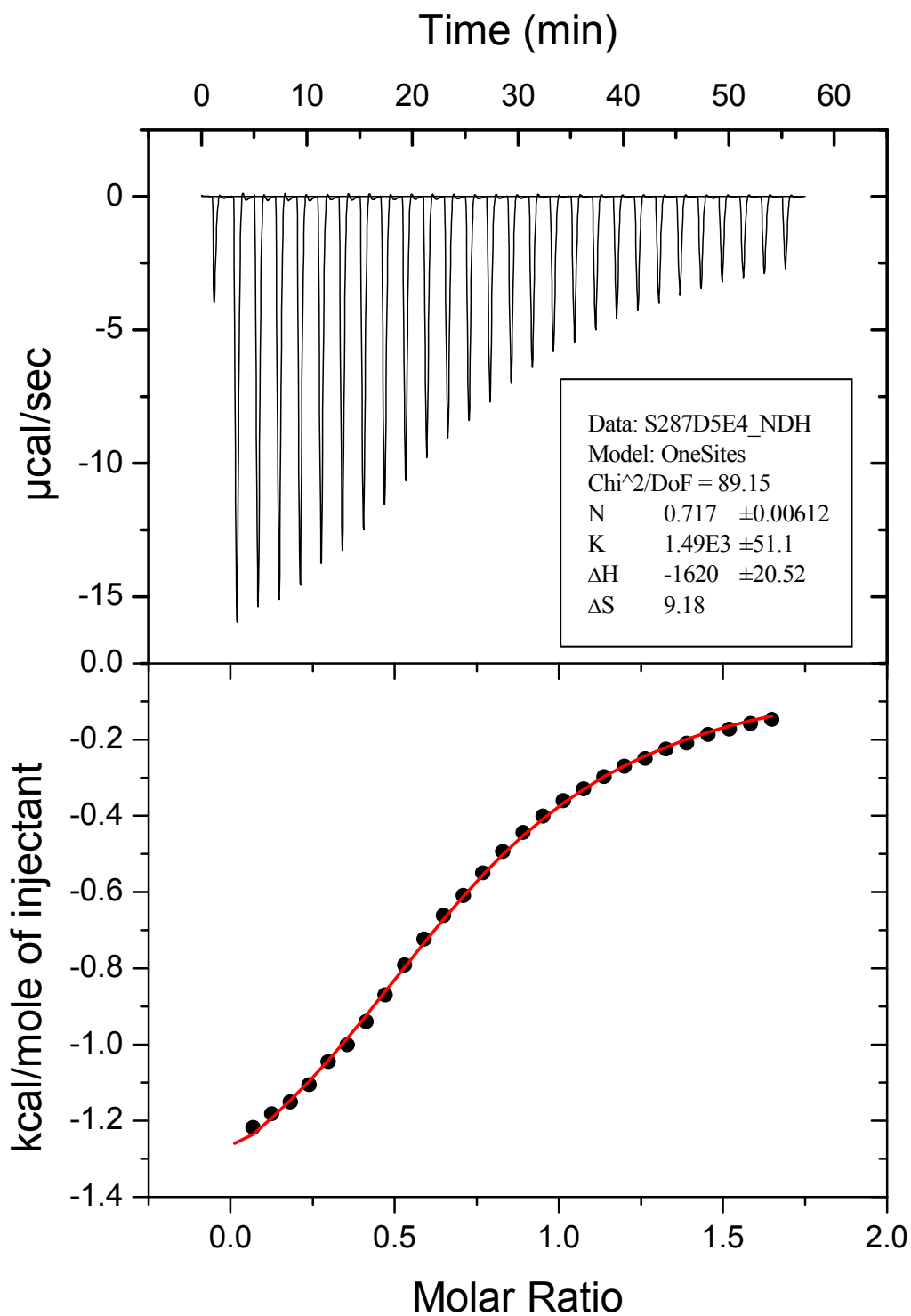
NBu<sub>4</sub>I to *m*-BrBr-1<sup>Me</sup>/OTf in CH<sub>3</sub>CN, 30 °C (see Table 1, entry 9)



NBu<sub>4</sub>Br to *m*-**HI-1**<sup>Me</sup>/OTf in CH<sub>3</sub>CN, 30 °C (see Table 1, entry 13)

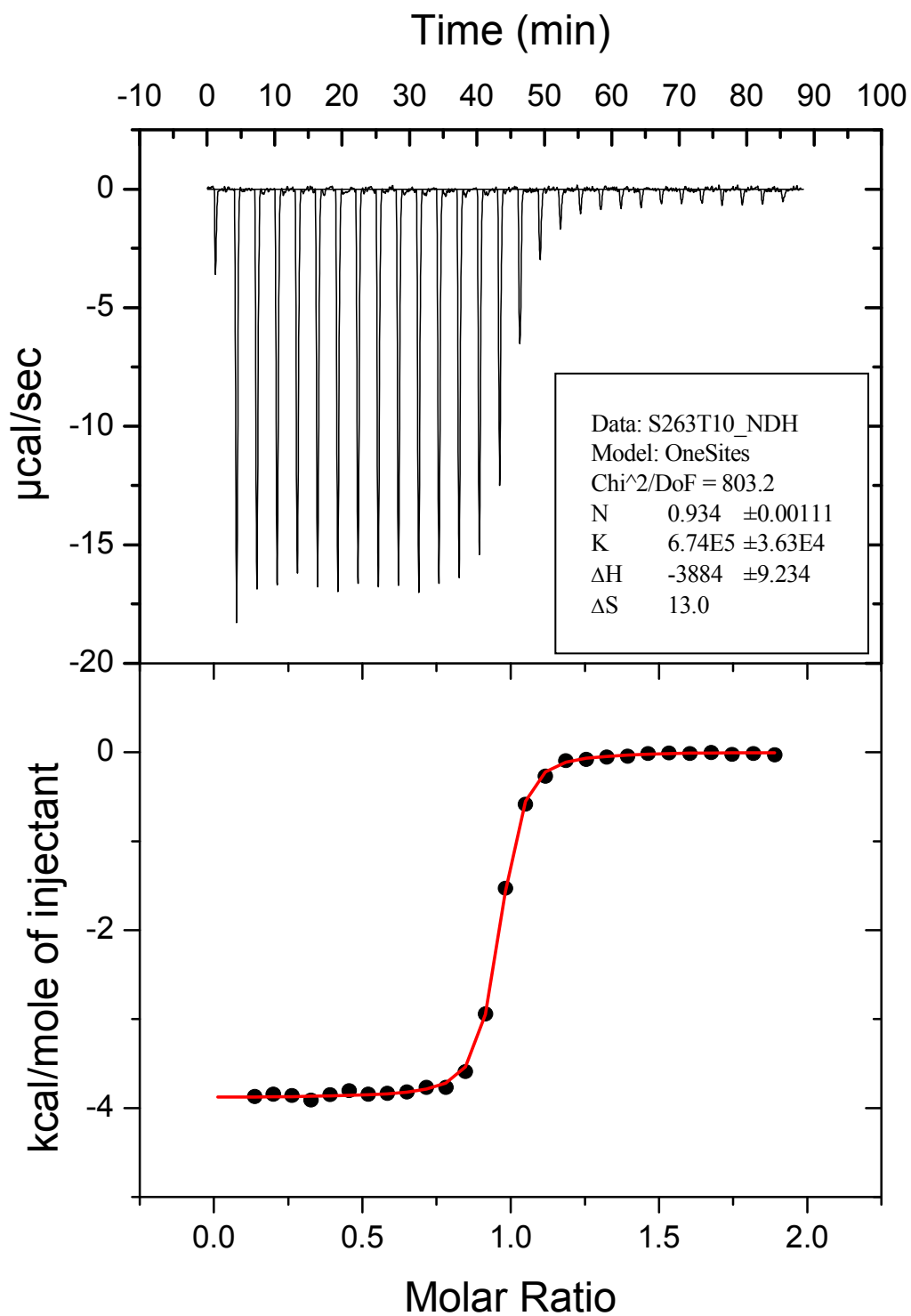


NBu<sub>4</sub>Br to **3** in CH<sub>3</sub>CN, 30 °C (*see Table 1, entry 14*)

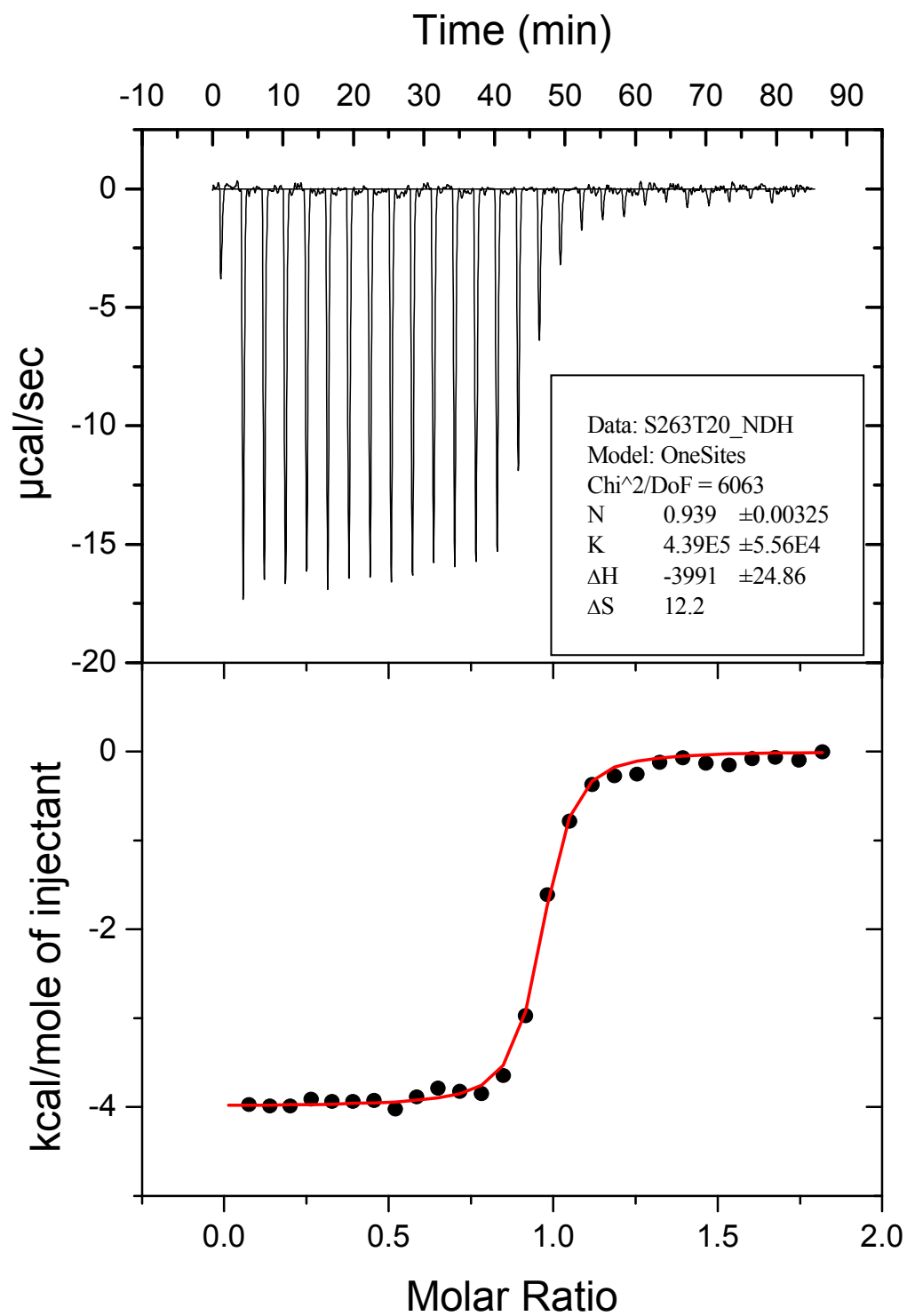


NBu<sub>4</sub>Br to **4** in CH<sub>3</sub>CN, 30 °C (*see Table 1, entry 16*)

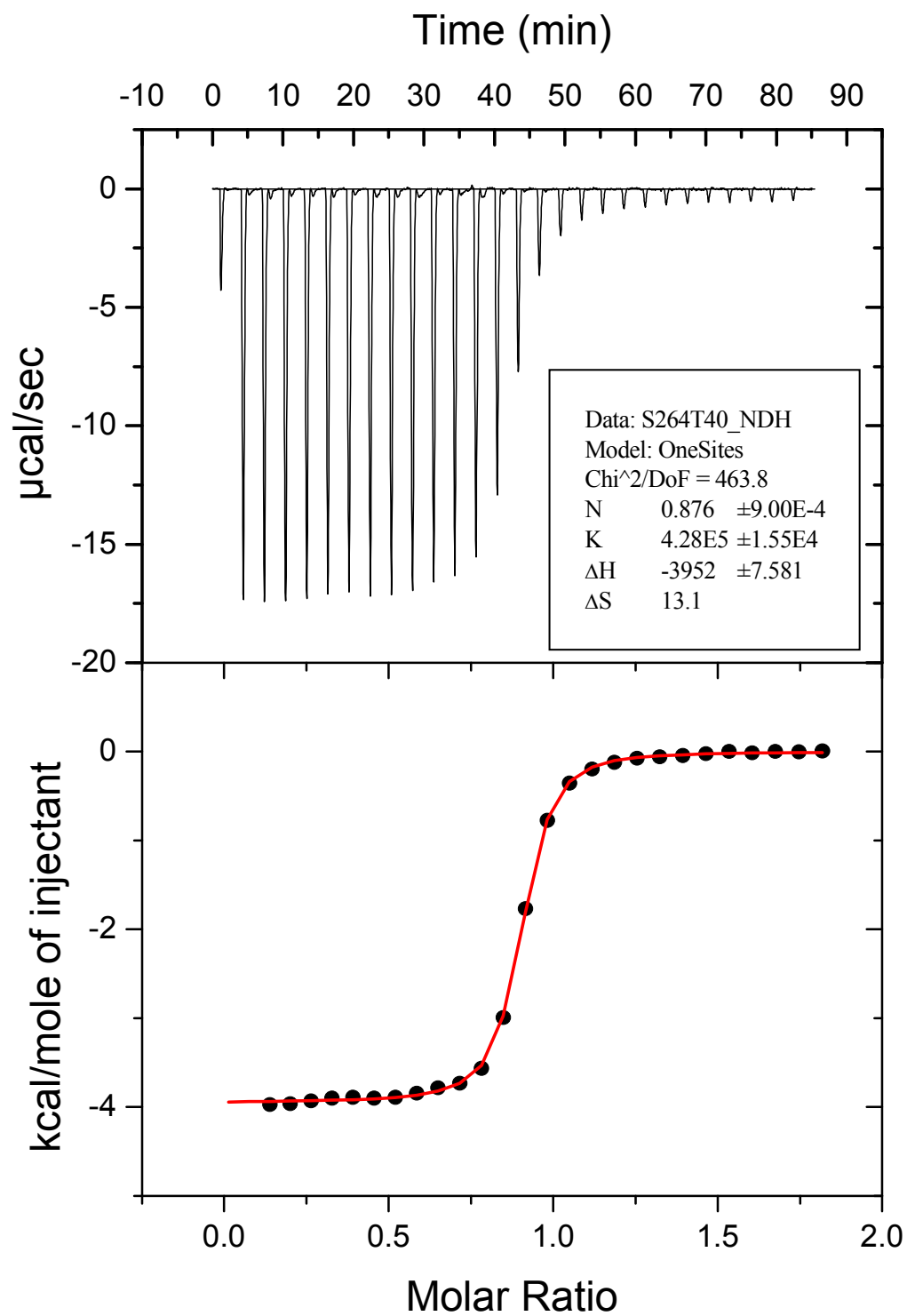




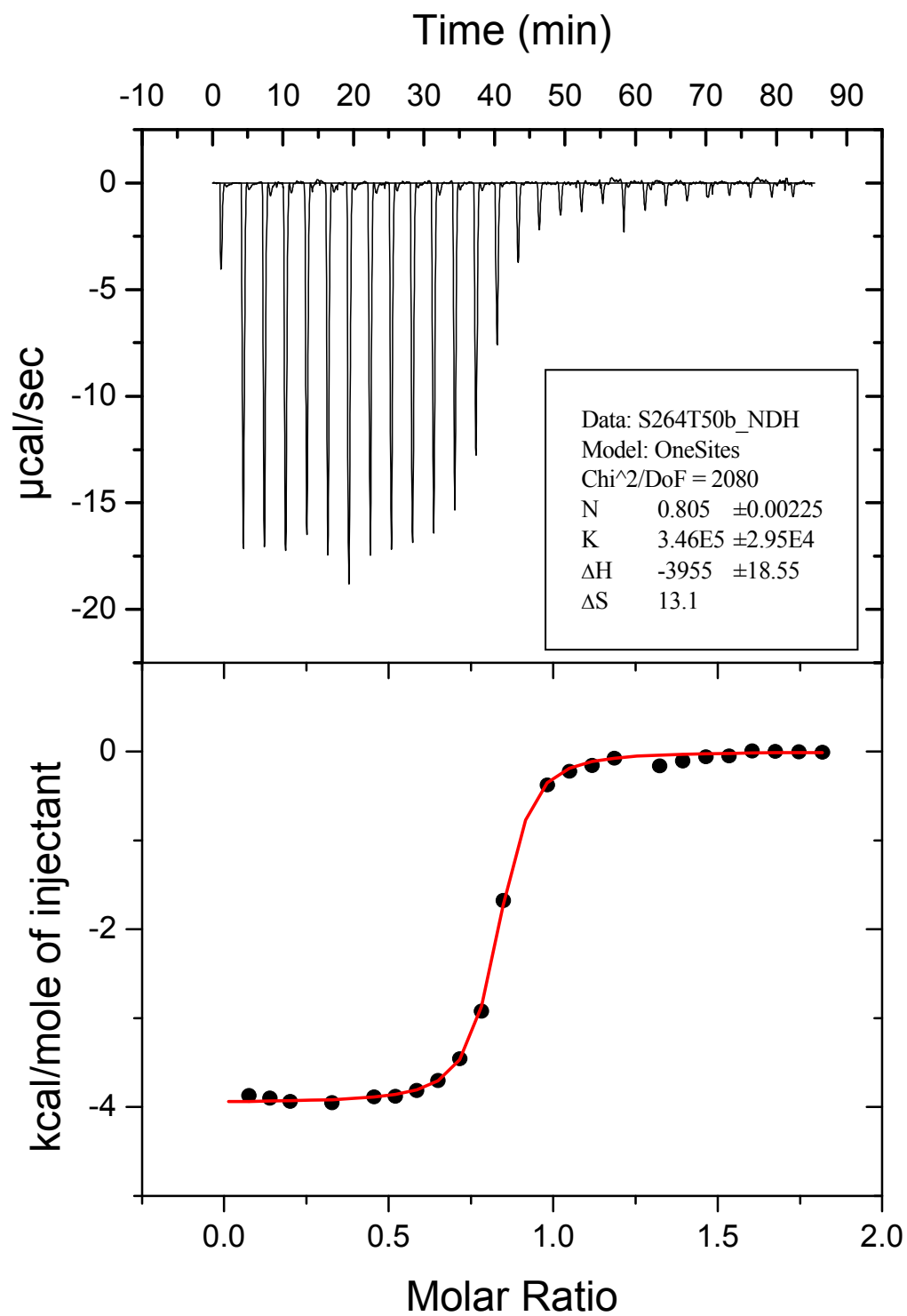
NBu<sub>4</sub>Br to *m*-**II-1**<sup>Me</sup>/OTf in CH<sub>3</sub>CN, 10 °C (see Table 1, entry 17)



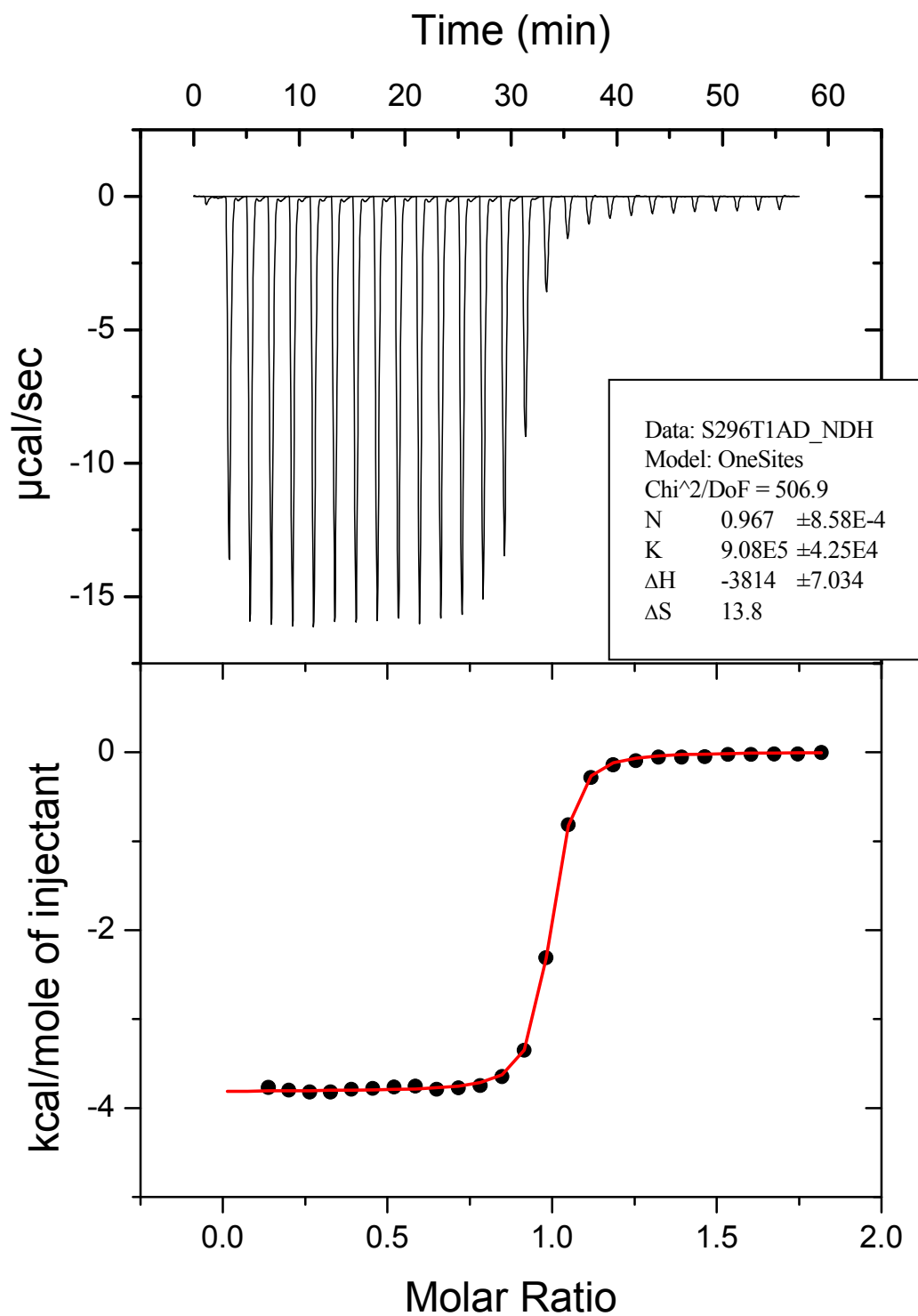
NBu<sub>4</sub>Br to *m*-**II-1**<sup>Me</sup>/OTf in CH<sub>3</sub>CN, 20 °C (see Table 1, entry 18)



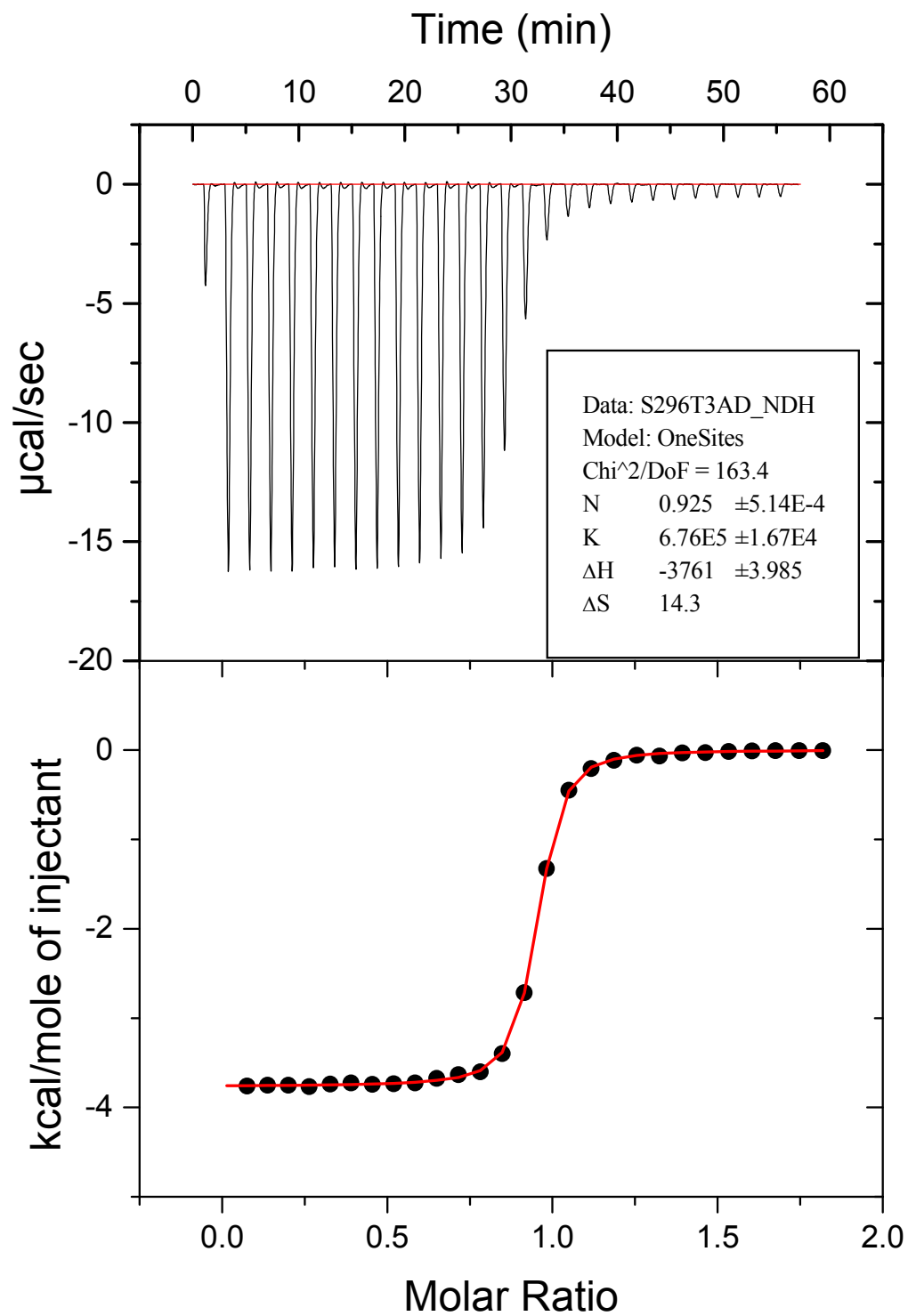
NBu<sub>4</sub>Br to *m*-II-1<sup>Me</sup>/OTf in CH<sub>3</sub>CN, 40 °C (see Table 1, entry 19)



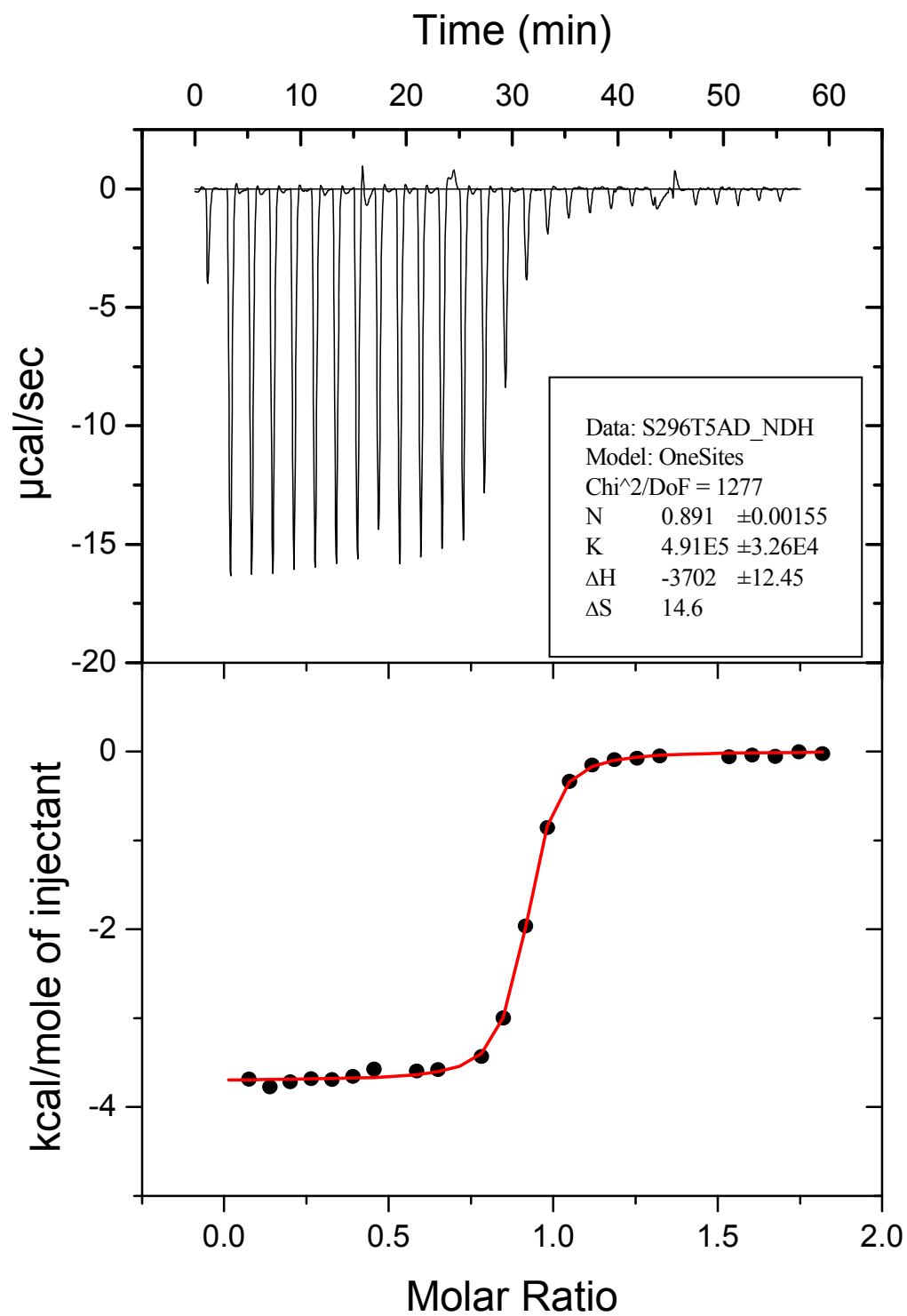
NBu<sub>4</sub>Br to *m*-**II-1**<sup>Me</sup>/OTf in CH<sub>3</sub>CN, 50 °C (see Table 1, entry 20)



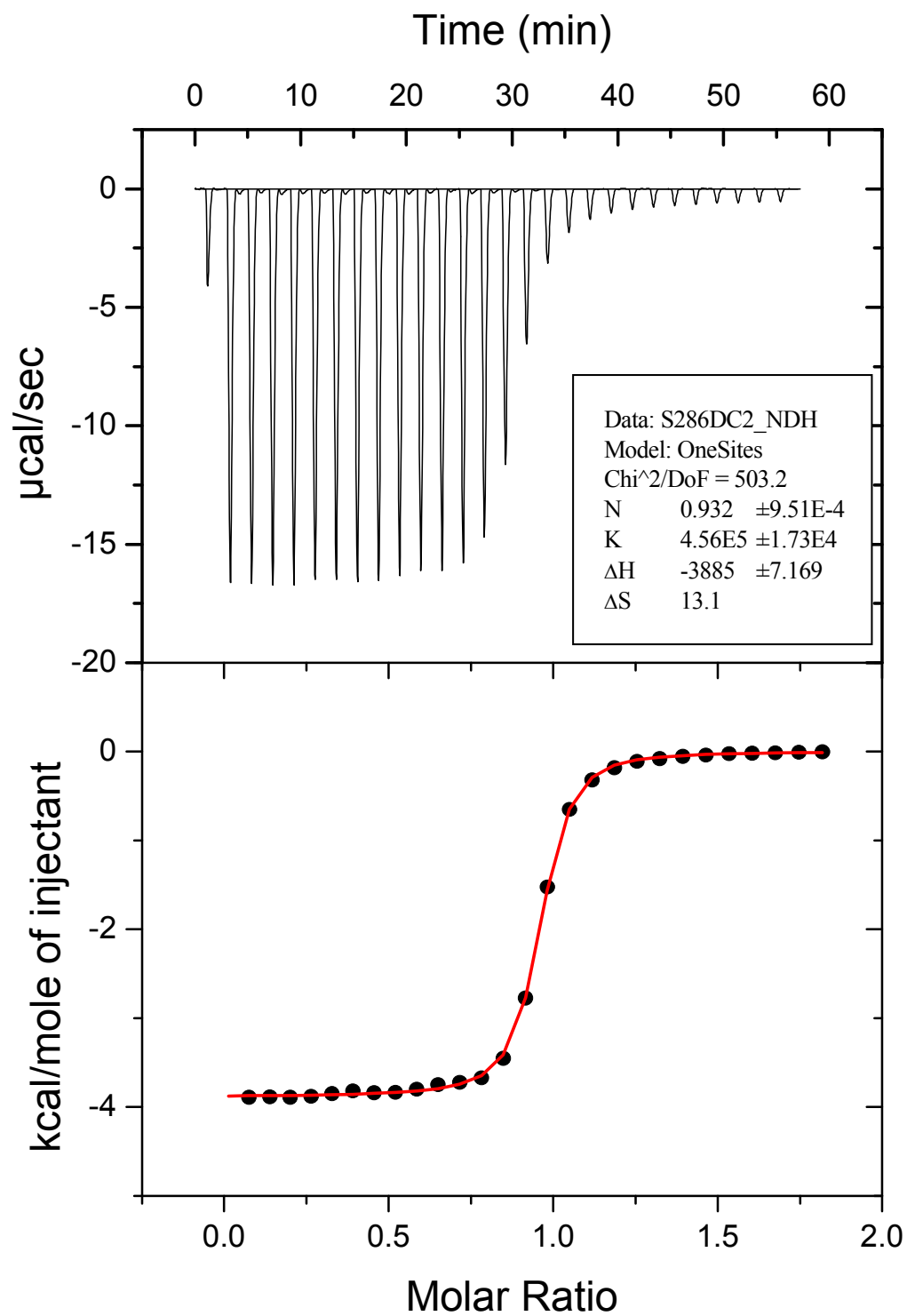
NBu<sub>4</sub>Br to *m*-II-1<sup>Me</sup>/BPh<sub>4</sub> in CH<sub>3</sub>CN, 10 °C (see Table 1, entry 21)



NBu<sub>4</sub>Br to *m*-**II-1**<sup>Me</sup>/BPh<sub>4</sub> in CH<sub>3</sub>CN, 30 °C (see Table 1, entry 22)

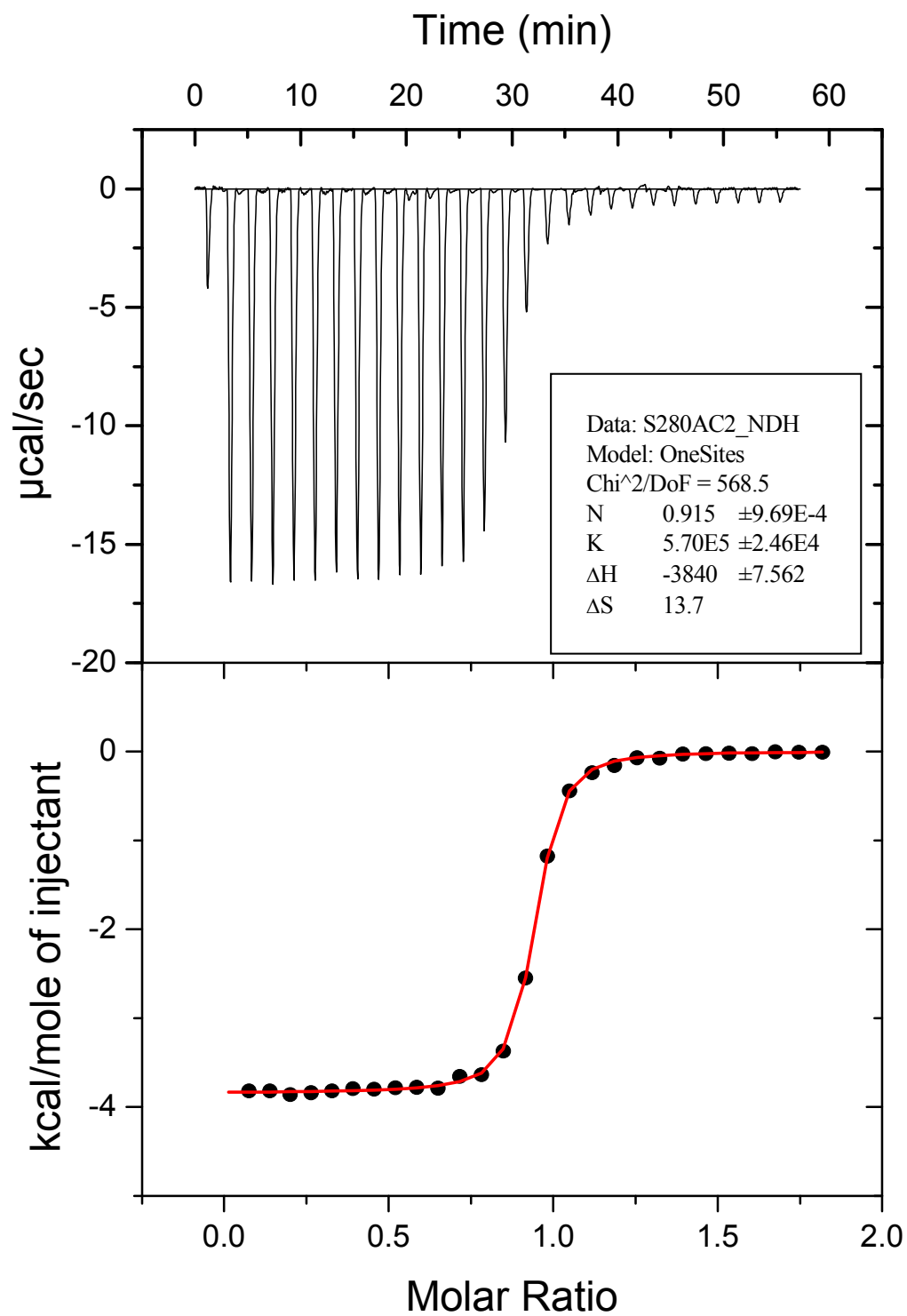


NBu<sub>4</sub>Br to *m*-**II-1**<sup>Me</sup>/**BPh**<sub>4</sub> in CH<sub>3</sub>CN, 50 °C (see Table 1, entry 23)

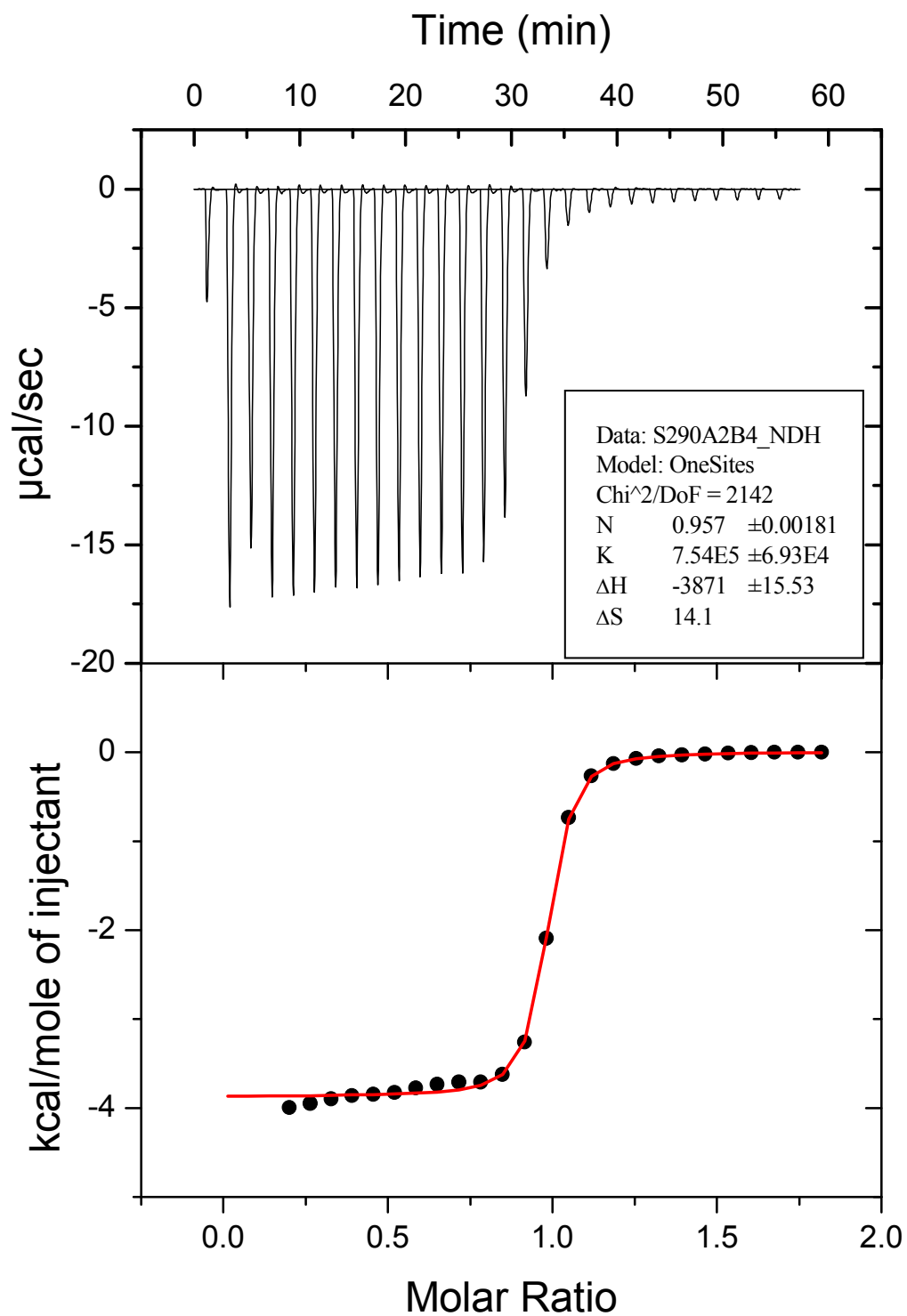


$\text{NBu}_4\text{Br}$  to  $m\text{-II-1}^{\text{Me}}/\text{BF}_4$  in  $\text{CH}_3\text{CN}$ ,  $30^\circ\text{C}$  (see Table 1, entry 29)

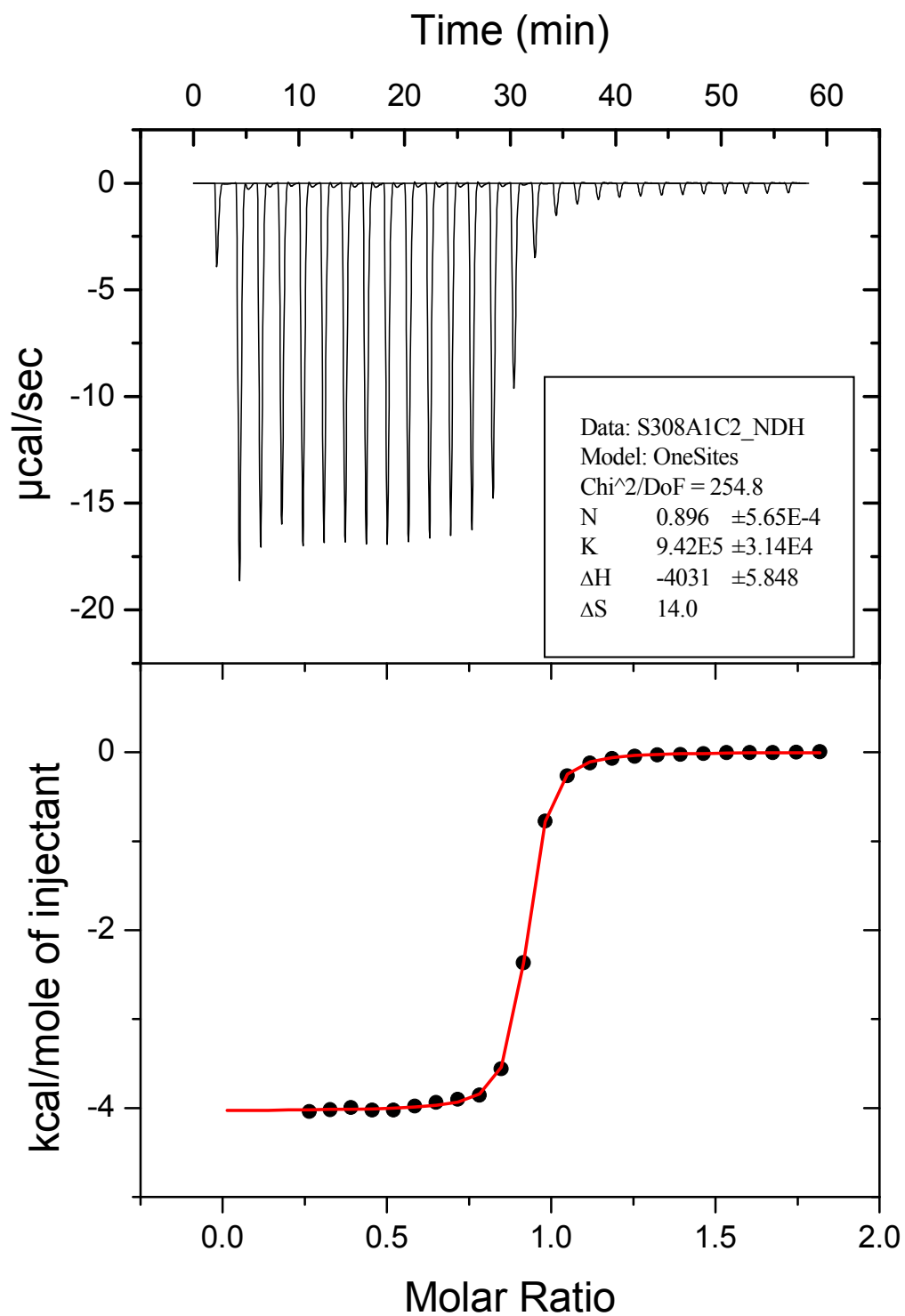




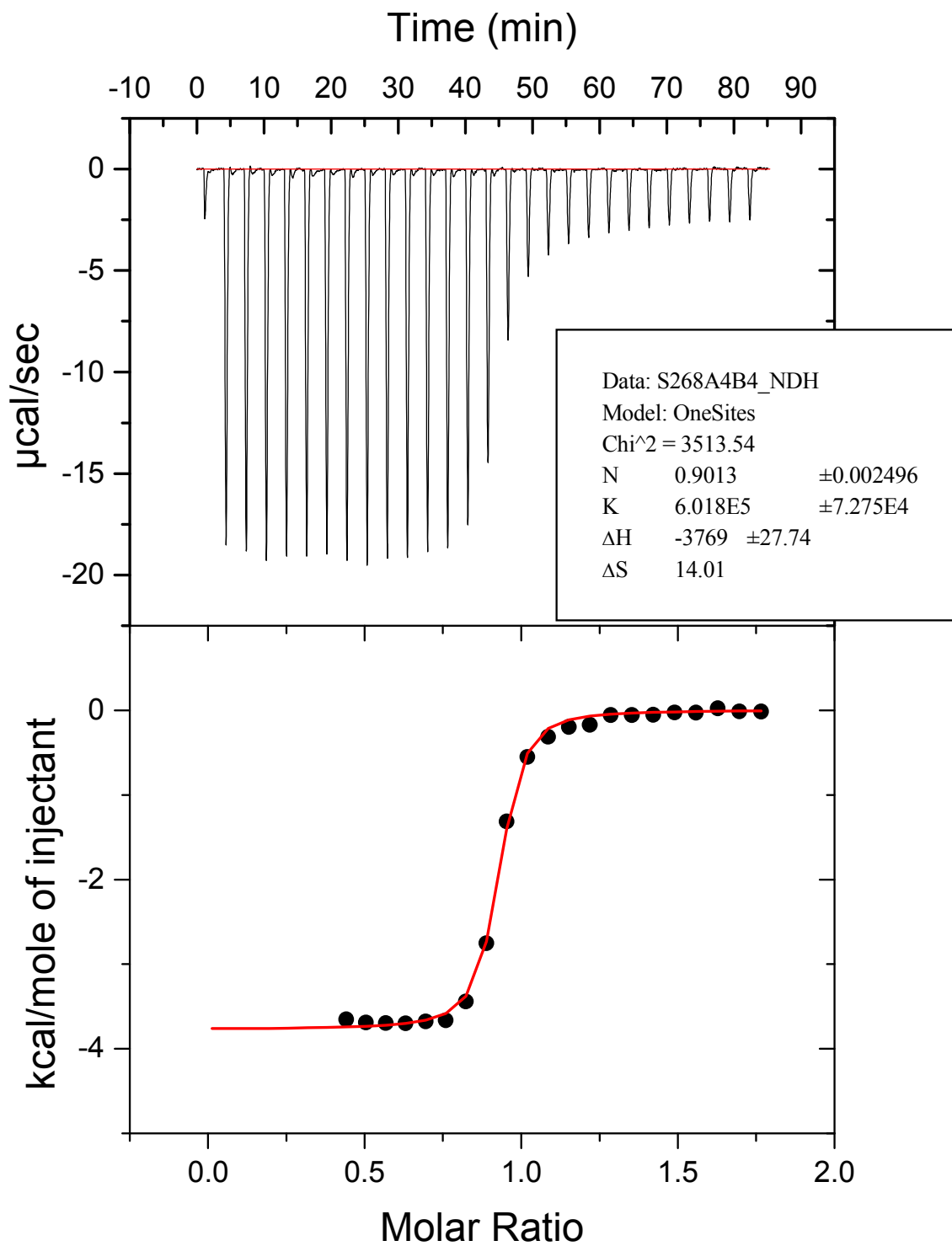
NBu<sub>4</sub>Br to *m*-II-1<sup>Me</sup>/PF<sub>6</sub> in CH<sub>3</sub>CN, 30 °C (see Table 1, entry 30)



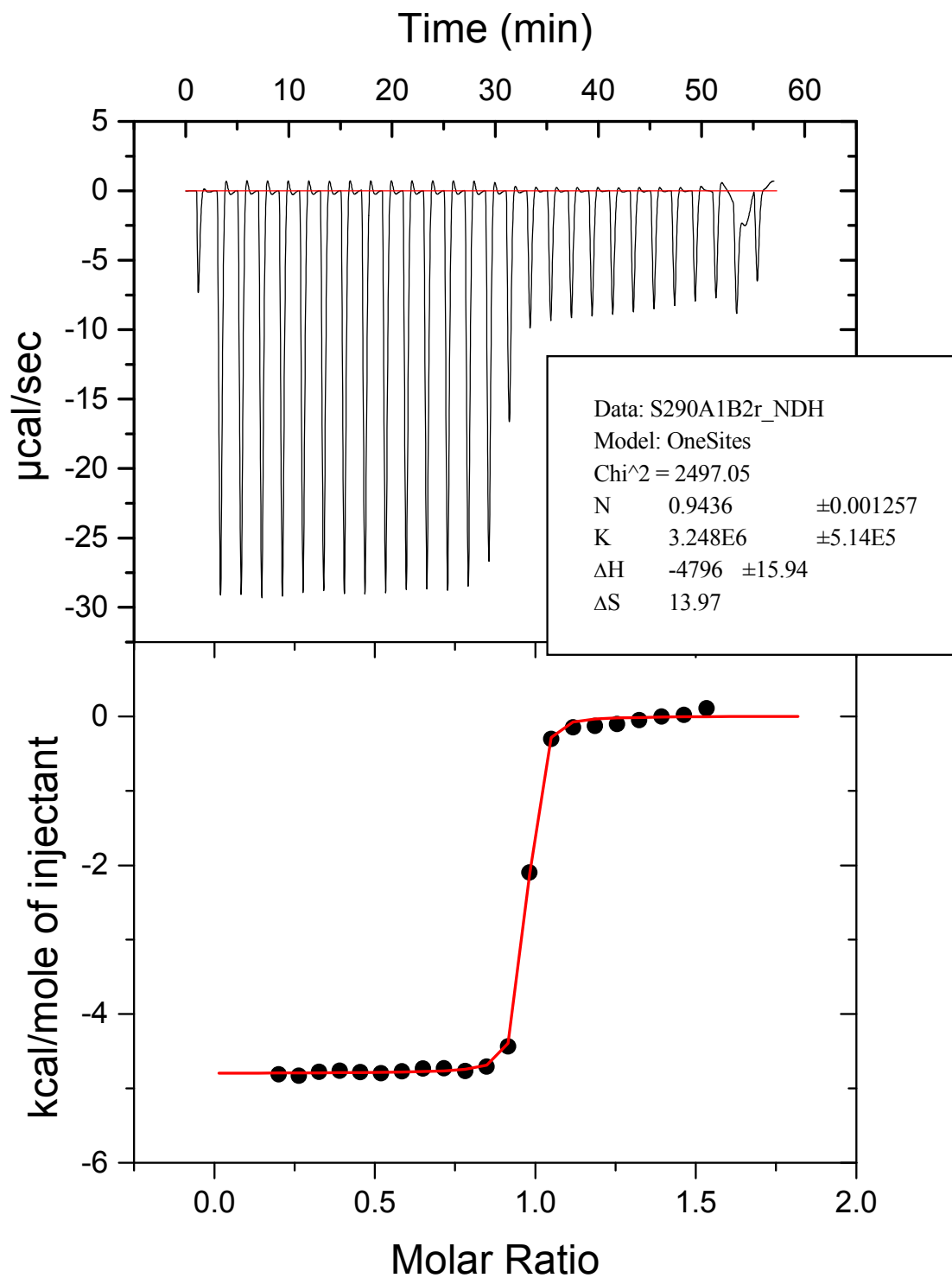
$\text{NBu}_4\text{Br}$  to *m*-**II-1**<sup>Oct</sup>/OTf in  $\text{CH}_3\text{CN}$ , 30 °C (see Table 1, entry 31)



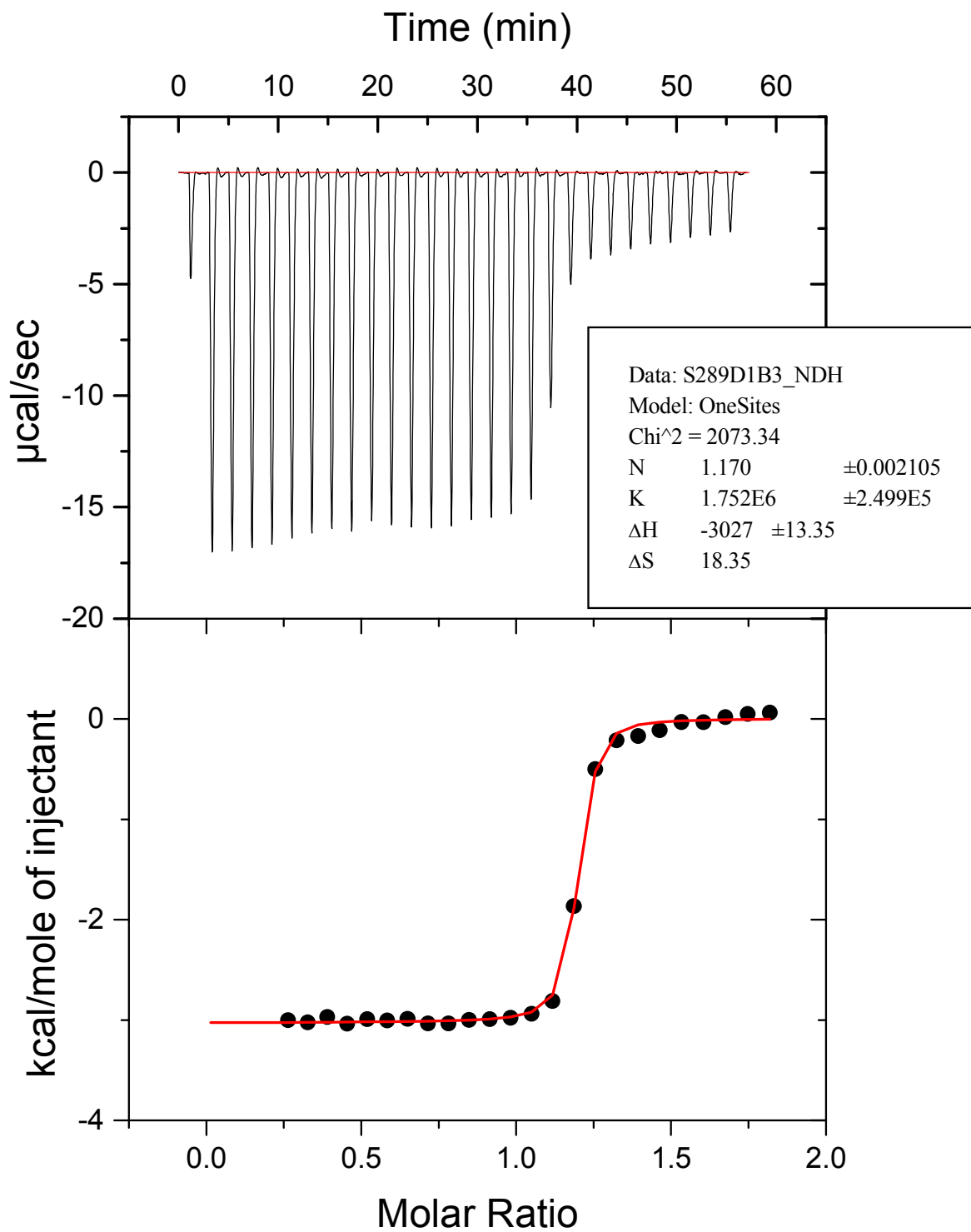
NBu<sub>4</sub>Br to *m*-**II-1**<sup>Oct</sup>/BPh<sub>4</sub> in CH<sub>3</sub>CN, 30 °C (see Table 1, entry 32)



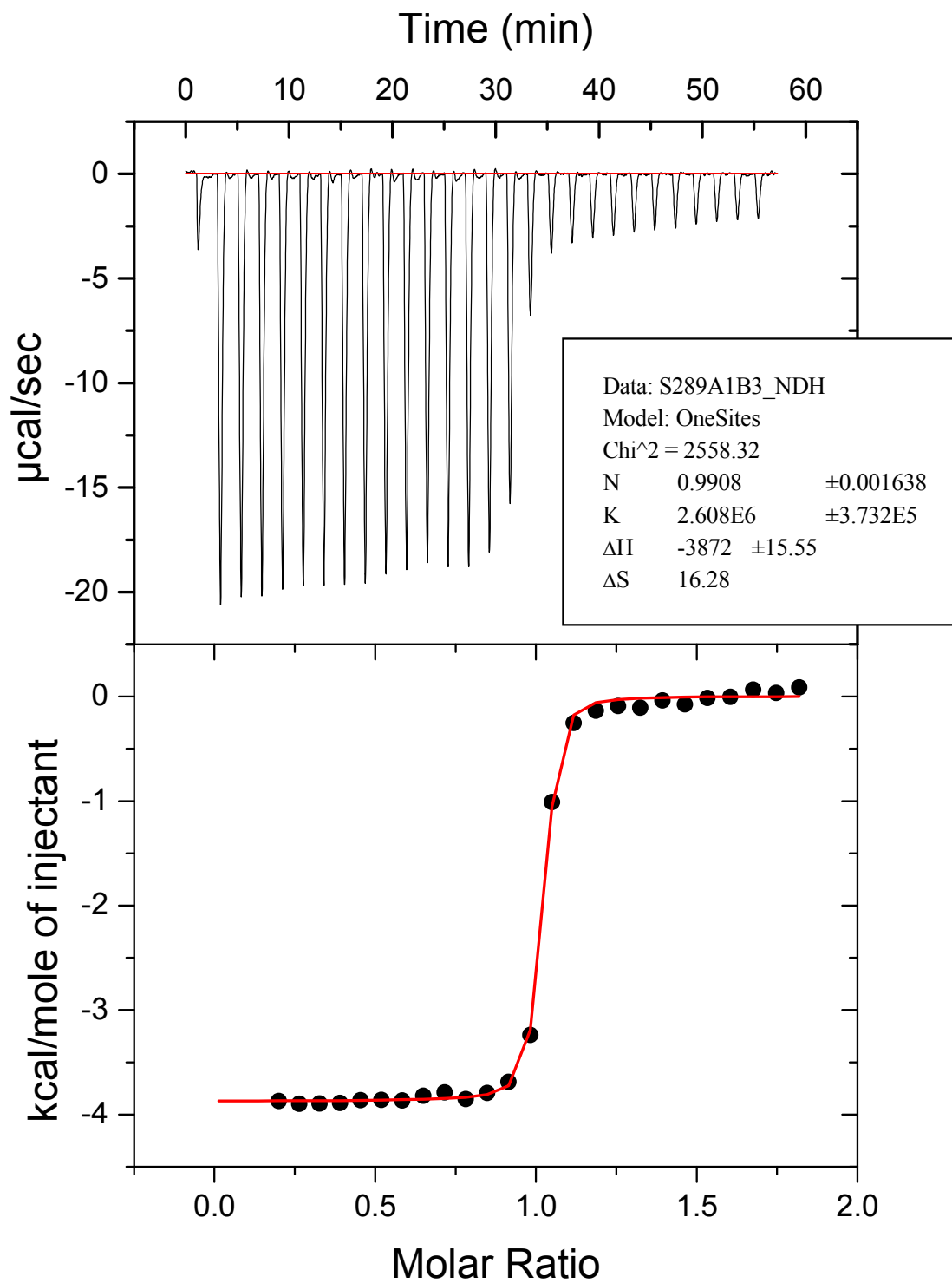
NBu<sub>4</sub>Br to *m*-II-1<sup>Me</sup>/OTf in acetone, 30 °C (see Table 1, entry 33)



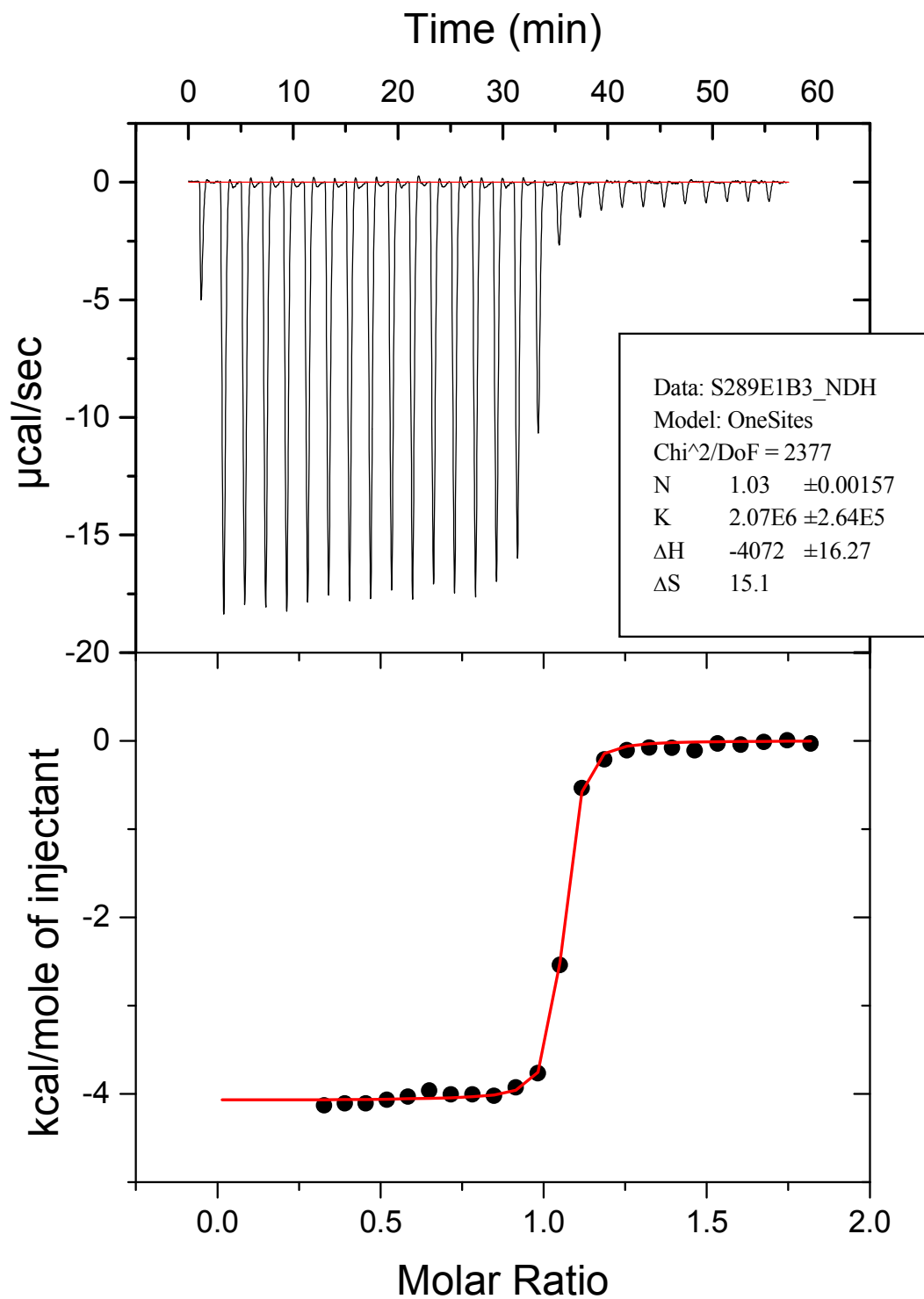
NBu<sub>4</sub>Br to *m*-II-1<sup>Oct</sup>/OTf in THF, 30 °C (see Table 1, entry 37)



$\text{NBu}_4\text{Cl}$  to  $m\text{-II-1}^{\text{Oct}}/\text{OTf}$  in  $\text{CH}_2\text{Cl}_2$ ,  $30^\circ\text{C}$  (see Table 1, entry 38)

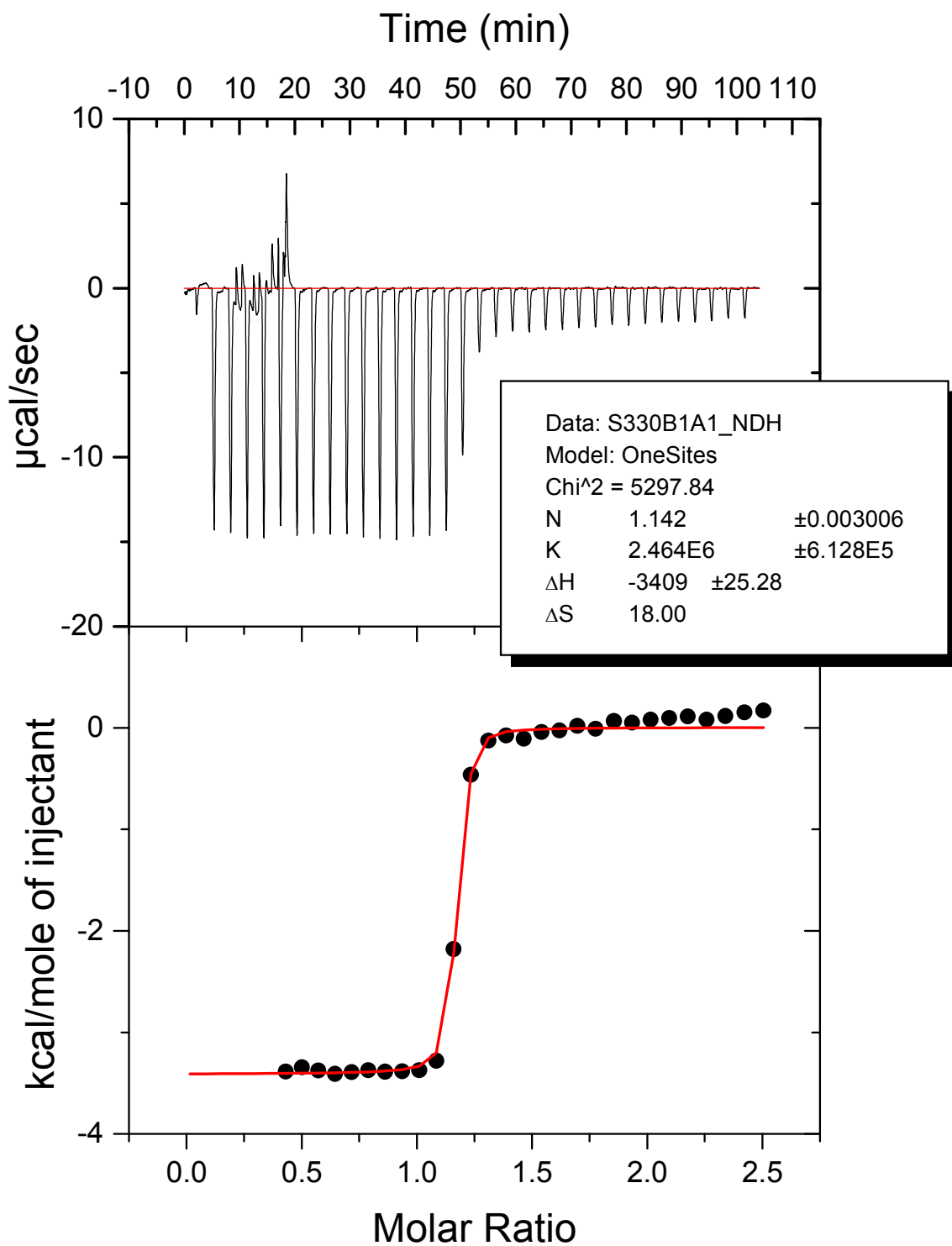


NBu<sub>4</sub>Br to *m*-II-1<sup>Oct</sup>/OTf in CH<sub>2</sub>Cl<sub>2</sub>, 30 °C (see Table 1, entry 39)

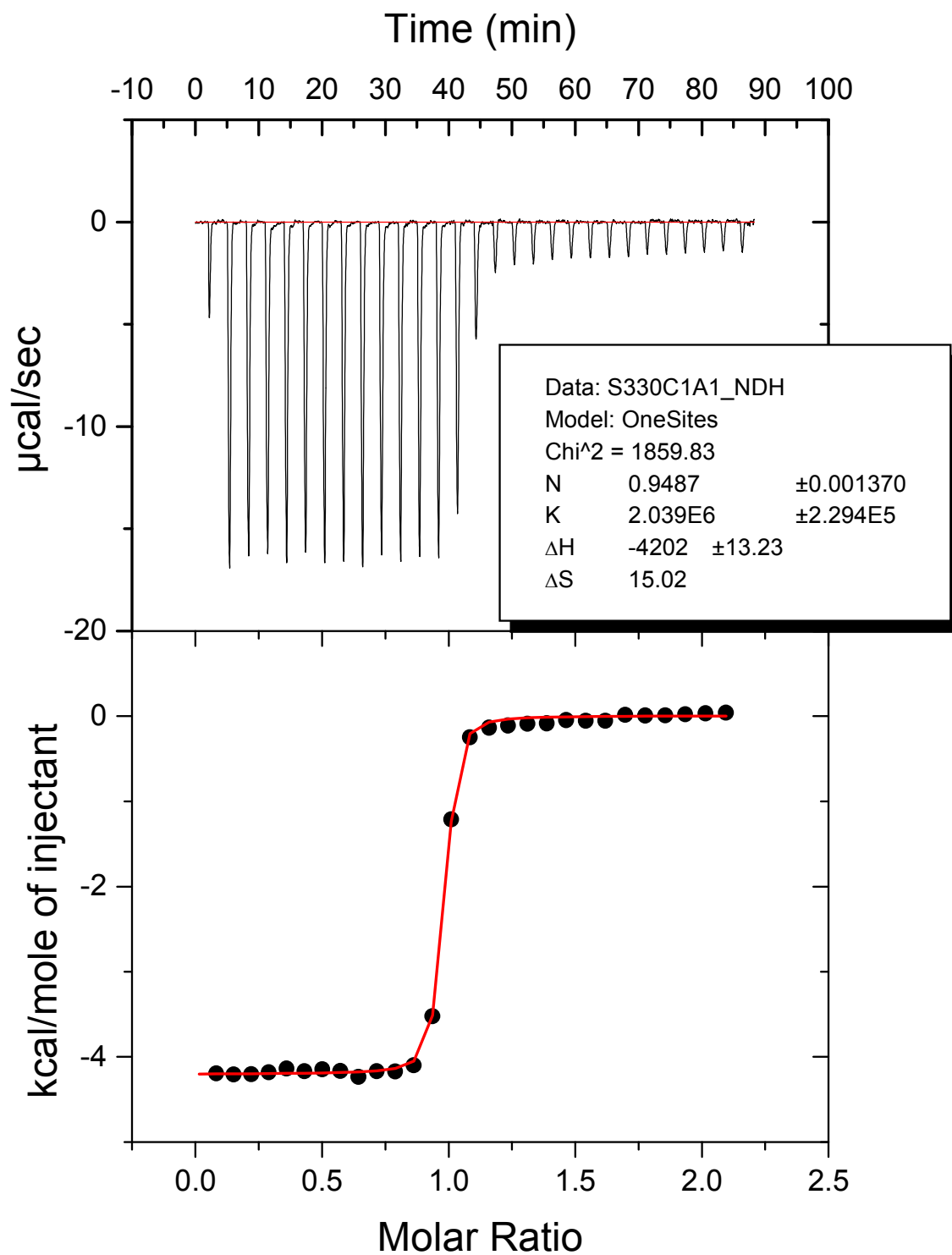


NBu<sub>4</sub>I to *m*-II-1<sup>Oct</sup>/OTf in CH<sub>2</sub>Cl<sub>2</sub>, 30 °C (see Table 1, entry 40)

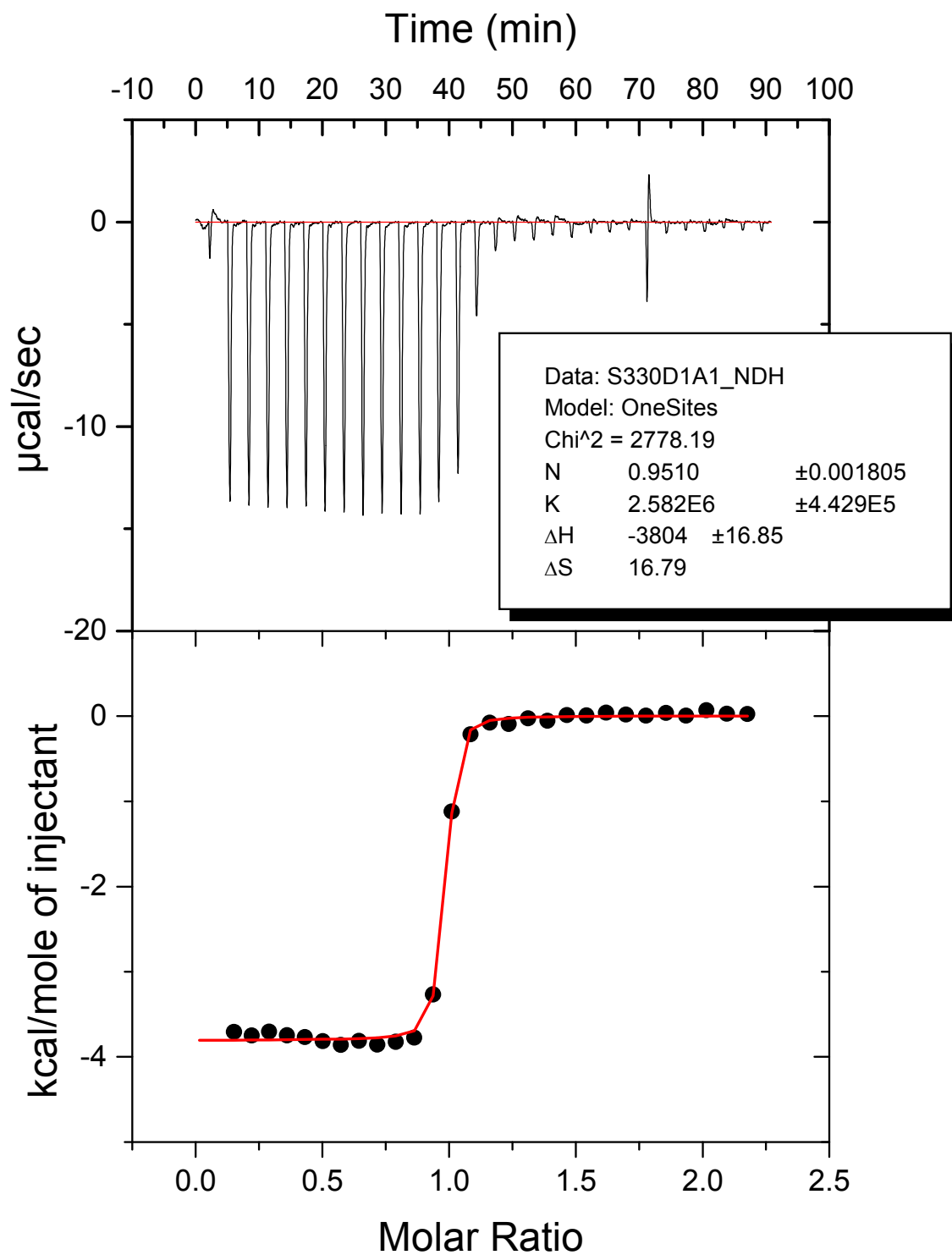




NBu<sub>4</sub>Cl to *m*-H-1<sup>Oct</sup>/OTf in acetone, 30 °C (see Table 1, entry 41)



NBu<sub>4</sub>Br to *m*-H-1<sup>Oct</sup>/OTf in acetone, 30 °C (see Table I, entry 42)



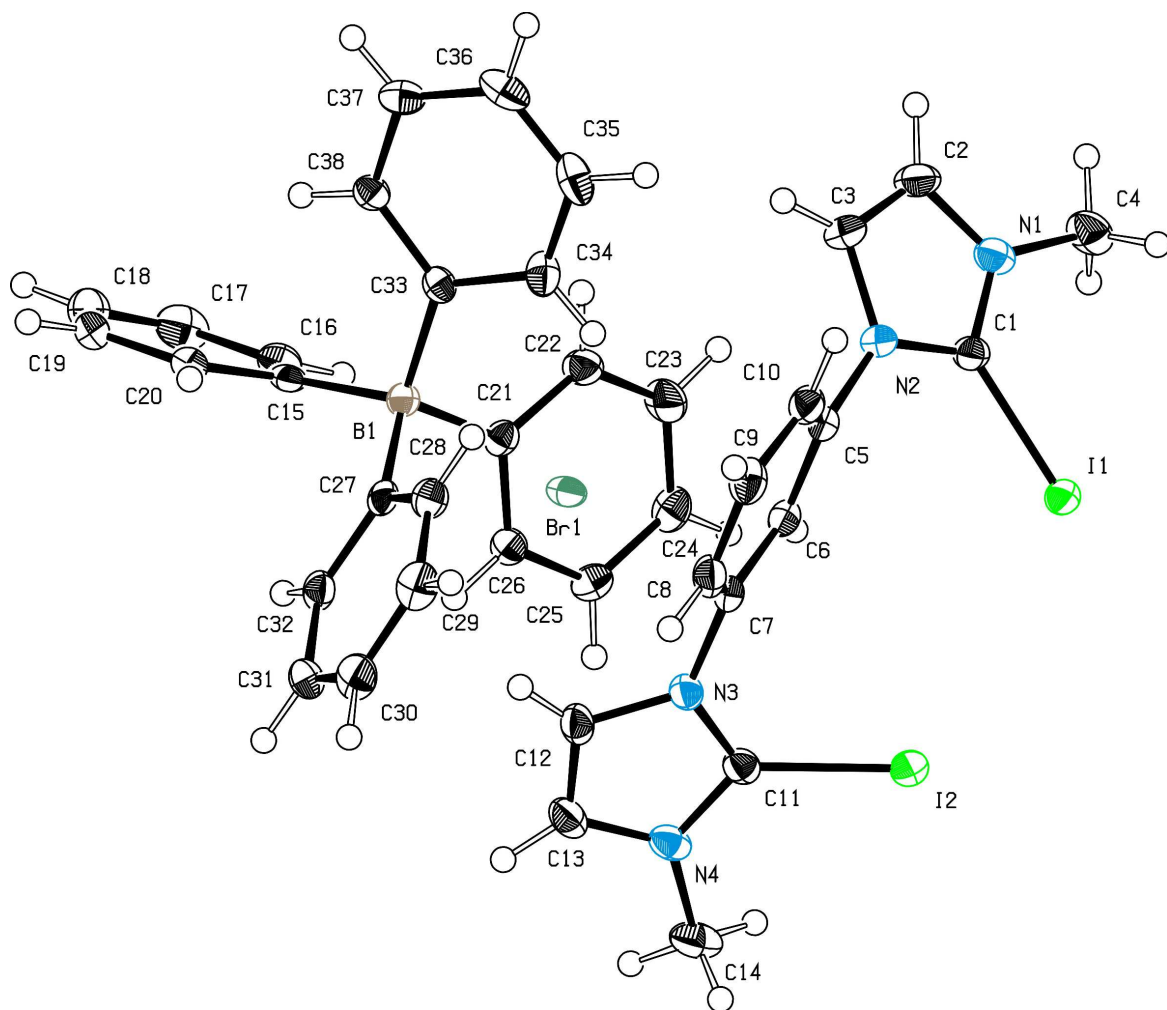
NBu<sub>4</sub>I to *m*-II-1<sup>Oct</sup>/OTf in acetone, 30 °C (see Table 1, entry 43)

### III) X-Ray Structural Analysis

#### **General:**

The data were collected on an X-ray single crystal diffractometer equipped with a CCD detector (APEX II,  $\kappa$ -CCD), a rotating anode (Bruker AXS, FR591) with MoK $_{\alpha}$  radiation ( $\lambda = 0.71073$  Å), and a graphite monochromator by using the SMART software package. [III-1] The measurements were performed on single crystals coated with perfluorinated ether. The crystals were fixed on the top of a glass fiber and transferred to the diffractometer. Crystals from *syn*-**15** and *anti*-**25a** were frozen under a stream of cold nitrogen. A matrix scan using three short runs was used to determine the initial lattice parameters. Reflections were merged and corrected for Lorentz and polarization effects, scan speed, and background using SAINT. [III-2] Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS. [III-2] Space group assignments were based upon systematic absences,  $E$  statistics, and successful refinement of the structures. Structures were solved by direct methods with the aid of successive difference Fourier maps, and were refined against all data using WinGX [III-7] based on SIR-92. [III-3] Hydrogen atoms could not be located in the difference Fourier maps and were calculated in ideal positions (riding model). If not mentioned otherwise, non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing  $\sum w(F_o^2 - F_c^2)^2$  with SHELXL-97 [III-5] weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*. [III-4] Images of the crystal structures were generated by PLATON [III-6].

# Single Crystal X-Ray Structure Determination of Compound *m*-II-1<sup>Me</sup>/BPh<sub>4</sub>



**Figure III-F2** – Ortep drawing drawing of compound *m*-II-1<sup>Me</sup>/BPh<sub>4</sub> with 50% ellipsoids. [III-6]

Operator:	*** Herdtweck ***
Molecular Formula:	C <sub>38</sub> H <sub>34</sub> B Br I <sub>2</sub> N <sub>4</sub> [(C <sub>14</sub> H <sub>14</sub> I <sub>2</sub> N <sub>4</sub> ) <sup>2+</sup> ], [(C <sub>24</sub> H <sub>20</sub> B) <sup>-</sup> ], [(Br) <sup>-</sup> ]
Crystal Color / Shape	Colorless needle
Crystal Size	Approximate size of crystal fragment used for data collection: 0.08 × 0.10 × 0.53 mm
Molecular Weight:	891.20 a.m.u.
F <sub>000</sub> :	1744
Systematic Absences:	h0l: h+l≠2n; 0k0: k≠2n
Space Group:	Monoclinic <i>P</i> 2 <sub>1</sub> /n (I.T.-No.: 14)

Cell Constants:	Least-squares refinement of 9628 reflections with the programs "APEX suite" and "SAINT" [III-1,2]; theta range $1.67^\circ < \theta < 25.35^\circ$ ; Mo(K $\overline{\alpha}$ ); $\lambda = 71.073$ pm		
	$a =$	1062.94(3) pm	
	$b =$	1426.71(4) pm	$\beta =$ 102.4990(12) $^\circ$
	$c =$	2387.57(7) pm	
	$V = 3534.95(18) \cdot 10^6$ pm <sup>3</sup> ; $Z = 4$ ; $D_{\text{calc}} = 1.675$ g cm <sup>-3</sup> ; Mos. = 0.65		
Diffractometer:	Kappa APEX II (Area Diffraction System; BRUKER AXS); rotating anode; graphite monochromator; 50 kV; 40 mA; $\lambda = 71.073$ pm; Mo(K $\overline{\alpha}$ )		
Temperature:	(-150 $\pm$ 1) $^\circ$ C; (123 $\pm$ 1) K		
Measurement Range:	$1.67^\circ < \theta < 25.35^\circ$ ; h: -12/12, k: -17/17, l: -28/28		
Measurement Time:	$2 \times 5$ s per film		
Measurement Mode:	measured: 9 runs; 4794 films / scaled: 9 runs; 4794 films		
	$\phi$ - and $\omega$ -movement; Increment: $\Delta\phi/\Delta\omega = 0.50^\circ$ ; dx = 45.0 mm		
LP - Correction:	Yes [III-2]		
Intensity Correction	No/Yes; during scaling [III-2]		
Absorption Correction:	Multi-scan; during scaling; $\mu = 2.942$ mm <sup>-1</sup> [III-2]		
	Correction Factors:	$T_{\text{min}} = 0.5799$	$T_{\text{max}} = 0.7452$
Reflection Data:	125780	reflections were integrated and scaled	
	3176	reflections systematic absent and rejected	
	122604	reflections to be merged	
	6464	independent reflections	
	0.030	$R_{\text{int}}$ : (basis $F_o^2$ )	
	6464	independent reflections (all) were used in refinements	
	6251	independent reflections with $I_o > 2\sigma(I_o)$	
	99.8 %	completeness of the data set	
	417	parameter full-matrix refinement	
	15.5	reflections per parameter	
Solution:	Direct Methods [III-3]; Difference Fourier syntheses		
Refinement Parameters:	In the asymmetric unit:		
	46	Non-hydrogen atoms with anisotropic displacement parameters	
Hydrogen Atoms:	In the difference map(s) calculated from the model containing all non-hydrogen atoms, not all of the hydrogen positions could be determined from the highest peaks. For this reason, the		

hydrogen atoms were placed in calculated positions ( $d_{C-H} = 95, 98$  pm). Isotropic displacement parameters were calculated from the parent carbon atom ( $U_H = 1.2/1.5 U_C$ ). The hydrogen atoms were included in the structure factor calculations but not refined.

Atomic Form Factors:	For neutral atoms and anomalous dispersion [III-4]	
Extinction Correction:	no	
Weighting Scheme:	$w^{-1} = \sigma^2(F_o^2) + (a*P)^2 + b*P$ with a: 0.0154; b: 3.2775; P: [Maximum(0 or $F_o^2$ ) + 2* $F_c^2$ ]/3	
Shift/Err:	Less than 0.002 in the last cycle of refinement:	
Resid. Electron Density:	+0.56 e <sub>0</sub> <sup>-</sup> /Å <sup>3</sup> ; -0.37 e <sub>0</sub> <sup>-</sup> /Å <sup>3</sup>	
R1:	$\Sigma( F_o  -  F_c )/\Sigma F_o $	
[ $F_o > 4\sigma(F_o)$ ]; N=6251]:		= 0.0150
[all reflctns; N=6464]:		= 0.0159
wR2:	$[\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)]^{1/2}$	
[ $F_o > 4\sigma(F_o)$ ]; N=6251]:		= 0.0383
[all reflctns; N=6464]:		= 0.0389
Goodness of fit:	$[\Sigma w(F_o^2 - F_c^2)^2 / (NO - NV)]^{1/2}$	
		= 1.093
Remarks:	Refinement expression $\Sigma w(F_o^2 - F_c^2)^2$	

## **References:**

- [III-1] APEX suite of crystallographic software. APEX 2 Version 2008.4. Bruker AXS Inc., Madison, Wisconsin, USA (2008).
- [III-2] SAINT, Version 7.56a and SADABS Version 2008/1. Bruker AXS Inc., Madison, Wisconsin, USA (2008).
- [III-3] Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, Moliterni A. G. G.; A.; Burla, M. C.; Polidori, G.; Camalli, M.; Spagna, R. "SIR97", A New Tool for Crystal Structure Determination and Refinement; *J. Appl. Crystallogr.* **1999**, 32, 115-119.
- [III-4] International Tables for Crystallography, Vol. C, Tables 6.1.1.4 (pp. 500-502), 4.2.6.8 (pp. 219-222), and 4.2.4.2 (pp. 193-199), Wilson, A. J. C., Ed., Kluwer Academic Publishers, Dordrecht, The Netherlands, 1992.
- [III-5] Sheldrick, G. M. "SHELXL-97", University of Göttingen, Göttingen, Germany, (1998).
- [III-6] Spek, A. L. "PLATON", A Multipurpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands, (2010).
- [III-7] L. J. Farrugia, "WinGX (Version 1.70.01 January 2005) ", *J. Appl. Cryst.* **1999**, 32, 837-838.