

## Supporting Information

### **Syntheses and characterization of bis(pyrazolyl)borate Ni(II) complexes: ligand rearrangement and transformation**

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#### **General Methods**

All manipulations were carried out under N<sub>2</sub> atmosphere by means of standard Schlenk techniques, unless otherwise stated. Solvents were dried and degassed using standard procedures prior to use. NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, Ni(acac)<sub>2</sub> and pyrazoles were used as received from commercial sources without further purification. All NMR spectra were recorded on a Bruker AV400 (<sup>1</sup>H 400.1 MHz; <sup>13</sup>C 100.6 MHz; <sup>11</sup>B 128.0 MHz) or a Bruker AV600 (<sup>1</sup>H 600.2 MHz; <sup>13</sup>C 150.9 MHz; <sup>11</sup>B 192.6 MHz) spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are referenced to residual solvent protons or TMS, and <sup>11</sup>B NMR spectra are externally referenced to BF<sub>3</sub>·OEt<sub>2</sub> in C<sub>6</sub>D<sub>6</sub> (δ = 0.00 ppm). Elemental analyses data were obtained on a Elementar (Vario EL) instrument.

#### **1. Preparation and Characterization of Compounds 1a-1d, 2a, 2b, 3, 4 and 5**

General synthetic method for **1a-1d**: To a stirred mixture of 9-BBN dimer (0.73 g, 3 mmol) and KH (0.24 g, 6 mmol) in 30 mL toluene was slowly added into a 20 mL toluene solution of pyrazole (12 mmol) using a syringe. Hydrogen evolution was immediately observed. The reaction mixture was refluxed for 3 h until no more gas was released. During reaction a white precipitate was formed. The mixture was cooled to room temperature, and

the solvent was removed to produce a white solid which was washed with hexane and dried under vacuum.

Compound **1a**. Yield: 1.73 g, 98%.

$^1\text{H}$  NMR(400 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.5 (d,  $J = 2.0$  Hz, 2H), 7.3 (d,  $J = 1.2$  Hz, 2H), 6.0 (t,  $J = 1.8$  Hz, 2H), 1.9-1.8 (m, 2H), 1.8-1.7 (m, 4H), 1.7-1.6 (m, 4H), 1.5 (br, 2H), 1.2 (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  138.1, 131.1, 102.3, 31.3, 24.4.  $^{11}\text{B}$  NMR (128 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  -0.1 (s).

Compound **1b**. Yield: 1.88 g, 97%.

$^1\text{H}$  NMR(600 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.4 (s, 2H), 5.7 (s, 2H), 2.1 (s, 6H), 1.9-1.7 (m, 6H), 1.6 (m, 4H), 1.4 (br, 2H), 1.3 (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  146.2, 132.2, 102.3, 32.0, 25.2, 24.2, 13.5.  $^{11}\text{B}$  NMR (193 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  -2.1 (s).

Compound **1c**. Yield: 2.77 g, 96%.

$^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.4 (s, 2H), 1.8 (m, 2H), 1.7 (m, 4H), 1.6 (m, 4H), 1.4 (br, 2H), 1.2 (m, 2H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  144.7, 132.3, 90.4, 31.8, 25.0, 23.2, 11.8.  $^{11}\text{B}$  NMR (193 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  -0.5 (s).

Compound **1d**. Yield: 2.22 g, 98%.

$^1\text{H}$  NMR(600 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  7.4 (s, 2H), 5.8 (s, 2H), 2.9 (Hept,  $J = 6.6$  Hz, 2H), 1.9-1.7 (m, 6H), 1.6-1.5 (m, 4H), 1.4 (br, 2H), 1.2 (d,  $J = 6.6$  Hz, 1H), 1.2 (d,  $J = 6.6$  Hz, 1H), 1.1 (d,  $J = 6.6$  Hz, 12H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  157.9, 132.1, 98.9, 32.2, 28.6, 25.3, 24.7, 24.0.  $^{11}\text{B}$  NMR (193 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  -1.9 (s).

Compound **2a**. At room temperature, a slurry of **1a** (0.29 g, 1 mmol) with  $\text{Ni}(\text{acac})_2$  (0.13 g, 0.5 mmol) in 50 mL dichloromethane was stirred vigorously for 12 h. The solution gradually turned from light-green to orange-red, and a little white precipitation was generated. Then the mixture was filtered to remove the insoluble substance. After concentration of the filtrate to saturation, orange crystals were obtained after a few days, which were collected by filtration and dried under vacuum. Yield: 0.20 g, 70%.

$^1\text{H}$  NMR plus  $^{13}\text{C}$ - $^1\text{H}$  HSQC (600 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  7.6 (d,  $J = 2.3$  Hz, 2H), 7.1 (s, 1H), 6.9 (d,  $J = 2.1$  Hz, 2H), 6.0 (t,  $J = 2.2$  Hz, 2H), 2.3-2.0 (m, 6H), 2.0-1.9 (m, 2H), 1.8 (dt,  $J = 12.1, 6.8$  Hz, 2H), 1.6 (dt,  $J = 13.8, 6.5$  Hz, 2H), 1.4 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (151 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  141.3, 135.2, 105.5, 32.5, 31.3, 30.6, 24.6, 20.4.  $^{11}\text{B}$  NMR (193 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  0.8 (s). Elemental Analysis Calcd. (%) for  $\text{C}_{28}\text{H}_{40}\text{B}_2\text{N}_8\text{Ni}$ : C, 59.11; H, 7.09; N, 19.70. Found: C,

59.40; H, 7.28; N, 19.63.

Compound **3**. At room temperature, a slurry of **1b** (0.64 g, 2 mmol) with NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.65 g, 1 mmol) or Ni(acac)<sub>2</sub> (0.26 g, 1 mmol) in 50 mL dichloromethane or toluene was stirred vigorously for 12 h. The solution gradually turned from dark- or light-green to green, and a little white precipitation was generated. Then the mixture was filtered to remove the insoluble substance. The filtrate was removed solvent under vacuum and redissolved in n-hexane. After concentration of the solution to near saturation, green crystals were obtained after a few days, which were collected by filtration and dried under vacuum. Yield: 0.59 g, 95%. Elemental Analysis Calcd. (%) for C<sub>32</sub>H<sub>48</sub>B<sub>2</sub>N<sub>8</sub>Ni: C, 61.49; H, 7.74; N, 17.93. Found: C, 61.31; H, 8.02; N, 18.05.

Compound **2b**. A solution of **3** (1.25 g, 2 mmol) in 30 mL toluene was stirred under reflux for 3 days. The solution gradually turned from green to orange-red. After concentration of the reaction mixture to saturation, orange crystals were obtained after a few days, which were collected by filtration and dried under vacuum. Yield: 0.81 g, 65%. Elemental Analysis Calcd. (%) for C<sub>32</sub>H<sub>48</sub>B<sub>2</sub>N<sub>8</sub>Ni: C, 61.49; H, 7.74; N, 17.93. Found: C, 61.70; H, 7.95; N, 17.65.

Compound **4**. At room temperature, a slurry of **1c** (0.96 g, 2 mmol) with NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.65 g, 1 mmol) or Ni(acac)<sub>2</sub> (0.26 g, 1 mmol) in 50 mL toluene was stirred vigorously for 12 h. The solution gradually turned from dark- or light-green to green, and a little white precipitation was generated. Then the mixture was filtered to remove the insoluble substance. The filtrate was removed solvent under vacuum and redissolved in n-hexane. After concentration of the solution to near saturation, green crystals were obtained after a few days, which were collected by filtration and dried under vacuum. Yield: 0.82 g, 87%. Elemental Analysis Calcd. (%) for C<sub>32</sub>H<sub>44</sub>B<sub>2</sub>N<sub>8</sub>Br<sub>4</sub>Ni: C, 40.86; H, 4.71; N, 11.91. Found: C, 40.56; H, 5.08; N, 12.25.

Compound **5**. At room temperature, a slurry of **1d** (0.76 g, 2 mmol) with NiCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.65 g, 1 mmol) in 50 mL toluene or CH<sub>2</sub>Cl<sub>2</sub> was stirred vigorously for 12 h. The solution gradually turned from dark-green to blue-green, and a little white precipitation was generated. Then the mixture was filtered to remove the insoluble substance. The filtrate was removed solvent under vacuum and redissolved in n-hexane. After concentration of the solution to near saturation, blue-green crystals were obtained via fast crystallization within one day, which

were collected by filtration and dried under vacuum. Yield: 0.68 g, 90%. Elemental Analysis Calcd. (%) for C<sub>40</sub>H<sub>66</sub>B<sub>2</sub>N<sub>8</sub>NiO: C, 40.86; H, 4.71; N, 11.91. Found: C, 41.13; H, 4.96; N, 11.63.

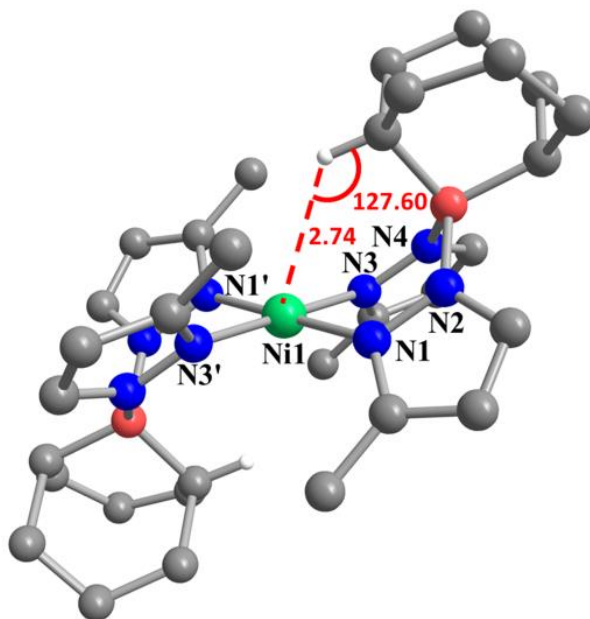
## 2. X-ray Crystallography

Single-crystal X-ray diffraction data were collected on a Bruker SMART6000 CCD detector with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), or on an Agilent Diffraction SuperNova Atlas using Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) or Cu K $\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ). Data reduction were performed using the SAINT software package and an absorption correction was applied using SADABS.<sup>[1-4]</sup> The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structures were solved by a combination of direct methods in SHELXT and the difference Fourier technique and refined by full-matrix least-squares procedures. Non-hydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model. CCDC-1917928 (**2a**), CCDC-1917929 (**2b**), CCDC-1917930 (**3**), CCDC-1917931 (**4**) and CCDC-1917932 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data-request/cif](http://www.ccdc.cam.ac.uk/data-request/cif). Crystal data and refinement parameters are summarized in Table S1. The X-ray crystal structure of **2b** is shown in Fig. S1.

**Table S1.** Crystallographic data and structure refinement results for **2a**, **2b**, **3**, **4** and **5**.

|                   | <b>2a</b>  | <b>2b</b>  | <b>3</b>   | <b>4•0.5C<sub>6</sub>H<sub>14</sub></b>  | <b>5</b>  |
|-------------------|--|--|--|--|---|
| Empirical formula | C <sub>28</sub> H <sub>40</sub> B <sub>2</sub> N <sub>8</sub> Ni | C <sub>32</sub> H <sub>48</sub> B <sub>2</sub> N <sub>8</sub> Ni | C <sub>32</sub> H <sub>48</sub> B <sub>2</sub> N <sub>8</sub> Ni | C <sub>35</sub> H <sub>51</sub> B <sub>2</sub> Br <sub>4</sub> N <sub>8</sub> Ni | C <sub>40</sub> H <sub>66</sub> B <sub>2</sub> N <sub>8</sub> NiO |
| <i>Mr</i>         | 569.01   | 625.11   | 625.11   | 983.80   | 754.33  |
| Temp, K           | 113.15   | 295.2(4)   | 293.99(18)   | 170.00(10)   | 100.01(10)  |
| Crystal system    | Triclinic  | Triclinic  | Monoclinic   | Monoclinic   | Monoclinic  |
| Space group       | <i>P</i> -1  | <i>P</i> -1  | <i>P</i> 2 <sub>1</sub> / <i>n</i>                               | <i>P</i> 2 <sub>1</sub> / <i>n</i>   | <i>P</i> 2 <sub>1</sub> / <i>c</i>                                |

|   |               |               |               |               |               |
|---|---------------|---------------|---------------|---------------|---------------|
| $a[\text{Å}]$                           | 7.5258(2)     | 7.5038(5)     | 8.8173(4)     | 11.1521(2)    | 11.00180(10)  |
| $b[\text{Å}]$                           | 9.3230(3)     | 9.7847(5)     | 24.0412(10)   | 19.2678(3)    | 10.8736(2)    |
| $c[\text{Å}]$                           | 10.6602(4)    | 11.3835(6)    | 15.2894(9)    | 18.7249(2)    | 34.0677(3)    |
| $\alpha[^\circ]$                        | 89.771(2)     | 87.799(4)     | 90            | 90            | 90            |
| $\beta[^\circ]$                         | 80.615(2)     | 79.365(5)     | 96.950(4)     | 102.2210(10)  | 90.9030(10)   |
| $\gamma[^\circ]$                        | 66.6289(18)   | 68.035(6)     | 90            | 90            | 90            |
| $V[\text{Å}^3]$                         | 675.87(4)     | 761.39(8)     | 3217.2(3)     | 3932.36(10)   | 4074.99(9)    |
| $Z$                                     | 1             | 1             | 4             | 4             | 4             |
| $\rho_{\text{calc}} [\text{g cm}^{-3}]$ | 1.398         | 1.363         | 1.291         | 1.662         | 1.230         |
| $\lambda [\text{Å}]$                    | 0.71073       | 1.54184       | 0.71073       | 1.54184       | 1.54184       |
| $\mu [\text{mm}^{-1}]$                  | 0.753         | 1.200         | 0.639         | 5.758         | 0.998         |
| $F(000)$                                | 302.0         | 334.0         | 1336.0        | 1980.0        | 1628.0        |
| $\theta$ range $[^\circ]$               | 2.97 to 36.47 | 3.95 to 72.53 | 3.39 to 25.00 | 4.26 to 71.26 | 4.02 to 72.34 |
| Reflns collected                        | 38704         | 7107          | 15648         | 18596         | 22863         |
| Independent                             | 6616          | 2935          | 5657          | 7491          | 7846          |
| reflns                                  |               |               |               |               |               |
| $R_{\text{int}}$                        | 0.0618        | 0.0248        | 0.0351        | 0.0246        | 0.0508        |
| GOF on $F^2$                            | 1.052         | 1.030         | 1.041         | 1.079         | 1.018         |
| $R_1/wR_2 [I \geq 2\sigma(I)]$          | 0.0350/0.0821 | 0.0464/0.1178 | 0.0449/0.1013 | 0.0382/0.0923 | 0.0621/0.1687 |
| $R_1/wR_2$ (all data)                   | 0.0479/0.0882 | 0.0542/0.1239 | 0.0601/0.1082 | 0.0436/0.0955 | 0.0901/0.1869 |



**Fig. S1** X-ray crystal structure of **2b**. Most hydrogen atoms on pyrazole and BBN rings are omitted for clarity. Selected bond lengths (Å) and angles (°): Ni1–N1, 1.9170(19); Ni1–N3, 1.9128(19); N1–Ni1–N3, 87.55(8).

### 3. Cartesian coordinates of calculated compounds

#### Compound 3

|    |             |             |             |
|----|-------------|-------------|-------------|
| Ni | -0.10782200 | 0.31283800  | 0.07691800  |
| N  | -1.51606500 | 1.45635700  | -0.90563300 |
| N  | 1.43497300  | 1.53148500  | 0.70867600  |
| N  | -2.82130000 | 1.10542100  | -0.71078500 |
| N  | 2.29043700  | -0.18923500 | -1.58686000 |
| N  | 0.92411300  | -0.19042000 | -1.62688800 |
| N  | 2.71098200  | 1.09447600  | 0.48418200  |
| N  | -2.63105900 | 0.11230200  | 1.54370500  |
| N  | -1.28744600 | 0.20108700  | 1.79135000  |
| C  | 1.50632500  | 2.80270100  | 1.15691600  |
| C  | -2.33695800 | -1.49701000 | -0.52661400 |
| H  | -1.23231300 | -1.35353700 | -0.57082200 |
| C  | -1.49892800 | 2.62716900  | -1.57752500 |
| C  | -4.71948200 | -0.65439300 | 0.04629200  |

|   |             |             |             |
|---|-------------|-------------|-------------|
| H | -5.38558700 | 0.13369600  | 0.43850000  |
| C | 2.85207800  | 3.19625100  | 1.21056700  |
| H | 3.24316100  | 4.15162400  | 1.53010600  |
| C | 2.77036600  | 0.05747100  | -2.83439900 |
| C | -3.61362400 | 2.06065700  | -1.22995500 |
| H | -4.68805700 | 1.98156000  | -1.16304600 |
| C | 0.55456800  | 0.00380300  | -2.90046900 |
| H | -0.49314900 | 0.04559200  | -3.15846600 |
| C | -2.76607200 | -1.71739400 | -1.99822100 |
| H | -2.44798800 | -0.84034000 | -2.57812100 |
| H | -2.23438600 | -2.57830000 | -2.43002900 |
| C | 5.04807100  | -0.93335000 | 1.30664700  |
| H | 6.06688300  | -1.34931100 | 1.28622200  |
| H | 5.15476700  | 0.08910800  | 1.69137700  |
| C | 3.56918900  | 2.08983800  | 0.77299600  |
| H | 4.63294100  | 1.95069000  | 0.65020400  |
| C | -1.14354900 | 0.53184300  | 3.09568100  |
| C | 4.48168500  | -0.87286700 | -0.13819800 |
| H | 5.15912200  | -0.21105200 | -0.69885900 |
| C | 1.68188500  | 0.15694700  | -3.70385800 |
| H | 1.72270000  | 0.33197500  | -4.76954200 |
| C | -2.81883600 | 3.04785500  | -1.79806900 |
| H | -3.14326900 | 3.94318700  | -2.30885500 |
| C | -0.23393600 | 3.28870600  | -2.03629800 |
| H | 0.59901600  | 3.09060000  | -1.35872000 |
| H | -0.37680400 | 4.37185500  | -2.10643900 |
| H | 0.06238900  | 2.92620800  | -3.02820100 |
| C | -4.28330200 | -1.90594600 | -2.21245600 |
| H | -4.50425900 | -1.80102600 | -3.28370800 |
| H | -4.56398800 | -2.93249500 | -1.96030600 |
| C | 2.12728200  | -1.46924100 | 0.74120200  |

|   |             |             |             |
|---|-------------|-------------|-------------|
| H | 1.04052200  | -1.24413800 | 0.86904100  |
| C | -2.40790900 | 0.67975700  | 3.68095600  |
| H | -2.62502800 | 0.93154000  | 4.70911200  |
| C | -5.16401000 | -0.91404900 | -1.42077900 |
| H | -6.20288900 | -1.27726300 | -1.43278800 |
| H | -5.17820200 | 0.03737000  | -1.96643500 |
| C | -3.31145600 | 0.41257600  | 2.66255300  |
| H | -4.39095200 | 0.41592900  | 2.66590000  |
| C | 0.29136300  | 3.58628100  | 1.55636900  |
| H | 0.12731300  | 3.53647900  | 2.64000400  |
| H | -0.60979000 | 3.20792700  | 1.06874800  |
| H | 0.41263000  | 4.64194300  | 1.29194000  |
| C | 2.16914000  | -2.83931000 | 0.02535900  |
| H | 1.64404500  | -3.60015300 | 0.62214300  |
| H | 1.60942600  | -2.74883700 | -0.91466300 |
| C | -2.53652900 | -2.72677800 | 0.39358200  |
| H | -2.04885100 | -2.50988800 | 1.35333800  |
| H | -2.01566200 | -3.60272400 | -0.02121300 |
| C | 3.59300500  | -3.34671200 | -0.29053800 |
| H | 4.02702700  | -3.80597200 | 0.60227100  |
| H | 3.52359700  | -4.15924200 | -1.02686700 |
| C | 2.68380600  | -1.49118300 | 2.18772500  |
| H | 2.46232000  | -0.52114600 | 2.64639400  |
| H | 2.14881700  | -2.24289700 | 2.78810400  |
| C | -4.94604000 | -1.90735400 | 0.93998400  |
| H | -4.82618900 | -1.62160700 | 1.99165800  |
| H | -5.98897800 | -2.24547700 | 0.84279800  |
| B | 2.93719700  | -0.35145300 | -0.13761400 |
| B | -3.14877900 | -0.22354600 | 0.09006000  |
| C | 4.54334100  | -2.26086000 | -0.84174200 |
| H | 4.30308400  | -2.12871500 | -1.90287500 |



|   |             |             |             |
|---|-------------|-------------|-------------|
| H | 5.57440300  | -2.64523900 | -0.81249900 |
| C | -4.01020700 | -3.10600900 | 0.66065100  |
| H | -4.39587500 | -3.68514100 | -0.18357100 |
| H | -4.04758500 | -3.79076500 | 1.51906500  |
| C | 0.17636600  | 0.64214100  | 3.79536400  |
| H | 0.54715400  | -0.34539200 | 4.09419800  |
| H | 0.06463400  | 1.24072900  | 4.70505300  |
| H | 0.93947400  | 1.10244400  | 3.16671700  |
| C | 4.20098200  | -1.73854700 | 2.31283000  |
| H | 4.41442300  | -2.80585700 | 2.20900700  |
| H | 4.51595300  | -1.48010000 | 3.33345800  |
| C | 4.20851000  | 0.29133900  | -3.19315400 |
| H | 4.64652500  | 1.08926500  | -2.58427300 |
| H | 4.26301100  | 0.60189200  | -4.24063300 |
| H | 4.83619400  | -0.59575500 | -3.07498800 |

**Compound 2b**

|    |            |             |             |
|----|------------|-------------|-------------|
| Ni | 0.00001300 | 0.00000500  | -0.00004800 |
| N  | 2.43434600 | 1.21452100  | 1.06181900  |
| N  | 1.07254600 | -1.33783900 | 0.92912900  |
| N  | 1.07239200 | 1.33768100  | 0.92950300  |
| N  | 2.43436400 | -1.21413200 | 1.06221700  |
| C  | 0.67318500 | -2.34895400 | 1.73796600  |
| C  | 0.67319100 | 2.34914600  | 1.73796400  |
| C  | 1.78703200 | -2.87882800 | 2.39581000  |
| H  | 1.79450500 | -3.69270600 | 3.10600900  |
| C  | 2.86207900 | 2.12741000  | 1.95196300  |
| H  | 3.90108300 | 2.17938300  | 2.22976200  |
| C  | 2.86184500 | -2.12624800 | 1.95327100  |
| H  | 3.90071600 | -2.17772600 | 2.23168100  |
| C  | 1.78728200 | 2.87988500  | 2.39470400  |

|   |             |             |             |
|---|-------------|-------------|-------------|
| H | 1.79490500  | 3.69416300  | 3.10444200  |
| C | 4.83893900  | 0.00010900  | 0.83289100  |
| H | 4.98650600  | 0.00036900  | 1.92669200  |
| C | 3.25098800  | -0.00021000 | -1.20794500 |
| H | 2.22746500  | -0.00025900 | -1.62199200 |
| C | 5.55981700  | 1.26936900  | 0.28748200  |
| H | 5.22045700  | 2.15757600  | 0.83066700  |
| H | 6.63642800  | 1.19279900  | 0.50266900  |
| C | -0.74236200 | 2.79226800  | 1.92169000  |
| H | -1.21123200 | 3.08558800  | 0.97939400  |
| H | -0.76511900 | 3.65047100  | 2.59990200  |
| H | -1.35432000 | 2.00153100  | 2.36346900  |
| C | -0.74231900 | -2.79255900 | 1.92092900  |
| H | -1.35455400 | -2.00235100 | 2.36328200  |
| H | -0.76507200 | -3.65137200 | 2.59836900  |
| H | -1.21088600 | -3.08511900 | 0.97825100  |
| C | 3.93231700  | 1.29688700  | -1.72042600 |
| H | 3.93214100  | 1.31943700  | -2.82149900 |
| H | 3.32317400  | 2.14944600  | -1.39997800 |
| C | 5.36988200  | 1.54275300  | -1.22032100 |
| H | 6.07644800  | 0.94462500  | -1.80124900 |
| H | 5.64164400  | 2.58736200  | -1.42694000 |
| B | 3.24709900  | 0.00006600  | 0.41888600  |
| C | 5.55958100  | -1.26953500 | 0.28806700  |
| H | 6.63617600  | -1.19319900 | 0.50341600  |
| H | 5.21985400  | -2.15747800 | 0.83146000  |
| C | 5.36981000  | -1.54329100 | -1.21966400 |
| H | 5.64158700  | -2.58795200 | -1.42601300 |
| H | 6.07645200  | -0.94530600 | -1.80064000 |
| C | 3.93230300  | -1.29751800 | -1.71997100 |
| H | 3.32308200  | -2.14993900 | -1.39931200 |

|   |             |             |             |
|---|-------------|-------------|-------------|
| H | 3.93221100  | -1.32040000 | -2.82103800 |
| N | -2.43435500 | -1.21450400 | -1.06180700 |
| N | -1.07253500 | 1.33781500  | -0.92926100 |
| N | -1.07240800 | -1.33771300 | -0.92947900 |
| N | -2.43437400 | 1.21415900  | -1.06220000 |
| C | -0.67323500 | 2.34889300  | -1.73817500 |
| C | -0.67323100 | -2.34918500 | -1.73793400 |
| C | -1.78715700 | 2.87886200  | -2.39582400 |
| H | -1.79468500 | 3.69273500  | -3.10602700 |
| C | -2.86209500 | -2.12732600 | -1.95201900 |
| H | -3.90109300 | -2.17924100 | -2.22985200 |
| C | -2.86196200 | 2.12639200  | -1.95308100 |
| H | -3.90088000 | 2.17796500  | -2.23129600 |
| C | -1.78731900 | -2.87983900 | -2.39474900 |
| H | -1.79495200 | -3.69409700 | -3.10451000 |
| C | -4.83892600 | -0.00010600 | -0.83281400 |
| H | -4.98653100 | -0.00036900 | -1.92660900 |
| C | -3.25091000 | 0.00024400  | 1.20798000  |
| H | -2.22737700 | 0.00031600  | 1.62199900  |
| C | -5.55977100 | -1.26936200 | -0.28736900 |
| H | -5.22041200 | -2.15757700 | -0.83054100 |
| H | -6.63638700 | -1.19280600 | -0.50253300 |
| C | 0.74230900  | -2.79240000 | -1.92153200 |
| H | 1.21112300  | -3.08558300 | -0.97916400 |
| H | 0.76506500  | -3.65070700 | -2.59961200 |
| H | 1.35432300  | -2.00175500 | -2.36340100 |
| C | 0.74226500  | 2.79239400  | -1.92141600 |
| H | 1.35440500  | 2.00205200  | -2.36366400 |
| H | 0.76496700  | 3.65104400  | -2.59906600 |
| H | 1.21097100  | 3.08516100  | -0.97887300 |
| C | -3.93221900 | -1.29683900 | 1.72050100  |

|   |             |             |             |
|---|-------------|-------------|-------------|
| H | -3.93201800 | -1.31934900 | 2.82157400  |
| H | -3.32307600 | -2.14940700 | 1.40006600  |
| C | -5.36980300 | -1.54269700 | 1.22043900  |
| H | -6.07634800 | -0.94453800 | 1.80136300  |
| H | -5.64157200 | -2.58729700 | 1.42709700  |
| B | -3.24707900 | -0.00005200 | -0.41884800 |
| C | -5.55956600 | 1.26952400  | -0.28797000 |
| H | -6.63616300 | 1.19316500  | -0.50329600 |
| H | -5.21986400 | 2.15747400  | -0.83137200 |
| C | -5.36976900 | 1.54325800  | 1.21976200  |
| H | -5.64157700 | 2.58790600  | 1.42613300  |
| H | -6.07636700 | 0.94523300  | 1.80075300  |
| C | -3.93223800 | 1.29753800  | 1.72001700  |
| H | -3.32305600 | 2.14997300  | 1.39931900  |
| H | -3.93210500 | 1.32043300  | 2.82108300  |

**Compound 4**

|    |             |             |             |
|----|-------------|-------------|-------------|
| Ni | 0.00004200  | 0.00001500  | 0.00013900  |
| N  | -2.65263000 | -1.21320500 | -0.08568800 |
| N  | -1.37007400 | 1.33774300  | 0.38908900  |
| N  | -1.37015900 | -1.33765900 | 0.38899700  |
| N  | -2.65256600 | 1.21337500  | -0.08556300 |
| C  | -1.35330100 | 2.34411000  | 1.29615700  |
| C  | -1.35346500 | -2.34409600 | 1.29599000  |
| C  | -2.65027400 | 2.86149600  | 1.39577600  |
| C  | -3.43178100 | -2.11796300 | 0.52910700  |
| H  | -4.48794800 | -2.18266900 | 0.33488000  |
| C  | -3.43167100 | 2.11805700  | 0.52940400  |
| H  | -4.48785200 | 2.18278600  | 0.33526900  |
| C  | -2.65045000 | -2.86148200 | 1.39546900  |
| C  | -4.71893300 | 0.00016300  | -1.33648900 |

|   |             |             |             |
|---|-------------|-------------|-------------|
| H | -5.32656500 | 0.00018100  | -0.41519500 |
| C | -2.40166900 | 0.00016000  | -2.48697100 |
| H | -1.29911700 | 0.00015800  | -2.41756000 |
| C | -5.13246000 | -1.26919300 | -2.14032900 |
| H | -5.06730300 | -2.15802800 | -1.50372600 |
| H | -6.19481300 | -1.18905200 | -2.41402700 |
| C | -0.15900600 | -2.78607600 | 2.07144700  |
| H | 0.68134000  | -3.03413600 | 1.42024100  |
| H | -0.41941100 | -3.67084800 | 2.65736000  |
| H | 0.17179000  | -2.00866300 | 2.76525100  |
| C | -0.15878800 | 2.78599300  | 2.07159200  |
| H | 0.17185200  | 2.00861900  | 2.76552200  |
| H | -0.41905800 | 3.67089000  | 2.65737700  |
| H | 0.68162000  | 3.03381100  | 1.42038200  |
| C | -2.79439900 | -1.29780300 | -3.24263100 |
| H | -2.31559400 | -1.32112500 | -4.23363100 |
| H | -2.38521400 | -2.15035200 | -2.68921300 |
| C | -4.30650100 | -1.54388000 | -3.41595200 |
| H | -4.69053800 | -0.94666400 | -4.24658800 |
| H | -4.46057000 | -2.58860800 | -3.71859300 |
| B | -3.10821600 | 0.00014000  | -1.02281900 |
| C | -5.13248200 | 1.26947000  | -2.14040800 |
| H | -6.19481900 | 1.18926500  | -2.41414700 |
| H | -5.06739900 | 2.15834000  | -1.50385200 |
| C | -4.30649400 | 1.54414900  | -3.41601000 |
| H | -4.46058600 | 2.58886400  | -3.71868300 |
| H | -4.69048200 | 0.94689800  | -4.24664300 |
| C | -2.79439500 | 1.29812600  | -3.24262200 |
| H | -2.38525900 | 2.15067700  | -2.68917100 |
| H | -2.31554700 | 1.32147600  | -4.23360100 |
| N | 2.65270200  | 1.21327200  | 0.08559100  |

|   |             |             |             |
|---|-------------|-------------|-------------|
| N | 1.37017700  | -1.33767900 | -0.38884900 |
| N | 1.37017800  | 1.33767000  | -0.38896800 |
| N | 2.65268800  | -1.21326100 | 0.08574400  |
| C | 1.35338000  | -2.34408100 | -1.29587400 |
| C | 1.35336500  | 2.34397900  | -1.29609700 |
| C | 2.65035400  | -2.86145600 | -1.39551800 |
| C | 3.43180700  | 2.11782300  | -0.52957400 |
| H | 4.48801800  | 2.18247400  | -0.33559900 |
| C | 3.43178600  | -2.11793700 | -0.52924500 |
| H | 4.48798300  | -2.18261300 | -0.33519000 |
| C | 2.65035600  | 2.86128100  | -1.39588300 |
| C | 4.71904400  | 0.00005900  | 1.33667800  |
| H | 5.32673300  | 0.00003300  | 0.41542100  |
| C | 2.40172400  | 0.00012900  | 2.48701400  |
| H | 1.29917800  | 0.00014800  | 2.41753500  |
| C | 5.13258100  | 1.26938900  | 2.14058400  |
| H | 5.06762200  | 2.15823300  | 1.50398500  |
| H | 6.19488600  | 1.18914200  | 2.41443500  |
| C | 0.15878800  | 2.78586700  | -2.07143100 |
| H | -0.68148300 | 3.03392800  | -1.42013200 |
| H | 0.41908200  | 3.67061500  | -2.65743100 |
| H | -0.17207000 | 2.00840000  | -2.76515000 |
| C | 0.15883300  | -2.78600800 | -2.07123000 |
| H | -0.17193100 | -2.00861600 | -2.76508000 |
| H | 0.41911800  | -3.67085000 | -2.65709100 |
| H | -0.68149700 | -3.03393100 | -1.41995700 |
| C | 2.79440600  | 1.29812400  | 3.24264700  |
| H | 2.31551700  | 1.32149700  | 4.23360600  |
| H | 2.38526900  | 2.15064900  | 2.68915700  |
| C | 4.30648900  | 1.54421600  | 3.41608700  |
| H | 4.69044400  | 0.94710400  | 4.24683000  |

|    |             |             |             |
|----|-------------|-------------|-------------|
| H  | 4.46052900  | 2.58897800  | 3.71862500  |
| B  | 3.10833200  | 0.00006100  | 1.02289500  |
| C  | 5.13253500  | -1.26926000 | 2.14061300  |
| H  | 6.19485200  | -1.18906100 | 2.41443600  |
| H  | 5.06750900  | -2.15811900 | 1.50403900  |
| C  | 4.30645100  | -1.54398800 | 3.41614500  |
| H  | 4.46044900  | -2.58874200 | 3.71873100  |
| H  | 4.69044600  | -0.94685400 | 4.24685500  |
| C  | 2.79437400  | -1.29783700 | 3.24272100  |
| H  | 2.38520200  | -2.15038000 | 2.68928500  |
| H  | 2.31550100  | -1.32113900 | 4.23368900  |
| Br | -3.23883600 | 4.27473200  | 2.49134400  |
| Br | 3.23889200  | -4.27473400 | -2.49104500 |
| Br | 3.23889400  | 4.27440000  | -2.49161500 |
| Br | -3.23909600 | -4.27483000 | 2.49084800  |

**Compound 4'**

|    |             |             |             |
|----|-------------|-------------|-------------|
| Ni | -0.00004300 | -0.00058200 | -0.40726100 |
| N  | -1.04528000 | 1.33661000  | 0.75744600  |
| N  | 1.04523500  | -1.33813700 | 0.75665800  |
| N  | -2.25906000 | 1.73252800  | 0.27022200  |
| N  | 2.88499000  | 0.37358400  | -0.83760300 |
| N  | 1.76646600  | 1.14183100  | -0.66058800 |
| N  | 2.25947200  | -1.73287800 | 0.26959700  |
| N  | -2.88542900 | -0.37334400 | -0.83748600 |
| N  | -1.76709000 | -1.14201100 | -0.66129900 |
| C  | 0.89668500  | -1.85356600 | 1.99391200  |
| C  | -1.65321900 | 1.43517000  | -2.30996400 |
| H  | -0.62481700 | 1.06013500  | -2.07815000 |
| C  | -0.89637100 | 1.85198100  | 1.99470200  |
| C  | -4.13301300 | 1.83731300  | -1.67513500 |

|   |             |             |             |
|---|-------------|-------------|-------------|
| H | -4.96521700 | 1.72457000  | -0.95900000 |
| C | 2.05735500  | -2.57733300 | 2.30492400  |
| C | 3.98493800  | 1.11409200  | -0.62926500 |
| C | -2.88866200 | 2.47125700  | 1.20029200  |
| H | -3.87487200 | 2.87483300  | 1.03444300  |
| C | 2.17878300  | 2.39674500  | -0.36487300 |
| C | -1.46742200 | 2.95831800  | -2.52409400 |
| H | -1.01496900 | 3.37407200  | -1.61796400 |
| H | -0.74904600 | 3.14288600  | -3.33654400 |
| C | 3.94436600  | -3.36261000 | -1.89421700 |
| H | 4.86867400  | -3.79458700 | -2.30531700 |
| H | 3.79615300  | -3.85216500 | -0.92321700 |
| C | 2.88969800  | -2.47088800 | 1.19979400  |
| H | 3.87633800  | -2.87349300 | 1.03410200  |
| C | -2.17964200 | -2.39683500 | -0.36557200 |
| C | 4.13311100  | -1.83648600 | -1.67606300 |
| H | 4.96543600  | -1.72355800 | -0.96010600 |
| C | 3.58150200  | 2.40537300  | -0.33538400 |
| C | -2.05634000 | 2.57696200  | 2.30549000  |
| C | 0.34013400  | 1.69069600  | 2.81969500  |
| H | 1.05273300  | 1.01801500  | 2.33973100  |
| H | 0.09702400  | 1.29837200  | 3.81287800  |
| H | 0.82986400  | 2.66013800  | 2.96996900  |
| C | -2.76334600 | 3.74697400  | -2.80948100 |
| H | -2.55329200 | 4.81869000  | -2.69108100 |
| H | -3.05157500 | 3.62435900  | -3.85696300 |
| C | 1.65304200  | -1.43505700 | -2.31025600 |
| H | 0.62452800  | -1.06039100 | -2.07826800 |
| C | -3.58234500 | -2.40497300 | -0.33511600 |
| C | -3.94383900 | 3.36338900  | -1.89321200 |
| H | -4.86810900 | 3.79569400  | -2.30405200 |



|   |             |             |             |
|---|-------------|-------------|-------------|
| H | -3.79523300 | 3.85284000  | -0.92222000 |
| C | -3.98550100 | -1.11348300 | -0.62850400 |
| H | -4.97618500 | -0.69405100 | -0.69899500 |
| C | -0.34030800 | -1.69372200 | 2.81844100  |
| H | -0.83278200 | -2.66269500 | 2.96286100  |
| H | -1.05074100 | -1.01667600 | 2.34139900  |
| H | -0.09713100 | -1.30755000 | 3.81398900  |
| C | 2.08039300  | -0.66143000 | -3.58241400 |
| H | 1.36310200  | -0.84314300 | -4.39604200 |
| H | 2.02629300  | 0.41296500  | -3.36367500 |
| C | -2.08106200 | 0.66190200  | -3.58216500 |
| H | -2.02709800 | -0.41255000 | -3.36369600 |
| H | -1.36396500 | 0.84367900  | -4.39595300 |
| C | 3.50144100  | -0.99727500 | -4.08986100 |
| H | 3.46675400  | -1.91944200 | -4.67680600 |
| H | 3.81342200  | -0.21837800 | -4.79848900 |
| C | 1.46767700  | -2.95825100 | -2.52453500 |
| H | 1.01555100  | -3.37420600 | -1.61833100 |
| H | 0.74919200  | -3.14295400 | -3.33685000 |
| C | -4.57954500 | 1.12336800  | -2.98516400 |
| H | -4.93007900 | 0.11443700  | -2.73890900 |
| H | -5.45325600 | 1.64290400  | -3.40575600 |
| B | 2.75108700  | -1.16993900 | -1.13634100 |
| B | -2.75108800 | 1.17017700  | -1.13585500 |
| C | 4.57910400  | -1.12230800 | -2.98612500 |
| H | 4.92939500  | -0.11327700 | -2.73991700 |
| H | 5.45287500  | -1.64154800 | -3.40696100 |
| C | -3.50218600 | 0.99812700  | -4.08917500 |
| H | -3.46743400 | 1.92033900  | -4.67604900 |
| H | -3.81455700 | 0.21936700  | -4.79777900 |
| C | -1.29257700 | -3.58245400 | -0.16258800 |

|    |             |             |             |
|----|-------------|-------------|-------------|
| H  | -1.22788200 | -4.17753700 | -1.08160800 |
| H  | -1.71161200 | -4.23283700 | 0.61182100  |
| H  | -0.28491500 | -3.29245600 | 0.12606800  |
| C  | 2.76377800  | -3.74649200 | -2.81024600 |
| H  | 3.05173900  | -3.62374200 | -3.85778800 |
| H  | 2.55407400  | -4.81827600 | -2.69184900 |
| Br | 2.40027300  | -3.51939700 | 3.89838500  |
| Br | -4.69797200 | -3.88181500 | 0.01527800  |
| Br | -2.39844500 | 3.51937600  | 3.89892100  |
| Br | 4.69676100  | 3.88256600  | 0.01468100  |
| H  | 4.97572900  | 0.69503400  | -0.70045400 |
| C  | 1.29155000  | 3.58201800  | -0.16058600 |
| H  | 1.70994600  | 4.23108800  | 0.61528500  |
| H  | 1.22768500  | 4.17871000  | -1.07862700 |
| H  | 0.28366800  | 3.29153200  | 0.12674500  |

## References

- [1] *SADABS: Area-Detector Absorption Correction*, Bruker, Madison, Wisconsin, 2001.
- [2] *TWINABS*, Bruker, Madison, Wisconsin, 2001.
- [3] *SAINT: SAX Area-Detector Integration Program*, Bruker, Madison, Wisconsin, 2008.
- [4] *XPREP*, Bruker, Madison, Wisconsin, 2008.