# Supplementary Materials

# New Sulfur-Containing Polyarsenicals from the New Caledonian sponge *Echinochalina bargibanti*

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## Contents

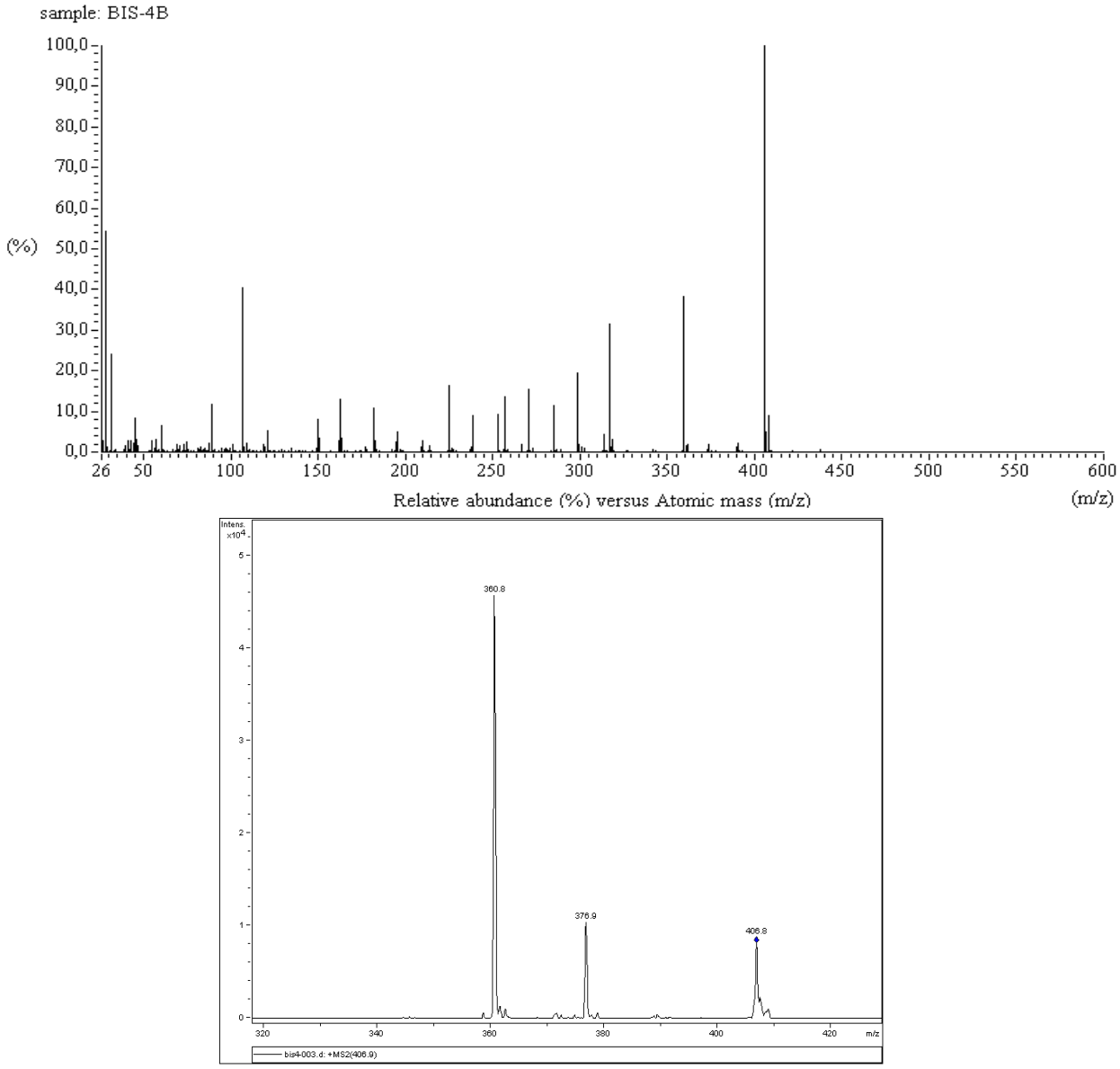


**Figure S1.** MS spectra of arsenicin B: EI-MS spectrum (top) and APCI(+)-MS tandem fragmentation experiment on *m*/*z* 407 $[M+H]^+$ (bottom).

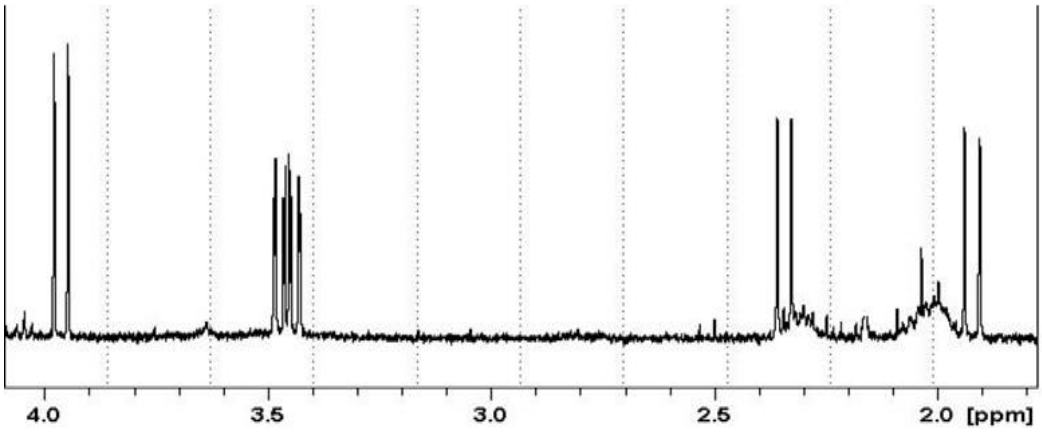


**Figure S2.** Detailed region in $^{1}$HNMR spectrum of arsenicin B in $CDCl_3$ (d at 1.56 ppm not shown because superimposed by water signal).

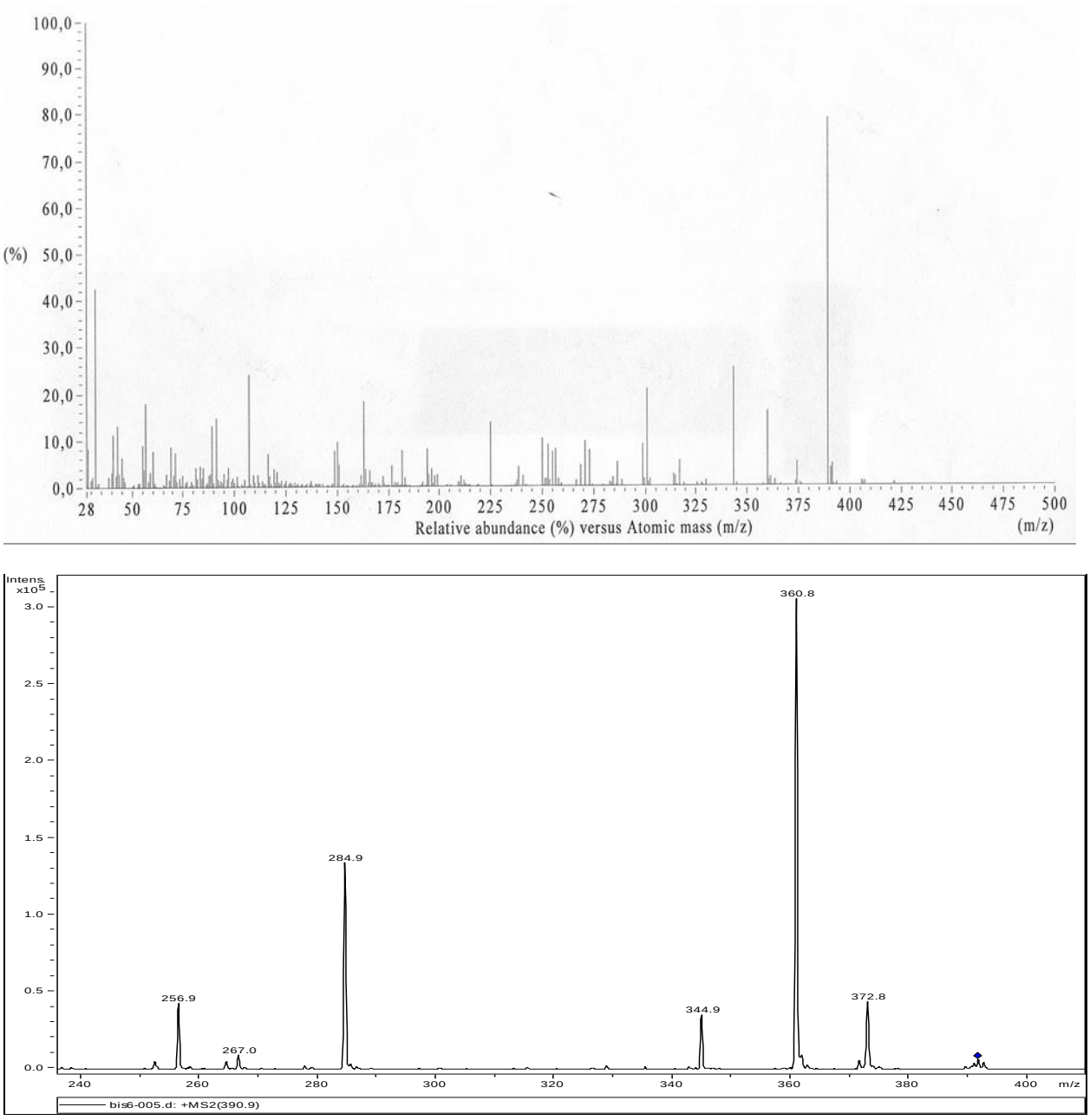


**Figure S3.** MS spectra of arsenicin C: EI-MS spectrum (top) and APCI(+)-MS tandem fragmentation experiment on *m*/*z* 391 $[M+H]^+$ (bottom).

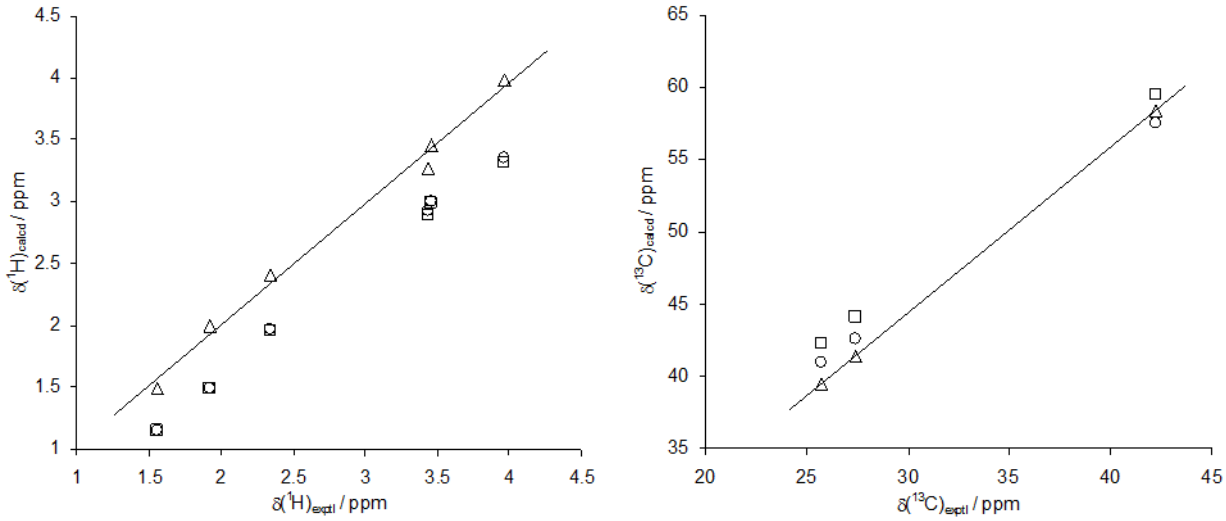


**Figure S4.** Correlations between experimental and calculated $^{1}H$ (left) and $^{13}C$ (right) chemical shifts for structure **B6** of Arsenicin B. Squares: non-relativistic (method A); circles: non-relativistic (method B); triangles: relativistic (method C). The correlation line refers to method C. Details on methods in the text, par.3.4.

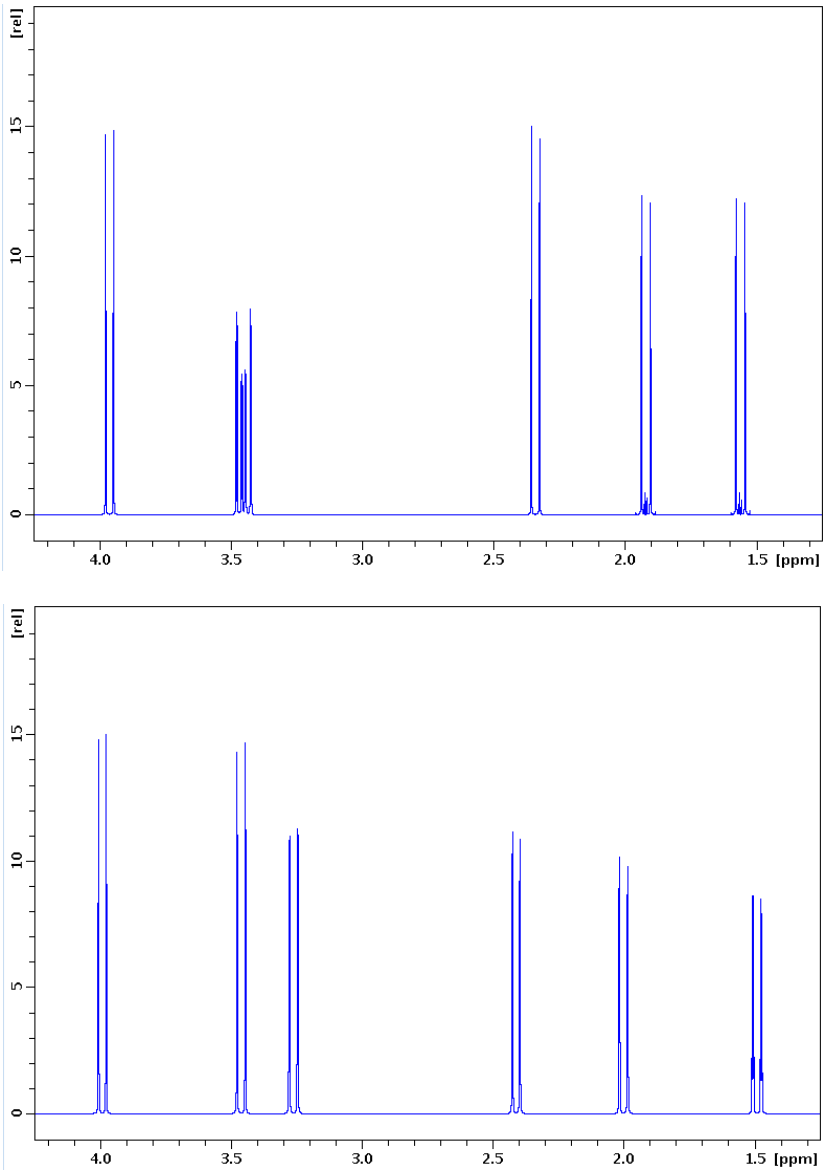


**Figure S5.** Experimental (top) and calculated (bottom) $^{1}H$ spectra of structure **B6** of arsenicin B. Spectrum recorded in $CDCl_3$ at 400MHz. Chemical shifts calculated with method (C), couplings with method (B). Simulations at 400 MHz. Details on methods in the text, par.3.4.

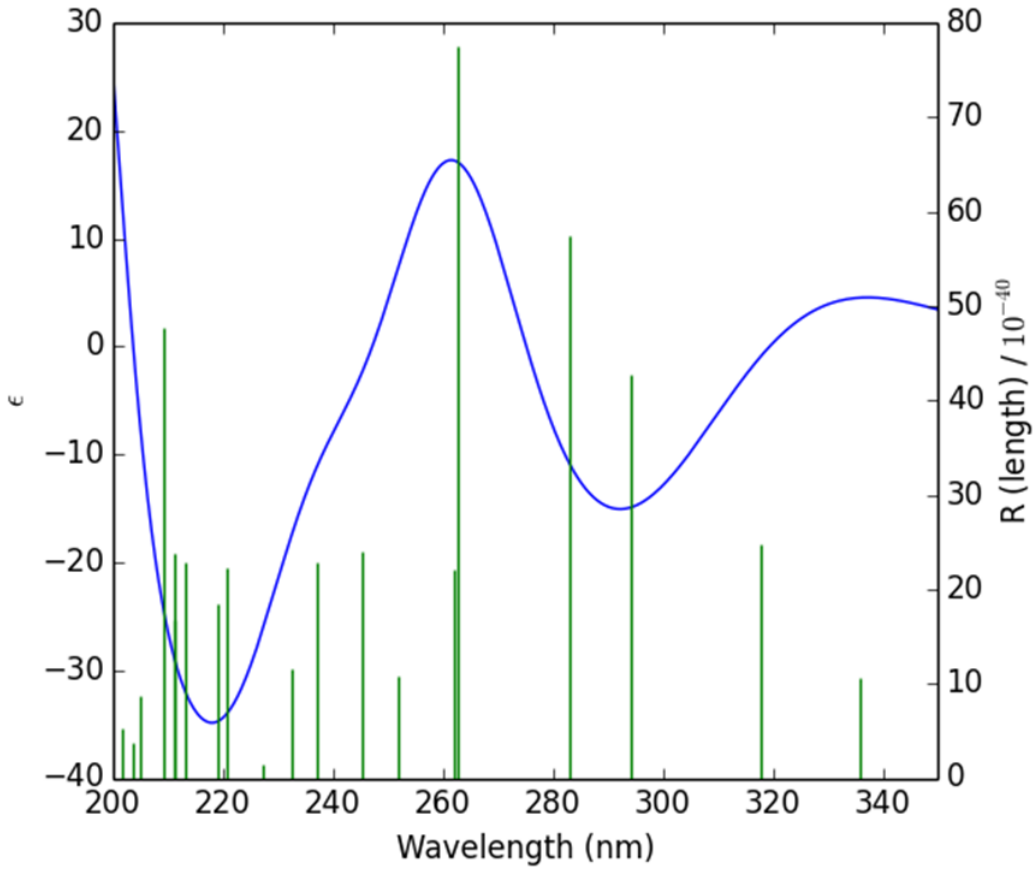


**Figure S6.** Theoretical ECD spectrum for the (1R,3S,5R,7R)-enantiomer of arsenicin B calculated at the TD-DFT B3LYP/6-311+G(3df,2pd) level for a structure optimized at the same level. Details on methods in the text, par.3.4.

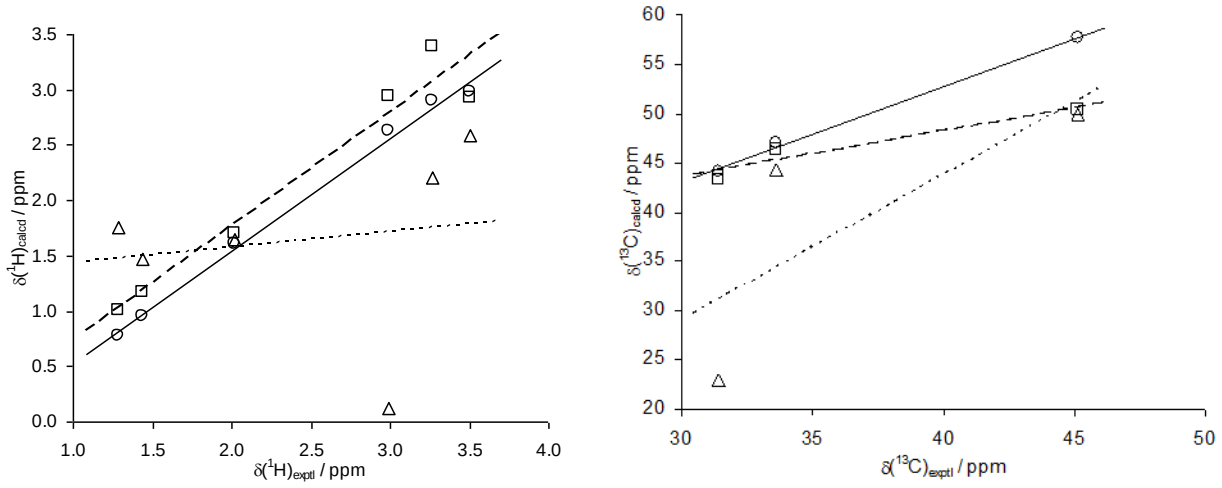


**Figure S7.** Correlations between the experimental and calculated (B3LYP/cc-pVTZ//B3LYP/6-311G(2d,2p) $^{1}H$ (left) and $^{13}C$ (right) chemical shifts for the proposed structures for arsenicin C. Squares: **C1** (– –); circles: **C2** (—); triangles: **C3** (····).

**Table S1.** Energies of trial structures **B1-B9** (reported in Figure 2) of arsenicin B calculated at B3LYP/6-311G(2d,2p) level.

| Structure | Symmetry group | *E* (au) | Δ*E* (kcal/mol) |
|---|---|---|---|
| **B1** | $C_1$ | -9857.86618198 | 316 |
| **B2'** | $C_1$ | -9857.92232084 | 281 |
| **B3** | $C_1$ | -9858.02119547 | 219 |
| **B4** | $C_1$ | -9858.02232713 | 218 |
| **B5** | $C_1$ | -9858.02109254 | 219 |
| **B6** | $C_1$ | -9858.36900792 | 0.5 |
| **B7** | $C_s$ | -9858.36937360 | 0.2 |
| **B8** | $C_s$ | -9858.36765298 | 1.3 |
| **B9** | $C_2$ | -9858.36972534 | (0.0) |

**Table S2.** Experimental and calculated $J(^1H,^1H)$ values (in Hz) for structure **B6** (Figure 2) of arsenicin B.

| | Exptl [a] | (A) | (B) | (C) |
|---|---|---|---|---|
| $^2J$(1a,1b) | 12.4 | -8.6 | -11.4 | -6.4 |
| $^2J$(2a,2b) | 13.5 | -9.7 | -12.6 | -7.5 |
| $^2J$(3a,3b) | 13.8 | -9.7 | -12.7 | -7.6 |
| $^4J$(1a,2a) | | 1.6 | 1.4 | 0.7 |
| $^4J$(1a,2b) | | -0.3 | -0.2 | -0.4 |
| $^4J$(1b,2a) | | -0.3 | -0.2 | -0.4 |
| $^4J$(1b,2b) | | -0.5 | -0.2 | -0.2 |
| $^4J$(2a,3a) | 1.7 | 0.2 | 0.7 | 0.5 |
| $^4J$(2a,3b) | | -0.8 | -0.7 | -0.7 |
| $^4J$(2b,3a) | | -0.8 | -0.7 | -0.7 |
| $^4J$(2b,3b) | | 1.0 | 0.9 | 0.6 |
| $^5J$(1a,3a ) | | -0.2 | 0.0 | 0.1 |
| $^5J$(1a,3b) | | -0.8 | -0.7 | -0.5 |
| $^5J$(1b,3a) | | -0.8 | -0.7 | -0.5 |
| $^5J$(1b,3b) | | -1.0 | -0.9 | -0.6 |
| MAE($J_{HH}$) [b] | | 3.3 | 1.0 | 4.9 |

[a] Experimental data are absolute values.

[b] Involves only $^2J$(H7,H8), $^2J$(H9,H10), $^2J$(H13,H14) and $^4J$(H7,H13).