

**Table S3.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectral assignments of halicyclamine A

| Carbon No. | $^1\text{H}$ (mult., $J$ in Hz)                   | $^{13}\text{C}$ | HMBC (# H)                        |
|------------|---|-----------------|-----------------------------------|
| 1          | 2.80(dd, 12.9 Hz), 3.32 <sup>a</sup>              | 51.0            | 32a, 32b, 2, 3, 5b, 11a, 11b      |
| 2          | 1.82(m)   | 31.6            | 31a, 31b, 32a, 32b, 3, 4a, 1a, 1b |
| 3          | 1.56(m)   | 40.6            | 8, 32a, 4b, 5b, 1b                |
| 4          | 1.73(m), 2.19(m)                                  | 26.2            | 2, 3, 5a, 5b                      |
| 5          | 3.30 <sup>a</sup> , 3.35 <sup>a</sup>             | 53.4            | 3, 4b, 11a, 1b, 1a, 1b            |
| 6          | 3.57 <sup>a</sup> , 3.62 <sup>a</sup>             | 52.2            | 8, 10a, 10b, 21a, 21b             |
| 7          |   | 133.3           | 20a, 20b, 6a, 6b                  |
| 8          | 5.90 (s)  | 120.3           | 10a, 10b, 3, 20b, 6a, 6b          |
| 9          | 2.71 <sup>a</sup>                                 | 41.5            | 8, 10a, 10b, 3                    |
| 10         | 3.26 <sup>a</sup> , 3.50 <sup>a</sup>             | 55.8            | 8, 21a, 21b, 3, 6a, 6b            |
| 11         | 3.22(dd, 13.2, 6.6 Hz)<br>4.04(dd, 13.2, 11.4 Hz) | 49.5            | 5a, 5b, 12a, 13, 1a, 1b           |
| 12         | 2.38(m), 2.75(m)                                  | 26.8            | 11a, 11b, 13, 14                  |
| 13         | 5.87(ddd, 16.2, 7.2, 3.6 Hz)                      | 129.5           | 11a, 11b, 12a, 12b, 14, 15        |
| 14         | 6.77(dd, 16.2, 10.2 Hz)                           | 128.4           | 12a, 12b, 15, 16                  |
| 15         | 5.94(dd, 10.8 Hz)                                 | 129.5           | 13, 14, 17a, 17b                  |
| 16         | 5.48(ddd, 10.8, 5.4 Hz)                           | 132.7           | 14, 17a, 17b, 18a, 18b            |
| 17         | 1.79 <sup>a</sup> , 2.66(m)                       | 28.5            | 15, 16, 18a, 18b, 19a, 19b        |
| 18         | 1.18 <sup>a</sup> , 1.30 <sup>a</sup>             | 29.5            | 16, 17a, 17b, 19a, 19b            |
| 19         | 1.62(m), 1.70(m)                                  | 26.0            | 17a, 17b, 18a, 18b, 20b           |
| 20         | 2.00 <sup>a</sup> , 2.40 <sup>a</sup>             | 33.5            | 8, 18a, 18b, 19a, 19b, 6a         |
| 21         | 3.48 <sup>a</sup> , 3.55 <sup>a</sup>             | 55.4            | 10b, 22b, 23, 6a                  |
| 22         | 2.54(m), 3.07(m)                                  | 23.4            | 21a, 21b, 23, 24                  |
| 23         | 5.57 <sup>a</sup>                                 | 127.6           | 21a, 21b, 24                      |
| 24         | 6.46(d, 7.2 or 9.6 Hz)                            | 124.0           | 23, 25                            |
| 25         | 6.46(d, 7.2 or 9.6 Hz)                            | 127.4           | 24, 26                            |
| 26         | 5.53 <sup>a</sup>                                 | 136.6           | 25, 27a, 27b                      |
| 27         | 2.07(m), 2.37 <sup>a</sup>                        | 26.2            | 25, 26, 28b, 29b                  |
| 28         | 1.41(m), 1.50 <sup>a</sup>                        | 28.5            | 29a, 29b, 30a, 30b                |
| 29         | 1.15 <sup>a</sup> , 1.20 <sup>a</sup>             | 29.1            | 28b, 30a, 30b                     |
| 30         | 1.07(m), 1.18 <sup>a</sup>                        | 27.0            | 29b, 31b                          |
| 31         | 0.89 <sup>a</sup> , 1.26 <sup>a</sup>             | 25.9            | 29b, 30a, 30b                     |
| 32         | 0.88 <sup>a</sup> , 1.30 <sup>a</sup>             | 33.0            | 30b, 31b, 2, 3, 1a                |

<sup>a</sup>  $J_{\text{H-H}}$  coupling could not be assigned due to their overlapped signals.