

**Conformational behaviour, hydrogen bond competition and  
intramolecular dynamics in vanillin derivatives:  
acetovanillone and 6-hydroxy-3-methoxyacetophenone**

**SUPPLEMENTARY INFORMATION**

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**Table S1.** Measured rotational transitions of acetovanillone *s-cis* conformer ( $\nu_{\text{obs}}$ ) together with calculated values ( $\nu_{\text{calc}}$ ) and residuals (diff =  $\nu_{\text{obs}} - \nu_{\text{calc}}$ ) for the fit of Table 1 of the manuscript.

| $J'$ | $K'_-$ | $K'_+$ | $J''$ | $K''_-$ | $K''_+$ | Sym | $\nu_{\text{obs}}/\text{MHz}$ | $\nu_{\text{calc}}/\text{MHz}$ | diff/MHz |
|------|--------|--------|-------|---------|---------|-----|-------------------------------|--------------------------------|----------|
| 5    | 1      | 4      | 4     | 1       | 3       | A   | 5859.0007                     | 5859.0006                      | 0.0001   |
| 5    | 1      | 4      | 4     | 1       | 3       | E   | 5858.9944                     | 5858.9953                      | -0.0009  |
| 4    | 1      | 3      | 3     | 1       | 2       | A   | 4737.9970                     | 4737.9995                      | -0.0025  |
| 4    | 1      | 3      | 3     | 1       | 2       | E   | 4737.9970                     | 4737.9952                      | 0.0018   |
| 5    | 2      | 3      | 4     | 2       | 2       | A   | 5882.9793                     | 5882.9803                      | -0.0010  |
| 5    | 2      | 3      | 4     | 2       | 2       | E   | 5882.9742                     | 5882.9746                      | -0.0004  |
| 6    | 1      | 6      | 5     | 1       | 5       | A   | 5924.5887                     | 5924.5892                      | -0.0005  |
| 6    | 1      | 6      | 5     | 1       | 5       | E   | 5924.5887                     | 5924.5873                      | 0.0013   |
| 6    | 0      | 6      | 5     | 0       | 5       | A   | 6022.9786                     | 6022.9799                      | -0.0013  |
| 6    | 0      | 6      | 5     | 0       | 5       | E   | 6022.9786                     | 6022.9770                      | 0.0016   |
| 6    | 2      | 5      | 5     | 2       | 4       | A   | 6521.8577                     | 6521.8598                      | -0.0021  |
| 6    | 2      | 5      | 5     | 2       | 4       | E   | 6521.8577                     | 6521.8563                      | 0.0014   |
| 6    | 4      | 2      | 5     | 4       | 1       | A   | 6727.1764                     | 6727.1755                      | 0.0009   |
| 6    | 4      | 2      | 5     | 4       | 1       | E   | 6726.2268                     | 6726.2271                      | -0.0002  |
| 6    | 2      | 4      | 5     | 2       | 3       | A   | 7129.1248                     | 7129.1234                      | 0.0013   |
| 6    | 2      | 4      | 5     | 2       | 3       | E   | 7129.1187                     | 7129.1174                      | 0.0013   |
| 8    | 4      | 4      | 7     | 4       | 3       | A   | 9057.8849                     | 9057.8856                      | -0.0007  |
| 8    | 4      | 4      | 7     | 4       | 3       | E   | 9057.7662                     | 9057.7662                      | 0.0000   |
| 8    | 3      | 5      | 7     | 3       | 4       | A   | 9354.4606                     | 9354.4594                      | 0.0011   |
| 8    | 3      | 5      | 7     | 3       | 4       | E   | 9354.4494                     | 9354.4508                      | -0.0014  |
| 9    | 2      | 8      | 8     | 2       | 7       | A   | 9533.7047                     | 9533.7049                      | -0.0001  |
| 9    | 2      | 8      | 8     | 2       | 7       | E   | 9533.7003                     | 9533.6991                      | 0.0012   |
| 9    | 1      | 8      | 8     | 1       | 7       | A   | 9778.1022                     | 9778.0999                      | 0.0023   |
| 9    | 1      | 8      | 8     | 1       | 7       | E   | 9778.0888                     | 9778.0914                      | -0.0025  |
| 9    | 4      | 6      | 8     | 4       | 5       | A   | 10156.2490                    | 10156.2498                     | -0.0008  |
| 9    | 4      | 6      | 8     | 4       | 5       | E   | 10156.2775                    | 10156.2788                     | -0.0014  |
| 10   | 2      | 9      | 9     | 2       | 8       | A   | 10496.5736                    | 10496.5721                     | 0.0015   |
| 10   | 2      | 9      | 9     | 2       | 8       | E   | 10496.5647                    | 10496.5658                     | -0.0011  |
| 11   | 1      | 11     | 10    | 1       | 10      | A   | 10568.4224                    | 10568.4255                     | -0.0030  |
| 11   | 1      | 11     | 10    | 1       | 10      | E   | 10568.4224                    | 10568.4231                     | -0.0007  |
| 10   | 4      | 7      | 9     | 4       | 6       | A   | 11298.9111                    | 11298.9115                     | -0.0004  |
| 10   | 4      | 7      | 9     | 4       | 6       | E   | 11298.9195                    | 11298.9168                     | 0.0026   |
| 11   | 2      | 10     | 10    | 2       | 9       | A   | 11444.3805                    | 11444.3784                     | 0.0021   |
| 11   | 2      | 10     | 10    | 2       | 9       | E   | 11444.3717                    | 11444.3718                     | -0.0001  |
| 12   | 0      | 12     | 11    | 0       | 11      | A   | 11491.1574                    | 11491.1575                     | -0.0001  |
| 12   | 0      | 12     | 11    | 0       | 11      | E   | 11491.1574                    | 11491.1551                     | 0.0023   |
| 11   | 3      | 9      | 10    | 3       | 8       | A   | 12129.5397                    | 12129.5377                     | 0.0020   |
| 11   | 3      | 9      | 10    | 3       | 8       | E   | 12129.5263                    | 12129.5292                     | -0.0029  |
| 13   | 1      | 13     | 12    | 1       | 12      | A   | 12408.9408                    | 12408.9419                     | -0.0011  |
| 13   | 1      | 13     | 12    | 1       | 12      | E   | 12408.9408                    | 12408.9395                     | 0.0012   |
| 11   | 5      | 6      | 10    | 5       | 5       | A   | 12483.8369                    | 12483.8373                     | -0.0004  |
| 11   | 5      | 6      | 10    | 5       | 5       | E   | 12483.6885                    | 12483.6877                     | 0.0008   |
| 12   | 3      | 10     | 11    | 3       | 9       | A   | 13139.7334                    | 13139.7334                     | 0.0000   |
| 12   | 3      | 10     | 11    | 3       | 9       | E   | 13139.7227                    | 13139.7240                     | -0.0013  |
| 15   | 1      | 15     | 14    | 1       | 14      | A   | 14248.3788                    | 14248.3799                     | -0.0012  |
| 15   | 1      | 15     | 14    | 1       | 14      | E   | 14248.3788                    | 14248.3775                     | 0.0012   |
| 15   | 0      | 15     | 14    | 0       | 14      | A   | 14248.6197                    | 14248.6207                     | -0.0010  |
| 15   | 0      | 15     | 14    | 0       | 14      | E   | 14248.6197                    | 14248.6183                     | 0.0014   |
| 16   | 0      | 16     | 15    | 0       | 15      | A   | 15168.1135                    | 15168.1135                     | 0.0001   |
| 16   | 0      | 16     | 15    | 0       | 15      | E   | 15168.1135                    | 15168.1111                     | 0.0025   |
| 16   | 1      | 16     | 15    | 1       | 15      | A   | 15167.9992                    | 15168.0011                     | -0.0020  |

**Table S2.** Measured rotational transitions of acetovanillone *s-trans* conformer ( $\nu_{\text{obs}}$ ) together with calculated values ( $\nu_{\text{calc}}$ ) and residuals (diff =  $\nu_{\text{obs}} - \nu_{\text{calc}}$ ) for the fit of Table 1 of the manuscript.

| $J'$ | $K'_-$ | $K'_+$ | $J''$ | $K''_-$ | $K''_+$ | Sym | $\nu_{\text{obs}}/\text{MHz}$ | $\nu_{\text{calc}}/\text{MHz}$ | diff/MHz |
|------|--------|--------|-------|---------|---------|-----|-------------------------------|--------------------------------|----------|
| 7    | 0      | 7      | 6     | 0       | 6       | A   | 6921.4496                     | 6921.4491                      | 0.0005   |
| 7    | 0      | 7      | 6     | 0       | 6       | E   | 6921.4496                     | 6921.4481                      | 0.0015   |
| 5    | 1      | 4      | 4     | 1       | 3       | A   | 5887.4314                     | 5887.4344                      | -0.0030  |
| 5    | 1      | 4      | 4     | 1       | 3       | E   | 5887.4314                     | 5887.4291                      | 0.0024   |
| 6    | 0      | 6      | 5     | 0       | 5       | A   | 6019.7836                     | 6019.7841                      | -0.0005  |
| 6    | 0      | 6      | 5     | 0       | 5       | E   | 6019.7836                     | 6019.7831                      | 0.0005   |
| 6    | 2      | 5      | 5     | 2       | 4       | A   | 6546.0847                     | 6546.0865                      | -0.0018  |
| 6    | 2      | 5      | 5     | 2       | 4       | E   | 6546.0847                     | 6546.0822                      | 0.0025   |
| 6    | 3      | 4      | 5     | 3       | 3       | A   | 6764.6928                     | 6764.6956                      | -0.0028  |
| 6    | 3      | 4      | 5     | 3       | 3       | E   | 6764.6928                     | 6764.6899                      | 0.0029   |
| 6    | 1      | 5      | 5     | 1       | 4       | A   | 6950.3874                     | 6950.3911                      | -0.0037  |
| 6    | 1      | 5      | 5     | 1       | 4       | E   | 6950.3874                     | 6950.3860                      | 0.0015   |
| 6    | 2      | 4      | 5     | 2       | 3       | A   | 7190.6404                     | 7190.6383                      | 0.0022   |
| 6    | 2      | 4      | 5     | 2       | 3       | E   | 7190.6261                     | 7190.6295                      | -0.0034  |
| 4    | 1      | 3      | 3     | 1       | 2       | A   | 4766.7431                     | 4766.7470                      | -0.0038  |
| 4    | 1      | 3      | 3     | 1       | 2       | E   | 4766.7431                     | 4766.7421                      | 0.0010   |
| 5    | 2      | 3      | 4     | 2       | 2       | A   | 5937.3906                     | 5937.3868                      | 0.0038   |
| 5    | 2      | 3      | 4     | 2       | 2       | E   | 5937.3770                     | 5937.3794                      | -0.0024  |
| 7    | 3      | 4      | 6     | 3       | 3       | A   | 8156.4031                     | 8156.4002                      | 0.0029   |
| 7    | 3      | 4      | 6     | 3       | 3       | E   | 8156.3890                     | 8156.3897                      | -0.0007  |
| 8    | 3      | 6      | 7     | 3       | 5       | A   | 8993.9620                     | 8993.9598                      | 0.0022   |
| 8    | 3      | 6      | 7     | 3       | 5       | E   | 8993.9504                     | 8993.9523                      | -0.0019  |
| 9    | 2      | 8      | 8     | 2       | 7       | A   | 9549.9235                     | 9549.9246                      | -0.0011  |
| 9    | 2      | 8      | 8     | 2       | 7       | E   | 9549.9235                     | 9549.9203                      | 0.0031   |
| 10   | 3      | 8      | 9     | 3       | 7       | A   | 11136.5422                    | 11136.5416                     | 0.0006   |
| 10   | 3      | 8      | 9     | 3       | 7       | E   | 11136.5325                    | 11136.5336                     | -0.0012  |
| 10   | 1      | 9      | 9     | 1       | 8       | A   | 10650.2570                    | 10650.2577                     | -0.0007  |
| 10   | 1      | 9      | 9     | 1       | 8       | E   | 10650.2570                    | 10650.2550                     | 0.0020   |
| 11   | 2      | 10     | 10    | 2       | 9       | A   | 11453.3903                    | 11453.3931                     | -0.0028  |
| 11   | 2      | 10     | 10    | 2       | 9       | E   | 11453.3903                    | 11453.3893                     | 0.0011   |
| 11   | 3      | 9      | 10    | 3       | 8       | A   | 12167.1422                    | 12167.1414                     | 0.0008   |
| 11   | 3      | 9      | 10    | 3       | 8       | E   | 12167.1321                    | 12167.1336                     | -0.0015  |
| 12   | 1      | 12     | 11    | 1       | 11      | A   | 11490.8400                    | 11490.8406                     | -0.0006  |
| 12   | 1      | 12     | 11    | 1       | 11      | E   | 11490.8400                    | 11490.8395                     | 0.0006   |
| 12   | 2      | 11     | 11    | 2       | 10      | A   | 12387.5462                    | 12387.5467                     | -0.0005  |
| 12   | 2      | 11     | 11    | 2       | 10      | E   | 12387.5462                    | 12387.5430                     | 0.0032   |
| 13   | 0      | 13     | 12    | 0       | 12      | A   | 12411.6451                    | 12411.6467                     | -0.0015  |
| 13   | 0      | 13     | 12    | 0       | 12      | E   | 12411.6451                    | 12411.6455                     | -0.0004  |
| 13   | 2      | 12     | 12    | 2       | 11      | A   | 13315.0698                    | 13315.0709                     | -0.0011  |
| 13   | 2      | 12     | 12    | 2       | 11      | E   | 13315.0698                    | 13315.0673                     | 0.0025   |
| 14   | 1      | 13     | 13    | 1       | 12      | A   | 14251.9106                    | 14251.9135                     | -0.0029  |
| 14   | 1      | 13     | 13    | 1       | 12      | E   | 14251.9106                    | 14251.9102                     | 0.0004   |
| 15   | 1      | 15     | 14    | 1       | 14      | A   | 14250.5138                    | 14250.5146                     | -0.0008  |
| 15   | 1      | 15     | 14    | 1       | 14      | E   | 14250.5138                    | 14250.5134                     | 0.0004   |
| 16   | 1      | 16     | 15    | 1       | 15      | A   | 15170.2613                    | 15170.2668                     | -0.0054  |
| 16   | 1      | 16     | 15    | 1       | 15      | E   | 15170.2613                    | 15170.2656                     | -0.0043  |
| 13   | 1      | 13     | 12    | 1       | 12      | A   | 12410.8764                    | 12410.8777                     | -0.0013  |
| 13   | 1      | 13     | 12    | 1       | 12      | E   | 12410.8764                    | 12410.8766                     | -0.0002  |
| 15   | 0      | 15     | 14    | 0       | 14      | A   | 14250.6751                    | 14250.6764                     | -0.0013  |
| 15   | 0      | 15     | 14    | 0       | 14      | E   | 14250.6751                    | 14250.6753                     | -0.0002  |
| 16   | 0      | 16     | 15    | 0       | 15      | A   | 15170.3461                    | 15170.3399                     | 0.0062   |
| 16   | 0      | 16     | 15    | 0       | 15      | E   | 15170.3461                    | 15170.3388                     | 0.0073   |
| 11   | 1      | 11     | 10    | 1       | 10      | A   | 10570.4078                    | 10570.4085                     | -0.0006  |
| 11   | 1      | 11     | 10    | 1       | 10      | E   | 10570.4078                    | 10570.4073                     | 0.0006   |
| 13   | 1      | 13     | 12    | 0       | 12      | A   | 12412.2951                    | 12412.2954                     | -0.0003  |
| 13   | 1      | 13     | 12    | 0       | 12      | E   | 12412.2951                    | 12412.2943                     | 0.0008   |
| 15   | 0      | 15     | 14    | 1       | 14      | A   | 14250.3819                    | 14250.3824                     | -0.0005  |
| 15   | 0      | 15     | 14    | 1       | 14      | E   | 14250.3819                    | 14250.3812                     | 0.0007   |
| 15   | 1      | 15     | 14    | 0       | 14      | A   | 14250.8073                    | 14250.8087                     | -0.0013  |

|    |   |    |    |   |    |   |            |            |         |
|----|---|----|----|---|----|---|------------|------------|---------|
| 15 | 1 | 15 | 14 | 0 | 14 | E | 14250.8073 | 14250.8075 | -0.0002 |
| 16 | 0 | 16 | 15 | 1 | 15 | A | 15170.2065 | 15170.2077 | -0.0013 |
| 16 | 0 | 16 | 15 | 1 | 15 | E | 15170.2065 | 15170.2066 | -0.0001 |
| 16 | 1 | 16 | 15 | 0 | 15 | A | 15170.3974 | 15170.3990 | -0.0015 |
| 16 | 1 | 16 | 15 | 0 | 15 | E | 15170.3974 | 15170.3978 | -0.0004 |
| 13 | 0 | 13 | 12 | 1 | 12 | A | 12410.2277 | 12410.2290 | -0.0013 |
| 13 | 0 | 13 | 12 | 1 | 12 | E | 12410.2277 | 12410.2278 | -0.0001 |
| 10 | 4 | 7  | 10 | 3 | 8  | A | 7232.4963  | 7232.4927  | 0.0036  |
| 10 | 4 | 7  | 10 | 3 | 8  | E | 7232.4829  | 7232.4869  | -0.0039 |
| 7  | 4 | 4  | 7  | 3 | 5  | A | 6775.0589  | 6775.0602  | -0.0013 |
| 7  | 4 | 4  | 7  | 3 | 5  | E | 6775.0589  | 6775.0580  | 0.0008  |
| 6  | 3 | 4  | 5  | 2 | 3  | A | 11015.3982 | 11015.3980 | 0.0002  |
| 6  | 3 | 4  | 5  | 2 | 3  | E | 11015.3982 | 11015.3972 | 0.0010  |

**Table S3.** Measured rotational transitions of 6-hydroxy-3-methoxyacetophenone (HMAP) *s-trans* conformer ( $\nu_{\text{obs}}$ ) together with calculated values ( $\nu_{\text{calc}}$ ) and residuals (diff =  $\nu_{\text{obs}} - \nu_{\text{calc}}$ ) for the fit of Table 2 of the manuscript.

| $J'$ | $K'_-$ | $K'_+$ | $J''$ | $K''_-$ | $K''_+$ | Sym | $\nu_{\text{obs}}/\text{MHz}$ | $\nu_{\text{calc}}/\text{MHz}$ | diff/MHz |
|------|--------|--------|-------|---------|---------|-----|-------------------------------|--------------------------------|----------|
| 8    | 1      | 8      | 7     | 1       | 7       | A   | 8147.6469                     | 8147.6478                      | -0.0009  |
| 8    | 1      | 8      | 7     | 1       | 7       | E   | 8147.6469                     | 8147.6465                      | 0.0004   |
| 8    | 0      | 8      | 7     | 0       | 7       | A   | 8159.5925                     | 8159.5942                      | -0.0017  |
| 8    | 0      | 8      | 7     | 0       | 7       | E   | 8159.5925                     | 8159.5931                      | -0.0005  |
| 7    | 1      | 6      | 6     | 1       | 5       | A   | 8296.2592                     | 8296.2620                      | -0.0029  |
| 7    | 1      | 6      | 6     | 1       | 5       | E   | 8296.2592                     | 8296.2583                      | 0.0008   |
| 7    | 3      | 5      | 6     | 3       | 4       | A   | 8444.4465                     | 8444.4446                      | 0.0018   |
| 7    | 3      | 5      | 6     | 3       | 4       | E   | 8444.4367                     | 8444.4359                      | 0.0008   |
| 7    | 3      | 4      | 6     | 3       | 3       | A   | 8933.0897                     | 8933.0872                      | 0.0025   |
| 7    | 3      | 4      | 6     | 3       | 3       | E   | 8933.0732                     | 8933.0724                      | 0.0008   |
| 8    | 2      | 7      | 7     | 2       | 6       | A   | 9019.4006                     | 9019.3982                      | 0.0024   |
| 8    | 2      | 7      | 7     | 2       | 6       | E   | 9019.3949                     | 9019.3934                      | 0.0015   |
| 7    | 2      | 5      | 6     | 2       | 4       | A   | 9046.4938                     | 9046.4917                      | 0.0021   |
| 7    | 2      | 5      | 6     | 2       | 4       | E   | 9046.4800                     | 9046.4807                      | -0.0007  |
| 9    | 1      | 9      | 8     | 1       | 8       | A   | 9110.2667                     | 9110.2688                      | -0.0021  |
| 9    | 1      | 9      | 8     | 1       | 8       | E   | 9110.2667                     | 9110.2675                      | -0.0008  |
| 9    | 0      | 9      | 8     | 0       | 8       | A   | 9115.4721                     | 9115.4744                      | -0.0023  |
| 9    | 0      | 9      | 8     | 0       | 8       | E   | 9115.4721                     | 9115.4732                      | -0.0011  |
| 8    | 1      | 7      | 7     | 1       | 6       | A   | 9220.1054                     | 9220.1064                      | -0.0010  |
| 8    | 1      | 7      | 7     | 1       | 6       | E   | 9220.1054                     | 9220.1035                      | 0.0020   |
| 8    | 3      | 6      | 7     | 3       | 5       | A   | 9597.8089                     | 9597.8076                      | 0.0013   |
| 8    | 3      | 6      | 7     | 3       | 5       | E   | 9597.8005                     | 9597.7985                      | 0.0020   |
| 8    | 4      | 5      | 7     | 4       | 4       | A   | 9769.4390                     | 9769.4369                      | 0.0021   |
| 8    | 4      | 5      | 7     | 4       | 4       | E   | 9769.4259                     | 9769.4253                      | 0.0006   |
| 8    | 4      | 4      | 7     | 4       | 3       | A   | 9931.8412                     | 9931.8401                      | 0.0012   |
| 8    | 4      | 4      | 7     | 4       | 3       | E   | 9931.8242                     | 9931.8248                      | -0.0006  |
| 9    | 2      | 8      | 8     | 2       | 7       | A   | 10019.7881                    | 10019.7870                     | 0.0011   |
| 9    | 2      | 8      | 8     | 2       | 7       | E   | 10019.7837                    | 10019.7825                     | 0.0011   |
| 10   | 1      | 10     | 9     | 1       | 9       | A   | 10071.2227                    | 10071.2243                     | -0.0016  |
| 10   | 1      | 10     | 9     | 1       | 9       | E   | 10071.2227                    | 10071.2230                     | -0.0004  |
| 10   | 0      | 10     | 9     | 0       | 9       | A   | 10073.4216                    | 10073.4230                     | -0.0014  |
| 10   | 0      | 10     | 9     | 0       | 9       | E   | 10073.4216                    | 10073.4218                     | -0.0002  |
| 9    | 1      | 8      | 8     | 1       | 7       | A   | 10136.1047                    | 10136.1060                     | -0.0013  |
| 9    | 1      | 8      | 8     | 1       | 7       | E   | 10136.1047                    | 10136.1031                     | 0.0016   |
| 8    | 2      | 6      | 7     | 2       | 5       | A   | 10211.5371                    | 10211.5361                     | 0.0010   |
| 8    | 2      | 6      | 7     | 2       | 5       | E   | 10211.5257                    | 10211.5261                     | -0.0005  |
| 8    | 3      | 5      | 7     | 3       | 4       | A   | 10349.5944                    | 10349.5930                     | 0.0013   |
| 8    | 3      | 5      | 7     | 3       | 4       | E   | 10349.5756                    | 10349.5762                     | -0.0007  |
| 9    | 3      | 7      | 8     | 3       | 6       | A   | 10713.8116                    | 10713.8096                     | 0.0020   |
| 9    | 3      | 7      | 8     | 3       | 6       | E   | 10713.8001                    | 10713.8005                     | -0.0004  |
| 9    | 5      | 5      | 8     | 5       | 4       | A   | 10994.8590                    | 10994.8590                     | 0.0000   |
| 9    | 5      | 5      | 8     | 5       | 4       | E   | 10994.8445                    | 10994.8466                     | -0.0021  |
| 9    | 4      | 6      | 8     | 4       | 5       | A   | 10999.7855                    | 10999.7832                     | 0.0023   |
| 9    | 4      | 6      | 8     | 4       | 5       | E   | 10999.7714                    | 10999.7704                     | 0.0010   |
| 10   | 2      | 9      | 9     | 2       | 8       | A   | 11002.3612                    | 11002.3622                     | -0.0010  |
| 10   | 2      | 9      | 9     | 2       | 8       | E   | 11002.3612                    | 11002.3580                     | 0.0032   |
| 9    | 5      | 4      | 8     | 5       | 3       | A   | 11030.6815                    | 11030.6812                     | 0.0003   |
| 9    | 5      | 4      | 8     | 5       | 3       | E   | 11030.6656                    | 11030.6648                     | 0.0008   |
| 11   | 1      | 11     | 10    | 1       | 10      | A   | 11031.4432                    | 11031.4438                     | -0.0007  |
| 11   | 1      | 11     | 10    | 1       | 10      | E   | 11031.4432                    | 11031.4426                     | 0.0006   |
| 11   | 0      | 11     | 10    | 0       | 10      | A   | 11032.3505                    | 11032.3509                     | -0.0004  |
| 11   | 0      | 11     | 10    | 0       | 10      | E   | 11032.3505                    | 11032.3497                     | 0.0008   |
| 10   | 1      | 9      | 9     | 1       | 8       | A   | 11063.5488                    | 11063.5489                     | -0.0001  |
| 10   | 1      | 9      | 9     | 1       | 8       | E   | 11063.5488                    | 11063.5458                     | 0.0030   |
| 9    | 2      | 7      | 8     | 2       | 6       | A   | 11270.1691                    | 11270.1677                     | 0.0014   |
| 9    | 2      | 7      | 8     | 2       | 6       | E   | 11270.1589                    | 11270.1598                     | -0.0009  |
| 9    | 4      | 5      | 8     | 4       | 4       | A   | 11336.0225                    | 11336.0226                     | -0.0001  |
| 9    | 4      | 5      | 8     | 4       | 4       | E   | 11336.0020                    | 11336.0036                     | -0.0016  |
| 9    | 3      | 6      | 8     | 3       | 5       | A   | 11717.4438                    | 11717.4451                     | -0.0013  |

|    |   |    |    |   |    |   |            |            |         |
|----|---|----|----|---|----|---|------------|------------|---------|
| 9  | 3 | 6  | 8  | 3 | 5  | E | 11717.4257 | 11717.4277 | -0.0020 |
| 10 | 3 | 8  | 9  | 3 | 7  | A | 11791.0354 | 11791.0336 | 0.0018  |
| 10 | 3 | 8  | 9  | 3 | 7  | E | 11791.0248 | 11791.0250 | -0.0002 |
| 11 | 2 | 10 | 10 | 2 | 9  | A | 11973.7084 | 11973.7105 | -0.0021 |
| 11 | 2 | 10 | 10 | 2 | 9  | E | 11973.7084 | 11973.7065 | 0.0019  |
| 12 | 1 | 12 | 11 | 1 | 11 | A | 11991.3600 | 11991.3613 | -0.0013 |
| 12 | 1 | 12 | 11 | 1 | 11 | E | 11991.3600 | 11991.3601 | -0.0001 |
| 12 | 0 | 12 | 11 | 0 | 11 | A | 11991.7275 | 11991.7287 | -0.0012 |
| 12 | 0 | 12 | 11 | 0 | 11 | E | 11991.7275 | 11991.7275 | 0.0001  |
| 11 | 1 | 10 | 10 | 1 | 9  | A | 12003.8218 | 12003.8217 | 0.0001  |
| 11 | 1 | 10 | 10 | 1 | 9  | E | 12003.8218 | 12003.8184 | 0.0034  |
| 10 | 6 | 4  | 9  | 6 | 3  | A | 12196.1034 | 12196.1047 | -0.0013 |
| 10 | 6 | 4  | 9  | 6 | 3  | E | 12196.0732 | 12196.0730 | 0.0002  |
| 10 | 4 | 7  | 9  | 4 | 6  | A | 12206.7538 | 12206.7541 | -0.0003 |
| 10 | 4 | 7  | 9  | 4 | 6  | E | 12206.7397 | 12206.7406 | -0.0009 |
| 10 | 2 | 8  | 9  | 2 | 7  | A | 12231.1899 | 12231.1887 | 0.0012  |
| 10 | 2 | 8  | 9  | 2 | 7  | E | 12231.1826 | 12231.1829 | -0.0003 |
| 10 | 5 | 6  | 9  | 5 | 5  | A | 12258.7571 | 12258.7576 | -0.0004 |
| 10 | 5 | 6  | 9  | 5 | 5  | E | 12258.7410 | 12258.7424 | -0.0014 |
| 10 | 5 | 5  | 9  | 5 | 4  | A | 12351.5874 | 12351.5894 | -0.0020 |
| 10 | 5 | 5  | 9  | 5 | 4  | E | 12351.5676 | 12351.5709 | -0.0033 |
| 11 | 1 | 11 | 10 | 0 | 10 | A | 11032.9593 | 11032.9593 | -0.0001 |
| 11 | 1 | 11 | 10 | 0 | 10 | E | 11032.9593 | 11032.9581 | 0.0011  |
| 11 | 0 | 11 | 10 | 1 | 10 | A | 11030.8348 | 11030.8354 | -0.0006 |
| 11 | 0 | 11 | 10 | 1 | 10 | E | 11030.8348 | 11030.8341 | 0.0007  |
| 8  | 0 | 8  | 7  | 1 | 7  | A | 8138.7275  | 8138.7281  | -0.0006 |
| 8  | 0 | 8  | 7  | 1 | 7  | E | 8138.7275  | 8138.7266  | 0.0009  |
| 8  | 1 | 8  | 7  | 0 | 7  | A | 8168.5127  | 8168.5139  | -0.0012 |
| 8  | 1 | 8  | 7  | 0 | 7  | E | 8168.5127  | 8168.5129  | -0.0003 |
| 9  | 1 | 9  | 8  | 0 | 8  | A | 9119.1869  | 9119.1885  | -0.0016 |
| 9  | 1 | 9  | 8  | 0 | 8  | E | 9119.1869  | 9119.1874  | -0.0005 |
| 9  | 0 | 9  | 8  | 1 | 8  | A | 9106.5533  | 9106.5547  | -0.0014 |
| 9  | 0 | 9  | 8  | 1 | 8  | E | 9106.5533  | 9106.5533  | 0.0000  |
| 9  | 1 | 8  | 8  | 2 | 7  | A | 9903.0253  | 9903.0233  | 0.0020  |
| 9  | 1 | 8  | 8  | 2 | 7  | E | 9903.0170  | 9903.0164  | 0.0006  |
| 10 | 2 | 9  | 9  | 1 | 8  | A | 11119.1267 | 11119.1259 | 0.0007  |
| 10 | 2 | 9  | 9  | 1 | 8  | E | 11119.1267 | 11119.1242 | 0.0025  |
| 9  | 2 | 8  | 8  | 1 | 7  | A | 10252.8703 | 10252.8697 | 0.0006  |
| 9  | 2 | 8  | 8  | 1 | 7  | E | 10252.8703 | 10252.8692 | 0.0011  |
| 10 | 1 | 10 | 9  | 0 | 9  | A | 10074.9376 | 10074.9385 | -0.0009 |
| 10 | 1 | 10 | 9  | 0 | 9  | E | 10074.9376 | 10074.9373 | 0.0003  |
| 11 | 1 | 10 | 10 | 2 | 9  | A | 11948.2428 | 11948.2447 | -0.0018 |
| 11 | 1 | 10 | 10 | 2 | 9  | E | 11948.2428 | 11948.2399 | 0.0029  |
| 10 | 1 | 9  | 9  | 2 | 8  | A | 10946.7874 | 10946.7852 | 0.0022  |
| 10 | 1 | 9  | 9  | 2 | 8  | E | 10946.7809 | 10946.7796 | 0.0013  |
| 9  | 3 | 7  | 8  | 2 | 6  | A | 12400.6461 | 12400.6523 | -0.0061 |
| 9  | 3 | 7  | 8  | 2 | 6  | E | 12400.6591 | 12400.6591 | 0.0000  |
| 11 | 2 | 9  | 10 | 3 | 8  | A | 12444.5084 | 12444.5079 | 0.0005  |
| 11 | 2 | 9  | 10 | 3 | 8  | E | 12444.4906 | 12444.4916 | -0.0009 |
| 13 | 0 | 13 | 12 | 1 | 12 | A | 12951.0709 | 12951.0717 | -0.0009 |
| 13 | 0 | 13 | 12 | 1 | 12 | E | 12951.0709 | 12951.0705 | 0.0004  |
| 13 | 1 | 13 | 12 | 0 | 12 | A | 12951.4067 | 12951.4072 | -0.0005 |
| 13 | 1 | 13 | 12 | 0 | 12 | E | 12951.4067 | 12951.4060 | 0.0008  |
| 3  | 3 | 0  | 2  | 2 | 1  | A | 7897.3326  | 7897.3314  | 0.0012  |
| 3  | 3 | 0  | 2  | 2 | 1  | E | 7897.3326  | 7897.3324  | 0.0002  |
| 7  | 5 | 3  | 7  | 4 | 4  | A | 7571.0798  | 7571.0818  | -0.0020 |
| 7  | 5 | 3  | 7  | 4 | 4  | E | 7571.0798  | 7571.0790  | 0.0008  |
| 8  | 5 | 4  | 8  | 4 | 5  | A | 7538.1499  | 7538.1504  | -0.0005 |
| 8  | 5 | 4  | 8  | 4 | 5  | E | 7538.1499  | 7538.1543  | -0.0045 |
| 9  | 5 | 5  | 9  | 4 | 6  | A | 7533.2262  | 7533.2262  | 0.0000  |
| 9  | 5 | 5  | 9  | 4 | 6  | E | 7533.2262  | 7533.2306  | -0.0045 |
| 5  | 2 | 4  | 4  | 1 | 3  | A | 7382.9792  | 7382.9777  | 0.0015  |
| 5  | 2 | 4  | 4  | 1 | 3  | E | 7382.9792  | 7382.9792  | 0.0001  |
| 6  | 1 | 5  | 5  | 1 | 4  | A | 7322.7523  | 7322.7558  | -0.0035 |
| 6  | 1 | 5  | 5  | 1 | 4  | E | 7322.7523  | 7322.7509  | 0.0015  |
| 8  | 5 | 3  | 8  | 4 | 4  | A | 7300.3611  | 7300.3497  | 0.0114  |
| 8  | 5 | 3  | 8  | 4 | 4  | E | 7300.3611  | 7300.3626  | -0.0015 |
| 6  | 4 | 3  | 5  | 4 | 2  | A | 7283.8342  | 7283.8396  | -0.0054 |

|   |   |   |   |   |   |   |           |           |         |
|---|---|---|---|---|---|---|-----------|-----------|---------|
| 6 | 4 | 3 | 5 | 4 | 2 | E | 7283.8342 | 7283.8340 | 0.0001  |
| 7 | 1 | 7 | 6 | 0 | 6 | A | 7228.6462 | 7228.6470 | -0.0009 |
| 7 | 1 | 7 | 6 | 0 | 6 | E | 7228.6462 | 7228.6464 | -0.0002 |
| 7 | 0 | 7 | 6 | 0 | 6 | A | 7207.7797 | 7207.7810 | -0.0012 |
| 7 | 0 | 7 | 6 | 0 | 6 | E | 7207.7797 | 7207.7799 | -0.0002 |
| 7 | 1 | 7 | 6 | 1 | 6 | A | 7181.5281 | 7181.5291 | -0.0011 |
| 7 | 1 | 7 | 6 | 1 | 6 | E | 7181.5281 | 7181.5277 | 0.0003  |

**Table S4.** Measured rotational transitions of HMAP *a-trans* conformer ( $\nu_{\text{obs}}$ ) together with calculated values ( $\nu_{\text{calc}}$ ) and residuals (diff =  $\nu_{\text{obs}} - \nu_{\text{calc}}$ ) for the fit of Table 2 of the manuscript.

| $J'$ | $K'_-$ | $K'_+$ | $J''$ | $K''_-$ | $K''_+$ | Sym | $\nu_{\text{obs}}/\text{MHz}$ | $\nu_{\text{calc}}/\text{MHz}$ | diff/MHz |
|------|--------|--------|-------|---------|---------|-----|-------------------------------|--------------------------------|----------|
| 8    | 2      | 7      | 7     | 2       | 6       | A   | 8454.0620                     | 8454.0620                      | 0.0000   |
| 8    | 2      | 7      | 7     | 2       | 6       | E   | 8454.0554                     | 8454.0554                      | 0.0000   |
| 8    | 2      | 6      | 7     | 2       | 5       | A   | 9254.2185                     | 9254.2172                      | 0.0012   |
| 8    | 2      | 6      | 7     | 2       | 5       | E   | 9254.2025                     | 9254.2029                      | -0.0005  |
| 8    | 3      | 6      | 7     | 3       | 5       | A   | 8745.9055                     | 8745.9052                      | 0.0003   |
| 8    | 3      | 6      | 7     | 3       | 5       | E   | 8745.8938                     | 8745.8950                      | -0.0012  |
| 8    | 4      | 5      | 7     | 4       | 4       | A   | 8767.3455                     | 8767.3463                      | -0.0008  |
| 8    | 4      | 5      | 7     | 4       | 4       | E   | 8767.3358                     | 8767.3358                      | 0.0000   |
| 7    | 1      | 7      | 6     | 1       | 6       | A   | 6838.0899                     | 6838.0924                      | -0.0025  |
| 7    | 1      | 7      | 6     | 1       | 6       | E   | 6838.0899                     | 6838.0903                      | -0.0004  |
| 7    | 2      | 6      | 6     | 2       | 5       | A   | 7443.2101                     | 7443.2144                      | -0.0043  |
| 7    | 2      | 6      | 6     | 2       | 5       | E   | 7443.2101                     | 7443.2079                      | 0.0022   |
| 7    | 2      | 5      | 6     | 2       | 4       | A   | 8075.9929                     | 8075.9911                      | 0.0018   |
| 7    | 2      | 5      | 6     | 2       | 4       | E   | 8075.9774                     | 8075.9779                      | -0.0005  |
| 7    | 3      | 5      | 6     | 3       | 4       | A   | 7654.6859                     | 7654.6840                      | 0.0019   |
| 7    | 3      | 5      | 6     | 3       | 4       | E   | 7654.6745                     | 7654.6748                      | -0.0003  |
| 7    | 4      | 4      | 6     | 4       | 3       | A   | 7655.5152                     | 7655.5148                      | 0.0004   |
| 7    | 4      | 4      | 6     | 4       | 3       | E   | 7655.5152                     | 7655.5076                      | 0.0075   |
| 9    | 1      | 8      | 8     | 1       | 7       | A   | 9788.4400                     | 9788.4443                      | -0.0043  |
| 9    | 1      | 8      | 8     | 1       | 7       | E   | 9788.4400                     | 9788.4387                      | 0.0013   |
| 9    | 2      | 7      | 8     | 2       | 6       | A   | 10398.2371                    | 10398.2360                     | 0.0010   |
| 9    | 2      | 7      | 8     | 2       | 6       | E   | 10398.2203                    | 10398.2213                     | -0.0010  |
| 9    | 3      | 6      | 8     | 3       | 5       | A   | 10210.3074                    | 10210.3062                     | 0.0012   |
| 9    | 3      | 6      | 8     | 3       | 5       | E   | 10210.2876                    | 10210.2882                     | -0.0006  |
| 9    | 4      | 5      | 8     | 4       | 4       | A   | 9927.2682                     | 9927.2683                      | -0.0001  |
| 9    | 4      | 5      | 8     | 4       | 4       | E   | 9927.2521                     | 9927.2542                      | -0.0021  |
| 10   | 1      | 10     | 9     | 1       | 9       | A   | 9630.1645                     | 9630.1662                      | -0.0017  |
| 10   | 1      | 10     | 9     | 1       | 9       | E   | 9630.1645                     | 9630.1644                      | 0.0001   |
| 10   | 0      | 10     | 9     | 0       | 9       | A   | 9652.0057                     | 9652.0083                      | -0.0025  |
| 10   | 0      | 10     | 9     | 0       | 9       | E   | 9652.0057                     | 9652.0068                      | -0.0011  |
| 10   | 2      | 9      | 9     | 2       | 8       | A   | 10424.2537                    | 10424.2564                     | -0.0027  |
| 10   | 2      | 9      | 9     | 2       | 8       | E   | 10424.2537                    | 10424.2499                     | 0.0038   |
| 10   | 3      | 8      | 9     | 3       | 7       | A   | 10893.1983                    | 10893.1979                     | 0.0004   |
| 10   | 3      | 8      | 9     | 3       | 7       | E   | 10893.1853                    | 10893.1863                     | -0.0010  |
| 10   | 4      | 7      | 9     | 4       | 6       | A   | 10999.5396                    | 10999.5403                     | -0.0007  |
| 10   | 4      | 7      | 9     | 4       | 6       | E   | 10999.5250                    | 10999.5263                     | -0.0013  |
| 11   | 1      | 10     | 10    | 1       | 9       | A   | 11585.1520                    | 11585.1539                     | -0.0019  |
| 11   | 1      | 10     | 10    | 1       | 9       | E   | 11585.1520                    | 11585.1500                     | 0.0020   |
| 11   | 0      | 11     | 10    | 0       | 10      | A   | 10565.2460                    | 10565.2475                     | -0.0016  |
| 11   | 0      | 11     | 10    | 0       | 10      | E   | 10565.2460                    | 10565.2460                     | -0.0001  |
| 11   | 2      | 9      | 10    | 2       | 8       | A   | 12550.1408                    | 12550.1405                     | 0.0003   |
| 11   | 2      | 9      | 10    | 2       | 8       | E   | 12550.1267                    | 12550.1273                     | -0.0006  |
| 11   | 3      | 8      | 10    | 3       | 7       | A   | 12692.6448                    | 12692.6475                     | -0.0027  |
| 11   | 3      | 8      | 10    | 3       | 7       | E   | 12692.6241                    | 12692.6253                     | -0.0012  |
| 11   | 3      | 9      | 10    | 3       | 8       | A   | 11942.6754                    | 11942.6746                     | 0.0009   |
| 11   | 3      | 9      | 10    | 3       | 8       | E   | 11942.6623                    | 11942.6627                     | -0.0004  |
| 13   | 1      | 12     | 12    | 1       | 11      | A   | 13362.1182                    | 13362.1172                     | 0.0010   |
| 13   | 1      | 12     | 12    | 1       | 11      | E   | 13362.1182                    | 13362.1133                     | 0.0050   |
| 14   | 0      | 14     | 13    | 0       | 13      | A   | 13314.7871                    | 13314.7877                     | -0.0006  |
| 14   | 0      | 14     | 13    | 0       | 13      | E   | 13314.7871                    | 13314.7860                     | 0.0010   |
| 15   | 0      | 15     | 14    | 0       | 14      | A   | 14232.7226                    | 14232.7234                     | -0.0008  |
| 15   | 0      | 15     | 14    | 0       | 14      | E   | 14232.7226                    | 14232.7218                     | 0.0009   |
| 8    | 0      | 8      | 7     | 1       | 7       | A   | 7688.0278                     | 7688.0305                      | -0.0027  |
| 8    | 0      | 8      | 7     | 1       | 7       | E   | 7688.0278                     | 7688.0269                      | 0.0009   |
| 8    | 1      | 8      | 7     | 0       | 7       | A   | 7922.4521                     | 7922.4526                      | -0.0006  |
| 8    | 1      | 8      | 7     | 0       | 7       | E   | 7922.4521                     | 7922.4530                      | -0.0009  |
| 7    | 0      | 7      | 6     | 1       | 6       | A   | 6690.1720                     | 6690.1744                      | -0.0025  |
| 7    | 0      | 7      | 6     | 1       | 6       | E   | 6690.1720                     | 6690.1700                      | 0.0020   |
| 8    | 2      | 7      | 7     | 1       | 6       | A   | 10012.8437                    | 10012.8384                     | 0.0053   |

|    |   |    |   |   |   |   |            |            |         |
|----|---|----|---|---|---|---|------------|------------|---------|
| 8  | 2 | 7  | 7 | 1 | 6 | E | 10012.8437 | 10012.8444 | -0.0007 |
| 7  | 1 | 7  | 6 | 0 | 6 | A | 7081.3731  | 7081.3740  | -0.0009 |
| 7  | 1 | 7  | 6 | 0 | 6 | E | 7081.3731  | 7081.3750  | -0.0019 |
| 7  | 2 | 6  | 6 | 1 | 5 | A | 9412.3216  | 9412.3165  | 0.0051  |
| 7  | 2 | 6  | 6 | 1 | 5 | E | 9412.3216  | 9412.3214  | 0.0002  |
| 7  | 3 | 5  | 6 | 2 | 4 | A | 12782.2340 | 12782.2348 | -0.0007 |
| 7  | 3 | 5  | 6 | 2 | 4 | E | 12782.2340 | 12782.2373 | -0.0032 |
| 7  | 3 | 4  | 6 | 2 | 5 | A | 13999.4463 | 13999.4466 | -0.0003 |
| 7  | 3 | 4  | 6 | 2 | 5 | E | 13999.4296 | 13999.4317 | -0.0021 |
| 6  | 1 | 6  | 5 | 0 | 5 | A | 6273.0645  | 6273.0633  | 0.0012  |
| 6  | 1 | 6  | 5 | 0 | 5 | E | 6273.0645  | 6273.0648  | -0.0003 |
| 6  | 2 | 5  | 5 | 1 | 4 | A | 8782.3718  | 8782.3685  | 0.0033  |
| 6  | 2 | 5  | 5 | 1 | 4 | E | 8782.3718  | 8782.3717  | 0.0001  |
| 6  | 3 | 4  | 5 | 2 | 3 | A | 12002.3746 | 12002.3739 | 0.0007  |
| 6  | 3 | 4  | 5 | 2 | 3 | E | 12002.3746 | 12002.3741 | 0.0005  |
| 6  | 3 | 3  | 5 | 2 | 4 | A | 12632.6686 | 12632.6687 | -0.0001 |
| 6  | 3 | 3  | 5 | 2 | 4 | E | 12632.6567 | 12632.6597 | -0.0030 |
| 5  | 2 | 4  | 4 | 1 | 3 | A | 8098.0210  | 8098.0179  | 0.0031  |
| 5  | 2 | 4  | 4 | 1 | 3 | E | 8098.0210  | 8098.0196  | 0.0014  |
| 4  | 2 | 3  | 3 | 1 | 2 | A | 7342.8835  | 7342.8824  | 0.0010  |
| 4  | 2 | 3  | 3 | 1 | 2 | E | 7342.8835  | 7342.8829  | 0.0005  |
| 3  | 2 | 2  | 2 | 1 | 1 | A | 6507.9354  | 6507.9358  | -0.0004 |
| 3  | 2 | 2  | 2 | 1 | 1 | E | 6507.9354  | 6507.9357  | -0.0003 |
| 3  | 3 | 1  | 2 | 2 | 0 | A | 9084.0729  | 9084.0754  | -0.0025 |
| 3  | 3 | 1  | 2 | 2 | 0 | E | 9084.0729  | 9084.0700  | 0.0028  |
| 3  | 3 | 0  | 2 | 2 | 1 | A | 9102.2412  | 9102.2386  | 0.0026  |
| 3  | 3 | 0  | 2 | 2 | 1 | E | 9102.2412  | 9102.2424  | -0.0012 |
| 10 | 0 | 10 | 9 | 1 | 9 | A | 9602.8716  | 9602.8744  | -0.0027 |
| 10 | 0 | 10 | 9 | 1 | 9 | E | 9602.8716  | 9602.8718  | -0.0002 |
| 9  | 1 | 8  | 8 | 2 | 7 | A | 8620.4791  | 8620.4783  | 0.0008  |
| 9  | 1 | 8  | 8 | 2 | 7 | E | 8620.4612  | 8620.4598  | 0.0014  |
| 9  | 0 | 9  | 8 | 1 | 8 | A | 8655.4387  | 8655.4411  | -0.0025 |
| 9  | 0 | 9  | 8 | 1 | 8 | E | 8655.4387  | 8655.4381  | 0.0005  |
| 8  | 1 | 7  | 7 | 2 | 6 | A | 7286.1040  | 7286.0960  | 0.0081  |
| 8  | 1 | 7  | 7 | 2 | 6 | E | 7286.0781  | 7286.0765  | 0.0016  |
| 8  | 3 | 5  | 7 | 3 | 4 | A | 8981.2403  | 8981.2406  | -0.0003 |
| 8  | 3 | 5  | 7 | 3 | 4 | E | 8981.2244  | 8981.2257  | -0.0012 |
| 7  | 0 | 7  | 6 | 0 | 6 | A | 6933.4535  | 6933.4560  | -0.0026 |

**Table S5.** *Ab initio* structure for *s-cis* acetovanillone (MP2-6-311++G(d,p), principal axis system).

| Atomic<br>Number | <i>a</i> /Å | <i>b</i> /Å | <i>c</i> /Å |
|------------------|-------------|-------------|-------------|
| 6                | 0.075726    | 0.744303    | -0.000279   |
| 6                | 1.139735    | -0.179830   | 0.000143    |
| 6                | 0.865216    | -1.555275   | 0.000253    |
| 6                | -0.457330   | -2.013019   | 0.000258    |
| 6                | -1.510010   | -1.101284   | 0.000011    |
| 6                | -1.237122   | 0.286128    | -0.000257   |
| 1                | 0.317962    | 1.801092    | -0.000454   |
| 1                | 1.672340    | -2.280636   | 0.000480    |
| 1                | -0.689538   | -3.073955   | 0.000438    |
| 8                | -2.793578   | -1.545343   | 0.000027    |
| 1                | -3.359131   | -0.760532   | 0.000154    |
| 8                | -2.361794   | 1.063760    | -0.000528   |
| 6                | -2.157556   | 2.474386    | 0.000433    |
| 1                | -1.610738   | 2.786966    | -0.894663   |
| 1                | -1.611144   | 2.785767    | 0.896198    |
| 1                | -3.152427   | 2.917491    | 0.000470    |
| 6                | 2.531606    | 0.365733    | 0.000039    |
| 8                | 2.730782    | 1.575336    | 0.000257    |
| 6                | 3.688904    | -0.614240   | -0.000375   |
| 1                | 3.646395    | -1.256711   | -0.885171   |
| 1                | 3.646764    | -1.257051   | 0.884192    |
| 1                | 4.623352    | -0.052323   | -0.000450   |

**Table S6.** *Ab initio* structure for *s-trans* acetovanillone (MP2-6-311++G(d,p), principal axis system).

| Atomic<br>Number | <i>a</i> /Å | <i>b</i> /Å | <i>c</i> /Å |
|------------------|-------------|-------------|-------------|
| 6                | 0.103136    | 0.728700    | -0.000191   |
| 6                | 1.140612    | -0.226866   | 0.000021    |
| 6                | 0.823651    | -1.593246   | 0.000116    |
| 6                | -0.507896   | -2.011893   | 0.000088    |
| 6                | -1.536891   | -1.070291   | -0.000015   |
| 6                | -1.226129   | 0.306094    | -0.000270   |
| 1                | 0.336124    | 1.786581    | -0.000336   |
| 1                | 1.633538    | -2.315899   | 0.000241    |
| 1                | -0.771145   | -3.065686   | 0.000224    |
| 8                | -2.831939   | -1.480888   | -0.000027   |
| 1                | -3.378309   | -0.682934   | 0.000272    |
| 8                | -2.329474   | 1.117418    | -0.000481   |
| 6                | -2.090957   | 2.520212    | 0.000697    |
| 1                | -3.074068   | 2.989047    | 0.000756    |
| 1                | -1.538624   | 2.820206    | 0.897425    |
| 1                | -1.538106   | 2.821662    | -0.895223   |
| 6                | 2.580481    | 0.178859    | 0.000033    |
| 8                | 3.470523    | -0.662389   | 0.000263    |
| 6                | 2.912779    | 1.660270    | -0.000329   |
| 1                | 2.494220    | 2.148922    | 0.885241    |
| 1                | 3.997207    | 1.774496    | -0.000326   |
| 1                | 2.494265    | 2.148487    | -0.886159   |

**Table S7.** DFT structure for *s-cis* acetovanillone (M05-2X-6-311++G(d,p), principal axis system).

| Atomic<br>Number | <i>a</i> /Å | <i>b</i> /Å | <i>c</i> /Å |
|------------------|-------------|-------------|-------------|
| 6                | 0.070547    | 0.736640    | -0.000119   |
| 6                | 1.131989    | -0.178574   | 0.000012    |
| 6                | 0.867306    | -1.543355   | 0.000147    |
| 6                | -0.443889   | -2.007068   | 0.000126    |
| 6                | -1.490577   | -1.103783   | -0.000020   |
| 6                | -1.228079   | 0.277627    | -0.000119   |
| 1                | 0.310472    | 1.789313    | -0.000241   |
| 1                | 1.675612    | -2.259969   | 0.000254    |
| 1                | -0.672814   | -3.062878   | 0.000239    |
| 8                | -2.767862   | -1.541089   | -0.000044   |
| 1                | -3.346462   | -0.769857   | -0.000008   |
| 8                | -2.352810   | 1.050999    | -0.000240   |
| 6                | -2.171056   | 2.461231    | 0.000305    |
| 1                | -1.629585   | 2.775399    | -0.892613   |
| 1                | -1.629346   | 2.774673    | 0.893331    |
| 1                | -3.166499   | 2.892121    | 0.000622    |
| 6                | 2.516389    | 0.372775    | -0.000004   |
| 8                | 2.706912    | 1.569714    | -0.000032   |
| 6                | 3.677314    | -0.593307   | -0.000031   |
| 1                | 3.640573    | -1.233244   | -0.882248   |
| 1                | 3.640641    | -1.233253   | 0.882181    |
| 1                | 4.599199    | -0.019981   | -0.000058   |

**Table S8.** DFT structure for *s-trans* acetovanillone (M05-2X-6-311++G(d,p), principal axis system).

| Atomic<br>Number | <i>a</i> /Å | <i>b</i> /Å | <i>c</i> /Å |
|------------------|-------------|-------------|-------------|
| 6                | 0.097195    | 0.722709    | -0.000127   |
| 6                | 1.132192    | -0.222420   | -0.000058   |
| 6                | 0.826634    | -1.579463   | 0.000039    |
| 6                | -0.492953   | -2.005589   | 0.000049    |
| 6                | -1.516683   | -1.073011   | -0.000021   |
| 6                | -1.217453   | 0.297667    | -0.000107   |
| 1                | 0.322435    | 1.777841    | -0.000213   |
| 1                | 1.640458    | -2.289684   | 0.000104    |
| 1                | -0.751625   | -3.054831   | 0.000135    |
| 8                | -2.805180   | -1.478301   | -0.000012   |
| 1                | -3.366091   | -0.694329   | 0.000105    |
| 8                | -2.321403   | 1.104272    | -0.000181   |
| 6                | -2.107970   | 2.507401    | 0.000327    |
| 1                | -3.092738   | 2.962274    | 0.000504    |
| 1                | -1.561364   | 2.811224    | 0.894506    |
| 1                | -1.561406   | 2.811891    | -0.893654   |
| 6                | 2.566885    | 0.183461    | -0.000060   |
| 8                | 3.448138    | -0.646541   | 0.000209    |
| 6                | 2.900680    | 1.658138    | -0.000146   |
| 1                | 2.484441    | 2.144247    | 0.882994    |
| 1                | 3.981122    | 1.763260    | -0.000109   |
| 1                | 2.484511    | 2.144122    | -0.883388   |

**Table S9.** *Ab initio* structure for *s-trans* HMAP (MP2-6-311++G(d,p), principal axis system).

| Atomic<br>Number | <i>a</i> /Å | <i>b</i> /Å | <i>c</i> /Å |
|------------------|-------------|-------------|-------------|
| 6                | -0.655469   | 0.616126    | -0.000294   |
| 6                | 0.683818    | 0.148837    | 0.000292    |
| 6                | 0.939466    | -1.242621   | 0.000003    |
| 6                | -0.146579   | -2.137377   | 0.000080    |
| 6                | -1.451853   | -1.669662   | -0.000063   |
| 6                | -1.717532   | -0.285724   | -0.000163   |
| 1                | -0.837514   | 1.682973    | -0.000327   |
| 1                | 0.064894    | -3.202678   | 0.000061    |
| 8                | -3.038859   | 0.057730    | -0.000301   |
| 6                | -3.328055   | 1.446840    | 0.000516    |
| 1                | -4.414770   | 1.523538    | 0.000607    |
| 1                | -2.926262   | 1.934467    | 0.896552    |
| 1                | -2.926392   | 1.935537    | -0.894995   |
| 6                | 1.814453    | 1.099387    | 0.000059    |
| 8                | 2.986051    | 0.696595    | 0.000319    |
| 6                | 1.538171    | 2.586920    | -0.000372   |
| 1                | 0.961338    | 2.870727    | 0.885061    |
| 1                | 2.491474    | 3.116167    | -0.000469   |
| 1                | 0.961422    | 2.870286    | -0.886000   |
| 8                | 2.181899    | -1.767098   | -0.000038   |
| 1                | 2.794402    | -0.999795   | -0.000860   |
| 1                | -2.292371   | -2.358044   | -0.000025   |

**Table S10.** *Ab initio* structure for *a-trans* HMAP (MP2-6-311++G(d,p), principal axis system).

| Atomic<br>Number | <i>a</i> /Å | <i>b</i> /Å | <i>c</i> /Å |
|------------------|-------------|-------------|-------------|
| 6                | -0.408007   | -0.887084   | -0.000082   |
| 6                | 0.799760    | -0.163530   | 0.000072    |
| 6                | 0.758998    | 1.256404    | -0.000067   |
| 6                | -0.486010   | 1.897370    | 0.000054    |
| 6                | -1.678046   | 1.170256    | -0.000083   |
| 6                | -1.642207   | -0.236178   | -0.000018   |
| 1                | -0.409196   | -1.972149   | -0.000029   |
| 1                | -0.503534   | 2.983445    | 0.000047    |
| 8                | -2.743954   | -1.044681   | -0.000064   |
| 6                | -4.006559   | -0.394735   | 0.000114    |
| 1                | -4.748946   | -1.192070   | 0.000143    |
| 1                | -4.134709   | 0.223582    | 0.895855    |
| 1                | -4.134914   | 0.223692    | -0.895522   |
| 6                | 2.104086    | -0.864563   | 0.000011    |
| 8                | 3.165641    | -0.228324   | 0.000044    |
| 6                | 2.135557    | -2.375971   | -0.000005   |
| 1                | 1.626264    | -2.769601   | -0.884538   |
| 1                | 3.176263    | -2.701069   | -0.000087   |
| 1                | 1.626400    | -2.769619   | 0.884599    |
| 8                | 1.867982    | 2.027748    | -0.000014   |
| 1                | 2.625654    | 1.406187    | 0.000149    |
| 1                | -2.618551   | 1.709938    | -0.000028   |

**Table S11.** DFT structure for *s-trans* HMAP (M05-2X-6-311++G(d,p), principal axis system).

| Atomic<br>Number | <i>a</i> /Å | <i>b</i> /Å | <i>c</i> /Å |
|------------------|-------------|-------------|-------------|
| 6                | 0.653932    | 0.607093    | -0.000018   |
| 6                | -0.680786   | 0.146230    | -0.000020   |
| 6                | -0.937505   | -1.233131   | 0.000006    |
| 6                | 0.141429    | -2.127914   | 0.000014    |
| 6                | 1.433430    | -1.663592   | 0.000008    |
| 6                | 1.702850    | -0.286441   | -0.000004   |
| 1                | 0.838481    | 1.669184    | -0.000038   |
| 1                | -0.075765   | -3.186357   | 0.000034    |
| 8                | 3.022314    | 0.055875    | -0.000011   |
| 6                | 3.332046    | 1.436125    | -0.000007   |
| 1                | 4.415162    | 1.501609    | -0.000003   |
| 1                | 2.936758    | 1.924659    | -0.893599   |
| 1                | 2.936751    | 1.924655    | 0.893584    |
| 6                | -1.806230   | 1.095047    | -0.000072   |
| 8                | -2.966797   | 0.700138    | -0.000088   |
| 6                | -1.532495   | 2.576827    | 0.000110    |
| 1                | -0.958658   | 2.859355    | -0.882943   |
| 1                | -2.485277   | 3.096745    | 0.000132    |
| 1                | -0.958726   | 2.859161    | 0.883271    |
| 8                | -2.171368   | -1.754438   | 0.000048    |
| 1                | -2.805693   | -1.008884   | 0.000162    |
| 1                | 2.271905    | -2.346078   | 0.000016    |

**Table S12.** DFT structure for *a-trans* HMAP (M05-2X-6-311++G(d,p), principal axis system).

| Atomic<br>Number | <i>a</i> /Å | <i>b</i> /Å | <i>c</i> /Å |
|------------------|-------------|-------------|-------------|
| 6                | -0.405008   | -0.878924   | -0.000013   |
| 6                | 0.795449    | -0.160559   | -0.000013   |
| 6                | 0.755109    | 1.248974    | 0.000003    |
| 6                | -0.482148   | 1.887174    | 0.000009    |
| 6                | -1.661596   | 1.161985    | 0.000005    |
| 6                | -1.628763   | -0.234708   | -0.000005   |
| 1                | -0.407689   | -1.958977   | -0.000028   |
| 1                | -0.496052   | 2.967616    | 0.000024    |
| 8                | -2.734918   | -1.033887   | -0.000012   |
| 6                | -3.999815   | -0.397481   | -0.000001   |
| 1                | -4.735336   | -1.195328   | -0.000006   |
| 1                | -4.129465   | 0.217054    | 0.893475    |
| 1                | -4.129472   | 0.217071    | -0.893464   |
| 6                | 2.096530    | -0.859006   | -0.000046   |
| 8                | 3.147057    | -0.230250   | -0.000068   |
| 6                | 2.131622    | -2.364285   | 0.000078    |
| 1                | 1.625929    | -2.757406   | -0.881887   |
| 1                | 3.170682    | -2.678725   | 0.000084    |
| 1                | 1.625962    | -2.757270   | 0.882123    |
| 8                | 1.856510    | 2.016302    | 0.000039    |
| 1                | 2.630450    | 1.419617    | 0.000123    |
| 1                | -2.600167   | 1.695299    | 0.000013    |