Supplementary tables for the manuscript:

# Fourier Transform Microwave Spectroscopic and *Ab Initio* Study of the Rotamers of 2-Fluorobenzaldehyde and 3-Fluorobenzaldehyde

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**Appendix I: Equilibrium Structures from MP2/aug-cc-pVTZ**

**Appendix II: Assigned Transitions for 2-Fluorobenzaldehydes and 3-Fluorobenzaldehydes**

**Appendix III: $R_s$ Coordinates**

**Appendix I: Equilibrium Structures from MP2/aug-cc-pVTZ**

Table S1: Z-matrix structure for O-*cis* 2-fluorobenzaldehyde

| | | | | | | |
|---|---|---|---|---|---|---|
| C1 | | | | | | |
| C2 | 1 | 1.397620 | | | | |
| C3 | 2 | 1.386234 | 1 | 121.7380 | | |
| C4 | 3 | 1.393078 | 2 | 119.2912 | 1 | 0.0000 |
| C5 | 4 | 1.394303 | 2 | 90.1078 | 1 | 0.0000 |
| C6 | 5 | 1.389336 | 4 | 119.3958 | 1 | 0.0000 |
| F7 | 2 | 1.337281 | 1 | 120.1140 | 6 | 180.0000 |
| H8 | 3 | 1.081203 | 2 | 118.9503 | 1 | 180.0000 |
| H9 | 4 | 1.081806 | 3 | 119.3982 | 2 | 180.0000 |
| H10 | 5 | 1.081097 | 4 | 120.2827 | 3 | 180.0000 |
| H11 | 6 | 1.084035 | 5 | 120.3824 | 4 | 180.0000 |
| C12 | 1 | 1.479234 | 6 | 117.7316 | 5 | 180.0000 |
| O13 | 12 | 1.215803 | 1 | 126.3429 | 6 | 180.0000 |
| H14 | 12 | 1.107118 | 1 | 112.8673 | 6 | 0.0000 |

Table S2: Z-matrix structure for O-*trans* 2-fluorobenzaldehyde

| | | | | | | |
|---|---|---|---|---|---|---|
| C1 | | | | | | |
| C2 | 1 | 1.393152 | | | | |
| C3 | 2 | 1.385461 | 1 | 122.4507 | | |
| C4 | 3 | 1.392101 | 2 | 118.4906 | 1 | 0.0000 |
| C5 | 4 | 1.397191 | 3 | 120.4719 | 2 | 0.0000 |
| C6 | 5 | 1.387876 | 4 | 119.9297 | 3 | 0.0000 |
| F7 | 2 | 1.349506 | 1 | 119.1529 | 3 | 180.0000 |
| H8 | 3 | 1.080942 | 2 | 119.5253 | 1 | 180.0000 |
| H9 | 4 | 1.081783 | 3 | 119.3792 | 2 | 180.0000 |
| H10 | 5 | 1.081242 | 4 | 119.9537 | 3 | 180.0000 |
| H11 | 6 | 1.082323 | 5 | 121.6782 | 4 | 180.0000 |
| C12 | 1 | 1.480111 | 2 | 121.5201 | 3 | 180.0000 |
| O13 | 12 | 1.219695 | 1 | 122.9704 | 2 | 180.0000 |
| H14 | 12 | 1.099307 | 1 | 116.1152 | 2 | 0.0000 |

Table S3: Z-matrix structure for O-*cis* 3-fluorobenzaldehyde

| | | | | | | |
|---|---|---|---|---|---|---|
| C1 | | | | | | |
| C2 | 1 | 1.397543 | | | | |
| C3 | 2 | 1.381674 | 1 | 117.9500 | | |
| C4 | 3 | 1.391004 | 2 | 122.5439 | 1 | 0.0000 |
| C5 | 4 | 1.392721 | 3 | 118.7812 | 2 | 0.0000 |
| C6 | 5 | 1.393129 | 4 | 120.0662 | 3 | 0.0000 |
| H7 | 2 | 1.081749 | 1 | 120.5600 | 3 | 180.0000 |
| F8 | 3 | 1.345309 | 2 | 119.1214 | 1 | 180.0000 |
| H9 | 4 | 1.081231 | 3 | 119.3972 | 2 | 180.0000 |
| H10 | 5 | 1.081628 | 4 | 119.5367 | 3 | 180.0000 |
| H11 | 6 | 1.083334 | 5 | 120.5575 | 4 | 180.0000 |
| C12 | 1 | 1.478598 | 2 | 119.8712 | 3 | 180.0000 |
| O13 | 12 | 1.218127 | 1 | 124.3568 | 2 | 0.0000 |
| H14 | 12 | 1.105373 | 1 | 114.8037 | 2 | 180.0000 |

Table S4: Z-matrix structure for O-*trans* 3-fluorobenzaldehyde

| | | | | | | |
|---|---|---|---|---|---|---|
| C1 | | | | | | |
| C2 | 1 | 1.396577 | | | | |
| C3 | 2 | 1.385037 | 1 | 118.3668 | | |
| C4 | 3 | 1.387016 | 2 | 122.1748 | 1 | 0.0000 |
| C5 | 4 | 1.396425 | 3 | 118.7014 | 2 | 0.0000 |
| C6 | 5 | 1.389943 | 4 | 120.5306 | 3 | 0.0000 |
| H7 | 2 | 1.082915 | 1 | 121.4446 | 3 | 180.0000 |
| F8 | 3 | 1.345620 | 2 | 118.9694 | 1 | 180.0000 |
| H9 | 4 | 1.081092 | 3 | 119.4947 | 2 | 180.0000 |
| H10 | 5 | 1.081756 | 4 | 119.2839 | 3 | 180.0000 |
| H11 | 6 | 1.081607 | 5 | 121.6315 | 4 | 180.0000 |
| C12 | 1 | 1.478906 | 2 | 118.6552 | 3 | 180.0000 |
| O13 | 12 | 1.217698 | 1 | 124.3514 | 2 | 180.0000 |
| H14 | 12 | 1.105901 | 1 | 114.8729 | 2 | 0.0000 |

Table S5: Z-matrix structure for benzaldehyde

| | | | | | | |
|---|---|---|---|---|---|---|
| C1 | | | | | | |
| C2 | 1 | 1.396417 | | | | |
| C3 | 2 | 1.392561 | 1 | 119.9728 | | |
| C4 | 3 | 1.394051 | 2 | 119.7242 | 1 | 0.0000 |

| | | | | | | |
|---|---|---|---|---|---|---|
| C5 | 4 | 1.397460 | 3 | 120.2655 | 2 | 0.0000 |
| C6 | 5 | 1.389501 | 4 | 120.1413 | 3 | 0.0000 |
| H7 | 2 | 1.084252 | 1 | 119.5217 | 6 | 180.0000 |
| H8 | 3 | 1.081966 | 2 | 120.2191 | 1 | 180.0000 |
| H9 | 4 | 1.082269 | 3 | 119.8538 | 2 | 180.0000 |
| H10 | 5 | 1.082129 | 4 | 119.8369 | 3 | 180.0000 |
| H11 | 6 | 1.082459 | 5 | 121.6046 | 4 | 180.0000 |
| C12 | 1 | 1.477486 | 2 | 119.1218 | 3 | 180.0000 |
| O13 | 12 | 1.218506 | 1 | 124.6072 | 2 | 180.0000 |
| H14 | 12 | 1.106320 | 1 | 114.7790 | 2 | 0.0000 |

**Appendix II: Assigned Transitions for 2-Fluorobenzaldehydes and 3-Fluorobenzaldehydes**

Table S6: O-*cis* 2-fluorobenzaldehyde (parent)

| J' | $K_a$' | $K_c$' | J'' | $K_a$'' | $K_c$'' | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 4 | 1 | 4 | 3 | 1 | 3 | 8770.9927 | 8770.9930 | -0.0003 |
| 4 | 0 | 4 | 3 | 0 | 3 | 9111.9227 | 9111.9228 | -0.0001 |
| 5 | 1 | 5 | 4 | 1 | 4 | 10853.3287 | 10853.3297 | -0.0010 |
| 5 | 0 | 5 | 4 | 0 | 4 | 11071.8263 | 11071.8261 | 0.0002 |
| 5 | 2 | 4 | 4 | 2 | 3 | 12149.4246 | 12149.4240 | 0.0006 |
| 5 | 4 | 2 | 4 | 4 | 1 | 12559.4607 | 12559.4627 | -0.0020 |
| 5 | 4 | 1 | 4 | 4 | 0 | 12568.6748 | 12568.6733 | 0.0015 |
| 5 | 3 | 3 | 4 | 3 | 2 | 12571.3571 | 12571.3562 | 0.0009 |
| 5 | 3 | 2 | 4 | 3 | 1 | 12792.5181 | 12792.5182 | -0.0001 |
| 6 | 0 | 6 | 5 | 1 | 5 | 12792.6488 | 12792.6491 | -0.0003 |
| 6 | 1 | 6 | 5 | 1 | 5 | 12898.9137 | 12898.9133 | 0.0004 |
| 6 | 0 | 6 | 5 | 0 | 5 | 13018.0317 | 13018.0315 | 0.0003 |
| 5 | 1 | 4 | 4 | 1 | 3 | 13024.0749 | 13024.0747 | 0.0002 |
| 6 | 1 | 6 | 5 | 0 | 5 | 13124.2960 | 13124.2957 | 0.0003 |
| 5 | 2 | 3 | 4 | 2 | 2 | 13422.8560 | 13422.8562 | -0.0002 |
| 6 | 2 | 5 | 5 | 2 | 4 | 14419.3075 | 14419.3074 | 0.0001 |
| 6 | 3 | 3 | 5 | 3 | 2 | 15609.8464 | 15609.8466 | -0.0002 |
| 6 | 2 | 4 | 5 | 2 | 3 | 16186.4167 | 16186.4172 | -0.0005 |
| 7 | 2 | 6 | 6 | 2 | 5 | 16618.3887 | 16618.3886 | 0.0002 |
| 8 | 1 | 8 | 7 | 1 | 7 | 16926.2458 | 16926.2460 | -0.0003 |
| 8 | 0 | 8 | 7 | 0 | 7 | 16953.2733 | 16953.2734 | -0.0001 |
| 8 | 1 | 8 | 7 | 0 | 7 | 16973.8942 | 16973.8939 | 0.0003 |
| 7 | 1 | 6 | 6 | 1 | 5 | 17271.2181 | 17271.2185 | -0.0004 |
| 7 | 3 | 5 | 6 | 3 | 4 | 17546.8326 | 17546.8327 | -0.0001 |
| 7 | 3 | 4 | 6 | 3 | 3 | 18538.5030 | 18538.5026 | 0.0004 |

Table S7: O-*trans* 2-fluorobenzaldehyde (parent)

| J' | $K_a$' | $K_c$' | J'' | $K_a$'' | $K_c$'' | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 2 | 1 | 2 | 1 | 1 | 1 | 4473.7155 | 4473.7149 | 0.0006 |
| 2 | 0 | 2 | 1 | 0 | 1 | 4870.3006 | 4870.3003 | 0.0003 |
| 4 | 1 | 3 | 4 | 1 | 4 | 5623.8691 | 5623.8699 | -0.0007 |
| 2 | 1 | 1 | 1 | 1 | 0 | 5653.5421 | 5653.5422 | -0.0001 |
| 6 | 2 | 4 | 6 | 2 | 5 | 6347.3668 | 6347.3671 | -0.0003 |
| 3 | 1 | 3 | 2 | 1 | 2 | 6604.3828 | 6604.3830 | -0.0002 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 8 | 3 | 5 | 8 | 3 | 6 | 6756.7779 | 6756.7782 | -0.0003 |
| 3 | 0 | 3 | 2 | 0 | 2 | 6928.4017 | 6928.4019 | -0.0002 |
| 4 | 2 | 3 | 4 | 0 | 4 | 7209.8445 | 7209.8445 | 0.0000 |
| 3 | 2 | 2 | 2 | 2 | 1 | 7595.4371 | 7595.4368 | 0.0002 |
| 5 | 1 | 4 | 5 | 1 | 5 | 7893.6380 | 7893.6378 | 0.0002 |
| 3 | 2 | 1 | 2 | 2 | 0 | 8262.4751 | 8262.4750 | 0.0001 |
| 3 | 1 | 2 | 2 | 1 | 1 | 8331.8835 | 8331.8835 | 0.0000 |
| 4 | 3 | 2 | 4 | 1 | 3 | 8535.7598 | 8535.7602 | -0.0005 |
| 5 | 3 | 3 | 5 | 1 | 4 | 8620.3960 | 8620.3958 | 0.0002 |
| 4 | 1 | 4 | 3 | 1 | 3 | 8655.3271 | 8655.3273 | -0.0002 |
| 5 | 2 | 4 | 5 | 0 | 5 | 8721.2123 | 8721.2127 | -0.0004 |
| 4 | 0 | 4 | 3 | 0 | 3 | 8830.1027 | 8830.1029 | -0.0002 |
| 7 | 2 | 5 | 7 | 2 | 6 | 8852.3710 | 8852.3710 | -0.0001 |
| 6 | 3 | 4 | 6 | 1 | 5 | 9302.9277 | 9302.9277 | 0.0000 |
| 9 | 3 | 6 | 9 | 3 | 7 | 9504.2263 | 9504.2264 | -0.0001 |
| 4 | 2 | 3 | 3 | 2 | 2 | 9972.8219 | 9972.8220 | -0.0001 |
| 6 | 1 | 5 | 6 | 1 | 6 | 10094.3862 | 10094.3862 | 0.0000 |
| 4 | 3 | 2 | 3 | 3 | 1 | 10419.3325 | 10419.3325 | 0.0000 |
| 6 | 2 | 5 | 6 | 0 | 6 | 10461.6355 | 10461.6354 | 0.0001 |
| 7 | 3 | 5 | 7 | 1 | 6 | 10519.1645 | 10519.1645 | 0.0000 |
| 5 | 1 | 5 | 4 | 1 | 4 | 10649.4745 | 10649.4747 | -0.0002 |
| 4 | 3 | 1 | 3 | 3 | 0 | 10652.3505 | 10652.3507 | -0.0002 |
| 4 | 1 | 3 | 3 | 1 | 2 | 10781.9549 | 10781.9552 | -0.0003 |
| 4 | 2 | 2 | 3 | 2 | 1 | 11262.3814 | 11262.3813 | 0.0001 |
| 8 | 2 | 6 | 8 | 2 | 7 | 11285.7632 | 11285.7630 | 0.0002 |
| 7 | 4 | 4 | 7 | 2 | 5 | 11339.0076 | 11339.0078 | -0.0001 |
| 8 | 4 | 5 | 8 | 2 | 6 | 11507.0652 | 11507.0651 | 0.0001 |
| 6 | 4 | 3 | 6 | 2 | 4 | 11832.7217 | 11832.7218 | -0.0001 |
| 8 | 3 | 6 | 8 | 1 | 7 | 12100.2900 | 12100.2902 | -0.0002 |
| 7 | 1 | 6 | 7 | 1 | 7 | 12179.2393 | 12179.2392 | 0.0001 |
| 10 | 3 | 7 | 10 | 3 | 8 | 12212.0196 | 12212.0191 | 0.0004 |
| 5 | 2 | 4 | 4 | 2 | 3 | 12233.4881 | 12233.4882 | -0.0001 |
| 7 | 2 | 6 | 7 | 0 | 7 | 12323.6927 | 12323.6927 | -0.0001 |
| 9 | 4 | 6 | 9 | 2 | 7 | 12354.1132 | 12354.1137 | -0.0005 |
| 6 | 1 | 6 | 5 | 1 | 5 | 12612.5694 | 12612.5695 | -0.0002 |
| 6 | 0 | 6 | 5 | 0 | 5 | 12638.7229 | 12638.7232 | -0.0002 |
| 5 | 1 | 4 | 4 | 1 | 3 | 12919.2423 | 12919.2426 | -0.0003 |
| 5 | 3 | 3 | 4 | 3 | 2 | 13003.8781 | 13003.8782 | -0.0001 |
| 5 | 4 | 2 | 4 | 4 | 1 | 13084.5806 | 13084.5807 | -0.0001 |
| 5 | 4 | 1 | 4 | 4 | 0 | 13142.1689 | 13142.1691 | -0.0002 |
| 9 | 2 | 7 | 9 | 2 | 8 | 13539.4084 | 13539.4080 | 0.0005 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 5 | 3 | 2 | 4 | 3 | 1 | 13682.4327 | 13682.4326 | 0.0000 |
| 10 | 4 | 7 | 10 | 2 | 8 | 13716.9989 | 13716.9989 | -0.0001 |
| 3 | 2 | 1 | 2 | 0 | 2 | 13855.8949 | 13855.8942 | 0.0007 |
| 10 | 5 | 6 | 10 | 3 | 7 | 13889.2520 | 13889.2522 | -0.0001 |
| 9 | 3 | 7 | 9 | 1 | 8 | 13891.5537 | 13891.5538 | -0.0001 |
| 5 | 2 | 3 | 4 | 2 | 2 | 14112.8277 | 14112.8276 | 0.0001 |
| 8 | 1 | 7 | 8 | 1 | 8 | 14188.9583 | 14188.9579 | 0.0004 |
| 8 | 2 | 7 | 8 | 0 | 8 | 14241.3356 | 14241.3359 | -0.0003 |
| 9 | 5 | 5 | 9 | 3 | 6 | 14281.9240 | 14281.9236 | 0.0004 |
| 6 | 2 | 5 | 5 | 2 | 4 | 14379.1459 | 14379.1459 | 0.0000 |
| 7 | 1 | 7 | 6 | 1 | 6 | 14561.8948 | 14561.8949 | -0.0001 |
| 7 | 0 | 7 | 6 | 0 | 6 | 14570.5618 | 14570.5619 | -0.0001 |
| 6 | 1 | 5 | 5 | 1 | 4 | 14813.3179 | 14813.3179 | -0.0001 |
| 8 | 5 | 4 | 8 | 3 | 5 | 15345.2619 | 15345.2620 | -0.0002 |
| 6 | 3 | 4 | 5 | 3 | 3 | 15495.8497 | 15495.8498 | -0.0001 |
| 10 | 2 | 8 | 10 | 2 | 9 | 15648.3722 | 15648.3723 | -0.0002 |
| 6 | 5 | 2 | 5 | 5 | 1 | 15694.3258 | 15694.3258 | 0.0001 |
| 6 | 5 | 1 | 5 | 5 | 0 | 15706.1269 | 15706.1266 | 0.0003 |
| 6 | 4 | 3 | 5 | 4 | 2 | 15779.0630 | 15779.0633 | -0.0003 |
| 6 | 4 | 2 | 5 | 4 | 1 | 16012.8941 | 16012.8941 | 0.0000 |
| 9 | 1 | 8 | 9 | 1 | 9 | 16162.6791 | 16162.6785 | 0.0006 |
| 9 | 2 | 8 | 9 | 0 | 9 | 16180.6244 | 16180.6244 | 0.0000 |
| 7 | 2 | 6 | 6 | 2 | 5 | 16432.6191 | 16432.6192 | -0.0001 |
| 8 | 1 | 8 | 7 | 1 | 7 | 16506.0147 | 16506.0147 | 0.0000 |
| 8 | 0 | 8 | 7 | 0 | 7 | 16508.7382 | 16508.7381 | 0.0001 |
| 7 | 1 | 6 | 6 | 1 | 5 | 16646.7476 | 16646.7478 | -0.0002 |
| 6 | 2 | 4 | 5 | 2 | 3 | 16697.2471 | 16697.2473 | -0.0002 |
| 6 | 3 | 3 | 5 | 3 | 2 | 16822.7486 | 16822.7488 | -0.0002 |
| 7 | 3 | 5 | 6 | 3 | 4 | 17862.9846 | 17862.9846 | 0.0001 |
| 7 | 6 | 2 | 6 | 6 | 1 | 18291.2491 | 18291.2487 | 0.0004 |
| 7 | 6 | 1 | 6 | 6 | 0 | 18293.4117 | 18293.4116 | 0.0001 |
| 7 | 5 | 3 | 6 | 5 | 2 | 18421.4794 | 18421.4795 | -0.0001 |
| 8 | 2 | 7 | 7 | 2 | 6 | 18426.3814 | 18426.3813 | 0.0001 |
| 7 | 4 | 4 | 6 | 4 | 3 | 18443.9088 | 18443.9091 | -0.0003 |
| 9 | 1 | 9 | 8 | 1 | 8 | 18448.4032 | 18448.4029 | 0.0003 |
| 9 | 0 | 9 | 8 | 0 | 8 | 18449.2278 | 18449.2275 | 0.0004 |
| 7 | 5 | 2 | 6 | 5 | 1 | 18482.1473 | 18482.1478 | -0.0005 |
| 8 | 1 | 7 | 7 | 1 | 6 | 18515.7337 | 18515.7334 | 0.0003 |
| 7 | 2 | 5 | 6 | 2 | 4 | 18937.6230 | 18937.6231 | -0.0002 |
| 7 | 4 | 3 | 6 | 4 | 2 | 19088.8077 | 19088.8075 | 0.0002 |
| 7 | 3 | 4 | 6 | 3 | 3 | 19846.7769 | 19846.7766 | 0.0003 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 8 | 3 | 6 | 7 | 3 | 5 | 20096.8591 | 20096.8591 | 0.0000 |
| 9 | 2 | 8 | 8 | 2 | 7 | 20388.5165 | 20388.5160 | 0.0006 |
| 10 | 1 | 10 | 9 | 1 | 9 | 20390.2864 | 20390.2858 | 0.0006 |
| 10 | 0 | 10 | 9 | 0 | 9 | 20390.5291 | 20390.5287 | 0.0004 |
| 9 | 1 | 8 | 8 | 1 | 7 | 20422.1238 | 20422.1236 | 0.0002 |
| 8 | 2 | 6 | 7 | 2 | 5 | 20859.7732 | 20859.7733 | -0.0001 |
| 8 | 7 | 1 | 7 | 7 | 0 | 20887.1473 | 20887.1477 | -0.0003 |
| 8 | 6 | 3 | 7 | 6 | 2 | 21018.6463 | 21018.6464 | -0.0002 |
| 8 | 4 | 5 | 7 | 4 | 4 | 21027.8305 | 21027.8306 | -0.0001 |
| 8 | 6 | 2 | 7 | 6 | 1 | 21032.0008 | 21032.0011 | -0.0003 |
| 8 | 5 | 4 | 7 | 5 | 3 | 21168.1652 | 21168.1653 | -0.0001 |
| 8 | 5 | 3 | 7 | 5 | 2 | 21385.0267 | 21385.0267 | 0.0000 |
| 9 | 3 | 7 | 8 | 3 | 6 | 22213.3874 | 22213.3872 | 0.0002 |
| 8 | 4 | 4 | 7 | 4 | 3 | 22326.7446 | 22326.7445 | 0.0001 |
| 11 | 1 | 11 | 10 | 1 | 10 | 22332.0524 | 22332.0515 | 0.0009 |
| 11 | 0 | 11 | 10 | 0 | 10 | 22332.1215 | 22332.1213 | 0.0002 |
| 10 | 2 | 9 | 9 | 2 | 8 | 22336.6410 | 22336.6407 | 0.0004 |
| 10 | 1 | 9 | 9 | 1 | 8 | 22348.4473 | 22348.4470 | 0.0003 |
| 8 | 3 | 5 | 7 | 3 | 4 | 22589.1361 | 22589.1361 | 0.0000 |
| 9 | 2 | 7 | 8 | 2 | 6 | 22642.1610 | 22642.1609 | 0.0001 |
| 9 | 8 | 2 | 8 | 8 | 1 | 23482.9514 | 23482.9504 | 0.0010 |
| 9 | 8 | 1 | 8 | 8 | 0 | 23483.0104 | 23483.0097 | 0.0007 |
| 9 | 4 | 6 | 8 | 4 | 5 | 23489.2099 | 23489.2096 | 0.0004 |
| 9 | 7 | 3 | 8 | 7 | 2 | 23606.8616 | 23606.8628 | -0.0012 |
| 9 | 7 | 2 | 8 | 7 | 1 | 23609.5067 | 23609.5071 | -0.0004 |
| 9 | 6 | 4 | 8 | 6 | 3 | 23783.7033 | 23783.7034 | -0.0001 |
| 9 | 6 | 3 | 8 | 6 | 2 | 23841.3421 | 23841.3425 | -0.0004 |
| 9 | 5 | 5 | 8 | 5 | 4 | 23897.4972 | 23897.4970 | 0.0003 |
| 10 | 3 | 8 | 9 | 3 | 7 | 24244.5129 | 24244.5124 | 0.0006 |
| 12 | 1 | 12 | 11 | 1 | 11 | 24273.8104 | 24273.8097 | 0.0007 |
| 12 | 0 | 12 | 11 | 0 | 11 | 24273.8265 | 24273.8272 | -0.0008 |
| 11 | 2 | 10 | 10 | 2 | 9 | 24279.5024 | 24279.5019 | 0.0005 |
| 11 | 1 | 10 | 10 | 1 | 9 | 24283.4533 | 24283.4573 | -0.0040 |
| 10 | 2 | 8 | 9 | 2 | 7 | 24445.6053 | 24445.6050 | 0.0003 |
| 9 | 5 | 4 | 8 | 5 | 3 | 24482.7845 | 24482.7846 | 0.0000 |
| 9 | 3 | 6 | 8 | 3 | 5 | 24960.8353 | 24960.8354 | -0.0001 |

Table S8: O-*trans* 2-fluorobenzaldehyde ($^{13}$C1)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 3 | 1 | 3 | 2 | 1 | 2 | 6600.9511 | 6600.9511 | 0.0000 |
| 3 | 0 | 3 | 2 | 0 | 2 | 6925.2242 | 6925.2249 | -0.0007 |
| 3 | 2 | 2 | 2 | 2 | 1 | 7590.7251 | 7590.7256 | -0.0005 |
| 4 | 1 | 4 | 3 | 1 | 3 | 8651.0636 | 8651.0637 | -0.0001 |
| 4 | 0 | 4 | 3 | 0 | 3 | 8826.2419 | 8826.2420 | -0.0001 |
| 4 | 2 | 3 | 3 | 2 | 2 | 9966.9667 | 9966.9671 | -0.0005 |
| 5 | 0 | 5 | 4 | 0 | 4 | 10717.3321 | 10717.3325 | -0.0005 |
| 4 | 1 | 3 | 3 | 1 | 2 | 10775.9566 | 10775.9566 | 0.0000 |
| 4 | 2 | 2 | 3 | 2 | 1 | 11254.1529 | 11254.1522 | 0.0007 |
| 6 | 1 | 6 | 5 | 1 | 5 | 12606.6779 | 12606.6777 | 0.0002 |
| 6 | 0 | 6 | 5 | 0 | 5 | 12632.9693 | 12632.9685 | 0.0008 |
| 5 | 1 | 4 | 4 | 1 | 3 | 12913.2012 | 12913.2001 | 0.0010 |
| 5 | 3 | 3 | 4 | 3 | 2 | 12995.4599 | 12995.4595 | 0.0005 |
| 5 | 3 | 2 | 4 | 3 | 1 | 13671.6323 | 13671.6328 | -0.0005 |
| 5 | 2 | 3 | 4 | 2 | 2 | 14103.3812 | 14103.3815 | -0.0003 |
| 6 | 2 | 5 | 5 | 2 | 4 | 14371.7411 | 14371.7416 | -0.0005 |
| 7 | 1 | 7 | 6 | 1 | 6 | 14555.1431 | 14555.1429 | 0.0002 |
| 7 | 0 | 7 | 6 | 0 | 6 | 14563.8676 | 14563.8673 | 0.0003 |
| 7 | 2 | 6 | 6 | 2 | 5 | 16424.5815 | 16424.5811 | 0.0004 |
| 8 | 1 | 8 | 7 | 1 | 7 | 16498.3824 | 16498.3818 | 0.0006 |
| 8 | 0 | 8 | 7 | 0 | 7 | 16501.1258 | 16501.1270 | -0.0012 |
| 7 | 1 | 6 | 6 | 1 | 5 | 16639.6472 | 16639.6474 | -0.0002 |
| 6 | 2 | 4 | 5 | 2 | 3 | 16687.4741 | 16687.4747 | -0.0005 |
| 6 | 3 | 3 | 5 | 3 | 2 | 16809.6342 | 16809.6338 | 0.0004 |
| 7 | 3 | 5 | 6 | 3 | 4 | 17852.7133 | 17852.7133 | -0.0001 |

Table S9: O-*trans* 2-fluorobenzaldehyde ($^{13}$C2)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 3 | 1 | 3 | 2 | 1 | 2 | 6593.9487 | 6593.9483 | 0.0005 |
| 3 | 0 | 3 | 2 | 0 | 2 | 6915.2507 | 6915.2506 | 0.0001 |
| 3 | 2 | 2 | 2 | 2 | 1 | 7587.3739 | 7587.3725 | 0.0014 |
| 4 | 1 | 4 | 3 | 1 | 3 | 8640.4436 | 8640.4439 | -0.0003 |
| 4 | 0 | 4 | 3 | 0 | 3 | 8812.3974 | 8812.3971 | 0.0003 |
| 4 | 2 | 3 | 3 | 2 | 2 | 9960.5144 | 9960.5146 | -0.0003 |
| 5 | 1 | 5 | 4 | 1 | 4 | 10630.2310 | 10630.2307 | 0.0002 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 5 | 0 | 5 | 4 | 0 | 4 | 10701.1475 | 10701.1471 | 0.0004 |
| 4 | 1 | 3 | 3 | 1 | 2 | 10766.8855 | 10766.8853 | 0.0002 |
| 4 | 2 | 2 | 3 | 2 | 1 | 11256.8156 | 11256.8159 | -0.0003 |
| 5 | 2 | 4 | 4 | 2 | 3 | 12216.0133 | 12216.0143 | -0.0010 |
| 6 | 1 | 6 | 5 | 1 | 5 | 12589.2371 | 12589.2368 | 0.0003 |
| 6 | 0 | 6 | 5 | 0 | 5 | 12614.5807 | 12614.5805 | 0.0001 |
| 5 | 1 | 4 | 4 | 1 | 3 | 12895.2685 | 12895.2691 | -0.0005 |
| 5 | 3 | 3 | 4 | 3 | 2 | 12991.8816 | 12991.8816 | 0.0000 |
| 5 | 3 | 2 | 4 | 3 | 1 | 13679.8886 | 13679.8889 | -0.0003 |
| 5 | 2 | 3 | 4 | 2 | 2 | 14101.3390 | 14101.3385 | 0.0006 |
| 6 | 2 | 5 | 5 | 2 | 4 | 14356.0321 | 14356.0327 | -0.0006 |
| 7 | 1 | 7 | 6 | 1 | 6 | 14534.7013 | 14534.7023 | -0.0010 |
| 7 | 0 | 7 | 6 | 0 | 6 | 14543.0406 | 14543.0414 | -0.0007 |
| 6 | 3 | 4 | 5 | 3 | 3 | 15478.9133 | 15478.9135 | -0.0002 |
| 7 | 2 | 6 | 6 | 2 | 5 | 16404.0296 | 16404.0290 | 0.0006 |
| 8 | 1 | 8 | 7 | 1 | 7 | 16475.0914 | 16475.0914 | -0.0001 |
| 8 | 0 | 8 | 7 | 0 | 7 | 16477.6944 | 16477.6936 | 0.0008 |
| 7 | 3 | 5 | 6 | 3 | 4 | 17839.7787 | 17839.7784 | 0.0003 |

Table S10: O-*trans* 2-fluorobenzaldehyde ($^{13}$C3)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 3 | 1 | 3 | 2 | 1 | 2 | 6553.6693 | 6553.6698 | -0.0005 |
| 3 | 0 | 3 | 2 | 0 | 2 | 6880.0135 | 6880.0131 | 0.0004 |
| 3 | 2 | 2 | 2 | 2 | 1 | 7528.4560 | 7528.4558 | 0.0002 |
| 4 | 1 | 4 | 3 | 1 | 3 | 8591.5233 | 8591.5234 | -0.0002 |
| 4 | 0 | 4 | 3 | 0 | 3 | 8770.6293 | 8770.6297 | -0.0004 |
| 4 | 2 | 3 | 3 | 2 | 2 | 9888.6110 | 9888.6112 | -0.0002 |
| 5 | 1 | 5 | 4 | 1 | 4 | 10573.0429 | 10573.0427 | 0.0002 |
| 5 | 0 | 5 | 4 | 0 | 4 | 10648.7842 | 10648.7839 | 0.0003 |
| 4 | 1 | 3 | 3 | 1 | 2 | 10694.5924 | 10694.5921 | 0.0003 |
| 4 | 2 | 2 | 3 | 2 | 1 | 11148.8653 | 11148.8657 | -0.0004 |
| 5 | 2 | 4 | 4 | 2 | 3 | 12135.3769 | 12135.3765 | 0.0004 |
| 6 | 1 | 6 | 5 | 1 | 5 | 12523.2683 | 12523.2681 | 0.0002 |
| 6 | 0 | 6 | 5 | 0 | 5 | 12550.9840 | 12550.9842 | -0.0003 |
| 5 | 1 | 4 | 4 | 1 | 3 | 12827.5901 | 12827.5902 | 0.0000 |
| 5 | 3 | 3 | 4 | 3 | 2 | 12885.1672 | 12885.1679 | -0.0007 |
| 5 | 3 | 2 | 4 | 3 | 1 | 13535.5953 | 13535.5951 | 0.0003 |
| 5 | 2 | 3 | 4 | 2 | 2 | 13980.3293 | 13980.3291 | 0.0003 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 6 | 2 | 5 | 5 | 2 | 4 | 14269.4918 | 14269.4909 | 0.0008 |
| 7 | 1 | 7 | 6 | 1 | 6 | 14459.3717 | 14459.3711 | 0.0005 |
| 7 | 0 | 7 | 6 | 0 | 6 | 14468.7007 | 14468.7013 | -0.0006 |
| 6 | 1 | 5 | 5 | 1 | 4 | 14716.0980 | 14716.0984 | -0.0004 |
| 6 | 3 | 4 | 5 | 3 | 3 | 15360.0913 | 15360.0921 | -0.0008 |
| 6 | 4 | 3 | 5 | 4 | 2 | 15628.3532 | 15628.3527 | 0.0005 |
| 7 | 2 | 6 | 6 | 2 | 5 | 16312.1477 | 16312.1475 | 0.0002 |
| 8 | 1 | 8 | 7 | 1 | 7 | 16390.0361 | 16390.0365 | -0.0004 |
| 8 | 0 | 8 | 7 | 0 | 7 | 16393.0140 | 16393.0138 | 0.0003 |
| 7 | 1 | 6 | 6 | 1 | 5 | 16536.8088 | 16536.8086 | 0.0002 |
| 7 | 3 | 5 | 6 | 3 | 4 | 17714.5034 | 17714.5037 | -0.0003 |

Table S11: O-*trans* 2-fluorobenzaldehyde ($^{13}$C4)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 3 | 1 | 3 | 2 | 1 | 2 | 6528.4161 | 6528.4161 | -0.0001 |
| 3 | 0 | 3 | 2 | 0 | 2 | 6856.9143 | 6856.9141 | 0.0002 |
| 3 | 2 | 2 | 2 | 2 | 1 | 7493.2543 | 7493.2517 | 0.0026 |
| 4 | 1 | 4 | 3 | 1 | 3 | 8560.3185 | 8560.3190 | -0.0005 |
| 4 | 0 | 4 | 3 | 0 | 3 | 8742.8560 | 8742.8558 | 0.0002 |
| 4 | 2 | 3 | 3 | 2 | 2 | 9845.0082 | 9845.0088 | -0.0007 |
| 5 | 1 | 5 | 4 | 1 | 4 | 10536.1424 | 10536.1425 | -0.0001 |
| 5 | 0 | 5 | 4 | 0 | 4 | 10614.2967 | 10614.2966 | 0.0001 |
| 4 | 1 | 3 | 3 | 1 | 2 | 10649.9029 | 10649.9036 | -0.0007 |
| 4 | 2 | 2 | 3 | 2 | 1 | 11086.4459 | 11086.4462 | -0.0003 |
| 5 | 2 | 4 | 4 | 2 | 3 | 12085.5489 | 12085.5488 | 0.0001 |
| 6 | 1 | 6 | 5 | 1 | 5 | 12480.4582 | 12480.4580 | 0.0002 |
| 6 | 0 | 6 | 5 | 0 | 5 | 12509.3936 | 12509.3935 | 0.0001 |
| 5 | 1 | 4 | 4 | 1 | 3 | 12783.3218 | 12783.3222 | -0.0004 |
| 5 | 3 | 3 | 4 | 3 | 2 | 12821.9824 | 12821.9828 | -0.0004 |
| 5 | 3 | 2 | 4 | 3 | 1 | 13453.7071 | 13453.7070 | 0.0001 |
| 5 | 2 | 3 | 4 | 2 | 2 | 13908.8942 | 13908.8946 | -0.0004 |
| 6 | 2 | 5 | 5 | 2 | 4 | 14214.9561 | 14214.9558 | 0.0004 |
| 7 | 1 | 7 | 6 | 1 | 6 | 14410.3748 | 14410.3749 | -0.0001 |
| 7 | 0 | 7 | 6 | 0 | 6 | 14420.2254 | 14420.2258 | -0.0005 |
| 6 | 1 | 5 | 5 | 1 | 4 | 14671.2351 | 14671.2351 | 0.0000 |
| 7 | 2 | 6 | 6 | 2 | 5 | 16253.3171 | 16253.3170 | 0.0000 |
| 8 | 1 | 8 | 7 | 1 | 7 | 16334.6746 | 16334.6742 | 0.0004 |
| 8 | 0 | 8 | 7 | 0 | 7 | 16337.8527 | 16337.8526 | 0.0001 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 6 | 2 | 4 | 5 | 2 | 3 | 16482.8492 | 16482.8477 | 0.0015 |
| 7 | 1 | 6 | 6 | 1 | 5 | 16486.1277 | 16486.1288 | -0.0011 |
| 6 | 3 | 3 | 5 | 3 | 2 | 16543.8079 | 16543.8087 | -0.0008 |
| 7 | 3 | 5 | 6 | 3 | 4 | 17637.9131 | 17637.9125 | 0.0005 |

Table S12: O-*trans* 2-fluorobenzaldehyde ($^{13}$C5)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 3 | 1 | 3 | 2 | 1 | 2 | 6550.4219 | 6550.4202 | 0.0017 |
| 3 | 0 | 3 | 2 | 0 | 2 | 6866.1662 | 6866.1667 | -0.0005 |
| 3 | 2 | 2 | 2 | 2 | 1 | 7543.3885 | 7543.3878 | 0.0007 |
| 4 | 1 | 4 | 3 | 1 | 3 | 8581.5341 | 8581.5342 | -0.0001 |
| 4 | 0 | 4 | 3 | 0 | 3 | 8748.4484 | 8748.4482 | 0.0002 |
| 4 | 2 | 3 | 3 | 2 | 2 | 9900.0849 | 9900.0850 | -0.0001 |
| 5 | 1 | 5 | 4 | 1 | 4 | 10556.3233 | 10556.3238 | -0.0005 |
| 5 | 0 | 5 | 4 | 0 | 4 | 10624.3276 | 10624.3281 | -0.0005 |
| 4 | 1 | 3 | 3 | 1 | 2 | 10698.7203 | 10698.7201 | 0.0002 |
| 4 | 2 | 2 | 3 | 2 | 1 | 11201.3819 | 11201.3822 | -0.0003 |
| 5 | 2 | 4 | 4 | 2 | 3 | 12138.1967 | 12138.1969 | -0.0001 |
| 6 | 1 | 6 | 5 | 1 | 5 | 12500.8856 | 12500.8860 | -0.0005 |
| 6 | 0 | 6 | 5 | 0 | 5 | 12524.9115 | 12524.9111 | 0.0004 |
| 5 | 3 | 2 | 4 | 3 | 1 | 13619.2407 | 13619.2410 | -0.0003 |
| 5 | 2 | 3 | 4 | 2 | 2 | 14024.8053 | 14024.8056 | -0.0002 |
| 6 | 2 | 5 | 5 | 2 | 4 | 14260.5955 | 14260.5959 | -0.0004 |
| 7 | 0 | 7 | 6 | 0 | 6 | 14440.1340 | 14440.1339 | 0.0000 |
| 6 | 1 | 5 | 5 | 1 | 4 | 14673.2288 | 14673.2292 | -0.0004 |
| 7 | 2 | 6 | 6 | 2 | 5 | 16291.6371 | 16291.6369 | 0.0002 |
| 8 | 1 | 8 | 7 | 1 | 7 | 16358.8871 | 16358.8867 | 0.0005 |
| 8 | 0 | 8 | 7 | 0 | 7 | 16361.2992 | 16361.2997 | -0.0005 |
| 7 | 1 | 6 | 6 | 1 | 5 | 16490.5427 | 16490.5415 | 0.0012 |
| 6 | 2 | 4 | 5 | 2 | 3 | 16574.3974 | 16574.3975 | -0.0001 |
| 6 | 3 | 3 | 5 | 3 | 2 | 16742.3850 | 16742.3843 | 0.0007 |
| 7 | 3 | 5 | 6 | 3 | 4 | 17729.6342 | 17729.6349 | -0.0007 |

Table S13: O-*trans* 2-fluorobenzaldehyde ($^{13}$C6)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 3 | 1 | 3 | 2 | 1 | 2 | 6584.0205 | 6584.0208 | -0.0003 |
| 3 | 0 | 3 | 2 | 0 | 2 | 6900.3098 | 6900.3097 | 0.0001 |
| 3 | 2 | 2 | 2 | 2 | 1 | 7583.9703 | 7583.9713 | -0.0010 |
| 4 | 1 | 4 | 3 | 1 | 3 | 8624.9723 | 8624.9722 | 0.0001 |
| 4 | 0 | 4 | 3 | 0 | 3 | 8791.5356 | 8791.5353 | 0.0003 |
| 4 | 2 | 3 | 3 | 2 | 2 | 9952.5054 | 9952.5066 | -0.0012 |
| 5 | 1 | 5 | 4 | 1 | 4 | 10609.3171 | 10609.3170 | 0.0000 |
| 5 | 0 | 5 | 4 | 0 | 4 | 10676.9227 | 10676.9225 | 0.0002 |
| 4 | 1 | 3 | 3 | 1 | 2 | 10754.4516 | 10754.4512 | 0.0004 |
| 4 | 2 | 2 | 3 | 2 | 1 | 11264.6740 | 11264.6732 | 0.0008 |
| 5 | 2 | 4 | 4 | 2 | 3 | 12201.3142 | 12201.3137 | 0.0006 |
| 6 | 1 | 6 | 5 | 1 | 5 | 12563.3899 | 12563.3901 | -0.0002 |
| 6 | 0 | 6 | 5 | 0 | 5 | 12587.1893 | 12587.1891 | 0.0002 |
| 5 | 1 | 4 | 4 | 1 | 3 | 12868.3364 | 12868.3361 | 0.0003 |
| 5 | 3 | 3 | 4 | 3 | 2 | 12989.6976 | 12989.6979 | -0.0003 |
| 5 | 3 | 2 | 4 | 3 | 1 | 13698.3324 | 13698.3321 | 0.0003 |
| 5 | 2 | 3 | 4 | 2 | 2 | 14101.8201 | 14101.8205 | -0.0004 |
| 6 | 2 | 5 | 5 | 2 | 4 | 14333.5105 | 14333.5111 | -0.0006 |
| 7 | 1 | 7 | 6 | 1 | 6 | 14504.3621 | 14504.3624 | -0.0003 |
| 7 | 0 | 7 | 6 | 0 | 6 | 14512.0809 | 14512.0801 | 0.0008 |
| 6 | 1 | 5 | 5 | 1 | 4 | 14744.8741 | 14744.8747 | -0.0006 |
| 6 | 3 | 4 | 5 | 3 | 3 | 15470.8374 | 15470.8361 | 0.0013 |
| 7 | 2 | 6 | 6 | 2 | 5 | 16373.9083 | 16373.9080 | 0.0003 |
| 8 | 1 | 8 | 7 | 1 | 7 | 16440.5065 | 16440.5066 | -0.0001 |
| 8 | 0 | 8 | 7 | 0 | 7 | 16442.8804 | 16442.8806 | -0.0002 |
| 7 | 1 | 6 | 6 | 1 | 5 | 16571.3457 | 16571.3460 | -0.0003 |
| 6 | 2 | 4 | 5 | 2 | 3 | 16661.8225 | 16661.8221 | 0.0004 |
| 6 | 3 | 3 | 5 | 3 | 2 | 16839.0024 | 16839.0031 | -0.0007 |
| 7 | 3 | 5 | 6 | 3 | 4 | 17822.8895 | 17822.8895 | -0.0001 |

Table S14: O-*trans* 2-fluorobenzaldehyde ($^{13}$C7)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 3 | 1 | 3 | 2 | 1 | 2 | 6549.6640 | 6549.6646 | -0.0006 |
| 3 | 0 | 3 | 2 | 0 | 2 | 6878.1114 | 6878.1109 | 0.0005 |
| 3 | 2 | 2 | 2 | 2 | 1 | 7519.6744 | 7519.6748 | -0.0004 |
| 4 | 1 | 4 | 3 | 1 | 3 | 8587.5555 | 8587.5556 | -0.0001 |
| 4 | 0 | 4 | 3 | 0 | 3 | 8769.3241 | 8769.3243 | -0.0002 |
| 4 | 2 | 3 | 3 | 2 | 2 | 9878.8587 | 9878.8602 | -0.0015 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 5 | 1 | 5 | 4 | 1 | 4 | 10569.1709 | 10569.1705 | 0.0004 |
| 5 | 0 | 5 | 4 | 0 | 4 | 10646.6807 | 10646.6802 | 0.0005 |
| 4 | 1 | 3 | 3 | 1 | 2 | 10685.7235 | 10685.7237 | -0.0002 |
| 4 | 2 | 2 | 3 | 2 | 1 | 11128.9357 | 11128.9354 | 0.0003 |
| 5 | 2 | 4 | 4 | 2 | 3 | 12125.8962 | 12125.8961 | 0.0001 |
| 6 | 1 | 6 | 5 | 1 | 5 | 12519.2844 | 12519.2841 | 0.0002 |
| 6 | 0 | 6 | 5 | 0 | 5 | 12547.8711 | 12547.8712 | -0.0001 |
| 5 | 1 | 4 | 4 | 1 | 3 | 12823.2478 | 12823.2469 | 0.0009 |
| 5 | 3 | 3 | 4 | 3 | 2 | 12868.1653 | 12868.1651 | 0.0002 |
| 5 | 3 | 2 | 4 | 3 | 1 | 13507.2548 | 13507.2550 | -0.0001 |
| 5 | 2 | 3 | 4 | 2 | 2 | 13959.9626 | 13959.9621 | 0.0004 |
| 6 | 2 | 5 | 5 | 2 | 4 | 14261.0791 | 14261.0783 | 0.0008 |
| 7 | 0 | 7 | 6 | 0 | 6 | 14464.7573 | 14464.7577 | -0.0004 |
| 6 | 1 | 5 | 5 | 1 | 4 | 14715.0816 | 14715.0827 | -0.0011 |
| 6 | 3 | 4 | 5 | 3 | 3 | 15342.5272 | 15342.5264 | 0.0008 |
| 7 | 2 | 6 | 6 | 2 | 5 | 16304.8941 | 16304.8945 | -0.0004 |
| 8 | 1 | 8 | 7 | 1 | 7 | 16385.2688 | 16385.2691 | -0.0003 |
| 8 | 0 | 8 | 7 | 0 | 7 | 16388.3868 | 16388.3864 | 0.0004 |
| 7 | 1 | 6 | 6 | 1 | 5 | 16535.4678 | 16535.4677 | 0.0001 |
| 6 | 2 | 4 | 5 | 2 | 3 | 16539.7155 | 16539.7158 | -0.0002 |
| 6 | 3 | 3 | 5 | 3 | 2 | 16609.4581 | 16609.4585 | -0.0004 |
| 7 | 3 | 5 | 6 | 3 | 4 | 17698.0747 | 17698.0748 | -0.0001 |

Table S15: O-*trans* 2-fluorobenzaldehyde ($^{18}$O)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 5 | 1 | 5 | 4 | 1 | 4 | 10313.8824 | 10313.8822 | 0.0002 |
| 4 | 1 | 3 | 3 | 1 | 2 | 10387.0284 | 10387.0288 | -0.0004 |
| 5 | 0 | 5 | 4 | 0 | 4 | 10404.3692 | 10404.3698 | -0.0006 |
| 4 | 2 | 2 | 3 | 2 | 1 | 10737.8472 | 10737.8466 | 0.0006 |
| 5 | 2 | 4 | 4 | 2 | 3 | 11793.3693 | 11793.3690 | 0.0003 |
| 6 | 1 | 6 | 5 | 1 | 5 | 12221.7987 | 12221.7990 | -0.0003 |
| 6 | 0 | 6 | 5 | 0 | 5 | 12257.2817 | 12257.2817 | 0.0000 |
| 5 | 3 | 3 | 4 | 3 | 2 | 12463.0151 | 12463.0143 | 0.0008 |
| 5 | 1 | 4 | 4 | 1 | 3 | 12512.5673 | 12512.5672 | 0.0002 |
| 5 | 3 | 2 | 4 | 3 | 1 | 13004.9472 | 13004.9475 | -0.0003 |
| 5 | 2 | 3 | 4 | 2 | 2 | 13502.6360 | 13502.6368 | -0.0008 |
| 6 | 2 | 5 | 5 | 2 | 4 | 13890.7928 | 13890.7926 | 0.0002 |
| 7 | 1 | 7 | 6 | 1 | 6 | 14114.0358 | 14114.0353 | 0.0005 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 7 | 0 | 7 | 6 | 0 | 6 | 14126.8004 | 14126.8005 | -0.0001 |
| 6 | 1 | 5 | 5 | 1 | 4 | 14392.3636 | 14392.3633 | 0.0003 |
| 7 | 3 | 5 | 6 | 3 | 4 | 17191.4799 | 17191.4810 | -0.0011 |
| 8 | 2 | 7 | 7 | 2 | 6 | 17847.2331 | 17847.2327 | 0.0004 |
| 9 | 1 | 9 | 8 | 1 | 8 | 17883.0617 | 17883.0616 | 0.0001 |
| 9 | 0 | 9 | 8 | 0 | 8 | 17884.4867 | 17884.4869 | -0.0002 |
| 8 | 1 | 7 | 7 | 1 | 6 | 17973.3378 | 17973.3378 | 0.0000 |
| 7 | 3 | 4 | 6 | 3 | 3 | 18930.7831 | 18930.7827 | 0.0005 |

Table S16: O-*cis* 3-fluorobenzaldehyde (parent)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 4 | 0 | 4 | 3 | 0 | 3 | 8091.3547 | 8091.3549 | -0.0003 |
| 5 | 3 | 2 | 5 | 2 | 3 | 8109.0486 | 8109.0486 | -0.0001 |
| 4 | 2 | 3 | 3 | 2 | 2 | 8571.8594 | 8571.8601 | -0.0008 |
| 5 | 2 | 4 | 5 | 1 | 5 | 8578.6076 | 8578.6095 | -0.0019 |
| 4 | 3 | 1 | 4 | 2 | 2 | 8619.0597 | 8619.0600 | -0.0004 |
| 4 | 1 | 4 | 3 | 0 | 3 | 8688.0345 | 8688.0348 | -0.0002 |
| 4 | 3 | 2 | 3 | 3 | 1 | 8722.5773 | 8722.5768 | 0.0005 |
| 4 | 3 | 1 | 3 | 3 | 0 | 8757.3544 | 8757.3530 | 0.0014 |
| 4 | 2 | 2 | 3 | 2 | 1 | 9098.6582 | 9098.6580 | 0.0002 |
| 4 | 1 | 3 | 3 | 1 | 2 | 9249.3991 | 9249.3994 | -0.0004 |
| 7 | 2 | 5 | 6 | 3 | 4 | 9250.4475 | 9250.4467 | 0.0008 |
| 5 | 0 | 5 | 4 | 1 | 4 | 9261.5103 | 9261.5098 | 0.0005 |
| 4 | 3 | 2 | 4 | 2 | 3 | 9395.1427 | 9395.1413 | 0.0014 |
| 5 | 1 | 5 | 4 | 1 | 4 | 9603.5522 | 9603.5522 | 0.0000 |
| 2 | 2 | 1 | 1 | 1 | 0 | 9642.7073 | 9642.7068 | 0.0006 |
| 5 | 3 | 3 | 5 | 2 | 4 | 9678.9748 | 9678.9755 | -0.0006 |
| 6 | 2 | 5 | 6 | 1 | 6 | 9810.3974 | 9810.3972 | 0.0002 |
| 7 | 1 | 6 | 7 | 0 | 7 | 9826.3545 | 9826.3537 | 0.0008 |
| 5 | 0 | 5 | 4 | 0 | 4 | 9858.1890 | 9858.1897 | -0.0006 |
| 2 | 2 | 0 | 1 | 1 | 1 | 10087.2339 | 10087.2330 | 0.0009 |
| 6 | 3 | 4 | 6 | 2 | 5 | 10134.7312 | 10134.7307 | 0.0004 |
| 5 | 1 | 5 | 4 | 0 | 4 | 10200.2331 | 10200.2321 | 0.0010 |
| 6 | 1 | 5 | 5 | 2 | 4 | 10481.4148 | 10481.4139 | 0.0010 |
| 5 | 2 | 4 | 4 | 2 | 3 | 10640.7071 | 10640.7079 | -0.0008 |
| 7 | 3 | 5 | 7 | 2 | 6 | 10790.5571 | 10790.5586 | -0.0016 |
| 5 | 3 | 3 | 4 | 3 | 2 | 10924.5422 | 10924.5420 | 0.0002 |
| 7 | 2 | 6 | 7 | 1 | 7 | 11209.5566 | 11209.5571 | -0.0005 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 8 | 4 | 4 | 8 | 3 | 5 | 11231.2780 | 11231.2775 | 0.0004 |
| 6 | 0 | 6 | 5 | 1 | 5 | 11249.3899 | 11249.3897 | 0.0003 |
| 5 | 1 | 4 | 4 | 1 | 3 | 11409.7459 | 11409.7464 | -0.0005 |
| 3 | 2 | 2 | 2 | 1 | 1 | 11412.6301 | 11412.6298 | 0.0002 |
| 6 | 1 | 6 | 5 | 1 | 5 | 11431.5575 | 11431.5577 | -0.0003 |
| 5 | 2 | 3 | 4 | 2 | 2 | 11551.9937 | 11551.9943 | -0.0006 |
| 6 | 0 | 6 | 5 | 0 | 5 | 11591.4323 | 11591.4321 | 0.0002 |
| 8 | 3 | 6 | 8 | 2 | 7 | 11660.1264 | 11660.1266 | -0.0003 |
| 6 | 1 | 6 | 5 | 0 | 5 | 11773.6000 | 11773.6001 | -0.0001 |
| 8 | 1 | 7 | 8 | 0 | 8 | 11868.0651 | 11868.0658 | -0.0007 |
| 7 | 4 | 3 | 7 | 3 | 4 | 11897.4114 | 11897.4110 | 0.0004 |
| 6 | 4 | 2 | 6 | 3 | 3 | 12360.1362 | 12360.1363 | -0.0001 |
| 5 | 4 | 1 | 5 | 3 | 2 | 12628.8617 | 12628.8623 | -0.0006 |
| 6 | 2 | 5 | 5 | 2 | 4 | 12663.3455 | 12663.3455 | 0.0001 |
| 9 | 3 | 7 | 9 | 2 | 8 | 12740.9436 | 12740.9434 | 0.0002 |
| 8 | 2 | 7 | 8 | 1 | 8 | 12741.5826 | 12741.5809 | 0.0017 |
| 5 | 4 | 2 | 5 | 3 | 3 | 12782.6870 | 12782.6871 | -0.0001 |
| 6 | 4 | 3 | 6 | 3 | 4 | 12789.6406 | 12789.6394 | 0.0011 |
| 3 | 2 | 1 | 2 | 1 | 2 | 12856.7963 | 12856.7962 | 0.0001 |
| 7 | 4 | 4 | 7 | 3 | 5 | 12858.1657 | 12858.1659 | -0.0002 |
| 4 | 2 | 3 | 3 | 1 | 2 | 12984.1506 | 12984.1522 | -0.0016 |
| 8 | 4 | 5 | 8 | 3 | 6 | 13032.0684 | 13032.0675 | 0.0009 |
| 6 | 3 | 4 | 5 | 3 | 3 | 13119.1001 | 13119.1007 | -0.0006 |
| 7 | 0 | 7 | 6 | 1 | 6 | 13144.4836 | 13144.4831 | 0.0004 |
| 7 | 1 | 6 | 6 | 2 | 5 | 13160.4363 | 13160.4396 | -0.0033 |
| 7 | 1 | 7 | 6 | 1 | 6 | 13236.6082 | 13236.6068 | 0.0014 |
| 7 | 0 | 7 | 6 | 0 | 6 | 13326.6510 | 13326.6512 | -0.0001 |
| 9 | 4 | 6 | 9 | 3 | 7 | 13355.7257 | 13355.7263 | -0.0006 |
| 7 | 1 | 7 | 6 | 0 | 6 | 13418.7747 | 13418.7748 | -0.0002 |
| 6 | 1 | 5 | 5 | 1 | 4 | 13447.1291 | 13447.1280 | 0.0011 |
| 9 | 1 | 8 | 9 | 0 | 9 | 13859.4083 | 13859.4079 | 0.0004 |
| 10 | 4 | 7 | 10 | 3 | 8 | 13866.6316 | 13866.6307 | 0.0009 |
| 6 | 2 | 4 | 5 | 2 | 3 | 13983.0375 | 13983.0373 | 0.0002 |
| 10 | 3 | 8 | 10 | 2 | 9 | 14015.2101 | 14015.2106 | -0.0005 |
| 9 | 2 | 8 | 9 | 1 | 9 | 14370.6449 | 14370.6453 | -0.0004 |
| 5 | 2 | 4 | 4 | 1 | 3 | 14375.4591 | 14375.4606 | -0.0015 |
| 7 | 2 | 6 | 6 | 2 | 5 | 14635.7658 | 14635.7667 | -0.0008 |
| 8 | 0 | 8 | 7 | 1 | 7 | 14981.3128 | 14981.3126 | 0.0002 |
| 8 | 1 | 8 | 7 | 1 | 7 | 15026.2152 | 15026.2155 | -0.0003 |
| 8 | 0 | 8 | 7 | 0 | 7 | 15073.4358 | 15073.4362 | -0.0004 |
| 8 | 1 | 8 | 7 | 0 | 7 | 15118.3399 | 15118.3391 | 0.0008 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 6 | 2 | 5 | 5 | 1 | 4 | 15629.0604 | 15629.0596 | 0.0007 |
| 8 | 1 | 7 | 7 | 2 | 6 | 15639.8218 | 15639.8213 | 0.0005 |
| 3 | 3 | 1 | 2 | 2 | 0 | 15648.6223 | 15648.6218 | 0.0005 |
| 3 | 3 | 0 | 2 | 2 | 1 | 15714.3011 | 15714.3013 | -0.0003 |
| 9 | 5 | 4 | 9 | 4 | 5 | 15718.3017 | 15718.3020 | -0.0002 |
| 8 | 5 | 3 | 8 | 4 | 4 | 16065.8097 | 16065.8097 | 0.0001 |
| 4 | 2 | 2 | 3 | 1 | 3 | 16103.4360 | 16103.4357 | 0.0002 |
| 10 | 5 | 6 | 10 | 4 | 7 | 16199.8491 | 16199.8496 | -0.0005 |
| 7 | 2 | 5 | 6 | 2 | 4 | 16337.4506 | 16337.4498 | 0.0008 |
| 9 | 0 | 9 | 8 | 1 | 8 | 16785.1294 | 16785.1290 | 0.0004 |
| 9 | 1 | 9 | 8 | 1 | 8 | 16806.4268 | 16806.4283 | -0.0015 |
| 9 | 0 | 9 | 8 | 0 | 8 | 16830.0322 | 16830.0319 | 0.0004 |
| 9 | 1 | 9 | 8 | 0 | 8 | 16851.3314 | 16851.3312 | 0.0003 |

Table S17: O-*cis* 3-fluorobenzaldehyde ($^{13}$C1)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 2 | 2 | 0 | 1 | 1 | 1 | 10079.5396 | 10079.5398 | -0.0002 |
| 3 | 2 | 2 | 2 | 1 | 1 | 11403.7086 | 11403.7084 | 0.0002 |
| 3 | 2 | 1 | 2 | 1 | 2 | 12842.6747 | 12842.6748 | -0.0001 |
| 3 | 3 | 1 | 2 | 2 | 0 | 15638.8396 | 15638.8387 | 0.0009 |
| 3 | 3 | 0 | 2 | 2 | 1 | 15704.0948 | 15704.0956 | -0.0008 |
| 4 | 3 | 2 | 3 | 2 | 1 | 17664.1232 | 17664.1238 | -0.0006 |
| 4 | 3 | 1 | 3 | 2 | 2 | 17992.6373 | 17992.6367 | 0.0005 |

Table S18: O-*cis* 3-fluorobenzaldehyde ($^{13}$C2)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 4 | 1 | 4 | 3 | 0 | 3 | 8671.5980 | 8671.5988 | -0.0009 |
| 6 | 0 | 6 | 5 | 1 | 5 | 11242.7855 | 11242.7842 | 0.0013 |
| 5 | 1 | 4 | 4 | 1 | 3 | 11404.1204 | 11404.1210 | -0.0006 |
| 6 | 1 | 6 | 5 | 0 | 5 | 11756.7287 | 11756.7289 | -0.0002 |
| 4 | 2 | 3 | 3 | 1 | 2 | 12948.5363 | 12948.5352 | 0.0011 |
| 7 | 0 | 7 | 6 | 1 | 6 | 13134.0429 | 13134.0428 | 0.0001 |
| 7 | 1 | 7 | 6 | 0 | 6 | 13401.9002 | 13401.9007 | -0.0006 |
| 3 | 3 | 0 | 2 | 2 | 1 | 15663.3816 | 15663.3817 | -0.0001 |
| 4 | 3 | 2 | 3 | 2 | 1 | 17623.2907 | 17623.2909 | -0.0003 |

Table S19: O-*cis* 3-fluorobenzaldehyde ($^{13}$C3)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 2 | 2 | 0 | 1 | 1 | 1 | 10067.7348 | 10067.7345 | 0.0003 |
| 3 | 2 | 2 | 2 | 1 | 1 | 11390.1306 | 11390.1311 | -0.0005 |
| 6 | 1 | 6 | 5 | 0 | 5 | 11736.4185 | 11736.4191 | -0.0006 |
| 3 | 2 | 1 | 2 | 1 | 2 | 12823.5020 | 12823.5020 | 0.0000 |
| 4 | 2 | 3 | 3 | 1 | 2 | 12956.7498 | 12956.7488 | 0.0010 |
| 7 | 1 | 7 | 6 | 0 | 6 | 13374.5021 | 13374.5018 | 0.0002 |
| 3 | 3 | 0 | 2 | 2 | 1 | 15687.4054 | 15687.4058 | -0.0004 |

Table S20: O-*cis* 3-fluorobenzaldehyde ($^{13}$C4)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 2 | 2 | 0 | 1 | 1 | 1 | 10046.0928 | 10046.0933 | -0.0005 |
| 6 | 0 | 6 | 5 | 1 | 5 | 11164.2771 | 11164.2781 | -0.0010 |
| 5 | 1 | 4 | 4 | 1 | 3 | 11321.9213 | 11321.9205 | 0.0007 |
| 6 | 1 | 6 | 5 | 0 | 5 | 11699.2802 | 11699.2802 | 0.0000 |
| 3 | 2 | 1 | 2 | 1 | 2 | 12788.9753 | 12788.9754 | -0.0002 |
| 4 | 2 | 3 | 3 | 1 | 2 | 12926.9813 | 12926.9805 | 0.0008 |
| 7 | 0 | 7 | 6 | 1 | 6 | 13049.0490 | 13049.0492 | -0.0003 |
| 7 | 1 | 7 | 6 | 0 | 6 | 13330.6087 | 13330.6087 | -0.0001 |
| 6 | 1 | 5 | 5 | 1 | 4 | 13347.8927 | 13347.8927 | 0.0000 |
| 5 | 2 | 4 | 4 | 1 | 3 | 14310.3153 | 14310.3152 | 0.0001 |
| 8 | 0 | 8 | 7 | 1 | 7 | 14875.0811 | 14875.0807 | 0.0003 |
| 3 | 3 | 1 | 2 | 2 | 0 | 15592.4646 | 15592.4653 | -0.0007 |
| 3 | 3 | 0 | 2 | 2 | 1 | 15656.5570 | 15656.5565 | 0.0005 |

Table S21: O-*cis* 3-fluorobenzaldehyde ($^{13}$C5)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 6 | 2 | 5 | 5 | 2 | 4 | 12593.4051 | 12593.4050 | 0.0001 |
| 7 | 0 | 7 | 6 | 1 | 6 | 13059.7952 | 13059.7947 | 0.0005 |
| 7 | 1 | 7 | 6 | 0 | 6 | 13303.6373 | 13303.6380 | -0.0006 |
| 6 | 1 | 5 | 5 | 1 | 4 | 13365.6576 | 13365.6577 | 0.0000 |
| 5 | 2 | 4 | 4 | 1 | 3 | 14156.6895 | 14156.6896 | -0.0001 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 3 | 3 | 1 | 2 | 2 | 0 | 15362.9256 | 15362.9255 | 0.0001 |
| 6 | 2 | 5 | 5 | 1 | 4 | 15397.1841 | 15397.1837 | 0.0004 |
| 3 | 3 | 0 | 2 | 2 | 1 | 15431.9697 | 15431.9694 | 0.0003 |
| 4 | 3 | 2 | 3 | 2 | 1 | 17375.8558 | 17375.8563 | -0.0005 |

Table S22: O-*cis* 3-fluorobenzaldehyde ($^{13}$C6)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 4 | 0 | 4 | 3 | 0 | 3 | 8053.6633 | 8053.6637 | -0.0005 |
| 4 | 2 | 3 | 3 | 2 | 2 | 8550.5489 | 8550.5479 | 0.0010 |
| 4 | 1 | 4 | 3 | 0 | 3 | 8615.3979 | 8615.3981 | -0.0002 |
| 2 | 2 | 0 | 1 | 1 | 1 | 9959.1727 | 9959.1737 | -0.0010 |
| 5 | 1 | 5 | 4 | 0 | 4 | 10124.5323 | 10124.5331 | -0.0007 |
| 6 | 0 | 6 | 5 | 1 | 5 | 11214.5581 | 11214.5580 | 0.0000 |
| 3 | 2 | 2 | 2 | 1 | 1 | 11269.7289 | 11269.7265 | 0.0025 |
| 6 | 1 | 6 | 5 | 0 | 5 | 11697.2667 | 11697.2671 | -0.0004 |
| 6 | 2 | 5 | 5 | 2 | 4 | 12623.4976 | 12623.4973 | 0.0002 |
| 3 | 2 | 1 | 2 | 1 | 2 | 12736.7936 | 12736.7937 | -0.0001 |
| 7 | 1 | 7 | 6 | 0 | 6 | 13341.2989 | 13341.2987 | 0.0002 |
| 5 | 2 | 4 | 4 | 1 | 3 | 14210.6165 | 14210.6158 | 0.0008 |
| 3 | 3 | 1 | 2 | 2 | 0 | 15428.3515 | 15428.3509 | 0.0007 |
| 6 | 2 | 5 | 5 | 1 | 4 | 15454.9427 | 15454.9438 | -0.0011 |
| 4 | 3 | 2 | 3 | 2 | 1 | 17446.7282 | 17446.7280 | 0.0002 |
| 4 | 3 | 1 | 3 | 2 | 2 | 17792.0867 | 17792.0881 | -0.0015 |
| 8 | 2 | 7 | 7 | 1 | 6 | 17862.0766 | 17862.0762 | 0.0004 |

Table S23: O-*cis* 3-fluorobenzaldehyde ($^{13}$C7)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 4 | 1 | 4 | 3 | 0 | 3 | 8633.4190 | 8633.4181 | 0.0010 |
| 2 | 2 | 0 | 1 | 1 | 1 | 10066.2057 | 10066.2043 | 0.0014 |
| 5 | 1 | 5 | 4 | 0 | 4 | 10127.1205 | 10127.1199 | 0.0007 |
| 6 | 0 | 6 | 5 | 1 | 5 | 11120.4767 | 11120.4771 | -0.0004 |
| 5 | 1 | 4 | 4 | 1 | 3 | 11275.2376 | 11275.2382 | -0.0005 |
| 6 | 1 | 6 | 5 | 1 | 5 | 11316.4299 | 11316.4304 | -0.0005 |
| 6 | 0 | 6 | 5 | 0 | 5 | 11482.7130 | 11482.7125 | 0.0005 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 6 | 1 | 6 | 5 | 0 | 5 | 11678.6658 | 11678.6658 | 0.0000 |
| 6 | 2 | 5 | 5 | 2 | 4 | 12519.9803 | 12519.9815 | -0.0013 |
| 7 | 1 | 6 | 6 | 2 | 5 | 12915.2768 | 12915.2756 | 0.0013 |
| 6 | 1 | 5 | 5 | 1 | 4 | 13299.8320 | 13299.8316 | 0.0004 |
| 7 | 1 | 7 | 6 | 0 | 6 | 13301.2696 | 13301.2713 | -0.0017 |
| 6 | 2 | 5 | 5 | 1 | 4 | 15572.5978 | 15572.5978 | 0.0000 |
| 3 | 3 | 1 | 2 | 2 | 0 | 15636.3884 | 15636.3881 | 0.0003 |
| 3 | 3 | 0 | 2 | 2 | 1 | 15698.4531 | 15698.4523 | 0.0008 |
| 7 | 2 | 6 | 6 | 1 | 5 | 16747.8537 | 16747.8524 | 0.0013 |
| 4 | 3 | 2 | 3 | 2 | 1 | 17645.1953 | 17645.1958 | -0.0005 |
| 4 | 3 | 1 | 3 | 2 | 2 | 17957.7958 | 17957.7976 | -0.0018 |

Table S24: O-*trans* 3-fluorobenzaldehyde (parent)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 4 | 1 | 3 | 3 | 1 | 2 | 8357.0808 | 8357.0807 | 0.0000 |
| 5 | 1 | 5 | 4 | 1 | 4 | 9121.4568 | 9121.4570 | -0.0002 |
| 4 | 1 | 4 | 3 | 0 | 3 | 9295.7399 | 9295.7414 | -0.0016 |
| 5 | 0 | 5 | 4 | 0 | 4 | 9494.1139 | 9494.1141 | -0.0002 |
| 5 | 2 | 4 | 4 | 2 | 3 | 9804.3774 | 9804.3786 | -0.0011 |
| 6 | 0 | 6 | 5 | 1 | 5 | 10010.3613 | 10010.3609 | 0.0003 |
| 5 | 2 | 3 | 4 | 2 | 2 | 10156.5321 | 10156.5319 | 0.0002 |
| 5 | 1 | 4 | 4 | 1 | 3 | 10404.7406 | 10404.7410 | -0.0004 |
| 5 | 1 | 5 | 4 | 0 | 4 | 10723.9367 | 10723.9373 | -0.0006 |
| 6 | 1 | 6 | 5 | 1 | 5 | 10905.7613 | 10905.7619 | -0.0006 |
| 6 | 0 | 6 | 5 | 0 | 5 | 11240.1840 | 11240.1841 | -0.0001 |
| 6 | 2 | 5 | 5 | 2 | 4 | 11730.7555 | 11730.7566 | -0.0010 |
| 6 | 3 | 4 | 5 | 3 | 3 | 11897.5532 | 11897.5530 | 0.0003 |
| 6 | 3 | 3 | 5 | 3 | 2 | 11944.9549 | 11944.9553 | -0.0004 |
| 7 | 0 | 7 | 6 | 1 | 6 | 12051.9228 | 12051.9236 | -0.0008 |
| 6 | 1 | 6 | 5 | 0 | 5 | 12135.5846 | 12135.5851 | -0.0005 |
| 6 | 2 | 4 | 5 | 2 | 3 | 12305.2260 | 12305.2258 | 0.0002 |
| 6 | 1 | 5 | 5 | 1 | 4 | 12419.9099 | 12419.9107 | -0.0008 |
| 7 | 1 | 7 | 6 | 1 | 6 | 12674.4239 | 12674.4243 | -0.0004 |
| 7 | 0 | 7 | 6 | 0 | 6 | 12947.3244 | 12947.3246 | -0.0002 |
| 7 | 1 | 7 | 6 | 0 | 6 | 13569.8257 | 13569.8253 | 0.0004 |
| 7 | 2 | 6 | 6 | 2 | 5 | 13638.8822 | 13638.8823 | -0.0001 |
| 7 | 4 | 4 | 6 | 4 | 3 | 13878.0792 | 13878.0795 | -0.0003 |
| 7 | 4 | 3 | 6 | 4 | 2 | 13881.9737 | 13881.9738 | -0.0001 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 7 | 3 | 5 | 6 | 3 | 4 | 13893.3705 | 13893.3709 | -0.0004 |
| 7 | 3 | 4 | 6 | 3 | 3 | 13997.5945 | 13997.5943 | 0.0001 |
| 8 | 0 | 8 | 7 | 1 | 7 | 14012.2017 | 14012.2028 | -0.0011 |
| 7 | 1 | 6 | 6 | 1 | 5 | 14391.9571 | 14391.9576 | -0.0005 |
| 8 | 1 | 8 | 7 | 1 | 7 | 14428.8122 | 14428.8133 | -0.0011 |
| 7 | 2 | 5 | 6 | 2 | 4 | 14472.7885 | 14472.7887 | -0.0002 |
| 8 | 0 | 8 | 7 | 0 | 7 | 14634.7017 | 14634.7035 | -0.0018 |
| 8 | 2 | 7 | 7 | 2 | 6 | 15526.4902 | 15526.4911 | -0.0009 |
| 8 | 4 | 5 | 7 | 4 | 4 | 15883.3931 | 15883.3925 | 0.0006 |
| 8 | 3 | 6 | 7 | 3 | 5 | 15886.8262 | 15886.8268 | -0.0005 |
| 8 | 4 | 4 | 7 | 4 | 3 | 15893.9924 | 15893.9916 | 0.0008 |
| 9 | 0 | 9 | 8 | 1 | 8 | 15900.4936 | 15900.4942 | -0.0006 |
| 8 | 3 | 5 | 7 | 3 | 4 | 16087.7514 | 16087.7508 | 0.0006 |
| 9 | 1 | 9 | 8 | 1 | 8 | 16171.0099 | 16171.0112 | -0.0014 |
| 8 | 1 | 7 | 7 | 1 | 6 | 16309.7146 | 16309.7161 | -0.0014 |
| 9 | 0 | 9 | 8 | 0 | 8 | 16317.1032 | 16317.1048 | -0.0016 |
| 8 | 2 | 6 | 7 | 2 | 5 | 16635.6024 | 16635.6038 | -0.0014 |
| 9 | 1 | 9 | 8 | 0 | 8 | 16587.6213 | 16587.6218 | -0.0005 |
| 9 | 2 | 8 | 8 | 2 | 7 | 17391.9451 | 17391.9475 | -0.0024 |
| 10 | 0 | 10 | 9 | 1 | 9 | 17731.8626 | 17731.8629 | -0.0003 |
| 9 | 5 | 5 | 8 | 5 | 4 | 17848.3705 | 17848.3711 | -0.0006 |
| 9 | 5 | 4 | 8 | 5 | 3 | 17849.1643 | 17849.1642 | 0.0001 |
| 9 | 3 | 7 | 8 | 3 | 6 | 17873.5070 | 17873.5086 | -0.0015 |
| 9 | 4 | 6 | 8 | 4 | 5 | 17895.6086 | 17895.6095 | -0.0009 |
| 10 | 1 | 10 | 9 | 1 | 9 | 17903.4004 | 17903.4013 | -0.0009 |

Table S25: O-*trans* 3-fluorobenzaldehyde ($^{13}$C1)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 4 | 1 | 3 | 3 | 1 | 2 | 8344.7541 | 8344.7542 | -0.0001 |
| 5 | 1 | 4 | 4 | 1 | 3 | 10389.5800 | 10389.5805 | -0.0005 |
| 6 | 0 | 6 | 5 | 0 | 5 | 11226.1767 | 11226.1763 | 0.0005 |
| 6 | 1 | 5 | 5 | 1 | 4 | 12402.1201 | 12402.1196 | 0.0005 |
| 7 | 1 | 7 | 6 | 1 | 6 | 12658.2208 | 12658.2207 | 0.0001 |
| 7 | 0 | 7 | 6 | 0 | 6 | 12931.4789 | 12931.4794 | -0.0005 |

Table S26: O-*trans* 3-fluorobenzaldehyde ($^{13}$C2)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 4 | 1 | 3 | 3 | 1 | 2 | 8352.4482 | 8352.4476 | 0.0006 |
| 5 | 0 | 5 | 4 | 0 | 4 | 9480.3582 | 9480.3583 | -0.0001 |
| 5 | 1 | 4 | 4 | 1 | 3 | 10398.0985 | 10398.0983 | 0.0002 |
| 6 | 1 | 6 | 5 | 1 | 5 | 10890.4053 | 10890.4055 | -0.0002 |
| 6 | 0 | 6 | 5 | 0 | 5 | 11222.0149 | 11222.0149 | 0.0000 |
| 6 | 2 | 5 | 5 | 2 | 4 | 11719.6849 | 11719.6854 | -0.0005 |
| 6 | 2 | 4 | 5 | 2 | 3 | 12302.7582 | 12302.7579 | 0.0003 |
| 6 | 1 | 5 | 5 | 1 | 4 | 12410.5448 | 12410.5453 | -0.0006 |
| 7 | 0 | 7 | 6 | 0 | 6 | 12925.0713 | 12925.0708 | 0.0006 |

Table S27: O-*trans* 3-fluorobenzaldehyde ($^{13}$C3)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 4 | 1 | 3 | 3 | 1 | 2 | 8316.9561 | 8316.9561 | -0.0001 |
| 5 | 0 | 5 | 4 | 0 | 4 | 9454.2207 | 9454.2218 | -0.0010 |
| 5 | 1 | 4 | 4 | 1 | 3 | 10355.3656 | 10355.3646 | 0.0010 |
| 6 | 0 | 6 | 5 | 0 | 5 | 11194.2289 | 11194.2288 | 0.0001 |
| 6 | 2 | 4 | 5 | 2 | 3 | 12243.2444 | 12243.2449 | -0.0005 |
| 6 | 1 | 5 | 5 | 1 | 4 | 12361.9231 | 12361.9226 | 0.0005 |
| 7 | 1 | 7 | 6 | 1 | 6 | 12621.3260 | 12621.3256 | 0.0005 |
| 7 | 1 | 6 | 6 | 1 | 5 | 14326.2129 | 14326.2135 | -0.0006 |

Table S28: O-*trans* 3-fluorobenzaldehyde ($^{13}$C4)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 4 | 1 | 3 | 3 | 1 | 2 | 8306.1427 | 8306.1426 | 0.0001 |
| 6 | 1 | 6 | 5 | 1 | 5 | 10836.5071 | 10836.5073 | -0.0002 |
| 6 | 0 | 6 | 5 | 0 | 5 | 11168.1130 | 11168.1132 | -0.0002 |
| 6 | 2 | 5 | 5 | 2 | 4 | 11657.8913 | 11657.8899 | 0.0013 |
| 6 | 2 | 4 | 5 | 2 | 3 | 12231.5130 | 12231.5132 | -0.0001 |
| 6 | 1 | 5 | 5 | 1 | 4 | 12343.4719 | 12343.4728 | -0.0009 |
| 7 | 1 | 7 | 6 | 1 | 6 | 12593.7267 | 12593.7271 | -0.0004 |
| 7 | 0 | 7 | 6 | 0 | 6 | 12863.9084 | 12863.9082 | 0.0002 |
| 7 | 1 | 6 | 6 | 1 | 5 | 14302.7332 | 14302.7330 | 0.0002 |

Table S29: O-*trans* 3-fluorobenzaldehyde ($^{13}$C5)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 4 | 1 | 3 | 3 | 1 | 2 | 8340.3759 | 8340.3747 | 0.0012 |
| 6 | 1 | 6 | 5 | 1 | 5 | 10849.9445 | 10849.9453 | -0.0008 |
| 6 | 2 | 5 | 5 | 2 | 4 | 11690.6105 | 11690.6102 | 0.0003 |
| 6 | 1 | 5 | 5 | 1 | 4 | 12385.8139 | 12385.8145 | -0.0007 |
| 7 | 1 | 7 | 6 | 1 | 6 | 12606.9661 | 12606.9656 | 0.0006 |
| 7 | 0 | 7 | 6 | 0 | 6 | 12866.3322 | 12866.3328 | -0.0006 |
| 7 | 2 | 5 | 6 | 2 | 4 | 14463.0653 | 14463.0656 | -0.0002 |
| 8 | 0 | 8 | 7 | 0 | 7 | 14541.2260 | 14541.2254 | 0.0006 |

Table S30: O-*trans* 3-fluorobenzaldehyde ($^{13}$C6)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 5 | 0 | 5 | 4 | 0 | 4 | 9463.8316 | 9463.8304 | 0.0011 |
| 5 | 1 | 4 | 4 | 1 | 3 | 10383.9738 | 10383.9752 | -0.0015 |
| 6 | 1 | 6 | 5 | 1 | 5 | 10871.6430 | 10871.6433 | -0.0003 |
| 6 | 0 | 6 | 5 | 0 | 5 | 11201.5639 | 11201.5633 | 0.0006 |
| 6 | 2 | 5 | 5 | 2 | 4 | 11702.0758 | 11702.0758 | 0.0000 |
| 6 | 2 | 4 | 5 | 2 | 3 | 12288.6187 | 12288.6183 | 0.0004 |
| 6 | 1 | 5 | 5 | 1 | 4 | 12393.0011 | 12393.0013 | -0.0003 |
| 7 | 1 | 7 | 6 | 1 | 6 | 12633.7318 | 12633.7327 | -0.0009 |
| 7 | 0 | 7 | 6 | 0 | 6 | 12900.8983 | 12900.8988 | -0.0006 |
| 7 | 2 | 6 | 6 | 2 | 5 | 13604.2335 | 13604.2322 | 0.0013 |

Table S31: O-*trans* 3-fluorobenzaldehyde ($^{13}$C7)

| J' | $K_a$' | $K_c$' | J" | $K_a$" | $K_c$" | $\upsilon_{obs}$/MHz | $\upsilon_{calc}$/MHz | $\upsilon_{obs-calc}$/MHz |
|---|---|---|---|---|---|---|---|---|
| 4 | 1 | 3 | 3 | 1 | 2 | 8273.4444 | 8273.4446 | -0.0002 |
| 6 | 0 | 6 | 5 | 0 | 5 | 11137.6571 | 11137.6579 | -0.0008 |
| 6 | 2 | 5 | 5 | 2 | 4 | 11617.1823 | 11617.1805 | 0.0018 |
| 6 | 2 | 4 | 5 | 2 | 3 | 12178.4771 | 12178.4780 | -0.0009 |
| 6 | 1 | 5 | 5 | 1 | 4 | 12297.6575 | 12297.6573 | 0.0002 |
| 7 | 1 | 7 | 6 | 1 | 6 | 12557.2299 | 12557.2303 | -0.0004 |
| 7 | 0 | 7 | 6 | 0 | 6 | 12830.3614 | 12830.3611 | 0.0004 |
| 7 | 1 | 6 | 6 | 1 | 5 | 14252.0962 | 14252.0966 | -0.0004 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 7 | 2 | 5 | 6 | 2 | 4 | 14323.5742 | 14323.5739 | 0.0003 |

## Appendix III: Kraitchman Structures ($r_s$)

Table S32: $r_s$ coordinates for O-*trans* 2-fluorobenzaldehyde

| | | | | | |
|---|---|---|---|---|---|
| 13C1 | | | | | |
| | a | | b | | |
| PLANAR: | 0.48373 | +- 0.00003 | 0.09409 | +- 0.00026 | |
| +Costain err. | 0.48373 | +- 0.00310 | 0.09409 | +- 0.01594 | |
| | a | | b | | c |
| NONPLANAR: | 0.48309 | +- 0.00003 | 0.09077 | +- 0.00018 | 0.02478 +- 0.00067 |
| +Costain err. | 0.48309 | +- 0.00311 | 0.09077 | +- 0.01653 | 0.02478 +- 0.06055 |
| 13C2 | | | | | |
| | a | | b | | |
| PLANAR: | 0.42391 | +- 0.00004 | 0.89596 | +- 0.00003 | |
| +Costain err. | 0.42391 | +- 0.00354 | 0.89596 | +- 0.00167 | |
| | a | | b | | c |
| NONPLANAR: | 0.42400 | +- 0.00005 | 0.89601 | +- 0.00002 | 0.00903*i+- 0.00225 |
| +Costain err. | 0.42400 | +- 0.00354 | 0.89601 | +- 0.00167 | 0.00903*i+- 0.16621 |
| 13C3 | | | | | |
| | a | | b | | |
| PLANAR: | 1.80379 | +- 0.00001 | 0.66739 | +- 0.00003 | |
| +Costain err. | 1.80379 | +- 0.00083 | 0.66739 | +- 0.00225 | |
| | a | | b | | c |
| NONPLANAR: | 1.80367 | +- 0.00001 | 0.66705 | +- 0.00002 | 0.02088 +- 0.00062 |
| +Costain err. | 1.80367 | +- 0.00083 | 0.66705 | +- 0.00225 | 0.02088 +- 0.07186 |
| 13C4 | | | | | |
| | a | | b | | |
| PLANAR: | 2.24990 | +- 0.00001 | 0.64760 | +- 0.00005 | |
| +Costain err. | 2.24990 | +- 0.00067 | 0.64760 | +- 0.00232 | |
| | a | | b | | c |
| NONPLANAR: | 2.24989 | +- 0.00001 | 0.64756 | +- 0.00003 | 0.00741 +- 0.00281 |
| +Costain err. | 2.24989 | +- 0.00067 | 0.64756 | +- 0.00232 | 0.00741 +- 0.20252 |

---

13C5

---

| | a | b | c |
|---|---|---|---|
| PLANAR: | 1.33422 +- 0.00001 | 1.71023 +- 0.00002 | |
| +Costain err. | 1.33422 +- 0.00112 | 1.71023 +- 0.00088 | |
| NONPLANAR: | 1.33440 +- 0.00001 | 1.71038 +- 0.00001 | 0.02212*i+- 0.00085 |
| +Costain err. | 1.33440 +- 0.00112 | 1.71038 +- 0.00088 | 0.02212*i+- 0.06781 |

---

13C6

---

| | a | b | c |
|---|---|---|---|
| PLANAR: | 0.08667*i+- 0.00015 | 1.44733 +- 0.00001 | |
| +Costain err. | 0.08667*i+- 0.01731 | 1.44733 +- 0.00104 | |
| NONPLANAR: | 0.08882*i+- 0.00017 | 1.44719 +- 0.00001 | 0.01970 +- 0.00078 |
| +Costain err. | 0.08882*i+- 0.01689 | 1.44719 +- 0.00104 | 0.01970 +- 0.07615 |

---

13C7

---

| | a | b | c |
|---|---|---|---|
| PLANAR: | 1.95662 +- 0.00001 | 0.15151 +- 0.00015 | |
| +Costain err. | 1.95662 +- 0.00077 | 0.15151 +- 0.00990 | |
| NONPLANAR: | 1.95645 +- 0.00001 | 0.14931 +- 0.00011 | 0.02550 +- 0.00063 |
| +Costain err. | 1.95645 +- 0.00077 | 0.14931 +- 0.01005 | 0.02550 +- 0.05882 |

---

18O12

---

| | a | b | c |
|---|---|---|---|
| PLANAR: | 2.79462 +- 0.00000 | 0.72899 +- 0.00002 | |
| +Costain err. | 2.79462 +- 0.00054 | 0.72899 +- 0.00206 | |
| NONPLANAR: | 2.79467 +- 0.00000 | 0.72919 +- 0.00001 | 0.01675*i+- 0.00049 |
| +Costain err. | 2.79467 +- 0.00054 | 0.72919 +- 0.00206 | 0.01675*i+- 0.08954 |

Table S33: $r_s$ coordinates for O-*cis* 3-fluorobenzaldehyde

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13C1

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| | a | b | c |
|---|---|---|---|
| PLANAR: | 0.89385 +- 0.00004 | 0.30915 +- 0.00001 | |
| +Costain err. | 0.89385 +- 0.00168 | 0.30915 +- 0.00485 | |
| NONPLANAR: | 0.89355 +- 0.00005 | 0.30829 +- 0.00014 | 0.02309 +- 0.00187 |
| +Costain err. | 0.89355 +- 0.00168 | 0.30829 +- 0.00487 | 0.02309 +- 0.06498 |

---

13C2

---

| | a | b | c |
|---|---|---|---|
| PLANAR: | 0.13953*i+- 0.00011 | 0.78050 +- 0.00000 | |
| +Costain err. | 0.13953*i+- 0.01075 | 0.78050 +- 0.00192 | |
| NONPLANAR: | 0.14284*i+- 0.00010 | 0.77989 +- 0.00002 | 0.03065 +- 0.00049 |
| +Costain err. | 0.14284*i+- 0.01050 | 0.77989 +- 0.00192 | 0.03065 +- 0.04895 |

---

13C3

---

| | a | b | c |
|---|---|---|---|
| PLANAR: | 1.32035 +- 0.00002 | 0.51511 +- 0.00001 | |
| +Costain err. | 1.32035 +- 0.00114 | 0.51511 +- 0.00291 | |
| NONPLANAR: | 1.32031 +- 0.00002 | 0.51500 +- 0.00005 | 0.01039 +- 0.00270 |
| +Costain err. | 1.32031 +- 0.00114 | 0.51500 +- 0.00291 | 0.01039 +- 0.14439 |

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13C4

---

| | a | b | c |
|---|---|---|---|
| PLANAR: | 1.84690 +- 0.00001 | 0.76576 +- 0.00000 | |
| +Costain err. | 1.84690 +- 0.00081 | 0.76576 +- 0.00196 | |
| NONPLANAR: | 1.84680 +- 0.00001 | 0.76551 +- 0.00002 | 0.01968 +- 0.00064 |
| +Costain err. | 1.84680 +- 0.00081 | 0.76551 +- 0.00196 | 0.01968 +- 0.07622 |

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13C5

---

| | a | b | |
|---|---|---|---|
| PLANAR: | 0.96200 +- 0.00002 | 1.84696 +- 0.00000 | |
| +Costain err. | 0.96200 +- 0.00156 | 1.84696 +- 0.00081 | |
| | a | b | c |
| NONPLANAR: | 0.96226 +- 0.00003 | 1.84710 +- 0.00002 | 0.02255*i+- 0.00129 |
| +Costain err. | 0.96226 +- 0.00156 | 1.84710 +- 0.00081 | 0.02255*i+- 0.06653 |

---

13C6

---

| | a | b | |
|---|---|---|---|
| PLANAR: | 0.41085 +- 0.00002 | 1.61975 +- 0.00000 | |
| +Costain err. | 0.41085 +- 0.00365 | 1.61975 +- 0.00093 | |
| | a | b | c |
| NONPLANAR: | 0.41160 +- 0.00002 | 1.61995 +- 0.00001 | 0.02515*i+- 0.00037 |
| +Costain err. | 0.41160 +- 0.00364 | 1.61995 +- 0.00093 | 0.02515*i+- 0.05963 |

---

13C7

---

| | a | b | |
|---|---|---|---|
| PLANAR: | 2.36964 +- 0.00000 | 0.07959 +- 0.00002 | |
| +Costain err. | 2.36964 +- 0.00063 | 0.07959 +- 0.01885 | |
| | a | b | c |
| NONPLANAR: | 2.36954 +- 0.00000 | 0.07625 +- 0.00015 | 0.02272 +- 0.00049 |
| +Costain err. | 2.36954 +- 0.00063 | 0.07625 +- 0.01967 | 0.02272 +- 0.06602 |

3. Table S34: $r_s$ coordinates for O-*trans* 3-fluorobenzaldehyde

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13C1

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| | a | b | c |
|---|---|---|---|
| PLANAR: | 0.84410 +- 0.00002 | 0.15539 +- 0.00057 | |
| +Costain err. | 0.84410 +- 0.00178 | 0.15539 +- 0.00967 | |
| NONPLANAR: | 0.84370 +- 0.00006 | 0.15318 +- 0.00031 | 0.02611 +- 0.00179 |
| +Costain err. | 0.84370 +- 0.00178 | 0.15318 +- 0.00980 | 0.02611 +- 0.05749 |

---

13C2

---

| | a | b | c |
|---|---|---|---|
| PLANAR: | 0.26191 +- 0.00006 | 0.95881 +- 0.00006 | |
| +Costain err. | 0.26191 +- 0.00573 | 0.95881 +- 0.00157 | |
| NONPLANAR: | 0.26094 +- 0.00012 | 0.95854 +- 0.00003 | 0.02262 +- 0.00143 |
| +Costain err. | 0.26094 +- 0.00575 | 0.95854 +- 0.00157 | 0.02262 +- 0.06633 |

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13C3

---

| | a | b | c |
|---|---|---|---|
| PLANAR: | 1.52357 +- 0.00001 | 0.31494 +- 0.00016 | |
| +Costain err. | 1.52357 +- 0.00098 | 0.31494 +- 0.00477 | |
| NONPLANAR: | 1.52360 +- 0.00002 | 0.31511 +- 0.00009 | 0.01036*i+- 0.00280 |
| +Costain err. | 1.52360 +- 0.00098 | 0.31511 +- 0.00476 | 0.01036*i+- 0.14479 |

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13C4

---

| | a | b | c |
|---|---|---|---|
| PLANAR: | 1.65175 +- 0.00001 | 1.05561 +- 0.00004 | |
| +Costain err. | 1.65175 +- 0.00091 | 1.05561 +- 0.00142 | |
| NONPLANAR: | 1.65176 +- 0.00002 | 1.05563 +- 0.00003 | 0.00643*i+- 0.00420 |
| +Costain err. | 1.65176 +- 0.00091 | 1.05563 +- 0.00142 | 0.00643*i+- 0.23346 |

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13C5

---

| | a | b | |
|---|---|---|---|
| PLANAR: | 0.48372 +- 0.00003 | 1.83413 +- 0.00003 | |
| +Costain err. | 0.48372 +- 0.00310 | 1.83413 +- 0.00082 | |
| NONPLANAR: | 0.48442 +- 0.00006 | 1.83432 +- 0.00002 | 0.02649*i+- 0.00122 |
| +Costain err. | 0.48442 +- 0.00310 | 1.83432 +- 0.00082 | 0.02649*i+- 0.05665 |

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13C6

---

| | a | b | |
|---|---|---|---|
| PLANAR: | 0.76144 +- 0.00002 | 1.22678 +- 0.00004 | |
| +Costain err. | 0.76144 +- 0.00197 | 1.22678 +- 0.00122 | |
| NONPLANAR: | 0.76138 +- 0.00004 | 1.22674 +- 0.00002 | 0.00961 +- 0.00307 |
| +Costain err. | 0.76138 +- 0.00197 | 1.22674 +- 0.00122 | 0.00961 +- 0.15604 |

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13C7

---

| | a | b | |
|---|---|---|---|
| PLANAR: | 2.17958 +- 0.00001 | 0.83441 +- 0.00006 | |
| +Costain err. | 2.17958 +- 0.00069 | 0.83441 +- 0.00180 | |
| NONPLANAR: | 2.17948 +- 0.00001 | 0.83414 +- 0.00003 | 0.02096 +- 0.00129 |
| +Costain err. | 2.17948 +- 0.00069 | 0.83414 +- 0.00180 | 0.02096 +- 0.07156 |