

Supporting Information for the manuscript entitled:

## Conformational Preferences and Basicity of Monofluorinated Cyclopropyl Amines in Comparison to Cyclopropylamine and 2-Fluoroethylamine

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**TableS1.** Selected optimized parameters of the conformers of **1**, **2**, and **3**. Bond distances are given in (Å), bond angles in (deg.).

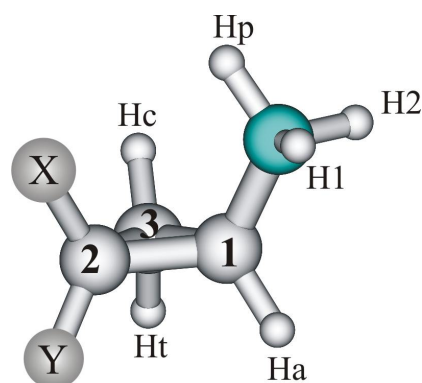
|                      | <b>1a</b> | <b>1b/1c</b> | <i>trans-2a</i> | <i>trans-2b</i> | <i>trans-2c</i> | <i>cis-2a</i> | <i>cis-2b</i> | <i>cis-2c</i> |
|----------------------|-----------|--------------|-----------------|-----------------|-----------------|---------------|---------------|---------------|
| C1–C2                | 1.500     | 1.493        | 1.487           | 1.479           | 1.492           | 1.496         | 1.500         | 1.491         |
| C1–C3                | 1.500     | 1.508        | 1.517           | 1.528           | 1.510           | 1.519         | 1.508         | 1.527         |
| C2–C3                | 1.509     | 1.514        | 1.489           | 1.493           | 1.495           | 1.488         | 1.496         | 1.491         |
| C1–N                 | 1.439     | 1.440        | 1.436           | 1.436           | 1.437           | 1.432         | 1.437         | 1.434         |
| N–H1                 | 1.012     | 1.012        | 1.011           | 1.011           | 1.012           | 1.011         | 1.012         | 1.011         |
| N–H2                 | 1.012     | 1.012        | 1.011           | 1.012           | 1.011           | 1.010         | 1.013         | 1.010         |
| C1–H <sub>a</sub>    | 1.085     | 1.081        | 1.085           | 1.081           | 1.081           | 1.085         | 1.081         | 1.081         |
| C2–H <sub>t</sub> /F | 1.078     | 1.078        | 1.370           | 1.368           | 1.370           | 1.079         | 1.079         | 1.078         |
| C2–H <sub>c</sub> /F | 1.078     | 1.080        | 1.078           | 1.081           | 1.080           | 1.364         | 1.371         | 1.372         |
| C3–H <sub>t</sub>    | 1.078     | 1.079        | 1.078           | 1.079           | 1.078           | 1.078         | 1.078         | 1.079         |
| C3–H <sub>c</sub>    | 1.078     | 1.080        | 1.078           | 1.080           | 1.080           | 1.079         | 1.080         | 1.080         |
| H1–F                 |           |              |                 |                 |                 | 3.025         | 2.610         | 2.257         |
| ∠C2–C1–N             | 116.2     | 118.7        | 116.6           | 119.8           | 123.2           | 116.9         | 121.9         | 118.1         |
| ∠C3–C1–N             | 116.2     | 122.6        | 116.6           | 123.8           | 119.3           | 115.7         | 118.6         | 122.2         |
| ∠C1–N–H1             | 110.5     | 110.1        | 110.5           | 110.7           | 110.9           | 111.0         | 109.7         | 110.1         |
| ∠C1–N–H2             | 110.5     | 110.3        | 110.7           | 110.4           | 110.7           | 110.6         | 109.6         | 111.0         |
| ∠C1–C2–C3            | 59.8      | 60.2         | 61.3            | 61.9            | 60.8            | 61.2          | 60.5          | 61.6          |
| ∠C1–C3–C2            | 59.8      | 59.2         | 59.3            | 58.6            | 59.5            | 59.6          | 59.9          | 59.1          |

**Table S2.** Vibrational frequencies ( $\text{cm}^{-1}$ ) of *s-trans-1a*, *gauche-1b/1c*, and the *trans*- and *cis*-isomers of **2** calculated at the MP2/TZVPP level.<sup>a)</sup>

| <i>s-trans-1a</i> | <i>gauche-1b/1c</i> | <i>trans-2a</i> | <i>trans-2b</i> | <i>trans-2c</i> | <i>cis-2c</i> | <i>cis-2a</i> | <i>cis-2b</i> |
|-------------------|---------------------|-----------------|-----------------|-----------------|---------------|---------------|---------------|
| 272.4 (29.8)      | 206.8 (45.2)        | 238.7 (11.1)    | 170.1 (41.0)    | 196.1 (44.8)    | 206.4 (47.7)  | 193.0 (15.2)  | 180.9 (50.8)  |
| 407.2 (6.4)       | 385.8 (10.2)        | 299.6 (14.0)    | 266.6 (2.0)     | 272.6 (5.4)     | 240.6 (1.5)   | 268.7 (17.2)  | 214.9 (9.7)   |
| 409.5 (5.4)       | 396.5 (1.5)         | 326.3 (23.6)    | 316.5 (10.7)    | 293.1 (7.3)     | 318.6 (5.3)   | 325.0 (3.3)   | 334.3 (1.3)   |
| 780.3 (3.4)       | 766.8 (2.4)         | 441.6 (1.9)     | 419.1 (3.9)     | 428.4 (12.0)    | 471.4 (7.1)   | 479.9 (6.5)   | 464.5 (1.5)   |
| 825.9 (67.6)      | 807.3 (89.6)        | 470.7 (1.1)     | 464.2 (7.4)     | 469.7 (1.1)     | 595.3 (9.1)   | 591.6 (15.5)  | 609.5 (7.3)   |
| 853.4 (3.7)       | 818.8 (17.5)        | 809.3 (28.7)    | 792.6 (41.6)    | 793.5 (123.5)   | 751.4 (10.2)  | 771.8 (22.5)  | 776.0 (25.9)  |
| 858.5 (75.0)      | 885.5 (22.0)        | 842.9 (103.7)   | 823.4 (42.6)    | 814.5 (3.1)     | 810.1 (127.4) | 811.6 (110.4) | 801.5 (21.2)  |
| 918.0 (10.4)      | 940.1 (53.5)        | 863.4 (35.5)    | 864.2 (65.2)    | 898.8 (49.1)    | 846.6 (46.9)  | 839.9 (28.8)  | 856.2 (53.3)  |
| 1029.8 (4.7)      | 1003.1 (3.6)        | 923.0 (2.9)     | 939.8 (58.5)    | 917.2 (1.6)     | 889.9 (6.3)   | 880.5 (8.5)   | 944.1 (96.6)  |
| 1049.2 (17.1)     | 1039.2 (12.8)       | 1002.3 (30.0)   | 1000.8 (6.8)    | 985.1 (24.6)    | 1010.3 (6.5)  | 1020.4 (16.4) | 991.3 (8.4)   |
| 1072.1 (1.9)      | 1065.9 (2.4)        | 1041.6 (8.5)    | 1023.7 (9.6)    | 1037.7 (9.2)    | 1032.1 (49.7) | 1044.0 (22.8) | 1039.3 (19.8) |
| 1141.1 (0.8)      | 1129.4 (3.0)        | 1105.4 (1.0)    | 1078.4 (16.6)   | 1095.7 (15.0)   | 1070.7 (5.4)  | 1099.4 (13.8) | 1079.8 (8.0)  |
| 1189.0 (4.1)      | 1158.8 (8.4)        | 1119.5 (21.7)   | 1103.2 (17.7)   | 1113.5 (27.2)   | 1137.2 (2.5)  | 1140.6 (0.4)  | 1126.0 (2.3)  |
| 1206.2 (0.3)      | 1201.0 (0.8)        | 1171.5 (5.2)    | 1169.0 (4.8)    | 1152.3 (4.3)    | 1168.0 (12.5) | 1169.4 (7.1)  | 1168.6 (3.8)  |
| 1259.2 (1.0)      | 1266.6 (4.3)        | 1201.7 (65.2)   | 1205.6 (78.2)   | 1203.6 (59.9)   | 1192.6 (25.9) | 1186.7 (19.6) | 1171.6 (24.3) |
| 1274.7 (0.9)      | 1293.3 (6.0)        | 1251.8 (5.7)    | 1257.9 (4.6)    | 1257.6 (0.7)    | 1263.8 (3.8)  | 1269.2 (8.0)  | 1254.3 (14.8) |
| 1426.0 (21.0)     | 1427.8 (13.1)       | 1277.6 (1.2)    | 1275.6 (12.1)   | 1282.5 (7.3)    | 1285.7 (17.8) | 1278.6 (17.8) | 1297.2 (8.2)  |
| 1469.9 (2.3)      | 1477.3 (2.2)        | 1352.1 (35.2)   | 1374.8 (18.6)   | 1361.8 (21.6)   | 1390.2 (14.7) | 1407.1 (24.4) | 1396.3 (23.0) |
| 1519.0 (16.0)     | 1522.6 (9.7)        | 1437.5 (0.5)    | 1442.3 (0.9)    | 1439.3 (1.1)    | 1430.3 (10.1) | 1429.5 (10.0) | 1433.8 (6.8)  |
| 1656.4 (15.3)     | 1653.4 (28.1)       | 1514.3 (27.6)   | 1519.3 (32.4)   | 1511.0 (21.7)   | 1500.4 (29.2) | 1506.8 (37.2) | 1503.5 (20.7) |
| 3150.9 (31.9)     | 3179.1 (12.4)       | 1657.0 (19.8)   | 1658.3 (27.1)   | 1654.8 (29.0)   | 1656.9 (26.9) | 1657.9 (17.1) | 1663.2 (30.9) |
| 3190.4 (11.3)     | 3186.3 (3.5)        | 3161.3 (20.2)   | 3184.1 (2.0)    | 3185.5 (2.4)    | 3184.4 (1.7)  | 3143.8 (29.8) | 3184.9 (1.6)  |
| 3197.3 (4.0)      | 3207.8 (10.1)       | 3197.1 (1.5)    | 3213.1 (6.0)    | 3210.5 (4.9)    | 3201.4 (11.1) | 3193.1 (2.6)  | 3210.7 (6.5)  |
| 3289.2 (0.2)      | 3275.2 (0.5)        | 3247.6 (5.4)    | 3218.1 (10.8)   | 3223.7 (12.7)   | 3244.0 (10.9) | 3231.1 (14.8) | 3233.9 (14.3) |
| 3301.7 (7.4)      | 3289.4 (13.0)       | 3304.5 (0.8)    | 3291.6 (2.4)    | 3291.9 (1.7)    | 3290.5 (4.2)  | 3301.0 (2.3)  | 3288.9 (4.4)  |
| 3531.9 (0.01)     | 3530.6 (0.3)        | 3536.9 (0.4)    | 3537.7 (1.1)    | 3538.2 (1.0)    | 3548.6 (3.3)  | 3548.4 (1.0)  | 3529.1 (1.7)  |
| 3626.7 (4.7)      | 3627.3 (4.2)        | 3632.3 (7.1)    | 3623.1 (6.1)    | 3638.3 (6.4)    | 3643.1 (14.7) | 3646.1 (8.4)  | 3622.3 (7.2)  |

a) Values in parentheses refer to IR intensity given in  $\text{Km mol}^{-1}$ .

**Scheme S1**



**Table S3.** NBO analysis of the important hyperconjugative interactions in  $1\mathbf{H}^+$ , *cis*- $2\mathbf{H}^+$  and *trans*- $2\mathbf{H}^+$ .  $\Delta E_{\sigma\sigma}^{(2)}$  is given in kcal mol<sup>-1</sup>, and  $\epsilon_{\sigma^*} - \epsilon_{\sigma}$ , and  $F_{\sigma\sigma^*}$  in E<sub>h</sub>.

| Donor<br>NBO( $\sigma$ ) | Acceptor<br>NBO( $\sigma^*$ ) | X = Y = H<br>$1\mathbf{H}^+$    |   |                      | X = F, Y = H<br><i>cis</i> - $2\mathbf{H}^+$ |   |                      | X = H, Y = F<br><i>trans</i> - $2\mathbf{H}^+$ |   |                      |
|--------------------------|-------------------------------|---------------------------------|---|----------------------|--|---|----------------------|--|---|----------------------|
|                          |                               | $\Delta E_{\sigma\sigma}^{(2)}$ | $\epsilon_{\sigma^*} - \epsilon_{\sigma}$ | $F_{\sigma\sigma^*}$ | $\Delta E_{\sigma\sigma}^{(2)}$              | $\epsilon_{\sigma^*} - \epsilon_{\sigma}$ | $F_{\sigma\sigma^*}$ | $\Delta E_{\sigma\sigma}^{(2)}$                | $\epsilon_{\sigma^*} - \epsilon_{\sigma}$ | $F_{\sigma\sigma^*}$ |
| $\sigma(\text{C1-N})$    | $\sigma^*(\text{C2-Y})$       | 0.55                            | 1.66                                      | 0.027                | 0.59   | 1.62                                      | 0.028                | 0.71   | 1.59                                      | 0.030                |
| $\sigma(\text{C1-N})$    | $\sigma^*(\text{C3-H}_t)$     | 0.55                            | 1.66                                      | 0.027                | 0.55   | 1.65                                      | 0.027                | –  | –   | –                    |
| $\sigma(\text{C2-X})$    | $\sigma^*(\text{C1-H}_a)$     | 1.62                            | 1.28                                      | 0.041                | 0.57   | 1.81                                      | 0.029                | 1.16   | 1.30                                      | 0.035                |
| $\sigma(\text{C2-X})$    | $\sigma(\text{C3-H}_t)$       | 1.46                            | 1.34                                      | 0.040                | –  | –   | –                    | 1.24   | 1.36                                      | 0.037                |
| $\sigma(\text{C2-Y})$    | $\sigma^*(\text{C1-N})$       | 3.13                            | 1.16                                      | 0.054                | 1.65   | 1.20                                      | 0.040                | 0.96   | 1.71                                      | 0.036                |
| $\sigma(\text{C2-Y})$    | $\sigma(\text{C3-H}_c)$       | 1.31                            | 1.31                                      | 0.037                | 0.89   | 1.34                                      | 0.031                | –  | –   | –                    |
| $\sigma(\text{C3-H}_t)$  | $\sigma^*(\text{C1-N})$       | 3.12                            | 1.16                                      | 0.054                | 3.25   | 1.18                                      | 0.055                | 3.37   | 1.17                                      | 0.056                |
| $\sigma(\text{C3-H}_t)$  | $\sigma^*(\text{C2-X})$       | 1.31                            | 1.31                                      | 0.037                | 2.69   | 1.23                                      | 0.051                | 1.28   | 1.28                                      | 0.036                |
| $\sigma(\text{N-H1})$    | $\sigma^*(\text{C1-C3})$      | 2.82                            | 1.46                                      | 0.058                | 2.99   | 1.44                                      | 0.059                | 2.99   | 1.45                                      | 0.059                |
| $\sigma(\text{N-H2})$    | $\sigma^*(\text{C1-C2})$      | 2.82                            | 1.46                                      | 0.058                | 2.07   | 1.44                                      | 0.049                | 2.65   | 1.46                                      | 0.056                |
| $\sigma(\text{N-H}_p)$   | $\sigma^*(\text{C1-H}_a)$     | 1.99                            | 1.53                                      | 0.049                | 2.10   | 1.51                                      | 0.050                | 2.09   | 1.53                                      | 0.050                |
| $\sigma(\text{C1-C3})$   | $\sigma^*(\text{N-H1})$       | 2.35                            | 1.28                                      | 0.049                | 2.11   | 1.28                                      | 0.047                | 2.37   | 1.27                                      | 0.049                |
| $\sigma(\text{C1-C2})$   | $\sigma^*(\text{N-H2})$       | 2.35                            | 1.28                                      | 0.049                | 2.33   | 1.30                                      | 0.049                | 2.25   | 1.30                                      | 0.048                |
| $\sigma(\text{C1-H}_a)$  | $\sigma^*(\text{N-H}_p)$      | 2.41                            | 1.27                                      | 0.049                | 1.93   | 1.29                                      | 0.044                | 2.39   | 1.27                                      | 0.049                |
| $\sigma(\text{C2-C3})$   | $\sigma^*(\text{C1-N})$       | 5.67                            | 1.18                                      | 0.073                | 3.58   | 1.23                                      | 0.059                | 7.27   | 1.21                                      | 0.084                |