Synthesis of halogenated bicyclic molecules involving Prins cyclization from aldehydes and non-conjugated diene alcohol

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X-ray crystal structure determinations

CCDC: 2070265 (3cCl).

Table S1. Crystallographic data for compound 3cCl.

| Compound | 3cCl |
|----------|------|
| Formula | C_{16}H_{21}ClO |
| Formula Weight | 264.79 |
| Crystal System | orthorhombic |
| Space Group | P2_12_2_1 (No. 19) |
| a /Å | 5.434(2) |
| b /Å | 11.961(3) |
| c /Å | 21.781(5) |
| α /° | 90.0 |
| β /° | 90.0 |
| γ /° | 90.0 |
| V /Å^3 | 1415.7(7) |
| $Z$ | 4 |
| $D_{\text{calc}}$ /gcm$^{-3}$ | 1.242 |
| $F(000)$ | 568.00 |
| $\mu$(MoKα) /mm$^{-1}$ | 0.256 |
| Temperature /K | 100(2) |
| Observed reflections | 8179 ($R_{\text{int}} = 0.1164$) |
| Refined reflections | 2589 (all data); 1691 ($I > 2\sigma(I)$) |
| $R$ | 0.1125 (all data) |
| $R_1$ | 0.0688 ($I > 2\sigma(I)$) |
| $wR_2$ | 0.1680 (all data) |
| GOF | 1.022 |

**Table S2.** Selected bond lengths (Å) and bond angles (°) of compound 3cCl.

(a) Selected bond lengths (Å)

| Atom 1 | Atom 2 | Bond lengths (Å) | Atom 1 | Atom 2 | Bond lengths (Å) |
|--------|--------|------------------|--------|--------|------------------|
| Cl1    | C5     | 1.805(6)         | O1     | C9     | 1.419(7)         |
| O1     | C1     | 1.430(6)         | C1     | C10    | 1.509(7)         |
| C1     | C2     | 1.547(8)         | C2     | C3     | 1.517(7)         |
| C2     | C7     | 1.519(7)         | C3     | C4     | 1.535(8)         |
| C4     | C5     | 1.506(8)         | C5     | C6     | 1.505(8)         |
| C6     | C7     | 1.531(8)         | C7     | C8     | 1.526(8)         |
| C8     | C9     | 1.506(9)         | C10    | C15    | 1.383(7)         |
| C10    | C11    | 1.398(8)         | C11    | C12    | 1.381(8)         |
| C12    | C13    | 1.388(8)         | C13    | C14    | 1.372(8)         |
| C13    | C16    | 1.505(7)         | C14    | C15    | 1.390(8)         |
| Cl1    | C5     | 1.805(6)         | O1     | C9     | 1.419(7)         |

(b) Selected bond angles (°)

| Atom 1 | Atom 2 | Atom 3 | Bond angles (°) | Atom 1 | Atom 2 | Atom 3 | Bond angles (°) |
|--------|--------|--------|-----------------|--------|--------|--------|-----------------|
| C9     | O1     | C1     | 111.5(4)        | O1     | C1     | C10    | 107.3(4)        |
| O1     | C1     | C2     | 110.9(5)        | C10    | C1     | C2     | 112.8(4)        |
|   |   |   | 110.8(4) |   |   | 112.7(4) |
|---|---|---|----------|---|---|----------|
| C3 | C2 | C7 |          | C3 | C2 | C1        |
| C7 | C2 | C1 | 110.7(4) | C2 | C3 | C4        |
| C5 | C4 | C3 | 110.1(5) | C6 | C5 | C4        |
| C6 | C5 | Cl1 | 111.2(5) | C4 | C5 | Cl1       |
| C5 | C6 | C7 | 111.3(5) | C2 | C7 | C8        |
| C2 | C7 | C6 | 110.2(5) | C8 | C7 | C6        |
| C9 | C8 | C7 | 109.8(5) | O1 | C9 | C8        |
| C15 | C10 | C11 | 117.8(5) | C15 | C10 | C1        |
| C11 | C10 | C1 | 121.6(5) | C12 | C11 | C10       |
| C11 | C12 | C13 | 120.1(6) | C14 | C13 | C12       |
| C14 | C13 | C16 | 120.6(6) | C12 | C13 | C16       |
| C13 | C14 | C15 | 121.0(6) | C10 | C15 | C14       |
Table S3. The DFT-optimized geometry of carbocation E. The Cartesian coordinates are given in Å.

| Atom | X    | Y    | Z    |
|------|------|------|------|
| H    | 5.822437 | 1.095260 | 0.396056 |
| O    | -0.472414 | -2.098587 | 0.022450 |
| C    | -0.245719 | -0.800053 | 0.575471 |
| H    | -0.415141 | -0.834332 | 1.671548 |
| C    | -1.778031 | -2.605229 | 0.288964 |
| H    | -1.803001 | -3.618305 | -0.136323 |
| C    | 1.201725  | -0.437324 | 0.313969 |
| C    | 1.772979  | -0.649022 | -0.952013 |
| H    | 1.175699  | -1.112511 | -1.739504 |
| C    | 3.098140  | -0.294845 | -1.202776 |
| H    | 3.522363  | -0.474063 | -2.194782 |
| C    | 3.900914  | 0.284074  | -0.203052 |
| C    | 3.327150  | 0.486016  | 1.059553 |
| H    | 3.928545  | 0.923845  | 1.860555 |
| C    | 1.998879  | 0.126310  | 1.316722 |
| H    | 1.583150  | 0.284741  | 2.315491 |
| C    | 5.333524  | 0.664694  | -0.489892 |
| H    | 5.393447  | 1.405767  | -1.304614 |
| H    | 5.922088  | -0.210969 | -0.810740 |
| H    | -3.784405 | 0.527034  | -1.574500 |
| C    | -1.246649 | 0.216497  | -0.032427 |
| H    | -1.042142 | 0.246843  | -1.119012 |
| C    | -1.085695 | 1.631555  | 0.542547 |
| H    | -0.073619 | 2.018796  | 0.365353 |
| H    | -1.231197 | 1.612735  | 1.635952 |
| C    | -2.099727 | 2.605567  | -0.060217 |
| H    | -2.201292 | 3.578783  | 0.456423 |
| H    | -1.787817 | 2.962510  | -1.084527 |
| C    | -3.397953 | 2.083839  | -0.404991 |
| H    | -4.168635 | 2.795045  | -0.730954 |
| C    | -3.706197 | 0.674431  | -0.461162 |
| H    | -4.761477 | 0.512020  | -0.166885 |
| C    | -2.693227 | -0.283286 | 0.178071 |
| H    | -2.892692 | -0.278522 | 1.265639 |
| C    | -2.856565 | -1.720423 | -0.329092 |
| H    | -3.855799 | -2.113041 | -0.077662 |
| H    | -2.758356 | -1.741300 | -1.428812 |
| H    | -1.934138 | -2.688442 | 1.383665 |
Table S4. The DFT-optimized geometry of TMSCI. The Cartesian coordinates are given in Å.

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | 0.895350 | -0.379985 | -1.764696 |
| Si   | 0.367210 | 0.000164  | 0.000079  |
| H    | 1.997016 | -0.393671 | -1.829743 |
| H    | 0.519356 | -1.364287 | -2.086492 |
| H    | 0.518833 | 0.384070  | -2.463422 |
| C    | 0.894855 | -1.338264 | 1.211714  |
| C    | 0.894337 | 1.718795  | 0.553511  |
| H    | 0.518544 | -1.125147 | 2.224996  |
| H    | 0.518333 | -2.325256 | 0.898904  |
| H    | 1.996493 | -1.387922 | 1.256468  |
| H    | 0.518520 | 2.489526  | -0.138211 |
| H    | 0.517147 | 1.941738  | 1.564341  |
| H    | 1.995967 | 1.782209  | 0.574800  |
| Cl   | -1.784823 | -0.000674 | -0.000519 |
Table S5. The DFT-optimized geometry of 3cCl (major)-TMS$^+$ cluster. The Cartesian coordinates are given in Å.

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | -6.745275 | -3.355151 | 0.418241 |
| O    | -2.581570  | 2.351772   | 0.485863  |
| C    | -2.118891  | 1.005464   | 0.637669  |
| H    | -1.755782  | 0.861814   | 1.676815  |
| C    | -1.582156  | 3.326577   | 0.773275  |
| H    | -2.074534  | 4.304102   | 0.668181  |
| C    | -3.306160  | 0.092893   | 0.406260  |
| C    | -4.177422  | 0.315354   | -0.673207 |
| H    | -4.011208  | 1.173893   | -1.326572 |
| C    | -5.260506  | -0.532944  | -0.901361 |
| H    | -5.927870  | -0.335712  | -1.745221 |
| C    | -5.514332  | -1.634317  | -0.064022 |
| C    | -4.645107  | -1.848035  | 1.014334  |
| H    | -4.821581  | -2.690039  | 1.688984  |
| C    | -3.560170  | -0.994957  | 1.249451  |
| H    | -2.906829  | -1.180639  | 2.106472  |
| C    | -6.691616  | -2.543843  | -0.322352 |
| H    | -6.630293  | -3.001773  | -1.323890 |
| H    | -7.642484  | -1.986306  | -0.283973 |
| H    | 0.983364   | 1.760661   | -2.120398 |
| H    | 2.669530   | 0.003044   | -1.846777 |
| C    | -0.936865  | 0.733990   | -0.326910 |
| H    | -1.329512  | 0.870748   | -1.352655 |
| C    | -0.371899  | -0.690069  | -0.208803 |
| H    | -1.153531  | -1.435772  | -0.413608 |
| H    | -0.030478  | -0.872401  | 0.825906  |
| C    | 0.792012   | -0.921809  | -1.180133 |
| H    | 1.237717   | -1.919322  | -1.060491 |
| H    | 0.422625   | -0.876064  | -2.224081 |
| C    | 1.851146   | 0.152763   | -1.135386 |
| Cl   | 2.878980   | -0.119550  | 0.581529  |
| C    | 1.337150   | 1.571284   | -1.087050 |
| H    | 2.157776   | 2.282149   | -0.911489 |
| C    | 0.179423   | 1.778663   | -0.100435 |
| H    | 0.574283   | 1.627661   | 0.923201  |
| C    | -0.388836  | 3.200760   | -0.168839 |
| H    | 0.381672   | 3.942257   | 0.101992  |
| H    | -0.714964  | 3.424385   | -1.199903 |
| H    | -1.248760  | 3.223431   | 1.826489  |
| C    | 5.678178   | 0.315054   | -1.11475  |
| Si   | 5.027674   | -0.904387  | 0.141109  |
| H    | 6.737910   | 0.062938   | -1.293568 |
Table S5. (Continued)

|   |    |    |    |
|---|----|----|----|
| H | 5.149452 | 0.247202 | -2.074250 |
| H | 5.630539 | 1.347171 | -0.733895 |
| C | 4.752453 | -2.640929 | -0.480594 |
| C | 5.720952 | -0.752838 | 1.866263 |
| H | 4.192522 | -3.245926 | 0.247862 |
| H | 4.231271 | -2.652242 | -1.449795 |
| H | 5.745741 | -3.102385 | -0.622637 |
| H | 5.721154 | 0.291013  | 2.214214  |
| H | 5.169234 | -1.380792 | 2.581799  |
| H | 6.766638 | -1.106717 | 1.834511  |
Table S6. The DFT-optimized geometry of 3cCl (minor)-TMS\(^+\) cluster. The Cartesian coordinates are given in Å.

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | -6.868504 | -3.383936 | 0.398802 |
| O    | -2.803763  | 2.390959  | 0.143961 |
| C    | -2.368887  | 1.106965  | 0.604286 |
| H    | -2.184237  | 1.156764  | 1.697580 |
| C    | -1.871101  | 3.432337  | 0.419232 |
| H    | -2.340670  | 4.360968  | 0.063985 |
| C    | -3.496476  | 0.128944  | 0.344682 |
| C    | -4.162591  | 0.118581  | -0.892252 |
| H    | -3.882239  | 0.844725  | -1.657646 |
| C    | -5.189351  | -0.791740 | -1.140796 |
| H    | -5.696390  | -0.777016 | -2.109818 |
| C    | -5.589061  | -1.725222 | -0.167357 |
| C    | -4.924306  | -1.706804 | 1.066241 |
| H    | -5.218270  | -2.413807 | 1.846611 |
| C    | -3.897082  | -0.790345 | 1.320976 |
| H    | -3.406630  | -0.791323 | 2.298288 |
| C    | -6.705875  | -2.701760 | -0.448395 |
| H    | -6.487904  | -3.312552 | -1.340337 |
| H    | -7.655018  | -2.175523 | -0.645847 |
| H    | 1.152314   | 1.461050  | -1.685578 |
| Cl   | 3.446041   | -0.294600 | -1.146590 |
| C    | -1.039828  | 0.714392  | -0.089541 |
| H    | -1.251690  | 0.660777  | -1.174019 |
| C    | -0.494526  | -0.644520 | 0.368147 |
| H    | -1.215886  | -1.449202 | 0.164099 |
| H    | -0.332138  | -0.634123 | 1.460887 |
| C    | 0.828902   | -0.998811 | -0.350219 |
| H    | 1.230148   | -1.947932 | 0.031851 |
| H    | 0.639806   | -1.113706 | -1.429389 |
| C    | 1.805963   | 0.130276  | -0.122949 |
| H    | 2.208177   | 0.154748  | 0.897044 |
| C    | 1.336021   | 1.484104  | -0.599145 |
| H    | 2.090466   | 2.257199  | -0.393504 |
| C    | 0.016018   | 1.817696  | 0.137487 |
| H    | 0.234192   | 1.853237  | 1.222829 |
| C    | -0.533558  | 3.187959  | -0.274706 |
| H    | 0.176367   | 3.989754  | -0.012072 |
| H    | -0.679042  | 3.217068  | -1.368582 |
| H    | -1.720146  | 3.522211  | 1.514620 |
| C    | 5.216628   | 0.584828  | 1.501457 |
| Si   | 5.218532   | -0.824122 | 0.278830 |
| H    | 6.085869   | 0.442019  | 2.167737 |
Table S6. (Continued)

|   |     |     |     |
|---|-----|-----|-----|
| H | 5.328081 | 1.554987 | 0.994628 |
| H | 4.313505 | 0.597196 | 2.129652 |
| C | 6.589264 | -0.797300 | -0.985829 |
| C | 4.745180 | -2.502220 | 0.939287 |
| H | 6.433302 | -1.551686 | -1.771515 |
| H | 6.698948 | 0.197424 | -1.443163 |
| H | 7.528832 | -1.040203 | -0.458706 |
| H | 3.834214 | -2.463177 | 1.555340 |
| H | 4.606245 | -3.225782 | 0.122121 |
| H | 5.574243 | -2.856097 | 1.577189 |
Table S7. The DFT-optimized geometry of 3cCl (major). The Cartesian coordinates are given in Å.

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | 6.054705 | -1.965165 | -0.434601 |
| O    | 0.438463  | 2.317697  | -0.324690 |
| C    | 0.380585  | 0.909511  | -0.587228 |
| H    | 0.104942  | 0.751756  | -1.651060 |
| C    | -0.790708 | 2.989750  | -0.590394 |
| H    | -0.599445 | 4.055030  | -0.392899 |
| C    | 1.773327  | 0.356894  | -0.359930 |
| C    | 2.516228  | 0.733659  | 0.771558  |
| H    | 2.093061  | 1.456782  | 1.471291  |
| C    | 3.790025  | 0.211591  | 0.995786  |
| H    | 4.349654  | 0.524311  | 1.882191  |
| C    | 4.370627  | -0.706102 | 0.101859  |
| C    | 3.628022  | -1.074021 | -1.028244 |
| H    | 4.055338  | -1.778623 | -1.746908 |
| C    | 2.351486  | -0.547184 | -1.258585 |
| H    | 1.801495  | -0.845443 | -2.155331 |
| C    | 5.750522  | -1.264379 | 0.356722  |
| H    | 5.793053  | -1.801231 | 1.319387  |
| H    | 6.504479  | -0.460754 | 0.405740  |
| H    | -2.889998 | 0.520784  | 2.038698  |
| H    | -3.984649 | -1.594410 | 1.556942  |
| C    | -0.703614 | 0.239305  | 0.292153  |
| H    | -0.399211 | 0.399854  | 1.344969  |
| C    | -0.835159 | -1.272607 | 0.050594  |
| H    | 0.123049  | -1.778297 | 0.244550  |
| H    | -1.081165 | -1.456569 | -1.010295 |
| C    | -1.919053 | -1.892585 | 0.941730  |
| H    | -2.036044 | -2.966622 | 0.732548  |
| H    | -1.612826 | -1.808251 | 2.001366  |
| C    | -3.268545 | -1.186595 | 0.832681  |
| Cl   | -4.065980 | -1.599925 | -0.802872 |
| C    | -3.146224 | 0.328024  | 0.979536  |
| H    | -4.121066 | 0.807535  | 0.798951  |
| C    | -2.064952 | 0.939494  | 0.078488  |
| H    | -2.364563 | 0.764791  | -0.972471 |
| C    | -1.924767 | 2.452836  | 0.276618  |
| H    | -2.866111 | 2.968799  | 0.020343  |
| H    | -1.706482 | 2.673956  | 1.336939  |
| H    | -1.051057 | 2.883372  | -1.664080 |
**Table S8.** The DFT-optimized geometry of 3cCl (minor). The Cartesian coordinates are given in Å.

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | -6.053540 | -2.186681 | 0.378561 |
| O    | -0.686458  | 2.385306  | -0.076491 |
| C    | -0.606971  | 1.097342  | 0.547609 |
| H    | -0.488697  | 1.233683  | 1.643219 |
| C    | 0.457353   | 3.200299  | 0.167881 |
| H    | 0.251070   | 4.163006  | -0.322868 |
| C    | -1.923163  | 0.393248  | 0.285497 |
| C    | -2.504390  | 0.417284  | -0.993345 |
| H    | -2.014786  | 0.977890  | -1.791771 |
| C    | -3.704880  | -0.246910 | -1.244321 |
| H    | -4.138955  | -0.209556 | -2.247717 |
| C    | -4.370178  | -0.960447 | -0.231123 |
| C    | -3.789125  | -0.976415 | 1.044064 |
| H    | -4.286486  | -1.514936 | 1.855315 |
| C    | -2.586995  | -0.306041 | 1.300052 |
| H    | -2.164206  | -0.327828 | 2.308163 |
| C    | -5.669645  | -1.675076 | -0.516261 |
| H    | -5.544751  | -2.429804 | -1.310878 |
| H    | -6.445166  | -0.971538 | -0.863105 |
| H    | 3.038921   | 0.313644  | -1.425317 |
| Cl   | 4.749663   | -1.824093 | -0.394548 |
| C    | 0.626086   | 0.319575  | 0.025321 |
| H    | 0.477022   | 0.184488  | -1.063243 |
| C    | 0.791282   | -1.065944 | 0.666826 |
| H    | -0.100481  | -1.685482 | 0.487110 |
| H    | 0.881016   | -0.954643 | 1.763523 |
| C    | 2.028794   | -1.800154 | 0.121264 |
| H    | 2.153732   | -2.770146 | 0.626281 |
| H    | 1.894045   | -2.005829 | -0.954607 |
| C    | 3.278228   | -0.946833 | 0.308190 |
| H    | 3.522359   | -0.850713 | 1.376135 |
| C    | 3.141134   | 0.429597  | -0.332116 |
| H    | 4.049224   | 1.025650  | -0.149573 |
| C    | 1.907208   | 1.159098  | 0.228055 |
| H    | 2.052309   | 1.278556  | 1.320663 |
| C    | 1.731979   | 2.558871  | -0.371322 |
| H    | 2.600331   | 3.196922  | -0.133915 |
| H    | 1.665963   | 2.487876  | -1.471590 |
| H    | 0.558162   | 3.387603  | 1.257244 |
Table S9. The DFT-optimized geometry of TMS⁺. The Cartesian coordinates are given in Å.

| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | -0.896957 | -0.959392 | 1.575453 |
| Si   | -0.933028 | -0.002655 | -0.000232 |
| H    | -1.754192 | -0.654495 | 2.200809 |
| H    | -0.916178 | -2.044197 | 1.406610 |
| H    | 0.018037  | -0.682024 | 2.130002 |
| C    | -0.929693 | -0.883610 | -1.618841 |
| C    | -0.975747 | 1.839749  | 0.044122 |
| H    | -0.797995 | -0.198086 | -2.466708 |
| H    | -0.143784 | -1.657234 | -1.618766 |
| H    | -1.898939 | -1.407637 | -1.717282 |
| H    | -1.071192 | 2.232576  | 1.064970 |
| H    | -0.042911 | 2.216187  | -0.414385 |
| H    | -1.807945 | 2.197874  | -0.586019 |