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	$P2_12_12_1$ (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	1415.7(7)

Z	4
D_{calc} /gcm^{-3}	1.242
F(000)	568.00
μ(MoKα) /mm^{-1}	0.256
Temperature /K	100(2)
Observed reflections	8179 (R_{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)

C3	C2	C7	110.8(4)	C3	C2	C1	112.7(4)
C7	C2	C1	110.7(4)	C2	C3	C4	111.2(5)
C5	C4	C3	110.1(5)	C6	C5	C4	113.1(5)
C6	C5	Cl1	111.2(5)	C4	C5	Cl1	108.7(4)
C5	C6	C7	111.3(5)	C2	C7	C8	110.8(5)
C2	C7	C6	110.2(5)	C8	C7	C6	113.8(5)
C9	C8	C7	109.8(5)	O1	C9	C8	112.0(5)
C15	C10	C11	117.8(5)	C15	C10	C1	120.7(5)
C11	C10	C1	121.6(5)	C12	C11	C10	121.4(5)
C11	C12	C13	120.1(6)	C14	C13	C12	119.0(5)
C14	C13	C16	120.6(6)	C12	C13	C16	120.3(6)
C13	C14	C15	121.0(6)	C10	C15	C14	120.7(6)

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 TMSCl. 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	-1.111475
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