Table S1. Selected interatomic distances (Å) in the reagents, prereaction complexes, transition states, and products of the reactions of atranes **1a-g**, **2a-g** (**a** OH, **b** F, **c** Cl, **d** Br, **e** $OClO_3$, **f** ONO_2, **g** SCN) with methanol. For X–N distances the Mayer bond order in the NAO basis are given in parentheses.

	X–N^{reagent}	X–N^{complex}	X–N^{TS}	X–N^{product}	X–O1^{TS}	X–O1^{product}	X–O4^{TS}	X–O4^{product}	O1–H1^{TS}	O1–H1^{product}	O4–H1^{TS}	O4–H1^{product}
1a	2.463 (0.1258)	2.405 (0.1496)	2.198 (0.2594)	3.053 (0.0286)	1.957	4.004	2.031	1.643	1.203	0.972	1.194	1.839
1b	2.344 (0.1673)	2.323 (0.1806)	2.120 (0.2832)	2.521 (0.1246)	1.920	3.709	1.913	1.658	1.186	0.972	1.219	1.793
1c	2.382 (0.1595)	2.359 (0.1727)	2.136 (0.2733)	2.689 (0.0854)	1.914	3.773	1.913	1.650	1.196	0.971	1.207	1.814
1d	2.378 (0.1626)	2.354 (0.1761)	2.133 (0.2708)	2.981 (0.0389)	1.912	3.954	1.911	1.636	1.200	0.970	1.204	1.884
1e	2.210 (0.2308)	2.191 (0.2442)	2.077 (0.3030)	2.279 (0.2276)	1.898	3.605	1.880	1.653	1.209	0.970	1.198	1.823
1f	2.248 (0.2128)	2.232 (0.2252)	2.097 (0.2942)	2.362 (0.1918)	1.909	3.633	1.890	1.653	1.209	0.971	1.196	1.811
1g	2.240 (0.2179)	2.223 (0.2307)	2.100 (0.2878)	2.400 (0.1822)	1.909	3.665	1.911	1.658	1.208	0.970	1.193	1.826
2a	2.343 (0.1997)	2.321 (0.2134)	2.251 (0.2691)	2.423 (0.1932)	2.090	3.730	2.031	1.794	1.196	0.976	1.204	1.747
2b	2.280 (0.2220)	2.259 (0.2357)	2.212 (0.2798)	2.316 (0.2326)	2.065	3.743	2.031	1.790	1.180	0.976	1.222	1.747
2c	2.315 (0.2155)	2.291 (0.2298)	2.235 (0.2746)	2.386 (0.2120)	2.070	3.769	2.053	1.793	1.184	0.975	1.215	1.758
2d	2.322 (0.2135)	2.297 (0.2276)	2.239 (0.2719)	2.407 (0.2051)	2.074	3.772	2.060	1.794	1.186	0.974	1.212	1.762
2e	2.210 (0.2578)	2.193 (0.2688)	2.179 (0.2960)	2.224 (0.2777)	2.040	3.677	2.003	1.778	1.196	0.974	1.206	1.778
2f	2.242 (0.2446)	2.223 (0.2566)	2.200 (0.2872)	2.251 (0.2639)	2.051	3.697	2.022	1.782	1.191	0.975	1.208	1.763
2g	2.254 (0.2434)	2.237 (0.2551)	2.212 (0.2863)	2.292 (0.2513)	2.069	3.756	2.062	1.797	1.190	0.974	1.204	1.768

Table S2. Selected interatomic distances (Å) in the reagents, prereaction complexes, transition states, and products of the reactions of ocanes **3a-g**, **4a-g** (**a** OH, **b** F, **c** Cl, **d** Br, **e** $OClO_3$, **f** ONO_2, **g** SCN) with methanol. For X–N distances the Mayer bond order in the NAO basis are given in parentheses.

	X–N^{reagent}	X–N^{complex}	X–N^{TS}	X–N^{product}	X–O1^{TS}	X–O1^{product}	X–O3^{TS}	X–O3^{product}	O1–H2^{TS}	O1–H2^{product}	O3–H2^{TS}	O3–H2^{product}
3a	2.271 (0.2137)	2.227 (0.2372)	2.032 (0.3366)	2.231 (0.2399)	1.940	3.683	1.946	1.671	1.167	0.970	1.238	1.847
3b	2.262 (0.2170)	2.207 (0.2470)	2.043 (0.3322)	2.195 (0.2562)	1.919	3.687	1.892	1.660	1.190	0.969	1.222	1.877
3c	2.344 (0.2080)	2.257 (0.2478)	2.050 (0.3304)	2.042 (0.3234)	1.910	2.206	1.885	1.732	1.196	0.973	1.218	1.922
3d	2.318 (0.2223)	2.236 (0.2582)	2.044 (0.3250)	2.033 (0.3183)	1.907	2.181	1.880	1.728	1.203	0.972	1.211	1.941
3e	2.109 (0.3193)	2.067 (0.3411)	1.984 (0.3827)	1.967 (0.3732)	1.866	1.962	1.840	1.692	1.194	0.963	1.229	2.778
3f	2.139 (0.2887)	2.105 (0.3086)	2.018 (0.3518)	2.134 (0.3038)	1.890	3.439	1.863	1.650	1.191	0.966	1.224	1.976
3g	2.123 (0.3220)	2.088 (0.3381)	1.993 (0.3606)	2.004 (0.3417)	1.896	2.097	1.855	1.698	1.197	0.969	1.222	2.085
4a	2.265 (0.2495)	2.235 (0.2698)	2.120 (0.3301)	2.257 (0.2661)	2.060	3.752	2.052	1.790	1.172	0.973	1.234	1.809
4b	2.245 (0.2572)	2.168 (0.2957)	2.122 (0.3274)	2.219 (0.2854)	2.031	3.761	1.997	1.778	1.192	0.971	1.225	1.832
4c	2.323 (0.2450)	2.280 (0.2693)	2.151 (0.3253)	2.343 (0.2512)	2.048	3.810	2.016	1.786	1.188	0.970	1.225	1.839
4d	2.336 (0.2423)	2.290 (0.2663)	2.159 (0.3194)	2.388 (0.2366)	2.056	3.833	2.020	1.788	1.192	0.970	1.220	1.837
4e	2.162 (0.3313)	2.098 (0.3528)	2.070 (0.3814)	2.058 (0.3826)	1.984	2.160	1.952	1.821	1.195	0.974	1.232	1.983
4f	2.182 (0.2965)	2.168 (0.3082)	2.143 (0.3387)	2.151 (0.3191)	2.013	2.281	1.967	1.814	1.204	0.971	1.211	1.995
4g	2.229 (0.3124)	2.195 (0.3307)	2.110 (0.3574)	2.115 (0.3441)	2.044	2.422	1.997	1.837	1.191	0.973	1.226	1.913

Table S3. Selected interatomic distances (Å) in the reagents, prereaction complexes, transition states, and products of the reactions of hypoatranes **5a-g**, **6a-g** (**a** OH, **b** F, **c** Cl, **d** Br, **e** $OClO_3$, **f** ONO_2, **g** SCN) with methanol. For X–N distances the Mayer bond order in the NAO basis are given in parentheses.

	X–N^{reagent}	X–N^{complex}	X–N^{TS}	X–N^{product}	X–O1^{TS}	X–O1^{product}	X–O2^{TS}	X–O2^{product}	O1–H3^{TS}	O1–H3^{product}	O2–H3^{TS}	O2–H3^{product}
5a	2.099 (0.3012)	2.114 (0.2951)	2.049 (0.3471)	2.072 (0.3248)	1.929	3.740	1.904	1.690	1.198	0.973	1.218	1.785
5b	2.138 (0.2813)	2.046 (0.3416)	2.033 (0.3528)	2.042 (0.3385)	1.891	2.116	1.863	1.724	1.197	0.971	1.228	2.019
5c	2.172 (0.2939)	2.041 (0.3579)	2.037 (0.3631)	2.033 (0.3547)	1.887	2.128	1.866	1.718	1.201	0.970	1.221	2.050
5d	2.158 (0.2996)	2.081 (0.3425)	2.036 (0.3557)	2.028 (0.3476)	1.886	2.133	1.865	1.712	1.204	0.970	1.218	2.083
5e	2.021 (0.3981)	1.967 (0.4346)	1.965 (0.4429)	1.956 (0.4364)	1.838	1.969	1.810	1.684	1.220	0.967	1.220	2.299
5f	2.037 (0.3618)	1.969 (0.4119)	1.968 (0.4179)	1.958 (0.4125)	1.863	2.086	1.828	1.684	1.203	0.966	1.226	2.287
5g	2.026 (0.3861)	1.988 (0.4034)	1.991 (0.4040)	1.990 (0.3924)	1.873	2.080	1.832	1.700	1.200	0.971	1.227	2.038
6a	2.175 (0.3004)	2.162 (0.3213)	2.135 (0.3414)	2.152 (0.3246)	2.049	3.757	2.016	1.808	1.199	0.974	1.220	1.786
6b	2.168 (0.3060)	2.121 (0.3388)	2.107 (0.3519)	2.123 (0.3335)	2.005	2.225	1.967	1.826	1.200	0.972	1.229	2.030
6c	2.286 (0.2773)	2.159 (0.3419)	2.149 (0.3513)	2.154 (0.34010	2.025	2.307	2.000	1.842	1.200	0.972	1.222	2.014
6d	2.307 (0.2693)	2.173 (0.3323)	2.159 (0.3417)	2.161 (0.3317)	2.034	2.348	2.009	1.845	1.201	0.971	1.220	2.021
6e	2.089 (0.4084)	2.054 (0.4347)	2.048 (0.4455)	2.042 (0.4381)	1.956	2.105	1.920	1.795	1.217	0.969	1.225	2.226
6f	2.119 (0.3613)	2.063 (0.4047)	2.059 (0.4134)	2.050 (0.4087)	1.983	2.209	1.944	1.800	1.202	0.967	1.230	2.256
6g	2.168 (0.3689)	2.116 (0.3943)	2.113 (0.3998)	2.119 (0.3845)	2.020	2.270	1.980	1.831	1.200	0.972	1.225	2.008

Table S4. Selected interatomic distances (Å) in the reagents, prereaction complexes, transition states, and products of the reactions of atranes **1a-d**, **2a-d** (**a** OH, **b** F, **c** Cl, **d** Br) with ethanol.

	X–N^{reagent}	X–N^{complex}	X–N^{TS}	X–N^{product}	X–O1^{TS}	X–O1^{product}	X–O4^{TS}	X–O4^{product}	O1–H1^{TS}	O1–H1^{product}	O4–H1^{TS}	O4–H1^{product}
1a	2.463	2.446	2.160	2.954	1.953	3.976	1.907	1.639	1.195	0.973	1.208	1.826
1b	2.344	2.323	2.121	2.536	1.922	3.686	1.912	1.658	1.185	0.972	1.221	1.816
1c	2.382	2.357	2.137	2.691	1.916	3.732	1.912	1.650	1.195	0.970	1.210	1.849
1d	2.378	2.351	2.135	2.714	1.914	3.743	1.910	1.649	1.199	0.970	1.206	1.860
2a	2.343	2.319	2.253	2.437	2.091	3.712	2.029	1.793	1.197	0.976	1.205	1.762
2b	2.280	2.259	2.213	2.328	2.065	3.721	2.030	1.790	1.179	0.976	1.224	1.763
2c	2.315	2.289	2.237	2.405	2.071	3.741	2.052	1.793	1.183	0.974	1.218	1.777
2d	2.322	2.295	2.242	2.426	2.074	3.747	2.059	1.794	1.185	0.974	1.215	1.782

Table S5. Selected interatomic distances (Å) in the reagents, prereaction complexes, transition states, and products of the reactions of ocanes **3a-d**, **4a-d** (**a** OH, **b** F, **c** Cl, **d** Br) with ethanol.

	X–N^{reagent}	X–N^{complex}	X–N^{TS}	X–N^{product}	X–O1^{TS}	X–O1^{product}	X–O3^{TS}	X–O3^{product}	O1–H2^{TS}	O1–H2^{product}	O3–H2^{TS}	O3–H2^{product}
3a	2.271	2.225	2.036	3.088	1.991	4.060	1.924	1.643	1.176	0.969	1.230	2.034
3b	2.262	2.205	2.043	2.202	1.921	3.672	1.890	1.660	1.189	0.969	1.224	1.884
3c	2.344	2.253	2.050	2.043	1.911	2.204	1.883	1.733	1.195	0.973	1.220	1.916
3d	2.318	2.233	2.044	2.033	1.909	2.172	1.877	1.729	1.202	0.973	1.213	1.935
4a	2.265	2.213	2.158	2.226	2.081	3.753	2.012	1.796	1.215	0.976	1.198	1.760
4b	2.245	2.163	2.163	2.187	2.029	2.295	1.976	1.833	1.206	0.974	1.216	1.943
4c	2.323	2.259	2.198	2.213	2.040	2.453	2.005	1.838	1.215	0.971	1.201	1.958
4d	2.336	2.270	2.205	2.303	2.044	3.763	2.017	1.794	1.214	0.973	1.200	1.800

Table S6. Selected interatomic distances (Å) in the reagents, prereaction complexes, transition states, and products of the reactions of hypoatranes **5a-d**, **6a-d** (**a** OH, **b** F, **c** Cl, **d** Br) with ethanol.

	X–N^{reagent}	X–N^{complex}	X–N^{TS}	X–N^{product}	X–O1^{TS}	X–O1^{product}	X–O2^{TS}	X–O2^{product}	O1–H3^{TS}	O1–H3^{product}	O2–H3^{TS}	O2–H3^{product}
5a	2.099	2.092	2.008	2.098	1.991	3.689	1.910	1.681	1.185	0.971	1.222	1.843
5b	2.138	2.047	2.034	2.042	1.892	2.119	1.860	1.724	1.196	0.971	1.230	2.018
5c	2.171	2.039	2.038	2.032	1.889	2.138	1.862	1.717	1.199	0.970	1.224	2.057
5d	2.158	2.080	2.036	2.027	1.888	2.144	1.860	1.717	1.203	0.969	1.221	2.094
6a	2.175	2.161	2.094	2.127	2.104	3.839	2.029	1.810	1.191	0.974	1.221	1.857
6b	2.168	2.121	2.108	2.124	2.006	2.228	1.964	1.826	1.200	0.972	1.231	2.027
6c	2.286	2.159	2.150	2.155	2.026	2.313	1.996	1.842	1.199	0.972	1.224	2.012
6d	2.308	2.172	2.159	2.161	2.035	2.357	2.005	1.843	1.199	0.971	1.222	2.024