Supplementary Material (ESI) for Dalton Transactions

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Paper Title: Molecular mechanism of acid-triggered aryl-halide cross-coupling reaction via reductive elimination in well-defined aryl-Cu^{III}-halide species

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1. Computational details

All geometry optimizations, with no symmetry constraints, have been performed with the Gaussian03 package,[1] using the B3LYP functional[2] and the standard 6-31G(d) basis set.[3] Intrinsic reaction pathways were calculated to confirm that the located transition states connected the expected minima. Analytical Hessians were computed to determine the nature of all located stationary points. Solvent effects including contributions of non electrostatic terms have been estimated in single point calculations on the gas phase optimized structures, based on the polarizable continuous solvation model (PCM) using CH_3CN as a solvent, the same solvent used experimentally. The solvent effect was introduced by the conductor polarizable calculation model (CPCM).[4] The cavity is created via a series of overlapping spheres.

The strength of some selected chemical bonds was evaluated with the Mayer Bond Order (MBO),[5] which is a valuable tool in the analysis of the bonding in main group and has been also used to characterize transition metal systems.[6]

Finally, the local aromaticity of the unique aromatic ring present in our system has been evaluated using the harmonic oscillator model of aromaticity (HOMA) index.[7] (Eq. S1), defined by Kruszewski and Krygowski as:[8]

$$HOMA = 1 - \frac{\alpha}{n}\sum_{i=1}^{n}\left(R_{opt} - R_i\right)^2 , \qquad \text{(Eq. S1)}$$

where n is the number of bonds considered, and α is an empirical constant (for CC bonds $\alpha = 257.7$) fixed to give HOMA = 0 for a model nonaromatic system, and HOMA = 1 for a system with all bonds equal to an optimal value R_{opt}, which is 1.388 Å for C-C bonds, assumed to be achieved for fully aromatic systems. R_i stands for a running bond length.

Figure S1. Transition state species for the transformation **B→C** in a) path A and b) path B, without the participation of triflate anions. The energy values in kcal mol^{-1} correspond to total free energy in solution with all non electrostatic terms in CH_3CN.

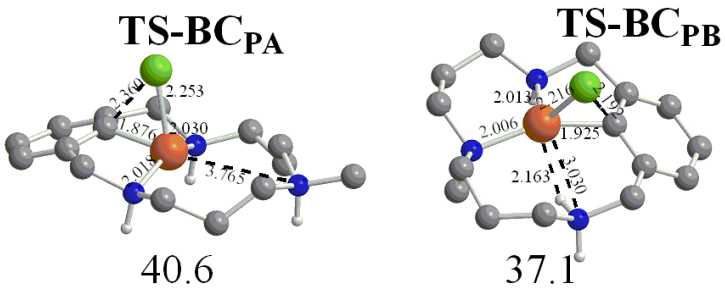

Figure S2. Proton transfer within a macrocyclic ligand from a protonated secondary amine to the tertiary amine moiety.

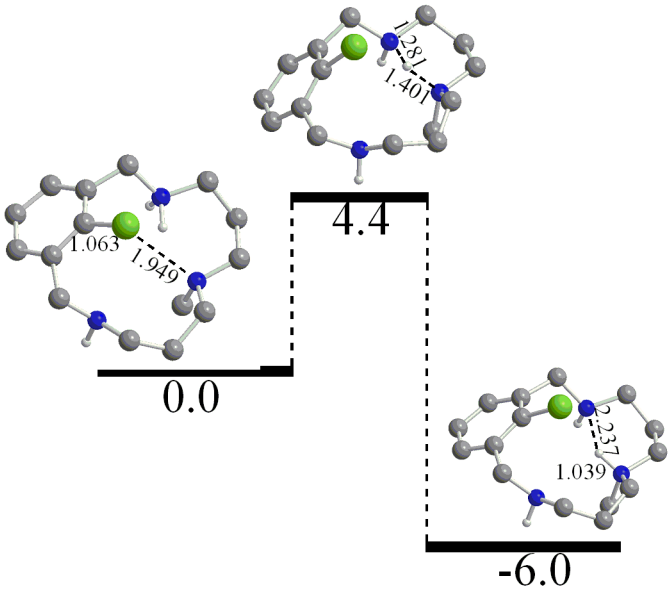

Table S1. Optimized xyz cartesian coordinates (Å) for all compounds and transition states calculated for path A.

1^{Cl}				A_{PA}				$TS\text{-}AB_{PA}$			
Cu	0.173603	0.000005	-0.008727	Cu	1.380577	0.290241	-0.001790	Cu	-1.607495	-0.023245	0.060539
N	-0.083554	1.979248	-0.430792	N	0.878568	0.194069	-1.966336	N	-0.905020	0.146631	1.890701
N	2.189900	0.000048	-0.472420	N	2.351658	-1.541115	0.014407	N	-0.395925	-2.528493	-0.029955
N	-0.083631	-1.979245	-0.430858	N	0.890886	0.234685	1.964693	N	-1.255907	0.116688	-1.878644
C	-1.704320	0.000038	-0.088689	C	0.123431	1.687303	-0.012681	C	-1.206676	1.797350	0.005408
C	-2.353113	1.223202	-0.171672	C	-0.347085	2.134704	-1.238255	C	-1.052065	2.438111	1.224350
C	-3.740468	1.217474	-0.352963	C	-1.335467	3.124821	-1.241625	C	-0.916894	3.831034	1.186149
H	-4.284501	2.155563	-0.424296	H	-1.724357	3.504034	-2.183109	H	-0.791318	4.395278	2.106252
C	-4.422196	0.000024	-0.441319	C	-1.817834	3.625217	-0.028484	C	-0.958523	4.494529	-0.045656
C	-3.740472	-1.217423	-0.352843	C	-1.334382	3.145520	1.192660	C	-1.164660	3.807673	-1.248235
H	-4.284507	-2.155518	-0.424086	H	-1.722467	3.540863	2.127792	H	-1.228766	4.354709	-2.184958
C	-2.353123	-1.223135	-0.171545	C	-0.344784	2.156703	1.205560	C	-1.301348	2.415081	-1.232158
C	-1.460370	2.406160	0.006619	C	0.329221	1.520426	-2.418063	C	-1.172284	1.530162	2.414005
H	-1.383985	2.660352	1.069349	H	1.187064	2.131942	-2.718151	H	-2.194129	1.545451	2.809189
H	-1.773463	3.304497	-0.537912	H	-0.315244	1.385840	-3.294894	H	-0.483470	1.757578	3.235630
C	0.950204	2.870436	0.164694	C	1.982700	-0.227562	-2.869591	C	-1.267226	-0.945627	2.838359
H	0.887285	2.732530	1.247999	H	2.764097	0.531900	-2.772934	H	-2.354153	-1.058356	2.818459
H	0.689208	3.911906	-0.066307	H	1.612976	-0.210218	-3.903920	H	-0.971918	-0.618533	3.844377
C	2.358976	2.561806	-0.325243	C	2.551093	-1.602156	-2.542691	C	-0.558141	-2.267825	2.519851
H	2.440594	2.712304	-1.409157	H	1.790455	-2.382388	-2.667341	H	0.529348	-2.115006	2.528900
H	3.027273	3.307845	0.120462	H	3.317309	-1.820334	-3.295918	H	-0.765581	-2.933142	3.366122
C	2.888650	1.195938	0.107193	C	3.242785	-1.687183	-1.183391	C	-1.017423	-3.000857	1.249099
H	2.802245	1.103851	1.193455	H	3.993406	-0.895468	-1.107360	H	-2.099080	-2.893137	1.155742
H	3.952501	1.123873	-0.158671	H	3.755998	-2.655822	-1.102273	H	-0.806580	-4.075105	1.363022
C	2.888672	-1.195980	0.106895	C	3.249572	-1.663080	1.209989	C	-1.203013	-3.042558	-1.181788
H	2.802392	-1.104093	1.193183	H	4.001184	-0.874653	1.112156	H	-2.257935	-2.964723	-0.913553
H	3.952496	-1.123893	-0.159072	H	3.760671	-2.634175	1.146662	H	-0.981704	-4.111819	-1.319817
C	2.358922	-2.561760	-0.325728	C	2.566189	-1.547524	2.571113	C	-0.981557	-2.313501	-2.517823
H	3.027289	-3.307885	0.119731	H	3.336988	-1.749389	3.324208	H	-1.320139	-2.990192	-3.311235
H	2.440378	-2.712057	-1.409683	H	1.805929	-2.324112	2.717932	H	0.087252	-2.151081	-2.716064
C	0.950224	-2.870487	0.164364	C	2.000312	-0.165832	2.870716	C	-1.754064	-1.003268	-2.728215
H	0.689222	-3.911935	-0.066733	H	1.635687	-0.126294	3.906189	H	-1.646441	-0.694001	-3.776587
H	0.887459	-2.732724	1.247695	H	2.780800	0.591754	2.753563	H	-2.818150	-1.129823	-2.514237
C	-1.460360	-2.406059	0.006881	C	0.335723	1.565600	2.394766	C	-1.653091	1.484404	-2.357935
H	-1.773550	-3.304540	-0.537357	H	-0.307067	1.442158	3.274399	H	-1.159892	1.708535	-3.310959
H	-1.383790	-2.659950	1.069670	H	1.190554	2.186717	2.683702	H	-2.735489	1.473404	-2.528084
C	2.320374	0.000209	-1.952232	C	1.343572	-2.633068	0.028127	C	0.965971	-3.118967	-0.116680
H	1.841263	0.881741	-2.380127	H	0.700445	-2.569962	-0.849386	H	1.609581	-2.738846	0.682047
H	1.841438	-0.881342	-2.380286	H	0.706499	-2.556476	0.908512	H	1.433411	-2.890078	-1.078454
H	3.376865	0.000344	-2.252574	H	1.839155	-3.613666	0.033701	H	0.923489	-4.214490	-0.022591
H	-0.048346	2.070122	-1.449195	H	0.111641	-0.483247	-2.010620	H	0.111316	0.104700	1.749750
H	-0.048661	-2.070078	-1.449272	H	0.127675	-0.445374	2.021319	H	-0.232343	0.102553	-1.907871
H	-5.497865	0.000020	-0.586818	S	-2.438147	-1.543985	0.011546	S	2.515104	0.642671	0.063638
Cl	0.337511	-0.000241	2.339712	O	-1.700899	-1.352407	1.250210	O	2.603942	1.984854	-0.462133
				O	-3.171146	-2.978166	0.135247	O	1.608998	-0.243029	-0.976985
				O	-1.790501	-1.430381	-1.294723	O	2.033231	0.337804	1.414476
				C	-3.921078	-0.395598	0.023012	C	4.169313	-0.218568	-0.147296
				F	-3.485352	0.836493	-0.198108	F	5.021787	0.330555	0.701103
				F	-4.521011	-0.476308	1.197635	F	4.576783	-0.064228	-1.395455
				F	-4.741810	-0.779714	-0.950311	F	4.003489	-1.511211	0.130067
				Cl	3.298184	1.685386	-0.027956	Cl	-3.634331	-1.001522	0.230795
				H	-3.417527	-3.311650	-0.752297	H	1.096777	-0.920302	-0.472353
				H	-2.585016	4.393411	-0.034640	H	-0.844641	5.573771	-0.067714

B_{PA}				$TS\text{-}BC_{PA}$				C_{PA}			
Cu	1.639443	0.593767	0.092320	Cu	0.748333	0.011480	0.083115	Cu	-0.814361	-0.296216	-0.084373
N	0.947370	0.081053	1.856111	N	1.053833	0.042788	2.086096	N	-1.224623	0.190458	-2.138241
N	-1.211102	2.493604	-0.030729	N	-1.870040	2.476651	0.140607	N	1.466552	2.904818	-0.133495
N	1.175345	0.352645	-1.812085	N	0.746130	0.234426	-1.922200	N	-0.712182	0.409750	1.955121
C	2.010577	-1.207820	-0.010115	C	2.546713	-0.417923	-0.057709	C	-2.770676	-0.443151	0.139391
C	2.141963	-1.868722	1.201269	C	3.061933	-0.933449	1.127206	C	-2.854131	-1.201641	-1.062218
C	2.597069	-3.189748	1.128121	C	4.016615	-1.946956	1.001126	C	-2.974978	-2.589077	-0.962675
H	2.740014	-3.774691	2.032480	H	4.447420	-2.400772	1.889874	H	-3.050283	-3.181229	-1.870903
C	2.857110	-3.759096	-0.125756	C	4.399170	-2.392348	-0.270669	C	-2.935936	-3.223261	0.285454
C	2.688192	-3.047782	-1.320936	C	3.821170	-1.867038	-1.432626	C	-2.644490	-2.484453	1.435418
H	2.903245	-3.524262	-2.273439	H	4.100744	-2.260738	-2.406353	H	-2.471295	-2.992894	2.380104
C	2.236531	-1.723815	-1.275635	C	2.863954	-0.851165	-1.338402	C	-2.516270	-1.091442	1.377818
C	1.813810	-1.020582	2.403351	C	2.496139	-0.327542	2.379407	C	-2.586724	-0.438526	-2.338178
H	2.715425	-0.575341	2.838432	H	3.026757	0.600645	2.611594	H	-3.313243	0.362422	-2.498607
H	1.275341	-1.557382	3.192477	H	2.556731	-0.987254	3.251253	H	-2.604130	-1.092030	-3.215941
C	0.580192	1.168370	2.807061	C	0.602604	1.260952	2.827464	C	-1.038765	1.520697	-2.759404
H	1.409768	1.876590	2.872373	H	1.366039	2.026672	2.668215	H	-1.898764	2.140806	-2.485927
H	0.447655	0.706031	3.793466	H	0.566218	1.036831	3.900330	H	-1.018467	1.457793	-3.855596
C	-0.748749	1.876726	2.449961	C	-0.773958	1.777853	2.363191	C	0.267168	2.173497	-2.268179
H	-1.523000	1.122566	2.259977	H	-1.462138	0.934639	2.251579	H	1.089367	1.451937	-2.355859
H	-1.060400	2.387411	3.367577	H	-1.174358	2.416604	3.156814	H	0.499057	3.014173	-2.930008
C	-0.725585	2.958677	1.345218	C	-0.665051	2.577738	1.049669	C	0.143141	2.649764	-0.815154
H	0.281616	3.351922	1.217652	H	0.204555	2.270249	0.466408	H	-0.342723	1.879773	-0.212321
H	-1.381441	3.788214	1.618385	H	-0.524358	3.644966	1.246070	H	-0.441899	3.571716	-0.741560
C	-0.502597	3.191753	-1.197590	C	-1.565537	3.000596	-1.266109	C	1.289966	3.354079	1.309521
H	0.460917	3.542645	-0.831471	H	-0.827894	3.799387	-1.147479	H	0.531605	4.143604	1.300264
H	-1.117356	4.063880	-1.431541	H	-2.497554	3.455275	-1.606367	H	2.243083	3.812965	1.581531
C	-0.317148	2.324659	-2.463494	C	-1.136423	1.975101	-2.338114	C	0.978554	2.265298	2.348381
H	-0.375996	3.019749	-3.308650	H	-1.391768	2.487907	-3.273122	H	1.273402	2.726921	3.297775
H	-1.156743	1.631719	-2.592128	H	-1.799004	1.105316	-2.319272	H	1.662051	1.418558	2.221247
C	1.018468	1.569424	-2.661491	C	0.346346	1.562228	-2.495336	C	-0.475427	1.764684	2.523458
H	1.049388	1.244011	-3.709203	H	0.555265	1.518764	-3.571343	H	-0.696348	1.745615	3.598894
H	1.874791	2.225587	-2.487183	H	1.022720	2.304057	-2.062214	H	-1.197526	2.452348	2.068721
C	2.026433	-0.739928	-2.396655	C	2.119092	-0.162668	-2.444468	C	-1.982308	-0.220808	2.488883
H	1.534441	-1.167121	-3.278340	H	2.015241	-0.773653	-3.346951	H	-1.782900	-0.797319	3.398028
H	2.976534	-0.297680	-2.717163	H	2.641774	0.760573	-2.712576	H	-2.680615	0.581089	2.743136
C	-2.702724	2.641557	-0.150266	C	-3.068032	3.168193	0.725230	C	2.325438	3.879326	-0.881416
H	-3.181796	2.060847	0.637279	H	-3.230714	2.799396	1.738407	H	2.495038	3.510395	-1.891888
H	-3.017814	2.250815	-1.117952	H	-3.937306	2.933422	0.109888	H	3.283225	3.966711	-0.366855
H	-2.959367	3.698442	-0.060932	H	-2.884755	4.244349	0.740472	H	1.824964	4.849970	-0.911538

H	0.062410	-0.406354	1.609407	H	0.465541	-0.735324	2.393696	H	-0.536432	-0.438689	-2.556381
H	0.233050	-0.049356	-1.668048	H	0.066253	-0.465011	-2.242565	H	0.069307	-0.176844	2.263573
S	-1.759487	-1.426233	-0.069317	S	-2.246172	-0.992887	-0.517418	S	2.154016	-0.829619	0.228005
O	-1.351154	-2.613991	-0.811494	O	-1.723837	-1.470789	-1.806522	O	2.044722	-0.887842	1.696865
O	-1.377787	-0.123137	-0.765562	O	-3.294132	0.053854	-0.551103	O	2.689510	0.454583	-0.318166
O	-1.417211	-1.352964	1.378767	O	-1.139130	-0.554687	0.444434	O	0.894258	-1.262194	-0.487568
C	-3.617511	-1.360646	-0.096798	C	-2.967346	-2.467456	0.365086	C	3.397610	-2.115811	-0.286332
F	-4.120761	-2.445996	0.474789	F	-2.007382	-3.376880	0.531476	F	2.984268	-3.308865	0.130057
F	-4.047123	-1.265883	-1.354361	F	-3.955107	-2.971675	-0.360617	F	4.571656	-1.823502	0.265519
F	-4.028058	-0.271912	0.583754	F	-3.424970	-2.078494	1.555909	F	3.509494	-2.113324	-1.614098
Cl	2.512718	2.618548	0.300689	Cl	2.682491	2.066903	0.053651	Cl	-3.398531	1.248155	0.144954
H	-1.079149	1.461912	-0.132247	H	-2.157654	1.485812	0.039306	H	1.974868	1.983438	-0.127545
H	3.195402	-4.789425	-0.173032	H	5.137127	-3.183514	-0.355952	H	-3.042046	-4.301105	0.347526

$[L_1\text{-Cl-H}]^+_{PA}$

N	-0.391890	-2.209793	-0.151372
N	-2.130542	0.207194	-0.408884
N	0.470917	2.371038	-0.431899
C	1.670732	-0.184349	0.605345
C	1.875408	-1.511672	0.215988
C	2.923268	-1.767721	-0.677036
H	3.115250	-2.792201	-0.985921
C	3.701419	-0.726271	-1.183499
C	3.381389	0.594939	-0.868696
H	3.932305	1.412358	-1.327056
C	2.339191	0.893136	0.017287
C	0.853455	-2.564270	0.573507
H	0.630681	-2.561518	1.644380
H	1.220154	-3.567914	0.315246
C	-1.600495	-2.923015	0.273346
H	-1.687024	-2.816157	1.361971
H	-1.570747	-4.004448	0.062645
C	-2.829644	-2.307642	-0.405279
H	-2.753519	-2.408847	-1.495368
H	-3.718071	-2.886302	-0.122994
C	-3.144527	-0.861305	-0.007317
H	-3.229028	-0.785436	1.080742
H	-4.096377	-0.544466	-0.443982
C	-2.530979	1.510841	0.288573
H	-2.302076	1.351558	1.345148
H	-3.618767	1.549298	0.179409
C	-1.950255	2.849748	-0.193572
H	-2.624632	3.602737	0.235453
H	-2.060641	2.957615	-1.279223
C	-0.522644	3.204788	0.244193
H	-0.372673	4.285841	0.085953
H	-0.428236	3.031889	1.321879
C	1.812090	2.300058	0.198872
H	2.515462	3.026681	-0.228178
H	1.709155	2.542482	1.260325
C	-2.004417	0.351041	-1.891150
H	-1.824386	-0.628835	-2.329577
H	-1.154074	0.999955	-2.092217
H	-2.926522	0.775702	-2.293432
H	-0.227587	-2.394663	-1.141645
H	0.583014	2.683703	-1.394187
Cl	0.476059	0.147767	1.880425
H	-1.210390	-0.129439	-0.064183
H	4.522379	-0.940530	-1.860710

Table S2. Optimized xyz cartesian coordinates (Å) for all compounds and transition states calculated for path B.

A_{PB}				$TS\text{-}AB_{PB}$				B_{PB}				$TS\text{-}BC_{PB}$			
Cu	1.380577	0.290241	-0.001790	Cu	-1.434322	0.407270	-0.041945	Cu	-0.984232	0.258887	-0.085582	Cu	-0.977655	0.073228	-0.173562
N	0.878568	0.194069	-1.966336	N	0.268006	-0.443515	2.500226	N	0.166397	-0.144386	2.943439	N	0.318445	-0.185400	2.913819
N	2.351658	-1.541115	0.014407	N	-2.189407	-1.478749	-0.234674	N	-2.290899	-1.308009	-0.209379	N	-2.097735	-1.650795	-0.108954
N	0.890886	0.234685	1.964693	N	-1.272542	0.828850	-1.960007	N	-1.051025	0.895834	-2.114981	N	-1.508256	0.950736	-2.016979
C	0.123431	1.687303	-0.012681	C	-0.218524	1.807326	0.268466	C	0.209567	1.683742	0.242387	C	-0.334288	1.838379	0.415027
C	-0.347085	2.134704	-1.238255	C	0.544519	1.859264	1.432698	C	0.870452	1.862099	1.457895	C	0.576363	1.935965	1.485042
C	-1.335467	3.124821	-1.241625	C	1.635025	2.749495	1.406429	C	2.005337	2.692620	1.438496	C	1.746679	2.680798	1.266387
H	-1.724357	3.504034	-2.183109	H	2.264989	2.824755	2.289288	H	2.565310	2.845683	2.357710	H	2.489485	2.736180	2.057693
C	-1.817834	3.625217	-0.028484	C	1.916605	3.534080	0.289545	C	2.403631	3.340399	0.270375	C	1.962742	3.361884	0.072822
C	-1.334382	3.145520	1.192660	C	1.142557	3.422507	-0.865380	C	1.671618	3.184597	-0.906077	C	1.010094	3.297263	-0.949739
H	-1.722467	3.540863	2.127792	H	1.393641	3.993598	-1.755156	H	1.975263	3.704685	-1.811097	H	1.185237	3.813862	-1.889695
C	-0.344784	2.156703	1.205560	C	0.059447	2.540313	-0.884066	C	0.545502	2.352157	-0.932474	C	-0.157247	2.559550	-0.787761
C	0.329221	1.520426	-2.418063	C	0.269919	1.058547	2.689844	C	0.368166	1.373118	2.800084	C	0.352753	1.349016	2.857841
H	1.187064	2.131942	-2.718151	H	-0.694014	1.355031	3.106759	H	-0.593509	1.833911	3.033162	H	-0.585641	1.693956	3.298907
H	-0.315244	1.385840	-3.294894	H	1.031783	1.309526	3.432300	H	1.079771	1.660938	3.575291	H	1.167041	1.660191	3.513653
C	1.982700	-0.227562	-2.869591	C	-0.967126	-1.156185	3.015381	C	-1.270351	-0.651691	3.118938	C	-1.057976	-0.815366	3.106675
H	2.764097	0.531900	-2.772934	H	-1.752409	-0.415597	3.163242	H	-1.925275	0.195379	2.926643	H	-1.783234	-0.050290	2.840018
H	1.612976	-0.210218	-3.903920	H	-0.720678	-1.559728	4.002451	H	-1.360138	-0.906826	4.176488	H	-1.155802	-0.993719	4.179761
C	2.551093	-1.602156	-2.542691	C	-1.498743	-2.321561	2.152782	C	-1.658750	-1.874369	2.243797	C	-1.301602	-2.117421	2.304110
H	1.790455	-2.382388	-2.667341	H	-0.665755	-2.899268	1.740604	H	-0.767660	-2.333077	1.804340	H	-0.377269	-2.452462	1.823620
H	3.317309	-1.820334	-3.295918	H	-1.986730	-3.004121	2.859698	H	-2.051167	-2.635495	2.925619	H	-1.553707	-2.905977	3.020076
C	3.242785	-1.687183	-1.183391	C	-2.597236	-2.051300	1.098766	C	-2.763911	-1.639549	1.178772	C	-2.468008	-2.038078	1.289822
H	3.993406	-0.895468	-1.107360	H	-3.350386	-1.380840	1.518662	H	-3.423320	-0.832531	1.505470	H	-3.209188	-1.316100	1.647440
H	3.755998	-2.655822	-1.102273	H	-3.091336	-3.010450	0.887838	H	-3.376055	-2.548264	1.107643	H	-2.972496	-3.013968	1.251839
C	3.249572	-1.663080	1.209989	C	-3.423094	-1.291223	-1.068416	C	-3.465753	-0.843574	-1.028387	C	-3.365746	-1.329711	-0.849573
H	4.001184	-0.874653	1.112156	H	-4.070600	-0.585067	-0.538122	H	-3.922773	-0.003923	-0.499776	H	-3.892413	-0.561293	-0.273447
H	3.760671	-2.634175	1.146662	H	-3.955125	-2.251319	-1.122217	H	-4.199774	-1.661207	-1.050439	H	-3.997437	-2.230321	-0.841638
C	2.566189	-1.547524	2.571113	C	-3.155191	-0.800446	-2.499419	C	-3.150859	-0.427262	-2.477061	C	-3.217905	-0.847317	-2.306436
H	3.336988	-1.749389	3.324208	H	-4.124403	-0.790918	-3.011786	H	-4.121178	-0.330961	-2.979071	H	-4.191917	-1.008796	-2.783784
H	1.805929	-2.324112	2.717932	H	-2.542439	-1.519580	-3.052614	H	-2.627883	-1.226887	-3.014533	H	-2.515365	-1.477222	-2.864054
C	2.000312	-0.165832	2.870716	C	-2.583299	0.613979	-2.638408	C	-2.421778	0.910558	-2.669635	C	-2.871299	0.635959	-2.496030
H	1.635687	-0.126294	3.906189	H	-2.478279	0.864315	-3.702418	H	-2.412529	1.165815	-3.739018	H	-3.001206	0.913585	-3.551585
H	2.780800	0.591754	2.753563	H	-3.279542	1.337323	-2.200235	H	-2.967992	1.703331	-2.147678	H	-3.568270	1.247664	-1.912504
C	0.335723	1.565600	2.394766	C	-0.801155	2.256470	-2.077467	C	-0.350153	2.209240	-2.143764	C	-1.198201	2.401731	-1.872159
H	-0.307067	1.442158	3.274399	H	-0.283980	2.409007	-3.030828	H	0.203973	2.354016	-3.078869	H	-0.861792	2.851235	-2.813382
H	1.190554	2.186717	2.683702	H	-1.694803	2.890885	-2.078028	H	-1.118426	2.990619	-2.104304	H	-2.123775	2.910369	-1.580086
C	1.343572	-2.633068	0.028127	C	-1.292123	-2.457644	-0.914957	C	-1.745068	-2.550504	-0.829023	C	-1.435401	-2.815521	-0.759747
H	0.700445	-2.569962	-0.849386	H	-0.471381	-2.737973	-0.261320	H	-1.003584	-3.016247	-0.184534	H	-0.592759	-3.163309	-0.164624
H	0.706499	-2.556476	0.908512	H	-0.860738	-2.037343	-1.820767	H	-1.249956	-2.326122	-1.770685	H	-1.036301	-2.538983	-1.734261
H	1.839155	-3.613666	0.033701	H	-1.860248	-3.360852	-1.174038	H	-2.564846	-3.259553	-1.002364	H	-2.152533	-3.640254	-0.875954
H	0.111641	-0.483247	-2.010620	H	1.034922	-0.788777	3.078966	H	0.695175	-0.442051	3.767712	H	0.911560	-0.485385	3.693226
H	0.127675	-0.445374	2.021319	H	-0.542851	0.224053	-2.345676	H	-0.482353	0.209554	-2.611068	H	-0.825773	0.544255	-2.658838
S	-2.438147	-1.543985	0.011546	S	2.056440	-1.455451	-0.685132	S	1.666607	-1.771534	-0.057891	S	1.876410	-1.511514	-0.304654
O	-1.700899	-1.352407	1.250210	O	2.291271	-2.696281	-1.399530	O	1.580924	-3.159817	-0.493008	O	1.876926	-2.851705	-0.881106
O	-3.171146	-2.978166	0.135247	O	1.560572	-1.760475	0.773578	O	1.832852	-1.528264	1.404499	O	1.897685	-1.441900	1.193152
O	-1.790501	-1.430381	-1.294723	O	1.210817	-0.409874	-1.291678	O	0.556689	-0.890476	-0.622670	O	0.824453	-0.573990	-0.861638
C	-3.921078	-0.395598	0.023012	C	3.705932	-0.651584	-0.346637	C	3.185990	-1.035233	-0.846481	C	3.466043	-0.694897	-0.827293
F	-3.485352	0.836493	-0.198108	F	4.179826	-0.151805	-1.482073	F	3.056449	-1.085525	-2.172374	F	3.487338	-0.575033	-2.153469
F	-4.521011	-0.476308	1.197635	F	4.545867	-1.549741	0.148089	F	4.256432	-1.721880	-0.467338	F	4.496156	-1.430628	-0.422528
F	-4.741810	-0.779714	-0.950311	F	3.528906	0.335528	0.540653	F	3.310098	0.239834	-0.464223	F	3.545845	0.522617	-0.273710
Cl	3.298184	1.685386	-0.027956	Cl	-2.773916	1.272587	1.443470	Cl	-2.363772	1.675053	0.914820	Cl	-2.265367	1.661736	1.020488
H	-3.417527	-3.311650	-0.752297	H	0.929430	-1.032820	1.328139	H	0.685675	-0.644976	2.171157	H	0.829289	-0.591332	2.075204
H	-2.585016	4.393411	-0.034640	H	2.759652	4.217438	0.312034	H	3.280688	3.979543	0.282641	H	2.869184	3.942174	-0.063178

C_{PB}				$[L_1\text{-}Cl\text{-}H]^+_{PB}$			
Cu	-0.874623	-0.664255	-0.513329	N	-0.670629	-2.054538	-0.063924
N	0.215633	1.009734	2.792561	N	-2.152045	0.350953	-0.414181
N	-1.654385	-2.199628	0.483950	N	0.769825	2.311870	-0.455195
N	-1.901696	0.108106	-2.032091	C	1.709421	-0.304180	0.620115
C	-1.105528	2.367013	0.066308	C	1.713699	-1.645711	0.218201
C	-0.010819	2.641849	0.904774	C	2.648585	-2.052390	-0.744099
C	1.210097	2.977223	0.299990	H	2.677756	-3.092862	-1.057903
H	2.067889	3.195861	0.928585	C	3.530397	-1.125957	-1.297386
C	1.343694	3.006175	-1.083855	C	3.409816	0.226673	-0.969674
C	0.274101	2.609936	-1.883981	H	4.034876	0.960689	-1.471784
H	0.398415	2.553366	-2.962219	C	2.473292	0.671071	-0.029395
C	-0.959462	2.256716	-1.327172	C	0.586964	-2.540325	0.649540
C	-0.055056	2.470957	2.403622	H	0.375502	-2.496585	1.718654
H	-1.014730	2.743189	2.846289	H	0.740010	-3.581314	0.355519
H	0.735198	3.053014	2.881880	C	-1.974219	-2.682175	0.354381
C	-0.905972	0.074619	2.441985	H	-2.050414	-2.535897	1.435855
H	-1.040690	0.183620	1.363432	H	-1.916507	-3.754965	0.150523
H	-1.804550	0.440698	2.943295	C	-3.132706	-2.010479	-0.384282
C	-0.672798	-1.410663	2.708353	H	-3.036116	-2.181340	-1.464023
H	0.316164	-1.733751	2.366021	H	-4.052572	-2.526721	-0.086616
H	-0.737901	-1.639067	3.778656	C	-3.307006	-0.516310	-0.061488
C	-1.785924	-2.193605	1.977528	H	-3.467579	-0.415026	1.018643
H	-2.752831	-1.743682	2.227805	H	-4.227335	-0.155309	-0.551353
H	-1.811760	-3.227489	2.344993	C	-2.390529	1.669398	0.259850
C	-3.005407	-2.372572	-0.146765	H	-2.227231	1.512292	1.332363
H	-3.694669	-1.690517	0.362052	H	-3.460434	1.907903	0.134063
H	-3.360546	-3.397166	0.042750	C	-1.628510	2.935071	-0.188079
C	-3.073134	-2.088494	-1.662651	H	-2.213525	3.765024	0.229539
H	-3.971671	-2.600672	-2.027702	H	-1.694768	3.066172	-1.275260
H	-2.240603	-2.562632	-2.197641	C	-0.180711	3.148048	0.278293
C	-3.205621	-0.615364	-2.085537	H	0.048445	4.225081	0.199133
H	-3.639820	-0.558147	-3.093419	H	-0.103627	2.892363	1.340390
H	-3.889447	-0.098908	-1.404178	C	2.112678	2.137203	0.128587
C	-2.025847	1.605764	-2.176304	H	2.875820	2.763512	-0.351804
H	-1.915365	1.896760	-3.225963	H	2.088381	2.422032	1.184461
H	-3.027257	1.897087	-1.856962	C	-2.039467	0.509333	-1.873110
C	-0.779127	-3.344165	0.093498	H	-1.993626	-0.469934	-2.360638
H	0.209176	-3.230781	0.539269	H	-1.116341	1.042350	-2.106052
H	-0.646204	-3.365067	-0.989819	H	-2.894544	1.053055	-2.307454

H	-1.227001	-4.297254	0.410066	H	-0.530165	-2.204623	-1.068813
H	0.411766	0.965451	3.798326	H	0.855571	2.638826	-1.414012
H	-1.356164	-0.206784	-2.837646	Cl	0.648207	0.167339	1.951754
S	2.224946	-0.806932	0.272064	H	-0.823770	-1.006391	0.022729
O	2.247676	-2.192547	0.756882	H	4.272395	-1.446709	-2.021594
O	2.352487	0.238095	1.336514				
O	1.102792	-0.499376	-0.692630				
C	3.739458	-0.559281	-0.779259				
F	3.716960	-1.427677	-1.788527				
F	4.828030	-0.752247	-0.041319				
F	3.745454	0.686656	-1.266019				
Cl	-2.727983	2.218539	0.764041				
H	1.091590	0.685569	2.282940				
H	2.291207	3.282349	-1.533491				

Table S3. Optimized xyz cartesian coordinates (Å) for all compounds and transition states calculated for path C.

A_{PC}				**TS-AB_{PC}**				**B_{PC}**			
Cu	-0.494721	-0.179752	-0.238280	Cu	1.661257	-0.226954	-0.079913	Cu	1.649942	-0.246276	-0.021811
N	-0.116251	-1.584327	1.180766	N	3.294306	0.202039	1.302586	N	3.255150	0.066657	1.362535
N	-2.216308	0.518354	0.672990	N	1.667971	-2.282783	0.030786	N	1.561251	-2.300365	-0.077663
N	-0.070878	1.583800	-1.153478	N	-0.590166	0.031079	-1.471797	N	-0.877673	0.315988	-1.691492
C	1.273016	-0.576121	-0.739762	C	1.606487	1.645458	-0.328212	C	1.602769	1.651872	-0.253066
C	1.897112	-1.656299	-0.135375	C	2.521520	2.356551	0.439769	C	2.517768	2.281959	0.585955
C	3.251288	-1.873107	-0.411493	C	2.312432	3.735157	0.575096	C	2.339317	3.652060	0.815246
H	3.772120	-2.713592	0.039896	H	2.996467	4.326644	1.178654	H	3.020719	4.178563	1.478719
C	3.930507	-1.004269	-1.270658	C	1.230080	4.342803	-0.064107	C	1.290927	4.333505	0.196041
C	3.279073	0.086547	-1.853706	C	0.353675	3.590567	-0.848582	C	0.425450	3.666089	-0.670157
H	3.820622	0.757780	-2.515253	H	-0.483532	4.074152	-1.345823	H	-0.381011	4.209668	-1.155053
C	1.925242	0.310106	-1.582814	C	0.538470	2.209100	-1.013644	C	0.579295	2.294954	-0.943196
C	0.998302	-2.484778	0.720470	C	3.697475	1.609849	1.015246	C	3.675513	1.481098	1.138732
H	0.534401	-3.276270	0.121800	H	4.493781	1.568312	0.263261	H	4.478686	1.464699	0.393038
H	1.490205	-2.955590	1.580112	H	4.114995	2.104375	1.901269	H	4.088890	1.932373	2.048516
C	-1.293331	-2.398816	1.586352	C	4.405001	-0.770218	1.216322	C	4.336884	-0.934720	1.209520
H	-1.617478	-2.934084	0.689060	H	4.890386	-0.614640	0.247710	H	4.827438	-0.732390	0.252160
H	-0.968244	-3.140519	2.328718	H	5.157118	-0.578633	1.995532	H	5.093753	-0.818877	1.997902
C	-2.446181	-1.572623	2.141186	C	3.920351	-2.220828	1.316748	C	3.804561	-2.375277	1.219233
H	-2.153361	-1.056566	3.063706	H	3.401711	-2.386527	2.269512	H	3.272675	-2.579735	2.156911
H	-3.231463	-2.277465	2.438743	H	4.815167	-2.853100	1.364352	H	4.680164	-3.035256	1.237815
C	-3.079075	-0.620082	1.128761	C	3.098907	-2.740562	0.124693	C	2.976737	-2.808438	-0.005466
H	-3.357096	-1.176952	0.229546	H	3.589310	-2.441415	-0.805033	H	3.484080	-2.476377	-0.914834
H	-3.993517	-0.192876	1.564276	H	3.090652	-3.839534	0.155534	H	2.936087	-3.906270	-0.033869
C	-3.052009	1.303535	-0.295181	C	1.106685	-2.855707	-1.245222	C	0.976522	-2.749378	-1.394008
H	-3.327631	0.613346	-1.097586	H	1.787665	-2.570509	-2.049428	H	1.699763	-2.492952	-2.170378
H	-3.971501	1.606580	0.225409	H	1.152172	-3.949984	-1.147028	H	0.916149	-3.845778	-1.355299
C	-2.388756	2.541655	-0.895358	C	-0.330275	-2.470152	-1.646118	C	-0.416009	-2.210179	-1.803893
H	-3.156044	3.046111	-1.494453	H	-0.642731	-3.248389	-2.353071	H	-0.806352	-2.958940	-2.502139
H	-2.097582	3.266837	-0.125899	H	-1.030664	-2.560795	-0.807297	H	-1.133424	-2.213764	-0.976635
C	-1.224717	2.235939	-1.828678	C	-0.549800	-1.129616	-2.369806	C	-0.476539	-0.861556	-2.557235
H	-0.874125	3.159906	-2.308512	H	-1.475857	-1.221996	-2.959948	H	-1.241736	-0.913027	-3.334963
H	-1.548513	1.545104	-2.612603	H	0.260204	-0.960679	-3.086617	H	0.477490	-0.629833	-3.028237
C	1.054206	1.389112	-2.133492	C	-0.330323	1.395007	-1.949889	C	-0.284689	1.670449	-2.024898
H	1.567169	2.339953	-2.321770	H	-1.252951	1.953531	-2.163743	H	-1.124267	2.331749	-2.244270
H	0.597007	1.059847	-3.072958	H	0.198046	1.290362	-2.904825	H	0.301590	1.547591	-2.939772
C	-1.858151	1.374613	1.834168	C	0.910189	-2.848732	1.177093	C	0.769405	-2.918323	1.020738
H	-1.265955	0.817263	2.557909	H	1.282541	-2.445073	2.118171	H	1.127510	-2.574364	1.990989
H	-1.252803	2.220314	1.514719	H	-0.145471	-2.594403	1.096583	H	-0.280916	-2.645090	0.931456
H	-2.765249	1.747382	2.329142	H	1.012343	-3.942243	1.193893	H	0.857612	-4.011636	0.976724
H	0.228822	-1.047619	1.981115	H	2.899172	0.167260	2.242640	H	2.873804	-0.007904	2.306119
H	0.275483	2.180158	-0.397188	H	-0.950710	-0.078504	-0.534079	H	-0.730577	0.129099	-0.696954
H	4.981189	-1.175892	-1.483708	S	-3.971846	0.693489	-0.189587	S	-3.840196	0.681507	-0.208246
Cl	-1.503863	-1.442144	-1.971167	O	-5.263919	1.325418	-0.308238	O	-5.086608	1.409591	-0.023371
N	1.494579	1.495347	1.996797	O	-3.472973	0.232945	-1.645364	O	-3.506766	0.272419	-1.620964
C	2.542529	1.804480	2.388815	O	-2.844498	1.299582	0.524571	O	-2.621692	1.203596	0.478933
C	3.857580	2.195615	2.888631	C	-4.199729	-0.974992	0.614081	C	-4.085054	-0.964688	0.624876
H	3.974846	1.875836	3.928779	F	-4.474354	-0.786155	1.906461	F	-4.376232	-0.796713	1.926024
H	3.969998	3.283302	2.841543	F	-5.163872	-1.663464	0.034851	F	-5.038382	-1.684798	0.053409
H	4.643471	1.731693	2.284705	F	-3.035692	-1.651195	0.519392	F	-2.918365	-1.676375	0.571850
				Cl	2.778106	-0.043443	-2.012995	Cl	2.734391	0.031777	-1.930495
				H	-2.472822	0.190534	-1.648032	H	-1.952292	0.379572	-1.739188
				H	1.069497	5.410830	0.046457	H	1.150187	5.393511	0.381908
				N	0.232121	0.001506	1.442612	N	0.138789	-0.082341	1.254788
				C	-0.511919	0.386541	2.243347	C	-0.629821	0.226345	2.065863
				C	-1.452107	0.874141	3.242478	C	-1.560283	0.600744	3.116314
				H	-1.679482	1.925236	3.041777	H	-1.902692	1.622795	2.932877
				H	-1.025311	0.771236	4.244780	H	-1.071888	0.524057	4.093039
				H	-2.382351	0.302988	3.177415	H	-2.433062	-0.056324	3.077197

TS-BC_{PC}				**C_{PC}**			
Cu	1.641535	-0.263055	0.112566	Cu	-1.390964	-0.481971	-0.701523
N	3.372411	0.131828	1.267458	N	-3.247695	0.295731	-1.252519
N	1.575243	-2.326354	-0.059471	N	-1.573081	-2.325943	0.035864
N	-0.853917	0.228034	-1.699516	N	0.533485	0.099336	1.867350
C	1.685874	1.626139	-0.459652	C	-1.823484	1.849603	1.004893
C	2.582568	2.278699	0.399769	C	-2.457700	2.332920	-0.148128
C	2.265879	3.578778	0.794685	C	-1.827130	3.371150	-0.842447
H	2.918390	4.098596	1.491523	H	-2.309538	3.782393	-1.725616
C	1.111435	4.203271	0.311925	C	-0.587956	3.864327	-0.431491
C	0.265383	3.534243	-0.571743	C	0.076576	3.272093	0.641944
H	-0.634063	4.022636	-0.935756	H	1.087762	3.574585	0.894368
C	0.555734	2.234913	-1.015874	C	-0.534171	2.252937	1.381898
C	3.793382	1.514992	0.885004	C	-3.674610	1.628872	-0.696701
H	4.519618	1.420213	0.070286	H	-4.411053	1.444490	0.087939
H	4.293371	2.035171	1.709891	H	-4.160541	2.235546	-1.468486
C	4.418322	-0.910510	1.132269	C	-4.313372	-0.741320	-1.217115
H	4.886761	-0.773489	0.151982	H	-4.813078	-0.667653	-0.245697

H	5.204183	-0.783156	1.889506	H	-5.073040	-0.551949	-1.987467
C	3.834220	-2.328693	1.226270	C	-3.739709	-2.155050	-1.380912
H	3.286882	-2.453098	2.169223	H	-3.116212	-2.218464	-2.282552
H	4.684673	-3.017478	1.295856	H	-4.586999	-2.823794	-1.574254
C	2.999094	-2.802625	0.019544	C	-3.018319	-2.714971	-0.141039
H	3.497127	-2.475227	-0.898599	H	-3.555096	-2.375235	0.750060
H	2.989357	-3.902375	0.005734	H	-3.075223	-3.813015	-0.151017
C	1.034861	-2.764915	-1.393291	C	-1.210445	-2.709657	1.446173
H	1.756785	-2.451947	-2.152654	H	-1.949079	-2.238744	2.101174
H	1.030546	-3.864661	-1.394361	H	-1.363516	-3.795942	1.525623
C	-0.373761	-2.283151	-1.818088	C	0.206749	-2.379488	1.967902
H	-0.735251	-3.046915	-2.515577	H	0.483373	-3.190923	2.649721
H	-1.095315	-2.302415	-0.994465	H	0.965521	-2.398453	1.178281
C	-0.471356	-0.942169	-2.576926	C	0.338028	-1.079237	2.773609
H	-1.259095	-1.002732	-3.331454	H	1.220304	-1.114700	3.416931
H	0.465356	-0.703569	-3.080080	H	-0.544338	-0.902060	3.393722
C	-0.319346	1.597288	-2.074220	C	0.230244	1.478587	2.426333
H	-1.188136	2.229823	-2.261050	H	1.188746	1.947181	2.653522
H	0.232953	1.484406	-3.011171	H	-0.333394	1.353542	3.353140
C	0.779782	-2.975681	1.013734	C	-0.747992	-3.139782	-0.906404
H	1.153754	-2.679708	1.994614	H	-1.063238	-2.955660	-1.935239
H	-0.263646	-2.668111	0.949840	H	0.304041	-2.866282	-0.825487
H	0.837294	-4.069675	0.927922	H	-0.862484	-4.212457	-0.693312
H	3.071199	0.155538	2.242589	H	-3.032867	0.464058	-2.236979
H	-0.622204	0.048202	-0.719529	H	-0.012921	-0.039862	1.005221
Cl	2.634463	0.302247	-1.874292	S	3.709555	0.474879	0.406078
H	-1.936064	0.268229	-1.695876	O	5.089770	0.925441	0.518409
H	0.872048	5.214614	0.623996	O	3.109204	-0.113734	1.663385
N	0.098551	-0.024434	1.353752	O	2.731367	1.367428	-0.269000
C	-0.680224	0.318153	2.141607	C	3.756355	-1.027574	-0.692405
C	-1.639303	0.744067	3.146589	F	4.123493	-0.701536	-1.941852
H	-2.481668	0.047406	3.160436	F	4.581718	-1.956152	-0.226361
H	-2.024124	1.728402	2.867011	F	2.506102	-1.571890	-0.768688
H	-1.162903	0.777887	4.131399	Cl	-2.699548	0.704606	2.045575
O	-3.472492	0.203325	-1.638050	H	1.584277	0.070571	1.606578
S	-3.852222	0.653610	-0.247143	H	-0.117738	4.676082	-0.977429
O	-2.677244	1.266485	0.434886	N	-0.037615	0.335676	-1.666475
O	-5.141365	1.316824	-0.118895	C	0.805317	0.824510	-2.295593
C	-4.027319	-0.974603	0.637761	C	1.851358	1.423306	-3.107688
F	-2.826374	-1.629085	0.616272	H	2.278861	2.268029	-2.561473
F	-4.343600	-0.784541	1.929333	H	1.446713	1.749018	-4.070984
F	-4.936830	-1.758562	0.077322	H	2.649483	0.692666	-3.264898

Table S4. HOMA aromaticity indexes for all species calculated in Paths A, B and C.

	HOMA
$\mathbf{1^{Cl}}$	0.980
$\mathbf{A_{PA}}$	0.981
$\mathbf{TS\text{-}AB_{PA}}$	0.976
$\mathbf{B_{PA}}$	0.973
$\mathbf{TS\text{-}BC_{PA}}$	0.977
$\mathbf{C_{PA}}$	0.880
$\mathbf{[L_1\text{-}Cl\text{-}H](CF_3SO_3)_{PA}}$	0.970
$\mathbf{[L_1\text{-}Cl\text{-}H]+_{PA}}$	0.974
$\mathbf{A_{PB}}$	0.981
$\mathbf{TS\text{-}AB_{PB}}$	0.973
$\mathbf{B_{PB}}$	0.972
$\mathbf{TS\text{-}BC_{PB}}$	0.937
$\mathbf{C_{PB}}$	0.957
$\mathbf{[L_1\text{-}Cl\text{-}H](CF_3SO_3)_{PB}}$	0.967
$\mathbf{[L_1\text{-}Cl\text{-}H]+_{PB}}$	0.970
$\mathbf{A_{PC}}$	0.981
$\mathbf{TS\text{-}AB_{PC}}$	0.977
$\mathbf{B_{PC}}$	0.973
$\mathbf{TS\text{-}BC_{PC}}$	0.966
$\mathbf{C_{PC}}$	0.967
$\mathbf{[L_1\text{-}Cl\text{-}H](CF_3SO_3)_{PC}}$	0.967
$\mathbf{[L_1\text{-}Cl\text{-}H]+_{PC}}$	0.970

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