Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Autocatalytic cathodic dehalogenation triggered by dissociative electron transfer through C−H···O hydrogen bond

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Supplementary Information

Complete description of the computational details

Our 'standard protocol' involved Gaussian[1] optimization of molecular structures and calculation of harmonic frequencies with a small basis set B1 (main group atoms: 6-31G(d,p), Mo: LANL2DZ with respective ECP[2]), followed by single-point energy calculations with a larger basis B2 (6-311++G(2d,2p) for main group atoms and LACV3P+[3] for Mo). In these calculations, the polarizable continuum solvation model (IEF-PCM)[4] was used with all parameters corresponding to the actual solvent (dichloromethane and where appropriate chloroform). In calculations with both B1 and B2, polarization and diffuse functions were omitted for the hydrogen atoms not involved in reactions (H atoms of Tp ligand and OCH_3 groups). Energy correction due to dispersion interactions was estimated from single-point calculations with TinyDFTD[5] (the DFT-D2 variant[6]). We consider the accuracy of this computational protocol satisfactory for description of organic species and their reactions.

However, for the Mo-containing complexes and especially their adducts with $CHCl_3$, $CHCl_2^{\bullet}$, CH_3OH, or an alkene, for which dispersive forces play a major role, we decided to optimize their geometries at DFT-D level. To this end, DFT-D (the DFT-D3 variant[7]) structure optimizations and frequency calculations were carried out with Turbomole,[8] employing the triple-ζ basis set B3 (def2-TZVPP[9] for all atoms, with respective ECP for Mo) and using conductor-like screening model (COSMO)[10] with the dielectric constant of dichloromethane ($\varepsilon = 8.93$). The starting geometry of the {Mo(NO)(Tp^{Me2})(OCH_2−)} fragment and chloroform molecule was taken from the crystal structure of *anti*-[Mo(NO)(Tp^{Me2}){1,4-$(OCH_2)_2C_6H_4$}]$_2$·4$CHCl_3$,[11] which contains two pairs of symmetry-related $CHCl_3$ molecules interacting with the complex via weak H···O_{alk} hydrogen-bonds. One of them, with a shorter H···O distance equal to 2.273 Å, was selected,[12] since it was assumed that one chloroform molecule takes part in the catalytic cycle. Geometries of the $CHCl_3$ solvates of the 16*e* (Mo^{II}) and 17*e* (Mo^{I}) complexes were optimized independently. Bonding energies for the $Mo^{II/I}$ adducts were corrected for basis-set superposition error (BSSE) estimated from the standard counterpoise procedure.[13]

Thermodynamic functions at 298 K were modeled based on the computed electronic energies and harmonic frequencies with aid of standard approximations[14] as implemented in Gaussian and Turbomole. The standard values of thermodynamic functions, calculated with these programs for ideal gas conditions, were corrected for the change of the standard state when passing from the gas to liquid phase (1 atm and 1 mol L^{-1}, respectively). Absolute reduction potentials were calculated from the total free energy of an electron attachment in solution $\Delta G^{EA}_{(sol)}$, as described elsewhere.[15] The absolute potentials were converted to experimentally measured potentials vs. the $Fc^{\bullet+/0}$ couple by subtracting the absolute potential of $Fc^{\bullet+/0}$ (4.84 V).[16] We found that B3LYP/B2 calculations best reproduced the experimental redox potential of the $\{Mo^{II/I}–O_{alk}\}^{0/\bullet-}$ couple (this is presumably because B2 contains a rather diffuse d function for Mo, important in its low +1 oxidation state) and this level was used to calculate the redox potentials reported in this work. However, B3LYP functional (even with very extensive basis set) underestimates the energy of the C−Cl bond in chlorinated compounds, even by 10 kcal·mol^{-1}.[17] Since $CHCl_3$ reduction invariably involves C−Cl dissociation, this problem translates into a comparably large systematic error in the $E°_{CHCl_3/CHCl_2^{\bullet}+Cl^-}$ computed at DFT (and DFT-D) level. Therefore, a reliable value of $E°_{CHCl_3/CHCl_2^{\bullet}+Cl^-}$ in CH_2Cl_2 was obtained here at coupled cluster CCSD(T)/aug-cc-pVTZ level (with Gaussian and PCM solvation model).

Table S1 Key structural parameters for DFT-D optimized geometries of $Mo^{II/I}(NO)(Tp^{Me2})(OMe)_2^{0/\bullet-}$ adducts with $CHCl_3$

	$\{Mo^{II}\}-HCCl_3$		$\{Mo^{I}\}^{\bullet-}-HCCl_3$
Parameter	Calcd	Exptl[a]	Calcd
	Distances (Å)		
$C-H\cdots O_{alk}$	2.160	2.273(3)	1.816
$C_{chl}\cdots O_{alk}$	3.125	3.198(9)	2.911
$C-H\cdots N_{pz}$[b]	2.656	3.091(5)	3.097
$C_{chl}\cdots N_{pz}$[b]	3.526	3.85(1)	3.772
$Mo-O_{alk}$[c]	1.923	1.923(3)	2.045
$Cl\cdots\pi_{pz}$[d]	3.600	3.597	3.426
	Angles (°)		
$C-H\cdots O_{alk}$	147.2	159.0(6)	172.2
$C-H\cdots N_{pz}$[b]	137.0	136.4(6)	120.1
$Mo-O-C$[c]	131.4	127.4(3)	125.9
Mo−N−O	178.2	178.2(5)	175.5

[a] X-ray data from Ref. 11; parameters for the stronger interacting $CHCl_3$ molecule (see Experimental for details). [b] H-bonding with the nearest N atom of the pyrazolyl (pz) ring. [c] Parameters for $Mo-O_{alk}-C$ interacting with $CHCl_3$. [d] Distances to the pz ring centroids.

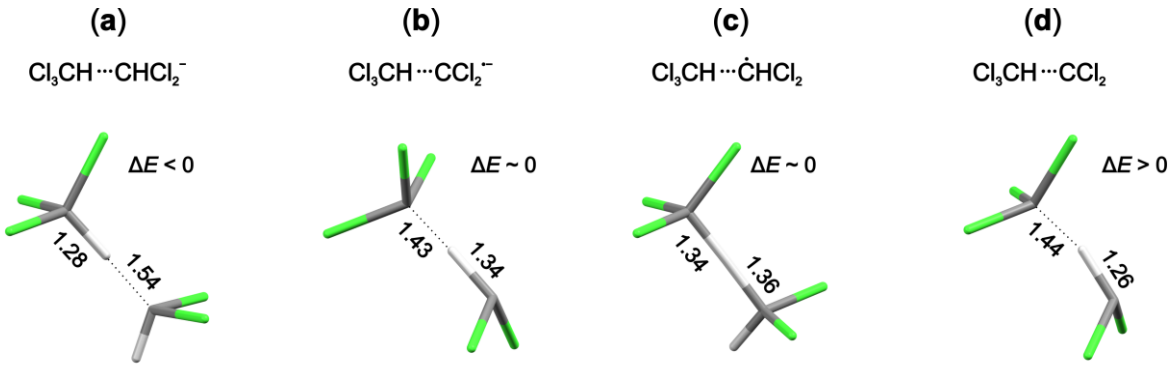

Fig. S1 TS geometries (distances in Å) for the $CHCl_3$ reactions with intermediates considered in the organic loop. The presented images are in accordance with the Hammond–Leffler postulate, i.e., the early (a) and late (d) TS correspond to exothermic and endothermic reactions, respectively, whereas intermediary (b) and (c) TS to virtually thermoneutral processes.

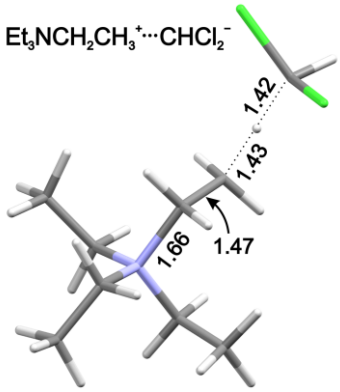

Fig. S2 TS geometry (distances in Å) for the proton transfer from the model molecule Et_4N^+ to $CHCl_2^-$ giving CH_2Cl_2, Et_3N and alkene (the Hoffmann elimination).

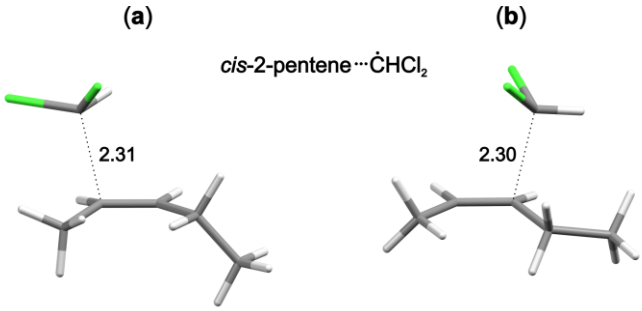

Fig. S3 Transition state geometry (distances in Å) for $CHCl_2^{\bullet}$ radical addition to *cis*-2-pentene yielding much more stable C2 (a) and C3-based (b) radicals.

Detailed description of reaction kinetics simulation

The process was divided into three stages: reduction of {Mo−O_{alk}}, autocatalytic process and electrocatalysis of chloroform reduction by {Mo−O_{alk}}. The process starts with the reduction of {Mo^{II}−O_{alk}} adducts with dichloromethane and chloroform. As mentioned in the main text, competitive binding of the solvent molecules results in a very low concentration of the chloroform adduct. Taking into account the equilibrium constant calculated from DFT results it can be shown that the concentration of {Mo^{I}−O_{alk}}$^{\bullet-}\cdots HCCl_3$ adduct is equal to 1% of [$CHCl_3$]. The comparison of the semiintegral of the {Mo^{II}−O_{alk}} reduction wave with the variation of the concentration of the Mo^{II} species with potential calculated from the Nernst equation demonstrated that the process is quasi-reversible with $\alpha = 0.61$. It was thus assumed that the concentration of {Mo^{I}−O_{alk}}$^{\bullet-}\cdots HCCl_3$ is equal to 0.01 times the concentration of {Mo^{I}−O_{alk}}$^{\bullet-}$ calculated from the Nernst equation with the above given α value. Chloroform reduction by ET from Mo^{I} center and the abstraction of the formed $CHCl_2^{\bullet}$ radical was treated as a single first order reaction with the k_{Mo} rate constant. Next, the radical is reduced at the electrode or by {Mo^{I}−O_{alk}}$^{\bullet-}$ with the pseudo first order rate k_{e1}. Then, the reactions of the organic loop ((6), (8), reduction of :CCl_2 with k_{e2} and (10)) occur. Anions formed in the cycle may abstract protons also from other sources in the reaction mixture, like *n*-Bu_4N^+ cation, above all. Reaction (8), as mentioned in the main text, should attain equilibrium immediately. Reduction processes that may use electrons from the electrode or Mo^{I} species are presented as pseudo first order reactions.

Since the concentration of the base electrolyte was much higher than that of the reactants and possibly other sources of protons may also take part in the process, the reactions are assumed to be pseudo first order. At some point of the reaction the protonation processes result in the removal of all the excess anions and, consequently, the reaction proceeds as ordinary electrocatalysis of chloroform reduction by {Mo−O_{alk}} species. The points in the simulation curve of this third stage (beyond −25 μA) are based on Nicholson's data for electrocatalysis with irreversible charge transfer for k_f/a value of 0.1 (k_f is the rate constant of the charge transfer reaction from the catalyst and $a = Fv/RT$ with v being the scan rate).

Fig. S4 The cross section of the electrode equipped with a small cap used for electrolysis.

Table S2 Optimized Cartesian coordinates (Å) for $Mo^{II}(NO)(Tp^{Me2})(OMe)_2{}^0$ obtained from B3LYP-D3/def2-TZVPP (COSMO:CH_2Cl_2) calculations

C	-1.1219976	-0.4281090	2.6038752
N	-0.7230923	-0.2024747	1.3457868
N	-0.9919063	1.1043965	1.0606518
C	-1.5562515	1.7049127	2.1275332
C	-1.6543894	0.7543058	3.1336941
Mo	0.2065051	-1.5759738	-0.2103744
N	0.9225077	-2.5542470	-1.4817484
O	1.4107158	-3.1854807	-2.3772827
B	-0.6525185	1.6718520	-0.3299703
N	0.8591884	1.5050218	-0.6014501
N	1.4126309	0.2586512	-0.7049440
C	2.7063665	0.4216694	-1.0194749
C	2.9853286	1.7881804	-1.1148570
C	1.7918850	2.4445263	-0.8480042
C	3.6573789	-0.7137371	-1.1944170
C	1.5084175	3.9086510	-0.8239436
C	-1.9712416	3.1379468	2.1391760
C	-0.9932969	-1.7570260	3.2709471
N	-1.1572574	-0.4545177	-1.6079128
C	-1.9013040	-0.8555270	-2.6494194
C	-2.6466352	0.2279298	-3.1237096
C	-2.3107375	1.3079162	-2.3195499
N	-1.4152884	0.8742934	-1.4118764
C	-1.9138035	-2.2575481	-3.1577425
C	-2.7979100	2.7163285	-2.3847549
O	1.4529272	-1.9934699	1.1834582
C	2.4390570	-2.9997086	1.2665668
O	-1.2449726	-2.7397697	0.2420281
C	-1.5012575	-4.0822646	-0.1100388
H	-1.2724714	-4.7300835	0.7424184
H	2.0701305	-3.8177742	1.8938594
H	-1.5848663	-2.5078404	2.7472852
H	0.0418097	-2.0969162	3.2551817
H	-1.3335214	-1.6904664	4.3029807
H	-2.0581083	0.8987364	4.1215120
H	-1.1243748	3.8007594	1.9561764
H	-2.3986695	3.3871102	3.1088003
H	-2.7186646	3.3436135	1.3714900
H	3.2598754	-1.4744063	-1.8644631
H	4.5964386	-0.3473527	-1.6054868
H	3.8704913	-1.1930529	-0.2387503
H	3.9333829	2.2407244	-1.3505558
H	2.4248168	4.4613829	-1.0222273
H	0.7698283	4.1836415	-1.5780520
H	1.1192585	4.2231417	0.1452107
H	-1.9819070	3.4112875	-2.5874592
H	-3.5352090	2.8112834	-3.1797801
H	-3.2616515	3.0216160	-1.4459934
H	-3.3393580	0.2260622	-3.9479446
H	-2.3978810	-2.9257618	-2.4454559
H	-2.4666553	-2.3040684	-4.0943465
H	-0.9067090	-2.6332655	-3.3318191
H	-2.5601243	-4.2049466	-0.3556343
H	-0.9016006	-4.4099720	-0.9637947
H	-0.9517627	2.8204350	-0.3839155
H	2.6998246	-3.4078135	0.2862820
H	3.3423831	-2.5947106	1.7311496

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C	-1.0391149	-0.4041608	2.5522040
N	-0.7005334	-0.1797076	1.2805902
N	-0.9761055	1.1283446	1.0098123
C	-1.4901624	1.7313643	2.1023287
C	-1.5484639	0.7800647	3.1104118
Mo	0.2736129	-1.5217143	-0.3428288
N	0.9925280	-2.3273896	-1.7181022
O	1.4876533	-2.8043452	-2.7444829
B	-0.6554523	1.7060279	-0.3852581
N	0.8634893	1.5779427	-0.6507780
N	1.4621140	0.3505125	-0.6506857
C	2.7607612	0.5361970	-0.9010437
C	3.0073130	1.9085532	-1.0613904
C	1.7817786	2.5376659	-0.8964966
C	3.7172987	-0.6069112	-0.9845406
C	1.4529113	3.9922011	-0.9598637
C	-1.8966232	3.1674826	2.1327576
C	-0.8462345	-1.7319668	3.2055085
N	-1.2515298	-0.4389470	-1.5986079
C	-2.0548972	-0.8484638	-2.5842870
C	-2.7706793	0.2488979	-3.0858807
C	-2.3528760	1.3453553	-2.3469577
N	-1.4363440	0.9083076	-1.4562998
C	-2.1255955	-2.2762717	-3.0111439
C	-2.7833037	2.7707949	-2.4535849
O	1.5677866	-2.0311333	1.1424058
C	1.9104356	-3.3452024	1.4439290
O	-1.1072733	-2.9266265	0.1938824
C	-1.0577782	-4.2660302	-0.1906077
H	-0.2138180	-4.8084890	0.2624149
H	1.0831901	-3.8946264	1.9217075
H	-1.1395047	-2.5312022	2.5259939
H	0.2085447	-1.8891297	3.4361158
H	-1.4252033	-1.7882190	4.1272997
H	-1.9120008	0.9242179	4.1142506
H	-1.0533465	3.8270118	1.9212922
H	-2.2876583	3.4173154	3.1179264
H	-2.6690977	3.3815716	1.3923145
H	3.5162566	-1.2159693	-1.8675613
H	4.7420871	-0.2403178	-1.0362784
H	3.5995875	-1.2568515	-0.1173232
H	3.9525341	2.3813954	-1.2696006
H	2.3558172	4.5624034	-1.1732969
H	0.7203930	4.2042071	-1.7403248
H	1.0358381	4.3508084	-0.0173517
H	-1.9432330	3.4277394	-2.6848842
H	-3.5237035	2.8702713	-3.2459377
H	-3.2267904	3.1272191	-1.5225135
H	-3.4960724	0.2445163	-3.8821992
H	-2.5205666	-2.8963453	-2.2062906
H	-2.7710374	-2.3764477	-3.8830753
H	-1.1353573	-2.6608738	-3.2554992
H	-1.9766179	-4.7888949	0.1167102
H	-0.9610311	-4.3909848	-1.2798999
H	-0.9728933	2.8528819	-0.4301745
H	2.2014189	-3.9230960	0.5515714
H	2.7613031	-3.3728627	2.1425377

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C	-1.1281939	-0.4267270	2.5955441
N	-0.7280875	-0.1984292	1.3364994
N	-1.0080584	1.1063647	1.0500399
C	-1.5745754	1.7026756	2.1167199
C	-1.6681847	0.7518587	3.1226216
Mo	0.1919513	-1.5710350	-0.2280021
N	0.9145286	-2.5592792	-1.4883801
O	1.4107649	-3.2029056	-2.3690921
B	-0.6695552	1.6737521	-0.3399042
N	0.8406727	1.5120757	-0.6159680
N	1.3982858	0.2668084	-0.7210357
C	2.6894350	0.4348995	-1.0474714
C	2.9616310	1.8014881	-1.1449962
C	1.7691222	2.4535485	-0.8671419
C	3.6429884	-0.6963005	-1.2284480
C	1.4880103	3.9159911	-0.8117959
C	-1.9723763	3.1393072	2.1371197
C	-0.9954066	-1.7548859	3.2616626
N	-1.1667990	-0.4562571	-1.6209783
C	-1.9065149	-0.8582989	-2.6657679
C	-2.6559136	0.2225135	-3.1379755
C	-2.3266080	1.3021855	-2.3300192
N	-1.4312684	0.8712815	-1.4214778
C	-1.9077501	-2.2586244	-3.1787208
C	-2.8203933	2.7083049	-2.3933723
O	1.4551925	-1.9517869	1.1709509
C	2.4560943	-2.9419945	1.2806305
O	-1.2443021	-2.7401943	0.2445087
C	-1.5117396	-4.0821760	-0.1033249
H	-1.3031285	-4.7256060	0.7572407
C	2.4005260	0.5591049	2.7742642
Cl	2.0977006	-0.1147892	4.3965189
Cl	1.8977311	2.2644705	2.6882203
Cl	4.1189590	0.3794967	2.3256500
H	2.0918362	-3.7551552	1.9162104
H	-1.6196479	-2.4971573	2.7642273
H	0.0328215	-2.1092238	3.2114104
H	-1.2941278	-1.6779835	4.3055517
H	-2.0636374	0.8970560	4.1134401
H	-1.1099447	3.7894350	1.9813543
H	-2.4157356	3.3833448	3.1007786
H	-2.6986243	3.3672219	1.3559210
H	3.2430003	-1.4610993	-1.8921572
H	4.5764184	-0.3263158	-1.6488090
H	3.8684223	-1.1675487	-0.2721919
H	3.9086960	2.2573738	-1.3772347
H	2.3979582	4.4721003	-1.0291256
H	0.7241234	4.2063213	-1.5338891
H	1.1332141	4.2098531	0.1772078
H	-2.0077715	3.4069922	-2.5967389
H	-3.5592439	2.8004524	-3.1872528
H	-3.2840586	3.0105703	-1.4536375
H	-3.3471894	0.2196696	-3.9633849
H	-2.3756647	-2.9358330	-2.4641031
H	-2.4696165	-2.3086806	-4.1096602
H	-0.8976621	-2.6206656	-3.3650173
H	-2.5683784	-4.1930009	-0.3629027
H	-0.9035255	-4.4217950	-0.9461554
H	-0.9734761	2.8208687	-0.3947258
H	2.7327351	-3.3589911	0.3088483
H	3.3460575	-2.5135223	1.7480018
H	1.8182828	-0.0211247	2.0697155

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C	-1.1112828	-0.3546676	2.5216502
N	-0.7536796	-0.1363322	1.2531870
N	-1.0307862	1.1679093	0.9704902
C	-1.5593100	1.7759351	2.0523402
C	-1.6318954	0.8305790	3.0637907
Mo	0.2435478	-1.4756541	-0.3519150
N	0.9882147	-2.3034018	-1.7004163
O	1.5019097	-2.8052337	-2.7033866
B	-0.7007560	1.7354553	-0.4250062
N	0.8180776	1.6165778	-0.6839616
N	1.4221871	0.3932641	-0.6781373
C	2.7208513	0.5838404	-0.9292891
C	2.9599711	1.9555391	-1.0925556
C	1.7324940	2.5792784	-0.9278042
C	3.6827895	-0.5535248	-1.0180214
C	1.4013470	4.0333854	-0.9705294
C	-1.9483490	3.2163740	2.0754423
C	-0.9312204	-1.6776295	3.1877529
N	-1.2750276	-0.4282209	-1.6231714
C	-2.0747891	-0.8554087	-2.6045965
C	-2.7980085	0.2308137	-3.1183278
C	-2.3888358	1.3386205	-2.3907156
N	-1.4697811	0.9193172	-1.4948485
C	-2.1332738	-2.2892080	-3.0126550
C	-2.8304345	2.7593527	-2.5128764
O	1.5375075	-1.9275217	1.1660527
C	1.9343599	-3.2063291	1.5465854
O	-1.1121659	-2.8968320	0.2014796
C	-1.0143809	-4.2429729	-0.1499194
H	-0.1219214	-4.7298781	0.2723720
C	2.6644207	0.1916504	2.8133416
Cl	2.3892888	-0.3286755	4.5081262
Cl	1.9633386	1.7996869	2.5322916
Cl	4.4178376	0.1920696	2.4489689
H	1.1122320	-3.7780318	2.0030903
H	-1.1566268	-2.4831046	2.4909109
H	0.1044362	-1.8048992	3.5041450
H	-1.5732228	-1.7473366	4.0661568
H	-2.0023270	0.9817417	4.0639577
H	-1.0888630	3.8630022	1.8894173
H	-2.3612189	3.4696592	3.0507607
H	-2.6965761	3.4454403	1.3150551
H	3.4869085	-1.1577590	-1.9053041
H	4.7048608	-0.1795680	-1.0632092
H	3.5746397	-1.2057384	-0.1528494
H	3.9050299	2.4327208	-1.2904647
H	2.3003665	4.6074766	-1.1898814
H	0.6557921	4.2559638	-1.7353448
H	0.9997623	4.3783222	-0.0158851
H	-1.9948039	3.4204964	-2.7479590
H	-3.5692166	2.8451011	-3.3083160
H	-3.2794996	3.1212159	-1.5865976
H	-3.5227678	0.2125528	-3.9149776
H	-2.5194360	-2.9022251	-2.1979562
H	-2.7801715	-2.4073737	-3.8811511
H	-1.1400698	-2.6677420	-3.2548677
H	-1.8887840	-4.8009927	0.2182615
H	-0.9668001	-4.3933553	-1.2394352
H	-1.0279172	2.8789025	-0.4843088
H	2.3077880	-3.7991763	0.6974141
H	2.7432785	-3.1482226	2.2902766
H	2.1809618	-0.5452283	2.1533237

Table S6 Optimized Cartesian coordinates (Å) for $Mo^{I}(NO)(Tp^{Me2})(OMe)_2^{\bullet-}\cdots HCCl_3$ adduct with C−Cl bond elongated to 2.20 Å, obtained from B3LYP-D3/def2-TZVPP (COSMO:CH_2Cl_2) calculations

C	-2.6512046	0.1836340	0.5849516
N	-1.5085584	0.2940279	-0.0977832
N	-1.3243113	1.6161420	-0.3721418
C	-2.3447885	2.3423025	0.1294526
C	-3.2166776	1.4585212	0.7454041
Mo	0.0676132	-1.2550472	-0.7924233
N	1.3767561	-2.2421070	-1.4023300
O	2.3406363	-2.8515507	-1.8696562
B	-0.0593950	2.0704387	-1.1250837
N	1.1939988	1.6559826	-0.3195604
N	1.4407587	0.3402447	-0.0605960
C	2.5841400	0.2715889	0.6286473
C	3.0761942	1.5684380	0.8291955
C	2.1698961	2.4201486	0.2152266
C	3.1729842	-1.0331984	1.0501667
C	2.1836264	3.9094191	0.1298528
C	-2.4290156	3.8272137	0.0087018
C	-3.1593797	-1.1243536	1.0916054
N	-0.0328929	0.0229456	-2.6233891
C	-0.0442229	-0.2726720	-3.9262973
C	-0.0483012	0.9158871	-4.6702370
C	-0.0396228	1.9461673	-3.7416218
N	-0.0292786	1.3857328	-2.5135427
C	-0.0648472	-1.6800223	-4.4202485
C	-0.0419369	3.4207773	-3.9713459
O	-0.0648145	-1.9025201	1.1470988
C	-0.2709931	-3.2214195	1.5492983
O	-1.5145662	-2.3765062	-1.4107539
C	-1.4246834	-3.7238637	-1.7605827
H	-1.1388631	-4.3653729	-0.9134012
H	-1.2635087	-3.5921633	1.2559313
H	-2.9109251	-1.9213873	0.3937603
H	-2.6931069	-1.3623891	2.0485757
H	-4.2390575	-1.0779232	1.2366392
H	-4.1353069	1.7047148	1.2512073
H	-2.4254717	4.1480786	-1.0341784
H	-1.5853156	4.3156077	0.4997336
H	-3.3470139	4.1823606	0.4741506
H	3.5477022	-1.5846991	0.1864732
H	3.9935591	-0.8690023	1.7468223
H	2.4152790	-1.6560641	1.5234850
H	3.9700807	1.8508488	1.3593039
H	3.0703653	4.2967649	0.6289342
H	2.1931205	4.2540483	-0.9053583
H	1.3037940	4.3442945	0.6074025
H	0.8317836	3.8976316	-3.5244294
H	-0.0340422	3.6238397	-5.0410164
H	-0.9254984	3.8930953	-3.5388271
H	-0.0559481	1.0127547	-5.7429645
H	-0.9892691	-2.1750030	-4.1222874
H	0.0115636	-1.6988013	-5.5064995
H	0.7579507	-2.2560636	-3.9964855
H	-2.3947016	-4.0905020	-2.1277662
H	-0.6848213	-3.9042916	-2.5546194
H	-0.0712824	3.2523360	-1.2613662
H	0.4740440	-3.9075387	1.1193198
H	-0.2054399	-3.2981028	2.6436349
H	0.0111830	-0.7281393	2.4208338
C	0.1732667	0.0102929	3.2333932
Cl	-1.4619223	-0.6365681	4.5554089
Cl	-0.1469191	1.6430494	2.8072379
Cl	1.6320868	-0.2362843	4.1281461

Table S7 Optimized Cartesian coordinates (Å) for $Mo^{II}(NO)(Tp^{Me2})(OMe)_2\cdots HCCl_3^{\bullet-}$ adduct with the C−Cl bond elongated to 2.20 Å, obtained from B3LYP-D3/def2-TZVPP ($COSMO:CH_2Cl_2$) calculations

C	-2.6430938	0.0275138	0.6889972
N	-1.5233899	0.2307115	-0.0167521
N	-1.3174432	1.5778623	-0.0781322
C	-2.2964238	2.2248864	0.5833723
C	-3.1665838	1.2666026	1.0780985
Mo	-0.0530929	-1.2255057	-0.9518953
N	1.1408646	-2.2754704	-1.6973999
O	1.9769049	-2.9582283	-2.2270513
B	-0.0730772	2.1281882	-0.7876915
N	1.2036238	1.5597511	-0.1348662
N	1.4743876	0.2203601	-0.1856496
C	2.6829571	0.0364622	0.3676552
C	3.1884295	1.2709779	0.7785728
C	2.2253030	2.2119787	0.4475723
C	3.3181690	-1.3010067	0.5363817
C	2.2249096	3.6816362	0.6909941
C	-2.3304095	3.7055460	0.7478295
C	-3.1645555	-1.3294291	1.0217714
N	0.0166960	0.3421436	-2.5813936
C	0.0641976	0.2499491	-3.9173720
C	-0.0019212	1.5340913	-4.4676085
C	-0.0872192	2.4076429	-3.3920737
N	-0.0776297	1.6680655	-2.2675439
C	0.1406855	-1.0496216	-4.6452427
C	-0.1674065	3.8972238	-3.3918335
O	-0.1504960	-2.0516039	0.7541980
C	0.3855338	-3.2326374	1.3020892
O	-1.6114745	-1.9564528	-1.8133168
C	-1.7679986	-3.1538421	-2.5410488
H	-2.1947276	-3.9254662	-1.8910966
H	-0.4227567	-3.9545597	1.4536377
H	-3.0050902	-2.0247798	0.2009349
H	-2.6481639	-1.7107639	1.9040772
H	-4.2296280	-1.2731259	1.2461468
H	-4.0510776	1.4404243	1.6669531
H	-2.2820175	4.2235032	-0.2105740
H	-1.4853095	4.0446195	1.3498593
H	-3.2491974	3.9982386	1.2531771
H	3.3212898	-1.8727244	-0.3897441
H	4.3470540	-1.1761456	0.8698358
H	2.7894300	-1.8799504	1.2922161
H	4.1243812	1.4521763	1.2783404
H	3.1688990	3.9781655	1.1448698
H	2.0911770	4.2463108	-0.2321199
H	1.4150523	3.9560356	1.3689814
H	0.6905601	4.3415036	-2.8852598
H	-0.1887878	4.2626834	-4.4169645
H	-1.0646564	4.2489230	-2.8810012
H	0.0137753	1.7938756	-5.5124917
H	-0.8156849	-1.5719532	-4.6092526
H	0.3895774	-0.8728983	-5.6903639
H	0.8931390	-1.7095448	-4.2167980
H	-2.4571172	-2.9928578	-3.3756096
H	-0.8200259	-3.5269912	-2.9385730
H	-0.0639528	3.3147335	-0.7340568
H	1.1411879	-3.6819745	0.6512494
H	0.8302760	-3.0085481	2.2740570
H	-0.2323079	-0.3349818	2.3924453
C	0.0133333	0.0217349	3.3859216
Cl	-1.5535428	-1.1097013	4.4369914
Cl	0.0118960	1.8856239	3.2524255
Cl	1.6916742	-0.5906027	3.7454701

Table S8 Optimized Cartesian coordinates (Å) for $Mo^{I}(NO)(Tp^{Me2})(OMe)_2^{\bullet-}\cdots H_2CCl_2$ adduct obtained from B3LYP-D3/def2-TZVPP (COSMO:CH_2Cl_2) calculations

C	-1.1173236	-0.3574875	2.5304009
N	-0.7607515	-0.1446471	1.2613028
N	-1.0743295	1.1477569	0.9621995
C	-1.6331771	1.7503390	2.0315915
C	-1.6855256	0.8146287	3.0529936
Mo	0.2154819	-1.5026698	-0.3466915
N	0.9538357	-2.3260836	-1.7014767
O	1.4719618	-2.8157703	-2.7098394
B	-0.7110048	1.7196433	-0.4224334
N	0.8158250	1.5909057	-0.6425709
N	1.4113902	0.3629731	-0.6489288
C	2.7203987	0.5513447	-0.8398167
C	2.9758994	1.9258763	-0.9482744
C	1.7455756	2.5534108	-0.8154434
C	3.6796311	-0.5905355	-0.9042591
C	1.4271527	4.0106826	-0.8216729
C	-2.0626925	3.1793534	2.0358751
C	-0.8737976	-1.6577939	3.2207057
N	-1.2886907	-0.4358724	-1.6273317
C	-2.0780094	-0.8558783	-2.6201927
C	-2.7718428	0.2393701	-3.1551511
C	-2.3559041	1.3450997	-2.4282542
N	-1.4609726	0.9155511	-1.5128205
C	-2.1539006	-2.2911258	-3.0204849
C	-2.7703821	2.7723067	-2.5677659
O	1.4954326	-1.9781733	1.1625433
C	1.8777824	-3.2601942	1.5386159
O	-1.1631482	-2.9022944	0.2024401
C	-1.0831538	-4.2508157	-0.1437162
H	-0.2106141	-4.7537181	0.3005640
C	2.7738531	0.3925077	2.5288202
Cl	3.3088910	-0.2985695	4.1051210
Cl	1.8311901	1.8956177	2.7438291
H	3.6634456	0.6399290	1.9638947
H	1.0560914	-3.8192014	2.0138145
H	-1.0770604	-2.4880723	2.5458649
H	0.1738747	-1.7354850	3.5164477
H	-1.4979495	-1.7364347	4.1111153
H	-2.0668158	0.9662729	4.0490614
H	-1.2158353	3.8481700	1.8704552
H	-2.5092691	3.4260722	2.9979314
H	-2.7954332	3.3844253	1.2538447
H	3.4781361	-1.2190108	-1.7732785
H	4.7030467	-0.2219095	-0.9655029
H	3.5690891	-1.2249313	-0.0242393
H	3.9308444	2.4017125	-1.0963245
H	2.3367561	4.5838714	-0.9945582
H	0.7070303	4.2644422	-1.6010574
H	0.9996934	4.3257600	0.1320248
H	-1.9184888	3.4179092	-2.7872641
H	-3.4896319	2.8658382	-3.3800378
H	-3.2342950	3.1469566	-1.6538067
H	-3.4820654	0.2281646	-3.9649309
H	-2.5450444	-2.8952129	-2.2016086
H	-2.8037282	-2.4066133	-3.8872041
H	-1.1654106	-2.6819428	-3.2630478
H	-1.9765675	-4.7913350	0.2046891
H	-1.0129346	-4.4042822	-1.2315529
H	-1.0271733	2.8656719	-0.4842178
H	2.2237866	-3.8649275	0.6848762
H	2.7011916	-3.2140295	2.2670238
H	2.1583866	-0.3631562	2.0400496

Table S9 Optimized Cartesian coordinates (Å) for $Mo^{II}(NO)(Tp^{Me2})(OMe)_2\cdots HCCl_2^{\bullet}$ adduct obtained from B3LYP-D3/def2-TZVPP (COSMO:CH_2Cl_2) calculations

C	-1.1348525	-0.5052500	2.5995472
N	-0.7466004	-0.2620627	1.3400203
N	-1.0161832	1.0493574	1.0768165
C	-1.5669642	1.6348425	2.1575323
C	-1.6603525	0.6696051	3.1498685
Mo	0.1762455	-1.6115097	-0.2438141
N	0.9008315	-2.5768150	-1.5201670
O	1.3985642	-3.2029692	-2.4131985
B	-0.6676731	1.6396774	-0.3016307
N	0.8434477	1.4721913	-0.5700709
N	1.3926584	0.2260141	-0.7015664
C	2.6896563	0.3921595	-1.0033605
C	2.9744122	1.7586797	-1.0586837
C	1.7829879	2.4128442	-0.7812179
C	3.6394173	-0.7403160	-1.1956031
C	1.5113124	3.8756487	-0.6952109
C	-1.9514742	3.0744447	2.2031349
C	-0.9921349	-1.8408550	3.2495733
N	-1.1729802	-0.4619994	-1.6234104
C	-1.9137682	-0.8407815	-2.6757738
C	-2.6557177	0.2530891	-3.1300767
C	-2.3209641	1.3160669	-2.3027235
N	-1.4293103	0.8632449	-1.4009055
C	-1.9244260	-2.2321994	-3.2124573
C	-2.8060623	2.7261147	-2.3412483
O	1.4164413	-2.0369960	1.1569411
C	2.4237333	-3.0211454	1.2497457
O	-1.2771896	-2.7791847	0.1883437
C	-1.5415409	-4.1143513	-0.1867500
H	-1.3250534	-4.7765503	0.6576813
H	2.0682676	-3.8440600	1.8780002
H	-1.5356490	-2.6013243	2.6895382
H	0.0535490	-2.1472362	3.2734574
H	-1.3760157	-1.8024779	4.2675172
H	-2.0497726	0.8021477	4.1449294
H	-1.0834136	3.7184941	2.0537508
H	-2.3878247	3.3069342	3.1728549
H	-2.6791957	3.3216865	1.4292806
H	3.2359172	-1.5003319	-1.8623305
H	4.5726139	-0.3699777	-1.6163019
H	3.8668558	-1.2173122	-0.2424901
H	3.9282435	2.2127775	-1.2653006
H	2.4292086	4.4296528	-0.8823854
H	0.7630886	4.1888949	-1.4241624
H	1.1412712	4.1476565	0.2942258
H	-1.9886250	3.4235561	-2.5292824
H	-3.5420477	2.8375353	-3.1352982
H	-3.2706153	3.0136316	-1.3972901
H	-3.3455568	0.2692960	-3.9565652
H	-2.4113622	-2.9149583	-2.5160140
H	-2.4733003	-2.2597866	-4.1520840
H	-0.9163609	-2.6039638	-3.3899096
H	-2.5992581	-4.2239762	-0.4427436
H	-0.9373761	-4.4335059	-1.0404906
H	-0.9628399	2.7898210	-0.3364646
H	2.6982029	-3.4257134	0.2720142
H	3.3134896	-2.5920339	1.7175310
C	2.4272775	0.6497400	2.6121641
Cl	1.8995808	2.2696576	2.7538461
Cl	4.0956808	0.3452025	2.3746860
H	1.7401292	-0.0811117	2.2125032

Table S10 Optimized Cartesian coordinates (Å) for $Mo^{I}(NO)(Tp^{Me2})(OMe)_2^{\bullet-}\cdots HCCl_2^{\bullet}$ (in triplet state) adduct obtained from B3LYP-D3/def2-TZVPP (COSMO:CH_2Cl_2) calculations

C	-1.0762210	-0.4372032	2.5361585
N	-0.7321820	-0.1984675	1.2682355
N	-1.0343352	1.1036879	1.0029884
C	-1.5716856	1.6881771	2.0932134
C	-1.6218506	0.7296684	3.0937878
Mo	0.2268382	-1.5233051	-0.3771873
N	0.9455832	-2.3263829	-1.7541405
O	1.4450560	-2.8052753	-2.7762813
B	-0.6897816	1.7007852	-0.3765711
N	0.8310746	1.5718635	-0.6234152
N	1.4218061	0.3421152	-0.6631665
C	2.7272153	0.5288166	-0.8788003
C	2.9852145	1.9036890	-0.9713919
C	1.7614997	2.5337772	-0.8017066
C	3.6798298	-0.6141979	-0.9881136
C	1.4486109	3.9920538	-0.7779620
C	-1.9869420	3.1208810	2.1346809
C	-0.8442477	-1.7577953	3.1905838
N	-1.2904998	-0.4296775	-1.6163069
C	-2.0962780	-0.8274907	-2.6051812
C	-2.7984166	0.2792752	-3.1042431
C	-2.3702080	1.3685810	-2.3599680
N	-1.4604733	0.9190217	-1.4691501
C	-2.1800204	-2.2534873	-3.0356912
C	-2.7864442	2.7986054	-2.4611059
O	1.5232546	-2.0348604	1.1116294
C	1.9089961	-3.3260489	1.4512564
O	-1.1435592	-2.9357244	0.1652874
C	-1.0741130	-4.2748676	-0.2182734
H	-0.1885554	-4.7886868	0.1862257
H	1.0892765	-3.8997954	1.9112434
H	-1.0596248	-2.5668073	2.4942355
H	0.2038599	-1.8559793	3.4790863
H	-1.4645331	-1.8530797	4.0819978
H	-1.9907460	0.8620750	4.0972301
H	-1.1377714	3.7853189	1.9643562
H	-2.4113039	3.3524439	3.1104926
H	-2.7335852	3.3478263	1.3721511
H	3.4602421	-1.2196917	-1.8688579
H	4.7029521	-0.2467822	-1.0560929
H	3.5850877	-1.2645173	-0.1192905
H	3.9394678	2.3780362	-1.1273235
H	2.3565076	4.5645755	-0.9618603
H	0.7122539	4.2606148	-1.5368001
H	1.0438804	4.2945594	0.1897387
H	-1.9380242	3.4490716	-2.6798170
H	-3.5183222	2.9103240	-3.2596859
H	-3.2354566	3.1527494	-1.5317787
H	-3.5220488	0.2859547	-3.9021232
H	-2.5666014	-2.8740907	-2.2270549
H	-2.8376018	-2.3479454	-3.8990859
H	-1.1950736	-2.6421637	-3.2947598
H	-1.9567347	-4.8247876	0.1427042
H	-1.0364848	-4.4007276	-1.3112947
H	-1.0041722	2.8487474	-0.4108181
H	2.2567974	-3.9046590	0.5809524
H	2.7346390	-3.2985197	2.1791464
C	2.7216610	0.2567569	2.5777353
Cl	1.9084008	1.7605310	2.7012161
Cl	4.4427930	0.2848173	2.4820576
H	2.2117228	-0.5724744	2.0754302

Table S11 Optimized Cartesian coordinates (Å) for $Mo^{I}(NO)(Tp^{Me2})(OMe)_2^{\bullet-}\cdots HOCH_3$ adduct obtained from B3LYP-D3/def2-TZVPP (COSMO:CH_2Cl_2) calculations

C	0.4043064	-1.3821840	-2.5013509
N	0.0035337	-0.7114358	-1.4185699
N	-1.3204139	-0.9835043	-1.2369147
C	-1.7608294	-1.8159000	-2.2034281
C	-0.6850257	-2.0896648	-3.0348602
Mo	1.1050148	0.6702438	0.0752877
N	1.7388866	1.7285823	1.3158460
O	2.0950379	2.4735879	2.2305519
B	-2.0700631	-0.3764490	-0.0324515
N	-1.3951128	-0.8430493	1.2787254
N	-0.0884684	-0.5372713	1.5277642
C	0.2272618	-1.0556874	2.7177901
C	-0.8959474	-1.7086175	3.2466860
C	-1.9049360	-1.5546116	2.3067179
C	1.5966181	-0.9289426	3.2968906
C	-3.3096418	-2.0570974	2.3417132
C	-3.1665340	-2.3111522	-2.2826337
C	1.8209148	-1.3741847	-2.9693615
N	-0.8029815	1.8181223	-0.1472943
C	-1.0587841	3.1256198	-0.2509447
C	-2.4463952	3.3236067	-0.2962740
C	-3.0142316	2.0608845	-0.2138531
N	-2.0055839	1.1674608	-0.1246209
C	0.0282514	4.1450178	-0.3157293
C	-4.4563269	1.6758775	-0.2152532
O	2.4981768	-0.8363199	0.0954381
C	3.8728081	-0.6460193	-0.0510650
O	1.9044820	1.5679707	-1.5717861
C	2.9893982	2.4443634	-1.5364054
H	3.9244261	1.9516243	-1.2290034
H	4.1424925	-0.3434229	-1.0734895
H	2.2599513	-0.3873560	-2.8323766
H	2.4100287	-2.0787918	-2.3795740
H	1.8743404	-1.6654342	-4.0186676
H	-0.6864454	-2.7246491	-3.9050860
H	-3.8782750	-1.4888714	-2.3740051
H	-3.4398324	-2.8798257	-1.3920427
H	-3.2790787	-2.9596395	-3.1500059
H	1.8479386	0.1165118	3.4821881
H	1.6615108	-1.4794362	4.2346359
H	2.3354517	-1.3164487	2.5947231
H	-0.9628411	-2.2324612	4.1854538
H	-3.4804565	-2.6018156	3.2689804
H	-4.0309019	-1.2398590	2.2855734
H	-3.5147841	-2.7289696	1.5066032
H	-4.7288243	1.1392295	0.6950141
H	-5.0730554	2.5707436	-0.2831208
H	-4.6977175	1.0271292	-1.0586950
H	-2.9680344	4.2625463	-0.3770966
H	0.6188041	4.0160815	-1.2229294
H	-0.3956906	5.1484199	-0.3098168
H	0.7104636	4.0427964	0.5284803
H	3.1669809	2.8763356	-2.5328208
H	2.8329784	3.2823097	-0.8405948
H	-3.2067149	-0.7303281	-0.0435695
H	4.2587966	0.1274485	0.6289598
H	4.4110878	-1.5795959	0.1664505
H	0.4901687	-4.8149008	0.3069968
C	0.6002822	-3.7294019	0.2493130
H	0.0631219	-3.3779203	-0.6365498
H	0.1231420	-3.2893942	1.1300716
O	1.9854249	-3.4304459	0.1868107
H	2.1071990	-2.4438942	0.1477889

Table S12 Optimized Cartesian coordinates (Å) for $Mo^{I}(NO)(Tp^{Me2})(OMe)_2^{\bullet-}\cdots H_3CCH_2{=}CHCHCH_3$ adduct obtained from B3LYP-D3/def2-TZVPP (COSMO:CH_2Cl_2) calculations

C	0.9660901	-0.5784982	2.4552474
N	0.3771996	0.0043819	1.4087962
N	1.1374072	1.0832361	1.0634640
C	2.2031856	1.1836989	1.8853747
C	2.1209126	0.1424839	2.7971568
Mo	-1.4349490	-0.6130524	0.0937149
N	-2.7541945	-0.8622086	-1.0260153
O	-3.6558306	-0.9481374	-1.8681658
B	0.7547196	1.9214992	-0.1736703
N	0.8127055	1.0217865	-1.4311277
N	0.0028302	-0.0729720	-1.5322548
C	0.2920453	-0.6828697	-2.6843756
C	1.3105768	0.0268411	-3.3371288
C	1.6196620	1.0972098	-2.5108839
C	-0.4027397	-1.9333247	-3.1081197
C	2.6614119	2.1502069	-2.6851178
C	3.2526515	2.2337624	1.7421015
C	0.4435702	-1.8359083	3.0635359
N	-1.7389104	1.6183306	0.1843900
C	-2.8342292	2.3692290	0.3266420
C	-2.4818012	3.7245797	0.2424847
C	-1.1098992	3.7486821	0.0406893
N	-0.6820612	2.4678900	0.0083565
C	-4.1823039	1.7702323	0.5509164
C	-0.2040738	4.9243345	-0.1206619
O	-0.5823823	-2.4503924	0.1450184
C	-1.2510306	-3.6317890	0.4249677
O	-2.4304677	-0.8788978	1.8598453
C	-3.6537357	-1.5377423	1.9669730
H	-3.5925773	-2.6000802	1.6845347
H	-1.5583112	-3.7036966	1.4817870
H	-0.6445201	-1.8141713	3.1034501
H	0.7176780	-2.6869734	2.4378963
H	0.8564626	-1.9770182	4.0628822
H	2.8158957	-0.0766563	3.5901737
H	2.8258700	3.2371107	1.7356608
H	3.8066238	2.1032626	0.8104333
H	3.9574162	2.1633930	2.5690604
H	-1.4660237	-1.7522890	-3.2742261
H	0.0384406	-2.3176560	-4.0270455
H	-0.3238960	-2.6815390	-2.3192563
H	1.7731305	-0.2151321	-4.2793730
H	3.1558446	2.0202364	-3.6466952
H	2.2359863	3.1539523	-2.6485585
H	3.4178611	2.0838835	-1.9005818
H	0.3144489	4.9028635	-1.0805671
H	-0.7855468	5.8434047	-0.0653769
H	0.5587487	4.9543719	0.6595106
H	-3.1388683	4.5749003	0.3171676
H	-4.2123485	1.2446782	1.5055261
H	-4.9450037	2.5483691	0.5517988
H	-4.4192689	1.0406055	-0.2235504
H	-4.0214860	-1.5029895	3.0043796
H	-4.4333299	-1.0899773	1.3309933
H	1.5157038	2.8284486	-0.2993944
H	-2.1653850	-3.7602135	-0.1787721
H	-0.6009567	-4.4982052	0.2207499
H	3.0866874	-1.9488499	0.7690538
C	2.9051871	-1.7119592	-0.2790786
C	4.0417704	-0.9334933	-0.8676046
C	5.1357323	-0.4737919	-0.2578198
H	3.9282430	-0.7112503	-1.9258875
C	2.5834530	-2.9920385	-1.0561682
C	5.5090115	-0.6305861	1.1869835

H	5.8470885	0.0889450	-0.8575315
H	2.0108191	-1.0907263	-0.2900561
H	4.7625334	-1.1823636	1.7546714
H	5.6267235	0.3473296	1.6624897
H	6.4695734	-1.1450542	1.2879580
H	1.6602115	-3.4254505	-0.6710977
H	3.3926675	-3.7230544	-0.9813600
H	2.4254805	-2.7696172	-2.1139953

Table S13 Optimized Cartesian coordinates (Å) for $Cl_3CH\cdots CHCl_2^-$ transition state geometry obtained from B3LYP/B1 (PCM:CH_2Cl_2) calculations

C	2.687996	-0.330194	2.792086
Cl	4.477108	-0.344989	2.417360
Cl	2.447324	-0.886532	4.512786
Cl	2.081375	1.387557	2.643186
H	2.062784	-1.083838	1.961782
C	1.327544	-1.966151	0.935561
Cl	2.071413	-3.677423	0.867314
Cl	-0.482981	-2.136095	1.355950
H	1.292330	-1.689179	-0.123190

Table S14 Optimized Cartesian coordinates (Å) for $Cl_3CH\cdots CCl_2^{\bullet-}$ transition state geometry obtained from B3LYP/B1 (PCM:CH_2Cl_2) calculations

C	-0.160099	0.370803	-0.151890
Cl	-0.304091	0.078041	1.629401
Cl	1.571610	0.260873	-0.668628
C	-1.479205	2.633656	-1.051359
H	-0.813262	1.450033	-0.599955
Cl	-3.193554	2.690949	-0.388453
Cl	-0.630446	4.181441	-0.548861
Cl	-1.590590	2.622894	-2.886945

Table S15 Optimized Cartesian coordinates (Å) for $Cl_3CH\cdots CHCl_2^{\bullet}$ transition state geometry obtained from B3LYP/B1 (PCM:CH_2Cl_2) calculations

C	2.659443	-0.366226	2.736747
Cl	4.321539	-0.276896	2.128788
Cl	2.554980	-1.130859	4.329388
Cl	1.826480	1.195588	2.672198
H	2.001119	-1.174414	1.893534
C	1.356280	-1.979748	1.012088
Cl	1.984930	-3.605771	1.250133
Cl	-0.368260	-1.794634	1.308756
H	1.628380	-1.593887	0.031201

Table S16 Optimized Cartesian coordinates (Å) for $Cl_3CH\cdots{:}CCl_2$ transition state geometry obtained from B3LYP/B1 (PCM:CH_2Cl_2) calculations

C	0.143287	0.107907	-0.108515
Cl	-0.564167	-0.525342	1.336949
Cl	1.799947	0.574188	0.059521
C	-1.258722	2.235285	-0.930560
H	-0.557087	1.009962	-0.639622
Cl	-2.638130	2.355706	0.166422
Cl	-0.147586	3.600828	-0.790385
Cl	-1.738732	1.909222	-2.605124

Table S17 Optimized Cartesian coordinates (Å) for $Et_3NCH_2CH_3^{+}\cdots CHCl_2^{-}$ transition state geometry obtained from B3LYP/B1 (PCM:CH_2Cl_2) calculations

N	2.054614	5.242801	-1.948959
C	0.949873	5.380973	-2.966319
H	0.500720	6.361460	-2.800745
H	1.434144	5.417996	-3.943413
C	-0.118744	4.293201	-2.939453
H	0.287762	3.300363	-3.147303
H	-0.850740	4.518345	-3.720307
H	-0.654743	4.256846	-1.987991
C	2.827337	3.950310	-2.104759
H	3.647754	4.024282	-1.388281
H	2.170382	3.141589	-1.777048
C	3.372293	3.655929	-3.497345
H	2.585008	3.513395	-4.241274
H	3.936096	2.720572	-3.437479
H	4.057986	4.427488	-3.853292
C	1.536387	5.268062	-0.526716
H	2.429089	5.234107	0.100657
H	0.983587	4.339338	-0.369309
C	0.676186	6.466867	-0.144744
H	1.205459	7.415709	-0.253583
H	0.413665	6.358270	0.911522
H	-0.258916	6.518719	-0.707414
C	3.087488	6.521195	-2.172081
H	3.351589	6.396220	-3.223549
H	2.397969	7.362866	-2.091766
C	4.255558	6.639461	-1.290576
H	4.008346	6.806341	-0.236723
H	4.977592	7.806333	-1.680016
H	4.977632	5.821929	-1.388971
H	6.482478	9.371250	-1.351958
C	5.721232	8.967316	-2.027069
Cl	6.653944	8.692284	-3.608159
Cl	4.551472	10.392253	-2.252416

Table S18 Optimized Cartesian coordinates (Å) for *cis*-2-pentene···$CHCl_2^{\bullet}$ (C2-based radical) transition state geometry obtained from B3LYP/B1 (PCM:CH_2Cl_2) calculations

C	-0.089607	0.601307	0.562279
C	0.732921	-0.070804	-0.496990
C	-1.445289	0.805350	0.562825
H	-1.837337	1.442353	1.353729
C	-2.349846	0.644886	-0.634410
H	1.159448	-0.997496	-0.084060
C	1.890886	0.817516	-0.990232
H	0.111076	-0.369264	-1.346045
H	-3.387892	0.500000	-0.324369
H	-2.063894	-0.199263	-1.265881
H	-2.318160	1.550469	-1.252841
H	1.513621	1.730907	-1.460798
H	2.503654	0.284471	-1.723926
H	2.541684	1.113616	-0.160458
C	-2.193993	-0.950506	1.855222
H	0.461932	0.915193	1.449163
Cl	-3.848276	-0.604342	2.376283
H	-1.505149	-0.893640	2.691365
Cl	-2.008209	-2.467633	0.977477

Table S19 Optimized Cartesian coordinates (Å) for *cis*-2-pentene···$CHCl_2^{\bullet}$ (C3-based radical) transition state geometry obtained from B3LYP/B1 (PCM:CH_2Cl_2) calculations

C	-0.217804	0.790568	0.380203
C	0.655439	0.296962	-0.762630
C	-1.586387	0.862559	0.322995
H	-2.098861	1.370481	1.138179
C	-2.462553	0.215418	-0.702700
H	0.523234	-0.782614	-0.903504
C	2.141929	0.620202	-0.577008
H	0.308046	0.759645	-1.695495
H	-3.069168	-0.581886	-0.251073
H	-1.895982	-0.223070	-1.527232
H	-3.172600	0.940227	-1.121550
H	2.300446	1.700097	-0.484945
H	2.727769	0.267802	-1.431149
H	2.553170	0.149251	0.322023
C	0.167671	-0.867846	1.918639
H	0.272768	1.442895	1.101250
Cl	-0.407187	-0.308875	3.489308
H	1.252068	-0.916964	1.896185
Cl	-0.546037	-2.385603	1.377224

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