

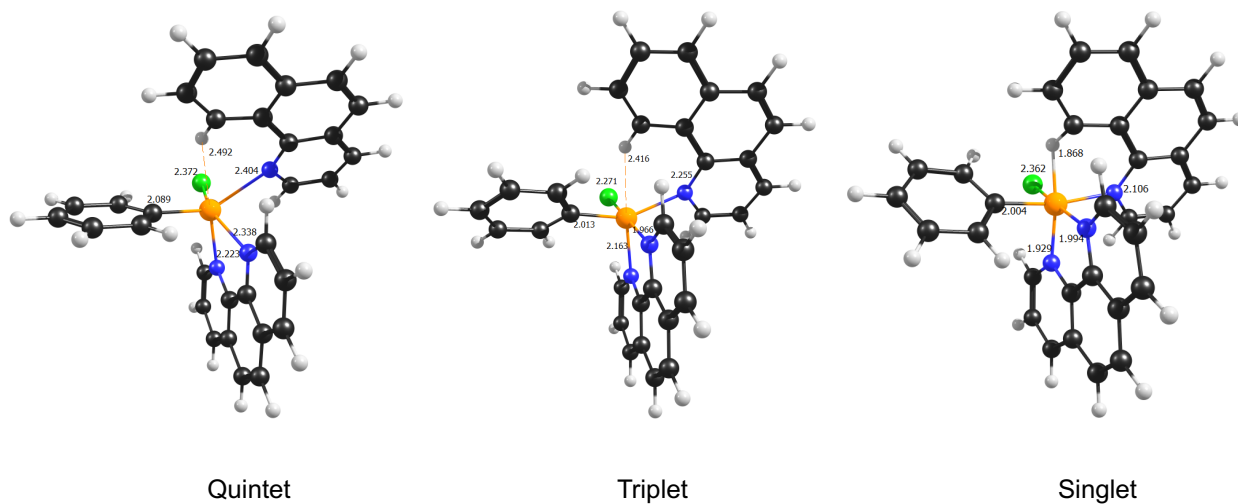
Role of Intermediate Triplet State in Iron-Catalyzed Multi-State C-H Activation

Electronic supplementary information

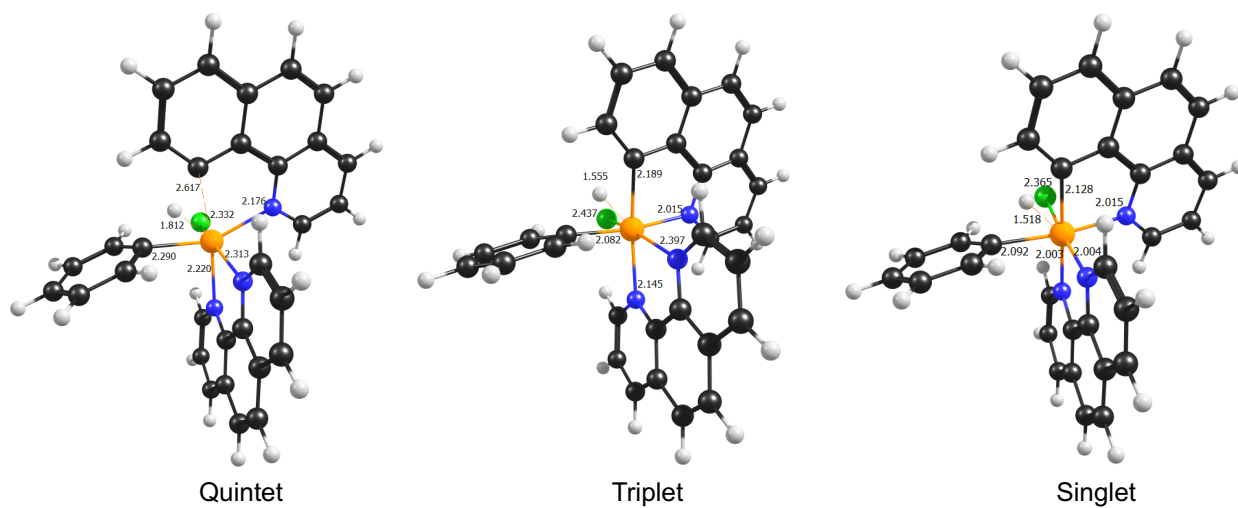
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(a) Reactants



(b) TSs

Figure S1. Bond distances (Å) between the iron center and the coordinated atoms in (a) reactant and (b) TS geometries.

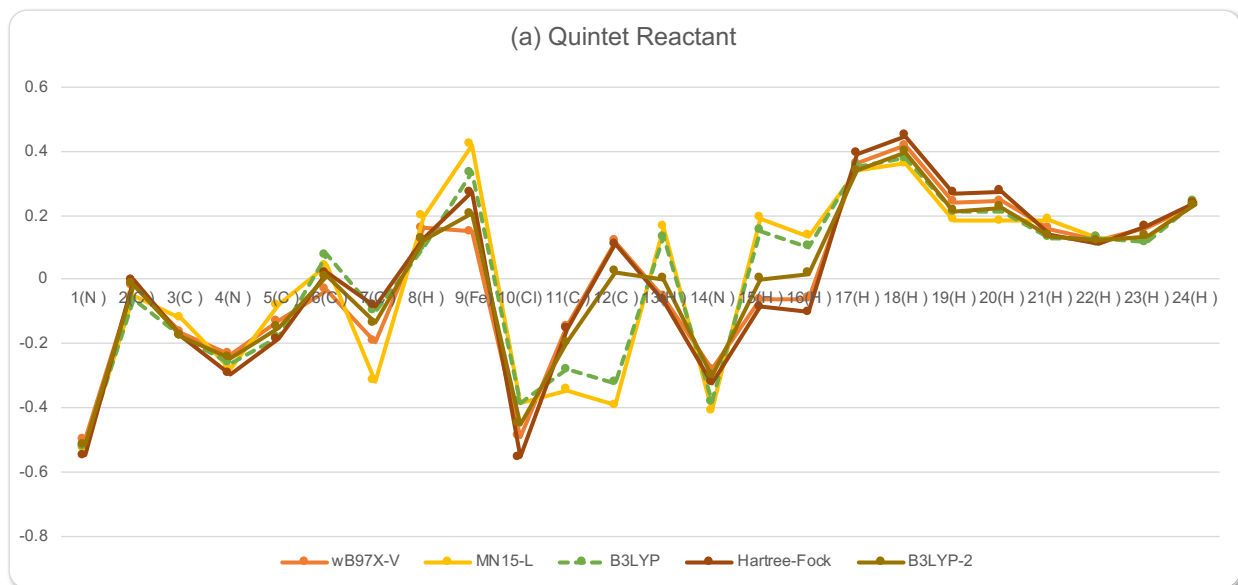


Figure S2. The Hirshfeld atomic dipole moment corrected charges obtained with different density functionals and the Hartree-Fock (HF) method for the quintet reactant geometry of the small model. The B3LYP and B3LYP-2 indicate the results obtained using the default and HF initial guess molecular orbitals in Molpro, respectively.

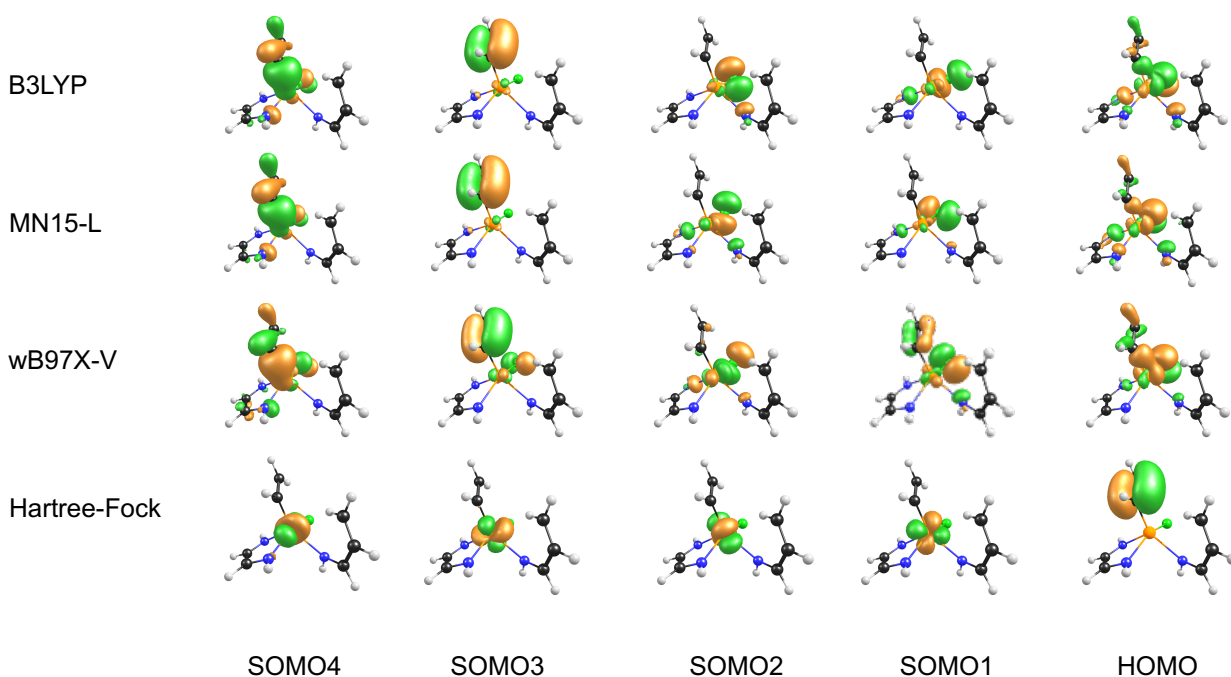


Figure S3. The highest doubly and singly occupied molecular orbitals (HOMO and SOMOs) obtained with different density functionals and the Hartree-Fock method for the quintet reactant geometry of the small model.

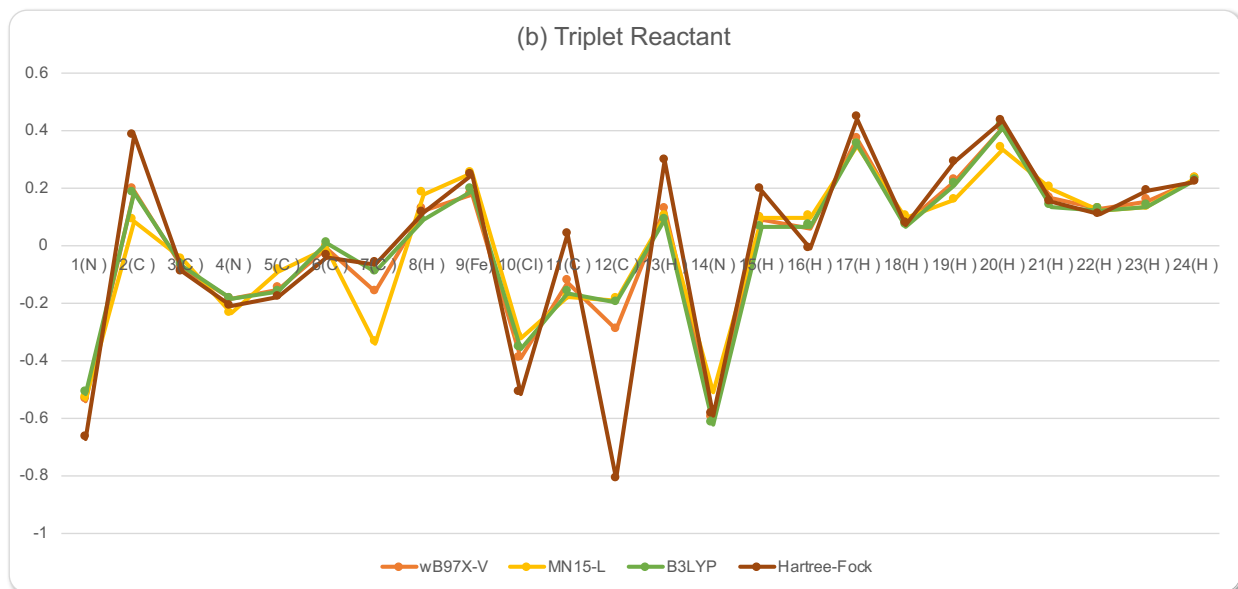


Figure S4. The Hirshfeld atomic dipole moment corrected charges obtained with different density functionals and the Hartree-Fock method for the triplet reactant geometry of the small model.

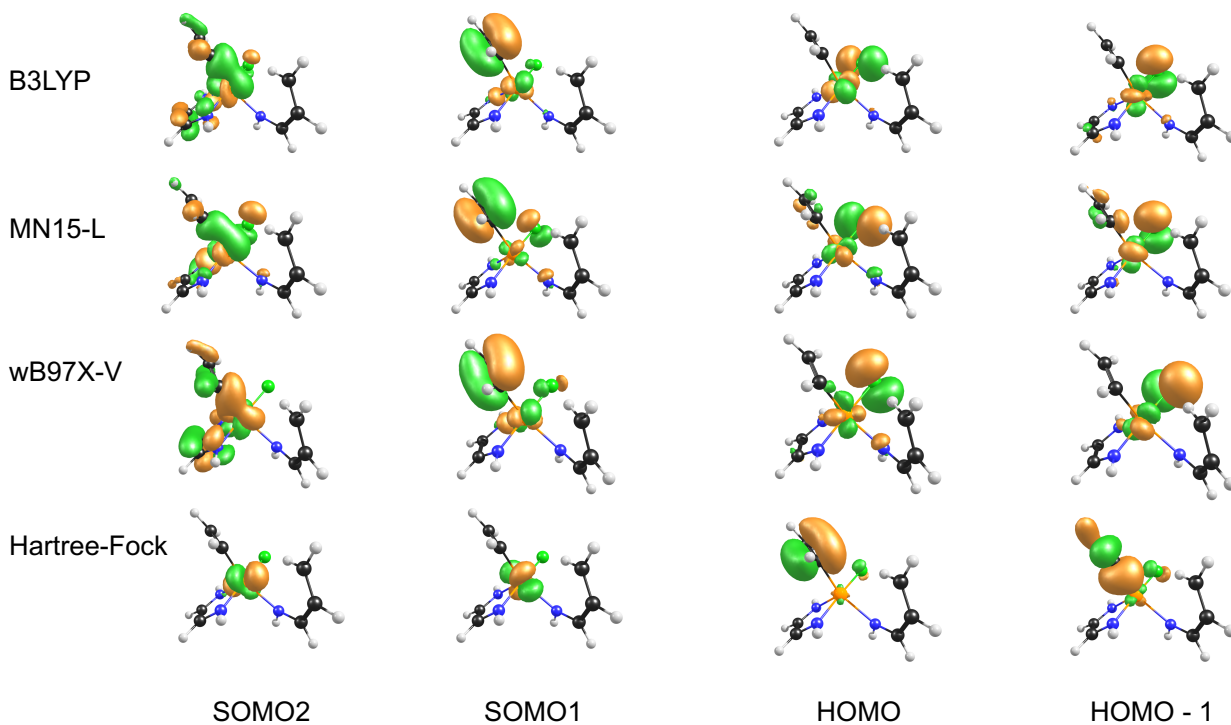


Figure S5. The highest doubly and singly occupied molecular orbitals (HOMOs and SOMOs) obtained with different density functionals and the Hartree-Fock method for the triplet reactant geometry of the small model.

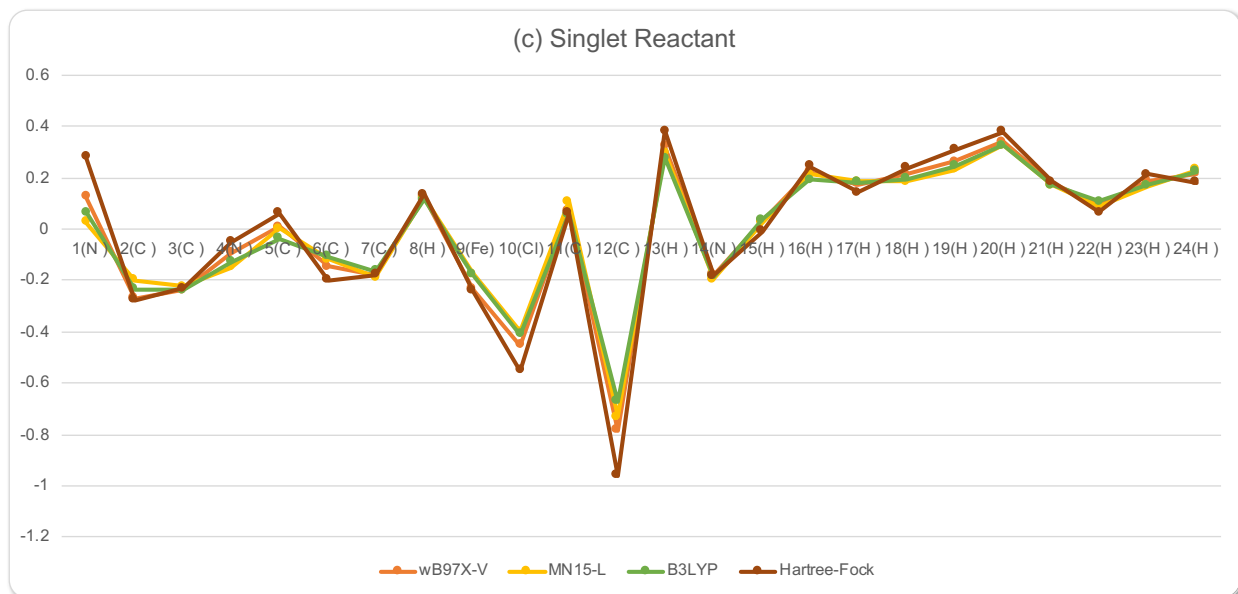


Figure S6. The Hirshfeld atomic dipole moment corrected charges obtained with different density functionals and the Hartree-Fock method for the singlet reactant geometry of the small model.

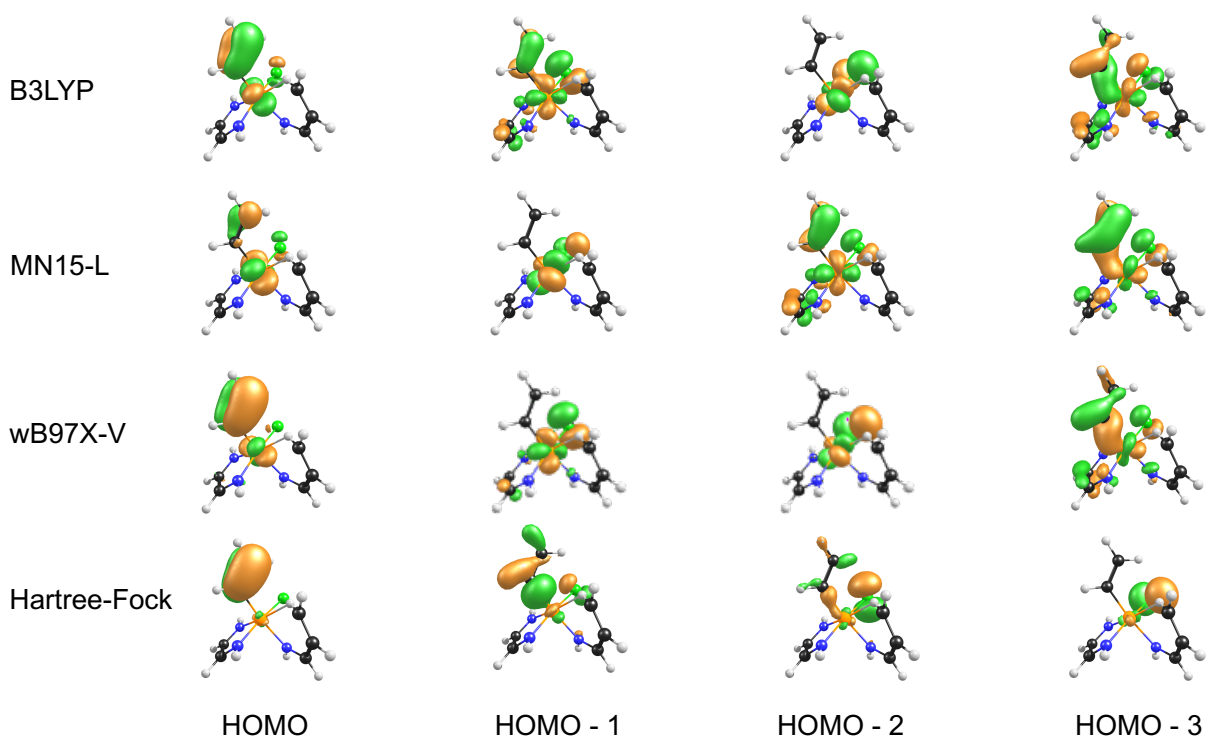


Figure S7. The highest doubly occupied molecular orbitals (HOMOs) obtained with different density functionals and the Hartree-Fock method for the singlet reactant geometry of the small model.

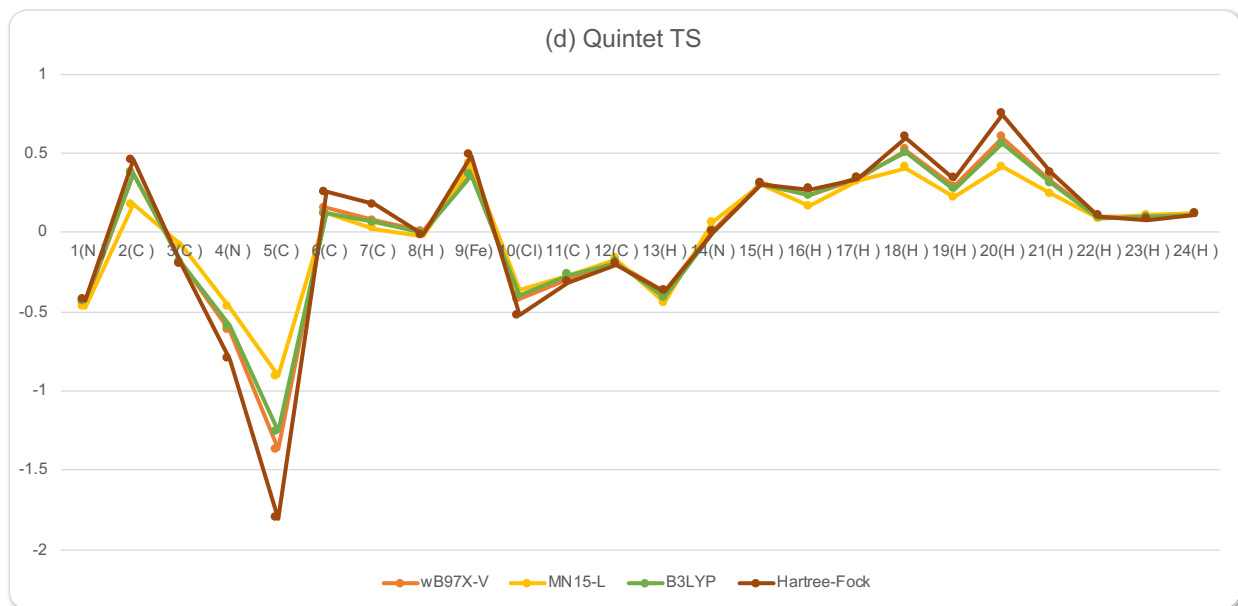


Figure S8. The Hirshfeld atomic dipole moment corrected charges obtained with different density functionals and the Hartree-Fock method for the quintet TS geometry of the small model.

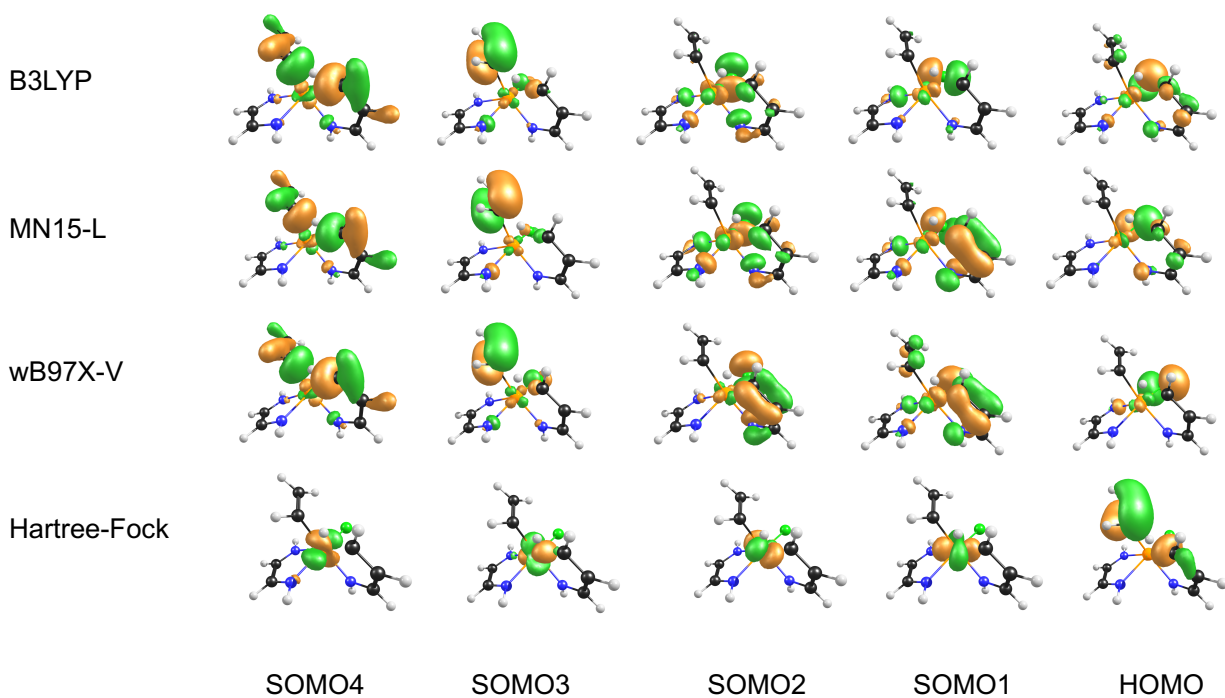


Figure S9. The highest doubly and singly occupied molecular orbitals (HOMO and SOMOs) obtained with different density functionals and the Hartree-Fock method for the quintet TS geometry of the small model.

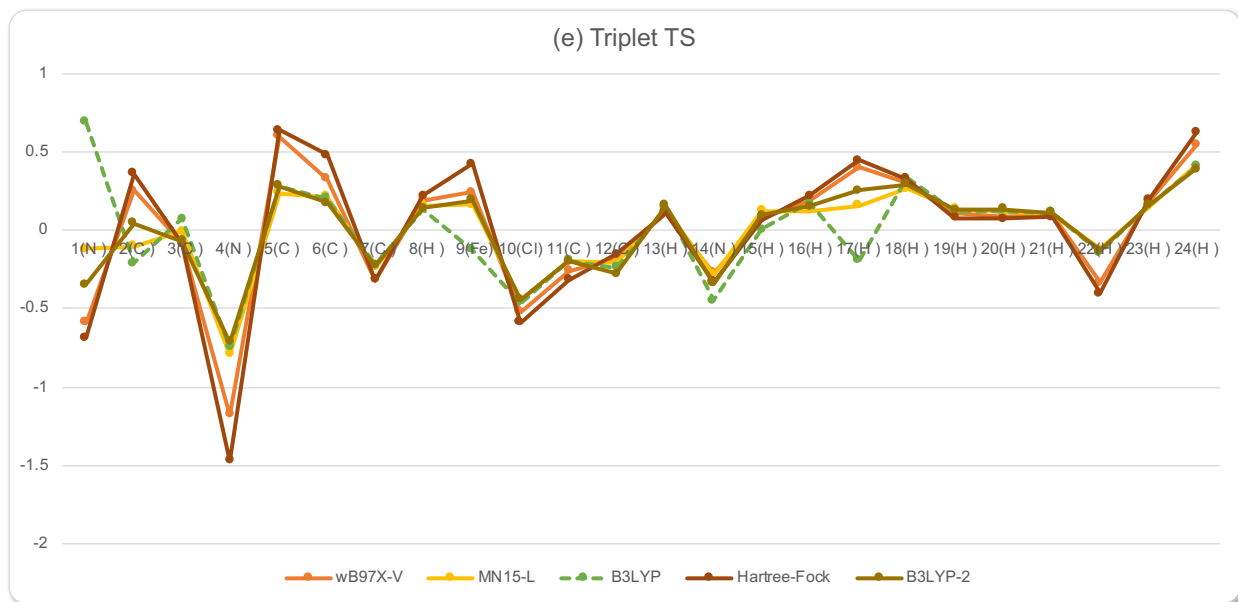


Figure S10. The Hirshfeld atomic dipole moment corrected charges obtained with different density functionals and the Hartree-Fock (HF) method for the triplet TS geometry of the small model. The B3LYP and B3LYP-2 indicate the results obtained using the default and HF initial guess molecular orbitals in Molpro, respectively.

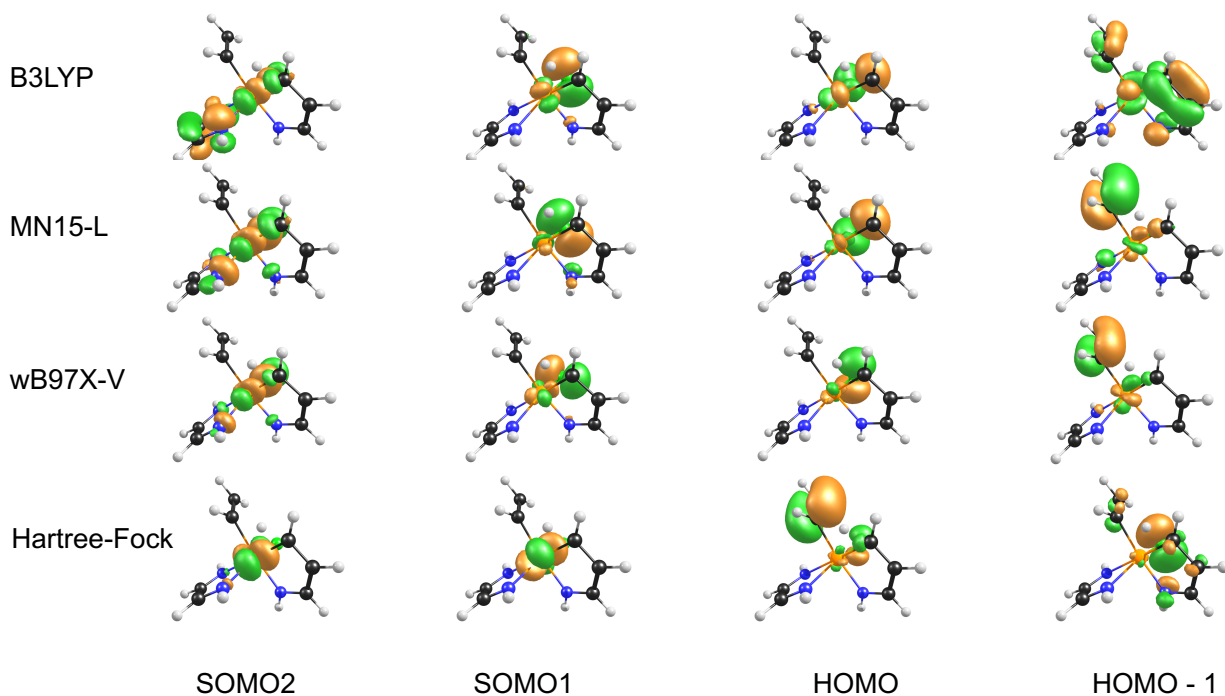


Figure S11. The highest doubly and singly occupied molecular orbitals (HOMOs and SOMOs) obtained with different density functionals and the Hartree-Fock method for the triplet TS geometry of the small model.

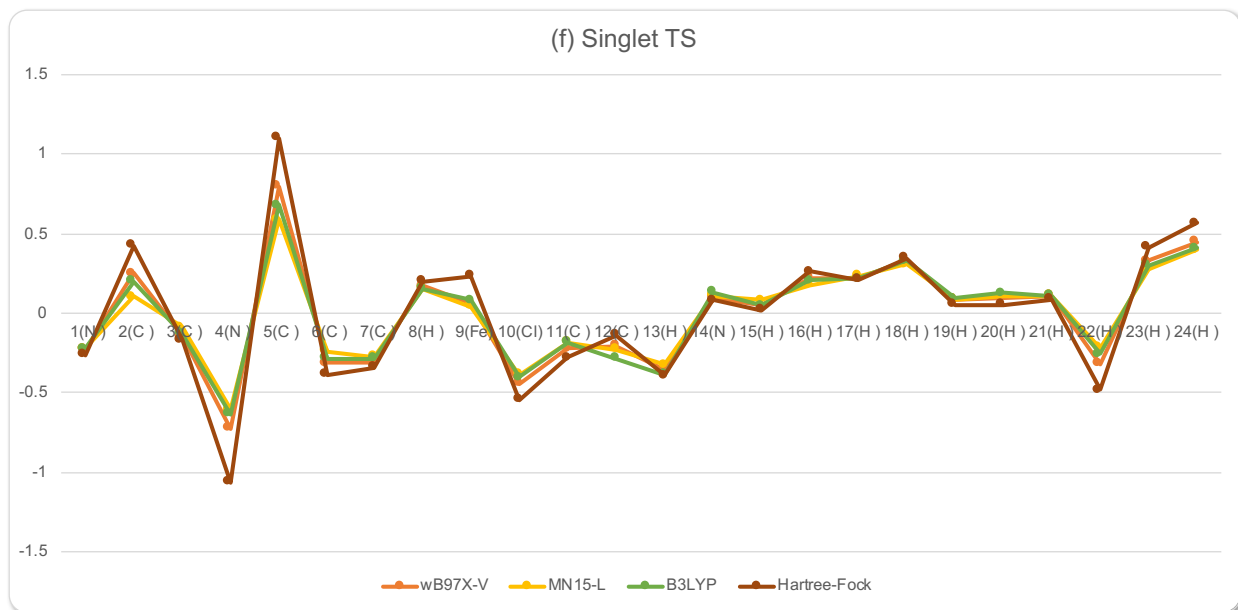


Figure S12. The Hirshfeld atomic dipole moment corrected charges obtained with different density functionals and the Hartree-Fock method for the singlet TS geometry of the small model.

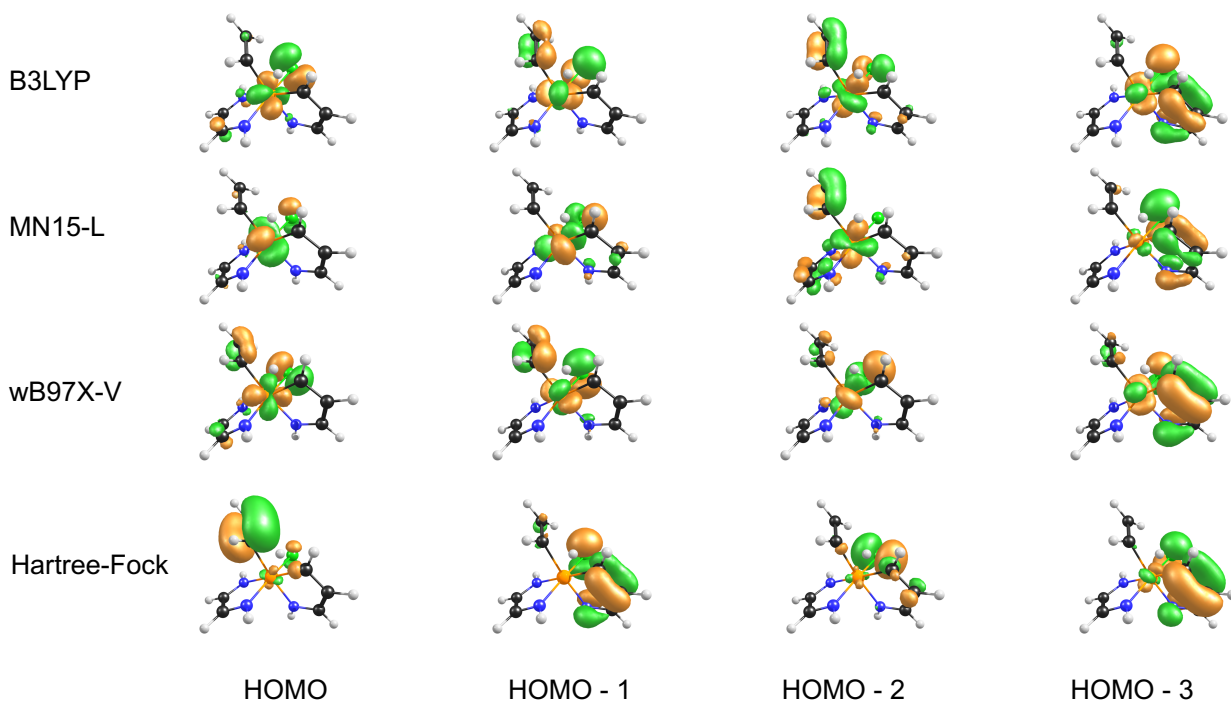


Figure S13. The highest doubly occupied molecular orbitals (HOMOs) obtained with different density functionals and the Hartree-Fock method for the singlet TS geometry of the small model.

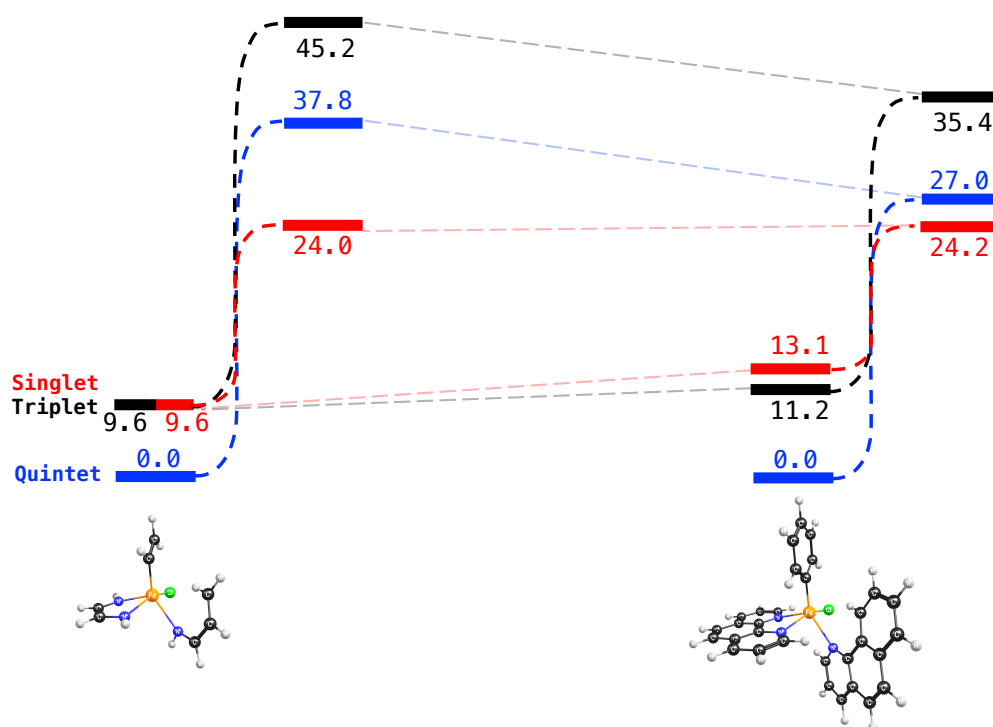


Figure S14. Relative energies (kcal/mol) of the spin states for the small and full-size models at the reactant and TS geometries calculated at the ω B97X-V/def2-TZVP level of theory.

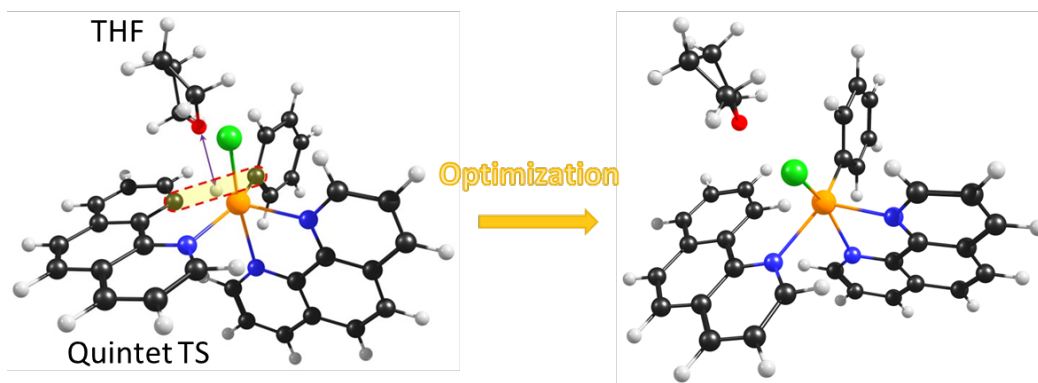


Figure S15. The initial and final optimized structures of the complex with a tetrahydrofuran (THF) solvent molecule. In the initial structure, the THF molecule is placed next to the quintet transition state geometry.

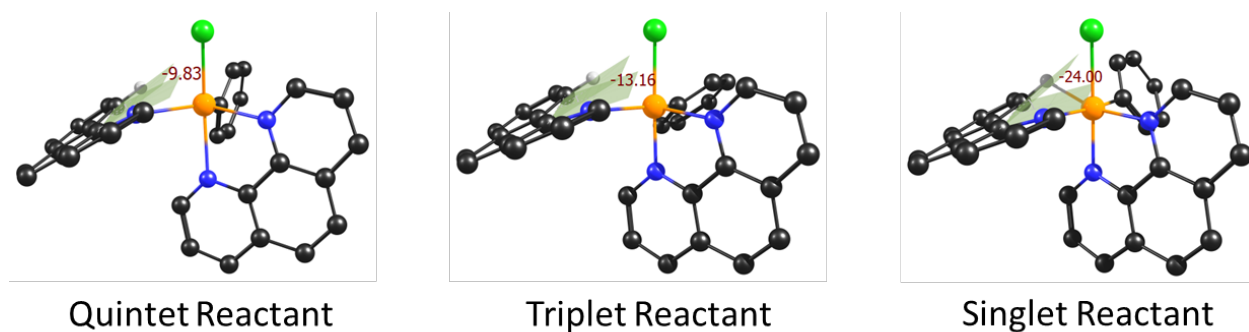


Figure S16. The out-of-plane C-H bond in the α -benzoquinoline ligand in different spin states. The dihedral angle values (9.83°, 13.16° and 24.00°) show how much the C-H bond goes out of the ligand's plane. Only the activated hydrogen atom (white ball) is shown.

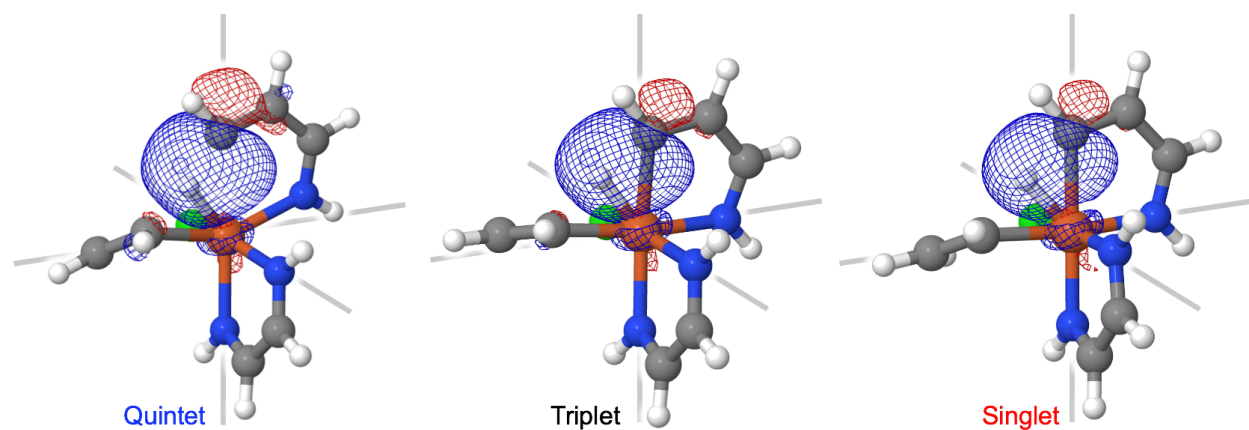
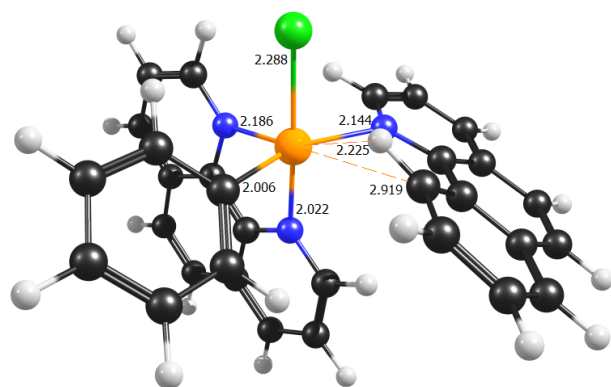
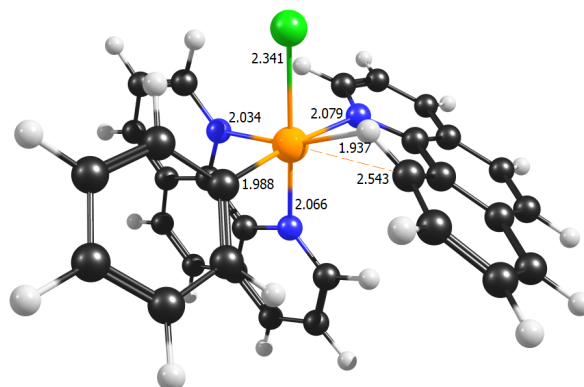


Figure S17. The C-H bond localized molecular orbital for three different spin states demonstrating the contribution of the d_{z^2} orbital of iron to this molecular orbital at the TS geometries.



(a) Quintet-Triplet MECP

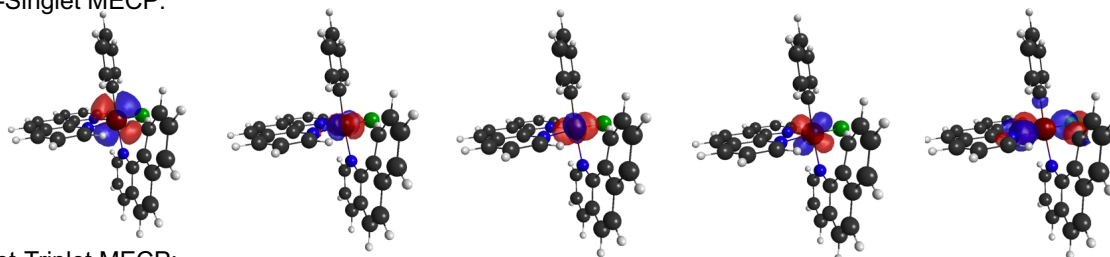


(b) Triplet-Singlet MECP

Figure S18. Geometries of the (a) quintet-triplet and (b) triplet-singlet MECPs in the full-size model. The bond lengths are in Å.

CASSCF Orbitals

Triplet-Singlet MECP:



Quintet-Triplet MECP:

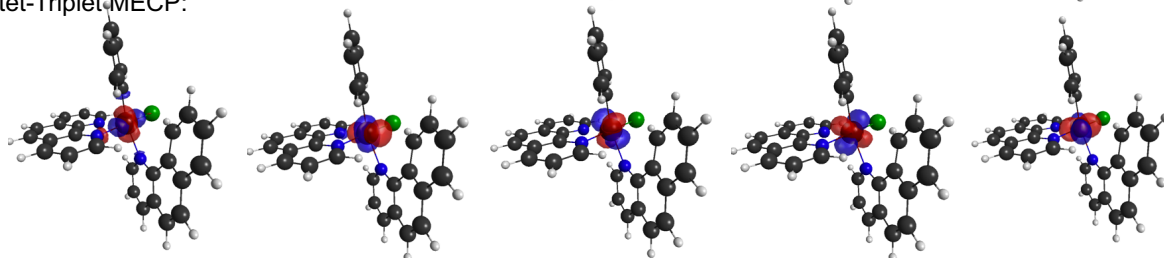


Figure S19. CASSCF active space orbitals for two MECP structures.

As shown in Table S1, the relative energies predicted by the DLPNO-CCSD(T₁) approximation with the recommended tight PNO settings and the full iterative triple excitations (T₁)¹ are comparable with the canonical CCSD(T) energies. However, the order of the quintet and singlet states at the transition state geometries predicted by the two methods is different. Also, the DLPNO-CCSD(T₁) energies at the reactant geometries are significantly different from the CCSD(T) energies for the singlet and triplet states. Analysis of the molecular orbitals showed that the DLPNO approximation sometimes converges to different reference wave functions than the “exact” CCSD(T).

Table S1. Relative energies in kcal/mol for the small model using def2-TZVP basis set.

State	B3LYP-D3(BJ)		MN15-L		ω B97X-V		DLPNO-CCSD(T ₁) ^a		CCSD(T)	
	Reactant	Transition State	Reactant	Transition State	Reactant	Transition State	Reactant	Transition State	Reactant	Transition State
Singlet	14.7	31.7	33.1	48.4	9.6	24.0	18.1	30.9	5.8	23.8
Triplet	10.2	47.3	14.2	56.4	9.6	45.2	23.4	62.0	11.2	52.9
Quintet	0.0	41.3	0.0	40.2	0.0	37.8	0.0	28.6	0.0	37.2

^a TightPNO thresholds were employed. T₁ refers to the full perturbative triple excitations.

Table S2. Relative energies (kcal/mol) for the full-size reactants, MECPs, and transition states in gas phase obtained with the ω B97X-V/def2-TZVP// ω B97X-V/def2-SVP level of theory.

	Reactant	MECP ^a	Transition State
Singlet	16.3	Triplet-Singlet 18.1	28.0
Triplet	13.8		39.6
Quintet	0.0	Quintet-Triplet 15.3	30.4

^a The def2-TZVP energies are calculated as an average of the energies of two spin-states at the MECP geometries optimized with def2-SVP basis set.

Table S3. Cartesian coordinates of optimized quintet reactant

Atomic Symbol	x	y	z
C	2.8926958167	4.2617547383	-1.6530792701
C	2.1300281219	5.2374243786	-1.0340728806
C	0.9601690337	4.8654689440	-0.3302292479
C	0.1093006894	5.8036011005	0.3506263530
C	-1.0069017669	5.3865931138	1.0181207056
C	-1.3738231756	3.9964454163	1.0556770766
C	-2.5171694344	3.5119470392	1.7325335988
C	-2.7915477855	2.1554811079	1.7177406505
C	-1.9231938717	1.2907154149	1.0210787009
N	-0.8475069948	1.7169136898	0.3725816550
C	-0.5597595783	3.0406169693	0.3869489161
C	0.6311848675	3.4835582494	-0.3052655864
N	-0.7914421014	-0.6017072499	-1.7406353418
C	2.4931683260	2.9131802355	-1.5594527248
H	3.7999969452	4.5168450936	-2.2045541660
H	2.4190661422	6.2911412554	-1.0814540067
H	0.3781621539	6.8631380447	0.3292755722
H	-1.6429356124	6.1076788116	1.5383695581
H	-3.1687965016	4.2118546006	2.2629831499
H	-3.6618846178	1.7466200701	2.2351375117
H	-2.1157587239	0.2145844123	0.9954103675
H	3.0563264065	2.0922106635	-2.0187106736
C	-0.3769018436	-3.2820903635	1.5600799036
C	-1.5107448099	-3.9839397268	2.0164369595
C	-1.6900085986	-2.2944909876	-0.2376229238
C	-0.8708549671	0.1000511170	-2.8662718698
C	-1.8235100179	-1.4135344927	-1.3887638705
C	-2.7130037627	-3.8752851909	1.3365436184
C	-2.8286863436	-3.0436663910	0.1959483058
C	-2.0083269380	0.1073120629	-3.6945216240
C	-3.0407543508	-1.4244210214	-2.1366070189
C	-4.0562650193	-2.9681958017	-0.5495303284
C	-3.1069743311	-0.6375605300	-3.3087358980
C	-4.1516582913	-2.2142378663	-1.6816050255
C	-0.4633869500	-2.4611386894	0.4462766745
H	0.4364654756	-1.9660233422	0.0793516892

H	-1.4359614107	-4.6280688535	2.8965717647
H	0.0221150225	0.6755400755	-3.1306654054
H	-3.5886301989	-4.4405579523	1.6683247621
H	-2.0132114437	0.7061516880	-4.6076178968
H	-4.9111633807	-3.5558214360	-0.2033940806
H	-4.0254354624	-0.6376449505	-3.9030546169
H	-5.0790791919	-2.1907544940	-2.2605295360
Fe	0.9333886968	0.4247903728	-0.4170048877
Cl	2.4031094427	-0.3682003241	-2.1020960979
H	0.0403211594	0.5515752941	2.7776409255
C	1.0984664618	0.2634245507	2.7345121863
C	1.7394029148	0.1168815981	1.4856082343
C	3.1036093430	-0.2544817772	1.5300953601
H	3.6499041243	-0.3909151464	0.5901546209
C	3.7823861086	-0.4651798626	2.7375740511
H	4.8397312418	-0.7513493490	2.7274919483
C	3.1121767803	-0.3132137997	3.9562568658
H	3.6372540954	-0.4783445709	4.9022820688
C	1.7617006870	0.0513534323	3.9508815647
H	1.2241914274	0.1725034203	4.8978503014
H	0.5795969637	-3.3806933577	2.0783970131
N	1.3991633750	2.5433672728	-0.9030471719

Table S4. Cartesian coordinates of optimized triplet reactant

C	2.7648030864	3.9677290896	-1.9400478343
C	2.0096038456	4.9850941183	-1.3641805287
C	0.9098258837	4.6546650820	-0.5452311234
C	0.0500354637	5.6088278459	0.1010348521
C	-1.0031314517	5.1972122159	0.8705870561
C	-1.2870404905	3.8001302671	1.0824541892
C	-2.3633023994	3.3222844755	1.8603399865
C	-2.5340427923	1.9446464089	1.9863253266
C	-1.6351534000	1.0668775308	1.3730240195
N	-0.5868542798	1.4845014525	0.6370341282
C	-0.4361256797	2.8412811830	0.4732309206
C	0.6406643164	3.2709546309	-0.3569626172
N	-0.7840395299	-0.3999461022	-1.6064392437
C	2.4112135917	2.6267539920	-1.7061340870

H	3.6248539336	4.1949536982	-2.5733350594
H	2.2610873954	6.0351689851	-1.5379744297
H	0.2510701266	6.6745107453	-0.0373749896
H	-1.6542796575	5.9335098543	1.3496138756
H	-3.0440647841	4.0238294326	2.3485795640
H	-3.3588387399	1.5318662350	2.5711401330
H	-1.7542345582	-0.0131821139	1.4754455630
H	2.9712660114	1.7889026403	-2.1354830187
C	-0.5567443726	-3.3742939516	1.4859701941
C	-1.7346632849	-4.0485112620	1.8657481449
C	-1.7705105738	-2.1950631673	-0.2674301069
C	-0.7950046643	0.3460139657	-2.7083439903
C	-1.8341670767	-1.2331275822	-1.3590278977
C	-2.9080327315	-3.8373908024	1.1605521735
C	-2.9497471865	-2.9291421816	0.0746462195
C	-1.8726492876	0.3872889439	-3.6075583763
C	-3.0100286237	-1.1849577462	-2.1707962154
C	-4.1433772264	-2.7709418733	-0.7113014791
C	-3.0020475837	-0.3537107088	-3.3119840189
C	-4.1626813121	-1.9630392414	-1.8082927159
C	-0.5724036375	-2.4706093229	0.4340491502
H	0.3652595702	-2.0099434318	0.1149522422
H	-1.7159222556	-4.7546758554	2.7000440601
H	0.0924190663	0.9593997661	-2.8818859022
H	-3.8181731566	-4.3837872137	1.4234966538
H	-1.8158577492	1.0212788510	-4.4944893664
H	-5.0307668514	-3.3441301578	-0.4291531826
H	-3.8874790342	-0.3124210338	-3.9527856376
H	-5.0591736387	-1.8817132557	-2.4287347008
Fe	0.7939187305	0.3494319863	-0.1811857035
Cl	2.3696948773	-0.8147136323	-1.3300419169
H	0.0578207942	-0.5255513312	2.8064969179
C	1.1148615143	-0.2427153258	2.7904076800
C	1.7236800852	0.1816913560	1.5960852810
C	3.0910344896	0.5197709368	1.6607353354
H	3.6214022600	0.8168664156	0.7522931934
C	3.8059625063	0.4544554608	2.8620149779
H	4.8665983145	0.7264229711	2.8754582105

C	3.1787162804	0.0284056712	4.0380059390
H	3.7389779223	-0.0313900136	4.9757509093
C	1.8284708022	-0.3268878882	3.9949176838
H	1.3213814950	-0.6688196912	4.9033259348
H	0.3812431704	-3.5631840501	2.0132515502
N	1.3724691374	2.2883426297	-0.9445918034

Table S5. Cartesian coordinates of optimized singlet reactant

C	2.6453341618	3.6222959741	-1.4704745788
C	1.9699032568	4.7453551451	-1.0127293852
C	0.7969940579	4.5674585504	-0.2451892662
C	0.0161987968	5.6331945056	0.3254367490
C	-1.0763934211	5.3733455208	1.1070391123
C	-1.4855292395	4.0240648305	1.3979699529
C	-2.5569395645	3.6779401455	2.2515990667
C	-2.8060556684	2.3357638104	2.4954932057
C	-2.0132829366	1.3486488356	1.8823946655
N	-1.0148620086	1.6380790652	1.0425720484
C	-0.7508567121	2.9593966517	0.8183525122
C	0.3808870763	3.2347318918	-0.0060584608
N	-1.2547709534	0.3944453430	-1.5257363965
C	2.1546128477	2.3334856498	-1.1933925657
H	3.5656797904	3.7189376426	-2.0503802727
H	2.3396272158	5.7523197512	-1.2233058097
H	0.3231435787	6.6647800244	0.1331827887
H	-1.6491268968	6.1955014934	1.5445218165
H	-3.1598251896	4.4595168004	2.7212341600
H	-3.6073311585	2.0251447327	3.1690452079
H	-2.1860219651	0.2928702540	2.0918890324
H	2.6440394802	1.4206220405	-1.5438388171
C	-1.2577506114	-2.4097145637	1.6321158613
C	-2.4822489390	-2.9832874555	2.0336473688
C	-2.3896131273	-1.2769219109	-0.2033653445
C	-1.1851847700	1.1500453305	-2.6172341371
C	-2.3761512559	-0.3480396669	-1.3117862465
C	-3.6352014942	-2.7529541271	1.2977664279
C	-3.6149969892	-1.9099440559	0.1591477933

C	-2.2491156785	1.2824753144	-3.5274722121
C	-3.5289654350	-0.2193822883	-2.1376440415
C	-4.7816811491	-1.6992102034	-0.6565726559
C	-3.4371094658	0.6208635136	-3.2699317276
C	-4.7321381677	-0.9186721600	-1.7752673537
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H	-0.2119322228	-1.3534886060	0.0992746812
H	-2.5142900490	-3.6363565234	2.9095755159
H	-0.2434895139	1.6781115865	-2.7812102561
H	-4.5762028043	-3.2315385215	1.5833622469
H	-2.1313341710	1.9216906673	-4.4049385657
H	-5.7108664276	-2.2020653477	-0.3748387254
H	-4.3019494926	0.7336396983	-3.9297700653
H	-5.6157552661	-0.7938573294	-2.4071110827
Fe	0.2062242317	0.4638429397	-0.0099981033
Cl	1.5367521642	-0.7795003107	-1.5145507993
H	0.9923312509	2.0489812187	2.6163827161
C	1.5511770321	1.1061080580	2.6253974549
C	1.4358592514	0.1960222783	1.5501739850
C	2.2234339260	-0.9750142199	1.6641932848
H	2.2252270393	-1.6979520940	0.8436597074
C	3.0359691189	-1.2305104162	2.7768040236
H	3.6238744187	-2.1542006232	2.8147985626
C	3.1148426480	-0.3095386964	3.8262976706
H	3.7529710506	-0.5033931091	4.6938083738
C	2.3696816422	0.8690678405	3.7385743667
H	2.4230743937	1.6124480674	4.5416329558
H	-0.3345749201	-2.6253632714	2.1747719638
N	1.0335244206	2.1399006490	-0.4880015025

Table S6. Cartesian coordinates of optimized quintet TS

C	3.1519549835	3.5625294180	-1.2972594028
C	2.7437678105	4.6842858267	-0.5949122493
C	1.5256608915	4.6466730489	0.1230219494
C	1.0095656605	5.7601960029	0.8721701873
C	-0.1793679899	5.6767830531	1.5377964010
C	-0.9581753163	4.4691175576	1.5186809052
C	-2.1959430902	4.3260353844	2.1860034008

C	-2.8708983353	3.1190383192	2.1151361215
C	-2.2997094810	2.0598415905	1.3838069874
N	-1.1389815928	2.1679768191	0.7478692572
C	-0.4738908798	3.3457503446	0.7956420491
C	0.7802949172	3.4378903803	0.0835942470
N	-1.8215372655	0.3528283012	-1.5248718558
C	2.3470337528	2.4065241558	-1.2767798958
H	4.0842448674	3.5571765707	-1.8658993209
H	3.3455037371	5.5978017035	-0.5850066959
H	1.5845527841	6.6892485397	0.8950957840
H	-0.5605417821	6.5353569100	2.0963687396
H	-2.6077130505	5.1666419493	2.7493037894
H	-3.8274479591	2.9773769216	2.6219387114
H	-2.7852961879	1.0813939540	1.3277450479
H	2.6198619540	1.4901781630	-1.8121876942
C	-1.4140786626	-2.2153720873	1.8803833003
C	-2.3911060152	-3.2054679051	2.1117255723
C	-2.5784557155	-1.4554035608	-0.0873859950
C	-1.9347886799	1.1197062525	-2.6031997321
C	-2.7436612308	-0.6091577213	-1.2635197012
C	-3.4636287647	-3.3274101943	1.2485632770
C	-3.5771649843	-2.4640606297	0.1344622159
C	-2.9968164273	1.0106870512	-3.5138140542
C	-3.8542178253	-0.7916063557	-2.1471375024
C	-4.6825399576	-2.6103068627	-0.7731368420
C	-3.9623700785	0.0484646949	-3.2770656829
C	-4.8215554842	-1.8106100661	-1.8662105960
C	-1.4703870892	-1.3263786960	0.8077013280
H	-0.2523578094	-0.5870926051	1.0762393923
H	-2.2926656908	-3.8791897607	2.9683456827
H	-1.1361849042	1.8485766671	-2.7663823199
H	-4.2276082516	-4.0952336655	1.4014263647
H	-3.0437154236	1.6725913305	-4.3804551362
H	-5.4237842856	-3.3878255814	-0.5666646249
H	-4.8090188062	-0.0748142136	-3.9597815222
H	-5.6823003354	-1.9090807432	-2.5295627657
Fe	0.0089373692	0.4907449966	-0.3572151851
Cl	1.2302921558	-0.6418643092	-1.9886763656

H	-0.1891331210	1.0601846131	3.1282759557
C	0.7807947716	0.6115345036	2.8959594382
C	0.9614483841	-0.0355538724	1.6579582553
C	2.2134998580	-0.6473573943	1.4403139186
H	2.3843330953	-1.1854863383	0.5028244165
C	3.2409579794	-0.5722983855	2.3903956603
H	4.2037273906	-1.0573725993	2.1943220675
C	3.0392556440	0.1020645630	3.5994951996
H	3.8430245604	0.1546008480	4.3424817543
C	1.7957152763	0.6886592098	3.8570587220
H	1.6149140049	1.1947332500	4.8115296655
H	-0.5703778544	-2.1494561694	2.5766040411
N	1.1975099396	2.3484993629	-0.6076932958

Table S7. Cartesian coordinates of optimized triplet TS

C	2.7707963985	3.3677499589	-1.3845813744
C	2.3404149706	4.5392048766	-0.7869280616
C	1.1663135082	4.5225344377	0.0018518571
C	0.6344117637	5.6925862523	0.6469503289
C	-0.5116948505	5.6325542159	1.3868861650
C	-1.2183662678	4.3917466272	1.5553253351
C	-2.4108510370	4.2716980563	2.3064172508
C	-3.0223833422	3.0351503718	2.4179189223
C	-2.4275369219	1.9209728105	1.7903431251
N	-1.3079440146	2.0033317431	1.0861795948
C	-0.7111524263	3.2089493047	0.9471203479
C	0.4913762839	3.2794442877	0.1448587313
N	-1.4960187073	0.4304954415	-1.4794563731
C	2.0312947523	2.1833284067	-1.1969703695
H	3.6721256259	3.3435153636	-2.0007444205
H	2.8922671183	5.4746500066	-0.9156237361
H	1.1689190689	6.6390758115	0.5279842799
H	-0.9097346422	6.5302378099	1.8677584676
H	-2.8365380244	5.1551182221	2.7905652643
H	-3.9450938573	2.9076033344	2.9878959358
H	-2.8746423179	0.9251163120	1.8791278837
H	2.3114778401	1.2255612247	-1.6534257540
C	-1.4501066445	-2.0633855524	1.9385621291

C	-2.5348102075	-2.9372007247	2.1691087168
C	-2.4742546871	-1.2924926913	-0.1091025595
C	-1.4668248614	1.1802578220	-2.5740177843
C	-2.5140247108	-0.4558552681	-1.2911100840
C	-3.5778203942	-3.0040393027	1.2654837370
C	-3.5686168088	-2.1869439299	0.1087029980
C	-2.4727798814	1.1338432064	-3.5548317605
C	-3.5810561895	-0.5569552215	-2.2282642939
C	-4.6429446175	-2.2514862360	-0.8466511081
C	-3.5362068627	0.2671374752	-3.3762456121
C	-4.6499008919	-1.4798310072	-1.9714299673
C	-1.3824581754	-1.2338126605	0.8192189985
H	-0.0662082739	-0.7714454437	1.0802475943
H	-2.5395022758	-3.5673712466	3.0630621612
H	-0.6054432562	1.8421020794	-2.6845398313
H	-4.4178074784	-3.6854770149	1.4277424056
H	-2.3997432252	1.7764992186	-4.4346043817
H	-5.4626800043	-2.9490292794	-0.6518470266
H	-4.3413198910	0.2064493532	-4.1142189806
H	-5.4689744699	-1.5489720916	-2.6923902500
Fe	-0.0783178436	0.2917466513	-0.0549734391
Cl	1.1872941765	-0.9653116979	-1.7148441354
H	0.0316376508	0.9010185486	3.0669204894
C	1.0040793155	0.4688302459	2.8155194257
C	1.2162820936	-0.0809710389	1.5325557805
C	2.4759782084	-0.6736325309	1.2951841823
H	2.6600257429	-1.1317977142	0.3200471509
C	3.4800678105	-0.6671403876	2.2692403501
H	4.4508082686	-1.1217416226	2.0464852744
C	3.2529648127	-0.0899106552	3.5239117089
H	4.0391408570	-0.0872902480	4.2847848481
C	2.0029602534	0.4717000315	3.7973023604
H	1.8001401106	0.9111663065	4.7792875533
H	-0.6333228346	-2.0499384189	2.6671038012
N	0.9257361444	2.1439523705	-0.4554323016

Table S8. Cartesian coordinates of optimized singlet TS

C	2.7251769355	3.1755014199	-1.5494609663
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C	2.3756061984	4.3686598454	-0.9366927413
C	1.2466266205	4.3956787445	-0.0854558956
C	0.7648023862	5.5654533113	0.5998160018
C	-0.3476293803	5.5143505368	1.3942240075
C	-1.0720259153	4.2857020403	1.5877898096
C	-2.2314478413	4.1591834339	2.3861746134
C	-2.8397250011	2.9180353181	2.4891774204
C	-2.2876327344	1.8086500700	1.8216204461
N	-1.1858131445	1.8904854940	1.0729502120
C	-0.6011996574	3.1152797097	0.9409725564
C	0.5465893312	3.1768563219	0.0900865571
N	-1.6003223976	0.5573785603	-1.4126462011
C	1.9598272347	2.0138595571	-1.3241705636
H	3.5907790136	3.1169413734	-2.2127761700
H	2.9568158394	5.2797491396	-1.1029660631
H	1.3066811097	6.5059377528	0.4689468964
H	-0.7049441800	6.4138618748	1.9022121020
H	-2.6353376641	5.0307716002	2.9080444434
H	-3.7412696436	2.7791235570	3.0893227017
H	-2.7454523620	0.8209359642	1.9057171480
H	2.1846716194	1.0481810384	-1.7898828772
C	-1.4716282480	-1.9844846088	1.9039953791
C	-2.4889358709	-2.9463864188	2.0839806906
C	-2.4876941137	-1.2744271110	-0.1593027883
C	-1.6097216954	1.3684357958	-2.4644529027
C	-2.5578580048	-0.4050291054	-1.3044182279
C	-3.4961252366	-3.0878811837	1.1475949156
C	-3.5167250331	-2.2504455501	0.0071421523
C	-2.5816909128	1.2944156409	-3.4773437144
C	-3.5915337752	-0.5398209330	-2.2739849256
C	-4.5545101656	-2.3627223066	-0.9838787293
C	-3.5796185313	0.3400886898	-3.3787153356
C	-4.5910121186	-1.5524920800	-2.0816983913
C	-1.4275525863	-1.1359076657	0.7938830131
H	-0.1481849425	-0.6649312754	1.0769133457
H	-2.4674032140	-3.5896517066	2.9682906485
H	-0.8102922345	2.1102797299	-2.5169825483
H	-4.2809345625	-3.8386703810	1.2753817878

H	-2.5356231394	1.9871265525	-4.3201452477
H	-5.3242414321	-3.1260426992	-0.8377703959
H	-4.3562459816	0.2576565784	-4.1444645848
H	-5.3834273887	-1.6578541735	-2.8276347249
Fe	-0.2242182752	0.4564688085	0.0561607948
Cl	0.8984926234	-1.0028641527	-1.4279441452
H	-0.1442373525	0.8908887563	3.2342936316
C	0.8546810434	0.5458311794	2.9511402994
C	1.1057030331	0.1076402136	1.6323745679
C	2.4074722535	-0.3715326710	1.3705563646
H	2.6259298020	-0.7625981753	0.3741472294
C	3.4079389990	-0.3623577459	2.3487264336
H	4.4089305371	-0.7303515642	2.1006745442
C	3.1374123198	0.1062154226	3.6390013943
H	3.9193488868	0.1129547477	4.4044061244
C	1.8480563209	0.5525784161	3.9392947394
H	1.6094406947	0.9069690544	4.9474072858
H	-0.6825040072	-1.9225836668	2.6593849423
N	0.8931676219	2.0142031253	-0.5235963202

Table S9. Cartesian coordinates of optimized quintet product

C	3.2013946268	1.2384077180	-2.2127172437
C	2.7784275600	2.1814936339	-1.2902653394
C	1.7585097461	1.8416475459	-0.3714476260
C	1.2643063405	2.7377650478	0.6392043767
C	0.2942237879	2.3451861880	1.5173529058
C	-0.2618623025	1.0195521425	1.4660845147
C	-1.2446363823	0.5473284464	2.3667420524
C	-1.7032448586	-0.7537638788	2.2480450807
C	-1.1818690671	-1.5759970998	1.2285726292
N	-0.2625866581	-1.1574076280	0.3666443721
C	0.1961052387	0.1127413322	0.4713938913
C	1.2124805019	0.5323930122	-0.4638969062
N	-0.9384523860	-1.7975202135	-2.8562785304
C	2.5965824704	-0.0344348008	-2.2251886480
H	3.9969382124	1.4621489458	-2.9266238507
H	3.2282734025	3.1777482244	-1.2556936562
H	1.6857153829	3.7451710874	0.6935213985

H	-0.0706559665	3.0346892117	2.2833375009
H	-1.6276325326	1.2108424529	3.1471537572
H	-2.4592676061	-1.1533989877	2.9271085512
H	-1.5218863008	-2.6080858655	1.1023586687
H	2.9152205895	-0.8275890498	-2.9097928183
C	-0.8624986011	-5.0672080085	-0.2382081435
C	-1.9338154983	-5.9891794419	-0.2362997681
C	-1.9642174089	-3.7772892389	-1.9271178009
C	-0.9260409599	-0.7741495267	-3.7028595821
C	-1.9962597838	-2.6578586559	-2.8496517861
C	-3.0260988256	-5.8036991182	-1.0707258051
C	-3.0642929183	-4.6909890557	-1.9430151888
C	-1.9673216000	-0.5179700436	-4.6110976315
C	-3.1012049181	-2.4693144298	-3.7342167845
C	-4.1684003894	-4.4664032695	-2.8380956661
C	-3.0599886719	-1.3706657496	-4.6196704146
C	-4.1922073203	-3.4041042852	-3.6959034602
C	-0.8400999740	-3.9371577117	-1.0615077253
H	-1.9020687820	-6.8591042830	0.4280063134
H	-0.0483896027	-0.1212059302	-3.6664042857
H	-3.8590856289	-6.5132682147	-1.0683194146
H	-1.9037523450	0.3365742938	-5.2880236390
H	-5.0003537755	-5.1773535620	-2.8219706205
H	-3.8935389923	-1.2057696711	-5.3089125847
H	-5.0362280363	-3.2524043739	-4.3748436940
Fe	0.5953948163	-2.4214460686	-1.3945100632
Cl	2.5117905537	-3.3134714981	-2.2872440308
H	-0.0199442901	-5.2646454582	0.4358175677
N	1.6211255234	-0.3705430441	-1.3856690118

Table S10. Cartesian coordinates of optimized triplet product

C	2.9446368955	2.7169909554	-0.7765188476
C	2.6841370304	3.7173964335	0.1599446303
C	1.6588775699	3.5306417884	1.1060498840
C	1.3092171935	4.4720586135	2.1351759477
C	0.3184672626	4.1938264272	3.0356628599
C	-0.4116068022	2.9502435622	3.0050373644
C	-1.4004444824	2.5936601774	3.9410883981

C	-2.0080744009	1.3366317386	3.8211421780
C	-1.6444284994	0.4741048469	2.7902864111
N	-0.7096423626	0.7815751975	1.8603631679
C	-0.0976631378	2.0152304946	1.9802357176
C	0.9242363051	2.3116430452	1.0402612101
N	-1.5697188592	0.5047030550	-1.1478352765
C	2.1709817492	1.5455464448	-0.7679677240
H	3.7405385761	2.8275804841	-1.5154050512
H	3.2731962591	4.6387251800	0.1723357211
H	1.8578944532	5.4163313749	2.1882317919
H	0.0688390948	4.9168488913	3.8171144883
H	-1.6759371319	3.2811839873	4.7441937096
H	-2.7734163239	1.0144121869	4.5305361407
H	-2.1163486090	-0.5040534046	2.6893475893
H	2.3557286327	0.7217554384	-1.4638678898
C	-1.4471249983	-2.8226323748	1.2441252765
C	-2.5500532996	-3.7062637695	1.2852319596
C	-2.6471987723	-1.4441822671	-0.3186429978
C	-1.5433936645	1.5899041828	-1.9176434215
C	-2.6805711096	-0.2836561373	-1.1608111034
C	-3.6957099337	-3.4642365360	0.5363677377
C	-3.7692297053	-2.3211090737	-0.2931203130
C	-2.6178843426	1.9597971592	-2.7461079601
C	-3.8154523317	0.0080282934	-1.9647787561
C	-4.9113090523	-2.0029443878	-1.1116481380
C	-3.7579133180	1.1677225126	-2.7693777273
C	-4.9376530611	-0.8918355345	-1.9097123951
C	-1.4829443792	-1.6734882869	0.4593806089
H	-2.4957948675	-4.6016471147	1.9120019946
H	-0.6338973410	2.1964697664	-1.8766765949
H	-4.5409531552	-4.1573893592	0.5757540055
H	-2.5420062931	2.8620189243	-3.3566328679
H	-5.7728473210	-2.6767372707	-1.0847828396
H	-4.6093366542	1.4322105723	-3.4031756841
H	-5.8147354637	-0.6707876496	-2.5243543928
Fe	-0.1114929299	-0.2753439180	0.2357431946
Cl	1.3761299957	-1.7173214425	-0.5906568466
H	-0.5519843386	-3.0606196111	1.8265066344

N	1.1785267842	1.3521101128	0.1012425858
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Table S11. Cartesian coordinates of optimized singlet product

C	2.9681579269	2.6538680460	-0.8019064051
C	2.7649325488	3.6429906791	0.1500200515
C	1.7239946534	3.4870997768	1.0942465142
C	1.4190240773	4.4236081669	2.1429460966
C	0.4039385837	4.1865487161	3.0288818036
C	-0.3965280194	2.9916253656	2.9525145597
C	-1.4409571377	2.6730589629	3.8495260315
C	-2.1277249869	1.4800953809	3.6769700482
C	-1.7846438872	0.6140619793	2.6241466072
N	-0.8037070835	0.8848424510	1.7536507194
C	-0.1229369486	2.0607632049	1.9185846471
C	0.9355824405	2.3133874126	0.9894836112
N	-1.6063117239	0.5182160234	-0.9542602964
C	2.1328035640	1.5195499427	-0.8234911268
H	3.7695897024	2.7388465445	-1.5388885603
H	3.4003067789	4.5322560053	0.1835201975
H	2.0204605900	5.3332651201	2.2208488573
H	0.1870568186	4.9066323617	3.8224054779
H	-1.6939932222	3.3576358924	4.6633021683
H	-2.9397192550	1.1957019649	4.3495446126
H	-2.3085253354	-0.3314126389	2.4739419648
H	2.2697663445	0.6944913262	-1.5297924390
C	-1.4138210827	-2.8527090731	1.2633167497
C	-2.4828048686	-3.7783072361	1.2610896544
C	-2.6437136903	-1.4916467865	-0.2571357942
C	-1.5941945858	1.6414045543	-1.6752372419
C	-2.6981187842	-0.3023750966	-1.0437831014
C	-3.6309664896	-3.5708124571	0.5013340715
C	-3.7343739882	-2.4053311280	-0.2910201129
C	-2.6533955467	2.0111446794	-2.5211836095
C	-3.8146272366	-0.0053081391	-1.8714233226
C	-4.8622714194	-2.0890284824	-1.1297282849
C	-3.7680402702	1.1885716101	-2.6218598428
C	-4.9042129312	-0.9468062648	-1.8850135608
C	-1.4608412024	-1.6727688334	0.5119335952

H	-2.4013056344	-4.6878800651	1.8655605328
H	-0.7091458078	2.2745066374	-1.5850965282
H	-4.4448405979	-4.3017927469	0.5081153356
H	-2.5827978040	2.9418003376	-3.0880198433
H	-5.7026011292	-2.7895883243	-1.1600120091
H	-4.6034837429	1.4564925482	-3.2752159501
H	-5.7705170725	-0.7323355565	-2.5172005430
Fe	-0.1988456776	-0.2103837339	0.2200077553
Cl	1.2219398606	-1.5718893820	-0.8666297651
H	-0.5261872631	-3.0862518734	1.8619199461
N	1.1332413957	1.3592658379	0.0427311081

Table S12. Cartesian coordinates of optimized benzene molecule

H	1.1447838067	-1.4184750743	2.0740796454
H	0.0226193434	-0.3973369428	4.0517541169
C	0.8326924267	0.1362125492	3.5467091482
C	1.4624995006	-0.4368345519	2.4364574095
C	2.4987061565	0.2458849697	1.7900992318
H	2.9906835803	-0.2021798579	0.9222813097
C	2.9051022462	1.5018109021	2.2539572151
H	3.7151466480	2.0353679273	1.7488977005
C	2.2752072812	2.0749444011	3.3641160218
H	2.5925787472	3.0568178855	3.7261798740
C	1.2391147404	1.3921300188	4.0105472055
H	0.7470920525	1.8401425932	4.8783541216

Table S13. Cartesian coordinates of quintet-triplet MECF

Atomic Symbol	x	y	z
C	2.8517048425	3.7090508265	-1.7223227710
C	2.3103001747	4.8032257683	-1.0726870107
C	1.1651679209	4.6344870535	-0.2591618539
C	0.5150691933	5.7032471125	0.4646049338
C	-0.5843585323	5.4598165111	1.2268304934
C	-1.1279955631	4.1251876479	1.3572987635
C	-2.2583533951	3.8172993577	2.1480865035
C	-2.6866357409	2.5068362515	2.2196810872

C	-1.9783754340	1.5086626616	1.5229276827
N	-0.9135577956	1.7679622842	0.7734019334
C	-0.5041553383	3.0623759675	0.6755289264
C	0.6417251544	3.3307125553	-0.1638402754
N	-1.3181940679	0.0494655285	-1.5273391749
C	2.2392207350	2.4465182738	-1.5736808796
H	3.7428636641	3.8075064685	-2.3481174833
H	2.7605160033	5.7964908857	-1.1750695399
H	0.9244121928	6.7154688434	0.3850814932
H	-1.0755532381	6.2737791428	1.7695708262
H	-2.7757256278	4.6129943338	2.6941025687
H	-3.5551982678	2.2231221885	2.8198947079
H	-2.2856853319	0.4603652057	1.5929640346
H	2.6193233217	1.5357885093	-2.0563938614
C	-1.4161973891	-2.6994816646	1.7135984821
C	-2.6716113935	-3.0852009002	2.2271674186
C	-2.5197350445	-1.4822168336	-0.0738219426
C	-1.2384707736	0.7539644714	-2.6473122842
C	-2.4812377779	-0.5802234226	-1.2187472042
C	-3.8325654237	-2.7299116049	1.5633765539
C	-3.7792340635	-1.9360116080	0.3925578351
C	-2.3326028267	0.9508762922	-3.5072623300
C	-3.6577455897	-0.3578137020	-1.9725891221
C	-4.9759499251	-1.6148563225	-0.3553695749
C	-3.5564310568	0.4235105637	-3.1442681411
C	-4.9144566325	-0.8999026723	-1.5070033473
C	-1.3388428119	-1.9251459904	0.5692147858
H	-0.3544840933	-1.7131402652	0.1315767632
H	-2.7251611392	-3.6939391345	3.1354083366
H	-0.2595876842	1.1944323458	-2.8668885412
H	-4.8075272424	-3.0672877370	1.9312414177
H	-2.2086656035	1.5409181141	-4.4190401751
H	-5.9352237445	-1.9944519827	0.0119476205
H	-4.4494410814	0.5982788697	-3.7541928464
H	-5.8175759338	-0.6961772656	-2.0915033275
Fe	0.2722311937	0.4051503616	-0.1338799652
Cl	1.6516174940	-0.8888443875	-1.4221583941
H	-0.3749245772	0.0267546656	2.9820971979

C	0.7171342667	0.0843074794	2.8667520885
C	1.2875078216	0.2265201152	1.5864754558
C	2.6982333349	0.2701147768	1.5466792682
H	3.2011241159	0.3334370453	0.5737755752
C	3.4815949895	0.2012316862	2.7024042917
H	4.5745784622	0.2434647350	2.6224137745
C	2.8806503075	0.0607455186	3.9572822770
H	3.4917570155	-0.0030459744	4.8644718505
C	1.4888656972	-0.0068934617	4.0329052052
H	0.9973196812	-0.1277639640	5.0061059451
H	-0.4927697557	-3.0161469380	2.2079958345
N	1.1607453140	2.2776734133	-0.8273488861

Table S14. Cartesian coordinates of triplet-singlet MECP

Atomic Symbol	x	y	z
C	2.7246464525	3.4450629250	-1.5891803019
C	2.1829718611	4.5688700600	-0.9960784060
C	1.0333012090	4.4326376836	-0.1831399265
C	0.3827802075	5.5335963421	0.4900529550
C	-0.7141118657	5.3280524874	1.2666741540
C	-1.2604908258	4.0021426331	1.4524574890
C	-2.3834290038	3.7275373419	2.2653387511
C	-2.8127235074	2.4220745978	2.3928184188
C	-2.1234538997	1.3983854154	1.7128323392
N	-1.0722005420	1.6267736658	0.9370661854
C	-0.6463472570	2.9109902661	0.8068386879
C	0.5092110681	3.1359143888	-0.0289866258
N	-1.2616304875	0.1787906669	-1.5780170212
C	2.1209330473	2.1872146641	-1.3807197106
H	3.6166870164	3.5114245065	-2.2178921051
H	2.6320887778	5.5569426292	-1.1420164383
H	0.7947908948	6.5399632009	0.3639741092
H	-1.2006943160	6.1659725062	1.7760032857
H	-2.8923521720	4.5447287289	2.7871399961
H	-3.6716489224	2.1626654837	3.0173313246
H	-2.4398809681	0.3567249779	1.8238005486
H	2.5012101599	1.2580455040	-1.8251419897

C	-1.4038641819	-2.3639019568	1.7757700418
C	-2.6674926682	-2.7371174222	2.2800186259
C	-2.4839469136	-1.3064615864	-0.1252588235
C	-1.1466795028	0.8529295322	-2.7113719205
C	-2.4265295259	-0.4624848334	-1.3067847492
C	-3.8154309474	-2.4638223229	1.5554654922
C	-3.7461866285	-1.7562294779	0.3306894879
C	-2.2095430600	0.9973855999	-3.6218269527
C	-3.5750626507	-0.2960714196	-2.1111579409
C	-4.9212306711	-1.5053887819	-0.4773645420
C	-3.4377503789	0.4507385030	-3.3022412021
C	-4.8338300503	-0.8493210017	-1.6632281559
C	-1.3109235880	-1.6728339702	0.5798851491
H	-0.3066829854	-1.5703902697	0.1197716419
H	-2.7357884065	-3.2782062852	3.2290659591
H	-0.1688779583	1.3065892279	-2.9041071339
H	-4.7925638181	-2.7990907869	1.9197308896
H	-2.0595201985	1.5643181394	-4.5444255867
H	-5.8852572707	-1.8858524626	-0.1237183196
H	-4.3040208141	0.5870305103	-3.9586183171
H	-5.7211868211	-0.6972872318	-2.2863434188
Fe	0.1570058213	0.3011124404	-0.0629903938
Cl	1.5270710538	-1.0091733230	-1.4357740937
H	-0.2101561706	0.2008339993	3.0436536156
C	0.8722692412	0.1895181528	2.8494073654
C	1.3526910281	0.2187167867	1.5226018022
C	2.7588122459	0.1778381151	1.3945969926
H	3.1960112128	0.1462381812	0.3892966800
C	3.6168631102	0.1339422174	2.4965674363
H	4.7021751172	0.1039226312	2.3403401202
C	3.1010598756	0.1137226612	3.7967827550
H	3.7703837479	0.0746312453	4.6634245114
C	1.7168980154	0.1339899266	3.9671230739
H	1.2872486480	0.1092644259	4.9763449626
H	-0.4874379646	-2.6246430332	2.3140717706
N	1.0412461308	2.0443351944	-0.6251325427

References:

- (1) Flöser, B. M.; Guo, Y.; Riplinger, C.; Tuzek, F.; Neese, F. Detailed Pair Natural Orbital-Based Coupled Cluster Studies of Spin Crossover Energetics. *J. Chem. Theory Comput.* **2020**, *16* (4), 2224–2235.