Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

The Role of Agostic Interaction in the Mechanism of Ethylene Polymerisation by Cr(III) Half-sandwich Complexes: What Dictates the Reactivity?

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Table S1: Compression of the structural parameter optimized Geometry with Experiments

Pre-catalyst 1	**Experimental Data**	**Computational Data**
Cr-N_{py}	2.107	2.134
Cr-Cp^c	1.890	1.963
Cr-Cl	2.287	2.266
Cr-Cl	2.281	2.261
∠N_{py}-Cr- Cp^c	109.3	108.9
∠ Cp^c-Cr-Cl	125.5	125.2
∠ Cp^c-Cr-Cl	124.7	123.0
∠Cl-Cr-Cl	97.4	100.4
Pre-catalyst 2	**Experimental Data**	**Computational Data**
Cr-N_{py}	2.077	2.108
C-N_{pyr}	1.348	1.353
Cr-Cp^c	1.888	1.969
Cr-Cl	2.293	2.272
Cr-Cl	2.288	2.267
∠N_{py}-Cr- Cp^c	109.9	109.0
∠ Cp^c-Cr-Cl	124.5	125.1
∠ Cp^c-Cr-Cl	123.3	123.2
∠Cl-Cr-Cl	98.8	99.4

Cp^c: center of the cyclopentadienyl ring

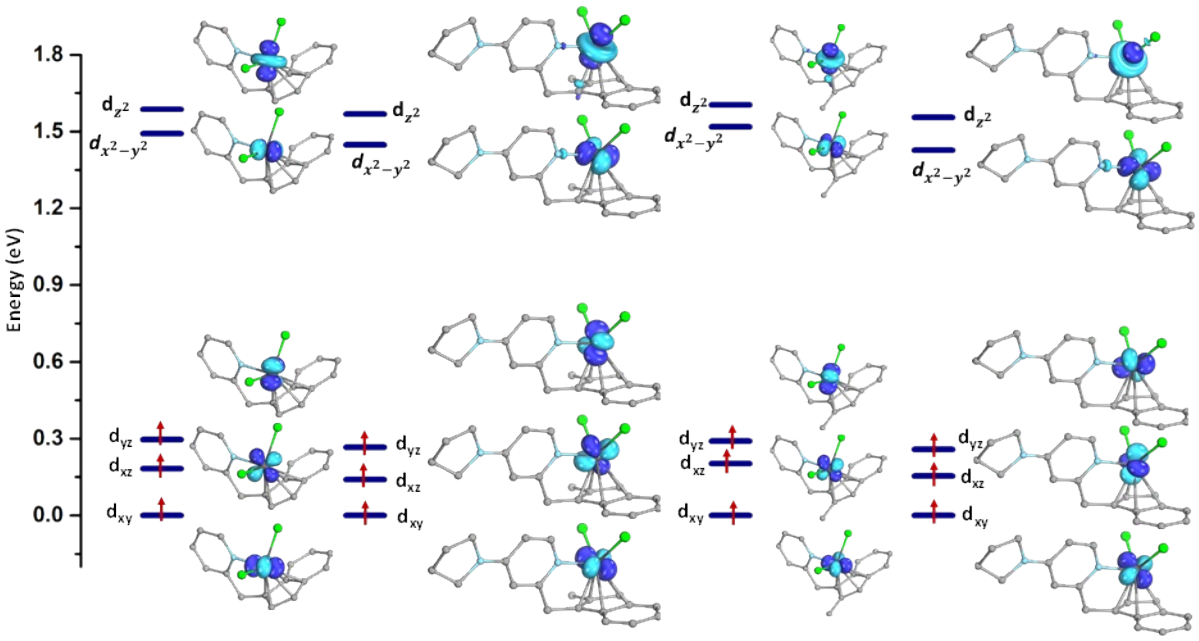

Figure S1. CASSCF/NEVPT2 computed ab initio ligand field theory (AILFT) metal d-orbitals pre-catalyst 1, pre-catalyst 2, Model 1 and Model2 (energies are in eV).

Table S2: DLPNO-CCSD(T) computed relative energies of each spin state of pre-catalysts

Catalysts	Spin	DLPNO-CCSD(T) Energies (Hartree)	Relative Energies (kJ/mol)
Pre-cat1	4	-2603.920589	0
	2	-2603.849689	186
Pre-cat2	4	-2854.39178	0
	2	-2854.319545	189

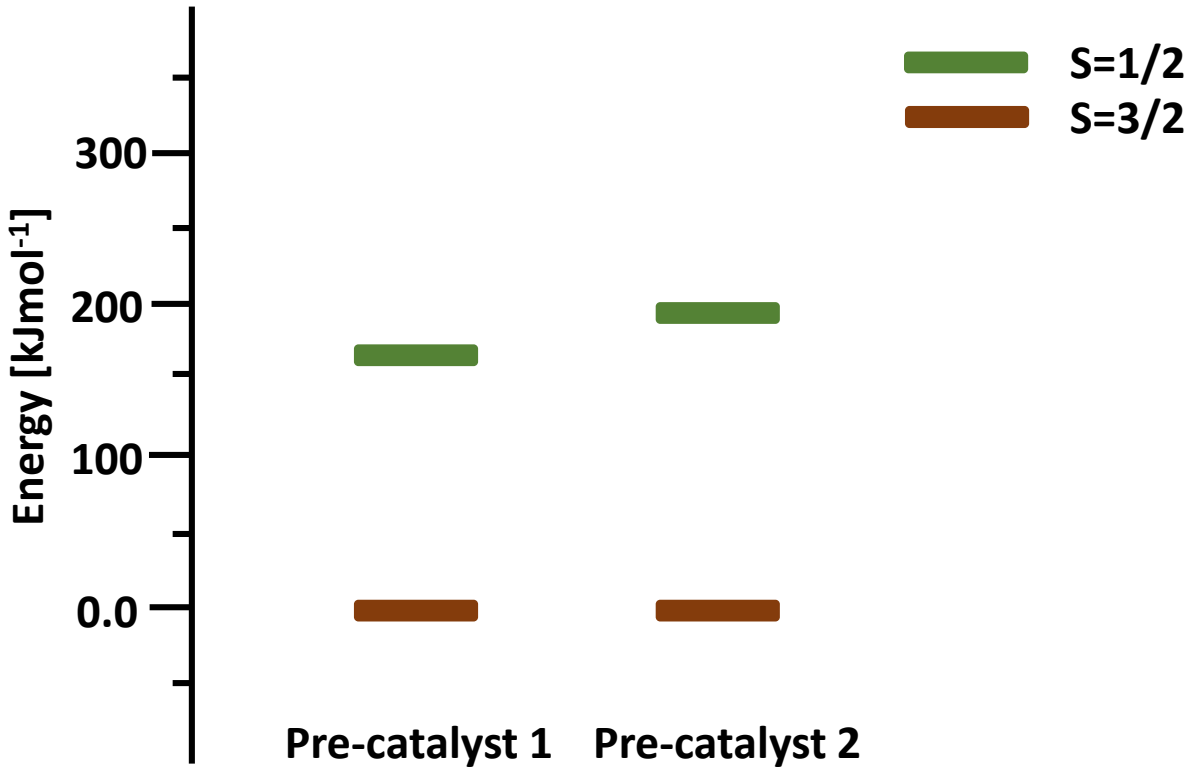

Figure S2. DLPNO-CCSD(T) computed energy separation between the ground state and other excited

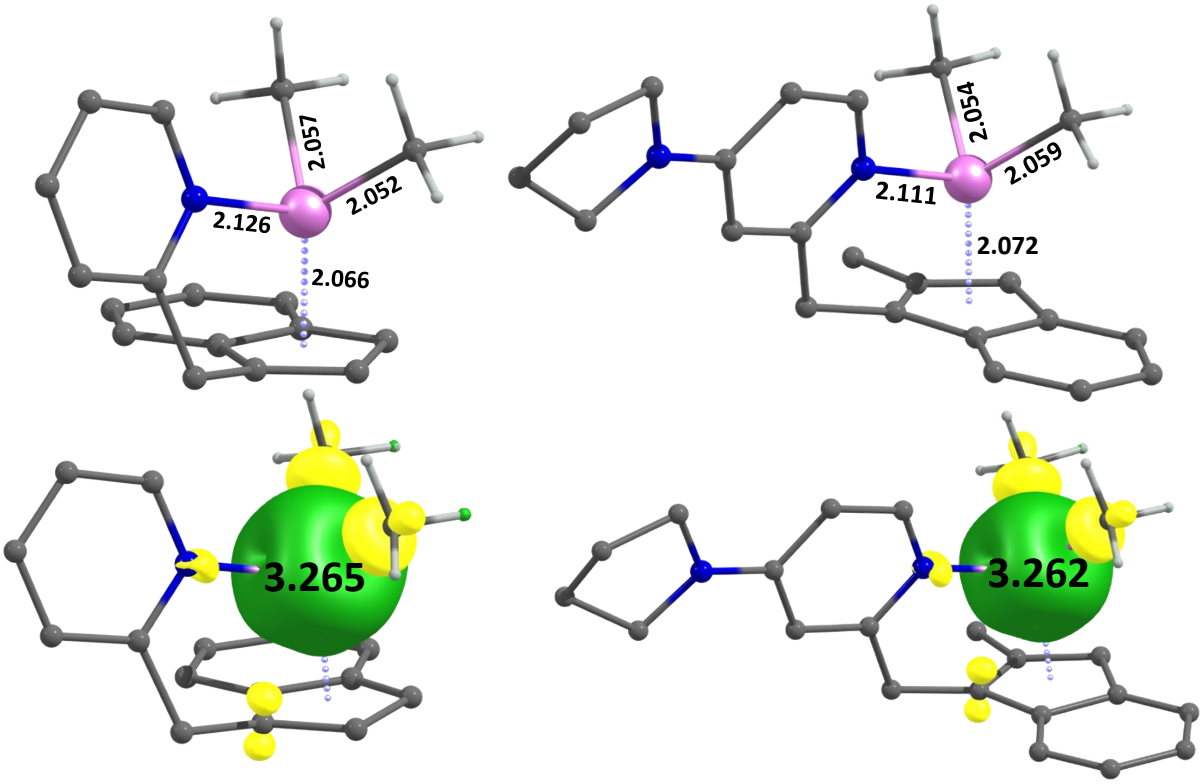

Figure S3. Optimized structure and spin density plots of **1**-R1 & **2**-R1.

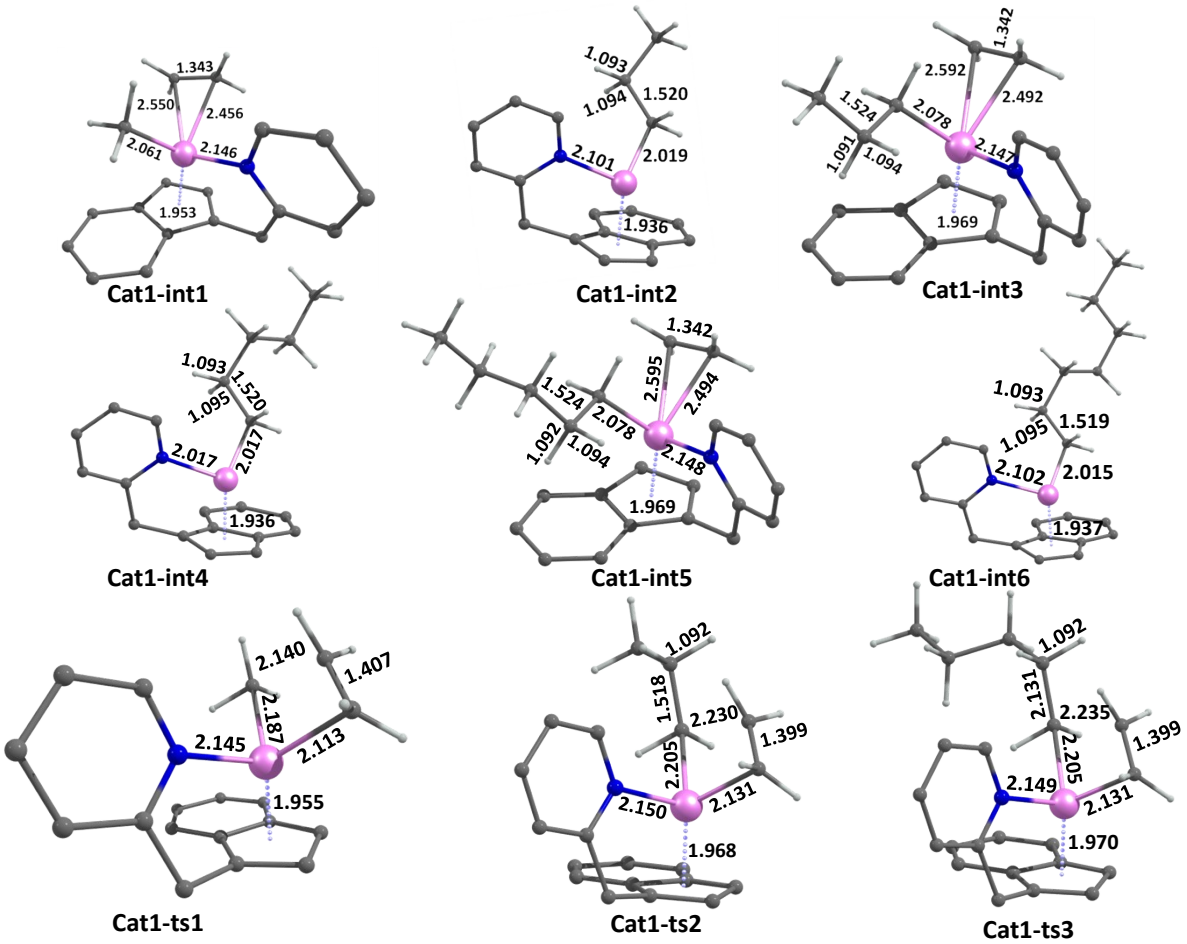

Figure S4. The DFT optimized geometry and structural parameters for 1-INT1 to 1-INT6 and 1-TS1 to 1-TS3.

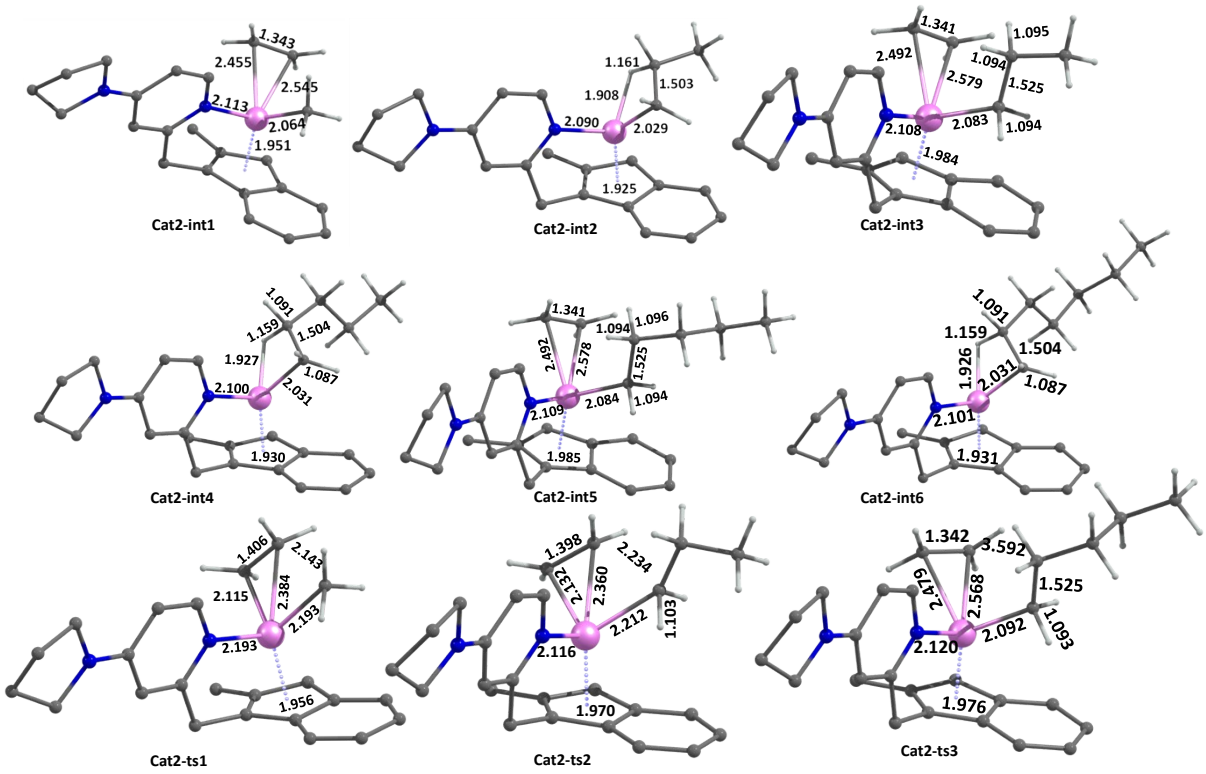

Figure S5. The DFT optimized geometry and structural parameters for 2-INT1 to 2-INT6 and 2-TS1 to 2-TS3.

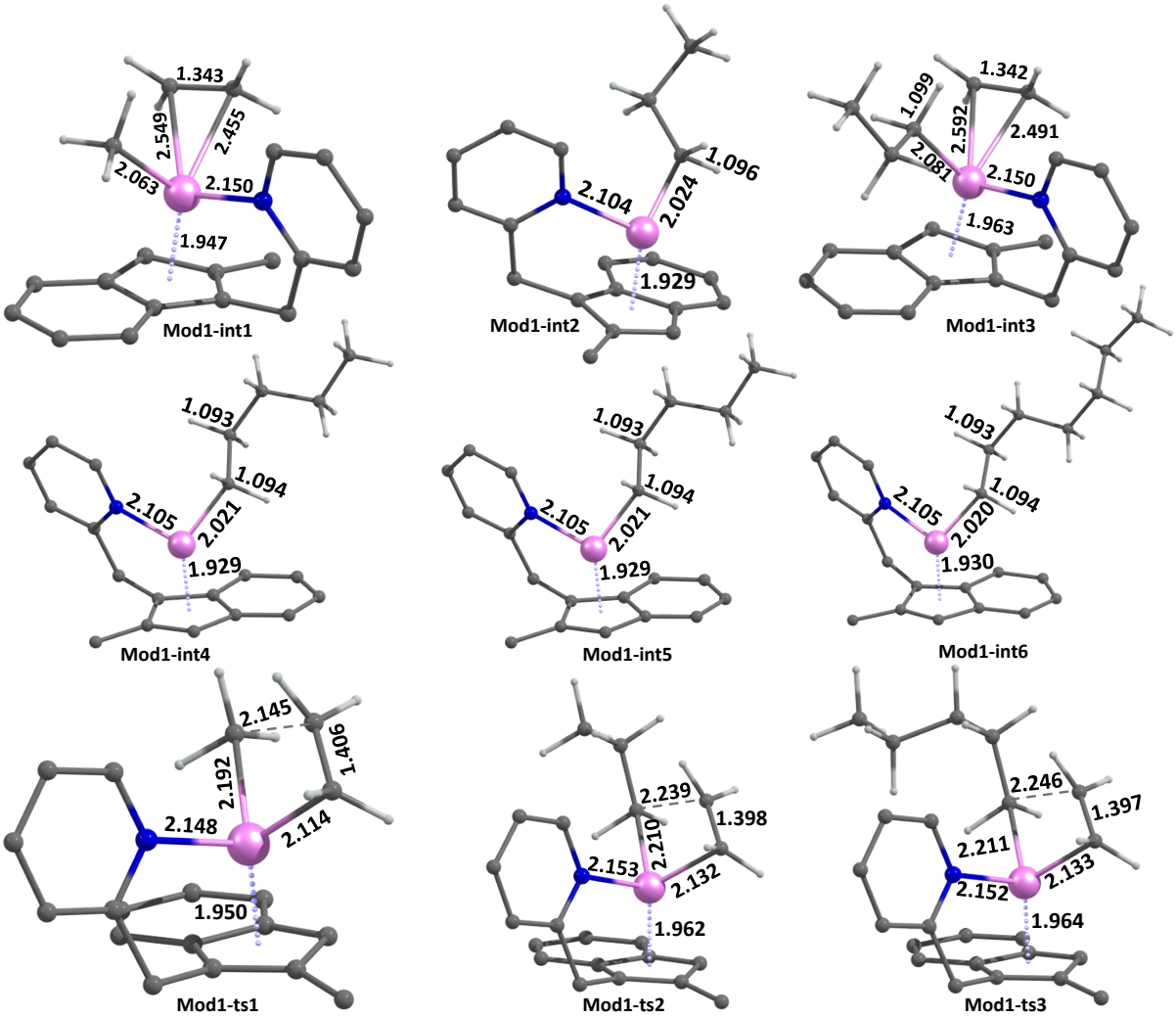

Figure S6. The DFT optimized geometry and structural parameters for mod1-INT1 to mod1-INT6 and mod1-TS1 to mod1-TS3.

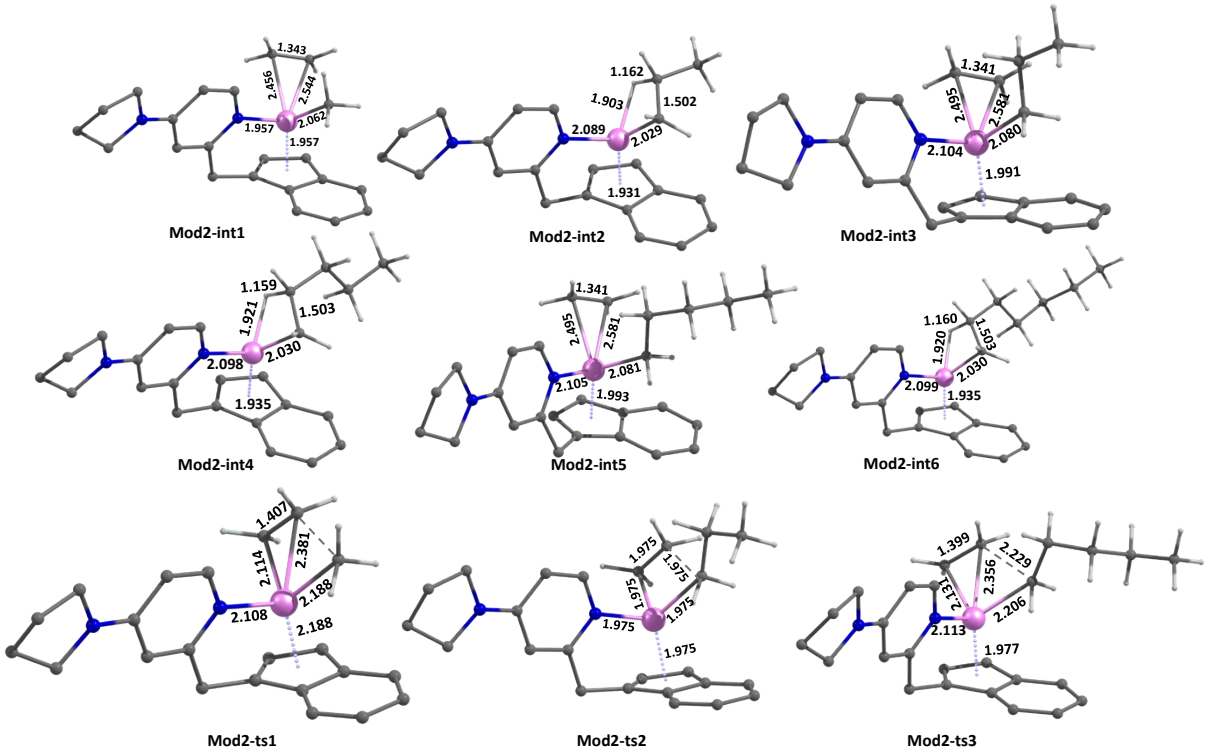

Figure S7. The DFT optimized geometry and structural parameters for mod2-INT1 to mod2-INT6 and mod2-TS1 to mod2-TS3.

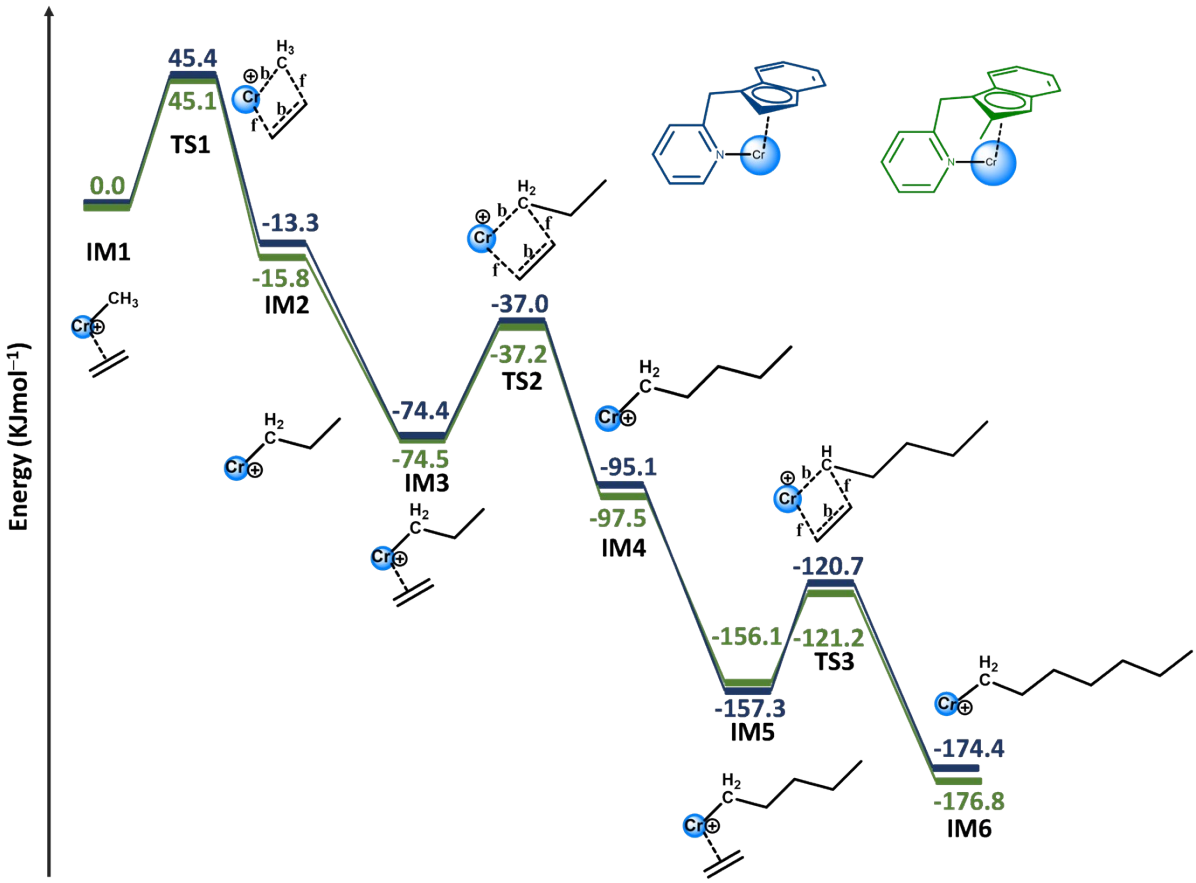

Figure S8: DFT-computed potential energy diagram (kJ/mol) of the ethylene polymerisation for catalyst 1 (Blue) and model 1 (Green).

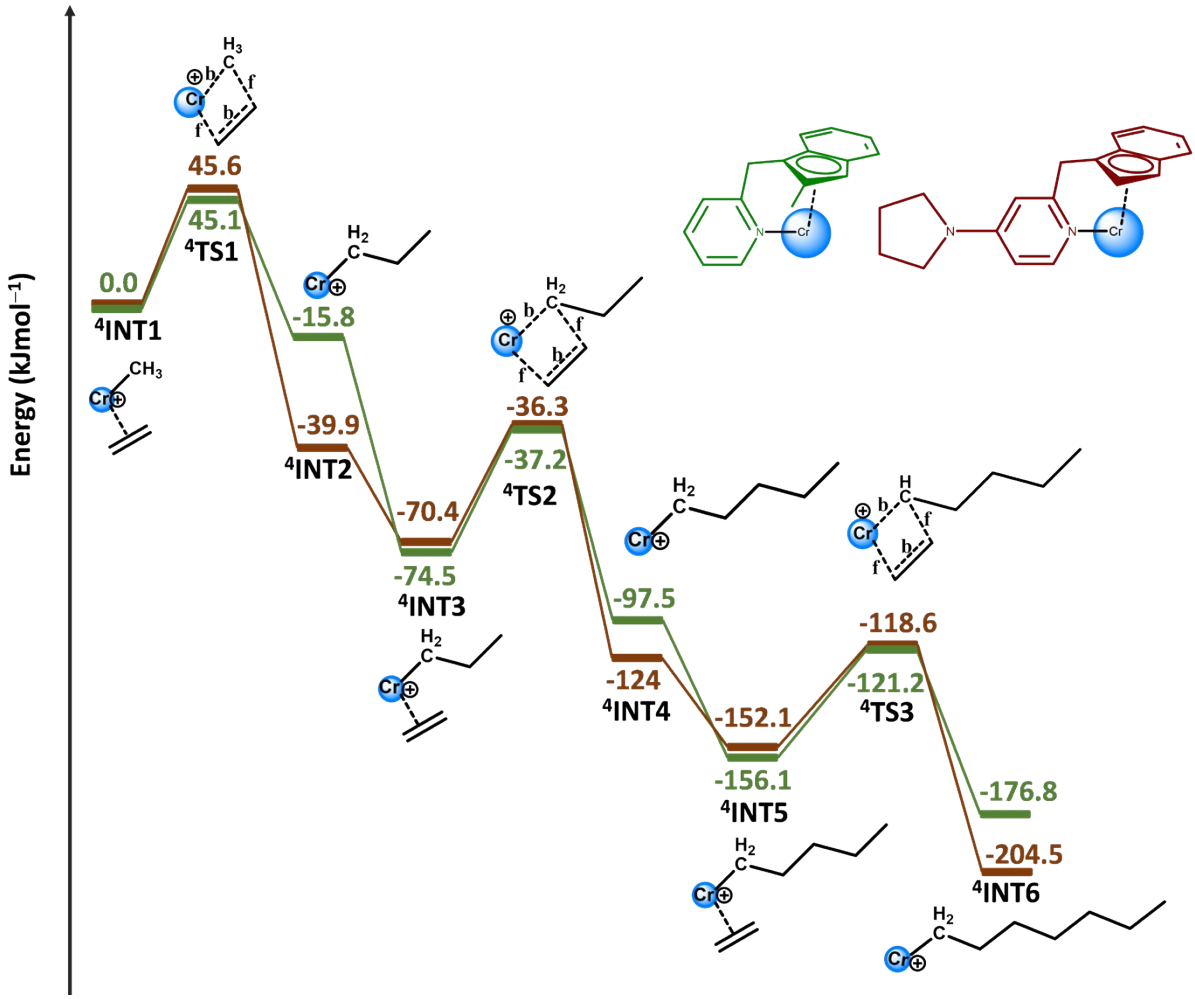

Figure S9: DFT-computed potential energy diagram (kJ/mol) of the ethylene polymerisation for model **1** (green) and model **2** (Brown).

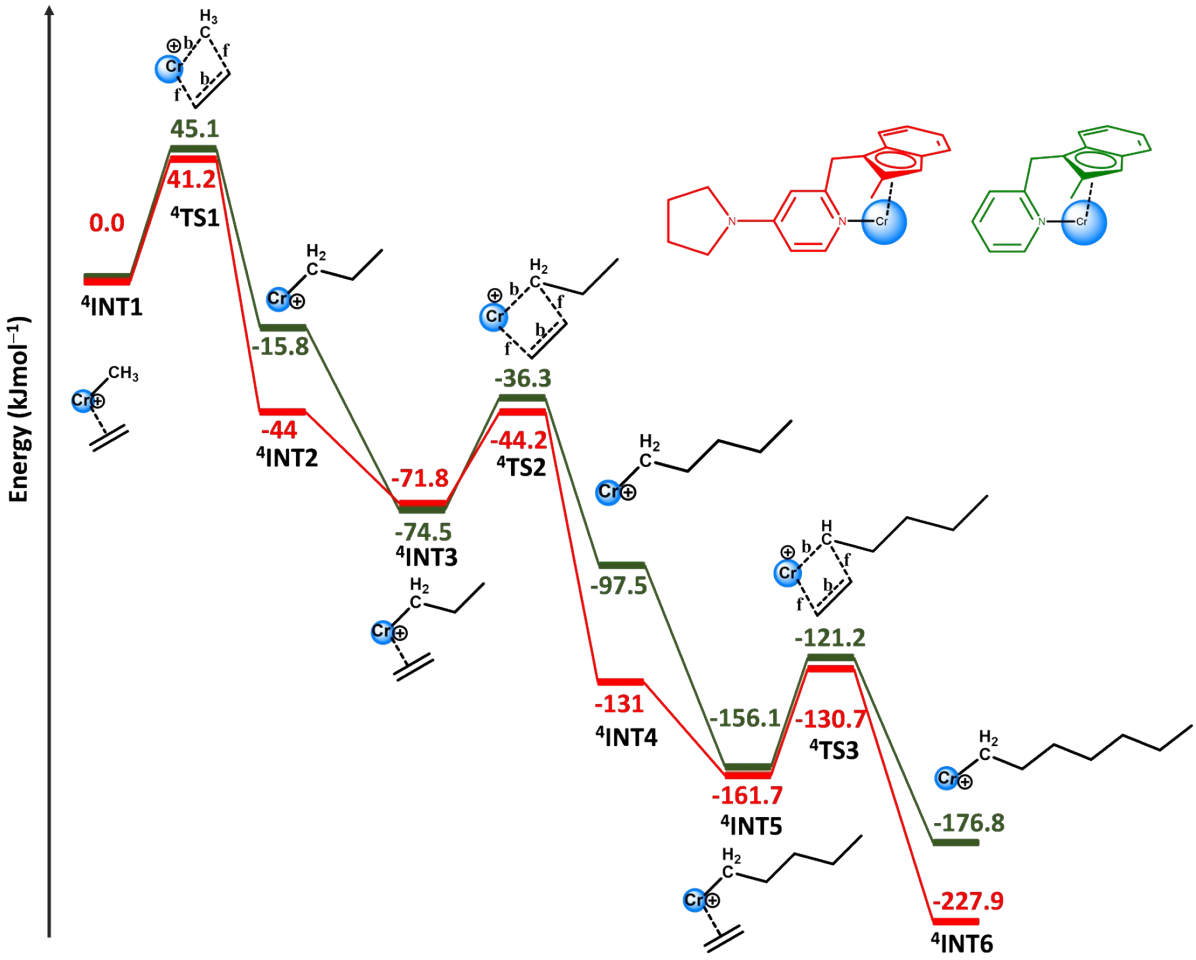

Figure S10: DFT-computed potential energy diagram (kJ/mol) of the ethylene polymerisation for catalyst **2** (Blue) and model **1** (Green).

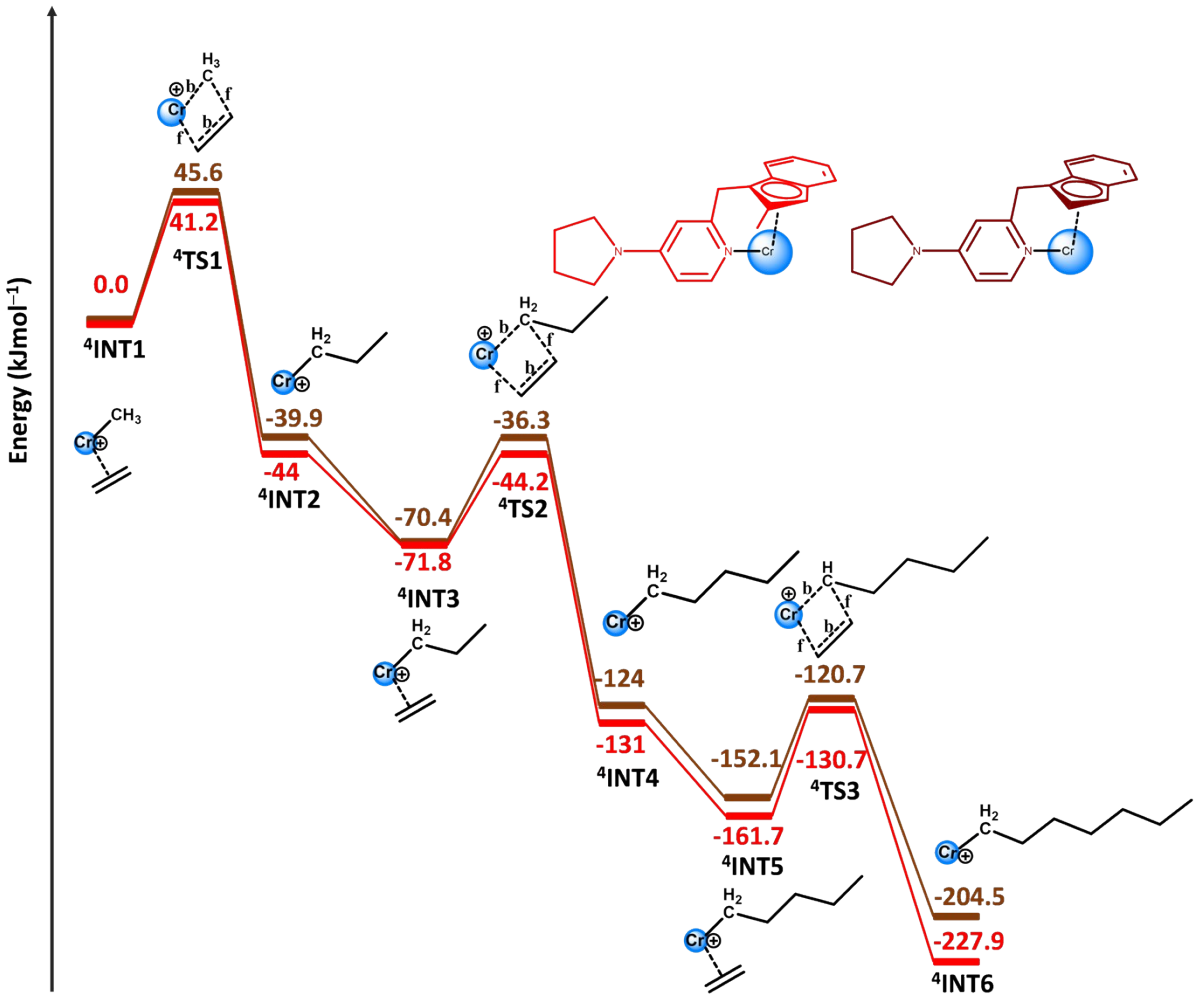

Figure S11: DFT-computed potential energy diagram (kJ/mol) of the ethylene polymerisation for catalyst **2** (Red) and model **2** (Brown).

Table S3. Calculated relevant bond parameters (bond lengths in Å and bond angles in °).

Species	**Cr-N_{py}**	**Cr-Cp^c**	**Cr-C_{Chain}**	**Cr-C_{ethene}**	**∠N_{py}-Cr-Cp^c**	**∠C_{chain}-Cr-Cp^c**	**∠C_{chain}-Cr-C_{ethene}**	**∠N_{py}-Cr-C_{chain}**	**∠N_{py}-Cr-C_{ethene}**
Pre-cat1	2.134	1.963	-	-	108.9	-	-	-	-
Pre-cat2	2.108	1.969	-	-	109.0	-	-	-	-
R1-cat1	2.126	2.066	2.057	2.052	108.2	124.9	125.7	101.7	97.3
R1-cat2	2.111	2.072	2.059	2.054	108.1	124.9	125.6	101.8	97.9
INT1-cat1	2.146	1.953	2.061	2.456/2.550	109.5	124.5	97.5	94.4	91.3
INT2-cat1	2.101	1.936	2.019	-	112.9	134.0	-	100.0	-
INT3-cat1	2.147	1.969	2.078	2.492/2.592	109.4	128.8	94.4	96.4	94.4
INT4-cat1	2.102	1.936	2.017	-	112.8	134.2	-	100.2	-
INT5-cat1	2.148	1.969	2.078	2.494/2.595	109.4	129.0	94.4	96.4	94.4
INT6-cat1	2.102	1.937	2.015	-	112.8	134.0	-	100.5	-
INT1-cat2	2.113	1.951	2.064	2.455/2.545	109.8	124.9	97.0	95.2	90.4
INT2-cat2	2.090	1.925	2.029	-	112.7	133.4	-	98.9	-
INT3-cat2	2.108	1.984	2.083	2.492/2.579	110.2	122.6	98.9	93.4	97.6
INT4-cat2	2.100	1.930	2.031	-	112.4	133.6	-	99.0	-
INT5-cat2	2.109	1.985	2.084	2.492/2.578	110.1	122.6	98.9	93.6	98.9
INT6-cat2	2.101	1.931	2.031	-	112.4	133.7	-	98.9	-
INT1-mod1	2.150	1.947	2.063	2.455/2.549	109.4	125.1	97.1	94.5	91.2
INT2- mod1	2.104	1.929	2.024	-	112.7	135.0	-	99.5	-
INT3- mod1	2.150	1.963	2.081	2.491/2.592	109.4	129.4	94.0	96.3	89.9
INT4- mod1	2.105	1.929	2.021	-	112.6	135.1	-	99.8	-
INT5- mod1	2.151	1.964	2.081	2.492/2.595	109.4	129.6	94.0	96.2	89.9
INT6- mod1	2.105	1.930	2.020	-	112.6	134.9	-	99.9	-
INT1-mod2	2.109	1.957	2.062	2.456/2.544	109.8	124.2	97.4	95.2	90.5
INT2- mod2	2.089	1.931	2.0293	-	112.9	132.2	-	99.3	-
INT3- mod2	2.104	1.991	2.080	2.495/2.581	110.3	122.0	99.2	93.7	97.6
INT4- mod2	2.098	1.935	2.030	-	112.5	132.6	-	99.4	-
INT5- mod2	2.105	1.993	2.081	2.495/2.581	110.2	122.0	99.2	93.9	97.7
INT6- mod2	2.099	1.935	2.030	-	112.4	132.5	-	99.4	-

Cp^c: center of the cyclopentadienyl ring

Table S4. The DFT computed Mulliken spin densities on selected atoms.

Spin Density (ρ)							
Species	Cr	N_{py}	C_{chain}	C_{ethene}	N_{pyr}	Cl	Cl’
Pre-cat1	3.106	-0.036	-	-	-	0.028/0.035	0.035
Pre-cat2	3.112	-0.040	-	-	0.006	0.031/0.022	0.022
R1-cat1	3.265	-0.038	-0.106	-0.122	-	-	-
R1-cat2	3.262	-0.037	-0.120	-0.106	-0.036	-	-
INT1-cat1	3.412	-0.063	-0.220	-0.022/0.023	-	-	-
TS1-cat1	3.371	-0.052	-0.091	-0.168/0.016	-	-	-
INT2-cat1	3.523	-0.058	-0.259	-	-	-	-
INT3-cat1	3.463	-0.065	-0.261	-0.025/0.023	-	-	-
TS2-cat1	3.389	-0.052	-0.110	-0.170/0.018	-	-	-
INT4-cat1	3.528	-0.058	-0.271	-	-	-	-
INT5-cat1	3.469	-0.064	-0.271	-0.025/0.024	-	-	-
TS3-cat1	3.390	-0.052	-0.112	-0.172/0.018	-	-	-
INT6-cat1	3.528	-0.058	-0.275	-	-	-	-
INT1-cat2	3.384	-0.066	-0.215	-0.016/0.021	0.012	-	-
TS1-cat2	3.356	-0.055	-0.090	-0.162/0.016	0.011	-	-
INT2-cat2	3.420	-0.059	-0.240	-	0.012	-	-
INT3-cat2	3.457	-0.075	-0.260	-0.012/0.027	0.011	-	-
TS2-cat2	3.376	-0.057	-0.111	-0.164/0.018	0.010	-	-
INT4-cat2	3.434	-0.061	-0.247	-	0.012	-	-
INT5-cat2	3.463	-0.075	-0.269	-0.013/0.027	0.011	-	-
TS3-cat2	3.449	-0.068	-0.268	-0.024/0.035	0.011	-	-
INT6-cat2	3.435	-0.062	-0.247	-	0.012	-	-
INT1-mod1	3.412	-0.064	-0.218	-0.020/0.023	-	-	-
TS1-mod1	3.378	-0.053	-0.092	-0.0163/0.017	-	-	-
INT2- mod1	3.522	-0.056	-0.252	-	-	-	-
INT3- mod1	3.462	-0.066	-0.256	-0.023/0.023	-	-	-
TS2-mod1	3.397	-0.054	-0.113	-0.165/0.018	-	-	-
INT4- mod1	3.527	-0.056	-0.263	-	-	-	-
INT5- mod1	3.468	-0.066	-0.266	-0.023/0.024	-	-	-
TS3-mod1	3.398	-0.054	-0.114	-0.166/0.019	-	-	-
INT6- mod1	3.527	-0.056	-0.267	-	-	-	-
INT1-mod2	3.382	-0.064	0.217	-0.018/0.021	0.013	-	-
TS1-mod2	3.348	-0.053	-0.089	-0.166/0.016	0.011	-	-
INT2- mod2	3.421	-0.059	-0.245	-	0.012	-	-
INT3- mod2	3.457	-0.077	-0.261	-0.013/0.025	0.011	-	-
TS2-mod2	3.368	-0.054	-0.108	-0.169/0.018	0.011	-	-
INT4- mod2	3.433	-0.060	-0.251	-	0.012	-	-
INT5- mod2	3.463	-0.077	0.270	-0.013/0.026	0.011	-	-
TS3-mod2	3.370	-0.054	-0.115	-0.170/0.019	0.011	--	
INT6- mod2	3.434	-0.060	-0.252	-	0.012	-	-

Table S5. The DFT computed NBO charges on pertinent atoms.

Species	Cr	N_{py}	C_{Chain}	C_{ethene}	N_{pyr}	Cl	Cl'
Pre-cat1	0.150	-0.375	-	-	-	-0.259	-0.282
Pre-cat2	0.256	-0.199	-	-	-0.039	-0.378	-0.396
R1-cat1	0.426	-0.315	-0.745	-0.272/-0.197	-	-	-
R1-cat2	0.379	-0.357	-0.730	-0.202/-0.262	-0.228	-	-
INT1-cat1	0.312	-0.412	-0.831	-0.367/-0.296	-	-	-
TS1-cat1	0.316	-0.178	-0.533	-0.138/-0.336	-	-	-
INT2-cat1	0.720	-0.445	-0.592	--	-	-	-
INT3-cat1	0.579	-0.423	-0.598	-0.372/-0.303	-	-	-
TS2-cat1	0.266	-0.170	-0.341	-0.300/-0.146	-	-	-
INT4-cat1	0.717	-0.444	-0.590	--	-	-	-
INT5-cat1	0.322	-0.143	-0.466	-0.208/-0.182	-	-	-
TS3-cat1	0.260	-0.171	-0.392	-0.296/-0.147	-	-	-
INT6-cat1	0.713	-0.444	-0.586	--	-	-	-
INT1-cat2	0.312	-0.179	-0.632	-0.174/-0.203	-0.024	-	-
TS1-cat2	0.294	-0.210	-0.535	-0.339/-0.129	-0.024	-	-
INT2-cat2	0.437	-0.462	-0.508	--	-0.329	-	-
INT3-cat2	0.644	-0.470	-0.609	-0.308/-0.384	-0.330	-	-
TS2-cat2	0.240	-0.199	-0.336	-0.305/-0.135	0.024	-	-
INT4-cat2	0.473	-0.467	-0.522	--	-0.330	-	-
INT5-cat2	0.654	-0.471	-0.613	-0.308/-0.385	-0.330	-	-
TS3-cat2	0.300	-0.189	-0.430	-0217/-0.194	-0.024	-	-
INT6-cat2	0.475	-0.467	-0.522	--	-0.330	-	-
INT1-mod1	0.526	-0.415	-0.845	-0.372/-0.297	-	-	-
TS1-mod1	0.274	-0.166	-0.354	-0.340/-0.130	-	-	-
INT2- mod1	0.739	-0.448	-0.605	--	-	-	-
INT3- mod1	0.635	-0.437	-0.616	-0.305/-0.377	-	-	-
TS2-mod1	0.222	-0.157	-0340	-0.306/-0.135	-	-	-
INT4- mod1	0.737	-0.448	-0.603	--	-	-	-
INT5- mod1	0.644	-0.428	-0.621	-0.378/-0.305	-	-	-
TS3-mod1	0.218	-0.156	-0.395	-0.303/-0.135	-	-	-
INT6- mod1	0.735	-0.447	-0.600	--	-	-	-
INT1-mod2	0.479	-0.457	-0.830	-0.302/-0.362	-0.328	-	-
TS1-mod2	0.337	-0223	-0.534	-0.335/-0.138	-0.023	-	-
INT2- mod2	0.417	-0.460	-0.501	--	-0.329	-	-
INT3- mod2	0.590	-0.462	-0.591	-0.379/-0.307	-0.329	-	-
TS2-mod2	0.285	-0214	-0.338	-0.299/-0.145	-0.024	-	-
INT4- mod2	0.447	0.465	-0.514	--	-0.329	-	-
INT5- mod2	0.598	-0.463	-0.595	-0.380/-0.307	-0.329	-	-
TS3-mod2	0.280	-0.214	-0.377	-0.294/-0.145	-0.024	-	-
INT6- mod2	0.448	-0.465	-0.513	--	-0.329	-	-

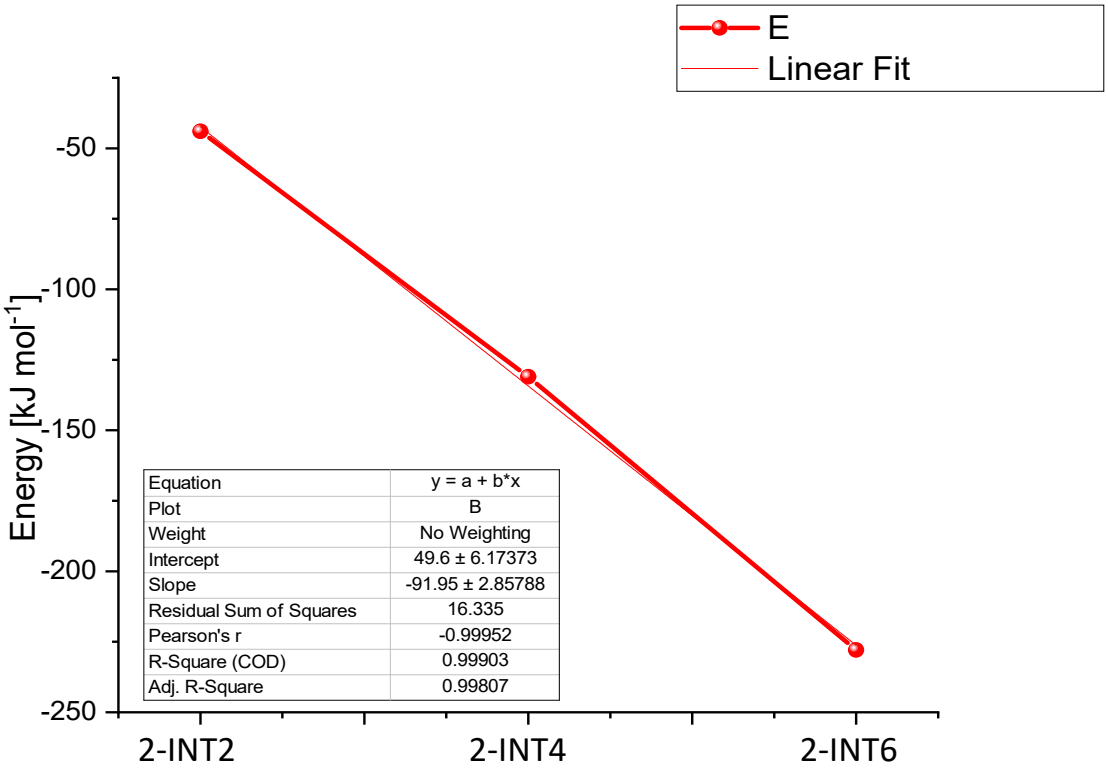

Figure S12. The linear variation of Energy vs **2**-INT2 – **2**-INT6 with continuous decrease for every successive alkyl migrated species for catalyst 2.

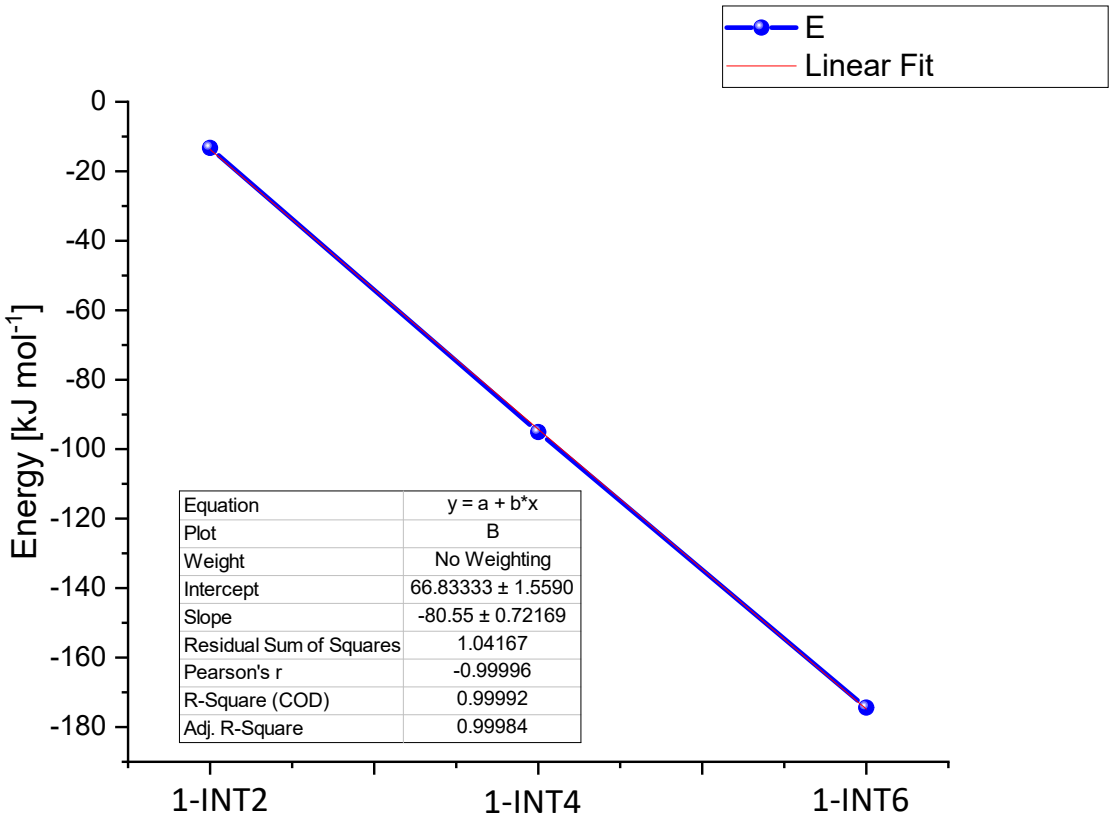

Figure S13. The linear variation of Energy vs **1**-INT2 – **1**-INT6 with continuous decrease for every successive alkyl migrated species for complex **1**.

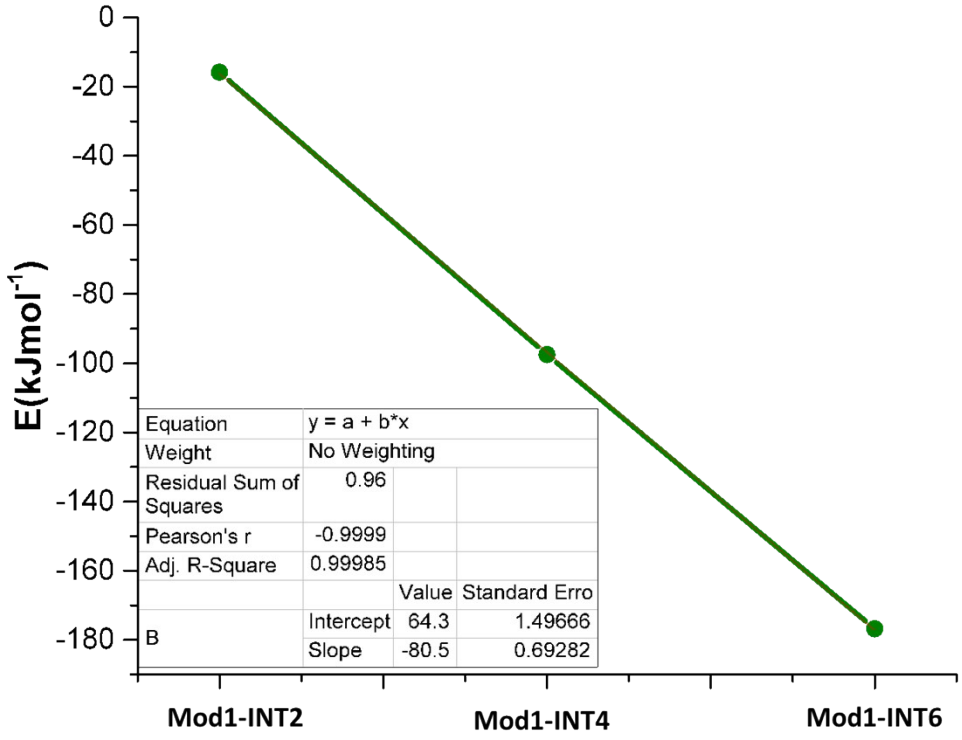

Figure S14. The linear variation of Energy vs **1**-INT2 – **1**-INT6 with continuous decrease for every successive alkyl migrated species for model **1**.

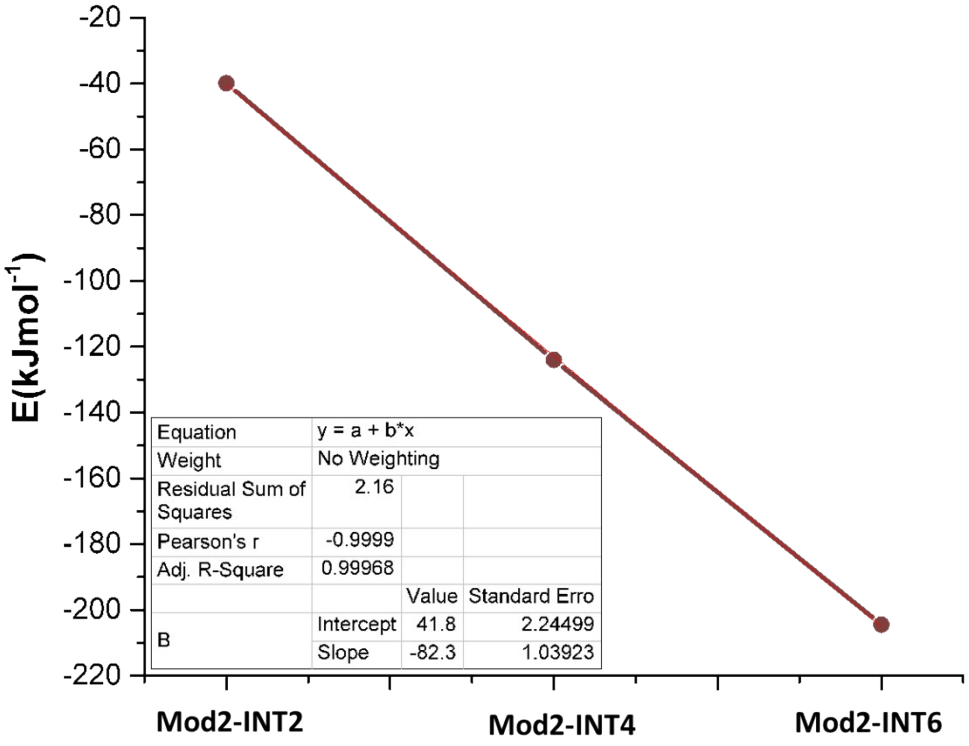

Figure S15. The linear variation of Energy vs **1**-INT2 – **1**-INT6 with continuous decrease for every successive alkyl migrated species for model **2**.

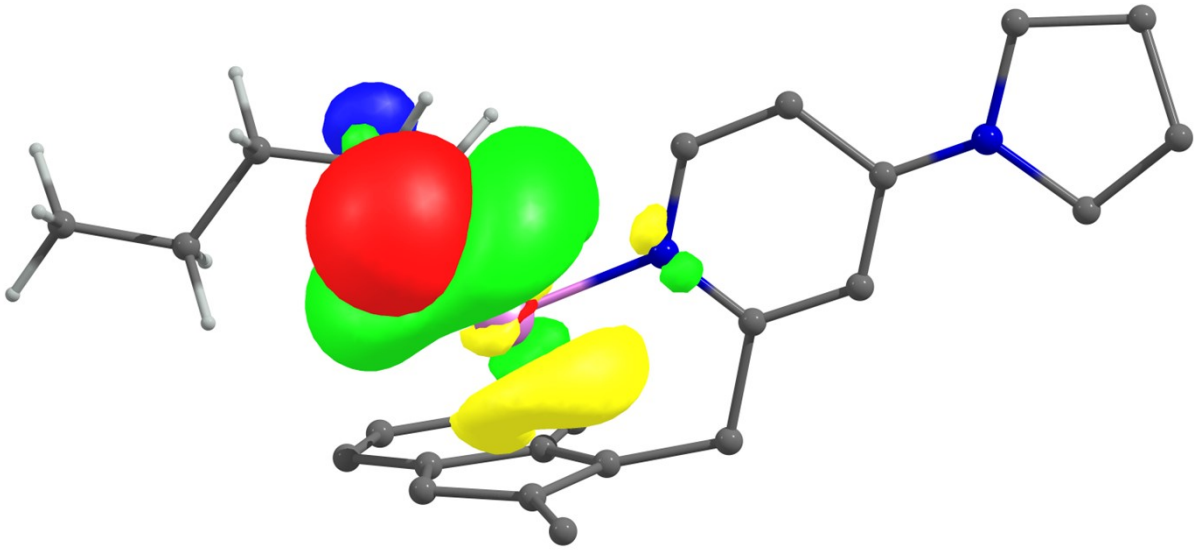

Figure S16. NBO plot of **2**-IN4 showing the orbital interaction diagram between the **σ**(C–H) → **Cr** (d_z^2)