DFT Study of C-C and C-N coupling on a quintuple-bonded Cr_2 template: MECP (Minimum Energy Crossing Point) Barriers Control Product Distribution

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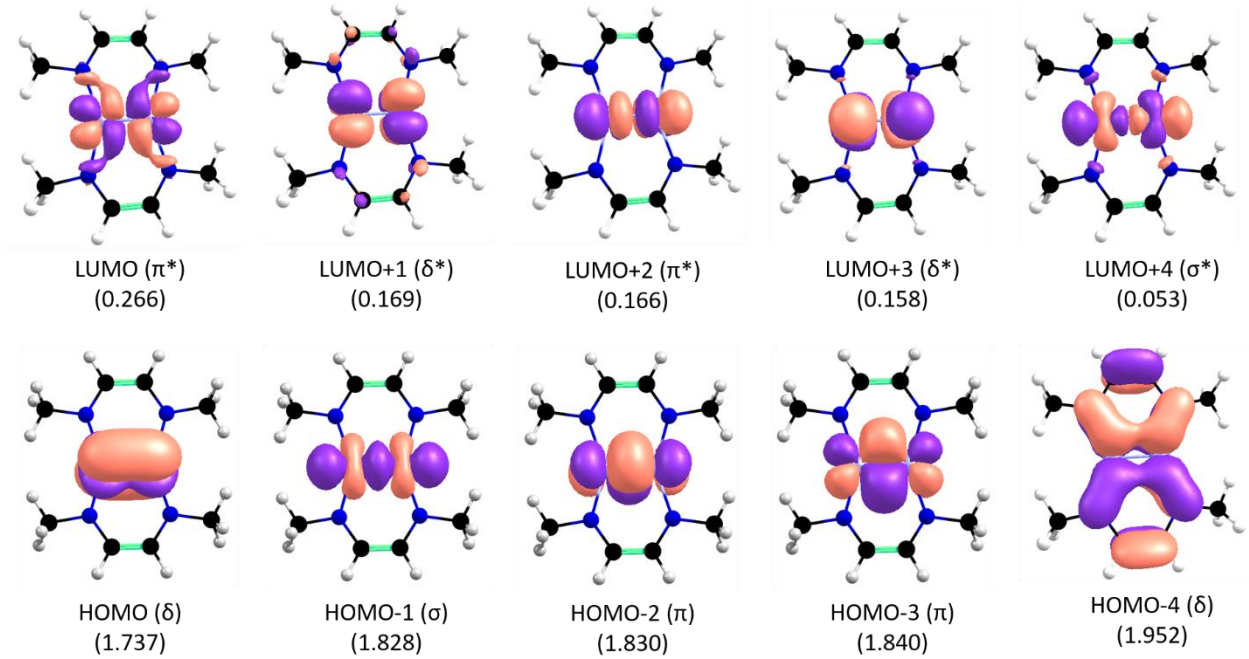


Figure S1. Natural orbitals of **^{1}1b** obtained from CASSCF (12e, 11o) calculation on the DFT optimized geometry considering def2-tzvp basis set for all atoms. Type of orbitals with their orbital occupation numbers are given in parenthesis.

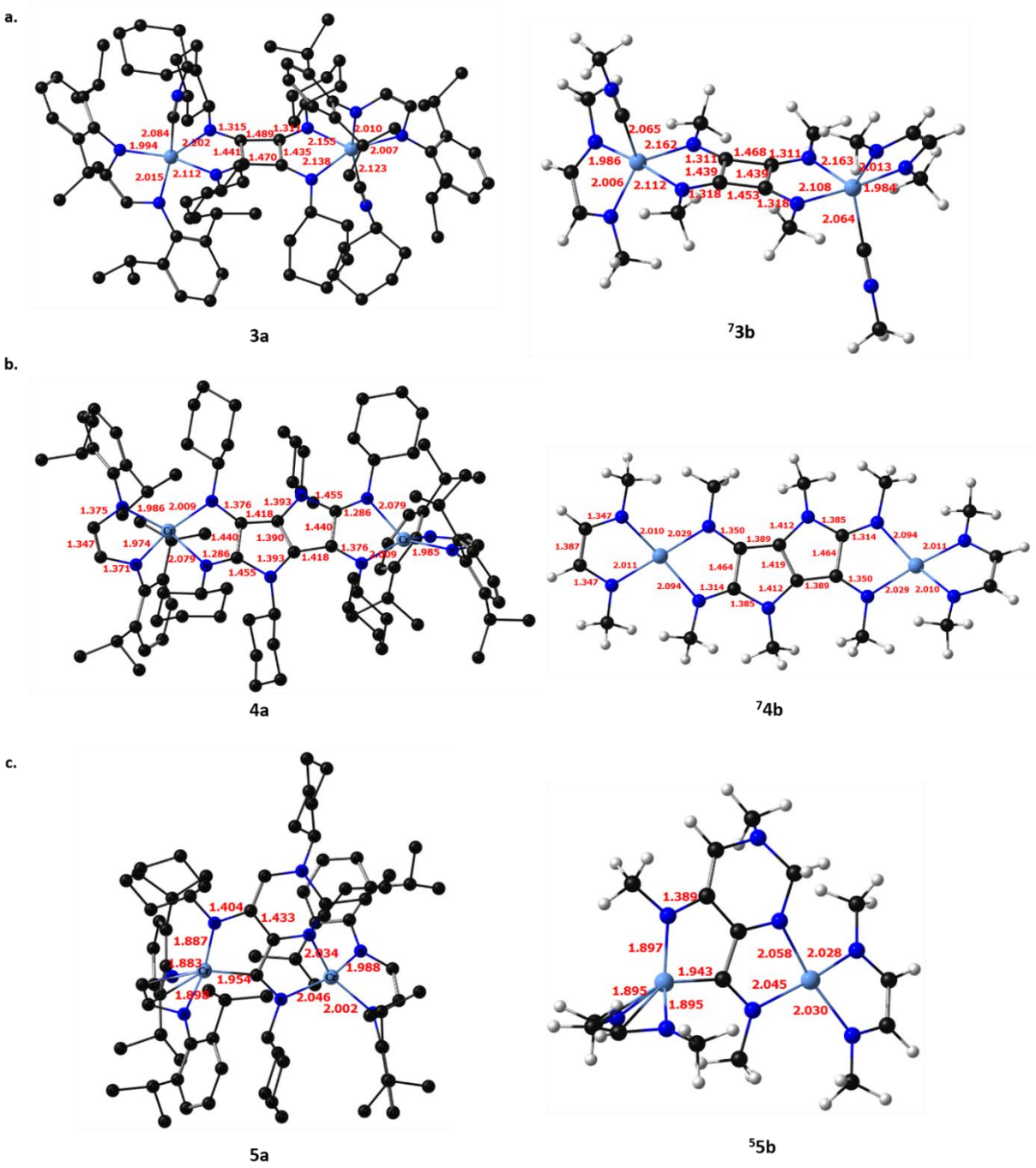


Figure S2. Important bond length comparison between X-ray data and optimize bond parameter of model complexes.

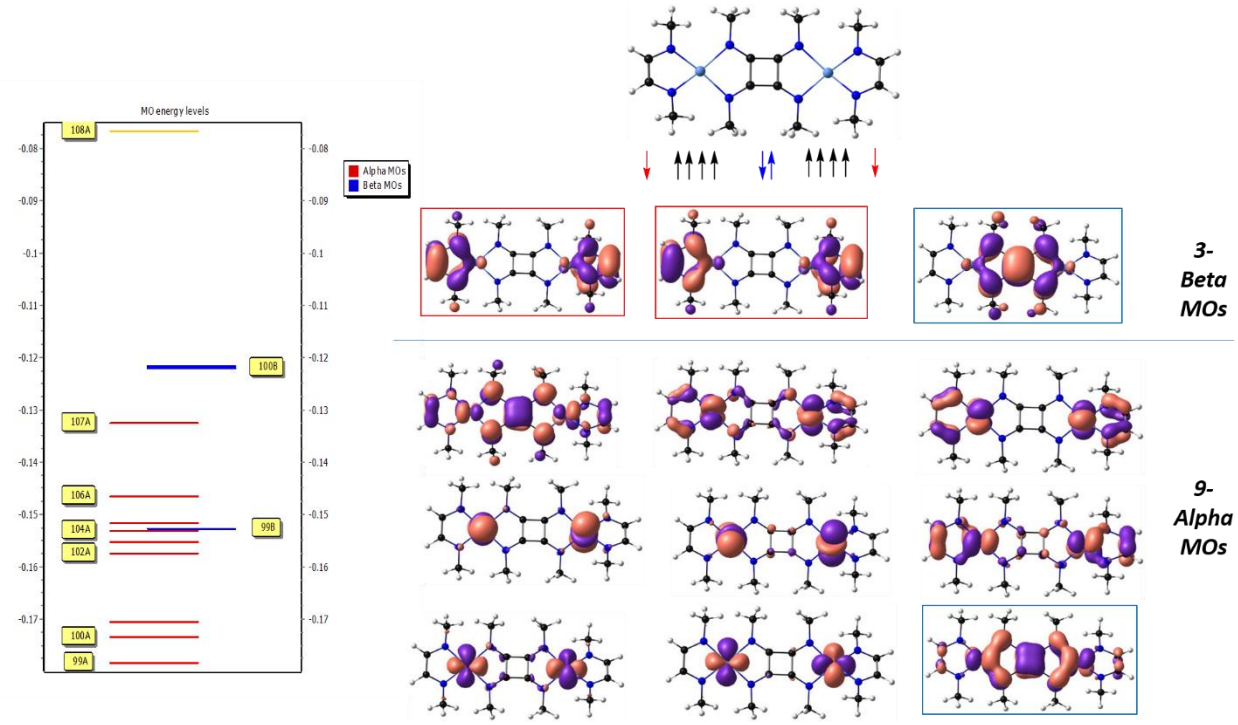


Figure S3. Ground state electronic structure description of the core of complex **3b** i.e. $L_2Cr_2[C_4(NMe)_4]$ (L = diimine ligand, Scheme 1) with important α and β type Kohn Sham molecular orbitals.

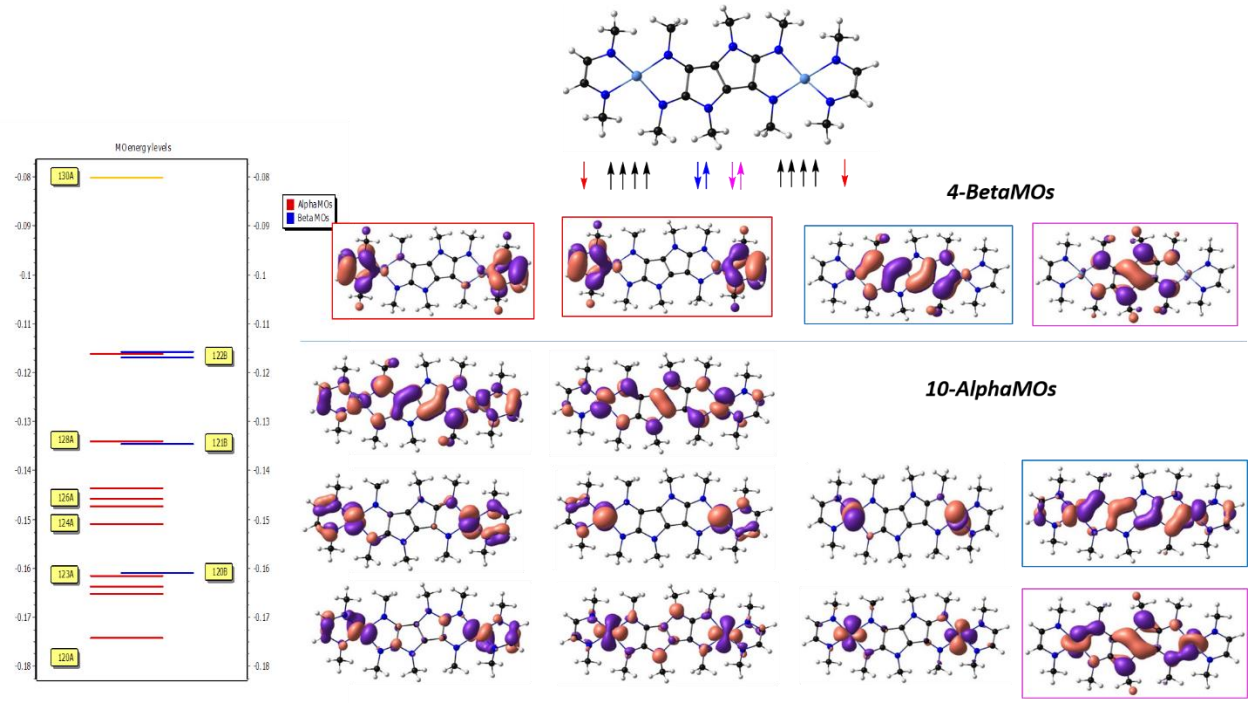
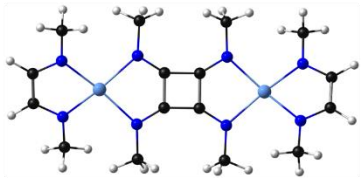


Figure S4. Ground state electronic structure description of the core of complex **4b** i.e. $L_2Cr_2[C_6(NMe)_6]$ (L = diimine ligand, Scheme 1) with important α and β type Kohn Sham molecular orbitals.

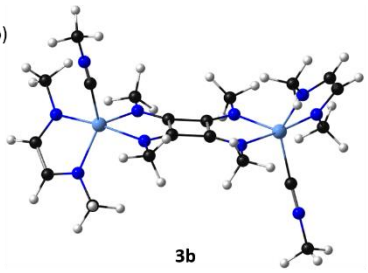
(a)



Core of **3b**

Spin Multiplicity	M06-L	BP86
3	26.1	40.0
5	25.9	19.4
7	0.0	0.0
9	10.9	12.3

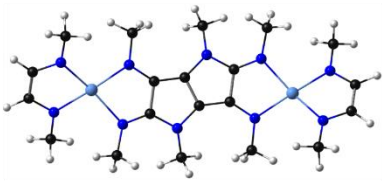
(b)



3b

Spin Multiplicity	M06-L	BP86
3	19.0	6.3
5	15.7	3.3
7	0.0	0.0
9	13.7	19.5

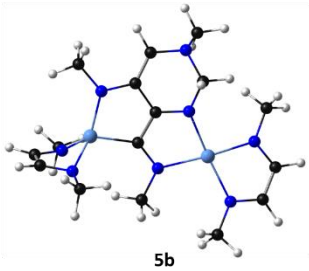
(c)



4b

Spin Multiplicity	M06-L	BP86
3	31.3	20.5
5	19.1	3.3
7	0.0	0.0
9	9.9	N.C.

(d)



5b

Spin Multiplicity	M06-L	BP86
3	2.8	5.5
5	0.0	0.0
7	6.0	6.6
9	6.5	N.C.

Figure S5. The relative stabilities of different spin states using M06-L functional with LANL2DZ basis set for Cr and 6-31G(d) basis set for other atoms and dispersion corrected functional BP86-GD3BJ with def2-tzvp basis set for Cr and 6-31G(d) basis set for other atoms; (a) Core of **3b**, (b) **3b**, (c) **4b** and (d) **5b**. N.C. stands for non-convergence.

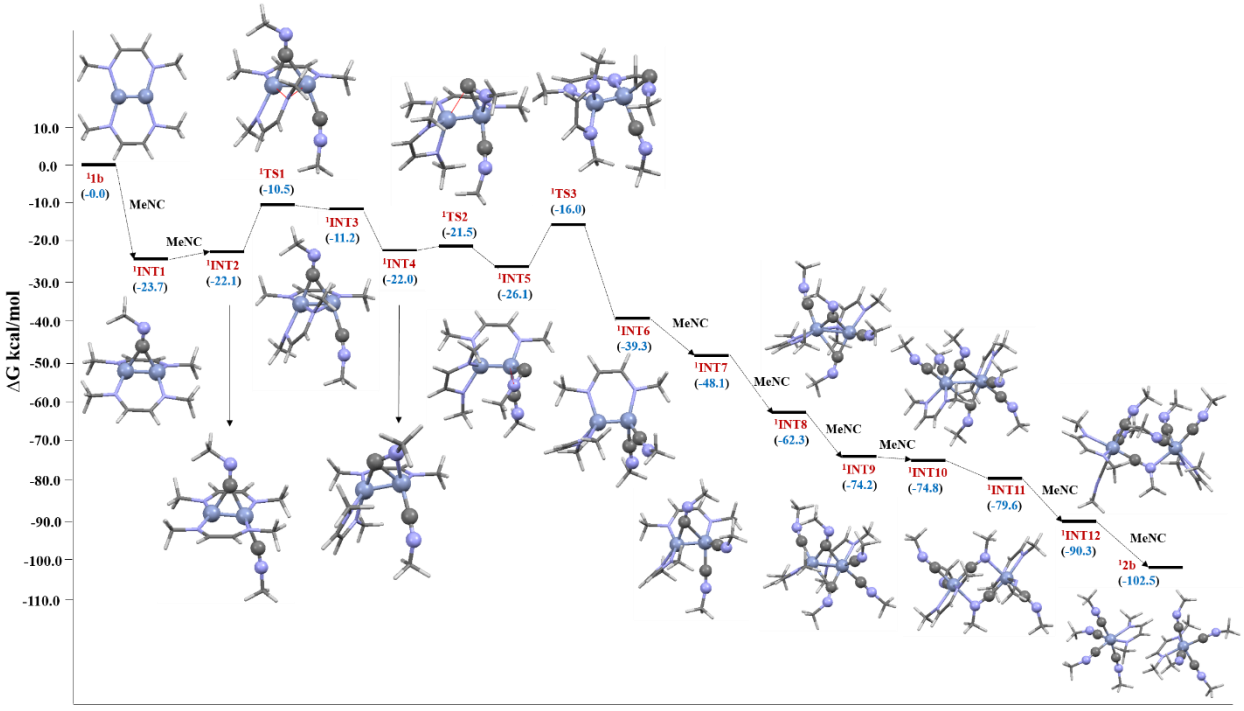


Figure S6. Free energy (kcal/mol) profile diagram for the formation of **^{1}2b** starting from **^{1}1b** at M06L level of theory with LANL2DZ basis set for Cr and 6-31G(d) basis set for all other atoms. (a) HOMO of **^{1}1b**; (b) HOMO of **^{1}INT1**.

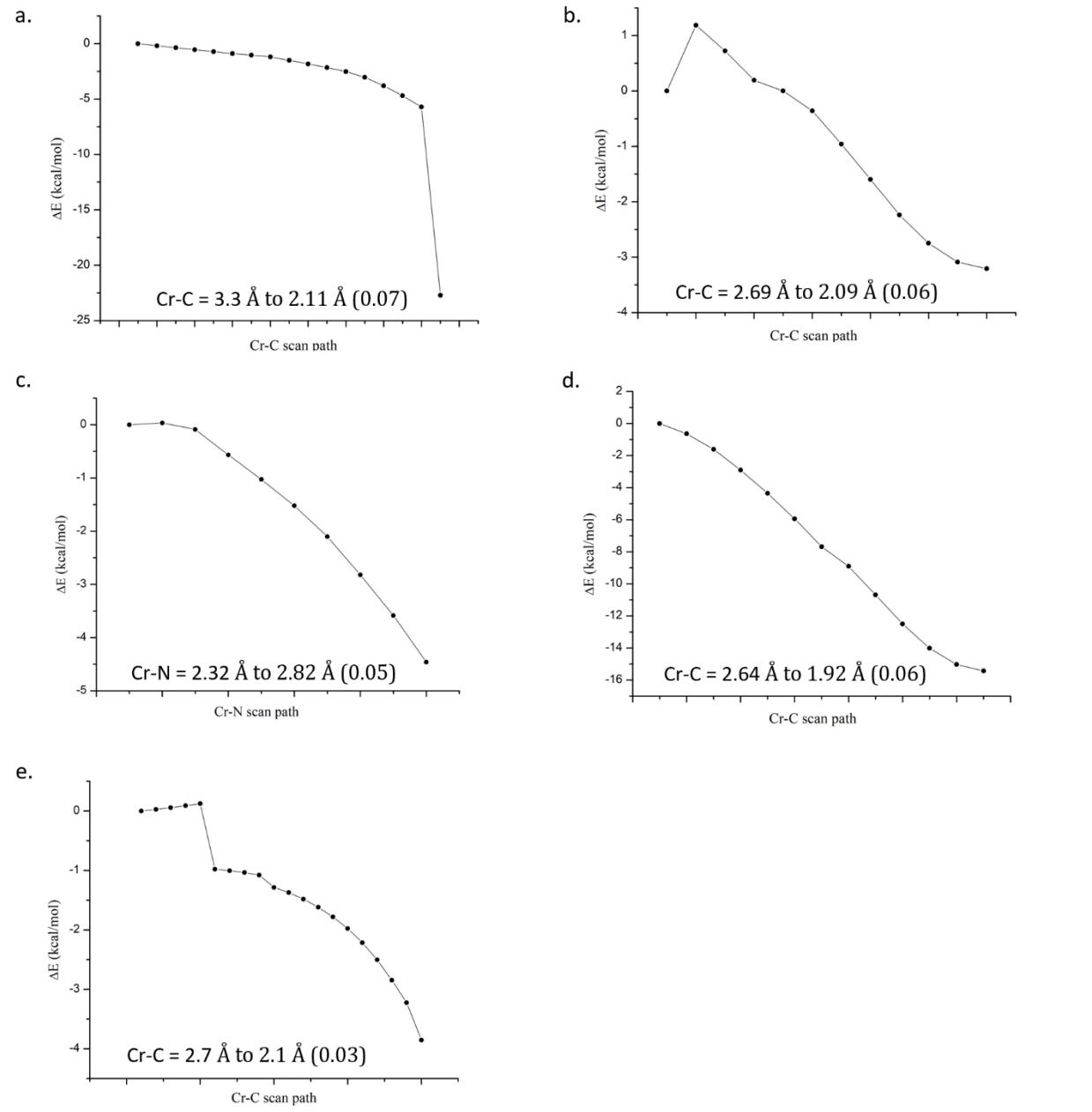


Figure S7. Energy (kcal/mol) profile diagram for the scanning pathways wherever transition states are not located due to flat nature of the PES at M06L level of theory with LANL2DZ basis set for Cr and 6-31G(d) basis set for all other atoms. (a) ^{1}**1b** to ^{1}**INT1**; (b) ^{1}**INT1** to ^{1}**INT2**; (c) ^{1}**INT3** to ^{1}**INT4**; (d) ^{1}**INT6** to ^{1}**INT7**; and (e) ^{1}**INT7** to ^{1}**INT8**. In all cases bond scanning are performed. The starting and end bond distances for different scanning pathways are given in the figure with step size (in Å) values in parenthesis.

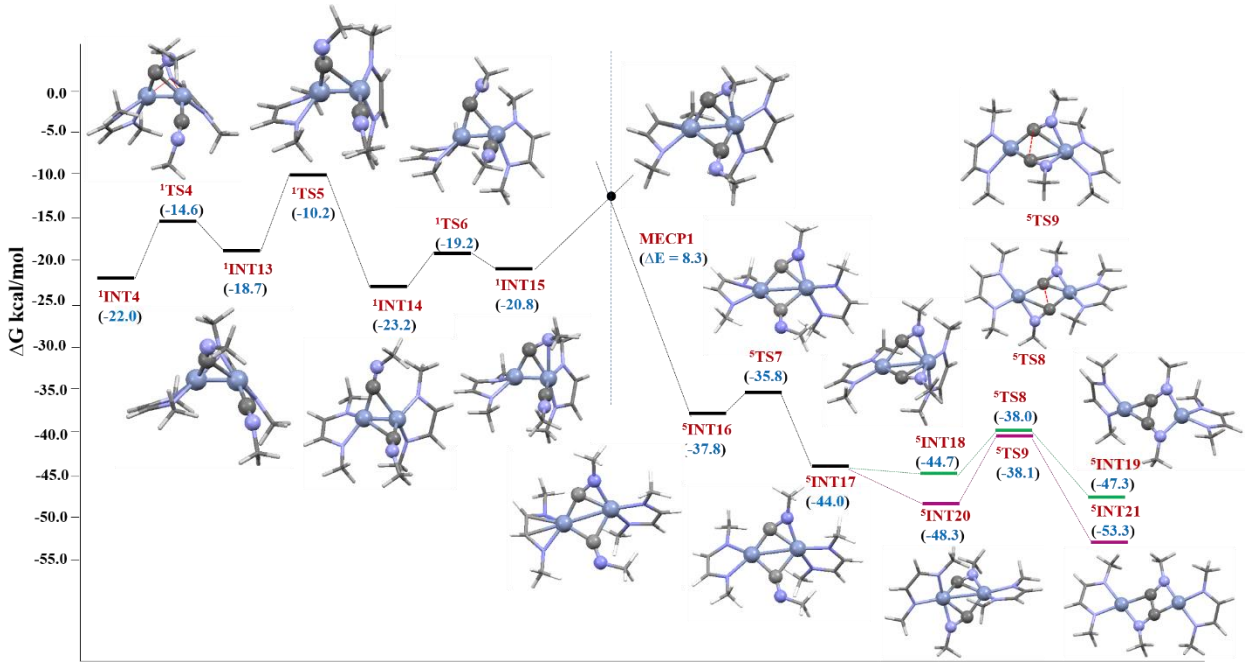


Figure S8. Free energy (kcal/mol) profile diagram for the formation of C-C coupled intermediates (**^{5}INT19** and **^{5}INT21**) starting from **^{1}INT4** at M06L level of theory with LANL2DZ basis set for Cr and 6-31G(d) basis set for all other atoms. The relative energy between **^{1}INT15** and **MECP1**, (ΔE), is the electronic energy difference.

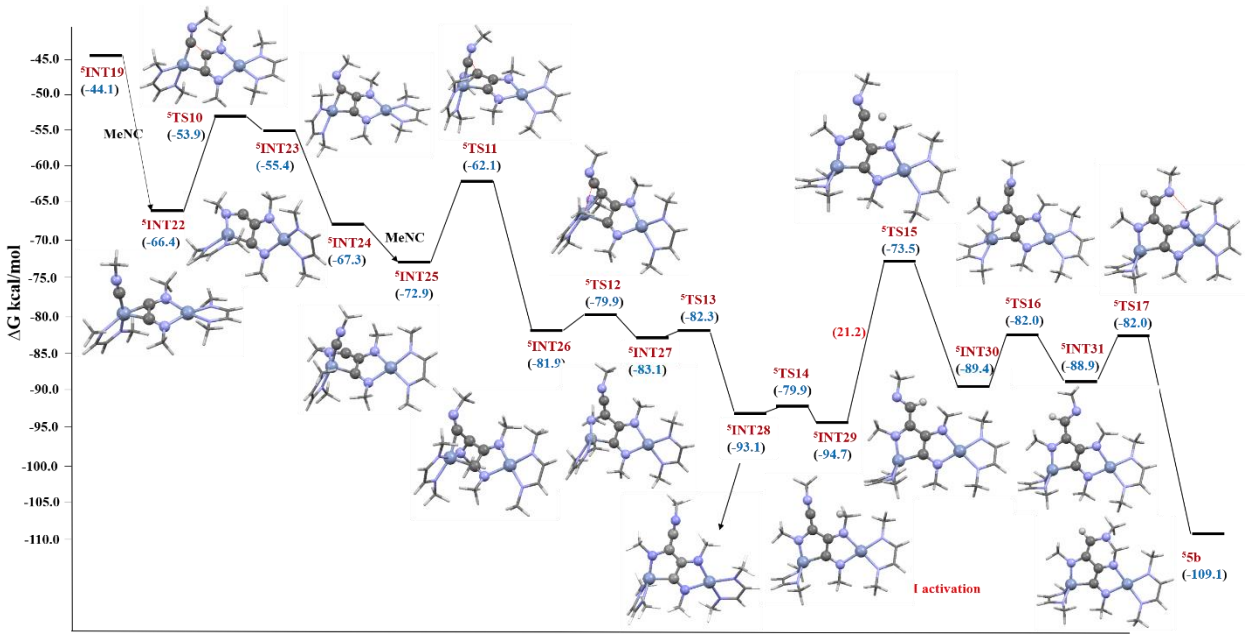


Figure S9. Free energy (kcal/mol) profile diagram for the formation complex **^{5}5b** from cis intermediate **^{5}INT19** at M06L level of theory with LANL2DZ basis set for Cr and 6-31G(d) basis set for all other atoms. Direct pathway is highlighted by red color.

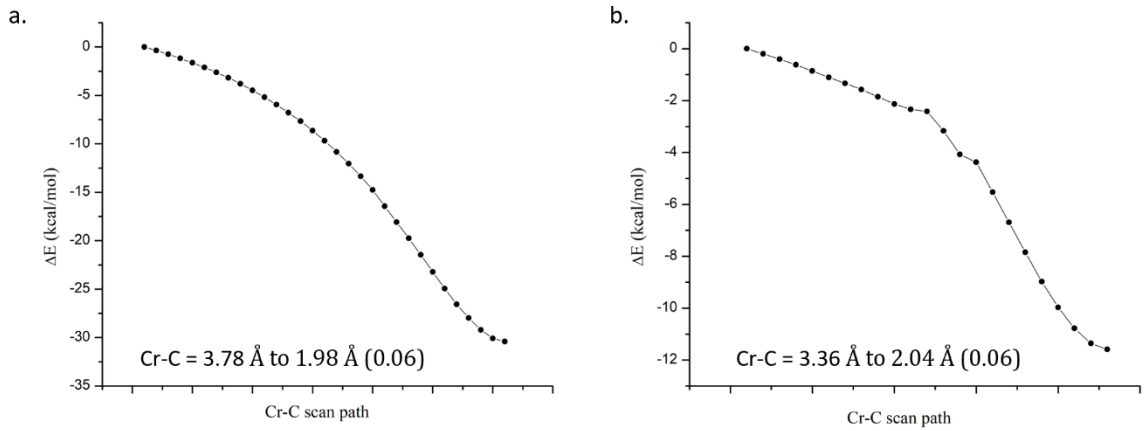


Figure S10. Energy (kcal/mol) profile diagram for the scanning pathways wherever transition states are not located due to flat nature of the PES at M06L level of theory with LANL2DZ basis set for Cr and 6-31G(d) basis set for all other atoms. (a) **^{5}INT19** to **^{5}INT22** and (b) **^{5}INT24** to **^{5}INT25**. In all cases bond scannings are performed. The starting and end bond distances for different scanning pathways are given in the figure with step size (in Å) values in parenthesis.

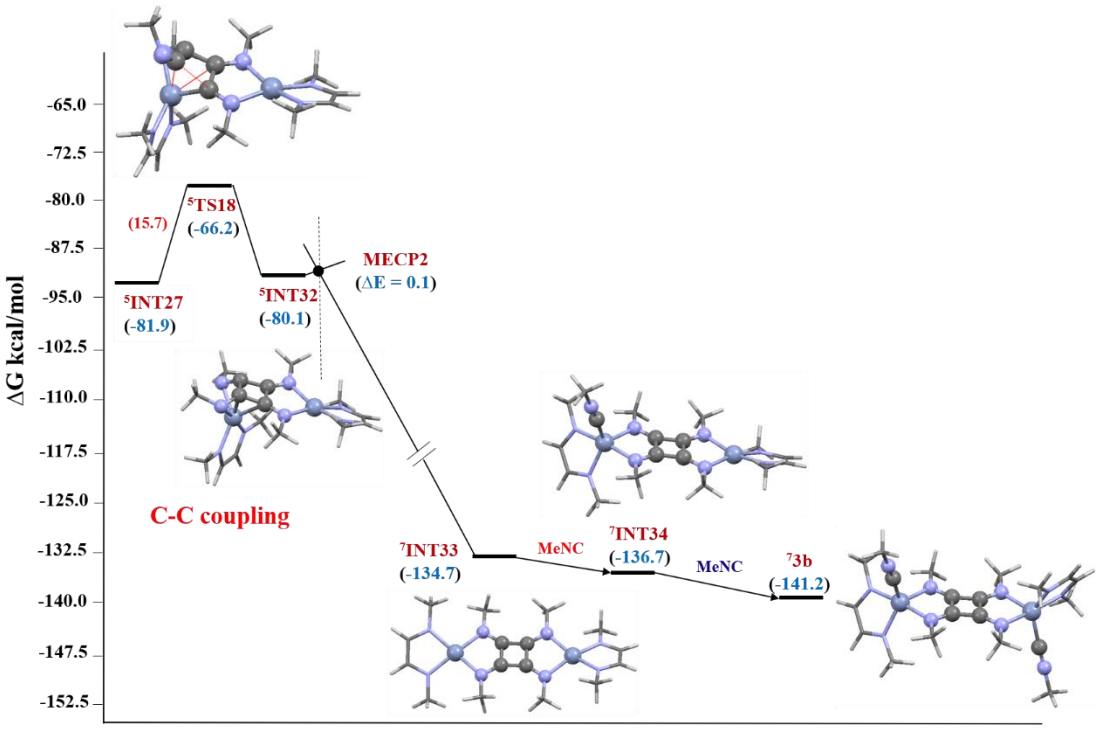


Figure S11. Free energy profile for the C-C coupling pathway leading to **^{7}3b** from **^{5}INT27** at M06L level of theory with LANL2DZ basis set for Cr and 6-31G(d) basis set for all other atoms.

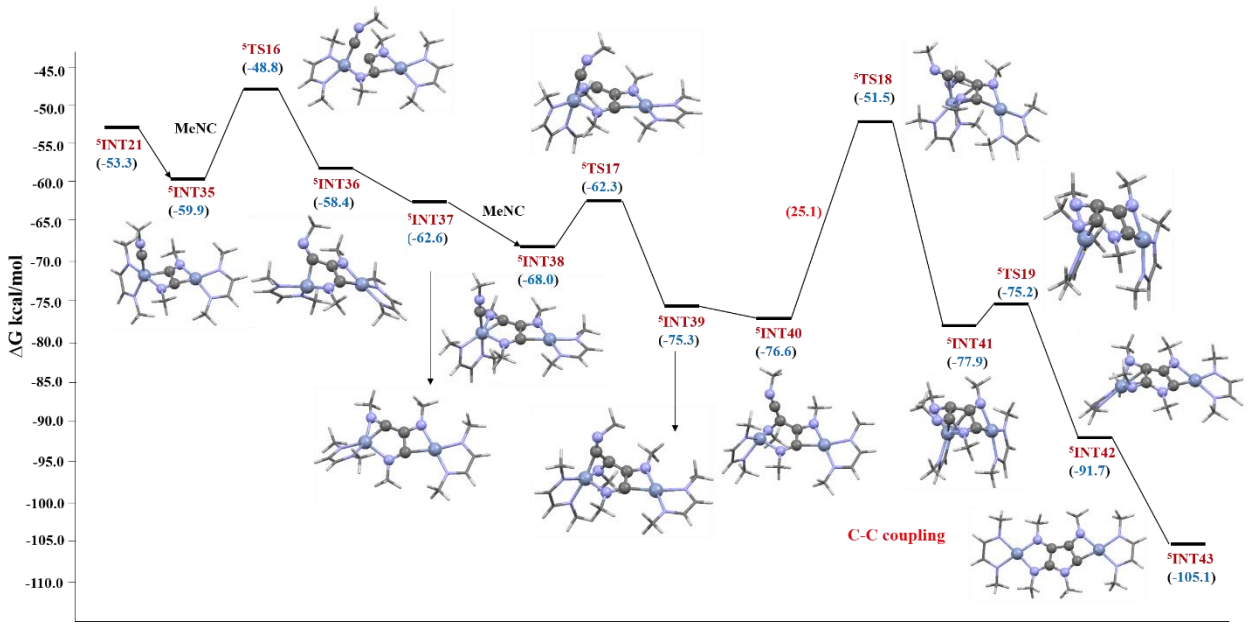


Figure S12. Free energy profile for the C-C coupling pathway leading to **^{5}INT43** from **^{5}INT21** at M06L level of theory with LANL2DZ basis set for Cr and 6-31G(d) basis set for all other atoms.

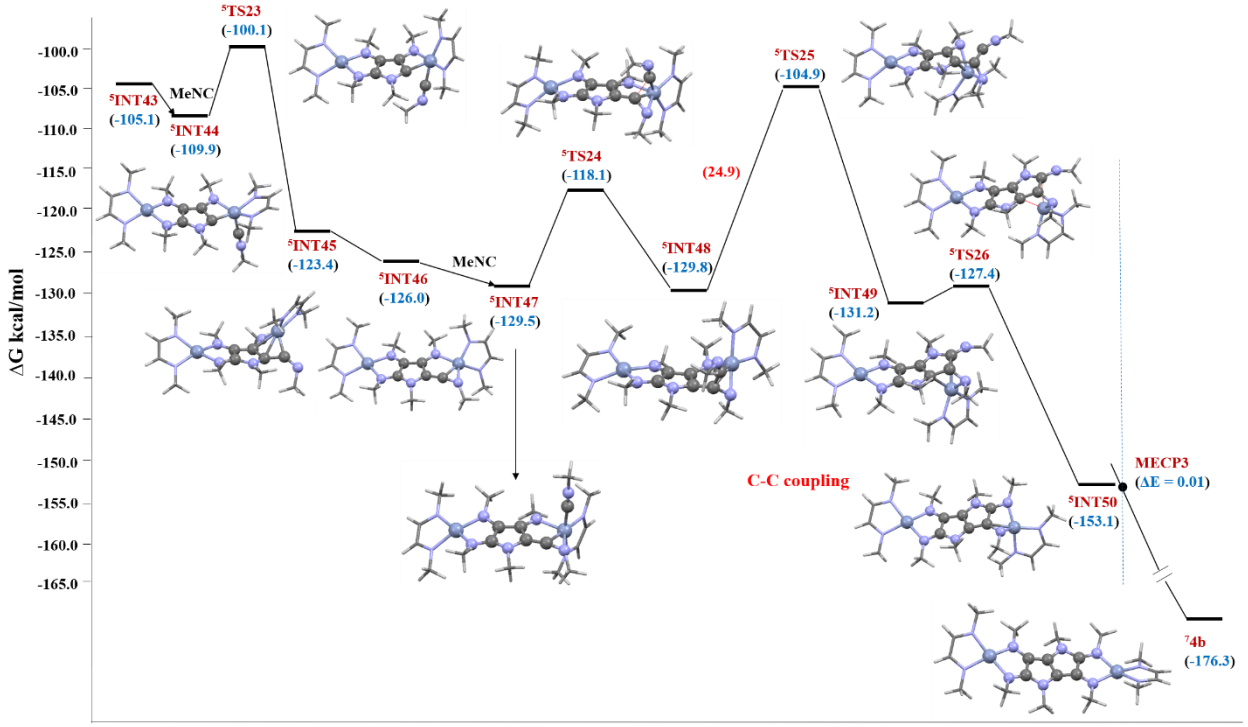


Figure S13. Free energy profile for the C-C coupling pathway leading to **^{7}4b** from **^{5}INT43** at M06L level of theory with LANL2DZ basis set for Cr and 6-31G(d) basis set for all other atoms.

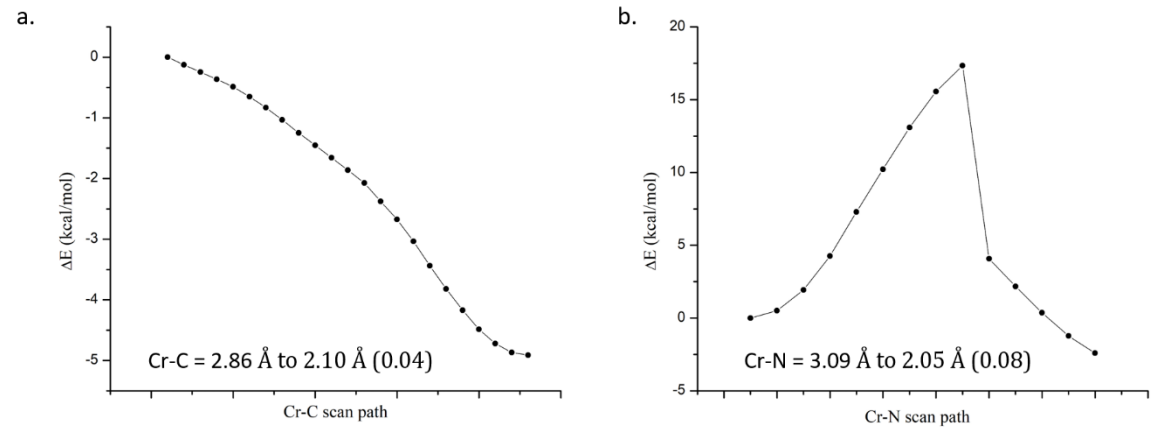


Figure S14. Energy (kcal/mol) profile diagram for the scanning pathways wherever transition states are not located at M06L level of theory with LANL2DZ basis set for Cr and 6-31G(d) basis set for all other atoms. (a) ^{5}**INT21** to ^{5}**INT35** and (b) ^{5}**INT45** to ^{5}**INT46**. In all cases bond scanning are performed. The starting and end bond distances for different scanning pathways are given in the figure with step size (in Å) values in parenthesis.

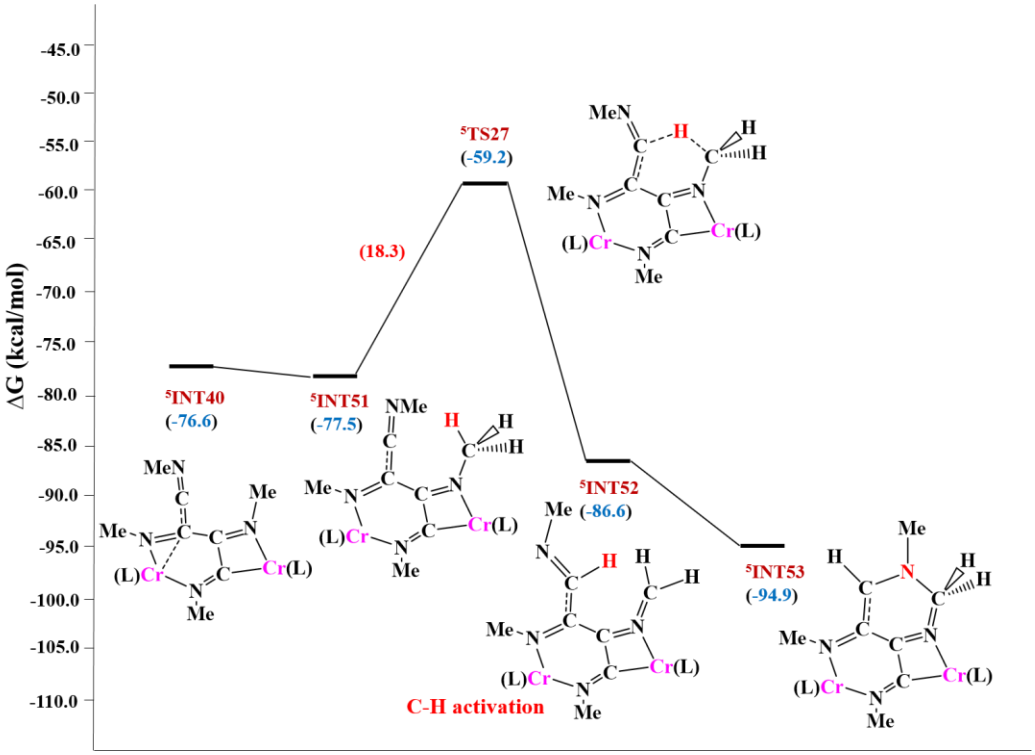


Figure S15. Free energy profile for the hypothetical C-H activation pathway from ^{5}**INT40** to give ^{5}**INT53** at M06L level of theory with LANL2DZ basis set for Cr and 6-31G(d) basis set for all other atoms.
Discussion: ^{5}**INT43** is thermodynamically more stable than ^{5}**INT53** by 10.2 kcal/mol. ^{5}**INT53** could also be a possible product but was not observed experimentally.

Table S1. WBI (Wiberg Bond Index) for intermediates with short Cr-Cr distances at M06L level of theory with LANL2DZ basis set for Cr and 6-31G(d) basis set for all other atoms.

Structure	WBI	Structure	WBI	Structure	WBI	Structure	WBI
^{1}1b	3.90	**^{1}INT4**	1.99	**^{1}INT8**	1.05	**^{5}INT16**	0.23
^{1}INT1	2.69	**^{1}INT5**	2.42	**^{1}INT13**	2.26	**^{5}INT17**	0.22
^{1}INT2	2.49	**^{1}INT6**	2.40	**^{1}INT14**	2.41	**^{5}INT18**	0.22
^{1}INT3	2.44	**^{1}INT7**	2.07	**^{1}INT15**	2.22	**^{5}INT20**	0.30