Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for

Mechanism of Co-C Photodissociation in Adenosylcobalamin

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Table S1. Selected geometrical parameters for Im-[Co^{III}(corrin)]-Ado^{+} model complex. The parameters for ground state of Im-[Co^{III}(corrin)]-Ado^{+} are compared with experimental data (atom numbering is given in Figure S1).

Structural parameter	S_0	Exp. [a]	S_1
r [Å]			
Co-C	2.014	2.032	2.060
C-N_{Im}	2.193	2.240	2.046
Co-N_{21}	1.877	1.880	1.886
Co-N_{22}	1.936	1.915	1.970
Co-N_{23}	1.938	1.912	1.972
Co-N_{24}	1.880	1.868	1.884
Bond angles			
C-Co-N_{Im}	176.7	171.3	165.1
N_{21}-Co-C	89.0	92.6	99.0
N_{22}-Co-C	89.0	84.07	82.9
N_{23}-Co-C	86.1	90.3	84.0
N_{24}-Co-C	88.8	93.2	94.9
N_{21}-Co-N_{Im}	88.0	91.8	92.6
N_{22}-Co-N_{Im}	89.6	88.5	87.7
N_{23}-Co-N_{Im}	87.0	86.2	85.5
N_{24}-Co-N_{Im}	92.3	94.8	95.9
N_{21}-Co-N_{22}	91.3	89.8	90.5
N_{22}-Co-N_{23}	94.7	96.8	96.3
N_{23}-Co-N_{24}	91.6	90.2	91.2
N_{24}-Co-N_{21}	82.5	83.2	82.1
Co-N_{21}-C_1	116.6	117.5	116.7
Co-N_{22}-C_9	124.8	122.9	122.7
Co-N_{23}-C_{11}	124.3	123.3	122.7
Co-N_{24}-C_{19}	116.9	115.4	116.9
Torsion angles			
N_{21}-N_{22}-N_{23}-Co	-3.4	-1.6	-1.5
N_{21}-N_{22}-N_{23}-N_{24}	-4.5	-3.5	-3.6
Co-N_{22}-C_9-C_{10}	1.4	-6.0	-1.3
Co-N_{22}-C_6-C_5	-8.4	-14.4	-5.7
Co-N_{23}-C_{14}-C_{15}	1.1	-3.9	-0.5
Co-N_{21}-C_1-C_{19}	33.5	33.3	33.6
N_{21}-C_1-C_{19}-N_{24}	-37.3	-38.4	-38.5
N_{21}-Co-N_{24}-C_{19}	-10.2	-11.1	-11.8
C_1-C_2-C_3-C_4	-24.6	-29.4	-25.7
C_6-C_7-C_8-C_9	-10.5	-28.7	-10.9
C_{11}-C_{12}-C_{13}-C_{14}	8.1	-25.0	0.7
C_{16}-C_{17}-C_{18}-C_{19}	-26.7	-31.5	-26.7

[a] Ouyang, L.; Rulis, P.; Ching, G.; Nardin, L.; Randaccio, L. *Inorg. Chem.* **2004**, *43*, 1235-1241. The structure contains in the "lower" axial position, the 5,6 – dimethylbenzimidazole (DBI) as an axial ligand.

Table S2. Selected geometrical parameters for Im-[Co^{III}(corrin)]-Ado^+ model complex and other species involved in the photoreaction process. The parameters for ground state of Im-[Co^{III}(corrin)]-Ado^+ are compared with experimental data (atom numbering is given in Figure S1).

Im-[Co^{III}(corrin)]-Ado^+	I (S_{0min})	I (S_{1min})	Exp. [a]
	Bond distances [Å]		
Co-C	2.014	2.060	2.032
C-N_{Im}	2.193	2.046	2.240
Co-N_{21}	1.877	1.886	1.880
Co-N_{22}	1.936	1.970	1.915
Co-N_{23}	1.938	1.972	1.912
Co-N_{24}	1.880	1.884	1.868
	Bond angles [deg]		
C-Co-N_{Im}	176.7	165.1	171.3
N_{21}-Co-N_{23}	172.2	172.8	172.9
N_{22}-Co-N_{24}	173.5	171.9	172.4
Im-[Co^{II}(corrin)]$^+$	IIIA (S_{0min})	IIIA (S_{1min})	IVA (S_{1min})
	Bond distances [Å]		
C-N_{Im}	2.162	4.863	1.882
Co-N_{21}	1.879	1.843	1.884
Co-N_{22}	1.940	1.913	1.945
Co-N_{23}	1.935	1.917	1.946
Co-N_{24}	1.882	1.843	1.894
	Bond angles [deg]		
N_{21}-Co-N_{23}	172.1	170.2	169.7
N_{22}-Co-N_{24}	165.6	170.3	164.2

[a] Ouyang, L.; Rulis, P.; Ching, G.; Nardin, L.; Randaccio, L. *Inorg. Chem.* **2004**, *43*, 1235-1241. The structure contains in the "lower" axial position, the 5,6 – dimethylbenzimidazol (DBI) as a axial ligand

Table S3. NBO charges for Im-[Co^{III}(corrin)]-Ado^{+} model complex and other species involved in the photoreaction process. Results for S_0 and S_1 optimized geometry.

	NBO charges			
	q_{S0}	q_{S0}	q_{S1}	Δq [a]
Im-[Co^{III}(corrin)]-Ado^{+}	I (S_{0min})	I (S_{1min})		
Co	0.767	0.782	0.885	0.104
C	-0.469	-0.502	-0.415	0.087
N_{Im}	-0.471	-0.468	-0.413	0.055
Ado	-0.133	-0.144	0.021	0.165
Im	0.153	0.179	0.291	0.112
Corr	0.213	0.183	-0.198	-0.381
Im-[Co^{II}(corrin)]$^{+}$	IIIA (S_{0min})	IIIA (S_{1min})		
Co	0.911	0.975	0.920	-0.055
N_{Im}	-0.475	-0.487	-0.486	0.001
Im	0.141	0.002	0.002	0.000
Corr	-0.052	0.023	0.078	0.055
		IVA (S_{1min})		
Co		0.863	0.883	0.020
N_{Im}		-0.471	-0.310	0.161
Im		0.167	0.414	0.247
Corr		-0.030	-0.297	-0.267

[a] Δq – difference between charge in excited state and ground state in geometry excited state.

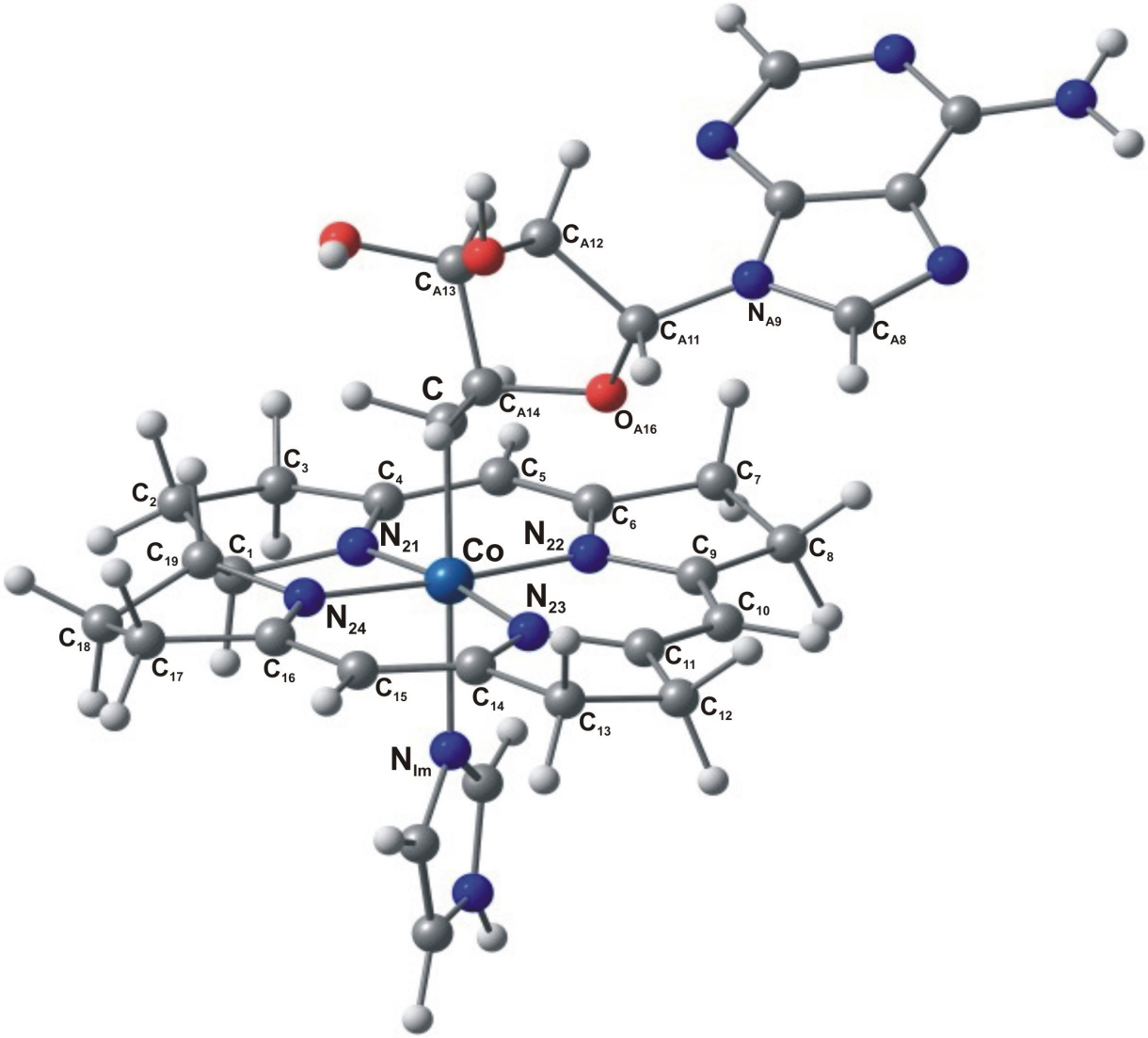

Figure S1. Structural model of AdoCbl used in the calculations.

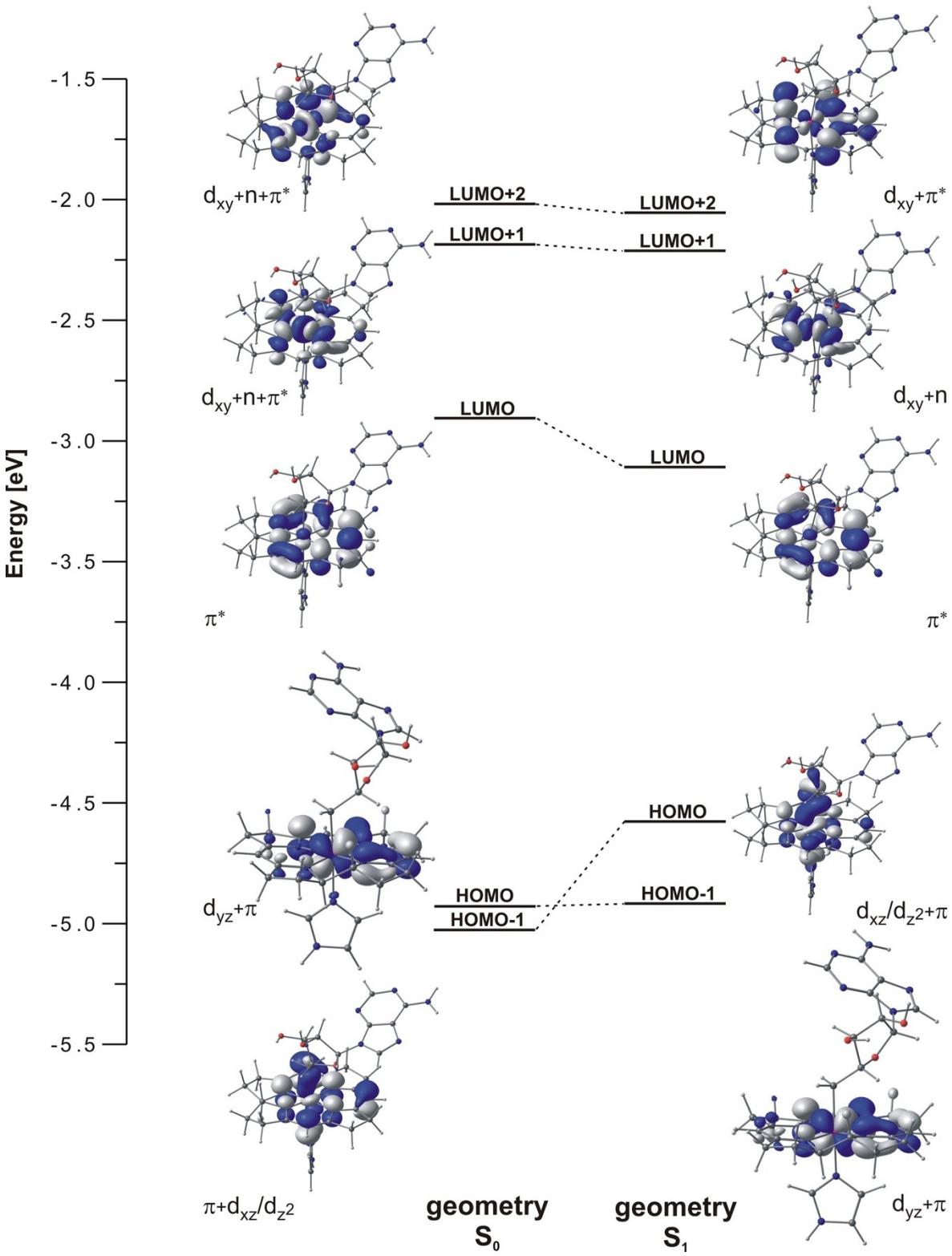

Figure S2. Molecular orbital diagram for Im-[Co^{III}(corrin)]-Ado$^+$ model complex in the S_0 and S_1 optimized geometry.

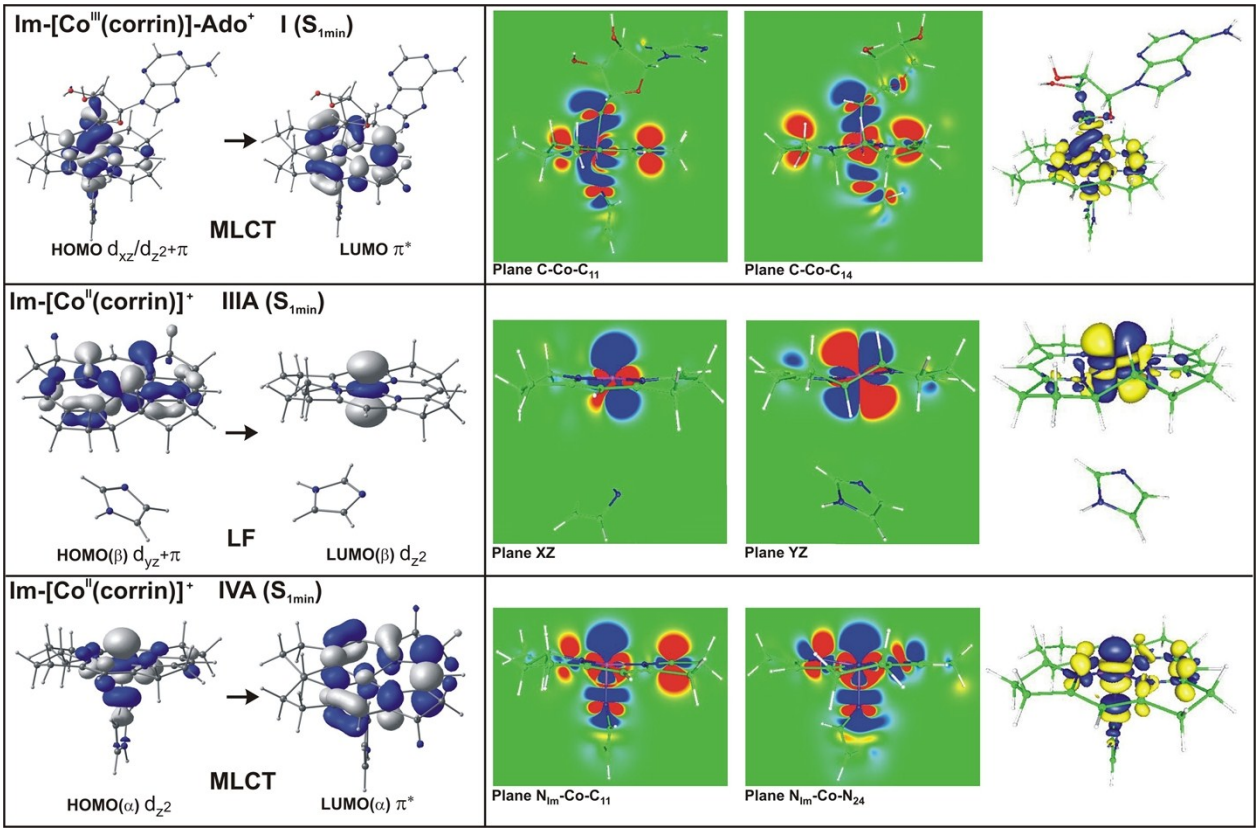

Figure S3. HOMO and LUMO molecular orbitals for electron excitations in the optimized geometries of S_1 states together with isosurface and cross-section contour along the axial bonding (in two different section planes) of electron density difference between the S_1 and S_0 states for substrate and products of photolysis process. The yellow and red colors denote electron space, blue color - hole space.

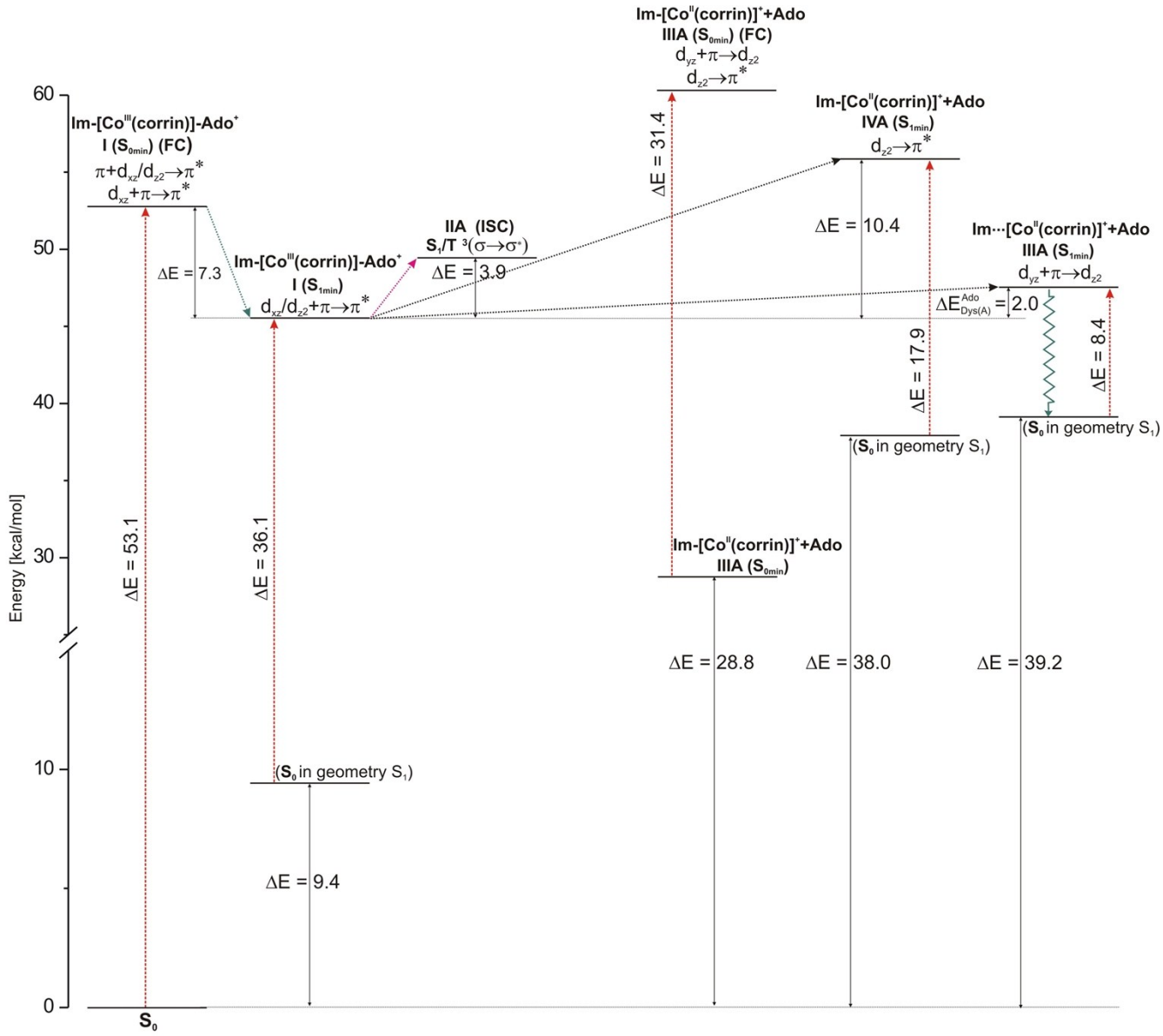

Figure S4. Energy diagram of photoreaction on Path A (ΔE values in kcal/mol).

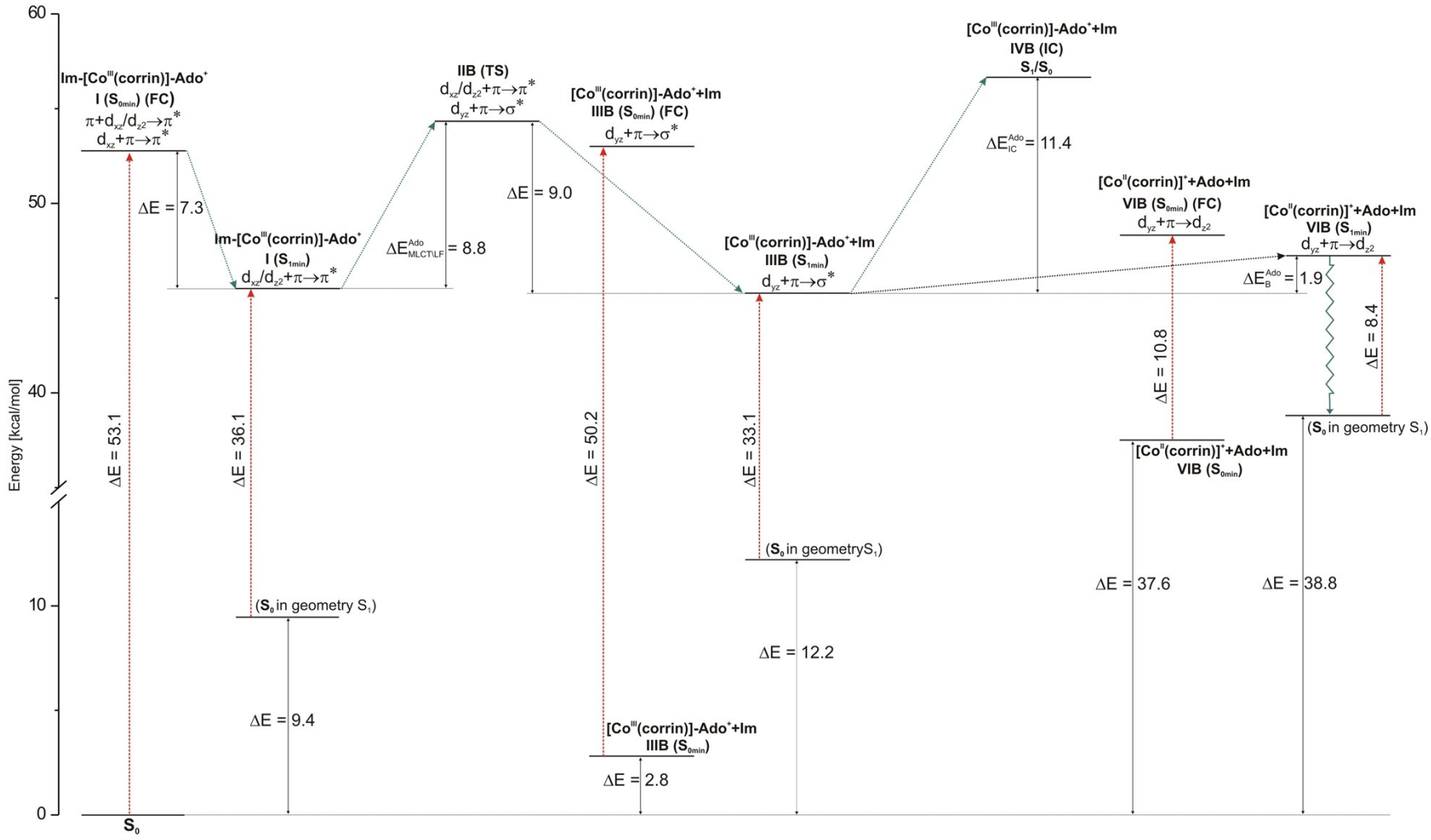

Figure S5. Energy diagram of photoreaction on Path B (ΔE values in kcal/mol).