Supporting Information

Computational Studies on Rhodium(III) Catalyzed C–H Functionalization versus Deoxygenation of Quinoline *N*-Oxides with Diazo Compounds

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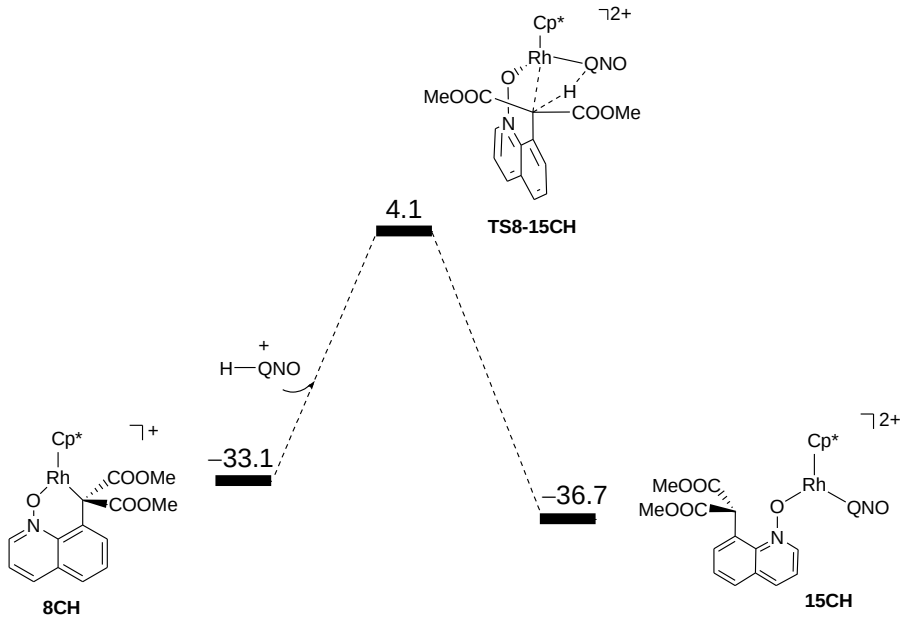

Figure S1. Free energy profile calculated for the protonation of **8CH** with $[QNO\text{-}H]^+$ via a metathesis step. The solvation-corrected free energies are given in kcal/mol.

Table S1. Comparison of results from single-point energy calculations using different DFT methods – relative free energies (kcal/mol) calculated for selected species

Reactions of dimethyl diazomalonate

Species	M06/6-311++G(d,p) //B3LYP/6-31G(d)[a]	wB97XD/6-311++G(d,p) //B3LYP/6-31G(d)[a]	B3LYP-D3/6-311++G(d,p) //B3LYP/6-31G(d)[a]
1 + $N_2C(COOMe)_2$	0.0	0.0	0.0
TS3-4CH + $N_2C(COOMe)_2$	25.3	26.5	25.9
TS6-7CH + H-QNO$^+$ + QNO	28.0	31.6	32.9
7CH + H-QNO$^+$ + QNO + N_2	4.4	4.3	3.4
TS3-4DO + QNO	30.6	32.6	30.4
4DO + QNO + N_2	12.2	13.3	8.6

Reactions of methyl phenyldiazoacetate

Species	M06/6-311++G(d,p) //B3LYP/6-31G(d)[a]	wB97XD/6-311++G(d,p) //B3LYP/6-31G(d)[a]	B3LYP-D3/6-311++G(d,p) //B3LYP/6-31G(d)[a]
1 + $N_2C(Ph)(COOMe)$	0.0	0.0	0.0
TS6-7CHPh + H-QNO$^+$ + QNO	23.6	24.8	27.7
7CHPh + H-QNO$^+$ + QNO + N_2	–6.3	–5.6	–4.9
TS3-4DOPh + QNO	21.4	21.0	21.1
4DOPh + QNO + N_2	–6.0	–6.5	–8.8

a) See the Computational Details section in the main text for the detailed description of the basis set. The single-point energy calculations were performed in conjunction with the solvation model density (SMD) continuum method in dichloroethane.

Table S2. Results compared with geometry optimization calculations using B3LYP-D3/6-31G(d)/SMD – relative free energies (kcal/mol) calculated for two selected transition states

Reactions of dimethyl diazomalonate

Species	M06/6-311++G(d,p) //B3LYP/6-31G(d)[a]	B3LYP-D3/6-31G(d)/SMD
1 + $N_2C(COOMe)_2$	0.0	0.0
TS6-7CH + H-QNO$^+$ + QNO	28.0	35.5
TS3-4DO + QNO	30.6	29.8

a) See the Computational Details section in the main text for the detailed description of the basis set. The single-point energy calculations were performed in conjunction with the solvation model density (SMD) continuum method in dichloroethane.