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A computational mapping of the R–NHC coupling pathway – the key process in the evolution of Pd/NHC catalytic systems

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Table S1. Relative enthalpies ΔH (kcal/mol) of calculated structures for various levels of theory

level of theory	1	TS-2	3b	3a	4	5	6a
PBE1PBE/Def2SVP, gas phase	0	21.4	9.4	22.2	121.5	42.0	117.2
PBEPBE/Def2SVP, gas phase	0	20.0	9.1	21.3	120.3	40.5	121.1
PBE1PBE/Def2TZVP, gas phase	0	22.0	10.1	19.5	119.9	44.1	107.0
PBE1PBE/Def2TZVP, SMD(DMF)	0	21.2	5.0	3.9	23.5	37.0	22.0
PBE1PBE/Def2TZVP, PCM(DMF)	0	20.4	5.2	5.9	25.7	34.5	16.9
PBEPBE/Def2TZVP, SMD(DMF)	0	19.8	5.7	4.8	25.4	38.7	23.9

Table S2. Relative free energies ΔG (kcal/mol) of the calculated structures for various levels of theory

level of theory	1	TS-2	3b	3a	4	5	6a
PBE1PBE/Def2SVP, gas phase	0	22.6	10.4	11.8	110.0	40.5	108.1
PBEPBE/Def2SVP, gas phase	0	20.8	9.8	11.1	109.3	40.2	112.7
PBE1PBE/Def2TZVP, gas phase	0	23.4	11.2	9.7	108.7	43.1	98.2
PBE1PBE/Def2TZVP, SMD(DMF)	0	22.1	5.4	-6.0	12.0	28.5	14.3
PBE1PBE/Def2TZVP, PCM(DMF)	0	22.3	6.3	-3.3	15.3	26.6	10.2
PBEPBE/Def2TZVP, SMD(DMF)	0	21.0	6.4	-4.4	15.3	31.8	17.0

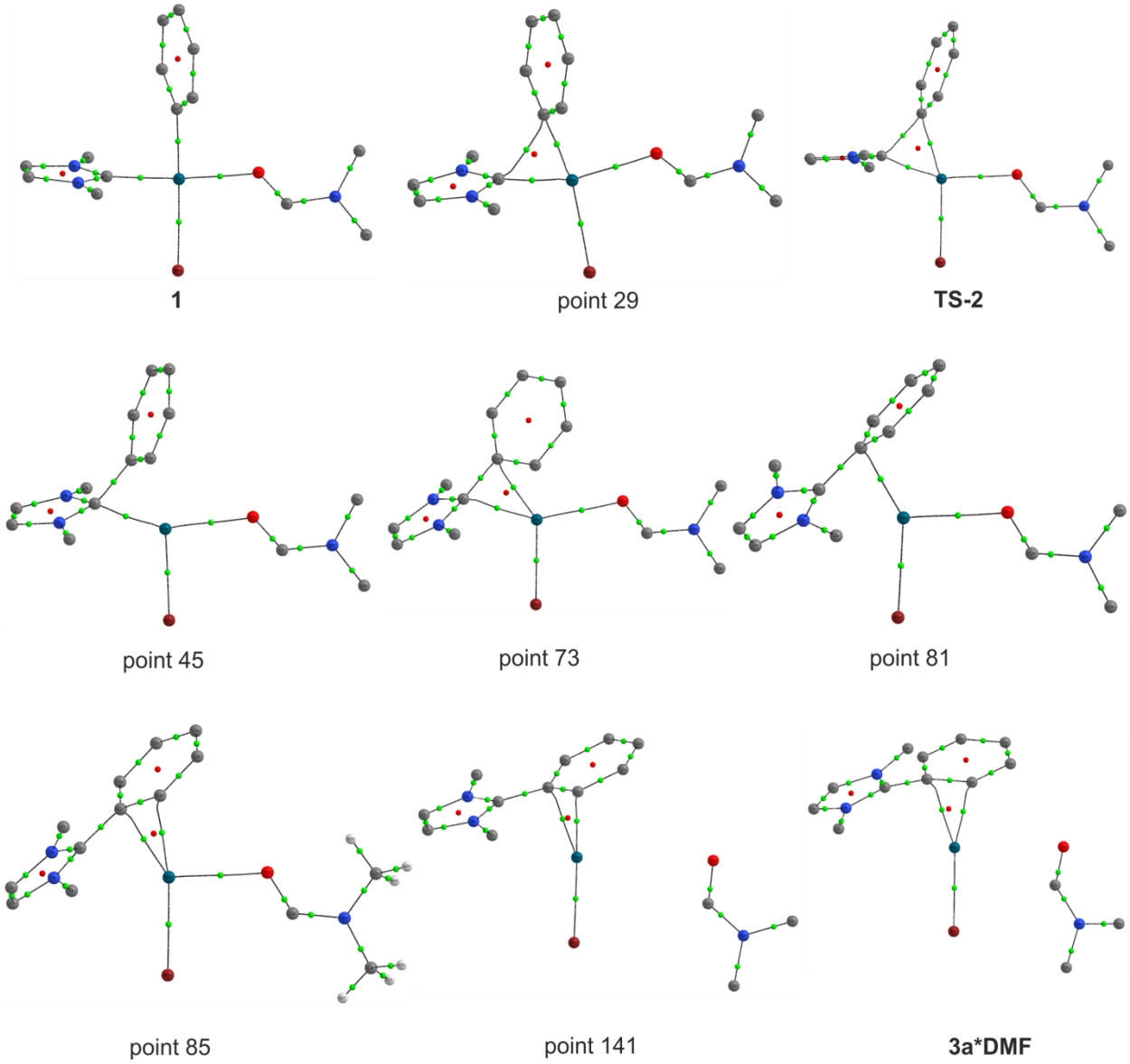

Figure S1. Key structures of the IRC trajectory of the R-NHC coupling. The bond critical points (BCPs) are shown as small green spheres. Ring critical points (RCPs) are shown as small red spheres.

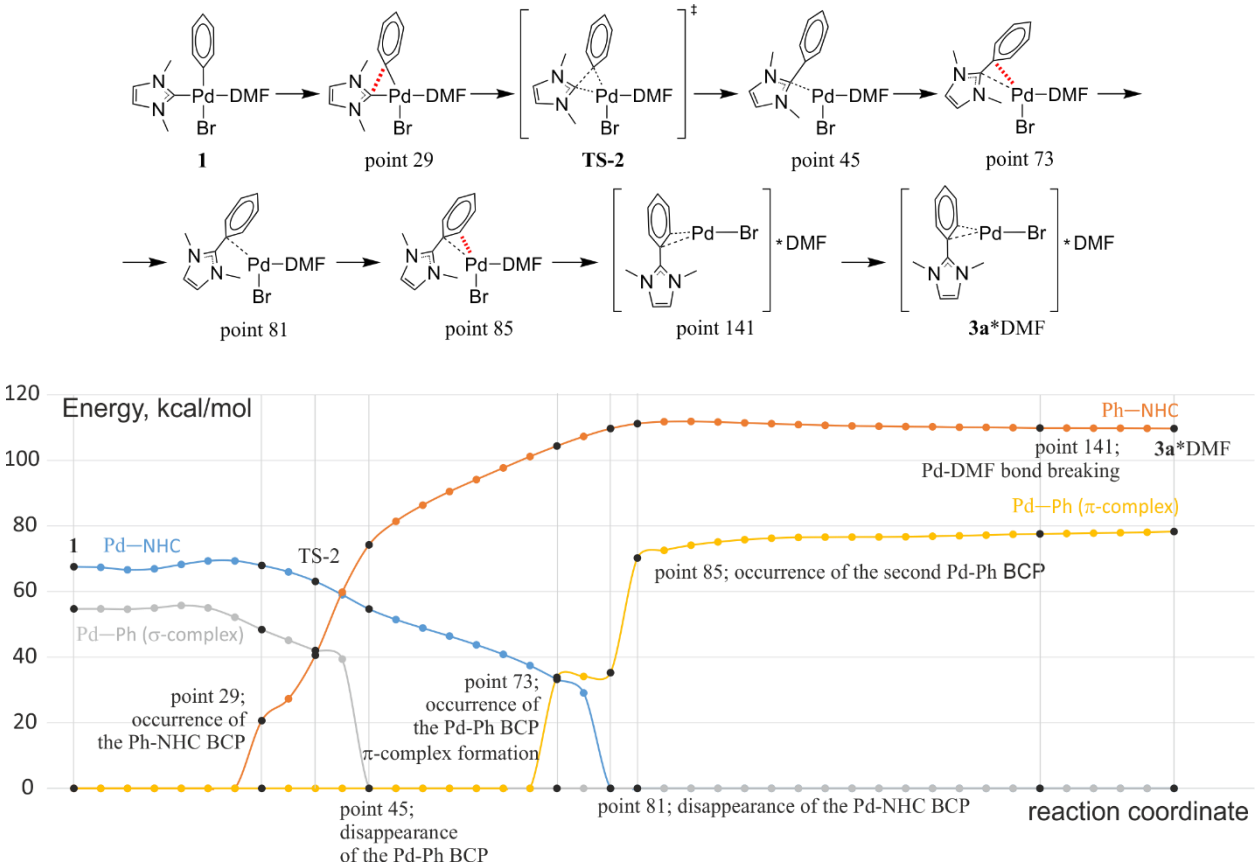

Figure S2. Bond energy-reaction coordinate dependences for R-NHC coupling: Pd-NHC (blue), Ph-NHC (red), and Pd-Ph (gray for sigma-complex and yellow for pi-complex) bonds. The bond energies are determined from the potential energy density at the bond critical points using the correlation by E. Espinosa, C. Lecomte and E. Molins [1].

[1] Espinosa, E., Molins, E., & Lecomte, C. Hydrogen bond strengths revealed by topological analyses of experimentally observed electron densities. *Chem. Phys. Lett.*, **1998**, *285*, 170-173.