Supporting Information

Computational Study on Gold-Catalyzed Cascade Reaction of 1,4-Diynes and Pyrroles: Mechanism, Regioselectivity, Role of Catalyst, Effects of Substituent and Solvent

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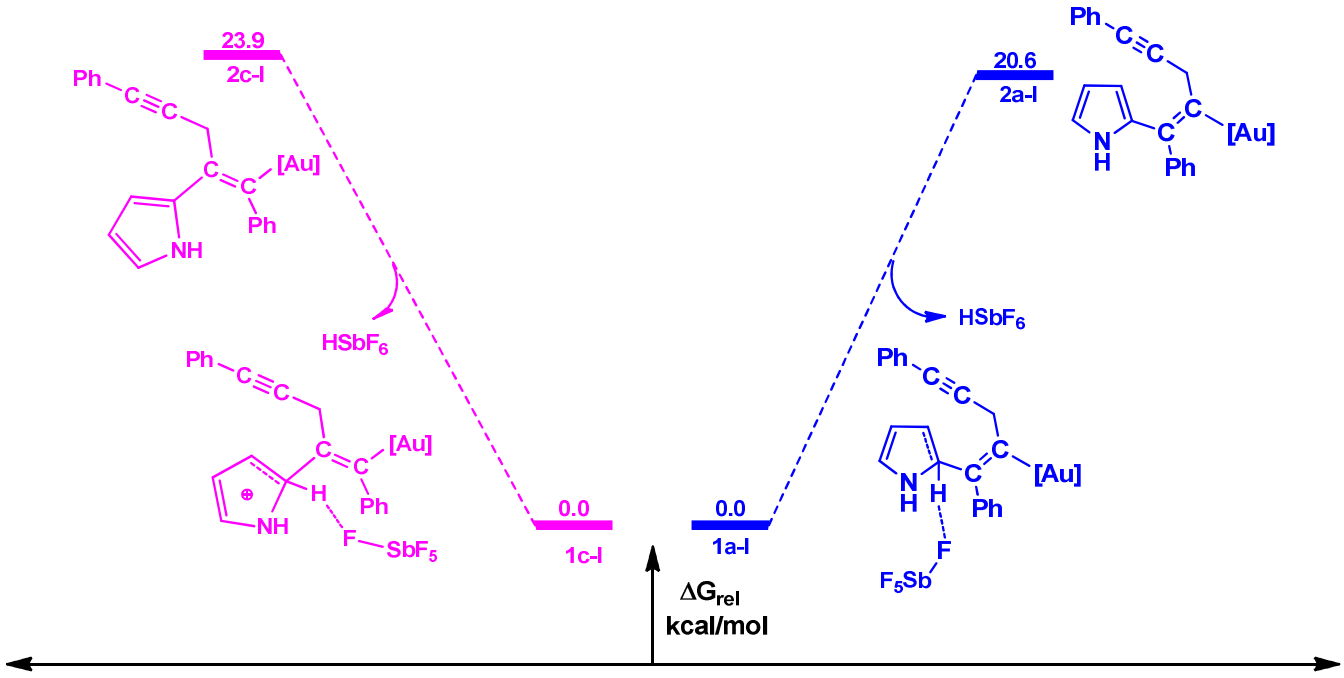

Figure S1 Energy profiles for the formation of $HSbF_6$, the relative energies are given in kcal/mol.

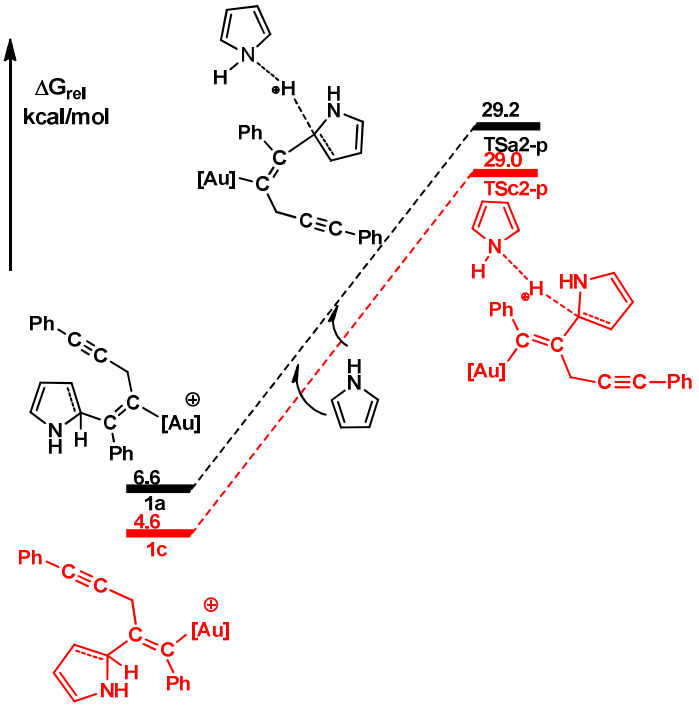

Figure S2 Energy profiles for the first [1,3] proton migration assisted by pyrroles. the relative energies are given in kcal/mol.

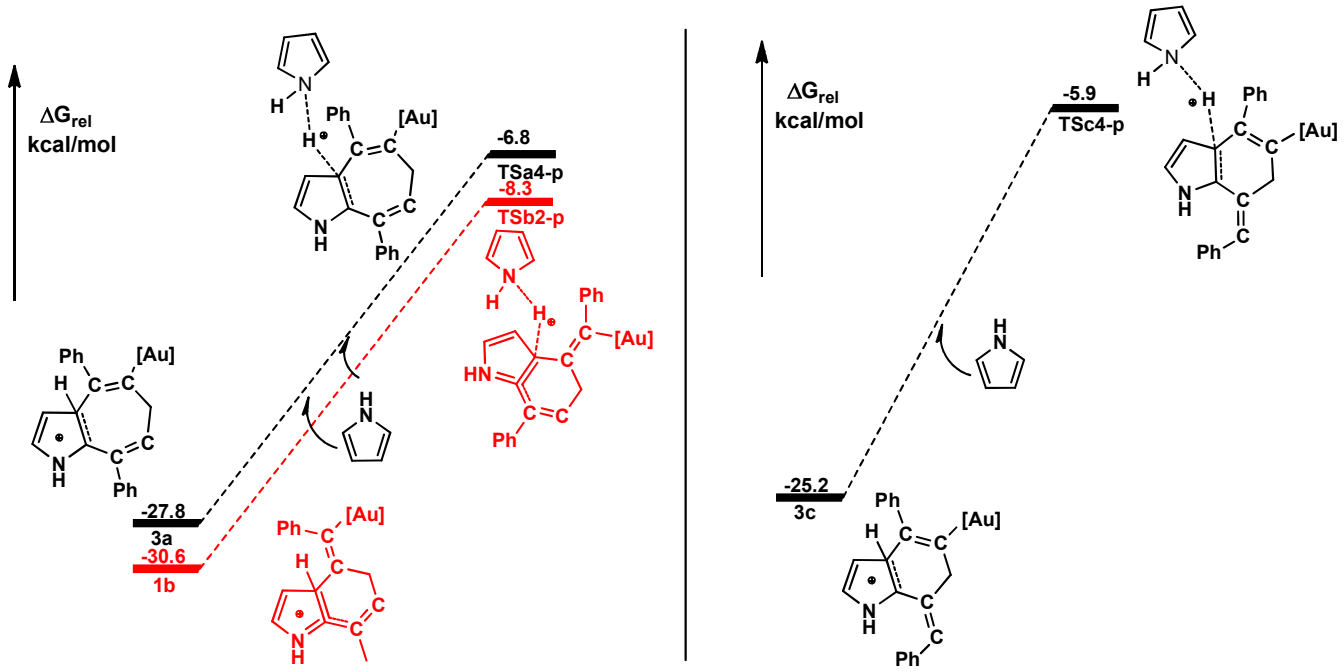

Figure S3 Energy profiles for the second [1,3] proton migration assisted by pyrroles; the relative energies are given in kcal/mol.

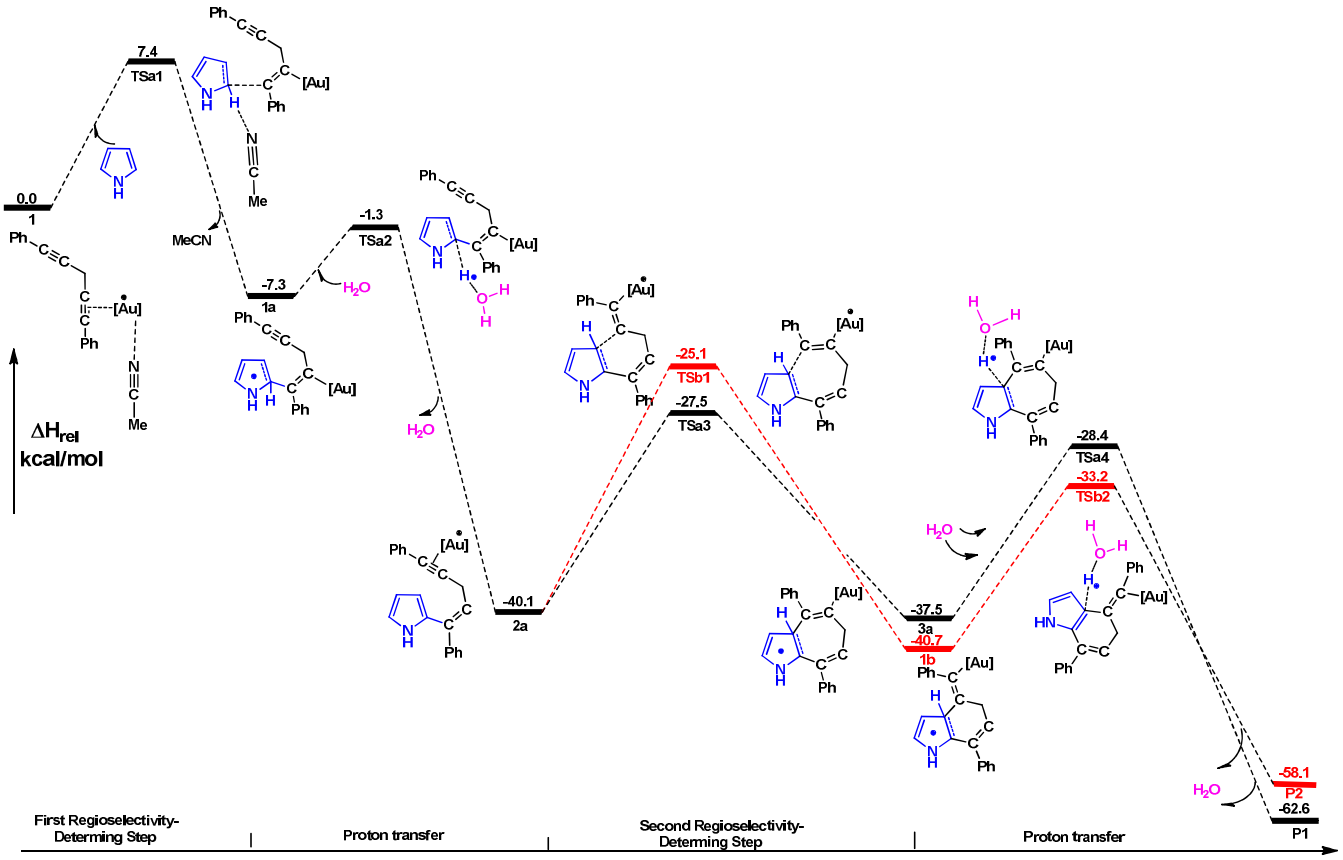

Figure S4 The enthalpy-based energy profiles for pathway **a** and **b**; the relative energies are given in kcal/mol.

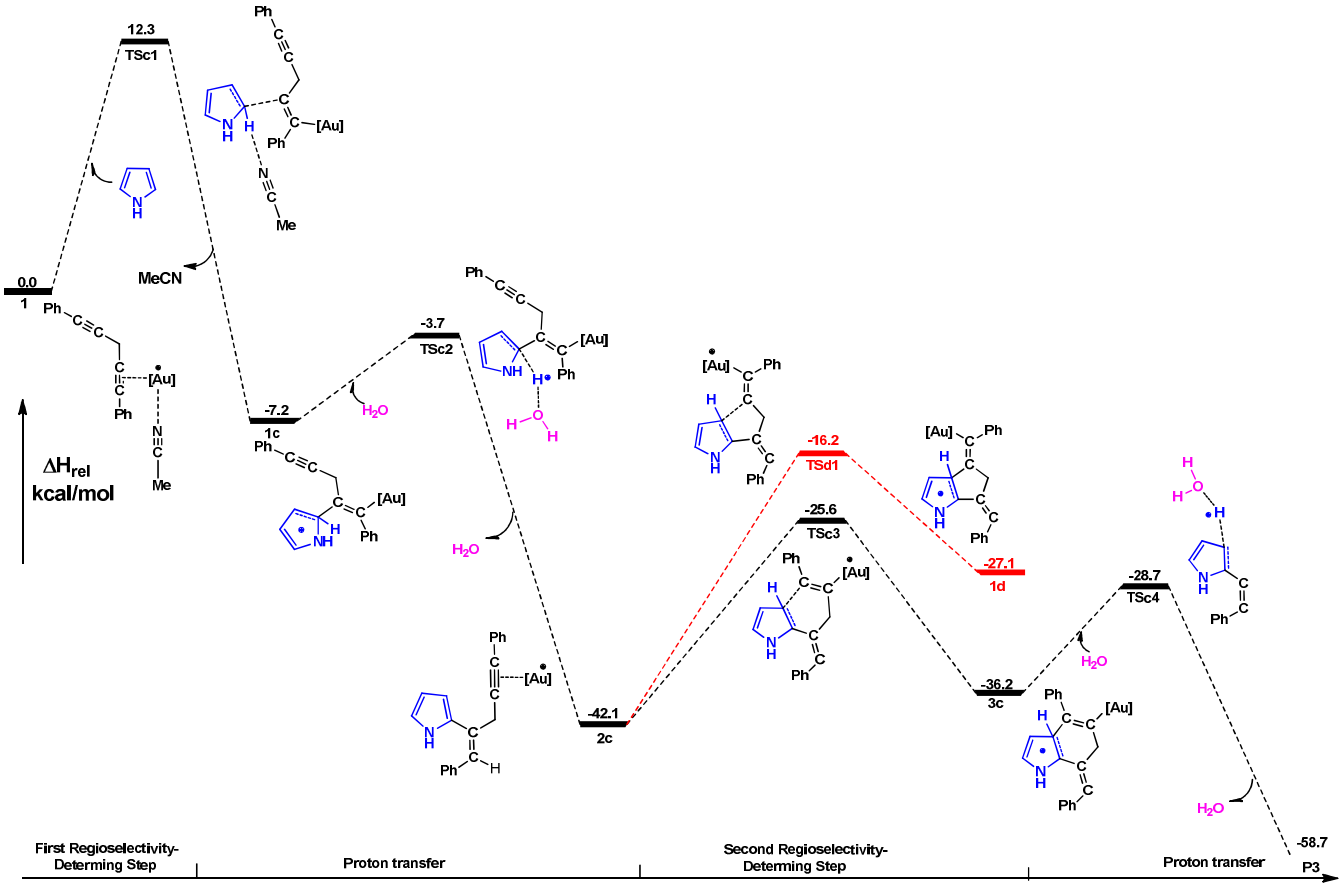

Figure S5 The enthalpy-based energy profiles for pathway **c** and **d**; the relative energies are given in kcal/mol.

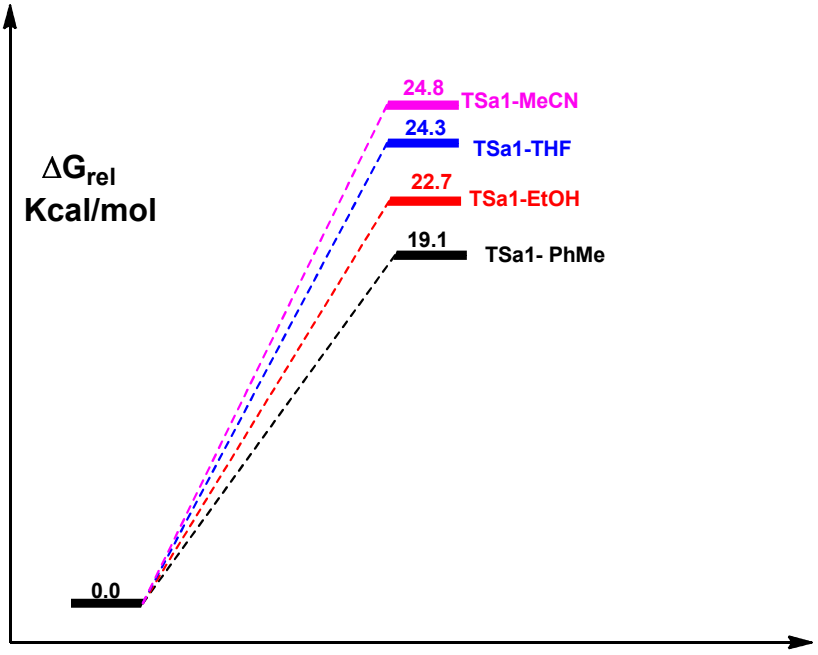

Figure S6. Energy profiles of the rate-limiting step for the different solvent. The relative energies are given in kcal/mol. (All the strucures were optimized in toluene, MeCN, EtOH and THF solution at the M06-2X/SMD/6-31G (d, p) level of theory.)

Table S1. Electronic chemical potential (μ, in a.u.), chemical hardness (η, in a.u.), global electrophilicity (ω, in eV), and global nucleophilicity (N, in eV), HOMO energy (E_H, in eV), LUMO energy (E_L, in eV) of **1** in different solvent.[a]

	μ	η	ω	N	E_H	E_L
1[b]	-0.14991	0.25894	3.52	2.99	-0.27938	-0.02044
1[c]	-0.14921	0.25898	3.52	3.01	-0.2787	-0.01972
1[d]	-0.158325	0.25925	3.53	2.76	-0.28795	-0.0287
1[e]	-0.18433	0.25936	3.53	2.05	-0.31401	-0.05465

[a] These values, were obtained at the M06-2X/BS1 level of theory by structural optimization in toluene, MeCN, EtOH and THF solution. [b] in EtOH, [c] in MeCN, [d] in THF, [e] in toluene.

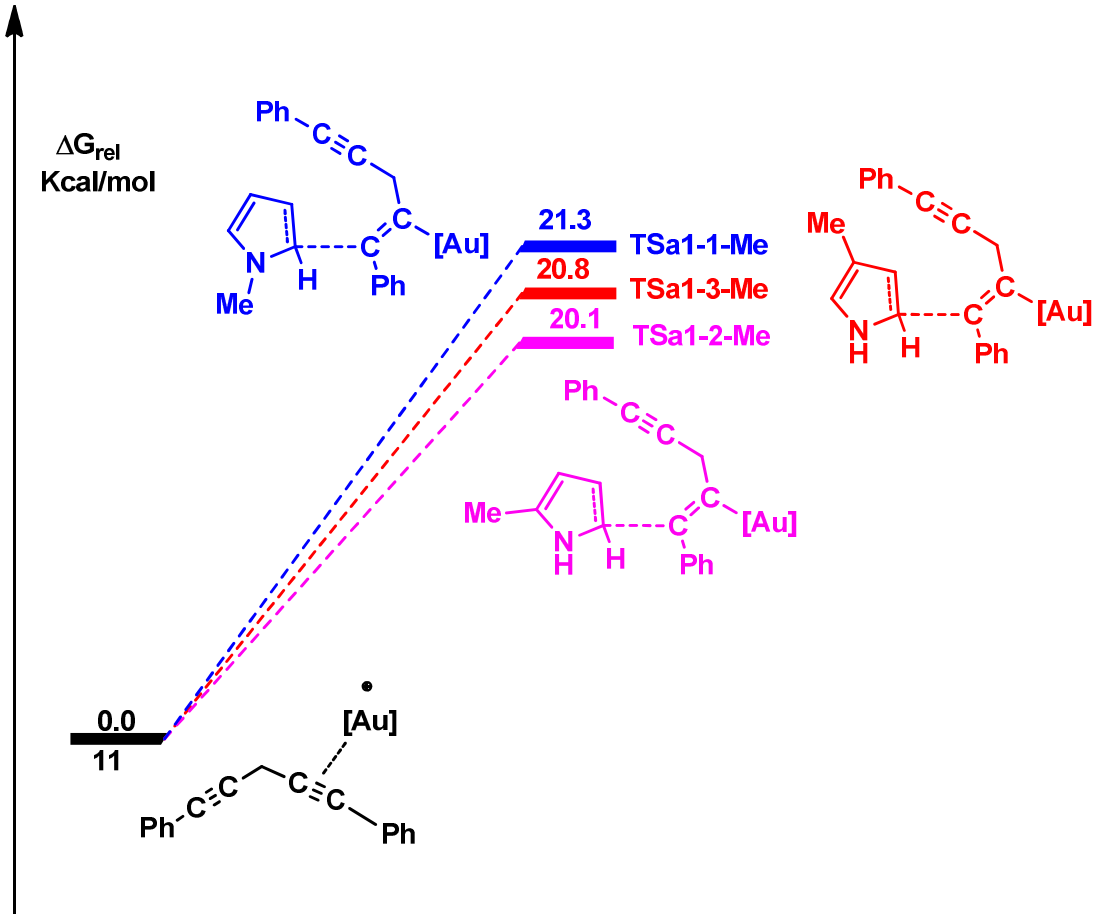

Figure S7. Energy profiles of the rate-limiting step for the different substituent on the pyrrole ring. The relative energies are given in kcal/mol.