

# Reactions of chemically activated C<sub>9</sub>H<sub>9</sub> species II: The reaction of phenyl radicals with allene and cyclopropopene, and of benzyl with acetylene

- Supporting information -

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## Content

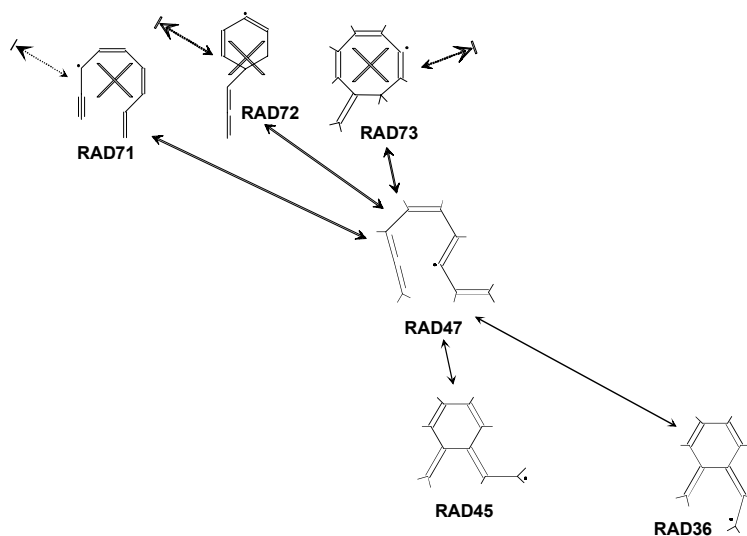
Page 1 : Additional B3LYP-DFT calculations

Page 2 : Additional CCSD(T) calculations on entrance channels

Page 3 : [C<sub>9</sub>H<sub>9</sub>] Reaction scheme (see L. Vereecken, H. F. Bettinger, R. I. KAiser, P. v. R. Schleyer, H. F. Schaefer, III, *J. Am. Chem. Soc.* 2002, **124**, 2781.)

## Additional B3LYP-DFT calculations

At elevated temperatures, it was found that a significant fraction of the chemically activated C<sub>9</sub>H<sub>9</sub> intermediates formed in the benzyl + C<sub>2</sub>H<sub>2</sub> reaction isomerized to the RAD47 intermediate at some point during their lifetime. To avoid biasing the predicted product distribution, this radical was unfrozen, and the most important of its subsequent reactions were included in the RRKM-Master Equation analyses. As can be seen from the table below, the most favorable reaction path by far for RAD47 is re-isomerization to RAD36 or RAD45. All other pathways conceivable were either estimated to have even higher barriers based on general chemical principle and analogous reactions, or the reaction products were proven to be unstable at the levels of theory used here.



The figure above fits into the main PES near RAD47 (upper left corner of the RHS half as shown lower in this supporting information).

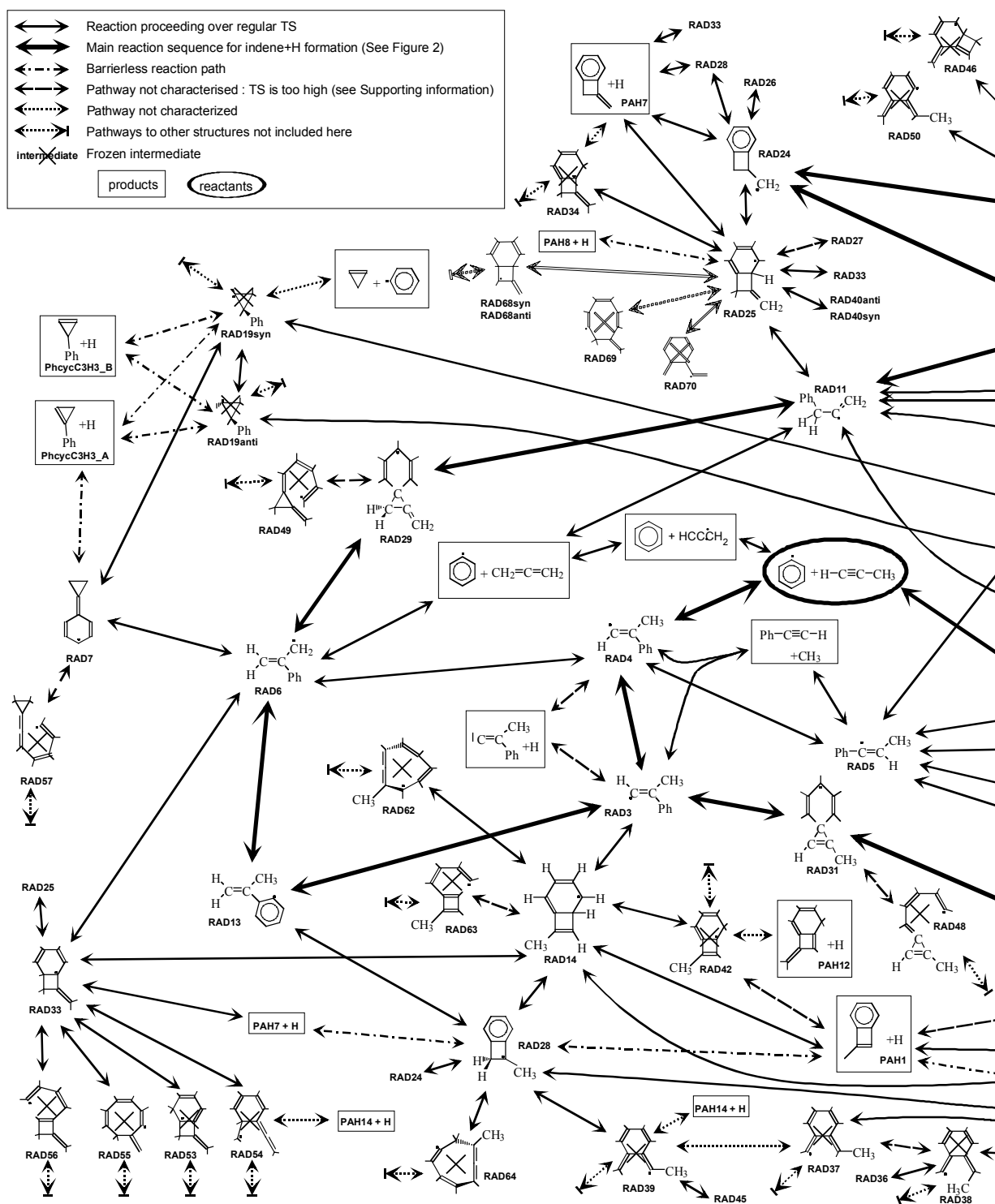
B3LYP-DFT energies in Hartree, ZPE in Hartree,  $E_{\text{rel}}$  is relative energy in kJ/mol relative to RAD23.

Compound	B3LYP-DFT 6-31G*	ZPE	$E_{\text{rel}}$ kJ/mol	B3LYP-DFT 6-311+G(d,p)	$E_{\text{rel}}$ kJ/mol
RAD47	-348.186705666	0.142489	385.95	-348.284764622	359.33
RAD71	-348.222705219	0.143964	295.31	-348.322545337	264.01
RAD72	-348.193562410	0.146983	379.75	-348.288696497	360.81
RAD73	-348.237588739	0.148043	266.94	-348.330930377	252.71
tsrad36_rad47	-348.182101842	0.142351	397.68	-348.279198142	373.59
tsrad45_rad47	-348.182318901	0.142265	396.88	-348.279817189	371.73
tsrad47_rad71	-348.152043865	0.139057	467.94	-348.250398657	440.55
tsrad47_rad72	-348.138035494	0.143478	516.33	-348.235192314	492.08
tsrad47_rad73	-348.164401736	0.144134	448.83	-348.260817793	426.52

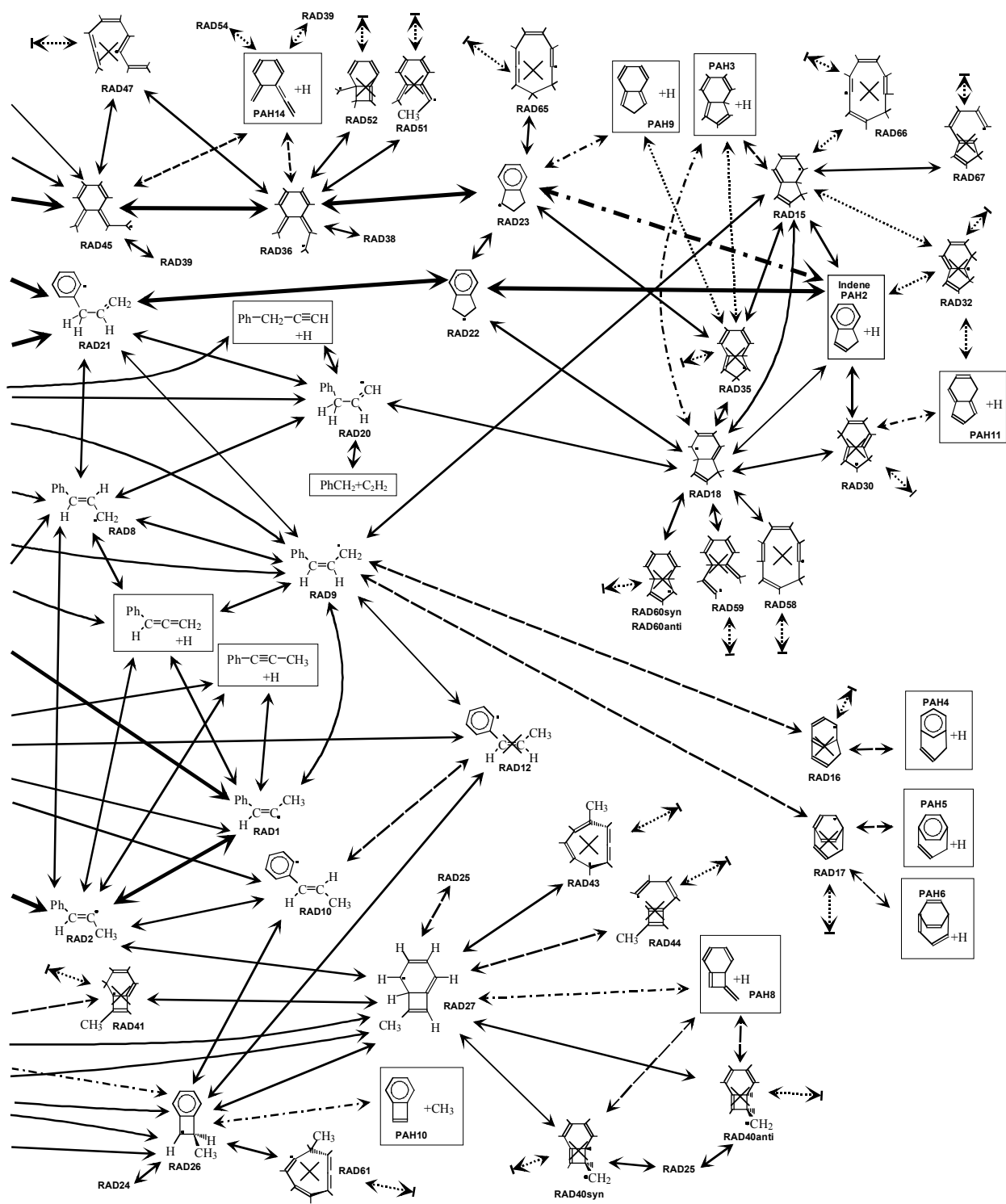
## Additional CCSD(T) calculations on entrance channels

Single point CCSD(T)/6-31G(d,p) calculations on reactants and entrance transition states, using the B3LYP-DFT/6-311+G(d,p) geometries. The relative energy  $E_{\text{rel}}$  is calculated using the ZPE-corrections at the same B3LYP level of theory.

Compound	CCSD(T)/6-311G(d,p) // B3LYP-DFT/6-311+G(d,p)	$E_{\text{rel}}$ kJ/mol
<b>phenyl+propyne</b>	-347.325773	285.0
TSrad1_Phenyl+propyne	-347.320725	299.1
TSrad4_Phenyl+propyne	-347.318793	304.2
TSPH+propyne_Benzene+2-propynyl	-347.313746	306.0
<b>phenyl+allene</b>	-347.322746	292.5
TSrad6_Phenyl+Allene	-347.315752	310.4
TSrad11_Phenyl+Allene	-347.317872	307.0
TSPhenyl+Allene_Benzene+2-propynyl	-347.308840	317.0
<b>C2H2+PhCH2</b>	-347.355316	202.8
TSrad20_C2H2+PhCH2	-347.335891	258.4
<b>phenyl+cyclopropene</b>	-347.288678	383.9
TSrad19_Phenyl+cyclopropene	-347.287705	387.6
TSPhenyl+cyclopropene_benzene+cycloprop-2-enyl	-347.275948	405.7
TSPhenyl+cyclopropene_benzene+cycloprop-1-enyl	-347.270399	420.1



**Figure SI - 1 : Reaction scheme for phenyl + propyne**  
 (Left Hand Side)



(Right Hand Side)