Table S3. Zero-point energies and electronic energies of reactants and transition state for the addition reaction of phenyl + acetylene with multi- and single-reference methods.

Multi-reference calculations			
Method	**$C_6H_5 + C_2H_2$**	**Transition state**	**Barrier height (kcal/mol)**
***Zero-Point Energy* (Hartree)**			
CASSCF(11e,11o)/aug-cc-pVTZ	0.1201816	0.1203603	(13.15)
***Single-Point Energy* (Hartree)**			
FIC-NEVPT2(11e,11o)			
cc-pVTZ	-308.1951293	-308.1905446	**2.99**
cc-pVQZ	-308.2891605	-308.2845441	**3.01**
CBS(cc-pVTZ, cc-pVQZ)	-308.3578033	-308.3531637	**3.02**
SC-NEVPT2(11e,11o)			
cc-pVTZ	-308.1936826	-308.1881823	**3.56**
cc-pVQZ	-308.2877437	-308.2820885	**3.66**
CBS(cc-pVTZ, cc-pVQZ)	-308.3312846	-308.3255577	**3.73**
MRCI(11e,11o)			
cc-pVDZ	-307.8170209	-307.8495567	**-20.30**
cc-pVTZ	-308.1016430	-308.1624778	**-38.06**
aug-cc-pVDZ	-307.8724421	-307.9366626	**-40.19**
CBS(cc-pVDZ, cc-pVTZ)	-308.2214688	-308.2942176	**-45.54**

Single-reference calculations				
Method	**C_6H_5**	**C_2H_2**	**Transition state**	**Barrier height (kcal/mol)**
***Zero-Point Energy* (Hartree)**				
M06-2X/ 6-311+G(d,p)	0.0879820	0.0275260	0.1156490	(4.01)
***Single-Point Energy* (Hartree)**				
B2PLYPD3/ def2-TZVPP	-231.4436114	-77.2938773	-308.7327118	**3.08**

Note:
(1) The active space (11e,11o) includes: (6e,6o) of C6 ring, (2e,2o) of the nonreactive π-orbital of acetylene, (2e,2o) of the reactive π-orbital of acetylene, and (1e,1o) of the radical orbital.
(2) Electronic energies are refined using the FIC-NEVPT2 and SC-NEVPT2 methods with cc-pVTZ and cc-pVQZ basis sets and are then extrapolated to the complete basis set (CBS) limit by the formula Eq. (E1)

$$E_{\mathrm{CBS}}^{\mathrm{NEVPT2}} = E_{\mathrm{cc-pVQZ}}^{\mathrm{NEVPT2}} + \left(E_{\mathrm{cc-pVQZ}}^{\mathrm{NEVPT2}} - E_{\mathrm{cc-pVTZ}}^{\mathrm{NEVPT2}}\right) \times 3^3/(4^3 - 3^3) \qquad \text{(E1)}$$

(3) Electronic energies are refined using the MRCI method with cc-pVDZ and cc-pVTZ basis sets and are then extrapolated to the complete basis set (CBS) limit by the formula Eq. (E2)

$$E_{\mathrm{CBS}}^{\mathrm{MRCI}} = E_{\mathrm{cc-pVTZ}}^{\mathrm{MRCI}} + \left(E_{\mathrm{cc-pVTZ}}^{\mathrm{MRCI}} - E_{\mathrm{cc-pVDZ}}^{\mathrm{MRCI}}\right) \times 2^3/(3^3 - 2^3) \qquad \text{(E2)}$$