

## Supplemental Material

# A Unified Reaction Network on the Formation of Five-Membered Ringed Polycyclic Aromatic Hydrocarbons (PAHs) and their Role in Ring Expansion Processes through Radical – Radical Reactions

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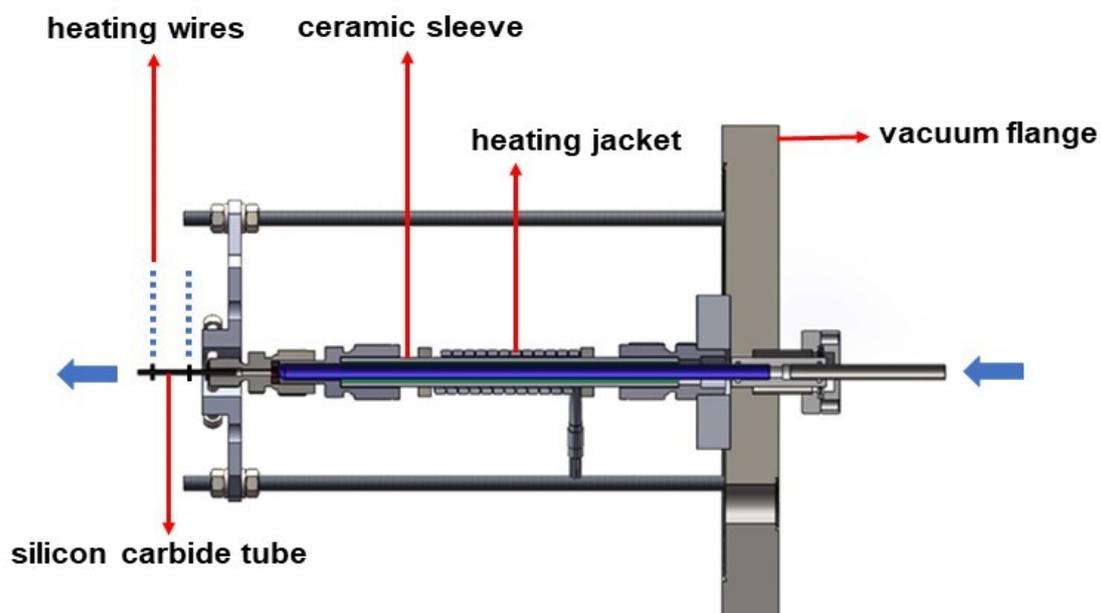
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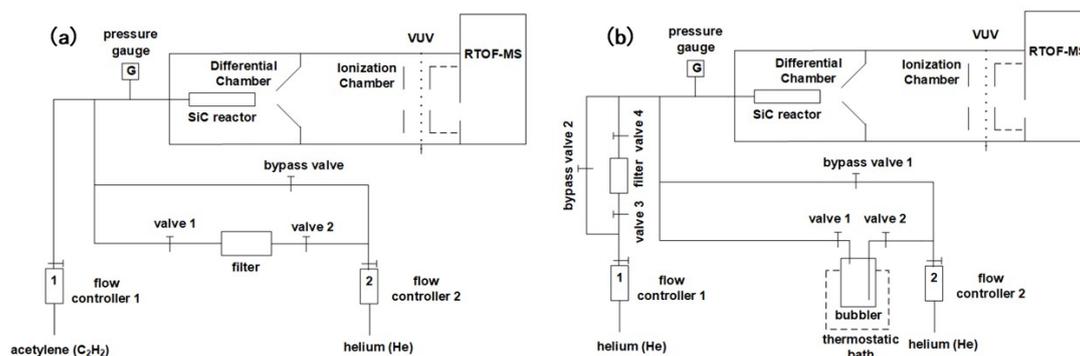
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**Section 1:** Simplified schematic diagram of experimental facility.

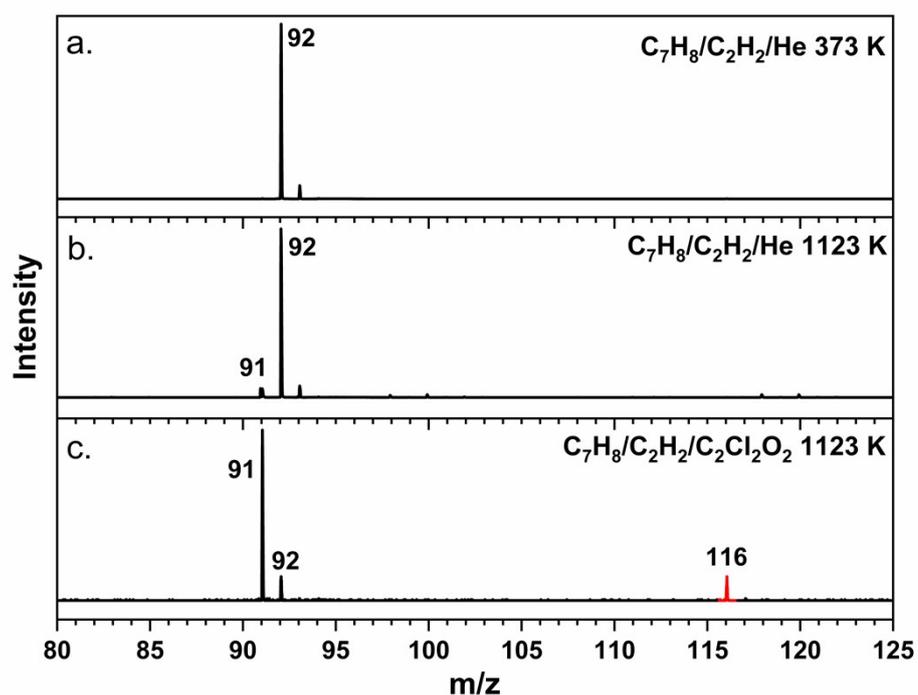


**Figure S1.** Schematic diagram of silicon carbide micro reactor.

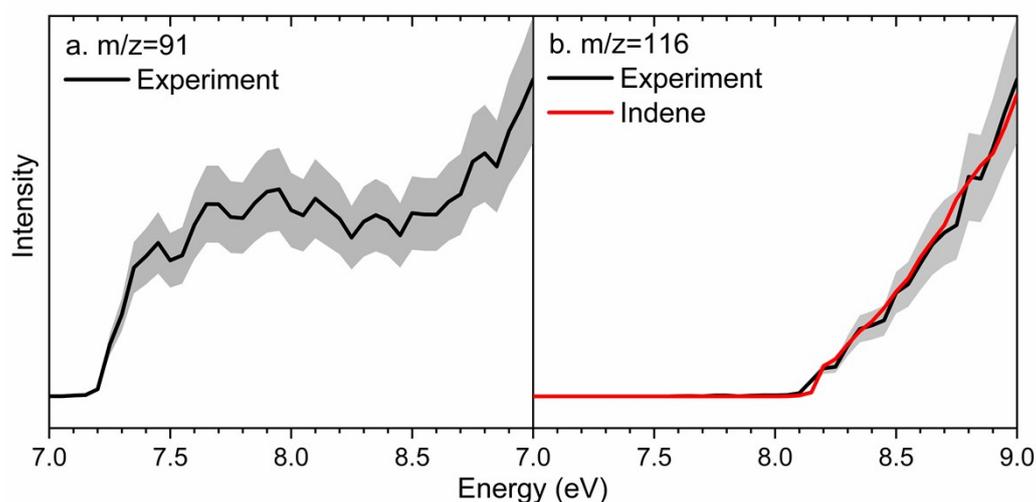


**Figure S2.** Simplified schematic diagram of experimental facility combined with SVUV and RTOF-MS.

## Section 2: Pre-experiment of oxalyl chloride/toluene/acetylene.



**Figure S3.** Mass spectra recorded at a photoionization energy of 9.00 eV for experiments (a-c). (a) toluene ( $C_7H_8$ )/acetylene ( $C_2H_2$ )/helium (He) system at 373 K; (b) toluene ( $C_7H_8$ )/acetylene ( $C_2H_2$ )/helium (He) system at 1123 K; (c) oxalyl chloride ( $C_2Cl_2O_2$ )/toluene ( $C_7H_8$ )/acetylene ( $C_2H_2$ ) system at 1123 K.



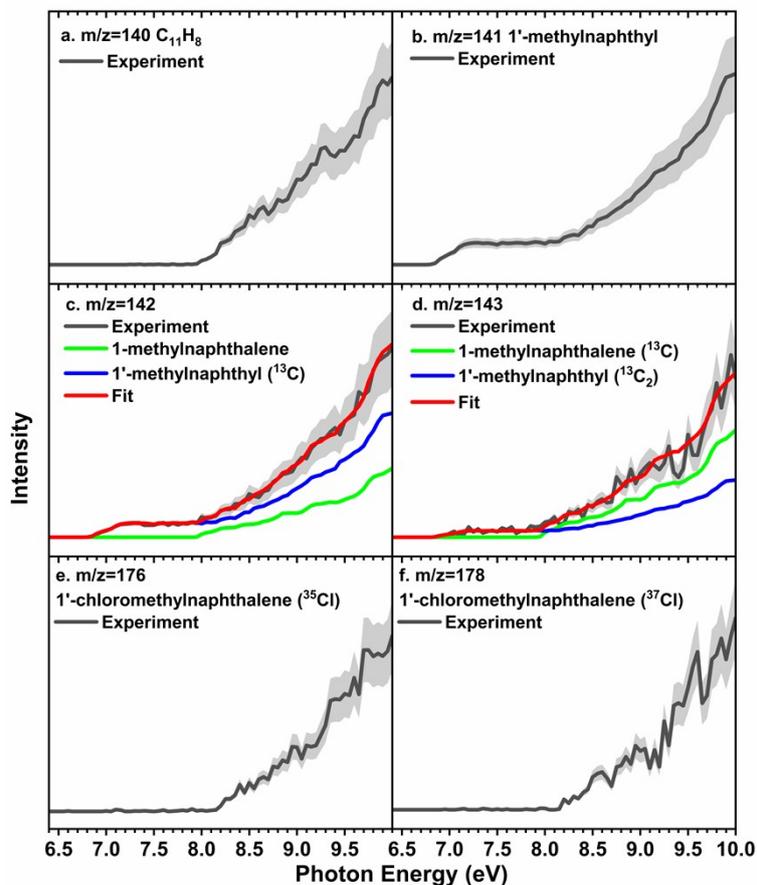
**Figure S4.** Experimental and reference PIE curves for species at  $m/z=91$  and 116 in oxalyl chloride ( $C_2Cl_2O_2$ )/toluene ( $C_7H_8$ )/acetylene ( $C_2H_2$ ) system at 1123 K. The black line refers to the normalized experimental data with  $1\sigma$  error limits defined in the shaded area. The red line refers to the reference PIE curves.

In order to verify the performance of our approach for reaction [R11], a test experiment of oxalyl chloride ( $C_2Cl_2O_2$ )/toluene ( $C_7H_8$ ,  $P_{\text{saturated}}$ : 22.0 mmHg at 293 K)/acetylene ( $C_2H_2$ ) was performed to explore whether indene ( $C_9H_8$ ,  $m/z=116$ ) would

be generated.  $C_2Cl_2O_2$  was selected as the precursor for atomic chlorine at elevated temperatures. Two bubblers which are the same as that in [R11] were adopted to contain liquid reactants of  $C_2Cl_2O_2$  and  $C_7H_8$ , respectively. One bubbler containing liquid  $C_2Cl_2O_2$  was cooled at 288 K through a thermostatic bath (Hangzhou Qiwei Instrument Co., Ltd); the second unit contained liquid  $C_7H_8$  was controlled at 273 K. The acetylene gas was seeded into the bubbler containing with a 10.0 ml/min flow rate through liquid  $C_2Cl_2O_2$ . Helium as the carrier gas with the flow rate of 10.0 ml/min entered into the bubbler containing liquid  $C_7H_8$ . The total pressure of the gas mixture mixtures was maintained at 250 Torr; the temperature of the SiC reactor was controlled at 1123 K.

Figures S3a-b show the mass spectrum at 9.00 eV of the control experiments without  $C_2Cl_2O_2$ . Ion counts for  $m/z=92$  ( $C_7H_8$ ) are obvious (Fig. S3a); weak signal at  $m/z=93$  from  $^{13}CC_6H_8$  is also observable. When  $C_2Cl_2O_2$  is added to the experiment at 1123 K, ion counts at  $m/z = 92$  decrease (Fig. S3c), and strong signal at  $m/z=91$  is emerging. Further, the target signal at  $m/z=116$  appears at 1,123 K. PIE curves of  $m/z = 116$  were acquired (Fig. S4). This PIE curve can be fit exceptionally well with the indene isomer ( $C_9H_8$ ).

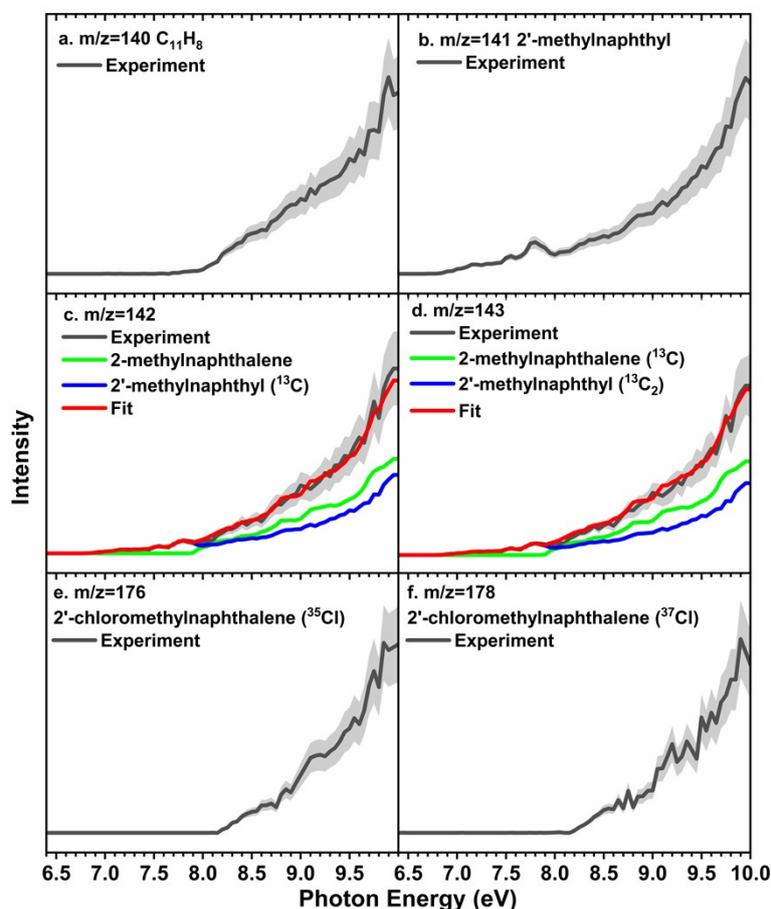
### Section 3: Additional PIE curves of three experiments.



**Figure S5.** Experimental and reference PIE curves for species at  $m/z=140$ ,  $141$ ,  $142$ ,  $143$ ,  $176$  and  $178$  in the 1'-chloromethylnaphthalene ( $C_{11}H_9Cl$ )/acetylene ( $C_2H_2$ ) system at  $1023$  K. The black line refers to the normalized experimental data with  $1\sigma$  error limits defined in the shaded area. The colored lines refer to the reference PIE curves of isomers. The red line shows the overall fit via the linear combination of the reference curves.

The experimental PIE curve of 1'-methylnaphthyl ( $C_{11}H_9$ ) at  $m/z=141$  is presented in Fig. S5b and the onset appears at about  $6.85 \pm 0.05$  eV. The H-loss and H-addition of this radical lead to the formation of the species at  $m/z = 140$  ( $C_{11}H_8$ , Fig. S5a) and  $142$  ( $C_{11}H_{10}$ , Fig. S5c), respectively. However, no corresponding PIE reference data for  $m/z=140$  can be acquired. Figure S5c exhibits the experimental PIE curve at  $m/z=142$  with the reference data of 1-methylnaphthalene ( $C_{11}H_{10}$ ) and the 1'-methylnaphthyl isotope ( $^{13}CC_{12}H_9$ ) taken into account. Except for the isotopic 1-methylnaphthalene ( $^{13}CC_{10}H_{10}$ , Fig. S5d), isotopes of  $^{13}C_2C_9H_9$  are also considered due to the abundant content of  $C_{11}H_9$  as the reactant while fitting with the experimental PIE curve at

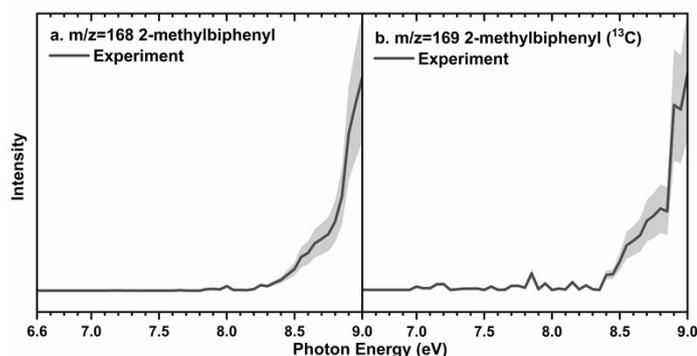
$m/z=143$ . PIE curves of the precursor 1'-chloromethylnaphthalene,  $m/z=176$  ( $C_{11}H_9^{35}Cl$ ) and 178 ( $C_{11}H_9^{37}Cl$ ), are presented in Figs. S5e-f, with the curves nearly identical after scaling.



**Figure S6.** Experimental and reference PIE curves for species at  $m/z=140$ , 141, 142, 143, 176 and 178 in 2'-chloromethylnaphthalene ( $C_{11}H_9Cl$ )/acetylene ( $C_2H_2$ ) system at 973 K. The black line refers to the normalized experimental data with  $1\sigma$  error limits defined in the shaded area. The colored lines refer to the reference PIE curves of isomers. The red line shows the overall fit via the linear combination of the reference curves.

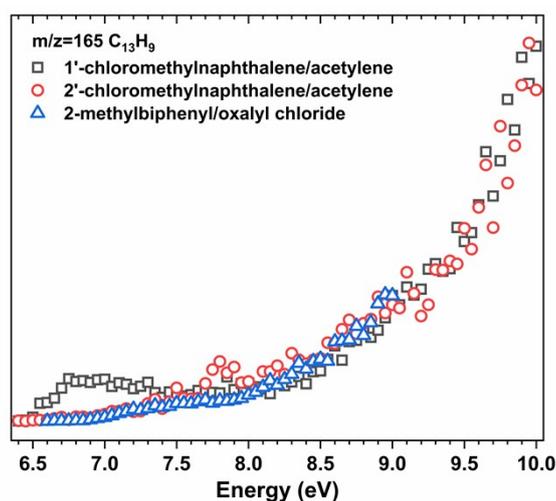
Experimental and reference PIE curves for species at  $m/z=140$ , 141, 142, 143, 176 and 178 in 2'-chloromethylnaphthalene ( $C_{11}H_9Cl$ )/acetylene ( $C_2H_2$ ) system at 973 K are shown in Fig. S6. Figure S6b displays the experimental PIE curve of 2'-methylnaphthyl,  $C_{11}H_9$ , with the onset of ion count of about  $6.85\pm 0.05$  eV. The species with  $C_{11}H_8$  molecular formulae with the initial value of  $7.65\pm 0.05$  eV of ion count could be formed through H-elimination from  $C_{11}H_9$  (Fig. S6a). It should be noted that the isotopes of  $C_{11}H_9$  have contributions to ion counts generated at  $m/z=142$  and 143 as

shown in Figs. S6c-d ( $^{13}\text{C}_{10}\text{H}_9$ -2, Fig. S6c;  $^{14}\text{C}_{10}\text{H}_9$ -1 and  $^{13}\text{C}_2\text{C}_9\text{H}_9$ -1, Fig. S6d). 2-Methylnaphthalene ( $\text{C}_{11}\text{H}_{10}$ -2,  $m/z=142$ ) is identified based on PIE match results of  $m/z=142$  (Fig. S6c). Figures S3e-f show the PIE curves of precursor 2'-chloromethylnaphthalene, at  $m/z=176$  ( $\text{C}_{11}\text{H}_9^{35}\text{Cl}$ -2, Fig. S6e) and 178 ( $\text{C}_{11}\text{H}_9^{37}\text{Cl}$ -2, Fig. S6f).



**Figure S7.** Experimental PIE curves for species at  $m/z=168$  and 169 in 2-methylbiphenyl ( $\text{C}_{13}\text{H}_{12}$ )/oxalyl chloride ( $\text{C}_2\text{Cl}_2\text{O}_2$ ) system at 1023 K.

Experimental PIE curve for the reactant, 2-methylbiphenyl, at  $m/z=168$  in 2-methylbiphenyl ( $\text{C}_{13}\text{H}_{12}$ )/oxalyl chloride ( $\text{C}_2\text{Cl}_2\text{O}_2$ ) system at 1023 K is presented in Fig. S7a. The PIE curve of the isotope of 2-methylbiphenyl,  $^{13}\text{C}_{12}\text{H}_{12}$ , is given in Fig. S7b.



**Figure S8.** Experimental PIE curves of  $m/z=165$  in three experiments.

Experimental PIE curves of species at  $m/z=165$  in three experiments are normalized and compiled in Fig. S8. Products at  $m/z=165$  are generated, respectively,

via the combination of the H-loss products from four distinct  $C_{13}H_{10}$  isomers: 3H-cyclopenta[a]naphthalene/1H-cyclopenta[a]naphthalene in 1'-chloromethylnaphthalene/acetylene system, 3H-cyclopenta[a]naphthalene/1H-cyclopenta[b]naphthalene in 2'-chloromethylnaphthalene/acetylene system, and fluorene in 2-methylbiphenyl/oxalyl chloride system. Shapes of the PIE curves of different  $C_{13}H_9$  isomers ( $m/z=165$ ) are diverse and therefore experimental PIE curves of  $m/z=165$  in three experiments are unique. As shown in Fig. S8, the onset value of PIE curve of  $m/z=165$  in 1'-chloromethylnaphthalene/acetylene system is about  $6.50\pm 0.05$  eV, whereas both of them are  $6.95\pm 0.05$  eV in 2'-chloromethylnaphthalene/acetylene and 2-methylbiphenyl/oxalyl chloride systems. The second ascending inflections of PIE curves at  $m/z=165$  in 1'-/2'-chloromethylnaphthalene with acetylene systems appear at about  $7.70\pm 0.05$  eV. However, due to the lack of PIE curves of these radicals, the radicals cannot be identified. In the 2-methylbiphenyl/oxalyl chloride system, considering the single  $C_{13}H_{10}$  isomer (fluorene) at  $m/z = 166$ , the H-loss product at  $m/z = 165$  is likely to be fluorenyl radical ( $IE=7.01\pm 0.02$  eV<sup>1</sup>).

## Reference.

- (1) Lang, M.; Holzmeier, F.; Fischer, I.; Hemberger, P., Threshold photoionization of fluorenyl, benzhydryl, diphenylmethylen, and their dimers. *J. Phys. Chem. A* **2013**, *117* (25), 5260-8.