

Supplementary Information

A Periodic System of Polycyclic Aromatic Hydrocarbons for Predictive Molecular Growth Processes

Wang Li,^a Hu Ju,^a Ming-Gao Xu,^a Shane J. Goettl,^b Jiu-Zhong Yang,^a Long Zhao,^{*ac} Ralf I.
Kaiser^{*b}

^a*National Synchrotron Radiation Laboratory, University of Science and Technology of China,
Hefei, Anhui 230029, China*

^b*Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI 96822, USA*

^c*School of Nuclear Science and Technology, University of Science and Technology of China,
Hefei, Anhui 230027, China*

Contents

Section 1: Experimental

1.1 Reactors

1.1.1 Silicon carbide microreactor

1.1.2 α -Al₂O₃ flow tube reactor

1.2 Conditions

1.2.1 Experiment 1

1.2.2 Experiment 2

1.2.3 Experiment 3

Section 2: Additional mass spectra

2.1 Experiment 1

2.2 Experiment 2

2.3 Experiment 3

Section 3: Simplified reaction pathways for the benzyl radical self-reaction

* Corresponding authors: Long Zhao zhaolong@ustc.edu.cn; Ralf I Kaiser ralfk@hawaii.edu

Section 1: Experimental

The experiments were performed at the Combustion Endstation (BL03U Beamline) in the National Synchrotron Radiation Laboratory (NSRL). These studies employed an isomer-selective product detection based on fragment-free photoionization with tunable vacuum ultraviolet (VUV) light coupled with a reflection time-of-flight mass spectrometer (Re-TOF-MS) for the detection of ionized molecules^{1,2}. Two high-temperature reactors with distinct residence times were exploited: a silicon carbide (SiC) chemical microreactor and an α -alumina (α -Al₂O₃) flow tube reactor (Figs. S1-S2; Table S1). The short residence time of only 10² μ s of the reactants in the chemical microreactor inhibits secondary reactions hence enabling a targeted investigation of elementary reactions^{3,4}. Conversely, the prolonged residence time provided in the flow tube reactor of 6 $\times$ 10³ μ s is optimal for investigating successive reactions of the primary reaction products⁵. In both reactors, benzyl (C₇H₇[•]) and (2-naphthyl)-methyl (2-C₁₁H₉[•]) radicals were prepared *in-situ* via pyrolysis of the benzyl chloride (C₇H₇Cl) and 2-chloromethylnaphthalene (2-C₁₁H₉Cl) precursors (Figs. S3-S4; Table S2), respectively.

1.1 Reactors

1.1.1 Silicon carbide microreactor

The chemical microreactor, mounted in a high vacuum differentially pumped chamber held at 10⁻⁶ Torr, comprises of a silicon carbide (SiC) tube (40.0 mm in length, 1.0 mm inner diameter, 2.0 mm outer diameter) interfaced to a stainless-steel Swagelok fitting via a graphite ferrule (Fig. S1a; Table S1). A stainless-steel nozzle with a 0.1 mm aperture is coupled to the SiC reactor. The nozzle assembly is thermally regulated using a heating jacket and a ceramic sleeve. The pressure of premixed gases was monitored through a pressure sensor (PMS 111, BD Sensor Co., Ltd) prior to entering the nozzle. The silicon carbide tube is resistively heated over a length of 20.0 mm with an accuracy of $\pm$ 10 K provided by a type-S thermocouple. The distance between the SiC tube outlet and the skimmer was optimized to 10.0 mm. A continuous molecular beam is generated by the expansion of the reactants after passing through the skimmer (2.0 mm diameter) before intersecting with the tunable vacuum ultraviolet (VUV) light perpendicularly in the ionization chamber held at 10⁻⁷ Torr (Fig. S2a). The ionized molecules are extracted and transported through an ion lens guide and then detected by a reflection time-of-flight mass spectrometer held at 10⁻⁸ Torr (Fig. S2c).

1.1.2 α -Al₂O₃ flow tube reactor

The flow tube reactor employed in this study was manufactured from corundum (α -Al₂O₃), with dimensions of 400.0 mm in length, an inner diameter of 7.0 mm, and an outer diameter of 10.0 mm (Fig. S1b; Table S1). A cylindrical quartz sleeve (13.0 mm inner diameter), externally fitted with a uniformly wound resistive heating wire (Cr20Ni80) was inserted coaxially into the α -Al₂O₃ tube. A Swagelok joint is adopted to hermetically connect the cylindrical quartz sleeve and the α -Al₂O₃ tube. To maintain the temperature of reactor, the exterior of cylindrical quartz sleeve is uniformly encased in insulation cotton with a thickness of 80.0 mm. The axial temperature distribution with an error of ± 5 K along the α -Al₂O₃ flow tube under various heating temperatures has been reported in previous literature⁶. The quartz nozzle with a diameter of 350 μ m, mounted in the difference chamber operating at 10⁻⁴ Torr, is positioned 10.0 mm from the outlet of the α -Al₂O₃ flow tube reactor. The reactants flow through the high-temperature reactor, after which the resulting products pass successively through a nozzle and a skimmer to form a molecular beam (Fig. S2b). The molecular beam is intersected perpendicularly by the VUV light within the ionization chamber held at 10⁻⁶ Torr; the resulting ions are subsequently detected by a high-resolution reflection time-of-flight mass spectrometer at 10⁻⁷ Torr (Fig. S2c).

Table S1. The main parameters of SiC microreactor and α -Al₂O₃ flow tube reactor.

	length (mm)	inner diameter (mm)	outer diameter (mm)	material	residence time	heating
microreactor	40.0	1.0	2.0	SiC	$\sim 10^2$ μ s	self-resistance heating
flow tube reactor	400.0	7.0	10.0	α -Al ₂ O ₃	$\sim 6 \times 10^3$ μ s	wrapped heating wire

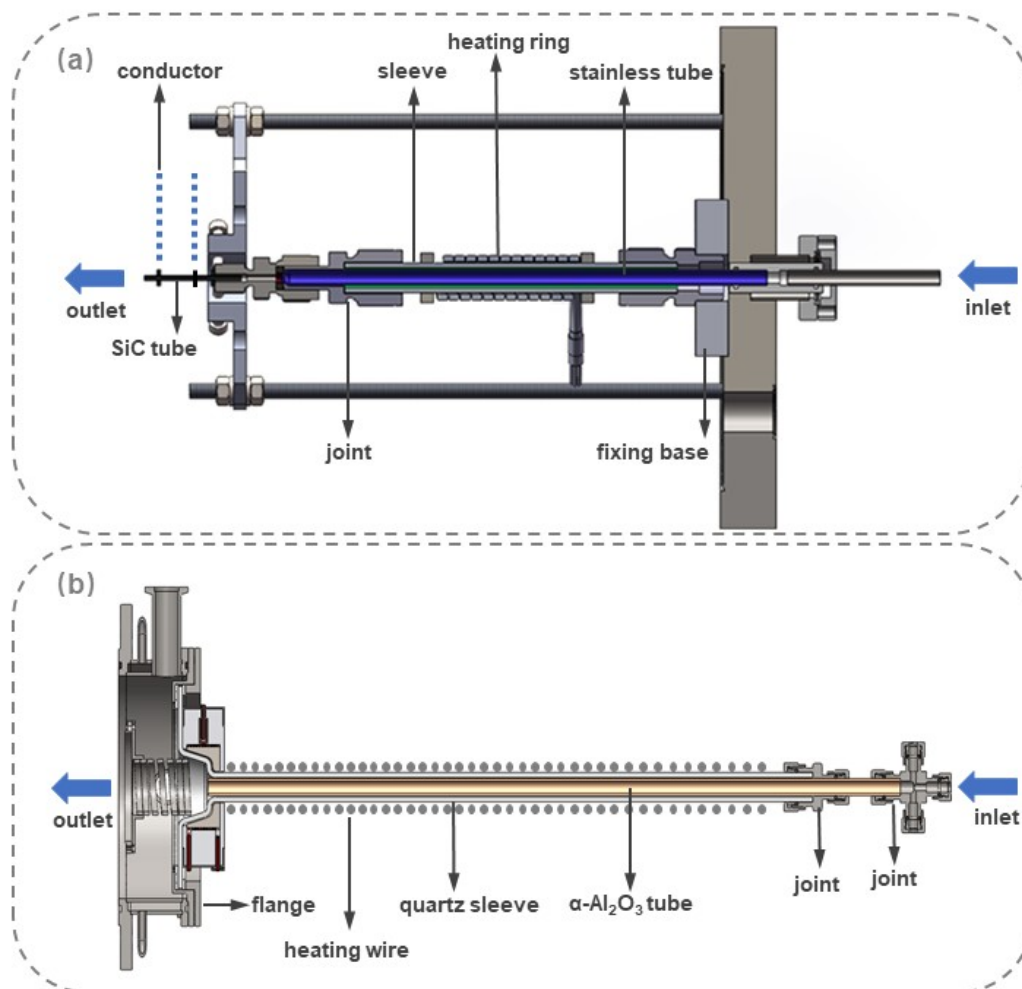


Fig. S1 Diagrams of reactors adopted in current studies are shown in panel (a) SiC microreactor and (b) α -Al₂O₃ flow tube reactor.

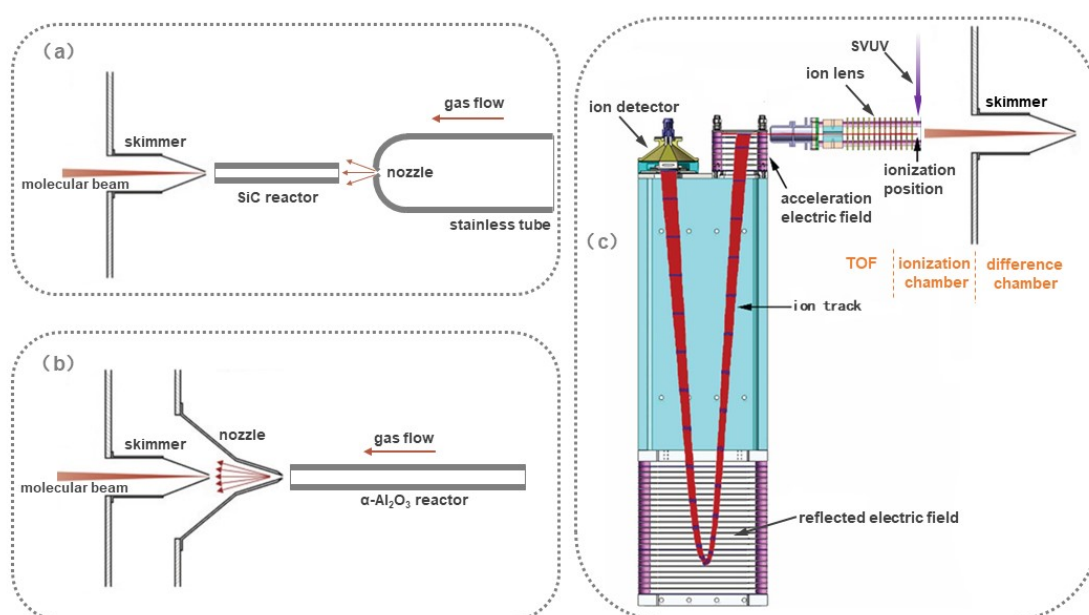


Fig. S2 Schematic diagram of the sampling systems used in the current studies are given in

panel (a) SiC microreactor (b) α -Al₂O₃ flow tube reactor; Schematic diagram of reflection time-of-flight mass spectrometer is presented in panel (c).

1.2 Conditions

1.2.1 Experiment 1

Figure S4a exhibits a schematic diagram of the injection system for experiment 1. In the present work, (2-naphthyl)-methyl ($2\text{-C}_{11}\text{H}_9^\bullet$) radicals were generated *in situ* within the SiC reactor through thermal-decomposition of the solid precursor, 2-chloromethylnaphthalene (Fig. S3a, purchased from Aladdin, >97%). A filter (Fig. S4c, Swagelok, SS-6F-MM-05) was used as the sample container. The solid 2-chloromethylnaphthalene was kept in the porous filter element (0.5 μm pore size) blocked with the quartz wool and the filter is maintained at 303 K to facilitate solid sample volatilization. The vapor of 2-chloromethylnaphthalene was introduced into a helium (He) carrier gas stream (20.0 SCCM) controlled by a mass flow controller (MKS, Andover, MA, USA) and carried out of the filter. The gas mixture passed through the stainless-steel nozzle with a 0.1 mm aperture, forming a continuous supersonic molecular beam before entering the SiC reactor, which was resistively heated to 1123 K. To prevent the condensation of the vaporized samples, the stainless-steel pipeline between the filter and the SiC reactor was heated to 473 K. Photoionization efficiency (PIE) curves from 6.50 to 9.00 eV with a step interval of 0.10 eV were recorded to identify the specific mass-to-charge ratios for the species of interest.

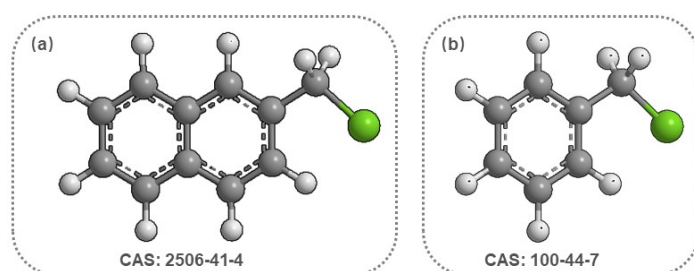


Fig. S3 Molecular structures of precursors used in the current studies are given in panel (a) 2-chloromethylnaphthalene ($2\text{-C}_{11}\text{H}_9\text{Cl}$); (b) benzyl chloride ($\text{C}_7\text{H}_7\text{Cl}$).

1.2.2 Experiment 2

In experiment 2, reactive (2-naphthyl)-methyl ($2\text{-C}_{11}\text{H}_9^\bullet$) and benzyl ($\text{C}_7\text{H}_7^\bullet$) radicals were prepared *in situ* in the SiC reactor, respectively through pyrolysis of the solid precursor, 2-chloromethylnaphthalene (Fig. S3a, purchased from Aladdin, >97%), and the liquid precursor,

benzyl chloride (C_7H_7Cl) (Fig. S3b, purchased from Aladdin, >99%). Figure S4b shows the schematic diagram of injection system. The filter (Swagelok, SS-6F-MM-05) was also used to keep the solid precursor of 2-chloromethylnaphthalene; a detailed description was provided in Section 1.2.1 of Supplementary Information. For the precursor of benzyl chloride (C_7H_7Cl), a home-made bubbler (Fig. S4d, height of 76.0 mm, diameter of 38.0 mm) equipped with a thermostatic bath instrument (Hangzhou Qiwei Instrument Co., Ltd) was employed to contain the liquid sample. Considering the relatively high saturation vapor pressure of benzyl chloride (1.3 ± 0.3 mmHg at 298 K)⁷, the bubbler is immersed in the thermostatic bath instrument (ethanol bath) and the cool-temperature was maintained at 263 K. Helium gas is introduced into the filter (35.0 SCCM) and bubbler (5.0 SCCM) as the carrier gas. The 2-chloromethylnaphthalene and benzyl chloride samples were therefore seeded into helium and sufficiently mixed reaching a total inlet pressure of 280-305 Torr. The SiC reactor was resistively heated and maintained at 1273 K; the stainless-steel gas delivery tube was heated to 473 K using a heating belt. Photoionization efficiency curves were recorded over the photon energy range of 6.90 to 9.00 eV in 0.10 eV increments to identify the specific mass-to-charge ratios corresponding to the species of interest.

1.2.3 Experiment 3

In experiment 3, the reactor was changed to the α - Al_2O_3 flow tube. In order to identify reaction species at specific mass-to-charge ratio, PIE curves ranged from 6.90 to 9.00 eV were also scanned with a more precise step interval of 0.05 eV. For a better comparison of three experiments in current study, the corresponding detailed conditions are summarized in Table S2.

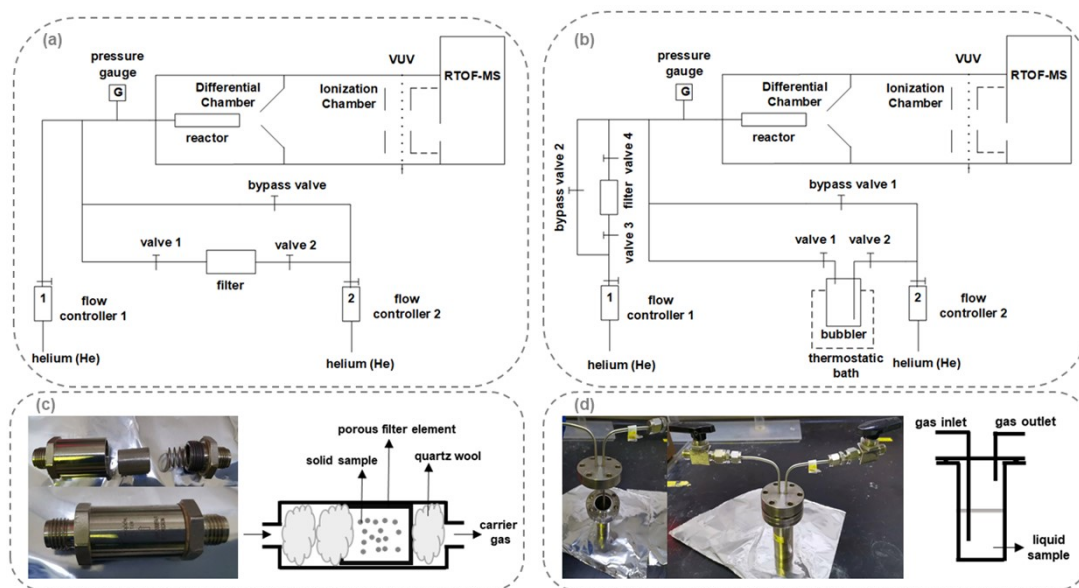


Fig. S4 Schematic diagrams of injection system are shown in panel (a) experiment 1; (b) experiments 2-3; Physical images and sample installation diagrams are shown in panel (c) filter; (d) bubbler.

Table S2. Detailed conditions of experiments 1-3.

	reactants	reactor	reaction temperature (K)	reaction pressure (Torr)	inlet pressure (Torr)	PIE
Experiment 1	$2\text{-C}_{11}\text{H}_9^{\bullet}$	SiC microtube	1123	~120	280-300	6.50-9.00/0.10
Experiment 2	$2\text{-C}_{11}\text{H}_9^{\bullet}/\text{C}_7\text{H}_7^{\bullet}$	SiC microtube	1273	~120	280-305	6.90-9.00/0.10
Experiment 3	$2\text{-C}_{11}\text{H}_9^{\bullet}/\text{C}_7\text{H}_7^{\bullet}$	$\alpha\text{-Al}_2\text{O}_3$ flow tube	1273	~30	270-300	6.90-9.00/0.05

Section 2: Additional mass spectra

2.1 Experiment 1

Figure S5a displays the experimental PIE curve recorded at $m/z = 140$ ($C_{11}H_8^+$), with an obvious onset value of approximately 7.60 eV. In Fig. S5b, the experimental PIE spectrum at $m/z = 142$ is accurately matched by the reference PIE curve of 2-methylnaphthalene, with a minor contribution from the isotope $^{13}CC_{10}H_9$ of (2-naphthyl)-methyl ($\sim 11.2\%$). The formation of 2-methylnaphthalene is attributed to hydrogen addition to (2-naphthyl)-methyl radicals in the reaction system. Figure S5c and S5d present the experimental PIE data for $m/z = 176$ ($C_{11}H_9^{35}Cl^+$) and 178 ($C_{11}H_9^{37}Cl^+$) corresponding to the precursors of 2-chloromethylnaphthalene.

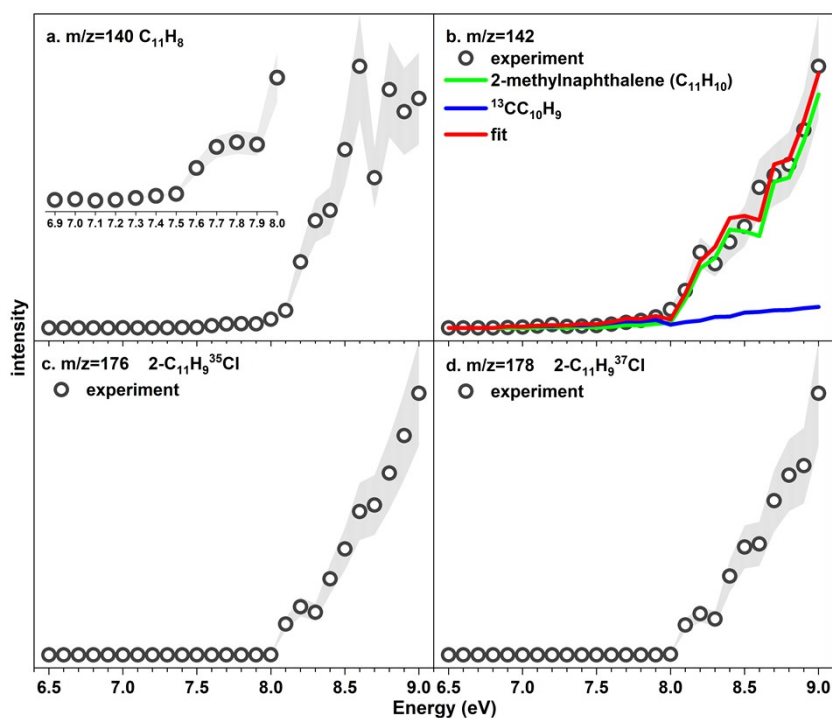


Fig. S5 Experimental and reference PIE curves for different species are shown in panel (a) $m/z = 140$, (b) 142, (c) 176, and (d) 178 in the 2-chloromethylnaphthalene ($C_{11}H_9Cl$)/helium (He) system at 1123 K. The black samples refer to the normalized experimental data with 1σ error limits defined in the shaded area. The colored lines refer to reference standard PIE curves.

To assess the purity of the reactant, (2-naphthyl)-methyl, generated in the reaction system, the experimental PIE curve at $m/z = 141$ ($C_{11}H_9^+$) was obtained and analyzed. As shown in Fig. S6, the experimental PIE data of $m/z = 141$ can be fitted well by the reference standard

PIE curve of (2-naphthyl)-methyl ($2\text{-C}_{11}\text{H}_9\cdot$)⁸, along with the isotope of $^{13}\text{CC}_{10}\text{H}_8$. This agreement confirms the successful *in-situ* preparation of (2-naphthyl)-methyl with the high-purity within the SiC microreactor.

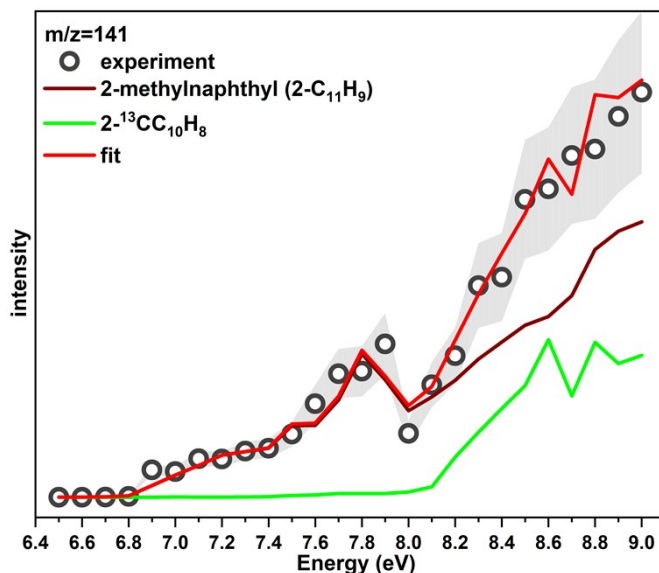


Fig. S6 Experimental and reference PIE curve at $m/z = 141$. It was collected at 1123 K in the 2-chloromethylnaphthalene ($\text{C}_{11}\text{H}_9\text{Cl}$)/helium (He) system. The black samples refer to the normalized experimental data with 1σ error limits defined in the shaded area. The colored lines refer to reference standard PIE curves.

Figure S7 exhibits the experimental PIE data collected at $m/z = 279\text{--}283$. As shown in Fig. S7b, the onset of ion signal at $m/z = 280$ ($\text{C}_{22}\text{H}_{16}^+$) occurs at 7.40 ± 0.03 eV, followed by a pronounced intensity enhancement around 8.50 eV. The PIE for $m/z = 282$ ($\text{C}_{22}\text{H}_{18}^+$) exhibits an onset of 6.90 ± 0.03 eV, with a marked increase in signal intensity observed near 7.70 eV (Fig. S7d). However, the detailed chemical structures of the products with the molecular formula $\text{C}_{22}\text{H}_{18}$ and $\text{C}_{22}\text{H}_{16}$ cannot be unambiguously assigned due to the lack of appropriate reference standards. Figure S7a presents the experimental PIE data of $m/z = 279$ and the integration intensity of collected ions at $m/z = 279$ is $\sim 23.08\%$ of that at $m/z = 278$ (Fig. 1b). Considering the contribution from ^{13}C isotopes ($22 \times 1.109\%$ natural abundance) of $\text{C}_{22}\text{H}_{14}$ isomers, ion signal at $m/z = 279$ is primarily attributed to $^{13}\text{CC}_{21}\text{H}_{14}$. Similarly, ion counts at $m/z = 281$ (Fig. S7c) and 283 (Fig. S7e) are believed to originate from $^{13}\text{CC}_{21}\text{H}_{16}$ and $^{13}\text{CC}_{21}\text{H}_{18}$, respectively.

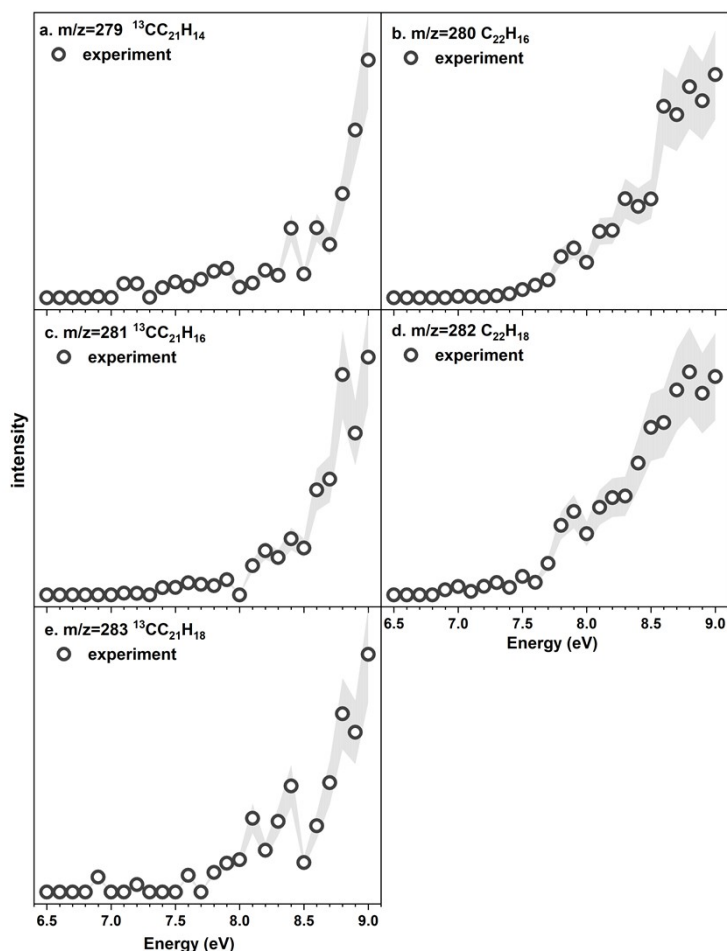


Fig. S7 Experimental PIE curves for different species are shown in panel (a) $m/z = 279$, (b) 280, (c) 281, (d) 282 and (e) 283 in 2-chloromethylnaphthalene ($C_{11}H_9Cl$)/helium (He) system at 1123 K. The black samples refer to the normalized experimental data with 1σ error limits defined in the shaded area.

Figure 2 shows the collected experimental PIE data at $m/z = 278$ ($C_{22}H_{14}^+$) and it can be well fitted with the standard PIE curves of [5]helicene, benzo[a]tetraphene and benzo[a]tetracene. The detailed fitting process of the experimental PIE data for $m/z = 278$ has been described in the main text (Fig. 2 and Figs. S8-S9). Briefly, the experimental ion onset at 7.00 ± 0.03 eV aligns well with the ionization energy (IE) of benzo[a]tetracene (6.97 ± 0.02 eV⁹). However, satisfactory fitting of the experimental PIE data using the benzo[a]tetracene reference curve is only achieved between 6.50 and 7.20 eV (Fig. S8a), with a pronounced intensity increase observed at 7.30 ± 0.03 eV. By incorporating the reference curve of benzo[a]tetraphene (7.30 ± 0.05 eV¹⁰) into the fit (Fig. S8b), the experimental PIE profile for $m/z = 278$ can be reproduced up to 7.50 eV. Finally, further inclusion of [5]helicene

($IE=7.51\pm0.02$ eV¹⁰) allows the entire experimental PIE dataset to be satisfactorily modeled by a linear combination of the reference curves for these three C₂₂H₁₄ isomers. Additional combinations of reference standard PIE curves (Fig. S8c: benzo[a]tetracene and pentaphene; Fig. S8d: benzo[a]tetracene, pentaphene and benzo[a]tetraphene; Fig. S8e: benzo[a]tetracene, benzo[a]tetraphene, pentaphene and benzo[k]tetraphene) were adopted to fit the experimental PIE data collected at $m/z=278$, but the experimental PIE data cannot be matched well in the whole energy range.

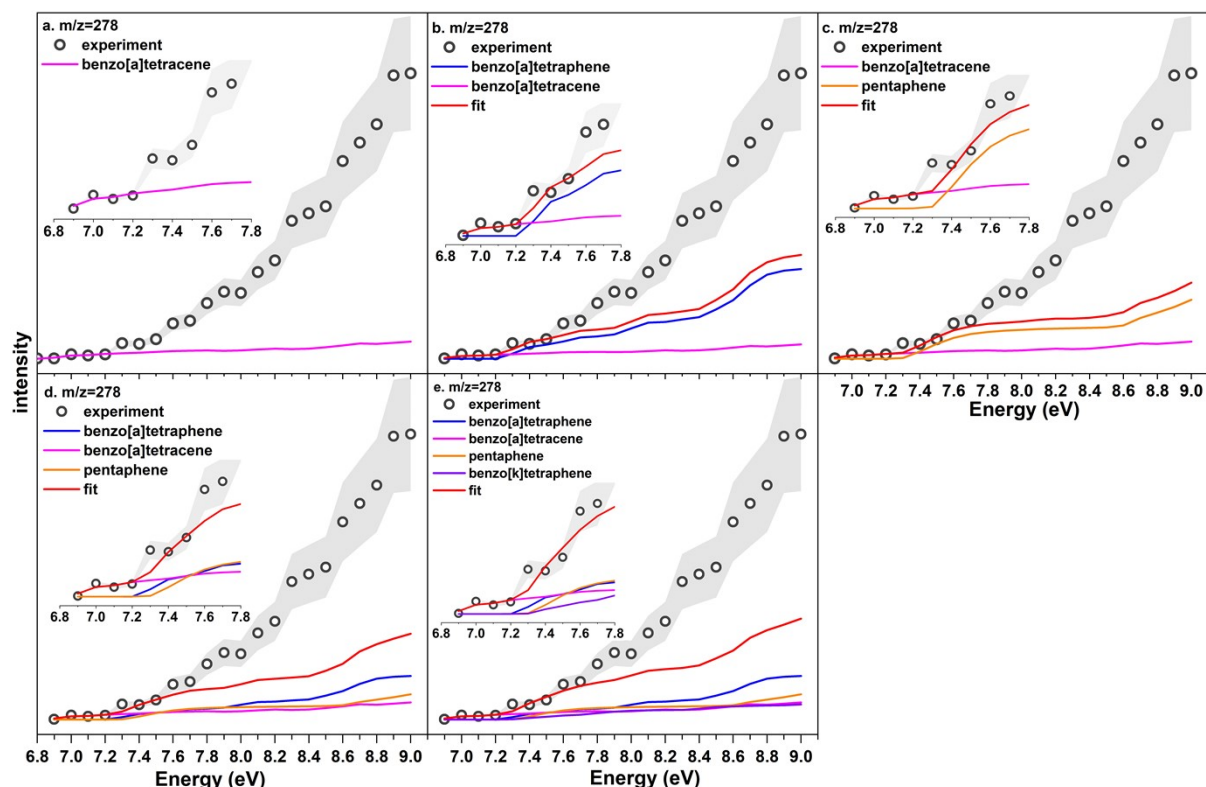


Fig. S8 Experimental PIE data for species at $m/z=278$, along with various combinations of reference standard PIE curves, in 2-chloromethylnaphthalene (C₁₁H₉Cl)/helium (He) system at 1123 K. The black samples refer to the normalized experimental data with 1σ error limits defined in the shaded area. The colored lines refer to reference standard PIE curves. (a) benzo[a]tetracene; (b) benzo[a]tetracene and benzo[a]tetraphene; (c) benzo[a]tetracene and pentaphene; (d) benzo[a]tetracene, pentaphene and benzo[a]tetraphene; (e) benzo[a]tetracene, benzo[a]tetraphene, pentaphene and benzo[k]tetraphene.

To enhance the accuracy of the experimental data analysis and assess the generation possibility of other C₂₂H₁₄ isomers, various combinations of the standard PIE curves of C₂₂H₁₄ isomers, including [5]helicene, benzo[a]tetracene, benzo[a]tetraphene, pentaphene, pentacene

and dibenz[a,h]anthracene, are also employed for reproducing the experimental datasets (Fig. S9). Figure S9a presents the experimental PIE data of $m/z=278$, along with the reference standard PIE curves of [5]helicene, benzo[a]tetraphene, benzo[a]tetracene, pentaphene, and the corresponding branching ratios of these four $C_{22}H_{14}$ isomers are extracted to be 74.3 ± 5.2 : 17.0 ± 1.2 : 6.0 ± 0.4 : $2.7\pm0.2\%$ at 8.80 ± 0.03 eV, taking 7% uncertainty of the experimental PIE data into consideration. The results of linear fitting of experimental data at $m/z=278$ using [5]helicene, benzo[a]tetraphene, benzo[a]tetracene and dibenz[a,h]anthracene are shown in Fig. S9b. After accounting for a 7% uncertainty in the experimental data, the derived branching ratios at 8.80 ± 0.03 eV were determined to be 74.1 ± 5.2 : 16.9 ± 1.2 : 6.5 ± 0.5 : $2.5\pm0.2\%$. Four reference PIE curves of [5]helicene, benzo[a]tetraphene, benzo[a]tetracene and pentacene, along with branching ratios of 72.9 ± 5.1 : 18.6 ± 1.3 : 7.4 ± 0.5 : $1.1\pm0.1\%$ at 8.80 ± 0.03 eV, were adopted into the fit of the experimental PIE data of $m/z=278$ (Fig. S9c). In Fig. S9d, five standard PIE profiles of $C_{22}H_{14}$ isomers, including [5]helicene, benzo[a]tetraphene, benzo[a]tetracene, pentaphene and dibenz[a,h]anthracene, were adopted to match the experimental PIE data of $m/z=278$. By linear fitting of these calibration PIE curves to the experimentally measured data, the branching ratios of [5]helicene, benzo[a]tetraphene, benzo[a]tetracene, pentaphene and dibenz[a,h]anthracene are extracted to be 75.5 ± 5.3 : 16.7 ± 1.2 : 5.4 ± 0.4 : 1.2 ± 0.1 : $1.2\pm0.1\%$ at 8.80 ± 0.03 eV. In Fig. S9e, all aforementioned six $C_{22}H_{14}$ isomers are considered into the match of the experimental PIE data for $m/z=278$ and the corresponding branching ratios are extracted as [5]helicene : benzo[a]tetraphene : benzo[a]tetracene : pentaphene : dibenz[a,h]anthracene : pentacene = 67.1 ± 5.3 : 20.9 ± 1.5 : 5.4 ± 0.4 : 3.1 ± 0.2 : 1.8 ± 0.1 : $1.7\pm0.1\%$. In summary, the (2-naphthyl)-methyl self-reaction system predominantly yields [5]helicene, benzo[a]tetraphene, and benzo[a]tetracene as the major products. Three additional $C_{22}H_{14}$ isomers of pentaphene, dibenz[a,h]anthracene, and pentacene, could potentially be generated as minor byproducts, with their formation yields remaining at trace levels.

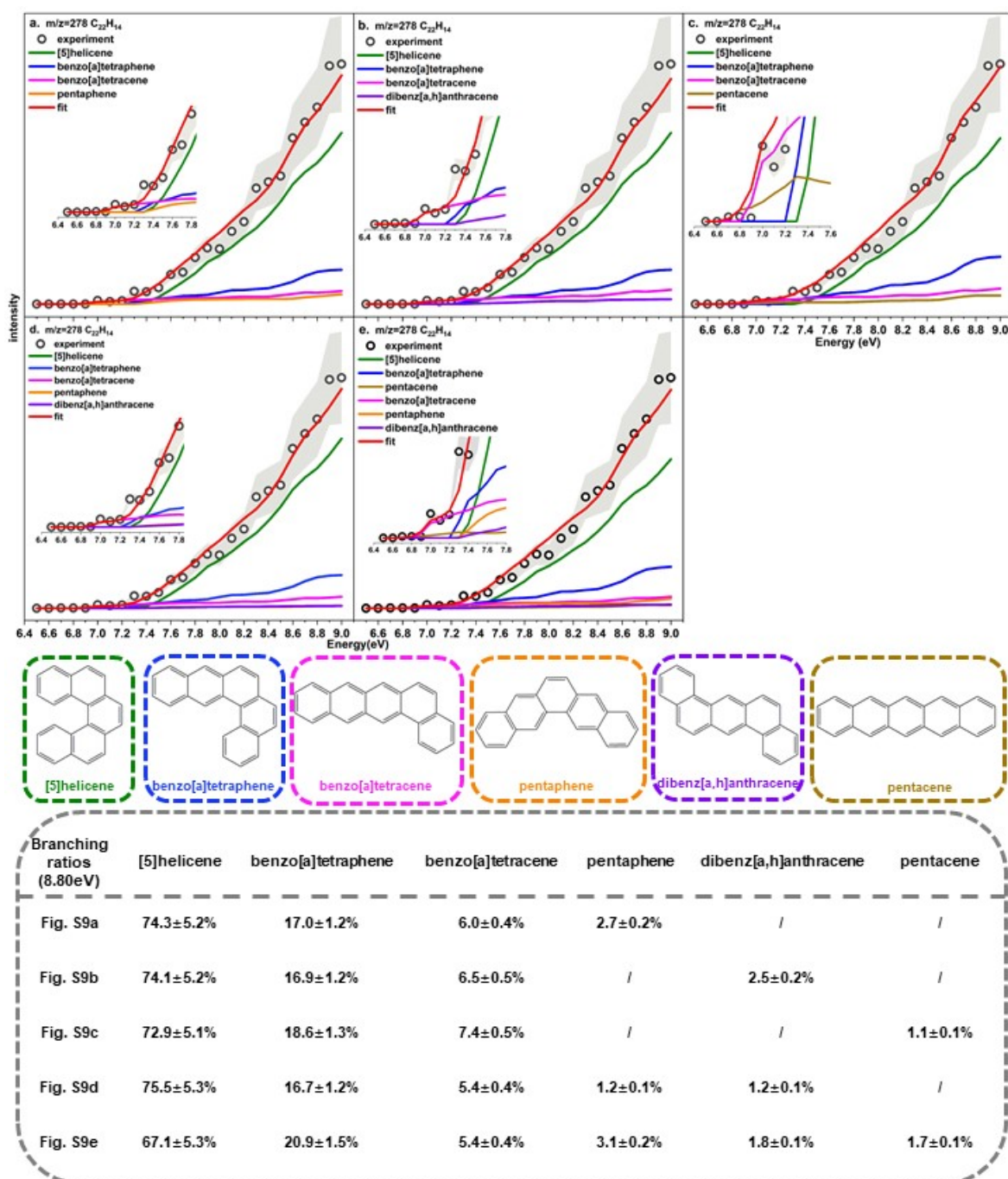


Fig. S9 Experimental PIE curve for $m/z = 278$. It was collected at 1123 K in 2-chloromethylnaphthalene ($C_{11}H_9Cl$)/helium (He) system. The black samples refer to the normalized experimental data with 1σ error limits defined in the shaded area. The colored lines refer to reference standard PIE curves. Various combinations of reference standard PIE curves are shown in panel (a) [5]helicene, benzo[a]tetrathene, benzo[a]tetracene and pentaphene; (b) [5]helicene, benzo[a]tetrathene, benzo[a]tetracene and dibenz[a,h]anthracene; (c) [5]helicene, benzo[a]tetrathene, benzo[a]tetracene and pentacene; (d) [5]helicene, benzo[a]tetrathene, benzo[a]tetracene, pentaphene and dibenz[a,h]anthracene; (e) [5]helicene, benzo[a]tetrathene, benzo[a]tetracene, pentaphene and pentacene.

benzo[a]tetraphene, pentaphene, pentacene and dibenz[a,h]anthracene.

2.2 Experiment 2

To evaluate the purity of benzyl and (2-naphthyl)-methyl radicals *in-situ* generated within the SiC reactor, we initially acquired and analyzed PIE curves of $m/z = 91$ (Fig. S10a) and 141 (Fig. S10b). It can be seen that both experimental PIE data of $m/z = 91$ and 141 can, respectively, be well matched with reference standard PIE curves of benzyl ($C_7H_7^+$, Fig. S10a)^{11,12} and (2-naphthyl)-methyl ($2-C_{11}H_9^+$, Fig. S10b)⁸, along with corresponding ^{13}C isotope contributions from $^{13}CC_6H_6$ (91 amu, Fig. S10a) and $^{13}CC_{10}H_8$ (141 amu, Fig. S10b), indicating satisfactory *in-situ* preparation of reactive radicals within the reactor.

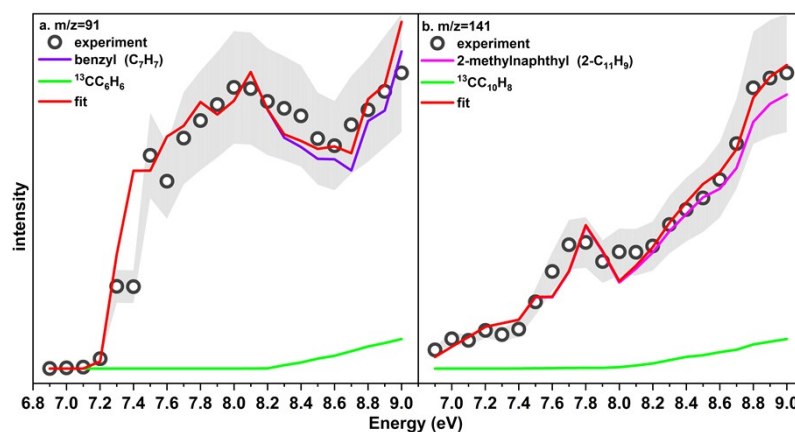


Fig. S10 Experimental and reference PIE curves for different species are shown in panel (a) $m/z = 91$ and (b) 141. The black samples refer to the normalized experimental data with 1σ error limits defined in the shaded area. The colored lines refer to reference standard PIE curves.

Figures S11a-S11c shows the experimental PIE data recorded at $m/z = 89$, 90 and 92, along with the corresponding reference curves. Figure S11a shows the experimental PIE data for $m/z=89$. The onset value of 8.20 ± 0.03 eV agrees well with the IE of fulvenallenyl (8.19 ± 0.01 eV) and the whole experimental PIE data can be reproduced by the reference PIE curve of fulvenallenyl¹³. Figure S11b presents the experimental PIE data for $m/z=90$. This spectrum is well-represented by a combination of the reference PIE curve for fulvenallene⁴ and the contribution from the $^{13}CC_6H_5$ isotope. Similarly, the experimental PIE data collected for $m/z=92$ is accurately reproduced by superimposing the standard PIE curve of toluene¹⁴ with the signal from its $^{13}CC_6H_7$ isotopologue (Fig. S11c). Through the PIE analysis method, the fulvenallenyl radical ($C_7H_5^+$), fulvenallene (C_7H_6) and toluene (C_7H_8) were identified at $m/z =$

89, 90 and 92. Benzyl radical ($C_7H_7^\bullet$) decomposes at elevated temperatures to yield fulvenallene (C_7H_6). Subsequent pyrolysis of fulvenallene (C_7H_6) then forms fulvenallenyl ($C_7H_5^\bullet$)^{14,15}. Toluene (C_7H_8) is formed through further H-addition of benzyl ($C_7H_7^\bullet$)¹⁵. Figures S11d-S11f present the experimental PIE data for $m/z = 139$, 140 and 142 which are assigned to products stemming from one or two step(s) of H-elimination/addition reactions of the (2-naphthyl)-methyl. Figures S11d and S11e exhibit the experimental PIE data for $m/z = 139$ and 140, respectively. However, further identifications of detailed chemical structures are hindered due to the lack of reference PIE curves. Figure S11f exhibits the experimental PIE data for $m/z = 142$ and it can be well fitted by the reference PIE curve of 2-methylnaphthalene (2- $C_{11}H_{10}$), along with the isotope of 2- $^{13}CC_{10}H_9$.

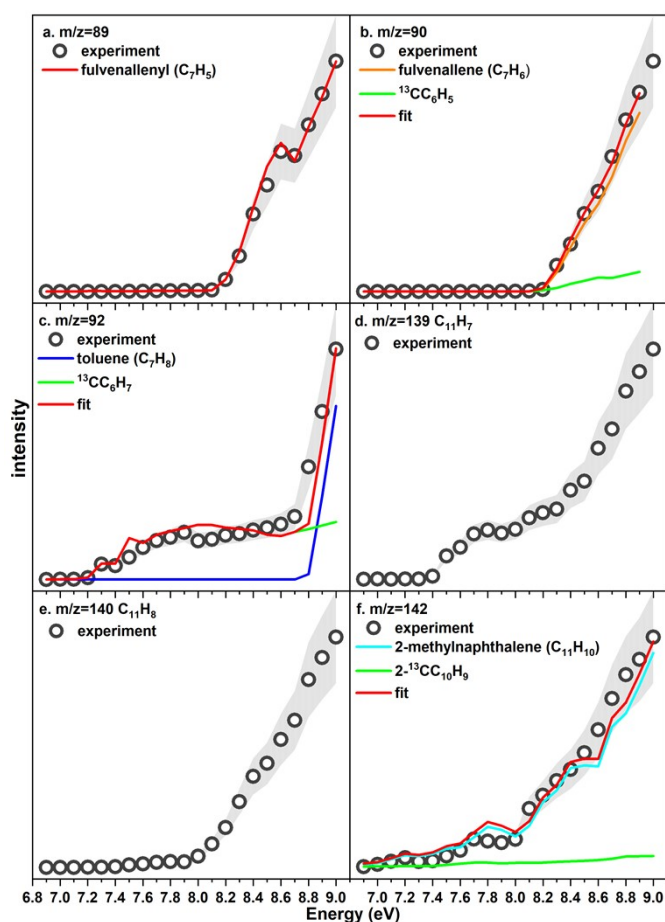


Fig. S11 Experimental and reference PIE curves for different species are shown in panel (a) $m/z = 89$, (b) 90, (c) 92, (d) 139, (e) 140 and (f) 142, in benzyl chloride (C_7H_7Cl)/2-chloromethylnaphthalene ($C_{11}H_9Cl$)/helium (He) system at 1273 K. The black samples refer to the normalized experimental data with 1σ error limits defined in the shaded area. The colored

lines refer to reference standard PIE curves.

Figure S12 presents experimental data recorded at $m/z = 154$ ($C_{12}H_{10}^+$), 156 ($C_{12}H_{12}^+$), 178 ($C_{14}H_{10}^+$), 180 ($C_{14}H_{12}^+$), 182 ($C_{14}H_{14}^+$), 278 ($C_{22}H_{14}^+$), 280 ($C_{22}H_{16}^+$), and 282 ($C_{22}H_{18}^+$). As shown in Fig. S12a, the experimental PIE curve for $m/z = 154$ exhibits an onset energy of 7.70 ± 0.03 eV, consistent with the ionization energy (IE) of ethynynaphthalene ($C_{12}H_{10}$, 7.70 eV¹⁶). Similarly, the PIE spectrum of $m/z = 156$ (Fig. S12b) shows an onset near 8.00 eV, which is close to the IE of ethynynaphthalene ($C_{12}H_{12}$, 7.95 eV⁷). It is proposed that ethynynaphthalene ($C_{12}H_{12}$) is formed through the reaction of (2-naphthyl)-methyl ($2-C_{11}H_9^{\bullet}$) with a methyl radical ($CH_3^{\bullet}$), which can subsequently undergo H-elimination to yield ethynynaphthalene ($C_{12}H_{10}$). Notably, ion signals at $m/z = 154$ and 156 were also observed in the previous reported studies of 1-/(2-naphthyl)-methyl^{8,17}. The signals observed at $m/z = 178$, 180 , and 182 have been attributed to products arising from the self-reaction of benzyl radicals, i.e. $C_{14}H_{10}$, $C_{14}H_{12}$ and $C_{14}H_{14}$ isomers¹². Similarly, the ion counts at $m/z = 278$, 280 , and 282 are assigned to products of the (2-naphthyl)-methyl radical self-reaction (Section 2.1 of Supplementary Information). By linear fitting of calibration PIE curves to the experimentally measured data ($m/z = 278$), the branching ratios of [5]helicene, benzo[a]tetraphene and benzo[a]tetracene are extracted to be 63.3 ± 4.4 : 31.8 ± 2.2 : $4.9 \pm 0.3\%$ at 8.80 eV, taking 7% uncertainty of the experimental PIE data into consideration.

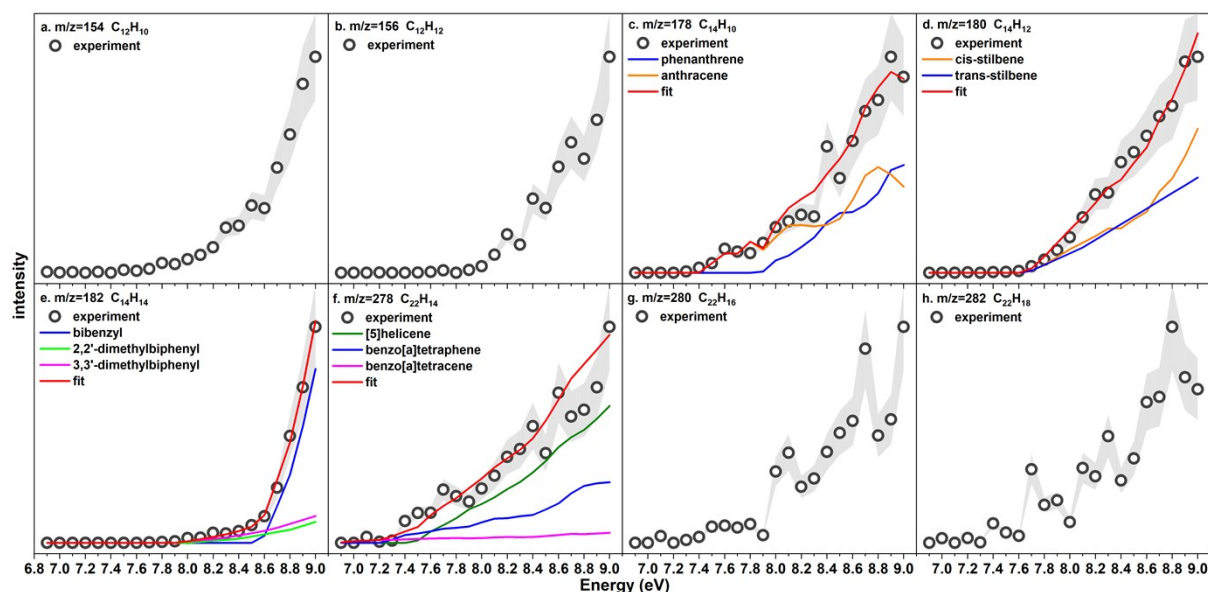


Fig. S12 Experimental and reference PIE curves for different species are shown in panel (a) $m/z = 154$, (b) 156 , (c) 178 , (d) 180 , (e) 182 , (f) 278 , (g) 280 and (h) 282 in benzyl chloride

(C₇H₇Cl)/2-chloromethylnaphthalene (C₁₁H₉Cl)/helium (He) system at 1273 K. The black samples refer to the normalized experimental data with 1 σ error limits defined in the shaded area. The colored lines refer to reference standard PIE curves.

Figure S13 shows the experimental PIE data collected at $m/z = 229$ -233. Figure S13b and S13d exhibit the experimental PIE data for $m/z = 230$ (C₁₈H₁₄⁺) and 232 (C₁₈H₁₆⁺); the analysis is precluded due to the lack of corresponding reference standard PIE curves. Briefly, the onset value of experimental PIE profile for $m/z = 230$ is 7.50 $\pm$ 0.03 eV (Fig. S13b). Similarly, an initial threshold near 7.80 eV can be determined from the experimental PIE curve of $m/z = 232$ (Fig. S13d), followed by a pronounced intensity enhancement at 8.50 $\pm$ 0.03 eV. Figure S13a shows the collected experimental PIE data at $m/z = 229$. The integrated ion intensity at $m/z = 229$ corresponds to approximately 20.11% of the intensity at $m/z = 228$ (Fig. 3b). Considering the contribution from ¹³C isotopes (natural abundance: 18 $\times$ 1.109%) within C₁₈H₁₂ isomers, the ion counts at $m/z = 229$ are primarily attributed to ¹³CC₁₇H₁₂. Similarly, the ion signals at $m/z = 231$ (Fig. S13c) and $m/z = 233$ (Fig. S13e) mainly come from ¹³CC₁₇H₁₄ and ¹³CC₁₇H₁₆, respectively. Figure S14 presents the experimental PIE data collected at $m/z = 228$ (C₁₈H₁₂⁺), along with different combinations of reference standard PIE curves with the detailed analysis provided in the main manuscript. To provide comprehensive experimental evidence, potential contributions of two additional C₁₈H₁₂ isomers, chrysene and triphenylene (their IEs $\geq$ 7.60 eV), were also evaluated. First, chrysene or triphenylene was elected as proxies for [4]helicene to fit the experimental PIE curve of $m/z=228$. As shown in Figs. S15a-S15b, the fitting result was less satisfactory than that achieved using benz[a]anthracene, [4]helicene, and tetracene and a discrepancy was particularly evident at energies greater than 8.40 eV. Building upon the successful fit with the three primary isomers of benz[a]anthracene, [4]helicene, and tetracene, we subsequently evaluated the individual and combined contributions of chrysene and triphenylene to the PIE curve (Figs. S15c–S15e). While a satisfactory fit could be reproduced, it is crucial to note that the branching ratios required for chrysene and triphenylene were minimal (<1%). Even if these additional C₁₈H₁₂ isomers, such as chrysene and triphenylene, are postulated to be formed in experiment 2, their yields would be negligible.

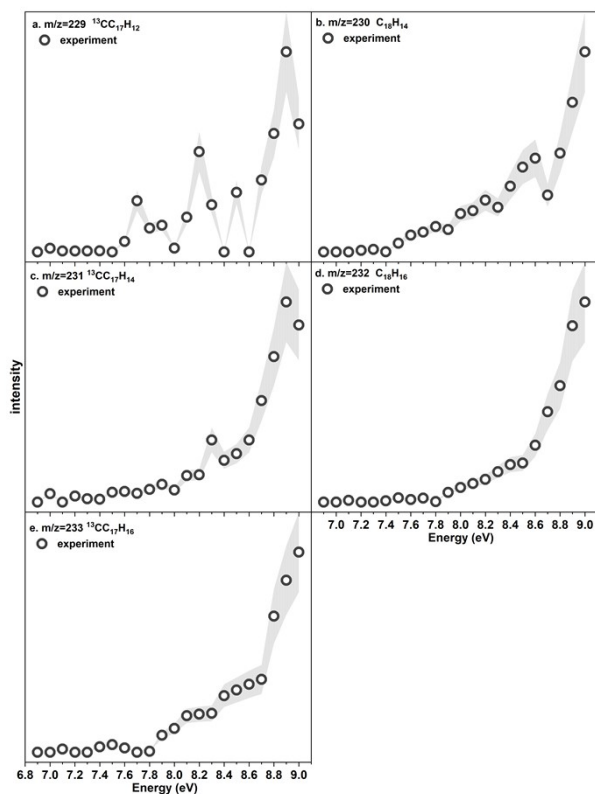


Fig. S13 Experimental PIE curves for different species are shown in panel (a) $m/z = 229$, (b) 230, (c) 231, (d) 232 and (e) 233, in benzyl chloride (C_7H_7Cl)/2-chloromethylnaphthalene ($C_{11}H_9Cl$)/helium (He) system at 1273 K. The black samples refer to the normalized experimental data with 1σ error limits defined in the shaded area.

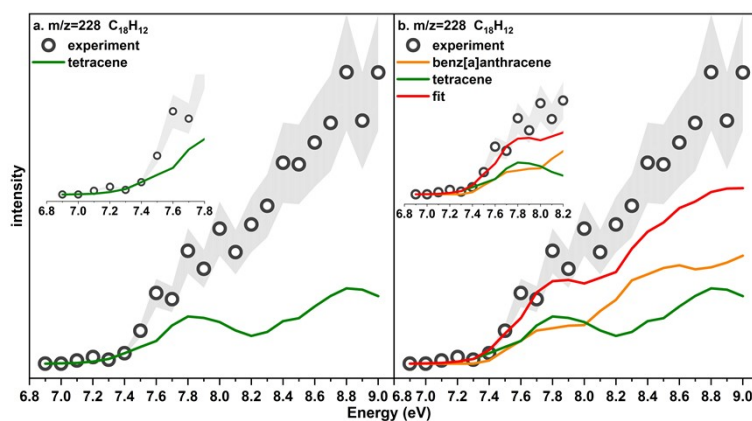


Fig. S14 Experimental PIE curve for $m/z = 228$. It was collected at 1273 K in benzyl chloride (C_7H_7Cl)/2-chloromethylnaphthalene ($C_{11}H_9Cl$)/helium (He) system. The black samples refer to the normalized experimental data with 1σ error limits defined in the shaded area. Various combinations of reference standard PIE curves are shown in panel (a) tetracene; (b) benz[a]anthracene and tetracene.

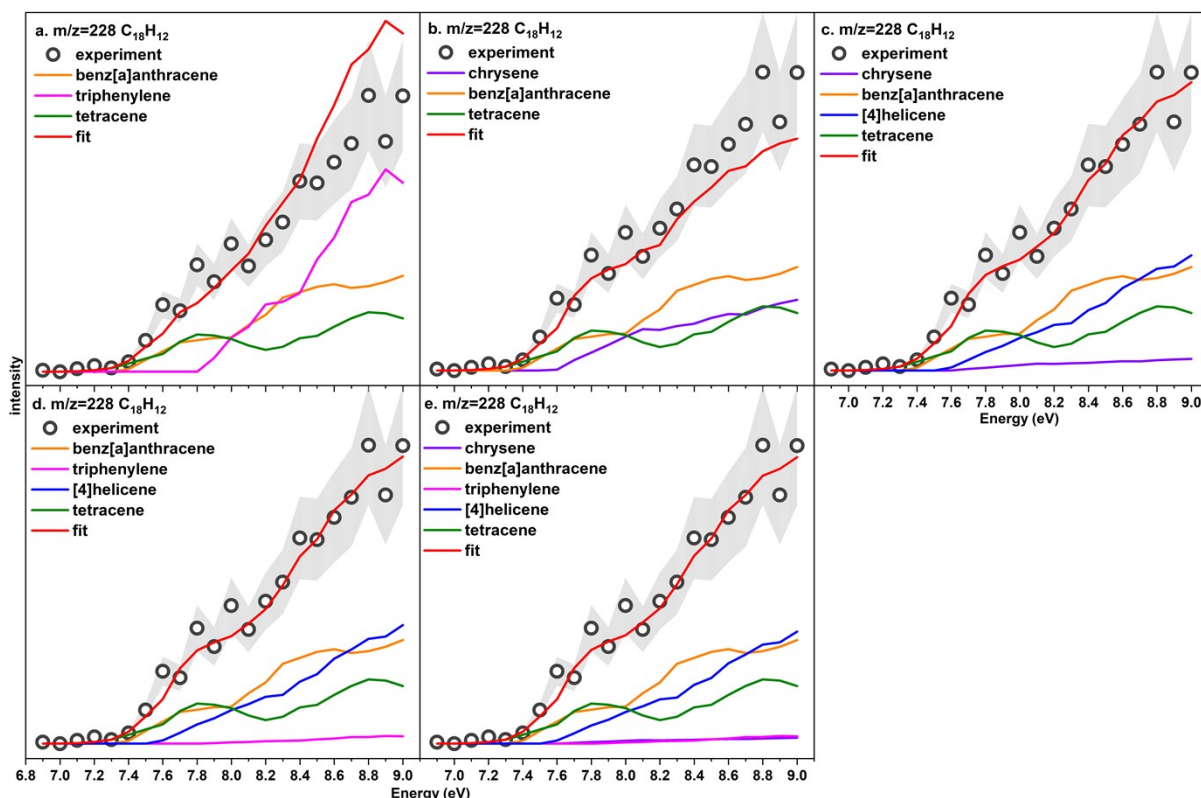


Fig. S15 Experimental PIE data for species at $m/z=228$, along with various combinations of reference standard PIE curves, in benzyl chloride (C_7H_7Cl)/2-chloromethylnaphthalene ($C_{11}H_9Cl$)/helium (He) system at 1273 K. The black samples refer to the normalized experimental data with 1σ error limits defined in the shaded area. The colored lines refer to reference standard PIE curves. (a) benz[a]anthracene, triphenylene and tetracene; (b) chrysene, benz[a]anthracene, and tetracene; (c) chrysene, benz[a]anthracene, [4]helicene, and tetracene; (d) benz[a]anthracene, triphenylene, [4]helicene, and tetracene; (e) chrysene, benz[a]anthracene, triphenylene, [4]helicene, and tetracene.

2.3 Experiment 3.

Figure S16a shows the mass spectrum recorded at the photoionization energy of 9.00 eV in experiment 3, using the α -Al₂O₃ flow tube reactor. the prolonged reactant residence time (Table S1) promotes secondary reactions and enhanced molecular mass growth within the system. The interested mass-to-charge ratio regions of 225–235 and 275–284 in the current study were displayed and discussed in detail in the main text (Fig. 5). Additionally, expanded views of the mass spectra at $m/z = 80$ –100 and 134–146 are provided in Figs. S16b and S16c, respectively. Notably, the signal intensities of the ions at $m/z = 91$ (C₇H₇⁺, Fig. S16b) and $m/z = 141$ (2-C₁₁H₉⁺, Fig. S16c) corresponding to benzyl and (2-naphthyl)-methyl, are markedly lower than those observed in experiments 1 and 2 (Figs. 1 and 3). Figure S17a exhibits the experimental PIE data collected at $m/z = 91$, which can be well fit with the reference PIE curve of the benzyl radical^{11,12}, along with the isotope of ¹³CC₆H₆. Likewise, the experimental PIE data of $m/z = 141$ (Fig. S17b) are accurately described by the reference profiles⁸ attributed to the (2-naphthyl)-methyl radical and ¹³CC₁₀H₈ isotope. Signals at $m/z = 92$ (C₇H₈⁺, Fig. S16b) and 142 (2-C₁₁H₁₀⁺, Fig. S16c) are significantly enhanced, respectively originating from further H-addition to benzyl and (2-naphthyl)-methyl forming toluene and 2-methylnaphthalene, separately. The integral intensity of ions at $m/z = 233$ (¹³CC₁₇H₁₆⁺) is about 20.65% of those at $m/z = 232$ (C₁₈H₁₆⁺), suggesting the ion counts at $m/z = 233$ primarily originates from ¹³C isotopes of C₁₈H₁₆ (232 amu, 18×1.109% natural abundance). Similarly, the signal at $m/z = 283$, with an intensity ratio of 23.50% relative to $m/z = 282$, is primarily attributable to the ¹³C isotope of C₂₂H₁₈ (282 amu, 22×1.109% natural abundance). Therefore, it can be concluded that the C₁₈H₁₆ and C₂₂H₁₈ hydrocarbons are mainly formed via (2-naphthyl)-methyl reacting with benzyl and self-reactions of (2-naphthyl)-methyl in experiment 3.

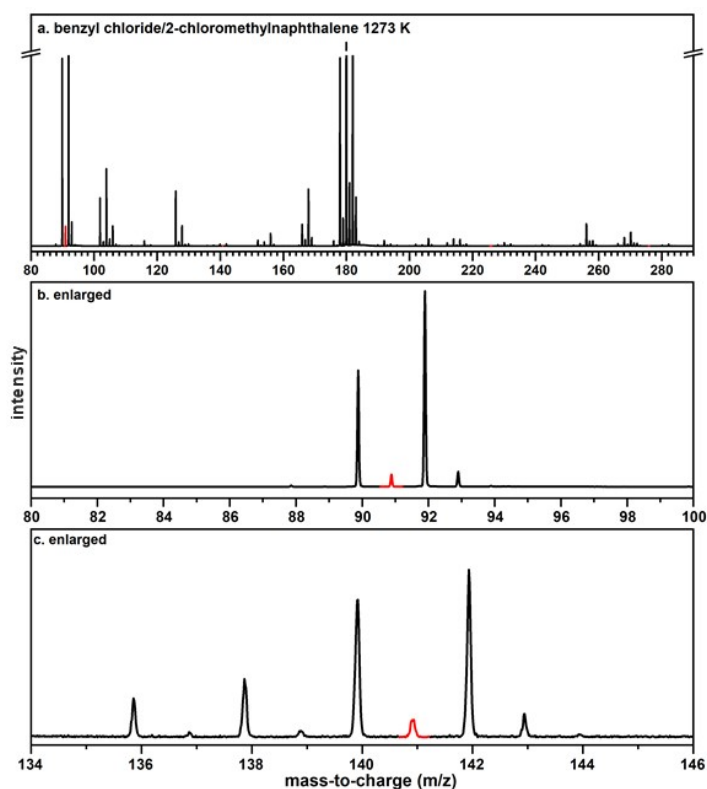


Fig. S16 Mass spectrum recorded at the photoionization energy of 9.00 eV in experiment 3, using the α -Al₂O₃ flow tube reactor. The whole mass spectrum is shown in panel (a) m/z =80-285. The enlarged spectra are shown in panel (b) m/z = 80-100 and (c) m/z = 134-146.

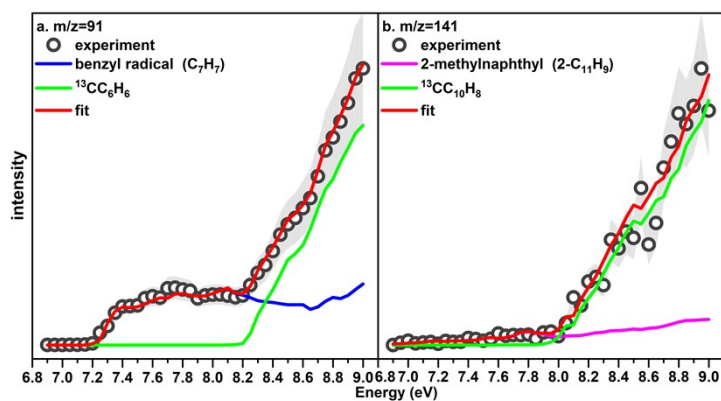


Fig. S17 Experimental and reference PIE curves for different species are shown in panel (a) m/z = 91 and (b) 141 in benzyl chloride (C_7H_7Cl)/2-chloromethylnaphthalene ($C_{11}H_9Cl$)/helium (He) system at 1273 K, using the α -Al₂O₃ flow tube reactor. The black samples refer to the normalized experimental data with 1σ error limits defined in the shaded area. The colored lines refer to reference standard PIE curves.

Figure S18a presents the experimental PIE data of $m/z=229$ ($^{13}CC_{17}H_{12}^+$), originating from ^{13}C isotope ($18 \times 1.109\%$ natural abundance) of $C_{18}H_{12}$ isomers. Note that ion counts at

$m/z=229$ ($^{13}\text{CC}_{17}\text{H}_{12}^+$) can be fit with the same overall branching ratios of benz[a]anthracene, [4]helicene, and tetracene (all $\text{C}_{18}\text{H}_{12}$) as those during the fitting for $m/z=228$. Additional experimental PIE data and fitting results are also presented in Figs. S18-S23. However, for some ion signals, further structure identifications cannot be performed due to lack of reference standard PIE curves.

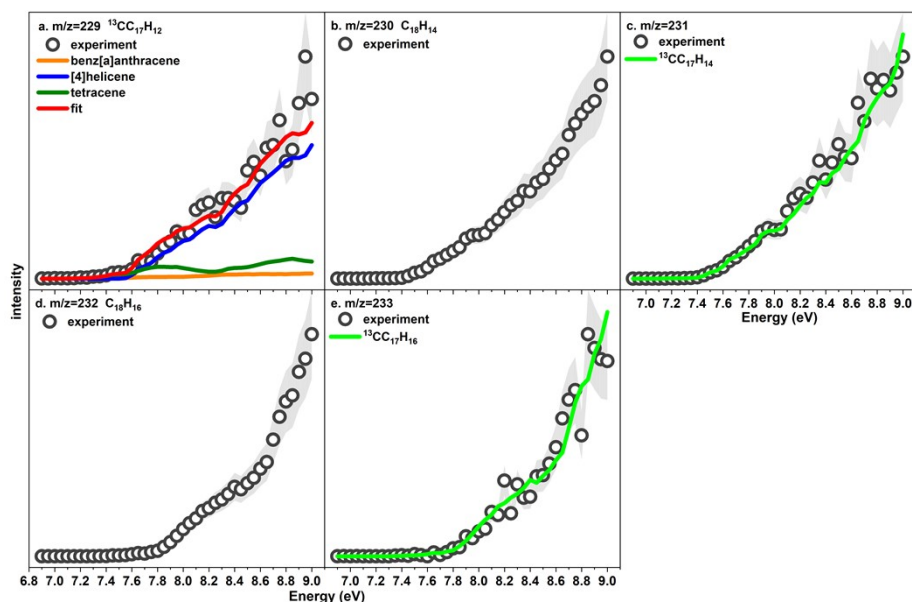


Fig. S18 Experimental and reference PIE curves for different species are shown in panel (a) $m/z = 229$, (b) 230, (c) 231, (d) 232 and (e) 233 in benzyl chloride ($\text{C}_7\text{H}_7\text{Cl}$)/2-chloromethylnaphthalene ($\text{C}_{11}\text{H}_9\text{Cl}$)/helium (He) system at 1273 K, using the $\alpha\text{-Al}_2\text{O}_3$ flow tube reactor. The black samples refer to the normalized experimental data with 1σ error limits defined in the shaded area. The colored lines refer to reference standard PIE curves.

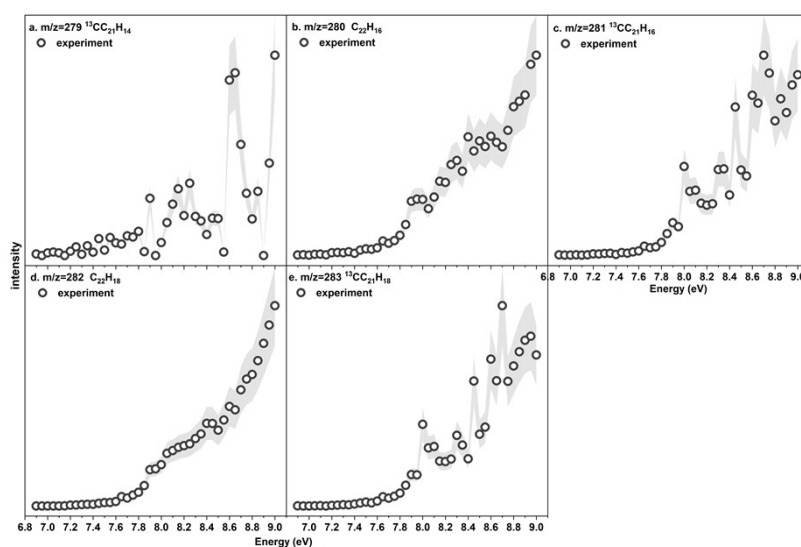


Fig. S19 Experimental PIE curves for different species are shown in panel (a) $m/z = 279$, (b) 280, (c) 281, (d) 282 and (e) 283 in benzyl chloride (C_7H_7Cl)/2-chloromethylnaphthalene ($C_{11}H_9Cl$)/helium (He) system at 1273 K, using the α - Al_2O_3 flow tube reactor. The black samples refer to the normalized experimental data with 1σ error limits defined in the shaded area.

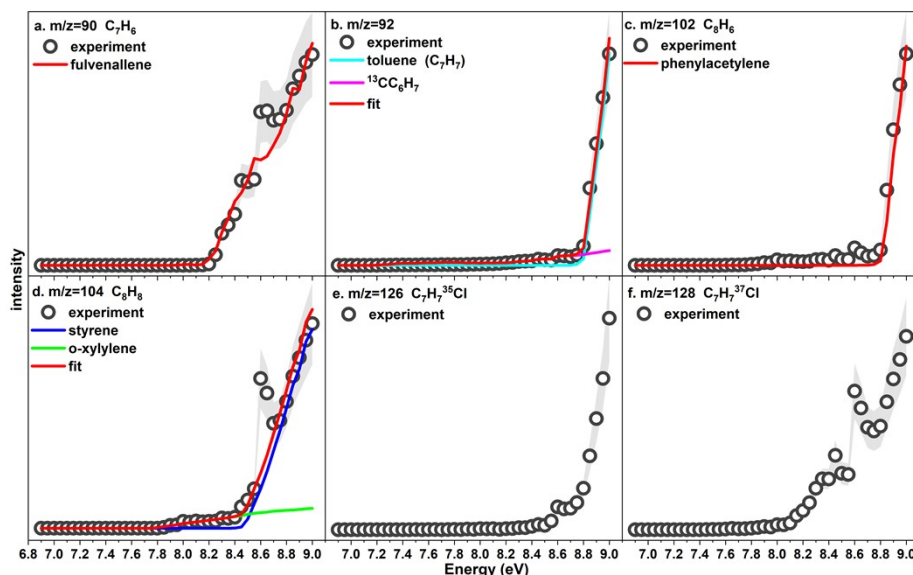


Fig. S20 Experimental and reference PIE curves for different species are shown in (a) $m/z = 90$, (b) 92, (c) 102, (d) 104, (e) 126 and (f) 128 in benzyl chloride (C_7H_7Cl)/2-chloromethylnaphthalene ($C_{11}H_9Cl$)/helium (He) system at 1273 K, using the α - Al_2O_3 flow tube reactor. The black samples refer to the normalized experimental data with 1σ error limits defined in the shaded area. The colored lines refer to reference standard PIE curves.

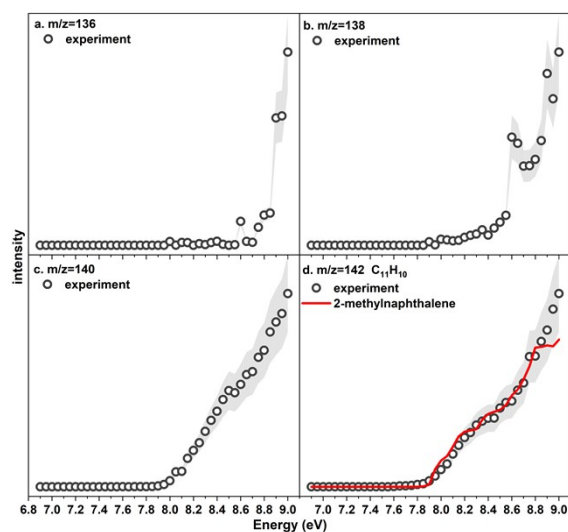


Fig. S21 Experimental and reference PIE curves for different species are shown in panel (a) $m/z = 136$, (b) 138, (c) 140 and (d) 142 in benzyl chloride (C_7H_7Cl)/2-chloromethylnaphthalene

(C₁₁H₉Cl)/helium (He) system at 1273 K, using the α -Al₂O₃ flow tube reactor. The black samples refer to the normalized experimental data with 1 σ error limits defined in the shaded area. The colored lines refer to reference standard PIE curves.

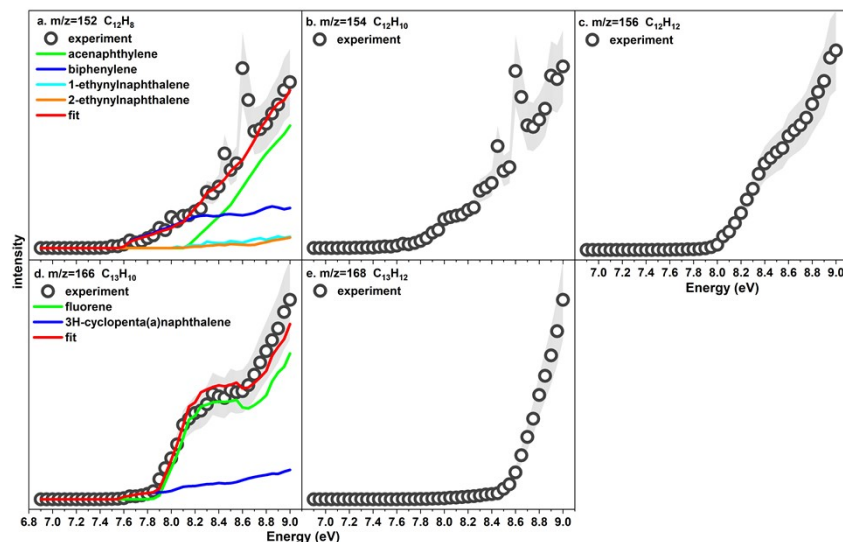


Fig. S22 Experimental and reference PIE curves for different species are shown in panel (a) $m/z = 152$, (b) 154, (c) 156, (d) 166 and (e) 168 in benzyl chloride (C₇H₇Cl)/2-chloromethylnaphthalene (C₁₁H₉Cl)/helium (He) system at 1273 K, using the α -Al₂O₃ flow tube reactor. The black samples refer to the normalized experimental data with 1 σ error limits defined in the shaded area. The colored lines refer to reference standard PIE curves.

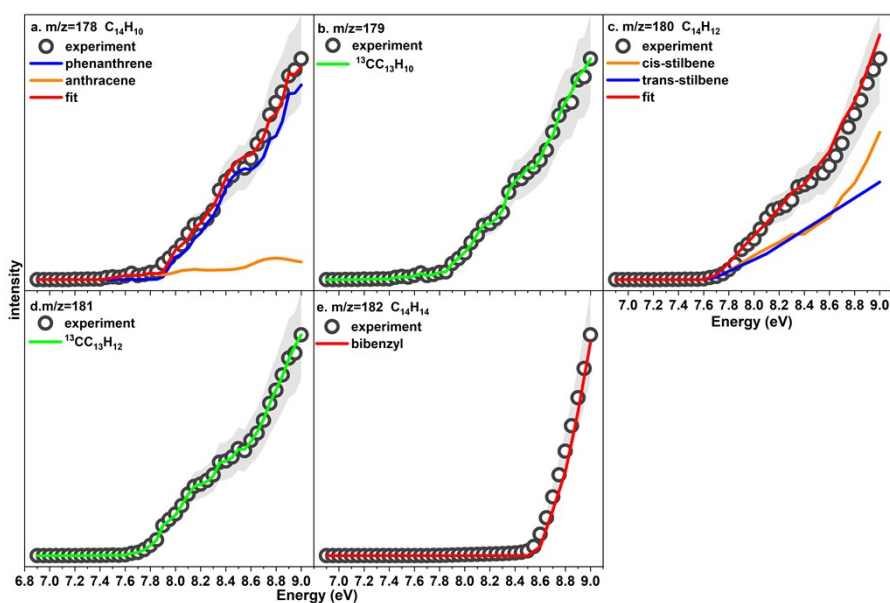


Fig. S23 Experimental and reference PIE curves for different species are shown in panel (a) $m/z = 178$, (b) 179, (c) 180, (d) 181 and (e) 182 in benzyl chloride (C₇H₇Cl)/2-

chloromethylnaphthalene ($C_{11}H_9Cl$)/helium (He) system at 1273 K, using the α - Al_2O_3 flow tube reactor. The black samples refer to the normalized experimental data with 1σ error limits defined in the shaded area. The colored lines refer to reference standard PIE curves.

Compared with experiment 2, the proportion of [4]helicene in the total formed $C_{18}H_{12}$ isomers rises markedly from $36.5 \pm 2.5\%$ to $86.5 \pm 6.1\%$ in experiment 3, whereas the proportions of benz[a]anthracene and tetracene decrease significantly to $3.8 \pm 0.3\%$ and $9.7 \pm 0.7\%$, respectively, from those of $44.6 \pm 3.0\%$ and $18.9 \pm 1.3\%$ in experiment 2 (Fig. S24a). A comparative analysis reveals that (Fig. S24b), in contrast to experiment 2, it exhibits significant increases in the branching ratios of [5]helicene ($63.3 \pm 4.4\%$ at 8.80 eV in experiment 2, Fig. S12f) and benzo[a]tetracene ($4.9 \pm 0.3\%$ at 8.80 eV in experiment 2, Fig. S12f), with the concomitant decreases in that of benzo[a]tetraphene ($31.8 \pm 2.2\%$ at 8.80 eV in experiment 2, Fig. S12f).

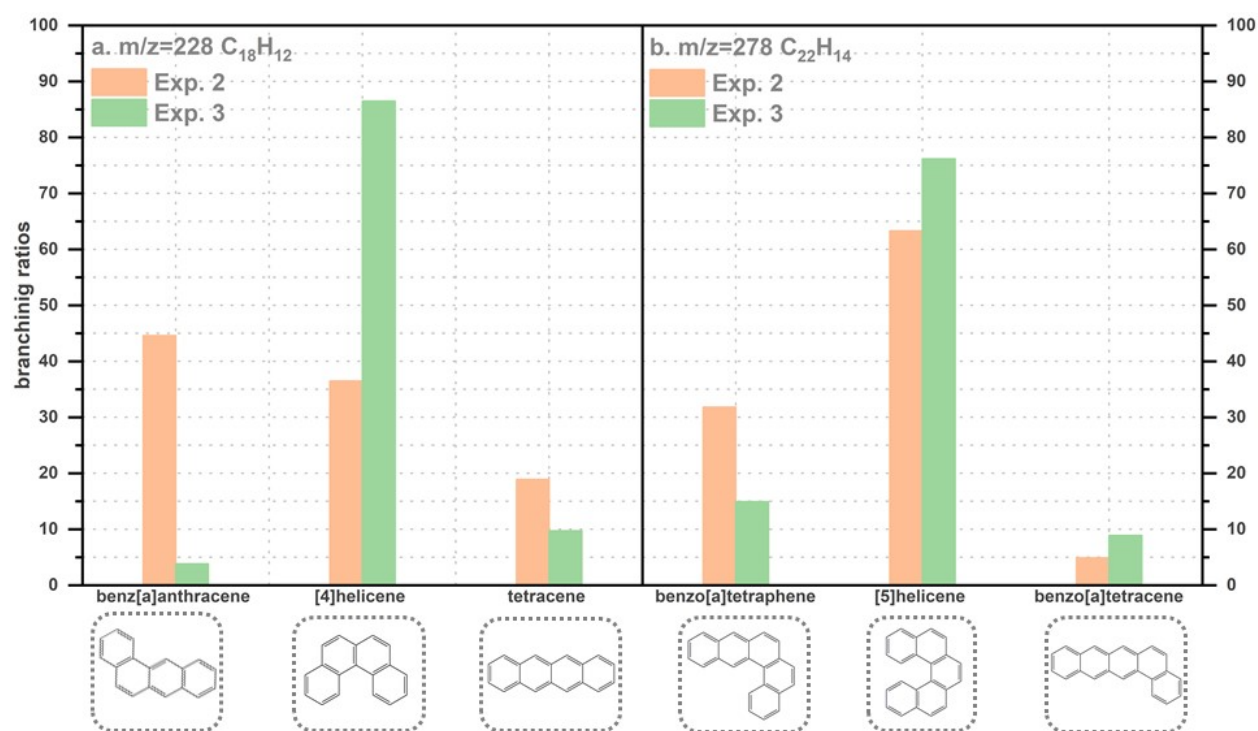


Fig. S24 Comparisons of branching ratios between experiment 3 (Exp. 3: benzyl/(2-naphthyl)-methyl, using the α - Al_2O_3 flow tube reactor) and experiment 2 (Exp. 2: benzyl/(2-naphthyl)-methyl, using the SiC microreactor) are shown in panel (a) $C_{18}H_{12}$; (b) $C_{22}H_{14}$.

Section 3: Simplified reaction pathways for the benzyl radical self-reaction

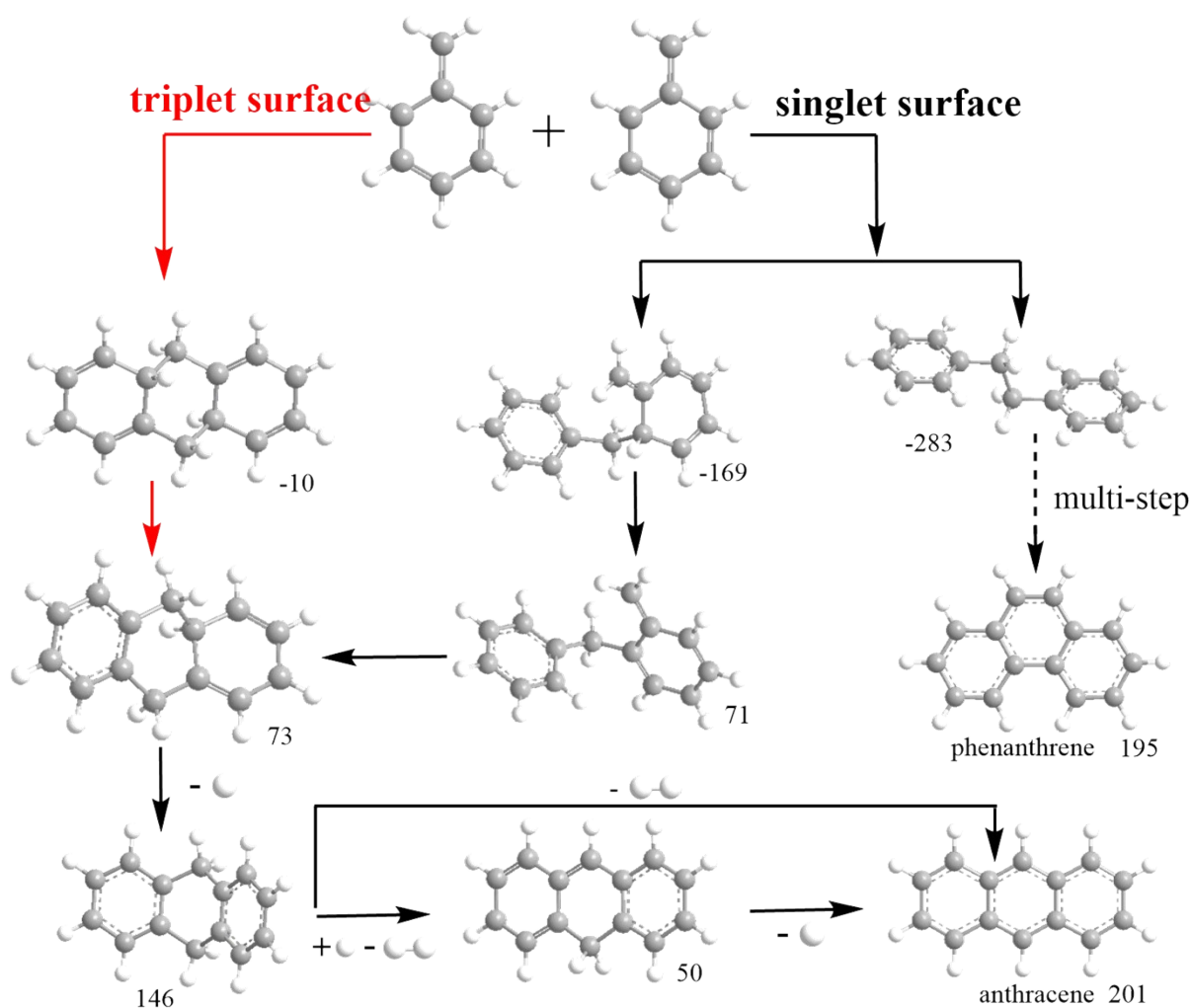


Fig. S25 Simplified reaction pathways for the benzyl self-reaction. The reaction pathways are extracted from the reference¹². Novel reaction pathways on the singlet and triplet surfaces are color coded in black and red, respectively. All energies are presented in the unit of kJ·mol⁻¹. Carbon and hydrogen atoms are color coded in gray and white, respectively.

Reference.

1. Z. Zhou, X. Du, J. Yang, Y. Wang, C. Li, S. Wei, L. Du, Y. Li, F. Qi and Q. Wang, The vacuum ultraviolet beamline/endstations at NSRL dedicated to combustion research, *J. Synchrotron Radiat.*, 2016, **23**, 1035-1045.
2. Z. Zhou, J. Yang, W. Yuan, Z. Wang, Y. Pan and F. Qi, Probing combustion and catalysis intermediates by synchrotron vacuum ultraviolet photoionization molecular-beam mass spectrometry: Recent progress and future opportunities, *Phys. Chem. Chem. Phys.*, 2022, **24**, 21567-21577.
3. L. Zhao, R. I. Kaiser, B. Xu, U. Ablikim, M. Ahmed, M. V. Zagidullin, V. N. Azyazov, A. H. Howlader, S. F. Wnuk and A. M. Mebel, VUV photoionization study of the formation of the simplest polycyclic aromatic hydrocarbon: Naphthalene ($C_{10}H_8$), *J. Phys. Chem. Lett.*, 2018, **9**, 2620-2626.
4. W. Li, Y. Zhang, J. Huang, C. Wang, F. Zhang, J. Yang and L. Zhao, A VUV photoionization study on the gas-phase synthesis of the first five-membered carbon ring - C_7H_6 isomers, *Chem. Phys. Lett.*, 2024, **835**, 140978.
5. D. Tian, Y. Liu, B. Wang, C. Cao, Z. Liu, Y. Zhai, Y. Zhang, J. Yang and Z. Tian, Pyrolysis study of iso-propylbenzene with photoionization and molecular beam mass spectrometry, *Combust. Flame*, 2019, **209**, 313-321.
6. W. Li, J. Yang, L. Zhao, D. Yu and Z. Tian, Pyrolysis investigation of n-propylamine with synchrotron photoionization and molecular-beam mass spectrometry, *Combust. Flame*, 2021, **232**, 111511.
7. National Institute of Standards and Technology, NIST Standard Reference Database, <https://webbook.nist.gov/chemistry/>, (accessed October 10, 2025).
8. W. Li, L. Zhao and R. I. Kaiser, 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, *Phys. Chem. Chem. Phys.*, 2023, **25**, 4141-4150.
9. L. Zhao, R. I. Kaiser, W. Lu, M. Ahmed, M. M. Evseev, E. K. Bashkirov, V. N. Azyazov, C. Tonshoff, F. Reicherter, H. F. Bettinger and A. M. Mebel, A free-radical prompted barrierless gas-phase synthesis of pentacene, *Angew. Chem. Int. Ed.*, 2020, **59**, 11334-11338.
10. R. I. Kaiser, L. Zhao, W. Lu, M. Ahmed, M. M. Evseev, V. N. Azyazov, A. M. Mebel, R. K. Mohamed, F. R. Fischer and X. Li, Gas-phase synthesis of racemic helicenes and their potential role in the enantiomeric enrichment of sugars and amino acids in meteorites, *Phys. Chem. Chem. Phys.*, 2022, **24**, 25077-25087.
11. G. Xu, H. Wang, J. Zhang, J. Gao, J. Guan, Q. Xu, D. G. Truhlar and Z. Wang, Combining synchrotron vacuum-ultraviolet photoionization mass spectrometry and gas chromatography-mass spectrometry for isomer-specific mechanistic analysis with application to the benzyl self-reaction, *Nat. Commun.*, 2024, **15**, 10755.
12. R. I. Kaiser, L. Zhao, W. Lu, M. Ahmed, V. S. Krasnoukhov, V. N. Azyazov and A. M. Mebel, Unconventional excited-state dynamics in the concerted benzyl (C_7H_7) radical self-reaction to anthracene ($C_{14}H_{10}$), *Nat. Commun.*, 2022, **13**, 786-794.
13. W. Li, J. Yang, L. Zhao, D. Couch, M. S. Marchi, N. Hansen, A. N. Morozov, A. M. Mebel and R. I. Kaiser, Gas-phase preparation of azulene ($C_{10}H_8$) and naphthalene

- (C₁₀H₈) via the reaction of the resonantly stabilized fulvenallenyl and propargyl radicals, *Chem. Sci.*, 2023, **14**, 9795-9805.
14. W. Yuan, Y. Li, P. Dagaut, J. Yang and F. Qi, Investigation on the pyrolysis and oxidation of toluene over a wide range conditions. I. Flow reactor pyrolysis and jet stirred reactor oxidation, *Combust. Flame*, 2015, **162**, 3-21.
 15. G. T. Buckingham, T. K. Ormond, J. P. Porterfield, P. Hemberger, O. Kostko, M. Ahmed, D. J. Robichaud, M. R. Nimlos, J. W. Daily and G. B. Ellison, The thermal decomposition of the benzyl radical in a heated micro-reactor. I. Experimental findings, *J. Chem. Phys.*, 2015, **142**, 044307.
 16. Yuyang Li, Jiuzhong Yang and Z. Cheng, Photonionization Cross Section Database (Version 2.0), <http://flame.nsrl.ustc.edu.cn/database/>, (accessed October 16, 2025).
 17. C. Y. Wang, L. Zhao and R. I. Kaiser, Gas-phase preparation of the 14 π Hückel polycyclic aromatic anthracene and phenanthrene isomers (C₁₄H₁₀) via the propargyl addition–benzannulation (PABA) mechanism, *Chemphyschem*, 2024, **25**, e202400151.