Supporting information

Observing C-N bond formation in plasma: a case study of benzene and

dinitrogen coupling via an arylnitrenium ion intermediate

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Experimental Methods

Chemicals

Benzene was provided by Sinopharm Co., Ltd. (China). Toluene was provided by Xilong Scientific Co., Ltd. (China). Aniline, 2,3,4-aminobiphenyl, *o, m, p*-toluidine, diphenylamine, methanol, benzyl-p-tolyl-amine and di-*p*-tolylamine were all purchased from Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). D4‑CH$_3$OH was purchased from Adama‑beta Reagent Co., Ltd. (Shanghai, China). All chemicals were used as received without further purification. High-purity dinitrogen (99.999%) was purchased from Xi'an Tenglong Chemical Co., Ltd. and was used as both the carrier and reagent gas.

Mass spectrometry

Real-time reaction monitoring experiments were performed using a commercial linear ion trap mass spectrometer (LTQ XL; Thermal Fisher, USA) coupled with an Ion Max APCI source. The liquid reactants in the bottle were bubbled with nitrogen at a flow rate (Q(N$_2$/C$_6$H$_6$) = 0.05 L/min, Q(N$_2$/C$_7$H$_8$) = 0.1 L/min), and the generated headspace vapor was carried along with nitrogen to the sheath gas inlet labeled "S" to enter the corona discharge region, where plasma induced reaction occurred and then the product ions were transferred to the mass analyzer. Methanol was also introduced through the headspace and mixed with benzene or toluene vapor into the discharge zone to investigate the reactivity of the PhNH$^+$ intermediate. In addition, some experiments were carried out with liquid samples; liquid benzene/CH$_3$OH mixture, and benzene/CD$_3$OD mixture were injected with a syringe at a flow rate of 2 μL/min to examine the influence of hydrogen donor on the reactions, as well as to investigate the KIE effect. The mass spectra of standard reagents such as aniline and diphenylamine were acquired by dissolving them in methanol to prepare 2 ppm solution and then being pumped with a syringe at a flow rate of 10 μL/min. To ensure precision and facilitate comparison, high-resolution mass spectra (HRMS) analysis was performed on a Q Exactive Orbitrap mass spectrometer (Thermal Fisher Scientific, USA) that was equipped with an APCI source.

The APCI ion source parameters in the positive mode were optimized and stable product signals were achieved with the following operating parameters: vaporizer temperature 350°C, auxiliary gas flow rate 5 arb, discharge current 5 μA, capillary temperature 250 °C, tube lens 15 V. Other parameters were set to the default instrument values. The Full MS mode was used to record mass spectra of the specified mass range. The SRM mode was also used to record fragment information of the selected precursors by collision-induced dissociation (CID)

experiments, with helium as the collision gas; the activation was set to 30 ms and the isolation window was 1 m/z, and the normalized collision energy (NCE) was set to 0%-50%. All spectra were collected under the automatic gain mode, where per spectrum was set 10 microscans at 100 ms maximum ion injection time. Thermo Scientific Xcalibur software version 4.0 was used to collect mass spectra and data analysis.

Sample introduction

For gas injection, assuming that the sample vapor was saturated in the headspace, the sample volumetric fraction (relative to standard atmospheric pressure (STP), 100 kPa) can be roughly calculated by using the ideal gas model based on the saturated vapor pressure (SVP) at ambient temperature (25℃) and pressure (12.8 kPa, 16.96 kPa and 3.8 kPa for benzene, methanol and toluene, respectively, with data from https://www.engineeringtoolbox.com). In most experiments, auxiliary nitrogen gas was used for better discharge, which was operated at a flow rate of 5 arb (approximately equivalent to 1.5 L/min), and hence the sample vapor in the carrier gas was further diluted when mixing with the auxiliary nitrogen gas. It should be noted that such a rough approximation can only provide an upper limit of the sample content in the gas injection, as the vapor pressure is far below saturation depending on the carrier gas flow rate. The sample volumetric fraction calculated by equations are listed as below. In the equations, for the benzene system, the dilution multiple is 30; and for the toluene system, this value is 15.

$$benzene/toluene\ volumetric\ fraction = \frac{SVP * (1 - flow\ rate\ ratio)}{STP * Dilution\ multiple}$$

$$CH_3OH\ volumetric\ fraction = \frac{SVP * flow\ rate\ ratio}{STP * Dilution\ multiple}$$

Table S1. Calculated sample volumetric fraction in the benzene system

flow rate ratio Q(N$_2$/CH$_3$OH): Q(N$_2$/C$_6$H$_6$)	benzene volumetric fraction	CH$_3$OH volumetric fraction
0	0.0043	0.0000
0.1	0.0039	0.0006
0.2	0.0034	0.0011
0.3	0.0030	0.0017
0.4	0.0026	0.0023
0.5	0.0022	0.0029
0.6	0.0017	0.0034
0.8	0.0009	0.0046
1	0.0000	0.0057

Table S2. Calculated sample volumetric fraction in the toluene system

flow rate ratio Q(N$_2$/CH$_3$OH): Q(N$_2$/C$_7$H$_8$)	toluene volumetric fraction	CH$_3$OH volumetric fraction
0	0.0025	0.0000
0.05	0.0024	0.0003
0.1	0.0023	0.0006
0.15	0.0021	0.0009
0.25	0.0019	0.0014
0.4	0.0015	0.0034
0.7	0.0008	0.0040
0.8	0.0005	0.0046
1	0.0000	0.0057

For liquid injection, the calculation of the sample volumetric fraction is more straightforward. Specifically, liquid samples were introduced with a syringe at a flow rate (F_l) of 2 µL/min, which were vaporized by and diluted in the auxiliary gas (F_a) and sheath gas both at the flow rate (F_s) of 5 arb (1.5 L/min). Thus, the sample volumetric fraction can be roughly approximated based the liquid injection rate and the auxiliary/sheath gas flow rate.

$$volumetric\ fraction = \frac{(F_l * c * \rho)/M}{(F_a + F_s)/22.4}$$

, where c is volume percentage in liquid sample, ρ is density, M is molar mass.

Table S3. Calculated sample volumetric fraction in the liquid injection for benzene/CH$_3$OH (1:9) and benzene/CD$_3$OD (1:9)

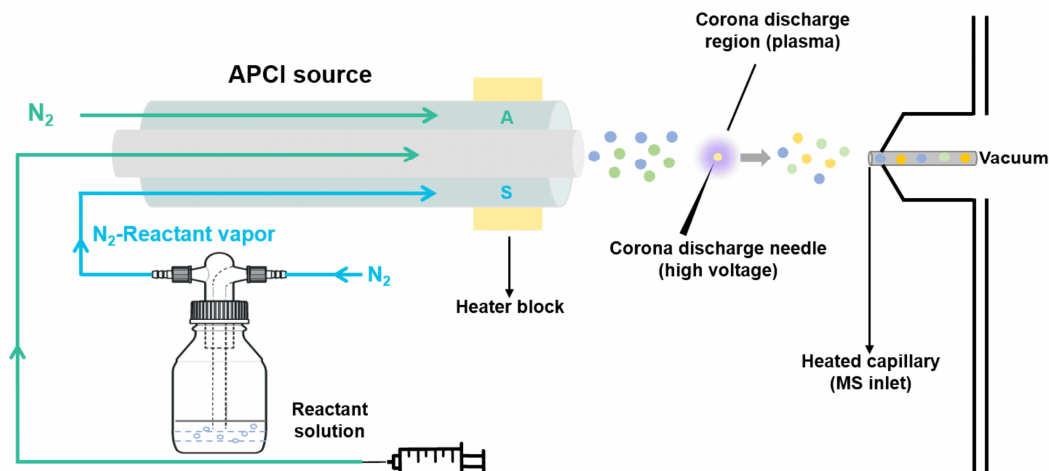| benzene	CH$_3$OH	CD$_3$OD
0.000017	0.00035	0.00031

Real-time reaction setup

Fig. S1 Schematic diagram of the experiment setup for corona discharge reactions and on-line MS monitoring.
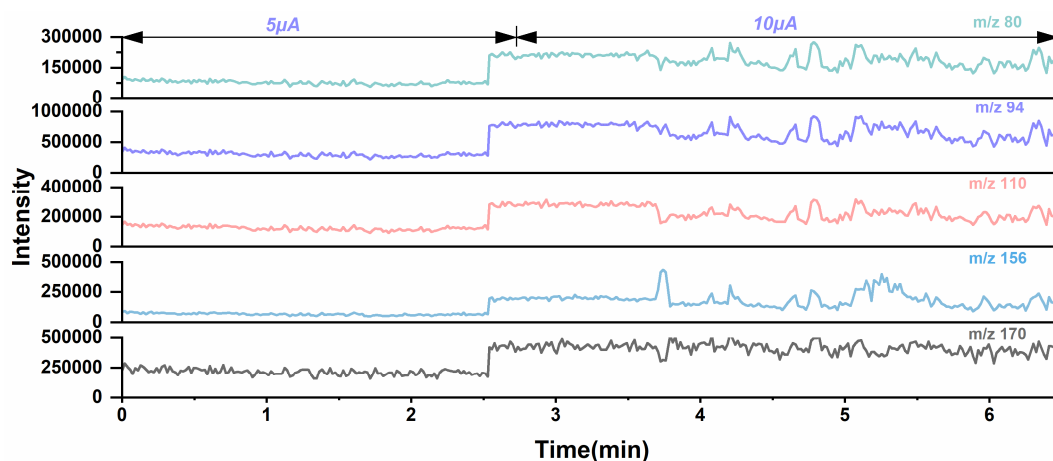
Optimization of corona discharge current

Fig. S2 Extracted ion chromatograms of benzene vapor reaction products obtained by headspace injection-mass spectrometry under the selected different conditions: 5μA and 10μA corona discharge.

Note: The signals' intensity at m/z 80, m/z 94, m/z 110, m/z 156, and m/z 170 notably increased with the increase of discharge current, However, the signal stability deteriorated obviously at the same time as the current increased, which would have a great influence on on-line monitoring of the reaction. Consequently, the current of 5 μA was chosen as the discharge condition without special instructions.

Mass spectra

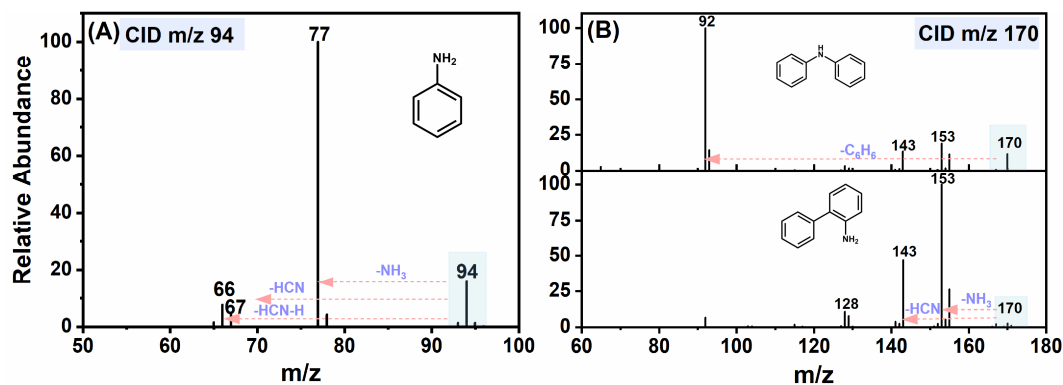MS/MS spectra of authentic aniline, diphenylamine and aminobiphenyl

Fig. S3 (A) MS^2 spectrum of m/z 94 generated by aniline; (B) MS^2 spectra of m/ 170 generated by diphenylamine and 2-aminobiphenyl (Three positional isomers of aminobiphenyl have identical fragmentation patterns).

Note： As for $C_{12}H_{12}N^+$ (m/z 170), the CID generated fragment ions mainly include m/z 153, m/z 143, and m/z 92 due to the loss of neutral NH_3, HCN, and C_6H_6, respectively, as shown in Fig. 2C; such a fragment pattern can be explained by the fact that precursor ions ($C_{12}H_{12}N^+$, m/z 170) were composed of both diphenylamine and aminobiphenyl, with the former producing fragment ions of m/z 92, while the latter fragmenting into m/z 153 and 143 upon CID.

HRMS data: Calculated for C_6H_8N 94.0651, experiment found 94.0650(-1.5214ppm); Calculated for $C_{12}H_{12}N$ 170.0964, experiment found 170.0957(-4.2573ppm); Calculated for key intermediate C_6H_6N 92.0495, experiment found 92.0494(-1.3002ppm)

Corona discharge results of toluene and associated MS/MS spectra
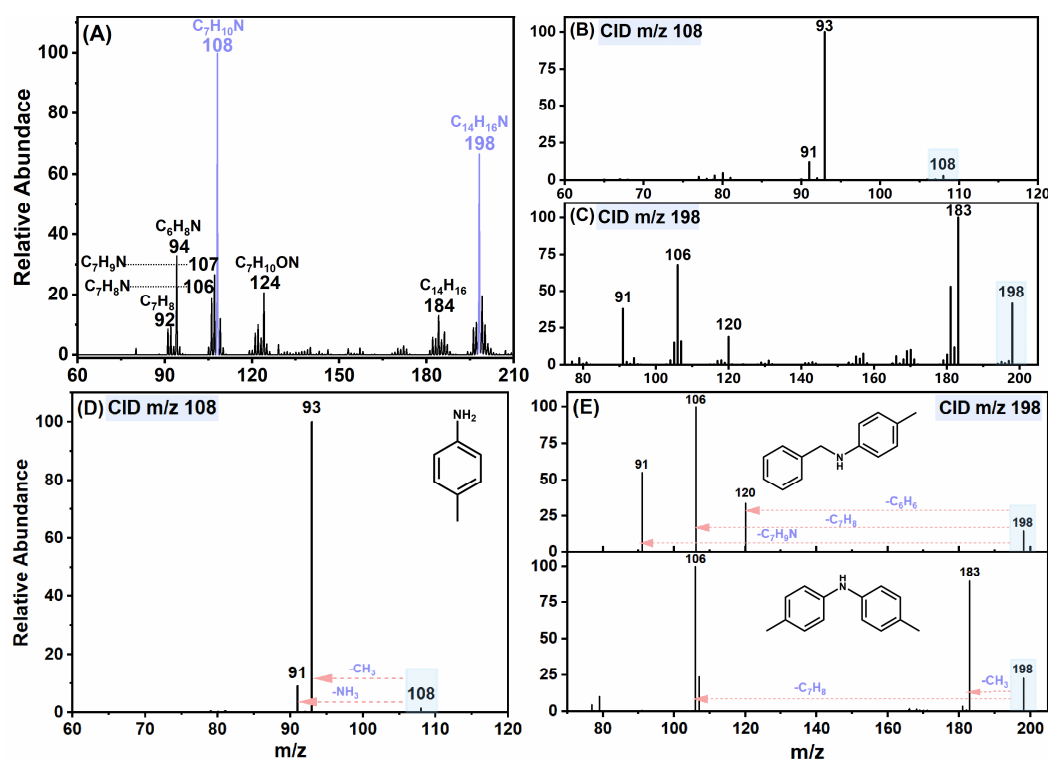

Fig. S4 (A) Typical mass spectra obtained upon introduction of toluene vapor into the plasma generated by corona discharge region. (B) MS^2 spectrum of m/z 108; (C) MS^2 spectrum of m/z 198. (D) MS^2 spectrum of m/z 108 generated by p-toluidine; (E) MS^2 spectra of m/z 198 generated by benzyl-p-tolyl-amine and di-p-tolylamine.

Note: The m/z 108 precursor ion generated major fragment ions of m/z 93, and m/z 91 due to the loss of CH_3 and NH_3, respectively, in agreement with the CID result of toluidine standard (Fig. S4D). Likewise, m/z 198 was fragmented under CID mode, into m/z 183($-CH_3$), m/z 181($-NH_3$), m/z 120 ($-C_6H_6$), m/z 106($-C_7H_8$), and m/z 91($-C_7H_9N$), respectively (Fig. S4C). By comparing the MS/MS spectrum with two of the standards, the ion at m/z 198 should also contain more than one structural isomer of diphenylamine derivatives (Fig. S4E). However, the exact identification of each isomer is challenging. The m/z 92 was assumed to be toluene radical ion, while m/z 184 was attributed to a toluene dimer ion complex ($C_{14}H_{16}^+$); m/z 94 was associated with methylpyridine ($C_6H_8N^+$).

Determination of the selectivity of the toluene amination product
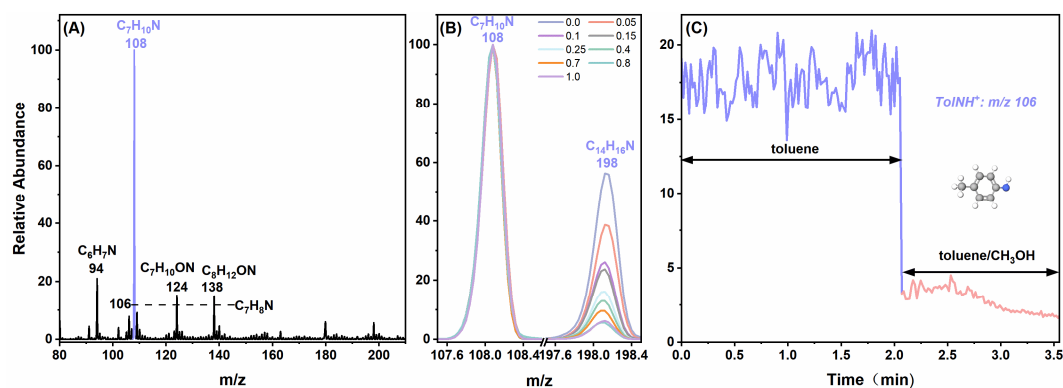

Fig. S5 (A) Typical mass spectrum obtained with toluene/CH_3OH vapor (Q(N_2/CH_3OH): Q(N_2/C_7H_8) =1:1) (B) Relative abundance of m/z 108 and m/z 198 by varying the carrier gas flow rate ratio (Q(N_2/CH_3OH): Q(N_2/$C_7H_{8)}$). (C) Two-stage ion chronograms recording the methylphenylnitrenium intermediate (m/z 106) with or without methanol in the feeding gas.

Note: The increase in methanol content resulted in gradual decrease in the signal at m/z 198 until its disappearance. In Fig. S5C, only toluene was introduced in the first 2.1 minutes, and a mixture vapor toluene/methanol (Q(N_2/CH_3OH): Q(N_2/C_7H_8) =1:1) was introduced in the second stage; the two-stage ion chronogram indicated that the methylphenylnitrenium intermediate at m/z 106 was involved in the hydrogen abstraction reaction and the signal decreased significantly in the second state due to the rapid consumption by reaction with methanol.

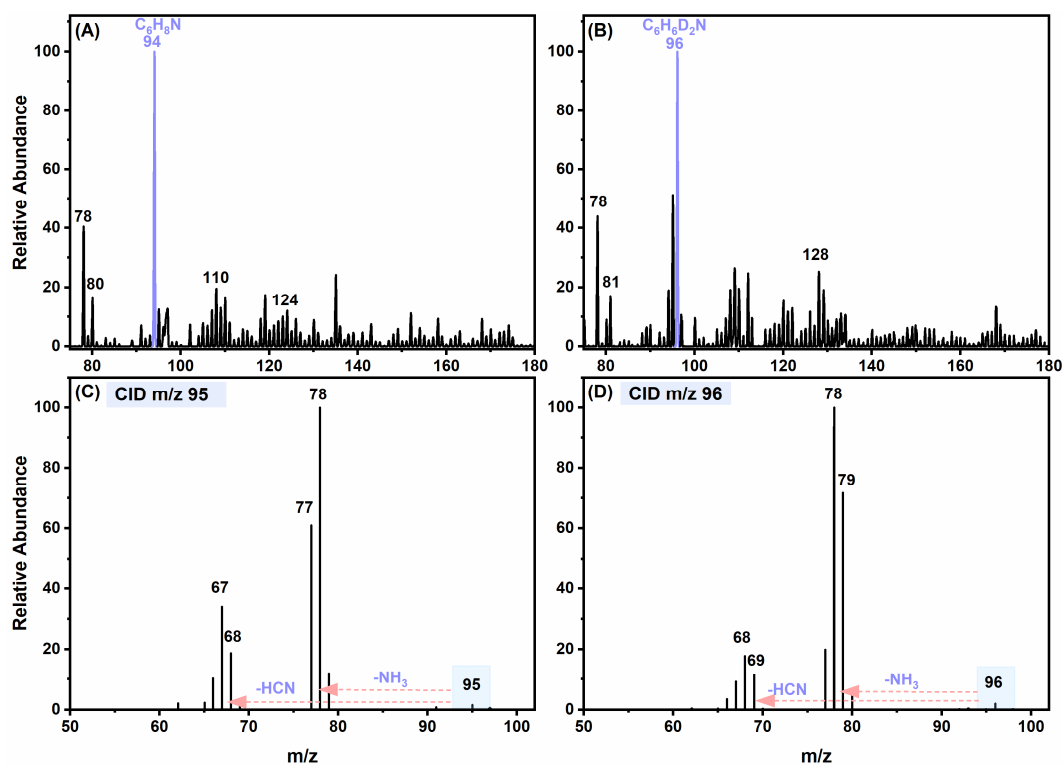# Deuterium reagent examination of phenylnitrenium intermediate

Fig. S6 (A) Typical mass spectrum obtained upon introduction upon introduction of liquid benzene/CH_3OH (1:9) into the 10μA corona discharge region. (B) Typical mass spectrum obtained upon introduction of benzene/CD_3OD (1:9). into the 10uA corona discharge region. (C) MS^2 spectrum of m/z 95. (D) MS^2 spectrum of m/z 96.

Note: Liquid reactants were introduced with a syringe at a flow rate of 2μL/min. The current was adjusted to 10μA because the corona discharge intensity was weakened by the introduction of large amounts of methanol. The mass spectrum obtained from the liquid injection was more complex, which is the reason we chose to introduce the reactant in the headspace manner.