

Supporting Information

Observing of Intermediates by Online Mass Spectrometry to Demonstrate Multi-mechanisms of Dye-Sensitized Photocatalysis

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Table of Contents

Experimental Procedures.....	S2
Figure S1. Characterizations of TiO ₂ nanoparticles.....	S3
Figure S2. Optimization of UV irradiation time in sUV-t Vis.....	S4
Figure S3. Confirmation of the product.....	S5
Figure S4. Control experiments to confirm the origin of m/z 108.....	S6
Figure S5. MS ² CID of m/z 213 and 215.....	S7
Figure S6. MS ² CID of m/z 319.....	S8
Figure S7. Schematic diagram of the fragmentation mechanism of Intermediate 9	S9
Figure S8. MS ² CID of m/z 107 and 317.....	S10
Figure S9. Role of H ₂ O ₂ in the DSP reaction.....	S11
Figure S10. DFT calculations.	S12
Table S1. Calculated bond dissociation energies (BDE) (kcal/mol) of the C _d -N _a bond in Intermediate 9 and its different protonation states via three different cleavage manners.	S13
Table S2. Calculated bond dissociation energies (kcal/mol) of the C _d -N _a bond in Intermediate 11 and its different protonation states via three cleavage manners.....	S14
DFT optimized Cartesian coordinates of all stationary point structures.	S15
References	S20

Experimental Procedures

Chemicals All reagents and solvents were purchased from commercial sources and used without further purification. HPLC grade methanol was purchased from Fisher Chemical (USA). *O*-Phenylenediamine was obtained from Alfa Aesar, and 2,3-diaminophenazine was obtained from Innochem. Titanium dioxide (P25) was purchased from Degussa Corp. Deionized water (Mill-Q, Millipore, 18.2 M Ω resistivity) was used in all experiments.

Mass spectrometry On-line monitoring was performed on an LTQ XL (Thermo Fisher Scientific, San Jose, CA, USA) instrument using a homemade ionization source of MF-EESI. The operational parameters were as follows: full-scan positive (+) ion spectra were obtained over the m/z range from 100 to 800; the temperature of the MS inlet capillary was 250 °C; the capillary voltage and tube lens voltage were set to 100 V and 120 V, respectively. The maximum ion injection time was 1000 ms. All MS results were obtained and processed using the Xcalibur or Microcal Origin (version 8.0) software.

Other instruments A Quantachrome NOVA 2000e sorption analyzer was used to examine the N₂ adsorption and desorption properties of three kinds of TiO₂ at liquid nitrogen temperature. Powder XRD patterns of all compounds were collected on a Shimadzu XRD-7000 automated diffraction system with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). The tube voltage and current were set at 40 kV and 30 mA, respectively. Measurements were made in a 2θ range of 20–40 ° at room temperature with a step of 0.02 ° (2θ). The scan speed was 2 degree/min. TEM were performed on a Tecnai G2 F20 transmission electron microscope (FEI Company, Hillsboro, OR, USA) under accelerating voltage of 200 kV. Fluorescence spectra were collected by an FS5 fluorescence spectrophotometer (Edinburgh Instruments, UK). UV–vis absorption spectra were carried out on a UV2450 spectrophotometer (Shimadzu, Japan). The product concentrations were determined by Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. ¹H NMR spectra was recorded on JEOL-400 spectrometers

General photocatalysis procedure Solutions of *ortho*-arylenediamine (0.9 mM) and DAP (0.1 mM) in water were placed in a quartz double-decker beaker (50 cm³). TiO₂ (1 mg/ml) were added to the beaker. The initial pH value was adjusted to ~5 by NaOH (1M) and HCl (1 M) solution. The mixture was vigorously stirred for 5 min before irradiation. Then, the reaction solution was photoirradiated for 25 min using a 250-W high-pressure mercury lamp (360 nm, from Shanghai Jiguang Special Lighting Appliance Factory) coupled to an additional longpass cut-off filters ($\lambda \geq 450 \text{ nm}$) under continuous magnetic stirring. In the sUV-t experiment, the reaction solution was photoirradiated (UV light, 365nm) for 3 min under continuous magnetic stirring. Then additional longpass cut-off filters ($\lambda \geq 450 \text{ nm}$) were used to control irradiation wavelength range during the reaction for 22 min visible light irradiation. After irradiation, the mixture was centrifuged to remove TiO₂ particles for further analysis. The on-line monitoring of MS was carried out under standard conditions. Before the spectrum measurements, TiO₂ was removed by centrifugation of aliquots (0.5 ml), after which the solution was diluted to 3 mL for the measurement.

Computational procedure Quantum chemical calculations were performed using density functional theory (DFT) at the B3LYP¹⁻³/6-311G(d) level with the Gaussian 09⁴ program package. Frequency calculations were performed to confirm all stationary points as local minima or transition states. The transition state was also verified with the intrinsic reaction coordinate (IRC) calculations. Moreover, the solvent effect was evaluated by using the SMD continuum solvent model with water as the solvent. The van der Waals effect was calculated by B3LYP-D using Grimme's D3 method⁶⁻⁷. The corrected Gibbs free energies were used in the energy profiles.

Results and Discussion

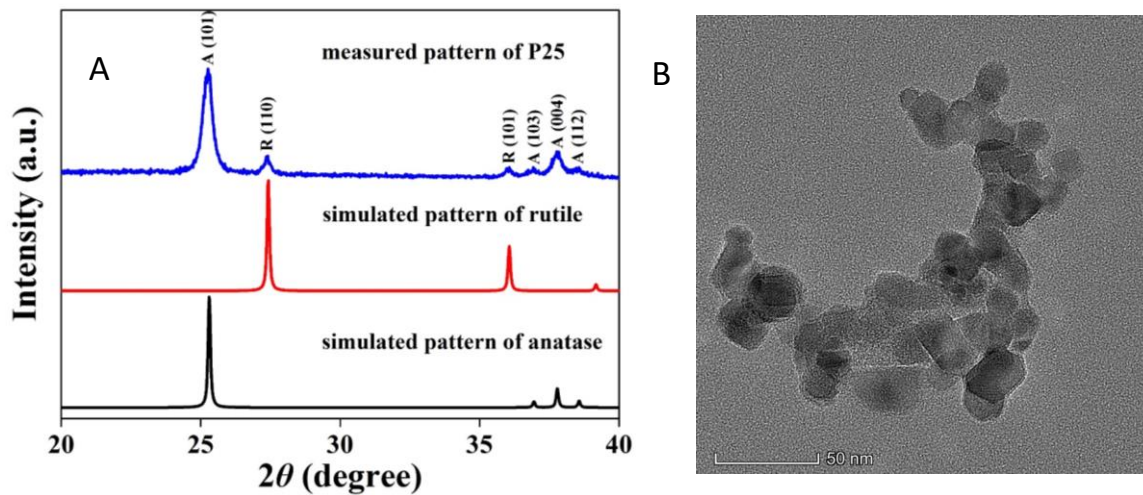


Figure S1. Characterizations of TiO₂ nanoparticles. (A) XRD patterns. (B) TEM image of P25.

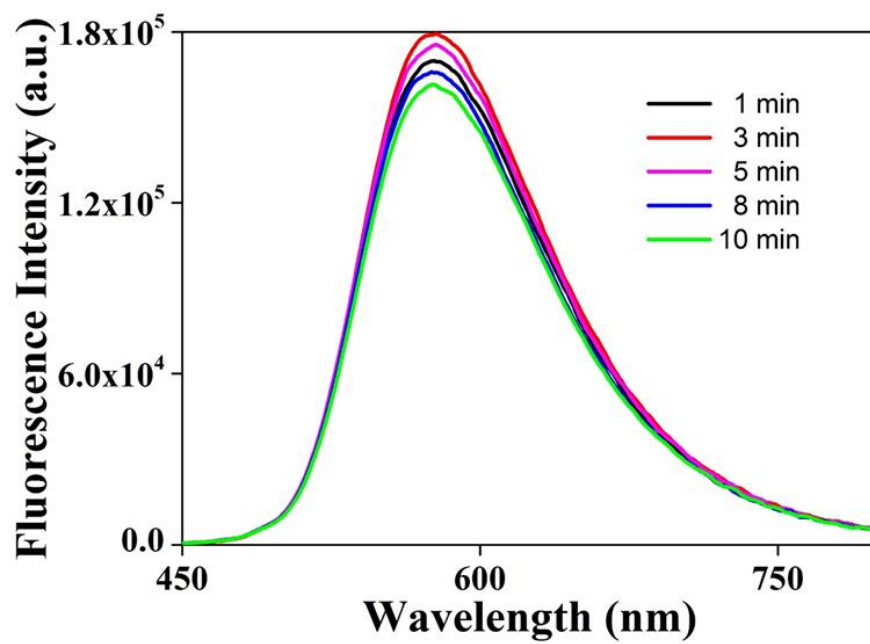


Figure S2. Optimization of UV irradiation time in sUV-t Vis. The FL spectra were obtained by increasing the UV irradiation time in the entire 25 min sUV-t Vis experiment.

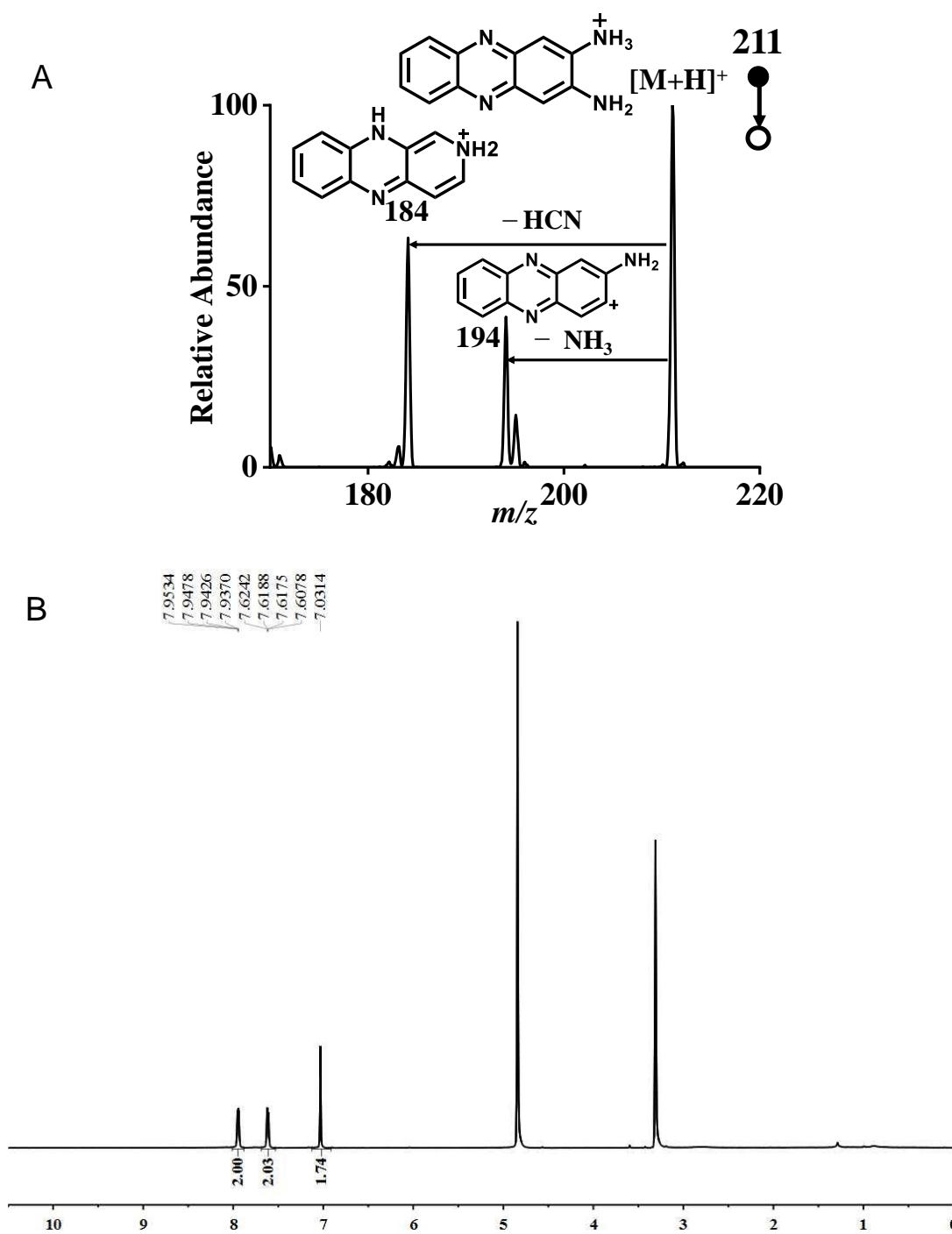


Figure S3. Confirmation of the product. (A) MS² CID of DAP at m/z 211; (B) ¹H NMR chart of DAP (CD₃OD, 600 MHz).⁸

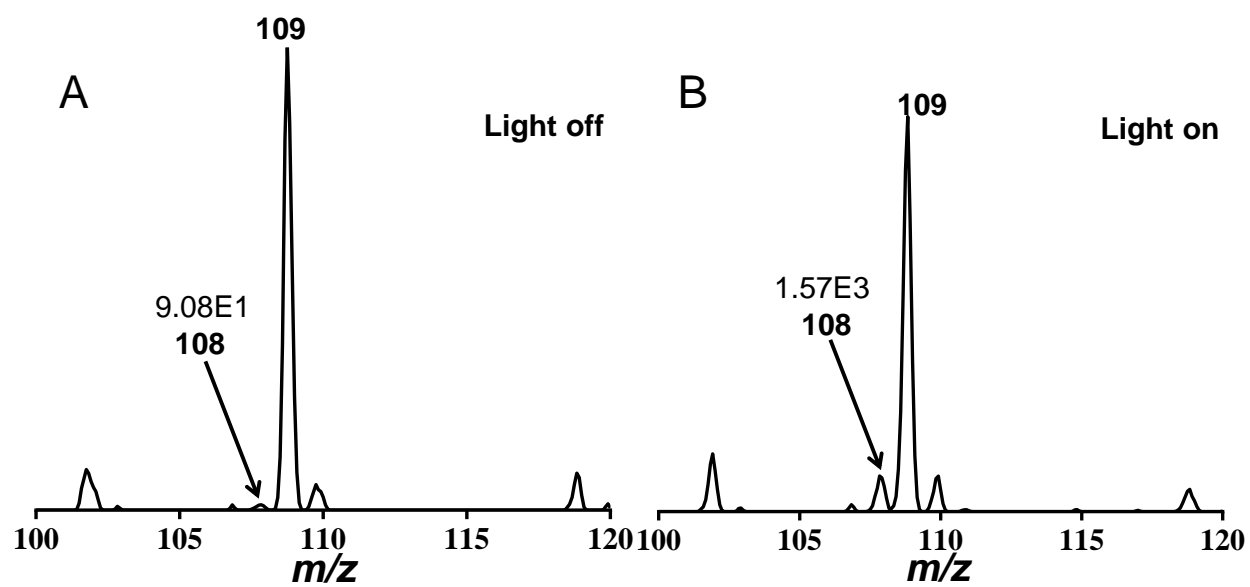


Figure S4. Control experiments to confirm the origin of m/z 108. (A) Self-sensitized DSP without visible-light irradiation. (B) Self-sensitized DSP with visible-light irradiation.

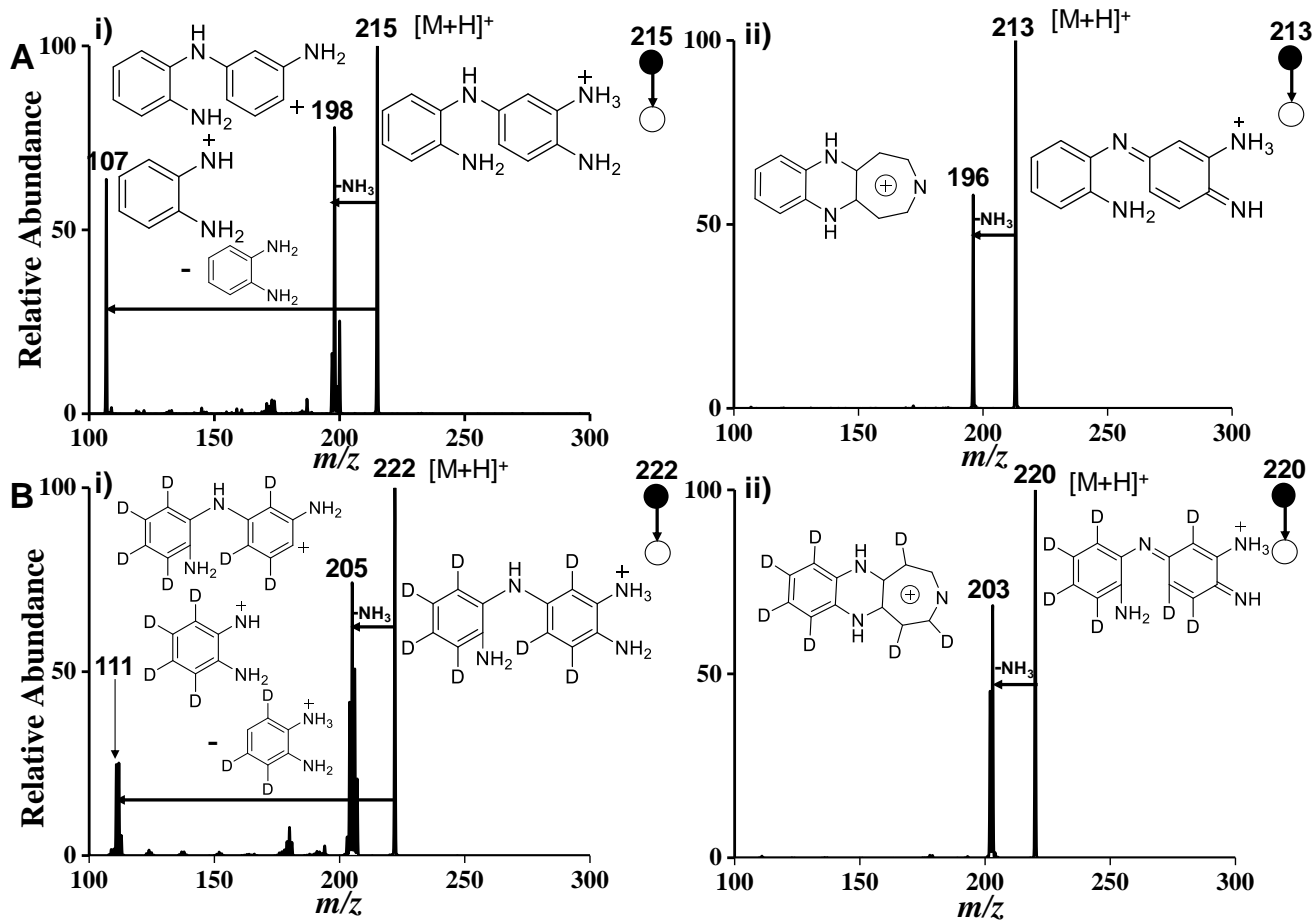


Figure S5. CID experiment to examine ions at m/z 213 and 215. (A) MS² CID of the two intermediate ions at m/z 213 (i) and m/z 215 (ii). (B) MS² CID of the two deuterated intermediate ions at m/z 222 (i) and m/z 220 (ii).

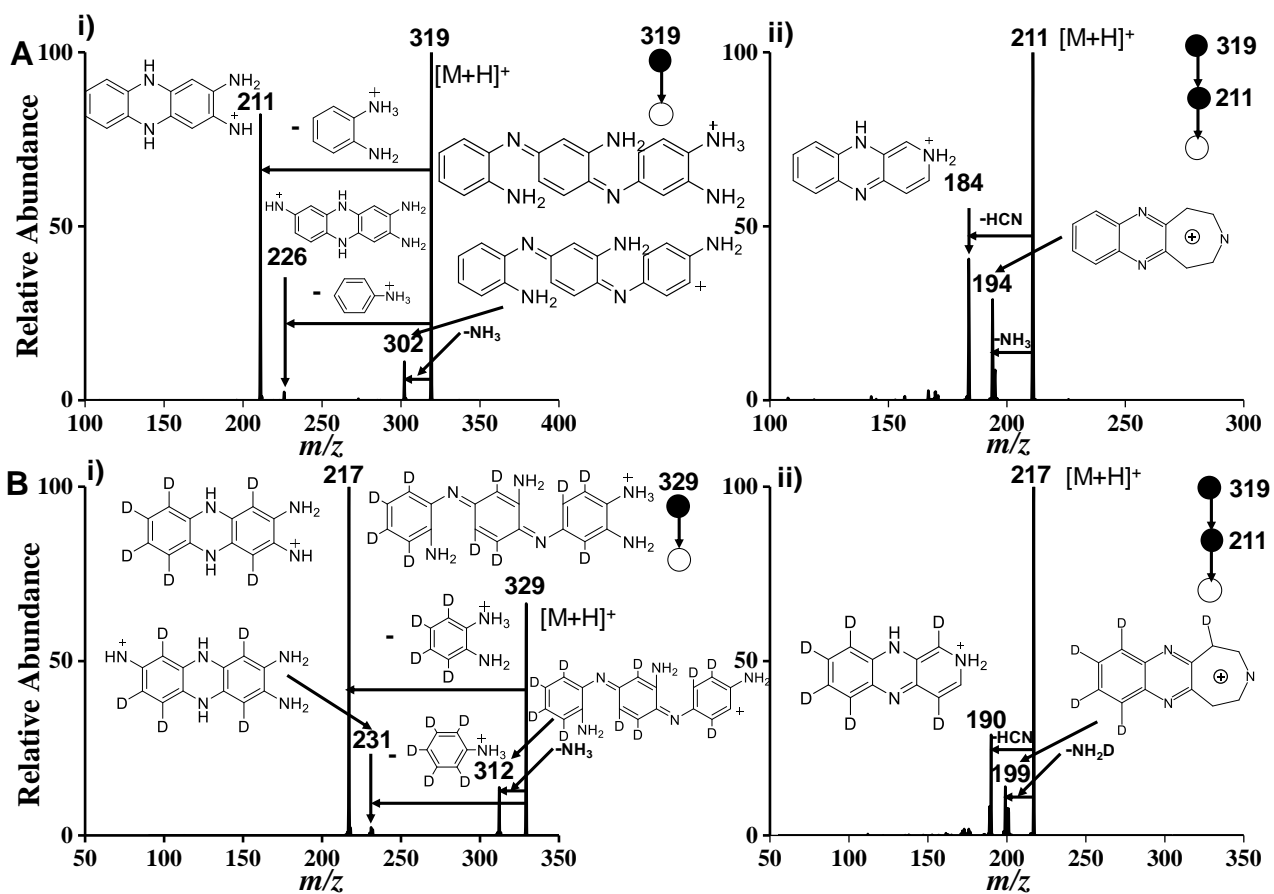


Figure S6. CID experiment to identify m/z 319. (A) MSⁿ CID of the ion at m/z 319. (i) MS² CID. (ii) MS³ CID. (B) MSⁿ CID of the deuterated ion at m/z 329. (i) MS² CID. (ii) MS³ CID.

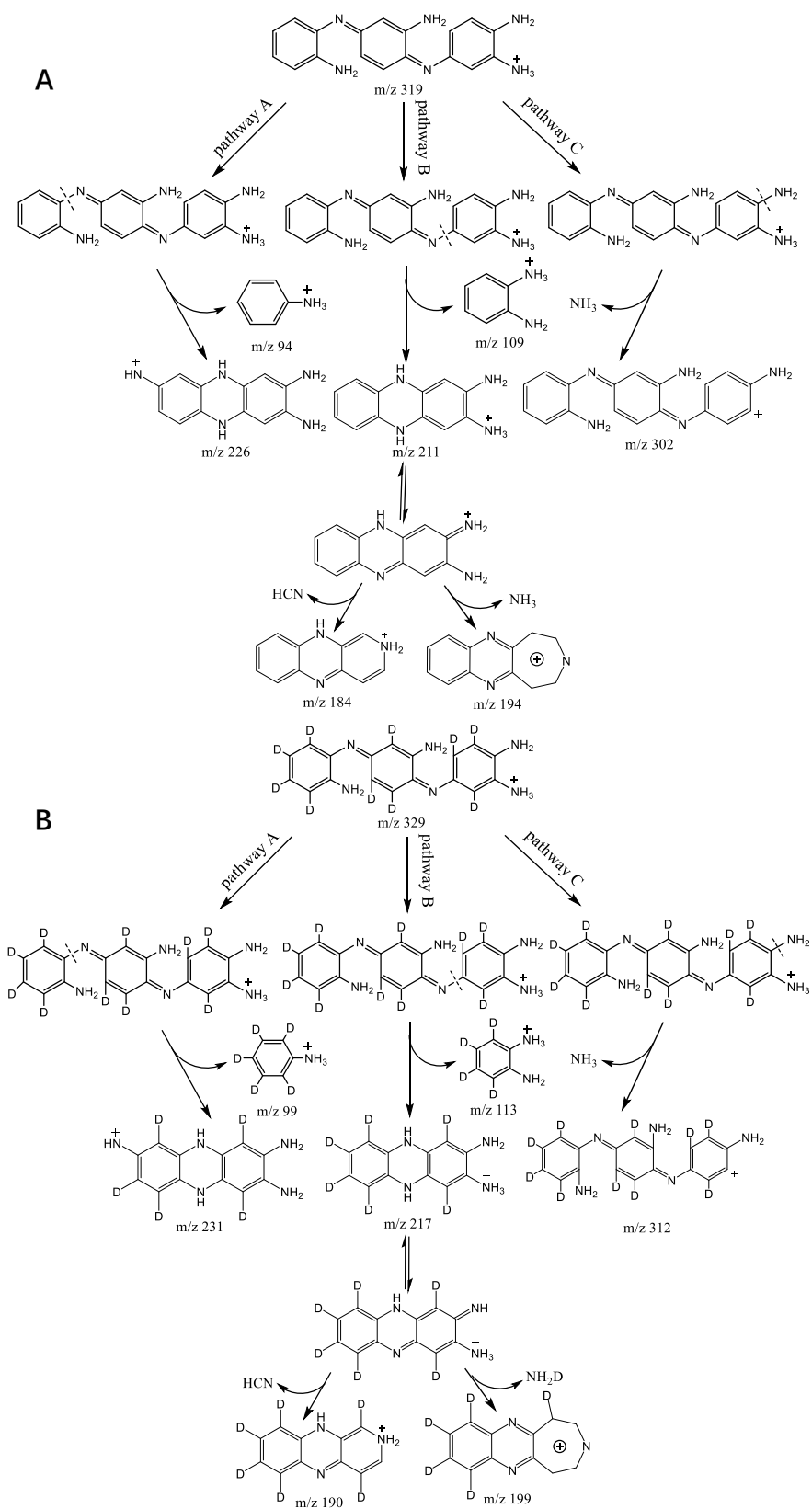


Figure S7. Schematic diagram of the fragmentation mechanism of Intermediate **9** generated by MSⁿ CID. (A) The intermediate ion at m/z 319. (B) The deuterated intermediate ion at m/z 329.

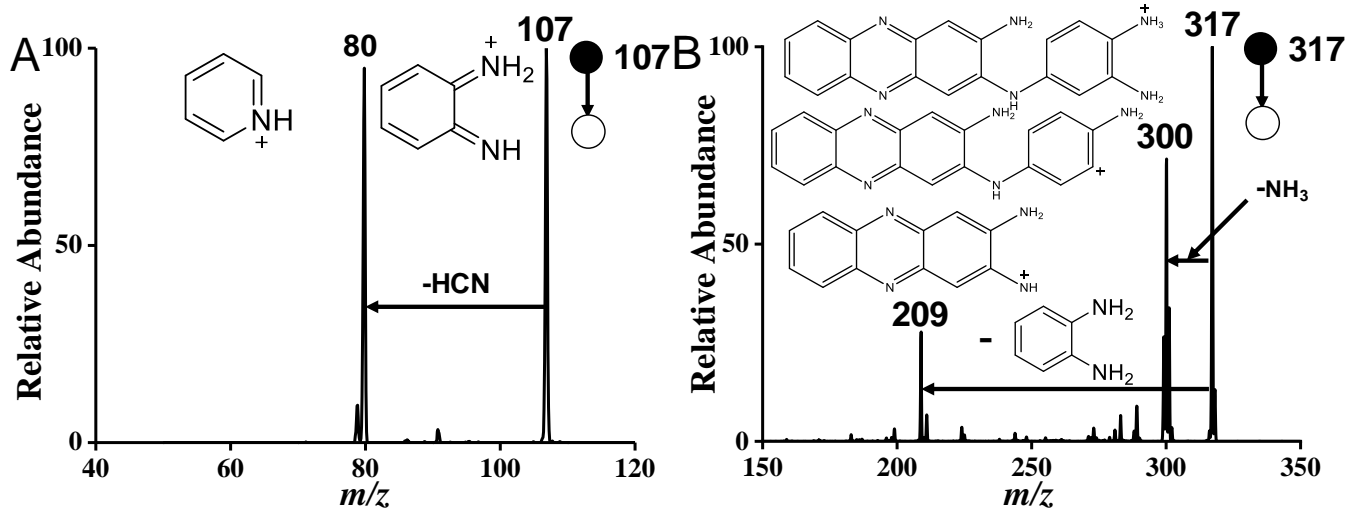


Figure S8. MS² CID of two intermediate ions at m/z 107 (A) and 317 (B).

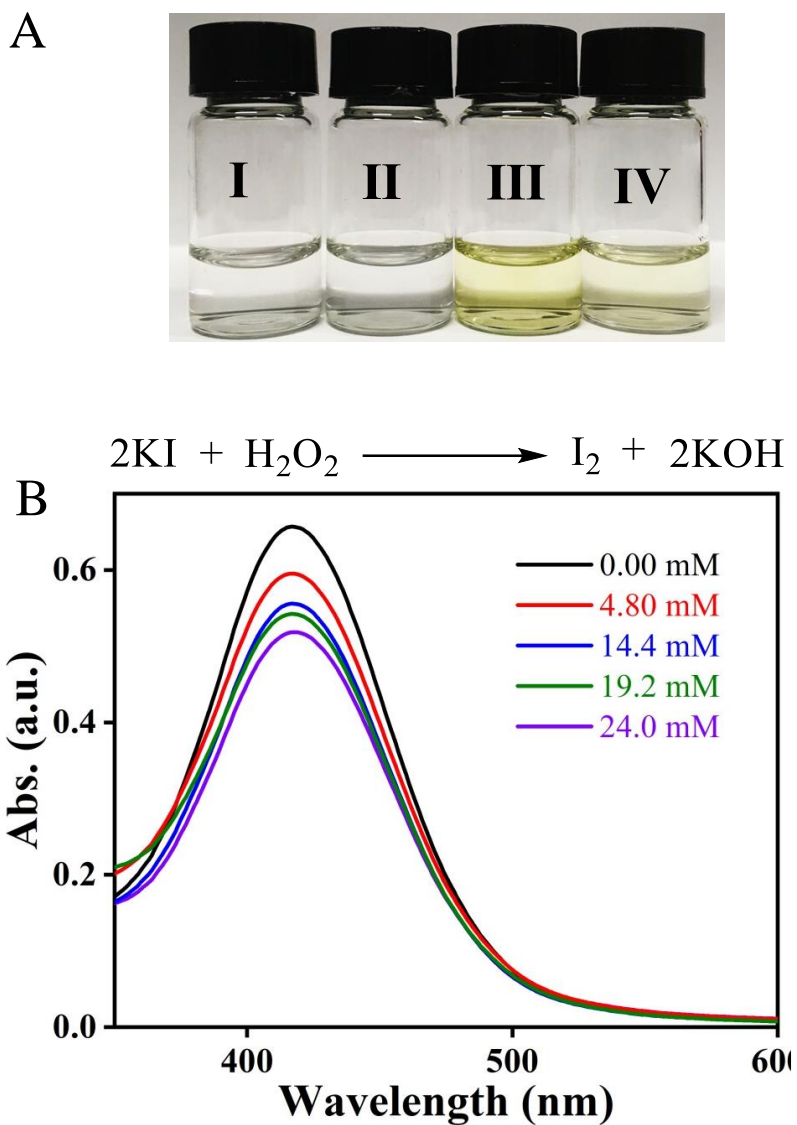


Figure S9. Role of H_2O_2 in the DSP reaction. (A) The detection of generated H_2O_2 by the titration reaction with KI. (I) Reaction system without visible irradiation. (II) Reaction system of (I) with the addition of KI. (III) Standard DSP reaction system with the addition of KI. (IV) Standard DSP reaction system without KI added. (B) Comparison of DSP reactions with the addition of different concentrations of DMTU.

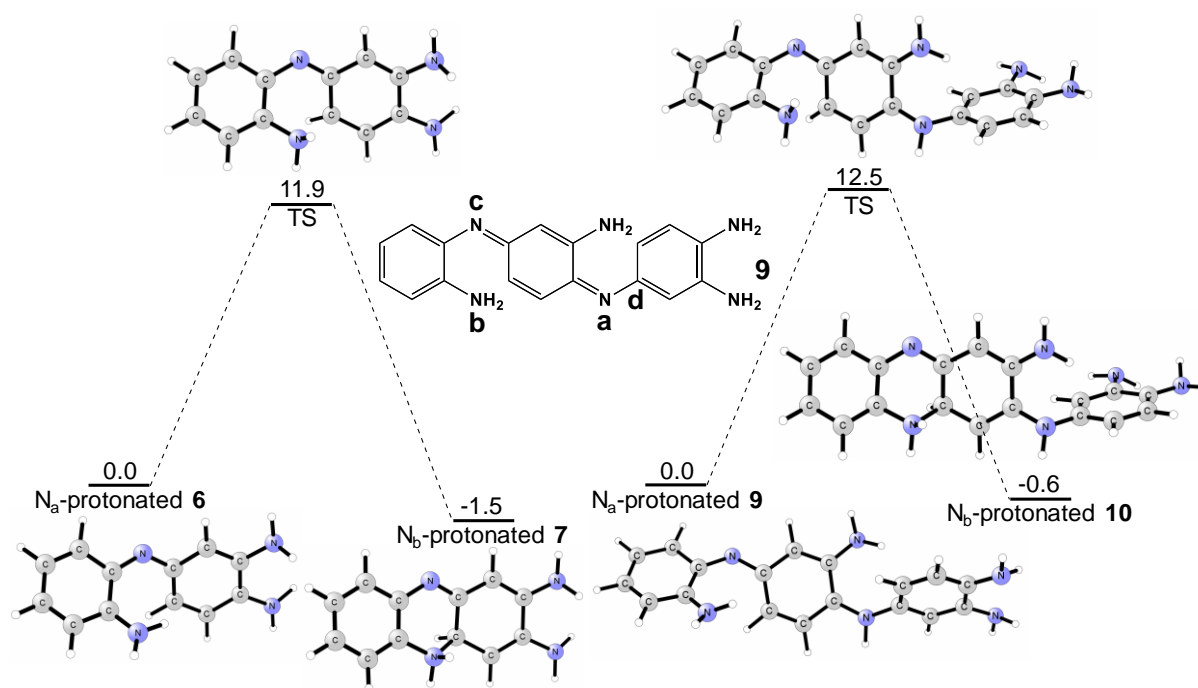


Figure S10. DFT-calculated energy profiles (kcal/mol) and the optimized geometries during the cyclization reaction of protonated intermediates **6** and **9**. Atom labels are shown on the structure of Intermediate **9**.

Table S1. Calculated bond dissociation energies (BDE) (kcal/mol) of the C_d-N_a bond in Intermediate **9** and its different protonation states via three different cleavage manners.

entry	complexes ^[a]	$E_{\text{Heterolysis1}}$ ^[b]	$E_{\text{Heterolysis2}}$ ^[c]	$E_{\text{Homolysis}}$ ^[d]
1	9	108.3	126.3	70.9
2	9 -H1-1	63.4	101.6	55.6
3	9 -H1-2	99.6	155.0	75.8
4	9 -H2	62.7	135.1	66.5

[a] Complexes **9**-H1-1 (N_a-protonated **9**), **9**-H1-2 and **9**-H2 represent protonation at N_a, N_c, N_a and N_c of Intermediate **9**, respectively. [b] $E_{\text{Heterolysis1}}$ represents the heterolysis cleavage energy of the C_d-N_a bond with the bond electrons transferring to the dimer side. [c] $E_{\text{Heterolysis2}}$ represents the heterolysis cleavage energy with the bond electrons transferring to the monomer side. [d] $E_{\text{Homolysis}}$ represents homolysis cleavage energy of the C_d-N_a bond.

Table S2. Calculated bond dissociation energies (kcal/mol) of the C_d-N_a bond in Intermediate **11** and its different protonation states via three cleavage manners.

entry	complexes ^[a]	$E_{\text{Heterolysis1}}$ ^[b]	$E_{\text{Heterolysis2}}$ ^[c]	$E_{\text{Homolysis}}$ ^[d]
1	11	91.1	110.8	64.3
2	11-H1	51.5	121.9	54.0
3	11-H2-1	43.6	129.5	53.8
4	11-H2-2	49.2	135.2	59.4
5	11-H2-3	66.6	146.8	72.9

[a] Complexes **11-H1**, **11-H2-1**, **11-H2-2** and **11-H2-3** represent protonation state of Intermediate **11** on N_a, N_a and N_b, N_a and N_c, N_b and N_c, respectively. [b] $E_{\text{Heterolysis1}}$ represents the heterolysis cleavage energy of the C_d-N_a bond with the bond electrons transferring to the dimer side. [c] $E_{\text{Heterolysis2}}$ represents the heterolysis cleavage energy of the C_d-N_a bond with the bond electrons transferring to the monomer side. [d] $E_{\text{Homolysis}}$ represents homolysis cleavage energy of the C_d-N_a bond.

DFT optimized Cartesian coordinates of all stationary point structures

N_a-protonated 6

C	-1.17140800	-4.15948200	-0.03295100
C	-0.39652800	-3.12208400	-0.46602400
C	-0.72209400	-1.74856400	-0.18870500
C	-2.01557900	-1.47999100	0.42989500
C	-2.79979200	-2.57783700	0.84079600
C	-2.38378800	-3.87467300	0.63763600
H	-0.87378300	-5.18568000	-0.20977200
H	0.53488900	-3.28787000	-0.99291200
H	-3.75518500	-2.38380400	1.31804600
H	-3.01482700	-4.68959400	0.97544200
N	-2.52449000	-0.22933000	0.55907100
H	-3.51281200	-0.12834300	0.73374400
H	-2.08043400	0.55908800	0.11615600
N	0.19507400	-0.88042200	-0.63126300
C	0.51172900	0.36380800	-0.27332400
C	1.37768500	1.06156300	-1.18292900
C	0.18461100	1.01823400	0.96442300
C	1.85294100	2.32076300	-0.93117400
H	1.62116300	0.55416600	-2.10979900
C	0.70663300	2.24303400	1.26305600
H	-0.41356300	0.50448300	1.70541000
C	1.56574300	2.91586100	0.34665600
H	0.51474200	2.69790900	2.22943000
N	2.71585900	3.04060200	-1.77668100
H	3.08096100	2.49467900	-2.54602100
H	2.31840000	3.90293500	-2.13554900
N	2.14091300	4.08450800	0.65405900
H	2.02734600	4.50321500	1.56416900
H	2.90185700	4.41602500	0.07625600

TS (6-7)

C	-5.09069800	1.82545800	-1.15574600
C	-4.08435900	2.63809200	-1.66886700
C	-4.15090500	4.03083700	-1.53681000
C	-5.28556100	4.59029700	-0.90467800
C	-6.31071900	3.78334200	-0.43870500
C	-6.20563500	2.39314900	-0.54648800
H	-5.01276600	0.74855700	-1.25050400
H	-3.22592100	2.21655600	-2.17832700
H	-7.18870700	4.22767200	0.01998900
H	-6.99834800	1.76476400	-0.15765000
N	-5.32844400	6.03712400	-0.78264000
H	-5.88430800	6.35253800	0.00640700
H	-5.66001900	6.50796800	-1.62427400
N	-3.17002600	4.80916400	-2.15247100
C	-2.87913400	5.98580500	-1.70118800
C	-2.09749400	6.87621800	-2.52765600
C	-3.42327000	6.51390100	-0.41291200
C	-1.92480900	8.18042400	-2.20285400
H	-1.75249500	6.47714400	-3.47480000
C	-3.18229600	7.85194400	-0.06604500
H	-3.46420700	5.78868900	0.39506400
C	-2.42329300	8.66823200	-0.89686800
H	-3.43287100	8.20157600	0.92994600
N	-1.21275500	9.10125200	-2.96544800

H	-0.77602600	8.71693000	-3.79236900
H	-1.70197400	9.96101900	-3.18547800
N	-2.04249200	9.90394300	-0.54194200
H	-2.29674600	10.28361800	0.35721100
H	-1.25967200	10.33211100	-1.01524200

N_b-protonated 7

C	-1.56692600	-4.05083100	-0.00957400
C	-0.55690100	-3.28778600	-0.58180300
C	-0.47827400	-1.90818400	-0.33815000
C	-1.46353800	-1.35678200	0.49594600
C	-2.49457100	-2.09296600	1.05503800
C	-2.53886000	-3.46292400	0.80401800
H	-1.60648800	-5.11630200	-0.20544800
H	0.18859900	-3.73029700	-1.23163200
H	-3.24712000	-1.62368200	1.68244000
H	-3.32647200	-4.06441500	1.24139900
N	-1.36505100	0.10843100	0.70814500
H	-1.84294300	0.37775700	1.56943200
H	-1.81800700	0.63264500	-0.05095000
N	0.49687400	-1.14208300	-0.96442500
C	0.76171800	0.04175500	-0.50041900
C	1.64397900	0.92169100	-1.18808700
C	0.10698100	0.54502500	0.78477100
C	1.77995900	2.23750100	-0.84078500
H	2.11153300	0.53222500	-2.08545700
C	0.24540700	1.99484400	1.07420300
H	0.48999500	-0.05784900	1.62043000
C	1.08881000	2.77730000	0.36033100
H	-0.17696200	2.36723100	2.00362800
N	2.56191300	3.11626800	-1.53258500
H	3.00780300	2.78692300	-2.37570200
H	2.27474200	4.08345200	-1.56584000
N	1.33218700	4.10512600	0.64320500
H	0.88956700	4.47426800	1.47244600
H	2.29290100	4.40930100	0.55869700

N_a-protonated 9

C	-5.14590200	1.85386300	-1.35822100
C	-4.21413800	2.70709500	-1.88444500
C	-4.15087100	4.09373600	-1.52640900
C	-5.21827400	4.61690300	-0.69284000
C	-6.17893100	3.71568400	-0.19287500
C	-6.13508600	2.37120000	-0.49549900
H	-5.13657600	0.80054100	-1.61086900
H	-3.44595500	2.35930000	-2.56413700
H	-6.97110400	4.10152100	0.44146600
H	-6.88999600	1.71110600	-0.08222000
N	-5.36373800	5.94613100	-0.42161200
H	-6.27160400	6.26498500	-0.11928600
H	-4.82412900	6.62654400	-0.93287700
N	-3.13829200	4.76073800	-2.11230400
C	-2.47384400	5.85589600	-1.75345600
C	-1.60920300	6.40834400	-2.75049200
C	-2.41377700	6.43762500	-0.43858200
C	-0.78007600	7.49250700	-2.54767800
H	-1.60083400	5.89905700	-3.70797100
C	-1.58310700	7.48992200	-0.20634700
H	-2.98216400	6.01212200	0.37731000
C	-0.79010100	8.09327300	-1.23268200

H	-1.52030500	7.91180400	0.79288300
N	0.13769000	7.86879600	-3.50696200
H	0.04030300	7.42497500	-4.40724400
H	0.43101200	8.83129600	-3.55815800
N	-0.02717000	9.15303200	-0.86649200
C	0.50060900	10.21656500	-1.64015400
C	1.75889300	10.73374100	-1.29798200
C	-0.25007800	10.81745700	-2.65445000
C	2.29140300	11.82037600	-1.97891300
H	2.32695300	10.27465700	-0.49398100
C	0.29060600	11.88772000	-3.36122600
H	-1.25687000	10.47766800	-2.86793800
C	1.56000600	12.38868500	-3.06317900
H	-0.28752000	12.34673900	-4.15705100
N	2.12155700	13.46306400	-3.72962900
H	3.12205500	13.40832200	-3.87207000
H	1.63084200	13.78804900	-4.54931500
N	3.55095000	12.34860700	-1.70555700
H	3.58449300	13.36110800	-1.69524500
H	4.01694900	11.95933200	-0.89860700
H	0.07446200	9.27500600	0.13366500

TS (9-10)

C	-4.13474900	1.81110500	-0.08498400
C	-3.21495800	2.49911900	-0.87059600
C	-3.26957700	3.89398300	-0.98670400
C	-4.30634400	4.57357000	-0.30664800
C	-5.24812100	3.88588200	0.44233000
C	-5.15431400	2.49748900	0.56871900
H	-4.06448900	0.73281900	0.00274400
H	-2.43484400	1.97579100	-1.41086700
H	-6.05065800	4.42460600	0.93729200
H	-5.87865800	1.96293500	1.17204300
N	-4.33012400	6.02115600	-0.43230900
H	-4.79120400	6.48140000	0.34649800
H	-4.74817200	6.34925200	-1.30278500
N	-2.39444300	4.53837100	-1.86010900
C	-2.05638200	5.77459600	-1.65481100
C	-1.38670400	6.51383500	-2.68191100
C	-2.42234700	6.50455800	-0.40267600
C	-1.18071000	7.86476300	-2.61793400
H	-1.17607000	5.97284100	-3.59806800
C	-2.13277900	7.87556600	-0.31262600
H	-2.33189200	5.92048200	0.50965600
C	-1.51981300	8.57474700	-1.35281600
H	-2.24337000	8.37477800	0.64486700
N	-0.81360700	8.58442000	-3.71785600
H	-0.59482500	8.07514200	-4.55955000
H	-0.37258800	9.48403000	-3.62569900
N	-1.25717100	9.88993700	-1.17900600
C	-0.21646100	10.69849300	-1.73422100
C	1.10079800	10.22070300	-1.80113600
C	-0.51048900	12.00048700	-2.13363000
C	2.11972100	11.02134700	-2.30850600
H	1.33645700	9.23274200	-1.41726700
C	0.50382200	12.80443500	-2.64474600
H	-1.52725200	12.37339400	-2.07932400
C	1.81273300	12.33281000	-2.76619900
H	0.26918000	13.80944200	-2.98085900
N	2.85475300	13.11012800	-3.25034400

H	3.52292900	12.61717400	-3.82929300
H	2.59387800	14.00205400	-3.64428600
N	3.44048800	10.58708300	-2.42935700
H	4.12567300	11.27522100	-2.13870800
H	3.63491300	9.68638800	-2.01547200
H	-1.72777000	10.30663100	-0.38510900

N_b-protonated 10

C	-2.84738200	-5.88787700	1.32950900
C	-2.08508200	-5.22457300	0.37725200
C	-1.95133900	-3.82650000	0.41076500
C	-2.62750900	-3.15815300	1.44480500
C	-3.41200000	-3.79697900	2.39125300
C	-3.51544900	-5.18471100	2.33621400
H	-2.93184100	-6.96794100	1.28605200
H	-1.58062700	-5.76054500	-0.41788000
H	-3.92880300	-3.23635600	3.16547400
H	-4.11128600	-5.71055100	3.07234200
N	-2.49118100	-1.68127800	1.43403600
H	-2.67663400	-1.29764400	2.36173200
H	-3.16779200	-1.24287600	0.79685000
N	-1.24182600	-3.16699700	-0.58048900
C	-0.86553000	-1.93588900	-0.37297900
C	-0.24541500	-1.16742600	-1.38448700
C	-1.07826800	-1.27291700	0.98358900
C	-0.01635400	0.18749600	-1.27501100
H	-0.06226700	-1.67239600	-2.32672500
C	-0.88461900	0.19603900	1.03096000
H	-0.44005800	-1.78199200	1.71989600
C	-0.34735800	0.89856600	-0.00184500
H	-1.02664500	0.69157200	1.98782000
N	0.42102000	0.90747600	-2.32527900
H	0.63071900	0.44855700	-3.19689900
H	0.64614500	1.88640200	-2.24701800
N	-0.20331100	2.26846300	0.06477900
C	0.96389800	3.00179100	-0.34774700
C	2.25142700	2.52575600	-0.06677600
C	0.80007400	4.22441200	-0.99395600
C	3.37806400	3.24709100	-0.45329800
H	2.37404300	1.59785800	0.48471500
C	1.92444500	4.95363000	-1.38074400
H	-0.19618400	4.59562200	-1.20761100
C	3.21330600	4.47826700	-1.14230100
H	1.79515600	5.89914300	-1.89858400
N	4.36419300	5.18478600	-1.48881700
H	5.10092600	4.61269200	-1.88400400
H	4.20737500	6.01682800	-2.03917000
N	4.68229100	2.79847700	-0.23406700
H	5.31501500	3.52797700	0.07412300
H	4.75880500	1.97988100	0.35259500
H	-0.70403100	2.69213400	0.83524800

9

C	-3.99947600	2.65312900	0.99622700
C	-3.26949600	3.52935000	0.20210800
C	-3.68192900	3.85052900	-1.10363100
C	-4.85697700	3.23151700	-1.62089000
C	-5.58881700	2.36384800	-0.80155400
C	-5.16771800	2.07924400	0.49241800
H	-3.64977600	2.40432900	1.99258400

H	-2.32955900	3.93120500	0.56410900
H	-6.49524500	1.90824500	-1.19141900
H	-5.74592000	1.39370700	1.10397500
N	-5.27626200	3.56261500	-2.89939500
H	-5.81360400	2.85666900	-3.38007600
H	-4.53829800	3.96923400	-3.46076300
N	-2.95223100	4.61720400	-2.00218600
C	-2.31675900	5.71639700	-1.69750900
C	-1.42404800	6.27092000	-2.68694900
C	-2.45232000	6.46352500	-0.44693700
C	-0.67839300	7.39937000	-2.50136600
H	-1.29389900	5.67916500	-3.58865800
C	-1.77142400	7.60724000	-0.25864100
H	-3.15523800	6.11477500	0.29851500
C	-0.88451300	8.20211400	-1.26192300
H	-1.89690200	8.20124100	0.63971800
N	0.34139300	7.73225100	-3.36728500
H	0.38123100	7.20159900	-4.22425000
H	0.58806400	8.70383500	-3.46883500
N	-0.38449000	9.35055400	-0.93798800
C	0.28155700	10.25409800	-1.76462700
C	1.47742900	10.82691200	-1.29513400
C	-0.26952600	10.74377900	-2.95995700
C	2.14816100	11.80423200	-2.01950700
H	1.86771800	10.49164000	-0.33909000
C	0.39502900	11.73631100	-3.68137400
H	-1.23228600	10.37747400	-3.29903100
C	1.61076700	12.25803300	-3.24841400
H	-0.04408300	12.10760400	-4.60404000
N	2.30311600	13.28087100	-3.92568600
H	3.29496100	13.08617900	-4.01411600
H	1.90871700	13.50326600	-4.82950900
N	3.37647400	12.34791300	-1.60900300
H	3.41451700	13.35421700	-1.72955900
H	3.63740900	12.09215700	-0.66657100

9-H1-2

C	-3.99669100	1.77954000	0.42166300
C	-3.11924200	2.42843500	-0.43571600
C	-3.53121000	3.54766800	-1.16140000
C	-4.85032000	4.03290900	-1.05934800
C	-5.71897300	3.37150100	-0.17491000
C	-5.29905700	2.26648500	0.55014600
H	-3.67110900	0.91318600	0.98480900
H	-2.09709600	2.08004000	-0.54542000
H	-6.73847800	3.73093800	-0.07224400
H	-5.99805400	1.77434500	1.21774100
N	-5.25770400	5.16469000	-1.75326300
H	-6.25611100	5.30030200	-1.80857300
H	-4.80006200	5.33230200	-2.63706500
N	-2.60486000	4.17338300	-2.06590500
C	-1.98750000	5.36286900	-1.88953800
C	-1.03273500	5.80084000	-2.82669200
C	-2.27139300	6.17343000	-0.73916200
C	-0.38453500	7.02271700	-2.71177500
H	-0.76924800	5.14525800	-3.65263900
C	-1.63500000	7.35914200	-0.59698200
H	-2.97625600	5.82045600	0.00052400
C	-0.73601800	7.91375600	-1.58881900
H	-1.81824800	7.99080600	0.26346500

N	0.60325600	7.34563000	-3.58425900
H	0.99625900	6.62177500	-4.16524700
H	1.19479700	8.14309300	-3.41636900
N	-0.29680900	9.11879500	-1.29791400
C	0.29972700	10.08837500	-2.03358800
C	0.96771600	11.09713700	-1.27779000
C	0.16824400	10.29697200	-3.43621100
C	1.58182500	12.17639100	-1.86795200
H	0.98355100	10.97715800	-0.20007100
C	0.73045200	11.40089800	-4.03349700
H	-0.43002300	9.62212300	-4.03433700
C	1.49977700	12.32367300	-3.28864200
H	0.60031400	11.56365300	-5.09885400
N	2.12708600	13.37575400	-3.86815000
H	2.88106000	13.81291500	-3.35718200
H	2.16039800	13.45349000	-4.87204900
N	2.33654600	13.13684400	-1.17048900
H	1.97967200	14.08244200	-1.26347500
H	2.46375500	12.91945800	-0.19119000
H	-2.28469800	3.60995100	-2.84326100

9-H2

C	-4.01569000	2.59423400	0.97022000
C	-3.37346300	3.56048400	0.22361700
C	-3.84495900	3.87076200	-1.06603500
C	-4.99680100	3.21306800	-1.59096800
C	-5.60446700	2.21064600	-0.82496400
C	-5.12795800	1.91385200	0.44027000
H	-3.63638900	2.32908300	1.94966700
H	-2.46516900	4.01770000	0.59477700
H	-6.47218400	1.69202800	-1.21827900
H	-5.61941900	1.14847100	1.02966300
N	-5.42597500	3.55035900	-2.86499200
H	-6.16792000	2.97727400	-3.24393500
H	-5.58378400	4.53096900	-3.05658300
N	-3.16953800	4.70885800	-1.95415400
C	-2.35395800	5.76864600	-1.72611700
C	-1.47151400	6.18560600	-2.74347500
C	-2.37702900	6.48420700	-0.48712600
C	-0.61280900	7.26606200	-2.59337900
H	-1.39800500	5.59203500	-3.64941000
C	-1.56307700	7.56276500	-0.32934200
H	-3.08009200	6.21538900	0.28893900
C	-0.69945700	8.03074500	-1.36492400
H	-1.62229800	8.13774800	0.58938700
N	0.30104100	7.55818600	-3.56487900
H	0.47451900	6.85981200	-4.27214500
H	1.09916200	8.13565900	-3.35427700
N	0.02860800	9.15153300	-1.07879200
C	0.55851000	10.17500600	-1.84357200
C	1.52622700	11.01083000	-1.23750200
C	0.06941100	10.49167600	-3.13759000
C	2.06242500	12.09418800	-1.90227000
H	1.85505200	10.80075100	-0.22377300
C	0.59166900	11.56110200	-3.81613700
H	-0.73501300	9.92017600	-3.57830700
C	1.63802800	12.34480600	-3.26180300
H	0.21239300	11.81117600	-4.80093700
N	2.22824200	13.32087600	-3.96455200
H	3.10283800	13.71991100	-3.65420200

H	1.95619000	13.51907400	-4.91619700
N	3.04640000	12.90982000	-1.37738900
H	2.90780700	13.90912400	-1.46366100
H	3.39589800	12.66552100	-0.46159100
H	0.13710600	9.30894900	-0.08129400
H	-3.26934500	4.41574700	-2.92464500

11

C	4.26078600	12.91371800	-2.84731700
C	5.51904400	13.51742700	-2.91570900
C	5.66774900	14.85696100	-3.25270200
C	4.51275700	15.61326200	-3.56371700
C	3.26065100	15.00906000	-3.50315700
C	3.11878200	13.66306300	-3.13215800
H	4.17319900	11.88010300	-2.53394600
H	2.37571800	15.57883600	-3.77536800
H	6.95604100	16.36761800	-2.83530700
N	6.92022600	15.50326800	-3.36680200
C	-1.28601200	5.40837100	-0.71817600
C	-0.52891400	5.86771600	-1.76197500
C	-1.73662300	6.29583000	0.29992800
C	-0.17833100	7.24641200	-1.84751900
H	-0.17442100	5.21154700	-2.54934600
C	-1.41986200	7.62670700	0.25341600
H	-2.33595500	5.90715000	1.11700300
C	-0.63417600	8.14348200	-0.81637600
H	-1.74942900	8.32475000	1.01530300
N	0.56454900	7.67911200	-2.88011900
H	7.69424700	14.90971600	-3.09926100
N	-0.33340500	9.45392300	-0.84708000
C	0.40294900	9.88121600	-1.87358000
C	0.78391200	11.25074200	-1.94930600
C	0.86337800	8.98252400	-2.91005000
C	1.53369800	11.74028100	-2.98655200
H	0.46696000	11.90161300	-1.14071600
C	1.63720400	9.50873900	-3.97562400
C	1.95204100	10.84700900	-4.05895100
H	1.93620900	8.82007400	-4.75958100
N	2.57033200	11.37319100	-5.17471000
H	3.08458200	12.23263200	-5.06567400
H	3.01914400	10.70767500	-5.78461200
N	1.81019700	13.11527000	-3.08524700
H	-1.54949200	4.35698200	-0.66027600
H	1.15222400	13.68986800	-2.57803100
N	4.68858200	16.96550900	-3.88602100
H	5.50048500	17.12262600	-4.47249900
H	3.86773600	17.40877000	-4.27408500
H	6.40070200	12.93177700	-2.66819900

11-H1

C	3.84813400	13.02785800	-2.34195600
C	5.10750300	13.56961900	-2.07539300
C	5.53626600	14.75257100	-2.67368600
C	4.68833600	15.40313600	-3.61754700
C	3.42762300	14.86985800	-3.87270500
C	3.02743600	13.69958500	-3.22605600
H	3.53514300	12.11486700	-1.85317200
H	2.77597400	15.36060800	-4.59113300
H	6.79988000	16.31598000	-2.37383000
N	6.78749100	15.30616500	-2.44752500

C	-0.93238300	5.46878200	-0.61341300
C	-0.45831000	5.95175700	-1.79955600
C	-1.08050400	6.32161500	0.52380300
C	-0.10280600	7.32810300	-1.91681000
H	-0.33883000	5.32322300	-2.67407400
C	-0.75179800	7.64517100	0.45765900
H	-1.46054500	5.90278600	1.44908300
C	-0.25245800	8.19411300	-0.76071300
H	-0.85595800	8.31026400	1.30682800
N	0.35741400	7.79339200	-3.08241800
H	7.33630000	14.86932100	-1.72142400
N	0.06823900	9.49037400	-0.81964800
C	0.52990600	9.94731300	-1.98929000
C	0.87375900	11.32583800	-2.10705400
C	0.67681000	9.09254000	-3.13850900
C	1.34621300	11.78267400	-3.29890400
H	0.73230600	11.96446800	-1.24139900
C	1.18068400	9.63188400	-4.35895400
C	1.52340200	10.95375700	-4.45148300
H	1.28164600	8.95894100	-5.20335400
N	1.94497700	11.62400100	-5.63677600
H	2.95297200	11.74599000	-5.68780700
H	1.64075400	11.14819900	-6.47782200
N	1.63913600	13.21170200	-3.51916700
H	-1.20372000	4.42259400	-0.52439200
H	0.95564500	13.78195000	-3.01623000
N	5.14991900	16.57601700	-4.19986000
H	6.12371400	16.55346900	-4.47725700
H	4.56453800	16.97702300	-4.91778000
H	5.75734500	13.06812900	-1.36581800
H	1.47954100	13.33178000	-4.53642700

11-H2-1

C	3.85285000	13.21682900	-2.15520900
C	5.14319900	13.73418000	-2.05169400
C	5.58130700	14.78538500	-2.86168900
C	4.70323400	15.30857900	-3.86734800
C	3.40877800	14.79724900	-3.96162500
C	3.00864800	13.77252200	-3.10024200
H	3.53769100	12.41884800	-1.49438200
H	2.73279200	15.19897600	-4.71216400
H	6.94134400	16.30557400	-2.93982800
N	6.84539500	15.31237900	-2.77483100
C	-0.98529000	5.33736700	-0.82767900
C	-0.41774800	5.90195500	-1.93400600
C	-1.26491400	6.12403900	0.32954200
C	-0.09931100	7.29452800	-1.93788200
H	-0.19359400	5.33393900	-2.82844200
C	-0.97859400	7.46856500	0.38014900
H	-1.71632900	5.64675000	1.19206900
C	-0.39415100	8.07039100	-0.74696500
H	-1.19855600	8.05206500	1.26818800
N	0.44759900	7.84465400	-3.01570200
H	7.44222200	14.97660600	-2.03364900
N	-0.07654800	9.38954000	-0.79131700
C	0.48540100	9.98571900	-1.87719800
C	0.79150200	11.36135200	-1.91997100
C	0.74412000	9.15672100	-3.01791600
C	1.35196800	11.86204200	-3.06750800
H	0.56313600	12.00538500	-1.07612000

C	1.34229500	9.72728600	-4.16713400
C	1.67063200	11.06722300	-4.21450800
H	1.53690000	9.06919000	-5.00582600
N	2.16501400	11.71521400	-5.33731800
H	3.01474000	12.25370500	-5.20676100
H	2.21963100	11.14724400	-6.17276700
N	1.57944200	13.31299400	-3.20019500
H	-1.23076400	4.28212300	-0.81726700
H	0.99074900	13.82188800	-2.53343300
N	5.16515600	16.33625500	-4.65859700
H	6.13060500	16.28077400	-4.95524200
H	4.55446600	16.69006100	-5.37936900
H	5.81317800	13.33339300	-1.29894200
H	1.24417300	13.56877900	-4.14006900
H	-0.27524800	9.95319000	0.03047900

11-H2-2

C	3.95620600	13.17597200	-2.19728900
C	5.24571400	13.70603900	-2.17739700
C	5.60624000	14.79595200	-2.97425800
C	4.64467600	15.35104600	-3.88084400
C	3.35129100	14.82659200	-3.89264100
C	3.03396900	13.75832800	-3.04742200
H	3.69895000	12.35226900	-1.54212100
H	2.60899000	15.26043900	-4.55861900
H	6.93758800	16.33764800	-3.08727500
N	6.86917400	15.33544400	-2.96795300
C	-1.11996300	5.34699400	-0.80602400
C	-0.49664200	5.84962600	-1.92989300
C	-1.42564800	6.16805200	0.31256400
C	-0.16121200	7.20957900	-1.95777300
H	-0.27235500	5.20625700	-2.77429500
C	-1.10512900	7.49894200	0.30279500
H	-1.91591700	5.72897000	1.17301600
C	-0.46151100	8.06396700	-0.83444700
H	-1.32323700	8.15482500	1.13667200
N	0.45523700	7.79180300	-3.02944400
H	7.52363500	14.97717600	-2.28829700
N	-0.14826200	9.36495600	-0.84429700
C	0.45291700	9.88269300	-1.91061300
C	0.76686000	11.27422400	-1.92582900
C	0.78999000	9.10999000	-3.07646300
C	1.38183700	11.82393600	-3.00554500
H	0.47371000	11.85512000	-1.05730300
C	1.43659900	9.69124000	-4.16936800
C	1.76639500	11.04674300	-4.16069100
H	1.70552300	9.08665500	-5.02937000
N	2.35540400	11.65556800	-5.22154100
H	2.96316900	12.45131400	-5.07571100
H	2.59077800	11.09638100	-6.02888300
N	1.60629400	13.28774900	-3.03463300
H	-1.38443500	4.29593000	-0.77586500
H	1.11131400	13.70209200	-2.23776900
N	5.03078900	16.42009300	-4.65784100
H	5.96992100	16.39179600	-5.03241000
H	4.36036600	16.80259900	-5.30711100
H	5.97762400	13.28486000	-1.49689000
H	1.14217000	13.67126300	-3.86663600
H	0.67174000	7.20506900	-3.82934600

11-H2-3

C	4.62962100	13.02648200	-2.81825700
C	5.76928300	13.75172100	-3.09353900
C	5.69553700	15.10470200	-3.49078000
C	4.40343800	15.70866800	-3.69227500
C	3.26883600	14.96699600	-3.40349000
C	3.36491200	13.63149800	-2.96620500
H	4.71496400	12.02365500	-2.41645600
H	2.29095000	15.41086800	-3.56252900
H	6.73993200	16.86076700	-3.61938900
N	6.80475600	15.85447800	-3.67793800
C	-1.68694100	5.36728700	-0.92015800
C	-0.79575400	5.81818800	-1.87659200
C	-2.16096600	6.23449000	0.08156400
C	-0.36840000	7.15007600	-1.83832800
H	-0.42920800	5.15072600	-2.64954100
C	-1.74607300	7.55288200	0.13001700
H	-2.85917700	5.86677400	0.82378000
C	-0.84435300	8.02268900	-0.83233500
H	-2.11316700	8.21995700	0.90293500
N	0.52339700	7.66475100	-2.76697800
H	7.71704000	15.46599600	-3.49211800
N	-0.39197400	9.32959400	-0.84583000
C	0.49079300	9.83542600	-1.75196900
C	0.95143500	11.13905800	-1.72428300
C	0.98116400	8.93833600	-2.77731100
C	1.87666700	11.62737500	-2.66256400
H	0.61454400	11.80306000	-0.93504300
C	1.88373500	9.40554000	-3.72278500
C	2.34337900	10.72876200	-3.72310300
H	2.22693000	8.73574900	-4.50418400
N	3.12132100	11.15488400	-4.73044100
H	3.52702100	12.07631300	-4.75256600
H	3.29440600	10.56194600	-5.52780200
N	2.19016900	12.95472000	-2.61694800
H	-2.02226700	4.33757600	-0.94337800
H	1.49598200	13.53402400	-2.15731900
N	4.36719200	17.02669600	-4.10235100
H	4.97779500	17.28708000	-4.86616900
H	3.45672500	17.45495000	-4.18637700
H	6.74309900	13.30714500	-2.91972000
H	-0.74431800	9.94994600	-0.12611200
H	0.85708000	7.03308900	-3.48667300

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