Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information for

Selective C-C and C-N Bond Activation in Dopamine and Norepinephrine under Deep Ultraviolet Laser Irradiation

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S1. Experimental and computational methods

Experimental Methods. The experiments were performed with the customized reflection time-of-flight mass spectrometer sketched (Fig. S1). The laser used was a all-solid-state DUV laser system (177.3 nm wavelength, 15.5 ps pulse duration, ~ 15 μJ pulse energy, 10 Hz repeating rate, Fig. S2b)[1]. The powder samples of dopamine hydrochloride (99% purity, Alfa Aesar) and norepinephrine (98% purity, Alfa Aesar) were loaded into a customized quartz container and heated to a certain proper temperature (140 ^{o}C for dopamine hydrochloride and 100 ^{o}C for norepinephrine, respectively) that produce enough vapor to form a stable molecular beam for photoionization. A high-vacuum plasma cleaning setup (XEI Evactron EP) was built for this instrument, helping to remove unwanted contamination especially organic chemicals. The 118nm and 177.3nm laser systems that used in the laser ionization mass spectrometry (LIMS) experiment are shown in Fig. S2, respectively. The vacuum ultraviolet (VUV) laser system (118 nm wavelength, ns-pulsed 355 nm radiation focused into a 1: 10 Xe/Ar gas cell to realize third harmonic.[2]

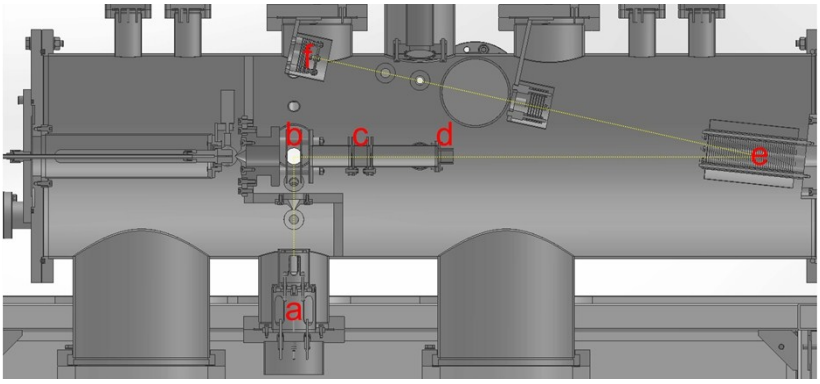


Fig. S1 The customized Re-TOF-MS based on the all-solid-state DUV laser system. Re-TOF-MS technical: (a) thermal evaporation source, (b) ionization zone with laser incidence, (c) focus, (d) deflection, (e) reflector, (f) MCP ions detector.

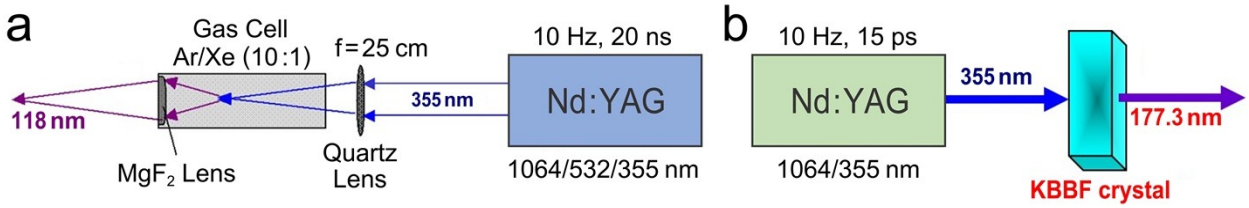


Fig. S2 The optional laser systems of (a) 118nm VUV and (b) 177.3nm DUV used in the LIMS experiment.

Computational Methods. All the optimization, frequency, and energy calculations are carried out on the basis of density functional theory (DFT) embedded within the Gaussian 09 program package.[3] The geometries of all species are fully optimized at the unrestricted b3lyp/6-311++g(d,p) level of theory.[4] All the energies are corrected with the zero-point vibrational contributions. The transition state (TS) structures are checked and confirmed by intrinsic reaction coordinate (IRC)[5] calculations. Natural population analysis (NPA)[6] is performed to reveal the charge distribution changes when the neurotransmitter molecules are ionized. Natural bond orbital (NBO)[7] analysis of neutral and cationic dopamine and norepinephrine was also performed to estimate the amount of charge transfer during the ionization process. The NBO orbitals were plotted with Multiwfn and VMD software.[8]

S2. Thermogravimetric analysis

Regarding the proper evaporation temperature, thermogravimetric analysis of samples dopamine hydrochloride and norepinephrine were performed to make sure the stability without thermal decomposition (Fig. S3).

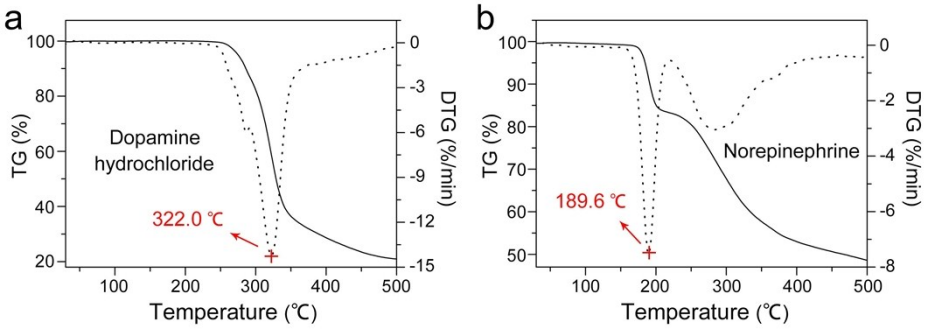


Fig. S3 Thermogravimetric curves of (a) dopamine hydrochloride (b) norepinephrine.

S3. VUV-LIMS details

As shown in Fig. S4, there are three peaks observed in the VUV-LIMS: m/z=153, 30, 124 amu, respectively. Among them, the mass peak at 153 amu aims at the molecule ion ($C_8NO_2H_{11}^{+\cdot}$), while the 30-amu peak corresponds to C_α-C_β bond cleavage fragment (CNH_4^+). Besides, the dominant peak 124 amu ($C_7O_2H_8^{+\cdot}$) indicates a gain of H atom induced by intramolecular hydrogen atom transfer (HAT) process, which is well consistent with the previously reported investigations on a basis of the McLafferty rearrangement.[9] Comparing with the DUV-LIMS results as mentioned in the main text due to the insufficient single-photon energy of the DUV light, the observation of fragmentation in VUV-LIMS is due to the relatively large pulses (20ns) of VUV laser (Xe/Ar gas cell to realize third harmonic) and there is residual 355 nm laser which readily give rise to fragmentation.[10]

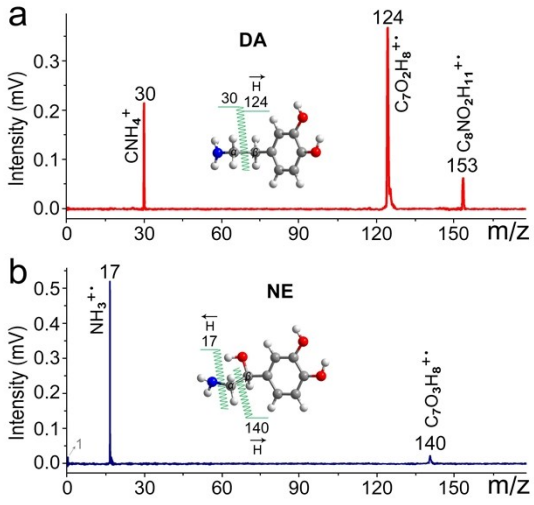


Fig. S4 Mass spectra of DA (a) and NE (b) ionized by VUV laser.

S4. DFT calculation details

Energies

Table S1 list the sum of electronic and zero-point energies (E_0), sum of electronic and thermal enthalpies (H), sum of electronic and thermal free energies (G) of nascent molecule and that after adiabatic ionization for dopamine (DA) and norepinephrine (NE) at the b3lyp/6-311++g(d,p) level of DFT. All the energies were corrected with zero-point vibrations.

Table S1. Thermodynamic energies of DA and NE at the b3lyp/6-311++g(d,p) level of DFT (hatree).

	DA			NE		
	Nascent molecule	After vertical ionization	After adiabatic ionization	Nascent molecule	After vertical ionization	After adiabatic ionization
E_0	-516.641525	-516.357890	-516.367700	-591.883493	-591.598261	-591.607422
H	-516.629343	-516.346805	-516.355806	-591.870690	-591.586398	-591.594882
G	-516.679052	-516.393885	-516.405003	-591.921428	-591.634819	-591.645478

UV absorption

Utilizing TD-DFT first-principles calculation, Fig. S5 present the absorption bands of nascent molecule and that after adiabatic ionization for DA and NE in the UV area at the b3lyp/6-311++g(d,p) level of DFT.

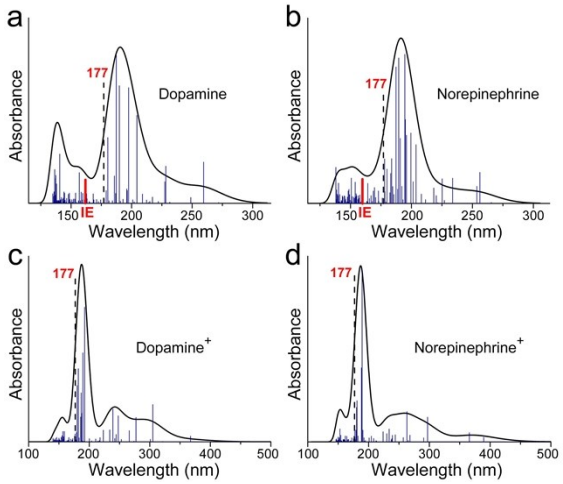


Fig. S5 Calculated UV spectra of neutral (upper) and cationic (bottom) (a/c) DA and (b/d) NE, respectively, at the b3lyp/6-311++g(d,p) level of DFT.

Bond lengths

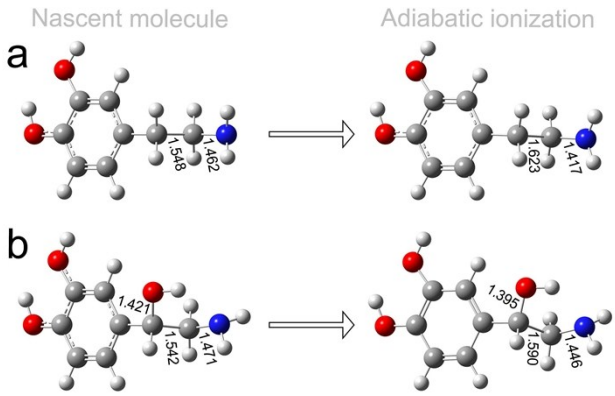


Fig. S6 The bond lengths of C_α-C_β and C_α-N in (a) DA and (b) NE respectively (Å).

Table S2. The bond lengths (Å) and relative changes of C_α-C_β and C_α-N in DA and NE, respectively, before and after ionization.

	C_α-C_β bond			C_α-N bond		
	Before ionization	After ionization	Increment	Before ionization	After ionization	Increment
DA	1.548	1.623	0.075	1.462	1.417	-0.045
NE	1.542	1.590	0.048	1.471	1.446	-0.025

Ionization energies & HOMO-LUMO gaps

Ionization energies and HOMO-LUMO gaps of DA and NE at the b3lyp/6-311++g(d,p) level of DFT are calculated. All energies were corrected with zero-point vibrations. As shown in Table S3, neutral DA bears a relatively smaller HOMO-LUMO gap, which is consistent with its relatively small ionization potential.

Table S3. Ionization energies and HOMO-LUMO gaps of DA and NE at the b3lyp/6-311++g(d,p) level of DFT (eV).

	Ionization energies		HOMO-LUMO gaps	
	Adiabatic	Vertical	Neutral	Cationic
DA	7.45	7.72	5.30	5.46
NE	7.51	7.76	5.34	5.26

HOMO-LUMO orbitals

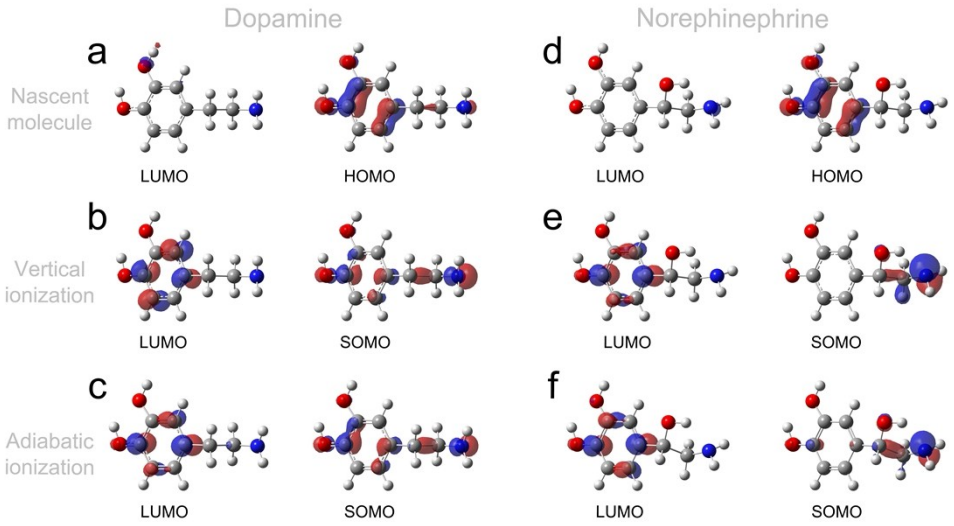


Fig. S7 Frontier molecular orbitals of the nascent molecule and that after ionization for (a-c) DA and (d-f) NE, at the b3lyp/6-311++g(d,p) level of DFT.

Molecular electrostatic potential (MEP) analysis

Fig. S8 depicts the Molecular electrostatic potential (MEP) of DA and NE, where red regions correspond to the maximal negative potentials and blue regions to positive. Different values of the MEPs at the surface are presented by different colors, with potential increasing in the order ‘‘red < orange < yellow < green < blue’’.

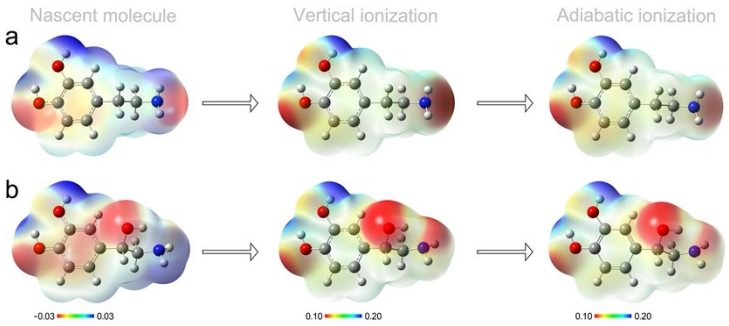


Fig. S8 Electrostatic potentials on the surface of (a) DA and (b) NE. Red and blue colors indicate negative and positive regions, respectively, at the b3lyp/6-311++g(d,p) level of DFT.

Natural Population Analysis (NPA)

The method of natural population analysis (NPA) was developed to calculate atomic charges and orbital populations of molecular wave functions in general atomic orbital basis sets. The atom labels and NPA of neutral and cationic DA and NE at the b3lyp/6-311++g(d,p) level of DFT are shown in Fig. S9-10 and Table S4-7. All the energies were corrected with zero-point-vibrations.

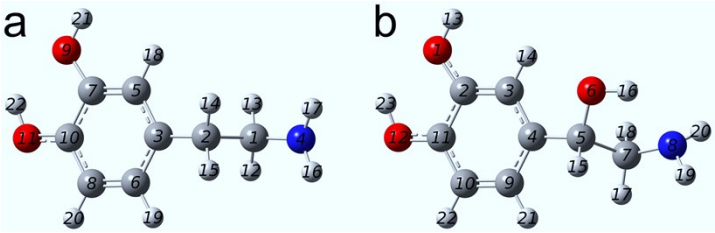


Fig. S9 Atom labels of (a) DA (b) NE for all analysis in this paper. Atoms in dark gray, blue, red and light gray atoms refer to C, N, O and H, respectively.

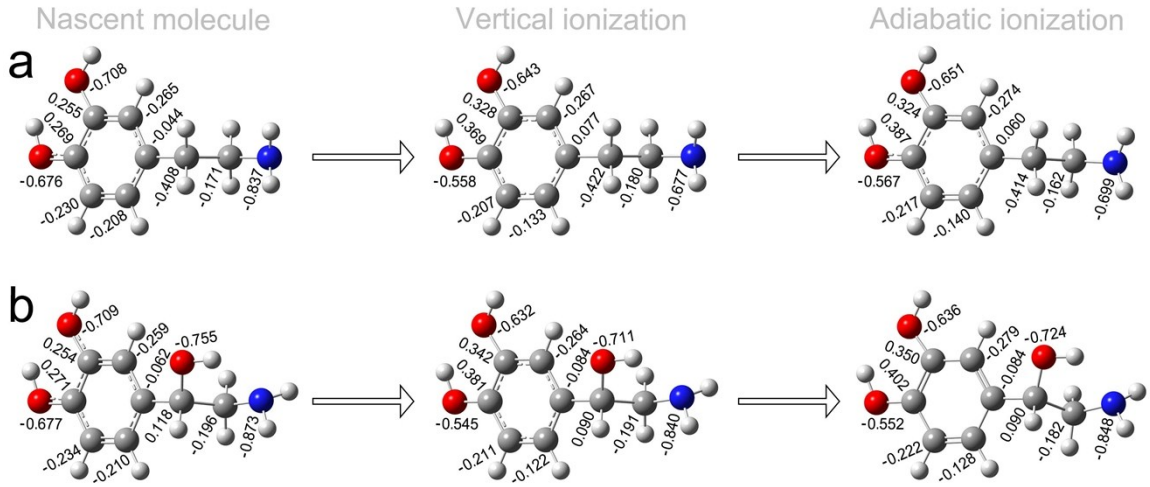


Fig. S10 Surface charge distribution from NPA of neutral and cationic (a) DA and (b) NE at the b3lyp/6-311++g(d,p) level of DFT. Atoms in dark gray, blue, red and light gray atoms refer to C, N, O and H, respectively.

Table S4. The natural charge increments between and after ionization in DA (*e*).

Atom	No.	Natural charge increment before and after vertical ionization	Natural charge increment before and after adiabatic ionization
C	1	-0.00892	0.01822
C	2	-0.01386	0.00847
C	3	0.1204	-0.01668
N	4	0.15976	-0.02168
C	5	-0.00109	-0.00746
C	6	0.07524	-0.00701
C	7	0.07284	-0.00414
C	8	0.02311	-0.00934
O	9	0.06506	-0.00851
C	10	0.10017	0.01726
O	11	0.11799	-0.0392

Note: The natural charge increment provided in the table is obtained by subtracting the natural charge of nascent molecule from the natural charge that after ionization.

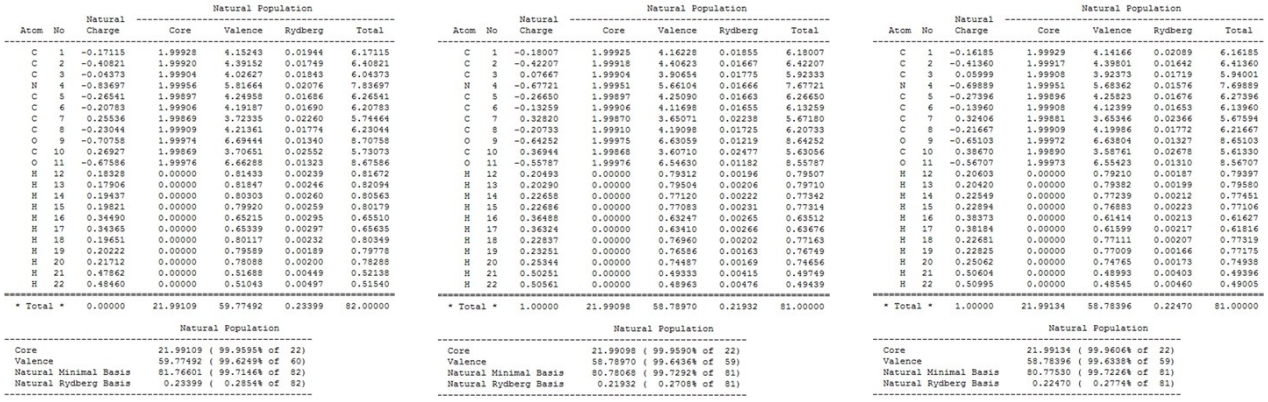
Table S5. The natural charge increments between and after ionization in NE (*e*).

Atom	No.	Natural charge increment before and after vertical ionization	Natural charge increment before and after adiabatic ionization
O	1	0.07718	-0.00353
C	2	0.08773	0.00788
C	3	-0.00473	-0.01553
C	4	0.14577	-0.00004
C	5	-0.02854	-0.00005
O	6	0.04313	-0.0124
C	7	0.00476	0.00906
N	8	0.03332	-0.00834
C	9	0.08757	-0.00593
C	10	0.02312	-0.01113
C	11	0.10984	0.02184
O	12	0.13227	-0.00751

Note: The natural charge increment provided in the table is obtained by subtracting the natural charge of nascent molecule from the natural charge that after ionization.

Table S6. Summary of Natural Population Analysis for nascent molecule (Left) and that after vertical (Middle) and adiabatic

ionization (Right) for DA.



Atom	No	Natural Charge	Core	Valence	Rydberg	Total
C	1	-0.17115	1.99928	4.15243	0.01944	6.17115
C	2	-0.40821	1.99920	4.39152	0.01749	6.40821
C	3	-0.04373	1.99904	4.02627	0.01843	6.04373
N	4	-0.83697	1.99956	5.81664	0.02076	7.83697
C	5	-0.26541	1.99897	4.24958	0.01686	6.26541
C	6	-0.20783	1.99906	4.19187	0.01690	6.20783
C	7	0.25536	1.99869	3.72335	0.02260	5.74464
C	8	-0.23044	1.99909	4.21361	0.01774	6.23044
O	9	-0.70758	1.99974	6.69444	0.01340	8.70758
C	10	0.26927	1.99869	3.70651	0.02552	5.73073
O	11	-0.67586	1.99976	6.66288	0.01323	8.67586
H	12	0.18328	0.00000	0.81493	0.00239	0.81672
H	13	0.17906	0.00000	0.81847	0.00246	0.82094
H	14	0.19437	0.00000	0.80303	0.00260	0.80563
H	15	0.19821	0.00000	0.79920	0.00259	0.80179
H	16	0.34490	0.00000	0.65215	0.00295	0.65510
H	17	0.34365	0.00000	0.65339	0.00297	0.65635
H	18	0.19651	0.00000	0.80117	0.00232	0.80349
H	19	0.20222	0.00000	0.79589	0.00189	0.79778
H	20	0.21712	0.00000	0.78088	0.00200	0.78288
H	21	0.47862	0.00000	0.51688	0.00449	0.52138
H	22	0.48460	0.00000	0.51043	0.00497	0.51540
* Total *		0.00000	21.99109	59.77492	0.23399	82.00000

Natural Population			
Core	21.99109	(99.9595% of	22)
Valence	59.77492	(99.6249% of	60)
Natural Minimal Basis	81.76601	(99.7146% of	82)
Natural Rydberg Basis	0.23399	(0.2854% of	82)

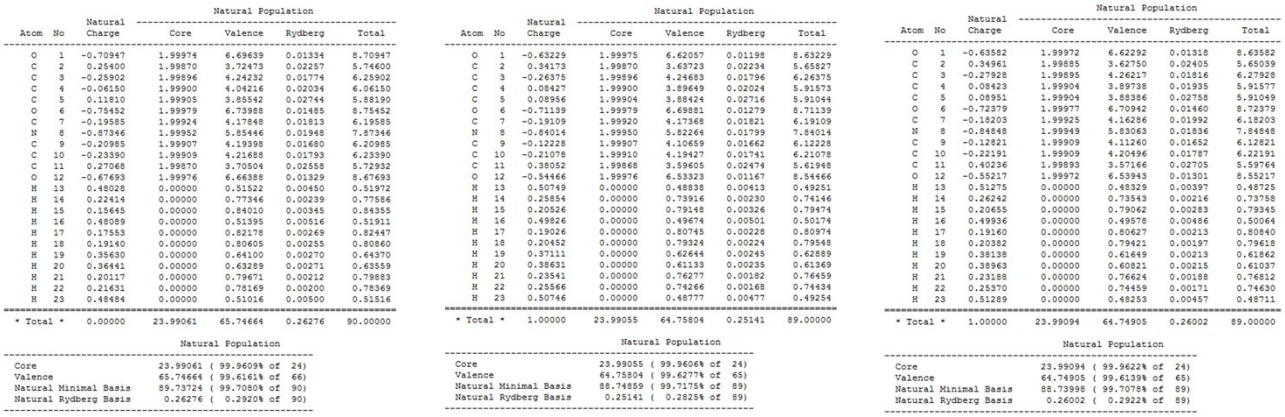
Atom	No	Natural Charge	Core	Valence	Rydberg	Total
C	1	-0.18007	1.99925	4.16228	0.01855	6.18007
C	2	-0.42207	1.99918	4.40623	0.01667	6.42207
C	3	0.07667	1.99904	3.90654	0.01775	5.92333
N	4	-0.67721	1.99951	5.66104	0.01666	7.67721
C	5	-0.26650	1.99897	4.25090	0.01663	6.26650
C	6	-0.13259	1.99906	4.11698	0.01655	6.13259
C	7	0.32820	1.99870	3.65071	0.02238	5.67180
C	8	-0.20733	1.99910	4.19098	0.01725	6.20733
O	9	-0.64252	1.99975	6.63059	0.01219	8.64252
C	10	0.36944	1.99868	3.60710	0.02477	5.63056
O	11	-0.55787	1.99976	6.54630	0.01182	8.55787
H	12	0.20493	0.00000	0.79312	0.00196	0.79507
H	13	0.20290	0.00000	0.79504	0.00206	0.79710
H	14	0.22658	0.00000	0.77120	0.00222	0.77342
H	15	0.22686	0.00000	0.77083	0.00231	0.77314
H	16	0.36488	0.00000	0.63247	0.00265	0.63512
H	17	0.36324	0.00000	0.63410	0.00266	0.63676
H	18	0.22837	0.00000	0.76960	0.00202	0.77163
H	19	0.23251	0.00000	0.76586	0.00163	0.76749
H	20	0.25344	0.00000	0.74487	0.00169	0.74656
H	21	0.50251	0.00000	0.49333	0.00415	0.49749
H	22	0.50561	0.00000	0.48963	0.00476	0.49439
* Total *		1.00000	21.99098	58.78970	0.21932	81.00000

Natural Population			
Core	21.99098	(99.9590% of	22)
Valence	58.78970	(99.6436% of	59)
Natural Minimal Basis	80.78068	(99.7292% of	81)
Natural Rydberg Basis	0.21932	(0.2708% of	81)

Atom	No	Natural Charge	Core	Valence	Rydberg	Total
C	1	-0.16185	1.99929	4.14166	0.02089	6.16185
C	2	-0.41360	1.99917	4.39801	0.01642	6.41360
C	3	0.05999	1.99908	3.92373	0.01719	5.94001
N	4	-0.69889	1.99951	5.68362	0.01576	7.69889
C	5	-0.27396	1.99896	4.25823	0.01676	6.27396
C	6	-0.13960	1.99908	4.12399	0.01653	6.13960
C	7	0.32406	1.99881	3.65346	0.02366	5.67594
C	8	-0.21667	1.99909	4.19886	0.01772	6.21667
O	9	-0.65103	1.99972	6.63804	0.01327	8.65103
C	10	0.38670	1.99890	3.58761	0.02678	5.61330
O	11	-0.56707	1.99973	6.55423	0.01310	8.56707
H	12	0.20603	0.00000	0.79210	0.00187	0.79397
H	13	0.20420	0.00000	0.79382	0.00199	0.79580
H	14	0.22549	0.00000	0.77239	0.00212	0.77451
H	15	0.22894	0.00000	0.76883	0.00223	0.77106
H	16	0.38373	0.00000	0.61414	0.00213	0.61627
H	17	0.38184	0.00000	0.61599	0.00217	0.61816
H	18	0.22681	0.00000	0.77111	0.00207	0.77319
H	19	0.22825	0.00000	0.77009	0.00166	0.77175
H	20	0.25062	0.00000	0.74765	0.00173	0.74938
H	21	0.50604	0.00000	0.48993	0.00403	0.49396
H	22	0.50995	0.00000	0.48545	0.00460	0.49005
* Total *		1.00000	21.99134	58.78396	0.22470	81.00000

Natural Population			
Core	21.99134	(99.9606% of	22)
Valence	58.78396	(99.6338% of	59)
Natural Minimal Basis	80.77530	(99.7226% of	81)
Natural Rydberg Basis	0.22470	(0.2774% of	81)

Table S7. Summary of Natural Population Analysis for nascent molecule (Left) and that after vertical (Middle) and adiabatic ionization (Right) for NE.



Atom	No	Natural Charge	Core	Valence	Rydberg	Total
O	1	-0.70947	1.99974	6.69639	0.01334	8.70947
C	2	0.25400	1.99870	3.72473	0.02257	5.74600
C	3	-0.25902	1.99896	4.24232	0.01774	6.25902
C	4	-0.06150	1.99900	4.04216	0.02034	6.06150
C	5	0.11810	1.99905	3.85542	0.02744	5.88190
O	6	-0.75452	1.99979	6.73988	0.01485	8.75452
C	7	-0.19585	1.99924	4.17848	0.01813	6.19585
N	8	-0.87346	1.99952	5.85446	0.01948	7.87346
C	9	-0.20985	1.99907	4.19398	0.01680	6.20985
C	10	-0.23390	1.99909	4.21688	0.01793	6.23390
C	11	0.27068	1.99870	3.70504	0.02558	5.72932
O	12	-0.67693	1.99976	6.66388	0.01329	8.67693
H	13	0.48028	0.00000	0.51522	0.00450	0.51972
H	14	0.22414	0.00000	0.77346	0.00239	0.77586
H	15	0.15645	0.00000	0.84010	0.00345	0.84355
H	16	0.48089	0.00000	0.51395	0.00516	0.51911
H	17	0.17553	0.00000	0.82178	0.00269	0.82447
H	18	0.19140	0.00000	0.80605	0.00255	0.80860
H	19	0.35630	0.00000	0.64100	0.00270	0.64370
H	20	0.36441	0.00000	0.63289	0.00271	0.63559
H	21	0.20117	0.00000	0.79671	0.00212	0.79883
H	22	0.21631	0.00000	0.78169	0.00200	0.78369
H	23	0.48484	0.00000	0.51016	0.00500	0.51516
* Total *		0.00000	23.99061	65.74664	0.26276	90.00000

Natural Population			
Core	23.99061	(99.9609% of	24)
Valence	65.74664	(99.6161% of	66)
Natural Minimal Basis	89.73724	(99.7080% of	90)
Natural Rydberg Basis	0.26276	(0.2920% of	90)

Atom	No	Natural Charge	Core	Valence	Rydberg	Total
O	1	-0.63229	1.99975	6.62057	0.01198	8.63229
C	2	0.34173	1.99870	3.63723	0.02234	5.65827
C	3	-0.26375	1.99896	4.24683	0.01796	6.26375
C	4	0.08427	1.99900	3.89649	0.02024	5.91573
C	5	0.08956	1.99904	3.88424	0.02716	5.91044
O	6	-0.71139	1.99979	6.69881	0.01279	8.71139
C	7	-0.19109	1.99920	4.17368	0.01821	6.19109
N	8	-0.84014	1.99950	5.82264	0.01799	7.84014
C	9	-0.12228	1.99907	4.10659	0.01662	6.12228
C	10	-0.21078	1.99910	4.19427	0.01741	6.21078
C	11	0.38052	1.99868	3.59605	0.02474	5.61948
O	12	-0.54466	1.99976	6.53323	0.01167	8.54466
H	13	0.50749	0.00000	0.48838	0.00413	0.49251
H	14	0.25854	0.00000	0.73916	0.00230	0.74146
H	15	0.20526	0.00000	0.79148	0.00326	0.79474
H	16	0.49826	0.00000	0.49674	0.00501	0.50174
H	17	0.19026	0.00000	0.80745	0.00228	0.80974
H	18	0.20452	0.00000	0.79324	0.00224	0.79548
H	19	0.37111	0.00000	0.62644	0.00245	0.62889
H	20	0.38631	0.00000	0.61133	0.00235	0.61369
H	21	0.23541	0.00000	0.76277	0.00182	0.76459
H	22	0.25566	0.00000	0.74266	0.00168	0.74434
H	23	0.50746	0.00000	0.48777	0.00477	0.49254
* Total *		1.00000	23.99055	64.75804	0.25141	89.00000

Natural Population			
Core	23.99055	(99.9606% of	24)
Valence	64.75804	(99.6277% of	65)
Natural Minimal Basis	88.74859	(99.7175% of	89)
Natural Rydberg Basis	0.25141	(0.2825% of	89)

Atom	No	Natural Charge	Core	Valence	Rydberg	Total
O	1	-0.63582	1.99972	6.62292	0.01318	8.63582
C	2	0.34961	1.99885	3.62750	0.02405	5.65039
C	3	-0.27928	1.99895	4.26217	0.01816	6.27928
C	4	0.08423	1.99904	3.89738	0.01935	5.91577
C	5	0.08951	1.99904	3.88386	0.02758	5.91049
O	6	-0.72379	1.99977	6.70942	0.01460	8.72379
C	7	-0.18203	1.99925	4.16286	0.01992	6.18203
N	8	-0.84848	1.99949	5.83063	0.01836	7.84848
C	9	-0.12821	1.99909	4.11260	0.01652	6.12821
C	10	-0.22191	1.99909	4.20496	0.01787	6.22191
C	11	0.40236	1.99893	3.57166	0.02705	5.59764
O	12	-0.55217	1.99972	6.53943	0.01301	8.55217
H	13	0.51275	0.00000	0.48329	0.00397	0.48725
H	14	0.26242	0.00000	0.73543	0.00216	0.73758
H	15	0.20655	0.00000	0.79062	0.00283	0.79345
H	16	0.49936	0.00000	0.49578	0.00486	0.50064
H	17	0.19160	0.00000	0.80627	0.00213	0.80840
H	18	0.20382	0.00000	0.79421	0.00197	0.79618
H	19	0.38138	0.00000	0.61649	0.00213	0.61862
H	20	0.38963	0.00000	0.60821	0.00215	0.61037
H	21	0.23188	0.00000	0.76624	0.00188	0.76812
H	22	0.25370	0.00000	0.74459	0.00171	0.74630
H	23	0.51289	0.00000	0.48253	0.00457	0.48711
* Total *		1.00000	23.99094	64.74905	0.26002	89.00000

Natural Population			
Core	23.99094	(99.9622% of	24)
Valence	64.74905	(99.6139% of	65)
Natural Minimal Basis	88.73998	(99.7078% of	89)
Natural Rydberg Basis	0.26002	(0.2922% of	89)

Fragment structures

The optimized fragment structures of DA and NE are shown in Fig. S11. Table S8 list the sum of electronic and zero-point energies (E_0) neutral and cationic DA and NE, respectively, at the b3lyp/6-311++g(d,p) level of DFT. All the energies were corrected with zero-point vibrations.

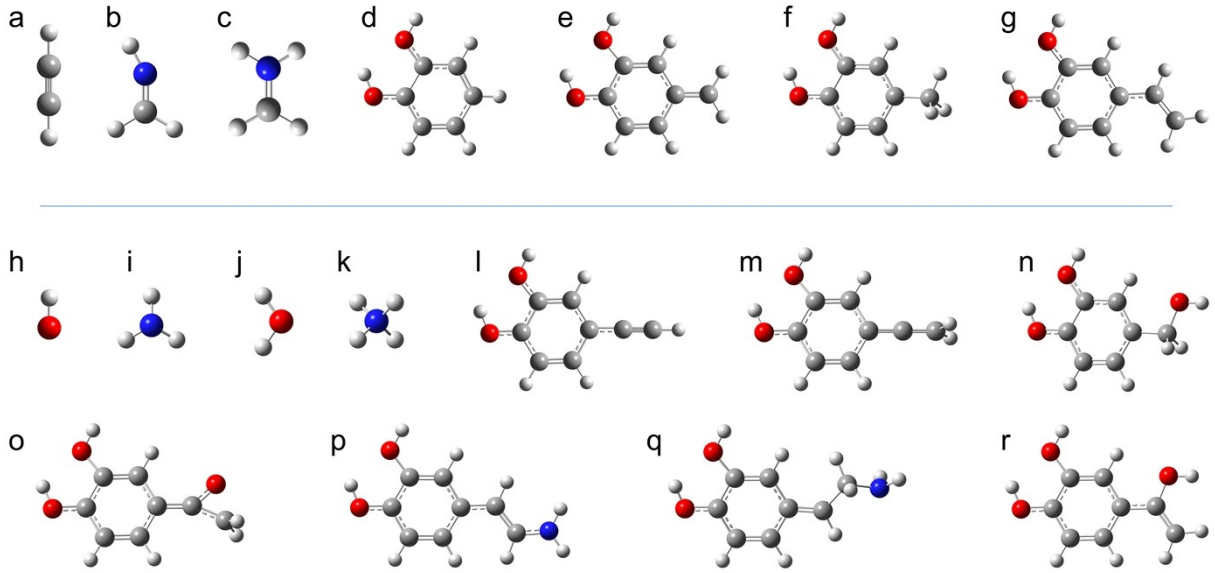


Fig. S11 The optimized fragment structures of (a-g) DA and (h-r) NE. Atoms in dark gray, blue, red and light gray atoms refer to C, N, O and H, respectively.

Table S8. Thermodynamic energies of the optimized fragment structures in Fig. **S11** (hatree).

Molecules	Labels	Energies	
		Neutral	Cationic
DA	Fig. **S11-a**	-77.329678	
	Fig. **S11-b**	-94.622715	-94.261393
	Fig. **S11-c**	-95.187901	-94.951334
	Fig. **S11-d**	-382.699050	-382.405706
	Fig. **S11-e**	-421.361997	-421.117744
	Fig. **S11-f**	-421.998627	-421.716566
	Fig. **S11-g**	-460.085947	-459.810170
NE	Fig. **S11-h**	-75.753961	-75.158167
	Fig. **S11-i**	-56.548470	-56.175409
NE	Fig. **S11-j**	-76.437242	-75.974059
	Fig. **S11-k**	-57.052664	-56.870873
	Fig. **S11-l**	-458.856353	-458.570614
	Fig. **S11-m**	-459.430231	-459.199329
	Fig. **S11-n**	-497.229872	-496.949924
	Fig. **S11-o**	-534.706866	-534.434296
	Fig. **S11-p**	-515.446017	-515.205512
	Fig. **S11-q**	-516.007584	-515.775951
	Fig. **S11-r**	-535.331098	-535.059407

Supplementary results of thermodynamics energy changes

1) Photo-induced 16-amu fragment removal for DA and NE

$$[C_8NO_2H_{11}]^{+\bullet} \rightarrow [C_8O_2H_9]^{+} + NH_2 \qquad \Delta E = 2.21 \text{ eV} \qquad \text{(S1)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8O_3H_9]^{+} + NH_2 \qquad \Delta E = 1.99 \text{ eV} \qquad \text{(S2)}$$

2) Photo-induced 30-amu fragment removal for DA and NE

$$[C_8NO_2H_{11}]^{+\bullet} \rightarrow C_7O_2H_7 + [CNH_4]^{+} \qquad \Delta E = 1.48 \text{ eV} \qquad \text{(S3)}$$

$$[C_8NO_2H_{11}]^{+\bullet} \rightarrow [C_7O_2H_7]^{+} + CNH_4 \qquad \Delta E = 1.69 \text{ eV} \qquad \text{(S4)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow C_7O_3H_7 + [CNH_4]^{+} \qquad \Delta E = 1.39 \text{ eV} \qquad \text{(S5)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_7O_3H_7]^{+} + CNH_4 \qquad \Delta E = 0.99 \text{ eV} \qquad \text{(S6)}$$

3) Photo-induced 17-amu fragment removal for DA and NE

$$[C_8NO_2H_{11}]^{+\bullet} \rightarrow C_8O_2H_8 + [NH_3]^{+\bullet} \qquad \Delta E = 2.89 \text{ eV} \qquad \text{(S7)}$$

$$[C_8NO_2H_{11}]^{+\bullet} \rightarrow [C_8O_2H_8]^{+\bullet} + NH_3 \qquad \Delta E = 0.25 \text{ eV} \qquad \text{(S8)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow C_8O_3H_8 + [NH_3]^{+\bullet} \qquad \Delta E = 2.75 \text{ eV} \qquad \text{(S9)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8O_3H_8]^{+\bullet} + NH_3 \qquad \Delta E = -0.01 \text{ eV} \qquad \text{(S10)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8NO_2H_{10}]^{+} + OH \qquad \Delta E = 2.11 \text{ eV} \qquad \text{(S11)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow C_8NO_2H_{10} + [OH]^{+} \qquad \Delta E = 12.02 \text{ eV} \qquad \text{(S12)}$$

4) Photo-induced secondary dissociation of $[C_8O_2H_8]^+$ fragment for DA

$$[C_8O_2H_8]^{+\bullet} \rightarrow [C_8O_2H_6]^{+\bullet} + C_2H_2 \qquad \Delta E = 1.99 \text{ eV} \qquad \text{(S13)}$$

5) Photo-induced 18-amu fragment removal for NE

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow C_8O_3H_7 + [NH_4]^+ \quad \Delta E = 0.81 \text{ eV} \quad \text{(S14)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8O_3H_7]^+ + NH_4 \quad \Delta E = 3.28 \text{ eV} \quad \text{(S15)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow C_8NO_2H_9 + [H_2O]^{+\bullet} \quad \Delta E = 5.10 \text{ eV} \quad \text{(S16)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8NO_2H_9]^{+\bullet} + H_2O \quad \Delta E = -0.96 \text{ eV} \quad \text{(S17)}$$

6) Photo-induced 29-amu fragment removal for DA and NE

$$[C_8NO_2H_{11}]^{+\bullet} \rightarrow C_7O_2H_8 + [CNH_3]^{+\bullet} \quad \Delta E = 2.93 \text{ eV} \quad \text{(S18)}$$

$$[C_8NO_2H_{11}]^{+\bullet} \rightarrow [C_7O_2H_8]^{+\bullet} + CNH_3 \quad \Delta E = 0.77 \text{ eV} \quad \text{(S19)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_7O_3H_8]^{+\bullet} + CNH_3 \quad \Delta E = 0.95 \text{ eV} \quad \text{(S20)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow C_7O_3H_8 + [CNH_3]^{+\bullet} \quad \Delta E = 3.17 \text{ eV} \quad \text{(S21)}$$

7) Photo-induced 134-amu, 17-amu and 18-amu fragments removal for NE

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8O_2H_6]^{+\bullet} + [H_2O]^{+\bullet} + [NH_3]^{+\bullet} + 2e^- \quad \Delta E = 0.89 \text{ eV} \quad \text{(S22)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8O_2H_6]^{+\bullet} + H_2O + [NH_3]^{+\bullet} + e^- \quad \Delta E = 11.54 \text{ eV} \quad \text{(S23)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow C_8O_2H_6 + [H_2O]^{+\bullet} + [NH_3]^{+\bullet} + e^- \quad \Delta E = 16.37 \text{ eV} \quad \text{(S24)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8O_2H_6]^{+\bullet} + [H_2O]^{+\bullet} + NH_3 + e^- \quad \Delta E = 0.51 \text{ eV} \quad \text{(S25)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8O_2H_6]^{+\bullet} + H_2O + NH_3 \quad \Delta E = 1.39 \text{ eV} \quad \text{(S26)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow C_8O_2H_6 + [H_2O]^{+\bullet} + NH_3 \quad \Delta E = 6.22 \text{ eV} \quad \text{(S27)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow C_8O_2H_6 + H_2O + [NH_3]^{+\bullet} \quad \Delta E = 3.77 \text{ eV} \quad \text{(S28)}$$

8) Photo-induced 135-amu and 17-amu fragments removal for NE

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8O_2H_7]^+ + [OH]^+ + [NH_3]^{+\bullet} + 2e^- \quad \Delta E = 1.07 \text{ eV} \quad \text{(S29)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8O_2H_7]^{+} + [OH]^{+} + NH_3 + e^{-} \quad \Delta E = 0.70 \text{ eV} \quad \text{(S30)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8O_2H_7]^{+} + OH + [NH_3]^{+\bullet} + e^{-} \quad \Delta E = 13.03 \text{ eV} \quad \text{(S31)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow C_8O_2H_7 + [OH]^{+} + [NH_3]^{+\bullet} + e^{-} \quad \Delta E = 22.95 \text{ eV} \quad \text{(S32)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8O_2H_7]^{+} + OH + NH_3 \quad \Delta E = 2.88 \text{ eV} \quad \text{(S33)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow C_8O_2H_7 + [OH]^{+} + NH_3 \quad \Delta E = 12.80 \text{ eV} \quad \text{(S34)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow C_8O_2H_7 + OH + [NH_3]^{+\bullet} \quad \Delta E = 6.74 \text{ eV} \quad \text{(S35)}$$

9) Photo-induced 135-amu, 17-amu and 16-amu fragments removal for NE

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8O_2H_7]^{+} + [H_2O]^{+\bullet} + [NH_2]^{+} + 2e^{-} \quad \Delta E = 1.02 \text{ eV} \quad \text{(S36)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8O_2H_7]^{+} + H_2O + [NH_2]^{+} + e^{-} \quad \Delta E = 15.15 \text{ eV} \quad \text{(S37)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8O_2H_7]^{+} + [H_2O]^{+\bullet} + NH_2 + e^{-} \quad \Delta E = 0.55 \text{ eV} \quad \text{(S38)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow C_8O_2H_7 + [H_2O]^{+\bullet} + [NH_2]^{+} + e^{-} \quad \Delta E = 21.47 \text{ eV} \quad \text{(S39)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow [C_8O_2H_7]^{+} + H_2O + NH_2 \quad \Delta E = 2.43 \text{ eV} \quad \text{(S40)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow C_8O_2H_7 + [H_2O]^{+\bullet} + NH_2 \quad \Delta E = 8.75 \text{ eV} \quad \text{(S41)}$$

$$[C_8NO_3H_{11}]^{+\bullet} \rightarrow C_8O_2H_7 + H_2O + [NH_2]^{+} \quad \Delta E = 8.87 \text{ eV} \quad \text{(S42)}$$

Supplementary results of hydrogen atom transfer (HAT) reaction pathways

As a supplementary information to the reaction pathways discussed in Fig. 4-5 (main text) and considering the likely HAT from other sites, we have also checked the reaction pathways for HAT, as shown below (Fig. S12-16). Comparing with the pathways having provided in the main text; these pathways show a relatively higher

transition-state energies, respectively.

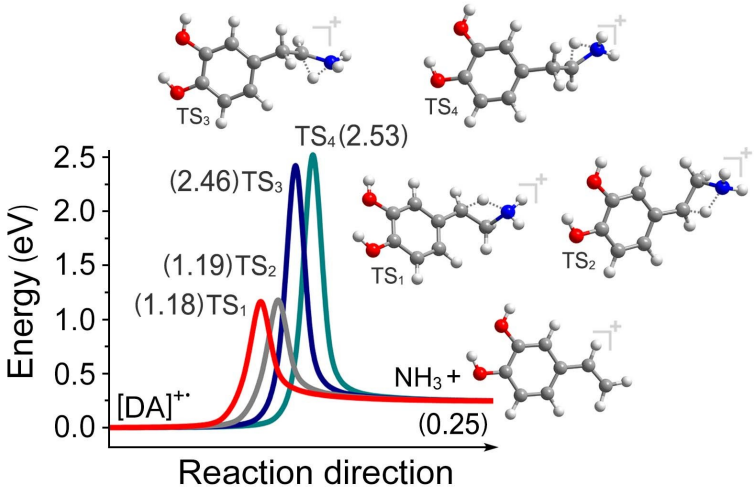


Fig. S12 Fragment pathways toward the NH_3 removal initiated by the HAT for DA. The atoms in dark gray, blue, red and light gray atoms refer to C, N, O and H, respectively.

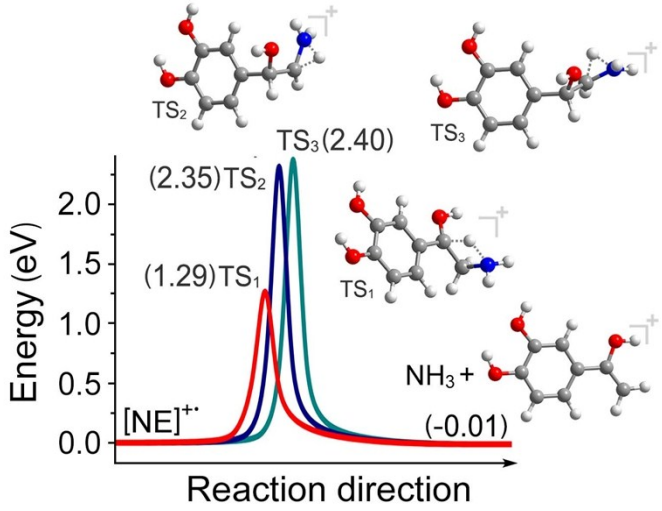


Fig. S13 Fragment pathways toward the NH_3 removal initiated by the HAT for NE. The atoms in dark gray, blue, red and light gray atoms refer to C, N, O and H, respectively.

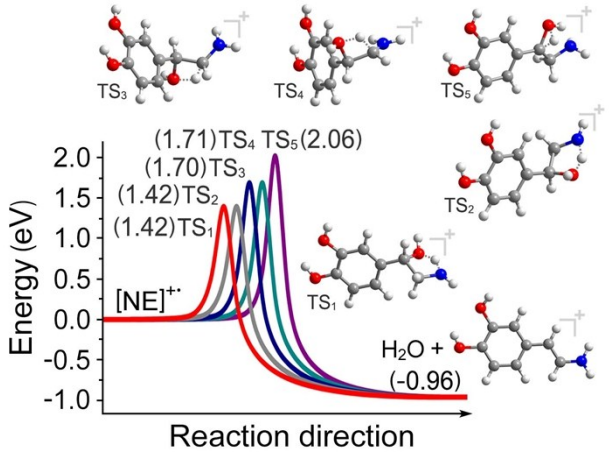


Fig. S14 Fragment pathways toward the H_2O removal initiated by the HAT for NE. The atoms in dark gray, blue, red and light gray atoms refer to C, N, O and H, respectively.

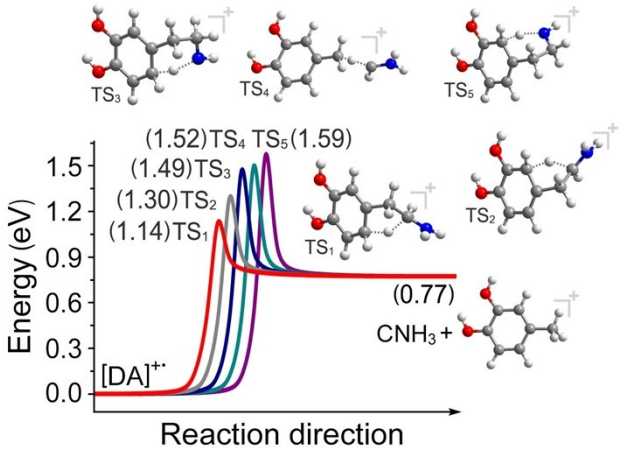


Fig. S15 Fragment pathways toward the CNH_3 removal initiated by the HAT for DA. The atoms in dark gray, blue, red and light gray atoms refer to C, N, O and H, respectively.

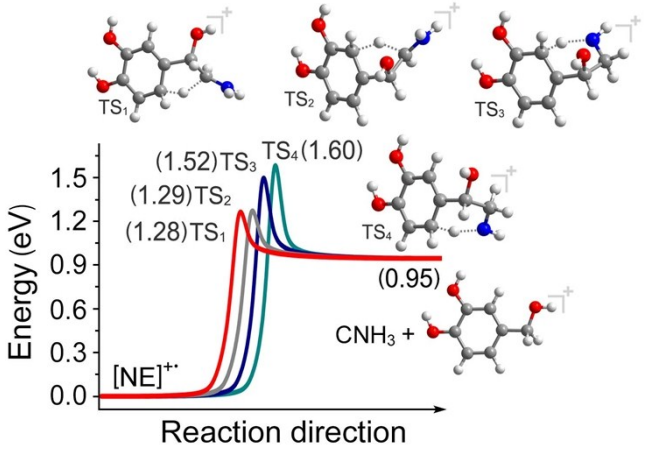


Fig. S16 Fragment pathways toward the CNH_3 removal initiated by the HAT for NE. The atoms in dark gray, blue, red and light gray atoms refer to C, N, O and H, respectively.

Natural bond orbital (NBO) analysis.

Table S9. Second order perturbation theory analysis of Fock matrix in NBO basis for nascent molecule of DA.

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis
Threshold for printing: 0.50 kcal/mol

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(2) eV
315. BD*(2) C 8 - C 10	/304. BD*(2) C 3 - C 6	252.73	10.96
308. BD*(2) C 5 - C 7	/304. BD*(2) C 3 - C 6	157.34	6.82
41. LP (2) O 11	/315. BD*(2) C 8 - C 10	26.58	1.15
39. LP (2) O 9	/308. BD*(2) C 5 - C 7	23.73	1.03
21. BD (2) C 8 - C 10	/308. BD*(2) C 5 - C 7	20.85	0.90
10. BD (2) C 3 - C 6	/315. BD*(2) C 8 - C 10	20.41	0.88
21. BD (2) C 8 - C 10	/304. BD*(2) C 3 - C 6	19.43	0.84
10. BD (2) C 3 - C 6	/308. BD*(2) C 5 - C 7	19.4	0.84
14. BD (2) C 5 - C 7	/304. BD*(2) C 3 - C 6	18.99	0.82
14. BD (2) C 5 - C 7	/315. BD*(2) C 8 - C 10	17.68	0.77
37. LP (1) N 4	/295. BD*(1) C 1 - C 2	8.14	0.35
38. LP (1) O 9	/307. BD*(1) C 5 - C 7	5.99	0.26
40. LP (1) O 11	/313. BD*(1) C 7 - C 10	5.3	0.23
17. BD (1) C 6 - H 19	/302. BD*(1) C 3 - C 5	4.72	0.20
8. BD (1) C 3 - C 5	/312. BD*(1) C 7 - O 9	4.62	0.20
25. BD (1) O 11 - H 22	/314. BD*(1) C 8 - C 10	4.57	0.20
13. BD (1) C 5 - C 7	/313. BD*(1) C 7 - C 10	4.39	0.19
15. BD (1) C 5 - H 18	/303. BD*(1) C 3 - C 6	4.23	0.18
19. BD (1) C 7 - C 10	/307. BD*(1) C 5 - C 7	4.18	0.18
16. BD (1) C 6 - C 8	/318. BD*(1) C 10 - O 11	4.16	0.18
7. BD (1) C 2 - H 15	/302. BD*(1) C 3 - C 5	3.93	0.17
19. BD (1) C 7 - C 10	/314. BD*(1) C 8 - C 10	3.92	0.17
15. BD (1) C 5 - H 18	/313. BD*(1) C 7 - C 10	3.84	0.17
22. BD (1) C 8 - H 20	/313. BD*(1) C 7 - C 10	3.79	0.16
20. BD (1) C 8 - C 10	/313. BD*(1) C 7 - C 10	3.76	0.16
16. BD (1) C 6 - C 8	/299. BD*(1) C 2 - C 3	3.7	0.16
13. BD (1) C 5 - C 7	/302. BD*(1) C 3 - C 5	3.68	0.16
22. BD (1) C 8 - H 20	/303. BD*(1) C 3 - C 6	3.6	0.16
6. BD (1) C 2 - H 14	/303. BD*(1) C 3 - C 6	3.56	0.15
8. BD (1) C 3 - C 5	/307. BD*(1) C 5 - C 7	3.38	0.15
16. BD (1) C 6 - C 8	/303. BD*(1) C 3 - C 6	3.37	0.15
3. BD (1) C 1 - H 12	/306. BD*(1) N 4 - H 17	3.36	0.15
4. BD (1) C 1 - H 13	/305. BD*(1) N 4 - H 16	3.33	0.14
9. BD (1) C 3 - C 6	/302. BD*(1) C 3 - C 5	3.31	0.14
23. BD (1) O 9 - H 21	/313. BD*(1) C 7 - C 10	3.23	0.14
13. BD (1) C 5 - C 7	/299. BD*(1) C 2 - C 3	3.22	0.14
8. BD (1) C 3 - C 5	/303. BD*(1) C 3 - C 6	3.22	0.14
17. BD (1) C 6 - H 19	/314. BD*(1) C 8 - C 10	3.22	0.14
20. BD (1) C 8 - C 10	/312. BD*(1) C 7 - O 9	3.22	0.14
13. BD (1) C 5 - C 7	/318. BD*(1) C 10 - O 11	3.21	0.14
40. LP (1) O 11	/195. RY*(1) C 10	3.2	0.14
10. BD (2) C 3 - C 6	/295. BD*(1) C 1 - C 2	3.18	0.14
9. BD (1) C 3 - C 6	/310. BD*(1) C 6 - C 8	3.09	0.13
304. BD*(2) C 3 - C 6	/129. RY*(3) C 6	2.99	0.13
25. BD (1) O 11 - H 22	/195. RY*(1) C 10	2.95	0.13
9. BD (1) C 3 - C 6	/309. BD*(1) C 5 - H 18	2.89	0.13
38. LP (1) O 9	/144. RY*(1) C 7	2.8	0.12
1. BD (1) C 1 - C 2	/304. BD*(2) C 3 - C 6	2.72	0.12
20. BD (1) C 8 - C 10	/310. BD*(1) C 6 - C 8	2.68	0.12
3. BD (1) C 1 - H 12	/300. BD*(1) C 2 - H 14	2.65	0.11
4. BD (1) C 1 - H 13	/301. BD*(1) C 2 - H 15	2.63	0.11
16. BD (1) C 6 - C 8	/314. BD*(1) C 8 - C 10	2.62	0.11
8. BD (1) C 3 - C 5	/311. BD*(1) C 6 - H 19	2.56	0.11
7. BD (1) C 2 - H 15	/298. BD*(1) C 1 - H 13	2.47	0.11
6. BD (1) C 2 - H 14	/297. BD*(1) C 1 - H 12	2.44	0.11
8. BD (1) C 3 - C 5	/145. RY*(2) C 7	2.43	0.11

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis
Threshold for printing: 0.50 kcal/mol

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	E(2) eV
9. BD (1) C 3 - C 6	/162. RY*(2) C 8	2.35	0.10
5. BD (1) C 2 - C 3	/310. BD*(1) C 6 - C 8	2.34	0.10
9. BD (1) C 3 - C 6	/316. BD*(1) C 8 - H 20	2.25	0.10
19. BD (1) C 7 - C 10	/309. BD*(1) C 5 - H 18	2.25	0.10
20. BD (1) C 8 - C 10	/311. BD*(1) C 6 - H 19	2.25	0.10
5. BD (1) C 2 - C 3	/303. BD*(1) C 3 - C 6	2.23	0.10
36. CR (1) O 11	/195. RY*(1) C 10	2.21	0.10
41. LP (2) O 11	/197. RY*(3) C 10	2.21	0.10
5. BD (1) C 2 - C 3	/296. BD*(1) C 1 - N 4	2.2	0.10
5. BD (1) C 2 - C 3	/307. BD*(1) C 5 - C 7	2.18	0.09
11. BD (1) N 4 - H 16	/298. BD*(1) C 1 - H 13	2.18	0.09
23. BD (1) O 9 - H 21	/144. RY*(1) C 7	2.18	0.09
12. BD (1) N 4 - H 17	/297. BD*(1) C 1 - H 12	2.15	0.09
39. LP (2) O 9	/146. RY*(3) C 7	2.09	0.09
33. CR (1) C 8	/196. RY*(2) C 10	2.07	0.09
5. BD (1) C 2 - C 3	/302. BD*(1) C 3 - C 5	2.03	0.09
9. BD (1) C 3 - C 6	/299. BD*(1) C 2 - C 3	2.03	0.09
34. CR (1) O 9	/144. RY*(1) C 7	2.03	0.09
19. BD (1) C 7 - C 10	/316. BD*(1) C 8 - H 20	2.01	0.09
15. BD (1) C 5 - H 18	/ 76. RY*(1) C 3	1.93	0.08
17. BD (1) C 6 - H 19	/ 76. RY*(1) C 3	1.92	0.08
20. BD (1) C 8 - C 10	/128. RY*(2) C 6	1.88	0.08
304. BD*(2) C 3 - C 6	/295. BD*(1) C 1 - C 2	1.87	0.08
39. LP (2) O 9	/283. RY*(1) H 21	1.86	0.08
41. LP (2) O 11	/289. RY*(1) H 22	1.85	0.08
19. BD (1) C 7 - C 10	/317. BD*(1) O 9 - H 21	1.81	0.08
16. BD (1) C 6 - C 8	/195. RY*(1) C 10	1.78	0.08
10. BD (2) C 3 - C 6	/112. RY*(3) C 5	1.76	0.08
10. BD (2) C 3 - C 6	/163. RY*(3) C 8	1.76	0.08
13. BD (1) C 5 - C 7	/196. RY*(2) C 10	1.76	0.08
35. CR (1) C 10	/145. RY*(2) C 7	1.76	0.08
8. BD (1) C 3 - C 5	/299. BD*(1) C 2 - C 3	1.75	0.08
1. BD (1) C 1 - C 2	/ 77. RY*(2) C 3	1.72	0.07
19. BD (1) C 7 - C 10	/161. RY*(1) C 8	1.68	0.07
31. CR (1) C 6	/ 78. RY*(3) C 3	1.68	0.07
5. BD (1) C 2 - C 3	/127. RY*(1) C 6	1.66	0.07
37. LP (1) N 4	/298. BD*(1) C 1 - H 13	1.64	0.07
37. LP (1) N 4	/ 42. RY*(1) C 1	1.61	0.07
35. CR (1) C 10	/162. RY*(2) C 8	1.6	0.07
32. CR (1) C 7	/195. RY*(1) C 10	1.58	0.07
30. CR (1) C 5	/144. RY*(1) C 7	1.57	0.07
18. BD (1) C 7 - O 9	/314. BD*(1) C 8 - C 10	1.55	0.07
30. CR (1) C 5	/ 78. RY*(3) C 3	1.55	0.07
19. BD (1) C 7 - C 10	/110. RY*(1) C 5	1.53	0.07
37. LP (1) N 4	/297. BD*(1) C 1 - H 12	1.49	0.06
13. BD (1) C 5 - C 7	/ 78. RY*(3) C 3	1.46	0.06
32. CR (1) C 7	/111. RY*(2) C 5	1.44	0.06
20. BD (1) C 8 - C 10	/319. BD*(1) O 11 - H 22	1.41	0.06
28. CR (1) C 3	/128. RY*(2) C 6	1.41	0.06
24. BD (1) C 10 - O 11	/307. BD*(1) C 5 - C 7	1.39	0.06
8. BD (1) C 3 - C 5	/309. BD*(1) C 5 - H 18	1.36	0.06
21. BD (2) C 8 - C 10	/212. RY*(1) O 11	1.35	0.06
8. BD (1) C 3 - C 5	/ 59. RY*(1) C 2	1.34	0.06
10. BD (2) C 3 - C 6	/300. BD*(1) C 2 - H 14	1.32	0.06
33. CR (1) C 8	/128. RY*(2) C 6	1.32	0.06
38. LP (1) O 9	/284. RY*(2) H 21	1.32	0.06

Table S10. Second order perturbation theory analysis of Fock matrix in NBO basis for adiabatic molecule of DA.

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis
Threshold for printing: 0.50 kcal/mol

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	eV
41. LP (2) O 11	/315. BD*(2) C 8 - C 10	13.57	0.59
39. LP (2) O 9	/308. BD*(2) C 5 - C 7	13.32	0.58
10. BD (2) C 3 - C 6	/315. BD*(2) C 8 - C 10	11.72	0.51
10. BD (2) C 3 - C 6	/308. BD*(2) C 5 - C 7	10.09	0.44
21. BD (2) C 8 - C 10	/304. BD*(2) C 3 - C 6	9.66	0.42
21. BD (2) C 8 - C 10	/308. BD*(2) C 5 - C 7	9.53	0.41
14. BD (2) C 5 - C 7	/304. BD*(2) C 3 - C 6	9.24	0.40
14. BD (2) C 5 - C 7	/315. BD*(2) C 8 - C 10	8.23	0.36
37. LP (1) N 4	/295. BD*(1) C 1 - C 2	5.66	0.25
38. LP (1) O 9	/307. BD*(1) C 5 - C 7	3.43	0.15
40. LP (1) O 11	/313. BD*(1) C 7 - C 10	3.24	0.14
8. BD (1) C 3 - C 5	/312. BD*(1) C 7 - O 9	2.4	0.10
25. BD (1) O 11 - H 22	/314. BD*(1) C 8 - C 10	2.4	0.10
17. BD (1) C 6 - H 19	/302. BD*(1) C 3 - C 5	2.23	0.10
15. BD (1) C 5 - H 18	/303. BD*(1) C 3 - C 6	2.22	0.10
15. BD (1) C 5 - H 18	/313. BD*(1) C 7 - C 10	2.12	0.09
6. BD (1) C 2 - H 14	/303. BD*(1) C 3 - C 6	2.07	0.09
7. BD (1) C 2 - H 15	/302. BD*(1) C 3 - C 5	2.07	0.09
22. BD (1) C 8 - H 20	/303. BD*(1) C 3 - C 6	2.02	0.09
10. BD (2) C 3 - C 6	/295. BD*(1) C 1 - C 2	1.97	0.09
1. BD (1) C 1 - C 2	/304. BD*(2) C 3 - C 6	1.92	0.08
22. BD (1) C 8 - H 20	/313. BD*(1) C 7 - C 10	1.92	0.08
3. BD (1) C 1 - H 12	/306. BD*(1) N 4 - H 17	1.91	0.08
40. LP (1) O 11	/195. RY*(1) C 10	1.88	0.08
17. BD (1) C 6 - H 19	/314. BD*(1) C 8 - C 10	1.85	0.08
23. BD (1) O 9 - H 21	/313. BD*(1) C 7 - C 10	1.85	0.08
4. BD (1) C 1 - H 13	/305. BD*(1) N 4 - H 16	1.82	0.08
16. BD (1) C 6 - C 8	/318. BD*(1) C 10 - O 11	1.75	0.08
25. BD (1) O 11 - H 22	/195. RY*(1) C 10	1.68	0.07
13. BD (1) C 5 - C 7	/302. BD*(1) C 3 - C 5	1.67	0.07
41. LP (2) O 11	/197. RY*(3) C 10	1.63	0.07
38. LP (1) O 9	/144. RY*(1) C 7	1.58	0.07
8. BD (1) C 3 - C 5	/307. BD*(1) C 5 - C 7	1.54	0.07
13. BD (1) C 5 - C 7	/313. BD*(1) C 7 - C 10	1.54	0.07
19. BD (1) C 7 - C 10	/307. BD*(1) C 5 - C 7	1.52	0.07
13. BD (1) C 5 - C 7	/299. BD*(1) C 2 - C 3	1.46	0.06
36. CR (1) O 11	/195. RY*(1) C 10	1.46	0.06
16. BD (1) C 6 - C 8	/299. BD*(1) C 2 - C 3	1.42	0.06
39. LP (2) O 9	/145. RY*(2) C 7	1.36	0.06
304. BD*(2) C 3 - C 6	/295. BD*(1) C 1 - C 2	1.31	0.06
9. BD (1) C 3 - C 6	/309. BD*(1) C 5 - H 18	1.3	0.06
9. BD (1) C 3 - C 6	/162. RY*(2) C 8	1.28	0.06
16. BD (1) C 6 - C 8	/303. BD*(1) C 3 - C 6	1.28	0.06
9. BD (1) C 3 - C 6	/310. BD*(1) C 6 - C 8	1.24	0.05
13. BD (1) C 5 - C 7	/318. BD*(1) C 10 - O 11	1.22	0.05
23. BD (1) O 9 - H 21	/144. RY*(1) C 7	1.2	0.05
37. LP (1) N 4	/298. BD*(1) C 1 - H 13	1.2	0.05
304. BD*(2) C 3 - C 6	/129. RY*(3) C 6	1.2	0.05
9. BD (1) C 3 - C 6	/316. BD*(1) C 8 - H 20	1.18	0.05
20. BD (1) C 8 - C 10	/311. BD*(1) C 6 - H 19	1.18	0.05
34. CR (1) O 9	/144. RY*(1) C 7	1.18	0.05
8. BD (1) C 3 - C 5	/146. RY*(3) C 7	1.17	0.05
19. BD (1) C 7 - C 10	/317. BD*(1) O 9 - H 21	1.16	0.05
20. BD (1) C 8 - C 10	/312. BD*(1) C 7 - O 9	1.16	0.05
20. BD (1) C 8 - C 10	/310. BD*(1) C 6 - C 8	1.15	0.05
19. BD (1) C 7 - C 10	/309. BD*(1) C 5 - H 18	1.14	0.05

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis
Threshold for printing: 0.50 kcal/mol

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	eV
19. BD (1) C 7 - C 10	/314. BD*(1) C 8 - C 10	1.13	0.05
5. BD (1) C 2 - C 3	/302. BD*(1) C 3 - C 5	1.07	0.05
9. BD (1) C 3 - C 6	/302. BD*(1) C 3 - C 5	1.07	0.05
8. BD (1) C 3 - C 5	/303. BD*(1) C 3 - C 6	1.05	0.05
16. BD (1) C 6 - C 8	/314. BD*(1) C 8 - C 10	1.04	0.05
5. BD (1) C 2 - C 3	/307. BD*(1) C 5 - C 7	1.03	0.04
20. BD (1) C 8 - C 10	/313. BD*(1) C 7 - C 10	1.01	0.04
21. BD (2) C 8 - C 10	/212. RY*(1) O 11	1.01	0.04
20. BD (1) C 8 - C 10	/128. RY*(2) C 6	0.99	0.04
20. BD (1) C 8 - C 10	/319. BD*(1) O 11 - H 22	0.99	0.04
5. BD (1) C 2 - C 3	/310. BD*(1) C 6 - C 8	0.98	0.04
8. BD (1) C 3 - C 5	/311. BD*(1) C 6 - H 19	0.97	0.04
33. CR (1) C 8	/196. RY*(2) C 10	0.95	0.04
11. BD (1) N 4 - H 16	/298. BD*(1) C 1 - H 13	0.93	0.04
12. BD (1) N 4 - H 17	/297. BD*(1) C 1 - H 12	0.93	0.04
8. BD (1) C 3 - C 5	/299. BD*(1) C 2 - C 3	0.92	0.04
29. CR (1) N 4	/ 44. RY*(3) C 1	0.9	0.04
1. BD (1) C 1 - C 2	/ 77. RY*(2) C 3	0.89	0.04
5. BD (1) C 2 - C 3	/303. BD*(1) C 3 - C 6	0.89	0.04
15. BD (1) C 5 - H 18	/ 76. RY*(1) C 3	0.87	0.04
37. LP (1) N 4	/297. BD*(1) C 1 - H 12	0.87	0.04
4. BD (1) C 1 - H 13	/301. BD*(1) C 2 - H 15	0.86	0.04
19. BD (1) C 7 - C 10	/161. RY*(1) C 8	0.86	0.04
17. BD (1) C 6 - H 19	/ 76. RY*(1) C 3	0.85	0.04
19. BD (1) C 7 - C 10	/316. BD*(1) C 8 - H 20	0.85	0.04
5. BD (1) C 2 - C 3	/127. RY*(1) C 6	0.84	0.04
6. BD (1) C 2 - H 14	/297. BD*(1) C 1 - H 12	0.84	0.04
9. BD (1) C 3 - C 6	/299. BD*(1) C 2 - C 3	0.84	0.04
13. BD (1) C 5 - C 7	/196. RY*(2) C 10	0.84	0.04
41. LP (2) O 11	/290. RY*(2) H 22	0.84	0.04
3. BD (1) C 1 - H 12	/300. BD*(1) C 2 - H 14	0.83	0.04
39. LP (2) O 9	/284. RY*(2) H 21	0.83	0.04
7. BD (1) C 2 - H 15	/298. BD*(1) C 1 - H 13	0.82	0.04
30. CR (1) C 5	/ 78. RY*(3) C 3	0.82	0.04
30. CR (1) C 5	/144. RY*(1) C 7	0.8	0.03
1. BD (1) C 1 - C 2	/ 93. RY*(1) N 4	0.78	0.03
31. CR (1) C 6	/ 78. RY*(3) C 3	0.78	0.03
35. CR (1) C 10	/146. RY*(3) C 7	0.78	0.03
10. BD (2) C 3 - C 6	/112. RY*(3) C 5	0.77	0.03
14. BD (2) C 5 - C 7	/178. RY*(1) O 9	0.77	0.03
35. CR (1) C 10	/162. RY*(2) C 8	0.76	0.03
9. BD (1) C 3 - C 6	/ 59. RY*(1) C 2	0.74	0.03
18. BD (1) C 7 - O 9	/307. BD*(1) C 5 - C 7	0.73	0.03
32. CR (1) C 7	/111. RY*(2) C 5	0.73	0.03
8. BD (1) C 3 - C 5	/ 59. RY*(1) C 2	0.72	0.03
10. BD (2) C 3 - C 6	/163. RY*(3) C 8	0.72	0.03
16. BD (1) C 6 - C 8	/316. BD*(1) C 8 - H 20	0.72	0.03
19. BD (1) C 7 - C 10	/110. RY*(1) C 5	0.71	0.03
38. LP (1) O 9	/283. RY*(1) H 21	0.71	0.03
315. BD*(2) C 8 - C 10	/165. RY*(5) C 8	0.71	0.03
13. BD (1) C 5 - C 7	/ 78. RY*(3) C 3	0.7	0.03
16. BD (1) C 6 - C 8	/195. RY*(1) C 10	0.7	0.03
11. BD (1) N 4 - H 16	/ 44. RY*(3) C 1	0.68	0.03
17. BD (1) C 6 - H 19	/161. RY*(1) C 8	0.68	0.03
18. BD (1) C 7 - O 9	/314. BD*(1) C 8 - C 10	0.68	0.03
28. CR (1) C 3	/128. RY*(2) C 6	0.68	0.03

Table S11. Second order perturbation theory analysis of Fock matrix in NBO basis for nascent molecule of NE.

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis
Threshold for printing: 0.50 kcal/mol

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	eV
338. BD*(2) C 10 - C 11	/325. BD*(2) C 4 - C 9	279.64	12.13
319. BD*(2) C 2 - C 3	/325. BD*(2) C 4 - C 9	231.78	10.05
45. LP (2) O 12	/338. BD*(2) C 10 - C 11	26.65	1.16
40. LP (2) O 1	/319. BD*(2) C 2 - C 3	23.12	1.00
23. BD (2) C 10 - C 11	/319. BD*(2) C 2 - C 3	20.12	0.87
10. BD (2) C 4 - C 9	/338. BD*(2) C 10 - C 11	19.88	0.86
23. BD (2) C 10 - C 11	/325. BD*(2) C 4 - C 9	19.63	0.85
4. BD (2) C 2 - C 3	/325. BD*(2) C 4 - C 9	19.44	0.84
10. BD (2) C 4 - C 9	/319. BD*(2) C 2 - C 3	19.36	0.84
4. BD (2) C 2 - C 3	/338. BD*(2) C 10 - C 11	18.69	0.81
42. LP (2) O 6	/328. BD*(1) C 5 - H 15	9.25	0.40
43. LP (1) N 8	/331. BD*(1) C 7 - H 17	6.16	0.27
39. LP (1) O 1	/318. BD*(1) C 2 - C 3	5.92	0.26
44. LP (1) O 12	/320. BD*(1) C 2 - C 11	5.27	0.23
21. BD (1) C 9 - H 21	/321. BD*(1) C 3 - C 4	4.79	0.21
6. BD (1) C 3 - C 4	/316. BD*(1) O 1 - C 2	4.69	0.20
26. BD (1) O 12 - H 23	/337. BD*(1) C 10 - C 11	4.59	0.20
7. BD (1) C 3 - H 14	/324. BD*(1) C 4 - C 9	4.49	0.19
3. BD (1) C 2 - C 3	/320. BD*(1) C 2 - C 11	4.4	0.19
5. BD (1) C 2 - C 11	/318. BD*(1) C 2 - C 3	4.19	0.18
20. BD (1) C 9 - C 10	/340. BD*(1) C 11 - O 12	4.16	0.18
5. BD (1) C 2 - C 11	/337. BD*(1) C 10 - C 11	3.91	0.17
7. BD (1) C 3 - H 14	/320. BD*(1) C 2 - C 11	3.9	0.17
43. LP (1) N 8	/329. BD*(1) O 6 - H 16	3.83	0.17
22. BD (1) C 10 - C 11	/320. BD*(1) C 2 - C 11	3.76	0.16
24. BD (1) C 10 - H 22	/320. BD*(1) C 2 - C 11	3.75	0.16
9. BD (1) C 4 - C 9	/321. BD*(1) C 3 - C 4	3.74	0.16
3. BD (1) C 2 - C 3	/321. BD*(1) C 3 - C 4	3.73	0.16
6. BD (1) C 3 - C 4	/324. BD*(1) C 4 - C 9	3.66	0.16
16. BD (1) C 7 - H 17	/326. BD*(1) C 5 - O 6	3.64	0.16
24. BD (1) C 10 - H 22	/324. BD*(1) C 4 - C 9	3.58	0.16
20. BD (1) C 9 - C 10	/323. BD*(1) C 4 - C 5	3.47	0.15
20. BD (1) C 9 - C 10	/324. BD*(1) C 4 - C 9	3.47	0.15
13. BD (1) C 5 - H 15	/321. BD*(1) C 3 - C 4	3.42	0.15
6. BD (1) C 3 - C 4	/318. BD*(1) C 2 - C 3	3.26	0.14
2. BD (1) O 1 - H 13	/320. BD*(1) C 2 - C 11	3.24	0.14
3. BD (1) C 2 - C 3	/340. BD*(1) C 11 - O 12	3.22	0.14
21. BD (1) C 9 - H 21	/337. BD*(1) C 10 - C 11	3.2	0.14
22. BD (1) C 10 - C 11	/316. BD*(1) O 1 - C 2	3.2	0.14
44. LP (1) O 12	/216. RY*(1) C 11	3.2	0.14
325. BD*(2) C 4 - C 9	/184. RY*(3) C 9	3.07	0.13
9. BD (1) C 4 - C 9	/335. BD*(1) C 9 - C 10	3.06	0.13
3. BD (1) C 2 - C 3	/323. BD*(1) C 4 - C 5	3.05	0.13
17. BD (1) C 7 - H 18	/333. BD*(1) N 8 - H 19	2.96	0.13
26. BD (1) O 12 - H 23	/216. RY*(1) C 11	2.93	0.13
10. BD (2) C 4 - C 9	/327. BD*(1) C 5 - C 7	2.8	0.12
39. LP (1) O 1	/ 63. RY*(1) C 2	2.8	0.12
13. BD (1) C 5 - H 15	/332. BD*(1) C 7 - H 18	2.7	0.12
22. BD (1) C 10 - C 11	/335. BD*(1) C 9 - C 10	2.7	0.12
9. BD (1) C 4 - C 9	/322. BD*(1) C 3 - H 14	2.66	0.12
20. BD (1) C 9 - C 10	/337. BD*(1) C 10 - C 11	2.6	0.11
43. LP (1) N 8	/327. BD*(1) C 5 - C 7	2.59	0.11
6. BD (1) C 3 - C 4	/336. BD*(1) C 9 - H 21	2.58	0.11
17. BD (1) C 7 - H 18	/328. BD*(1) C 5 - H 15	2.5	0.11
12. BD (1) C 5 - C 7	/325. BD*(2) C 4 - C 9	2.49	0.11
42. LP (2) O 6	/327. BD*(1) C 5 - C 7	2.48	0.11

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis
Threshold for printing: 0.50 kcal/mol

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	eV
14. BD (1) O 6 - H 16	/323. BD*(1) C 4 - C 5	2.47	0.11
9. BD (1) C 4 - C 9	/200. RY*(2) C 10	2.39	0.10
9. BD (1) C 4 - C 9	/339. BD*(1) C 10 - H 22	2.31	0.10
22. BD (1) C 10 - C 11	/336. BD*(1) C 9 - H 21	2.31	0.10
8. BD (1) C 4 - C 5	/335. BD*(1) C 9 - C 10	2.26	0.10
38. CR (1) O 12	/216. RY*(1) C 11	2.21	0.10
45. LP (2) O 12	/218. RY*(3) C 11	2.2	0.10
2. BD (1) O 1 - H 13	/ 63. RY*(1) C 2	2.18	0.09
41. LP (1) O 6	/327. BD*(1) C 5 - C 7	2.18	0.09
6. BD (1) C 3 - C 4	/ 64. RY*(2) C 2	2.16	0.09
5. BD (1) C 2 - C 11	/322. BD*(1) C 3 - H 14	2.14	0.09
21. BD (1) C 9 - H 21	/ 97. RY*(1) C 4	2.13	0.09
36. CR (1) C 10	/217. RY*(2) C 11	2.07	0.09
8. BD (1) C 4 - C 5	/318. BD*(1) C 2 - C 3	2.05	0.09
8. BD (1) C 4 - C 5	/324. BD*(1) C 4 - C 9	2.05	0.09
8. BD (1) C 4 - C 5	/321. BD*(1) C 3 - C 4	2.04	0.09
11. BD (1) C 5 - O 6	/324. BD*(1) C 4 - C 9	2.04	0.09
5. BD (1) C 2 - C 11	/339. BD*(1) C 10 - H 22	2.02	0.09
10. BD (2) C 4 - C 9	/ 82. RY*(3) C 3	2.01	0.09
27. CR (1) O 1	/ 63. RY*(1) C 2	2.01	0.09
325. BD*(2) C 4 - C 9	/327. BD*(1) C 5 - C 7	1.98	0.09
40. LP (2) O 1	/ 65. RY*(3) C 2	1.96	0.08
22. BD (1) C 10 - C 11	/183. RY*(2) C 9	1.95	0.08
41. LP (1) O 6	/114. RY*(1) C 5	1.95	0.08
18. BD (1) N 8 - H 19	/148. RY*(1) C 7	1.94	0.08
3. BD (1) C 2 - C 3	/ 97. RY*(1) C 4	1.93	0.08
29. CR (1) C 3	/ 98. RY*(2) C 4	1.92	0.08
18. BD (1) N 8 - H 19	/332. BD*(1) C 7 - H 18	1.85	0.08
20. BD (1) C 9 - C 10	/ 98. RY*(2) C 4	1.84	0.08
8. BD (1) C 4 - C 5	/182. RY*(1) C 9	1.82	0.08
20. BD (1) C 9 - C 10	/216. RY*(1) C 11	1.82	0.08
8. BD (1) C 4 - C 5	/330. BD*(1) C 7 - N 8	1.8	0.08
45. LP (2) O 12	/310. RY*(1) H 23	1.78	0.08
9. BD (1) C 4 - C 9	/323. BD*(1) C 4 - C 5	1.77	0.08
12. BD (1) C 5 - C 7	/334. BD*(1) N 8 - H 20	1.77	0.08
5. BD (1) C 2 - C 11	/317. BD*(1) O 1 - H 13	1.76	0.08
3. BD (1) C 2 - C 3	/217. RY*(2) C 11	1.75	0.08
40. LP (2) O 1	/250. RY*(1) H 13	1.71	0.07
10. BD (2) C 4 - C 9	/201. RY*(3) C 10	1.7	0.07
6. BD (1) C 3 - C 4	/323. BD*(1) C 4 - C 5	1.67	0.07
19. BD (1) N 8 - H 20	/327. BD*(1) C 5 - C 7	1.67	0.07
5. BD (1) C 2 - C 11	/199. RY*(1) C 10	1.66	0.07
42. LP (2) O 6	/269. RY*(2) H 16	1.66	0.07
5. BD (1) C 2 - C 11	/ 80. RY*(1) C 3	1.64	0.07
7. BD (1) C 3 - H 14	/ 97. RY*(1) C 4	1.63	0.07
37. CR (1) C 11	/200. RY*(2) C 10	1.6	0.07
28. CR (1) C 2	/216. RY*(1) C 11	1.58	0.07
1. BD (1) O 1 - C 2	/337. BD*(1) C 10 - C 11	1.57	0.07
37. CR (1) C 11	/ 64. RY*(2) C 2	1.57	0.07
15. BD (1) C 7 - N 8	/323. BD*(1) C 4 - C 5	1.56	0.07
28. CR (1) C 2	/ 81. RY*(2) C 3	1.56	0.07
29. CR (1) C 3	/ 63. RY*(1) C 2	1.56	0.07
6. BD (1) C 3 - C 4	/322. BD*(1) C 3 - H 14	1.49	0.06
35. CR (1) C 9	/ 97. RY*(1) C 4	1.44	0.06
22. BD (1) C 10 - C 11	/341. BD*(1) O 12 - H 23	1.41	0.06
25. BD (1) C 11 - O 12	/318. BD*(1) C 2 - C 3	1.39	0.06

Table S12. Second order perturbation theory analysis of Fock matrix in NBO basis for adiabatic molecule of NE.

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis
Threshold for printing: 0.50 kcal/mol

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	eV
320. BD*(2) C 2 - C 11	/322. BD*(2) C 3 - C 4	35.47	1.54
320. BD*(2) C 2 - C 11	/336. BD*(2) C 9 - C 10	28.65	1.24
45. LP (2) O 12	/320. BD*(2) C 2 - C 11	14.83	0.64
40. LP (2) O 1	/320. BD*(2) C 2 - C 11	13.81	0.60
7. BD (2) C 3 - C 4	/320. BD*(2) C 2 - C 11	11.83	0.51
21. BD (2) C 9 - C 10	/320. BD*(2) C 2 - C 11	9.89	0.43
5. BD (2) C 2 - C 11	/322. BD*(2) C 3 - C 4	9.67	0.42
7. BD (2) C 3 - C 4	/336. BD*(2) C 9 - C 10	9.2	0.40
5. BD (2) C 2 - C 11	/336. BD*(2) C 9 - C 10	9.19	0.40
21. BD (2) C 9 - C 10	/322. BD*(2) C 3 - C 4	9.09	0.39
42. LP (2) O 6	/328. BD*(1) C 5 - H 15	5.25	0.23
39. LP (1) O 1	/318. BD*(1) C 2 - C 3	3.4	0.15
44. LP (1) O 12	/319. BD*(1) C 2 - C 11	3.32	0.14
43. LP (1) N 8	/329. BD*(1) O 6 - H 16	2.7	0.12
43. LP (1) N 8	/331. BD*(1) C 7 - H 17	2.62	0.11
43. LP (1) N 8	/327. BD*(1) C 5 - C 7	2.53	0.11
8. BD (1) C 3 - H 14	/325. BD*(1) C 4 - C 9	2.42	0.10
6. BD (1) C 3 - C 4	/316. BD*(1) O 1 - C 2	2.41	0.10
26. BD (1) O 12 - H 23	/338. BD*(1) C 10 - C 11	2.39	0.10
22. BD (1) C 9 - H 21	/321. BD*(1) C 3 - C 4	2.21	0.10
8. BD (1) C 3 - H 14	/319. BD*(1) C 2 - C 11	2.17	0.09
24. BD (1) C 10 - H 22	/325. BD*(1) C 4 - C 9	2.03	0.09
2. BD (1) O 1 - H 13	/319. BD*(1) C 2 - C 11	1.93	0.08
22. BD (1) C 9 - H 21	/338. BD*(1) C 10 - C 11	1.91	0.08
24. BD (1) C 10 - H 22	/319. BD*(1) C 2 - C 11	1.91	0.08
44. LP (1) O 12	/216. RY*(1) C 11	1.88	0.08
322. BD*(2) C 3 - C 4	/ 82. RY*(3) C 3	1.83	0.08
7. BD (2) C 3 - C 4	/327. BD*(1) C 5 - C 7	1.75	0.08
26. BD (1) O 12 - H 23	/216. RY*(1) C 11	1.73	0.08
20. BD (1) C 9 - C 10	/340. BD*(1) C 11 - O 12	1.72	0.07
42. LP (2) O 6	/327. BD*(1) C 5 - C 7	1.72	0.07
45. LP (2) O 12	/218. RY*(3) C 11	1.7	0.07
3. BD (1) C 2 - C 3	/321. BD*(1) C 3 - C 4	1.68	0.07
39. LP (1) O 1	/ 63. RY*(1) C 2	1.64	0.07
16. BD (1) C 7 - H 17	/326. BD*(1) C 5 - O 6	1.51	0.07
14. BD (1) O 6 - H 16	/324. BD*(1) C 4 - C 5	1.5	0.07
38. CR (1) O 12	/216. RY*(1) C 11	1.5	0.07
40. LP (2) O 1	/ 64. RY*(2) C 2	1.47	0.06
6. BD (1) C 3 - C 4	/318. BD*(1) C 2 - C 3	1.46	0.06
12. BD (1) C 5 - C 7	/322. BD*(2) C 3 - C 4	1.46	0.06
13. BD (1) C 5 - H 15	/321. BD*(1) C 3 - C 4	1.44	0.06
13. BD (1) C 5 - H 15	/322. BD*(2) C 3 - C 4	1.44	0.06
41. LP (1) O 6	/114. RY*(1) C 5	1.44	0.06
3. BD (1) C 2 - C 3	/319. BD*(1) C 2 - C 11	1.37	0.06
4. BD (1) C 2 - C 11	/318. BD*(1) C 2 - C 3	1.36	0.06
3. BD (1) C 2 - C 3	/324. BD*(1) C 4 - C 5	1.34	0.06
17. BD (1) C 7 - H 18	/333. BD*(1) N 8 - H 19	1.33	0.06
10. BD (1) C 4 - C 9	/200. RY*(2) C 10	1.31	0.06
2. BD (1) O 1 - H 13	/ 63. RY*(1) C 2	1.25	0.05
20. BD (1) C 9 - C 10	/324. BD*(1) C 4 - C 5	1.25	0.05
41. LP (1) O 6	/327. BD*(1) C 5 - C 7	1.25	0.05
20. BD (1) C 9 - C 10	/325. BD*(1) C 4 - C 9	1.24	0.05
10. BD (1) C 4 - C 9	/323. BD*(1) C 3 - H 14	1.23	0.05
27. CR (1) O 1	/ 63. RY*(1) C 2	1.23	0.05
10. BD (1) C 4 - C 9	/339. BD*(1) C 10 - H 22	1.22	0.05
11. BD (1) C 5 - O 6	/325. BD*(1) C 4 - C 9	1.22	0.05

Second Order Perturbation Theory Analysis of Fock Matrix in NBO Basis
Threshold for printing: 0.50 kcal/mol

Donor NBO (i)	Acceptor NBO (j)	E(2) kcal/mol	eV
23. BD (1) C 10 - C 11	/337. BD*(1) C 9 - H 21	1.2	0.05
7. BD (2) C 3 - C 4	/328. BD*(1) C 5 - H 15	1.19	0.05
3. BD (1) C 2 - C 3	/340. BD*(1) C 11 - O 12	1.18	0.05
4. BD (1) C 2 - C 11	/317. BD*(1) O 1 - H 13	1.18	0.05
10. BD (1) C 4 - C 9	/335. BD*(1) C 9 - C 10	1.16	0.05
23. BD (1) C 10 - C 11	/335. BD*(1) C 9 - C 10	1.13	0.05
6. BD (1) C 3 - C 4	/ 65. RY*(3) C 2	1.12	0.05
10. BD (1) C 4 - C 9	/321. BD*(1) C 3 - C 4	1.11	0.05
9. BD (1) C 4 - C 5	/318. BD*(1) C 2 - C 3	1.1	0.05
23. BD (1) C 10 - C 11	/316. BD*(1) O 1 - C 2	1.1	0.05
6. BD (1) C 3 - C 4	/325. BD*(1) C 4 - C 9	1.09	0.05
4. BD (1) C 2 - C 11	/323. BD*(1) C 3 - H 14	1.08	0.05
13. BD (1) C 5 - H 15	/332. BD*(1) C 7 - H 18	1.03	0.04
23. BD (1) C 10 - C 11	/183. RY*(2) C 9	1.03	0.04
23. BD (1) C 10 - C 11	/341. BD*(1) O 12 - H 23	1.03	0.04
32. CR (1) O 6	/114. RY*(1) C 5	1.03	0.04
29. CR (1) C 3	/ 98. RY*(2) C 4	1.01	0.04
4. BD (1) C 2 - C 11	/338. BD*(1) C 10 - C 11	1	0.04
9. BD (1) C 4 - C 5	/321. BD*(1) C 3 - C 4	1	0.04
20. BD (1) C 9 - C 10	/338. BD*(1) C 10 - C 11	0.99	0.04
9. BD (1) C 4 - C 5	/335. BD*(1) C 9 - C 10	0.95	0.04
22. BD (1) C 9 - H 21	/ 97. RY*(1) C 4	0.95	0.04
6. BD (1) C 3 - C 4	/337. BD*(1) C 9 - H 21	0.94	0.04
36. CR (1) C 10	/217. RY*(2) C 11	0.93	0.04
5. BD (2) C 2 - C 11	/233. RY*(1) O 12	0.92	0.04
3. BD (1) C 2 - C 3	/ 97. RY*(1) C 4	0.91	0.04
17. BD (1) C 7 - H 18	/328. BD*(1) C 5 - H 15	0.9	0.04
23. BD (1) C 10 - C 11	/319. BD*(1) C 2 - C 11	0.88	0.04
9. BD (1) C 4 - C 5	/182. RY*(1) C 9	0.86	0.04
4. BD (1) C 2 - C 11	/199. RY*(1) C 10	0.85	0.04
4. BD (1) C 2 - C 11	/339. BD*(1) C 10 - H 22	0.85	0.04
322. BD*(2) C 3 - C 4	/327. BD*(1) C 5 - C 7	0.85	0.04
3. BD (1) C 2 - C 3	/217. RY*(2) C 11	0.83	0.04
6. BD (1) C 3 - C 4	/324. BD*(1) C 4 - C 5	0.83	0.04
45. LP (2) O 12	/311. RY*(2) H 23	0.83	0.04
28. CR (1) C 2	/ 81. RY*(2) C 3	0.82	0.04
336. BD*(2) C 9 - C 10	/201. RY*(3) C 10	0.82	0.04
5. BD (2) C 2 - C 11	/ 46. RY*(1) O 1	0.81	0.04
8. BD (1) C 3 - H 14	/321. BD*(1) C 3 - C 4	0.81	0.04
20. BD (1) C 9 - C 10	/ 98. RY*(2) C 4	0.81	0.04
7. BD (2) C 3 - C 4	/184. RY*(3) C 9	0.8	0.03
40. LP (2) O 1	/251. RY*(2) H 13	0.8	0.03
18. BD (1) N 8 - H 19	/148. RY*(1) C 7	0.79	0.03
18. BD (1) N 8 - H 19	/332. BD*(1) C 7 - H 18	0.79	0.03
29. CR (1) C 3	/ 63. RY*(1) C 2	0.78	0.03
320. BD*(2) C 2 - C 11	/ 70. RY*(8) C 2	0.78	0.03
6. BD (1) C 3 - C 4	/323. BD*(1) C 3 - H 14	0.77	0.03
12. BD (1) C 5 - C 7	/334. BD*(1) N 8 - H 20	0.76	0.03
4. BD (1) C 2 - C 11	/ 80. RY*(1) C 3	0.74	0.03
37. CR (1) C 11	/200. RY*(2) C 10	0.74	0.03
42. LP (2) O 6	/269. RY*(2) H 16	0.74	0.03
8. BD (1) C 3 - H 14	/ 97. RY*(1) C 4	0.73	0.03
20. BD (1) C 9 - C 10	/339. BD*(1) C 10 - H 22	0.73	0.03
10. BD (1) C 4 - C 9	/114. RY*(1) C 5	0.72	0.03
1. BD (1) O 1 - C 2	/318. BD*(1) C 2 - C 3	0.71	0.03
10. BD (1) C 4 - C 9	/326. BD*(1) C 5 - O 6	0.71	0.03

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