

Electronic Supplementary Information

π Complexes in the Benzidine Rearrangement

Shinichi Yamabe* Hazuki Nakata and Shoko Yamazaki

Department of Chemistry, Nara University of Education, Takabatake-cho, Nara 630-8528,

Japan

yamabes@nara-edu.ac.jp

Table of Contents

Scheme S1. Geometry models to seek isomers of π complexes.	S3
Scheme S2. Canonical resonance structures which stabilize the transition state of [3,3] sigmatropy (Claisen) rearrangement.	S4
Scheme S3. The charge-transfer (CT) interaction to support the Dewar's π complex derived from mono-protonated 2,2'-dimethoxyhydrazobenzene (14H⁺).	S4
Figure S1. Geometric changes along the path from the protonated parent hydrazobenzene (1H⁺) to the protonated benzidine (2H⁺), which corresponds to Scheme 9.	S5-S11
Figure S2. The water-free geometry of the π complex int2a is converted to the other one with the C-C covalent bond.	S11
Figure S3. Geometric changes along the path from the intermediate Int5 to the protonated diphenylene (3H⁺), which corresponds to Scheme 10.	S12-S15
Figure S4. Geometric changes along the path from the intermediate Int5 to the protonated <i>o</i> -semidine (7H⁺ X=H), which corresponds to Scheme 11.	S16-S17
Figure S5. Geometric changes along the path from the protonated parent hydrazobenzene (1H⁺) to the protonated 2,2'-diamino-biphenyl (16H⁺), which corresponds to Scheme 12.	S18-S21
Figure S6. Optimization results of initial geometries rotated along the way shown in Scheme	

S1.

S22

Figure S7. Optimization results of initial geometries shifted along the way shown in Scheme

S1.

S23

Figure S8. Two Claisen rearrangements in the mono-protonated form.

S24

Figure S9. The gas-phase π complex of the mono-protonated 2,2'-dimethoxy-hydrazobenzene.

The left geometry is an assumed one which is taken from that of the π complex one in Figure

3.

S25

Figure S10. A π complex intermediate of the mono-protonated hydrazobenzene is absent. The

left geometry is an assumed one which is taken from that of the π complex one in Figure 3.

S25

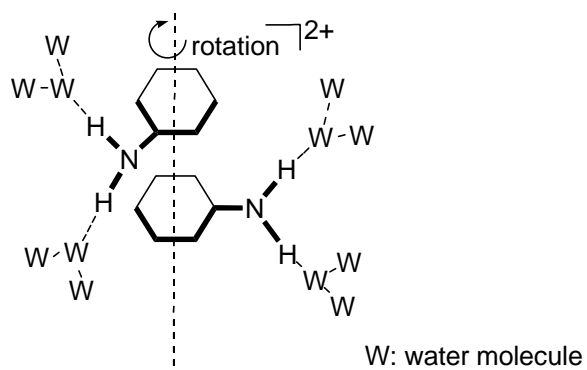
Figure S11. Geometric changes via disproportionation (Scheme 5) in a system composed of the π complex of the di-protonated 4,4'-dichlorohydrazobenzene and a neutral one.

S26-S27

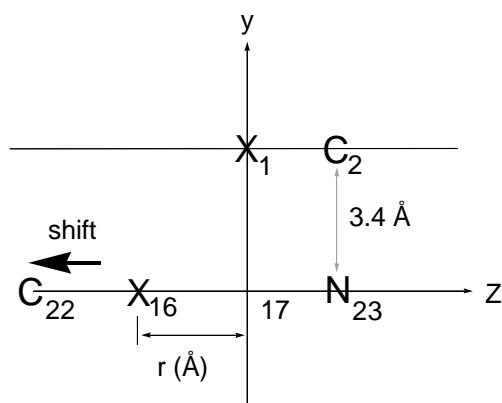
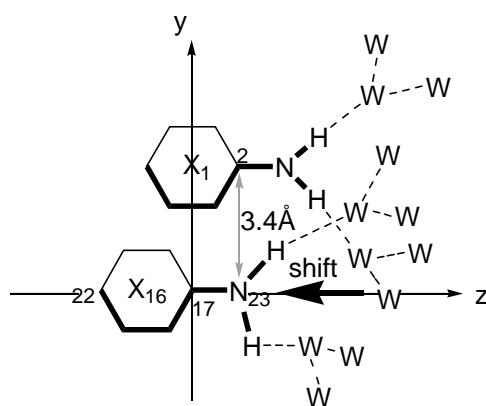
Figure S12. Geometries of two mono-protonated π complexes in the system of 2-methoxyhydrazobenzene and $(\text{H}_3\text{O}^+)_2(\text{H}_2\text{O})_{10}$.

S28

Type 1
Rotation

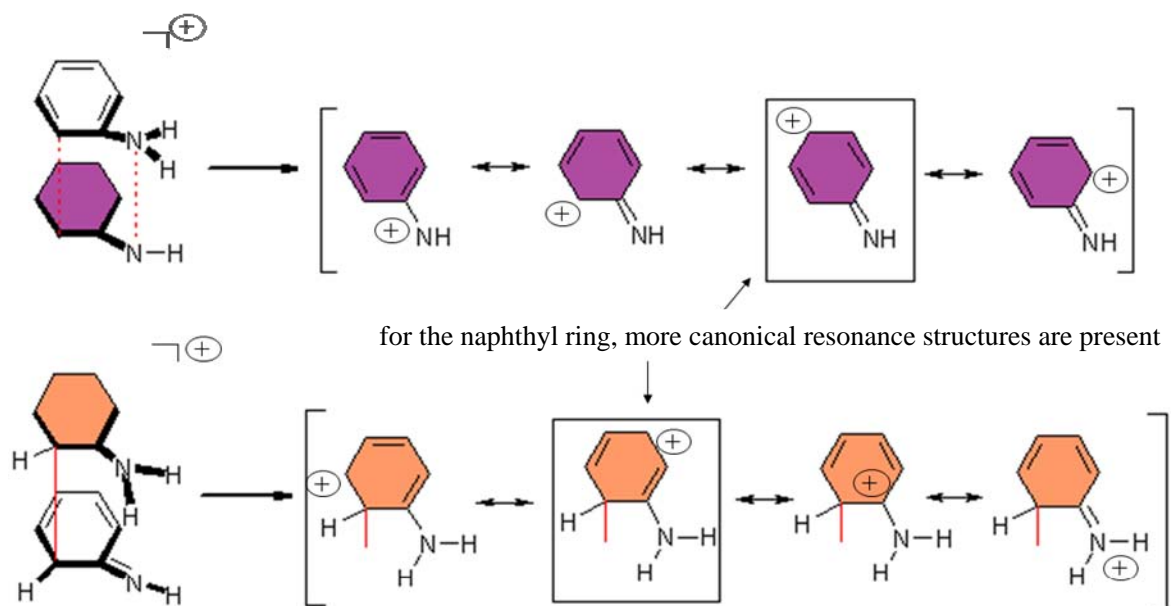


Type 2
Shift

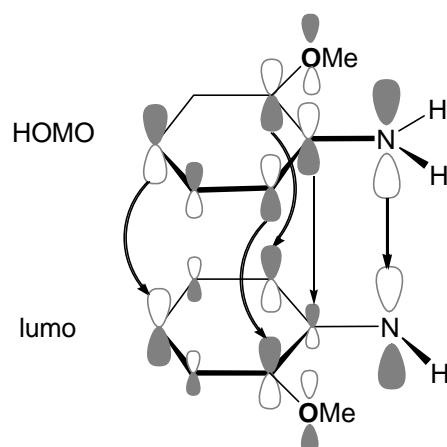


side view

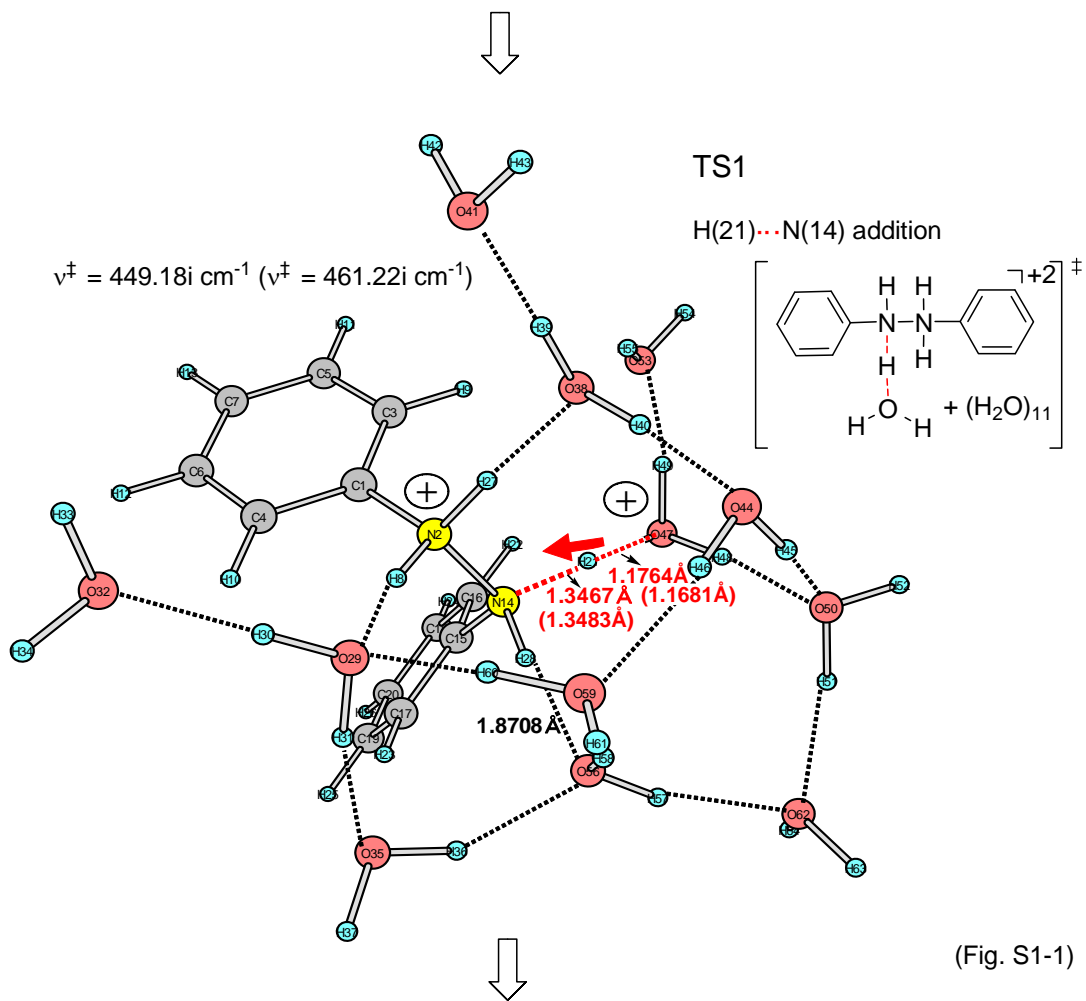
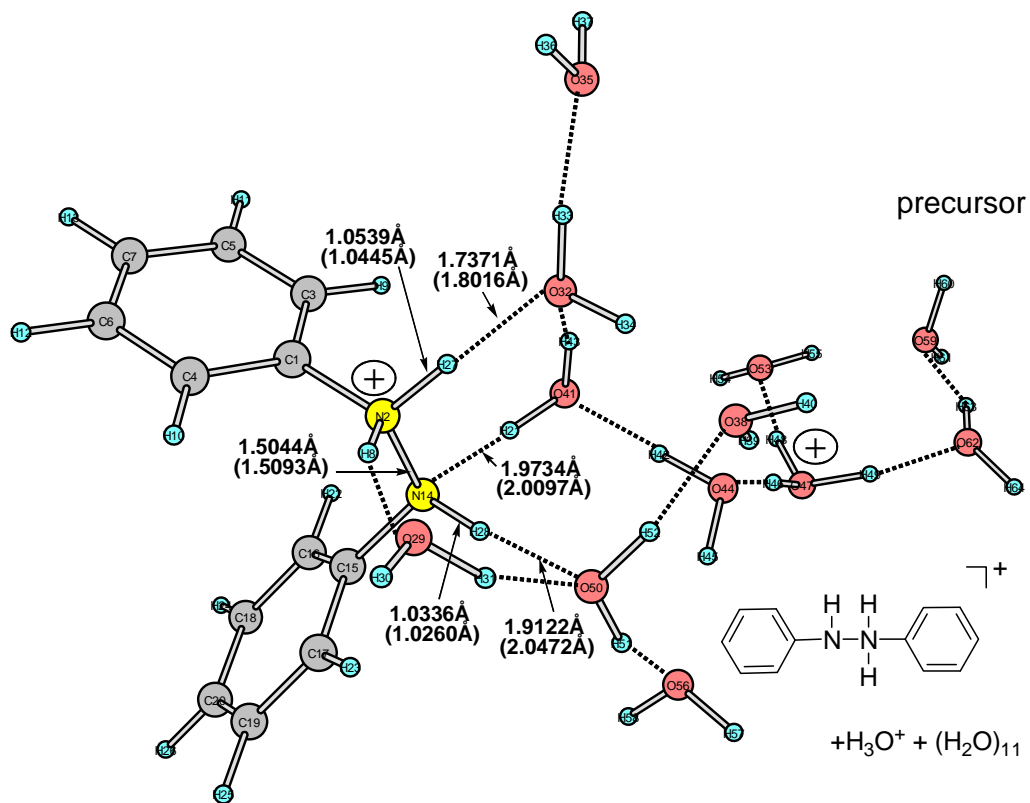
Scheme S1. Geometry models to seek isomers of π complexes.



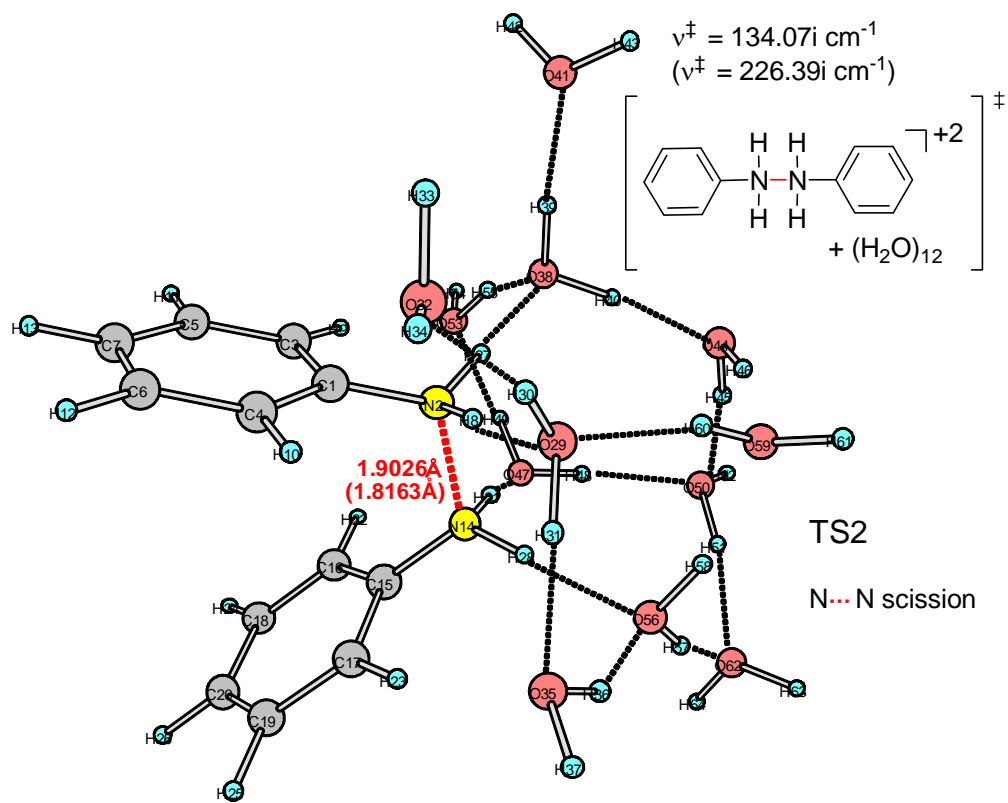
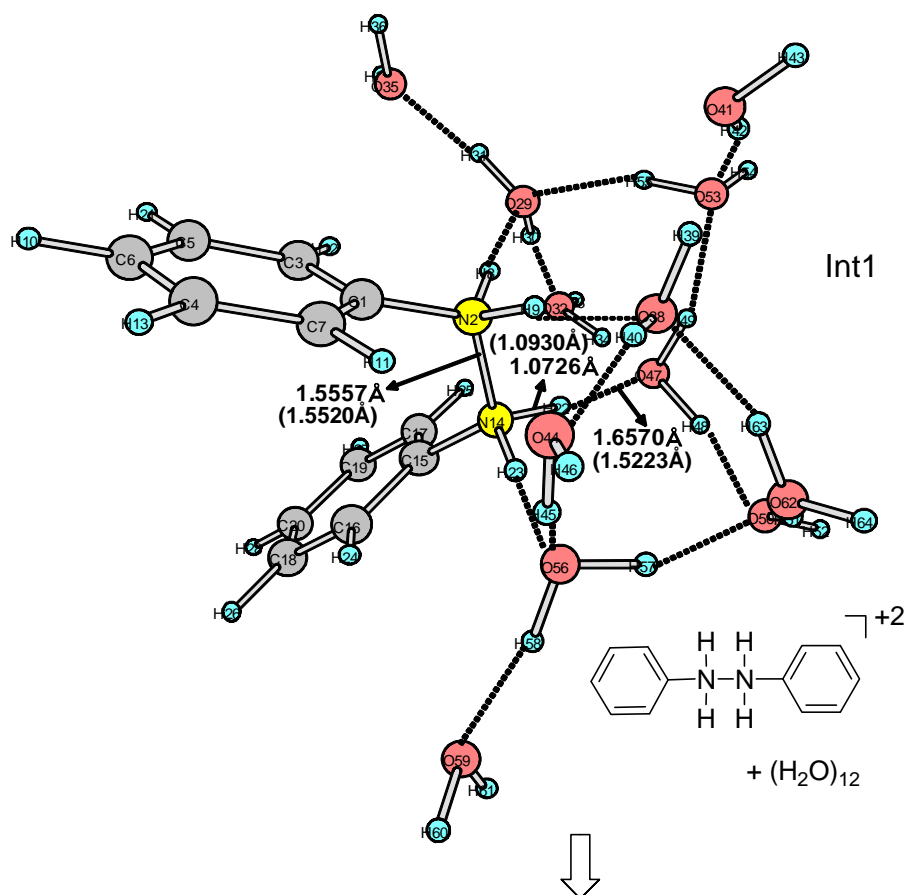
Scheme S2. Canonical resonance structures which stabilize the transition state of [3,3] sigmatropy (Claisen) rearrangement.



Scheme S3. The charge-transfer (CT) interaction to support the Dewar's π complex derived from mono-protonated 2,2'-dimethoxyhydrazobenzene ($\mathbf{14H}^+$). The Dewar's mono-protonated π complex shown by (ii) in Scheme 2 has been obtained in the substrate, 2,2'-dimethoxyhydrazobenzene (Figure 3). The complex may be present even in the gas phase (Figure S9). However, the complex is absent for the parent substrate, $\mathbf{1H}^+$ (Figure S10). The mono-protonated complex arises from CT from HOMO of 2-methoxyaniline to lumo of its H⁻ subtracted form (2-MeO-C₆H₄=NH⁺) (Scheme S3). One methoxy group gives the aniline higher donor ability, and the other relaxes the cation destabilization. Thus, the two methoxy groups may give the donor-acceptor Dewar's π complex. On the other hand, the π complex from the parent hydrazobenzene is supported by the non-classical mutual charge transfer in the di-protonated form.

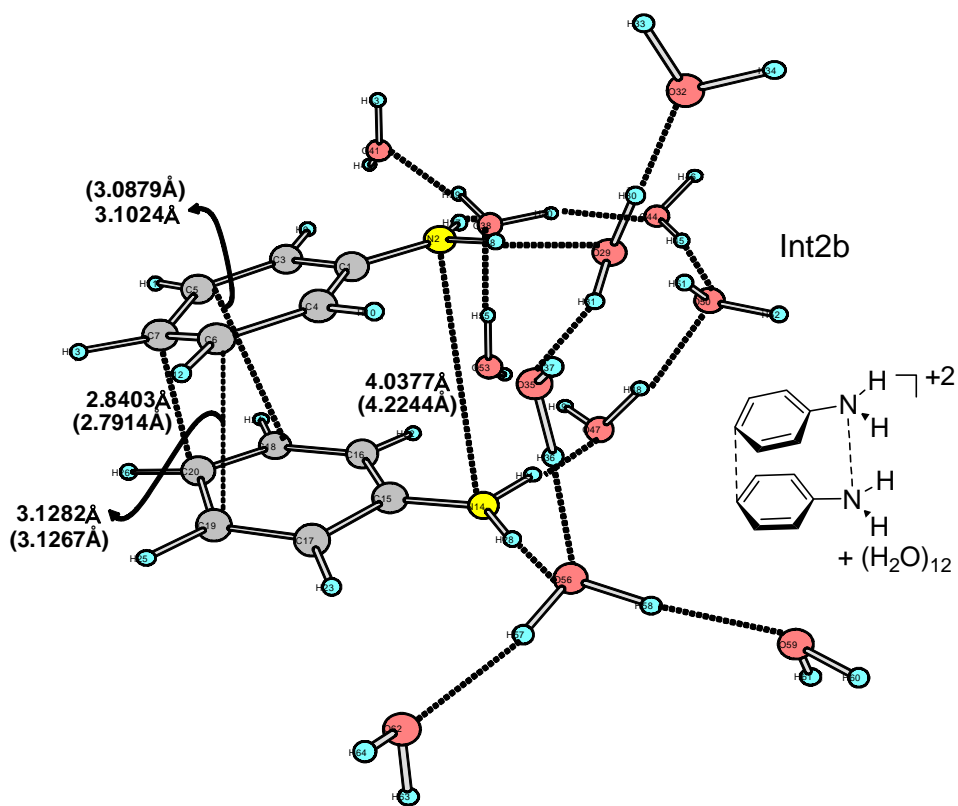
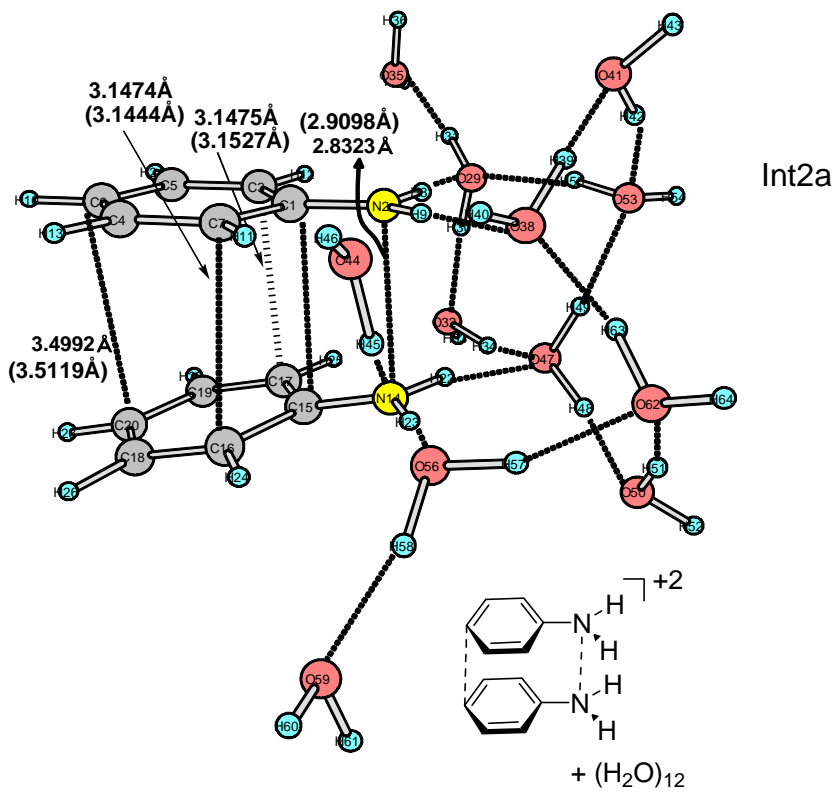


S5

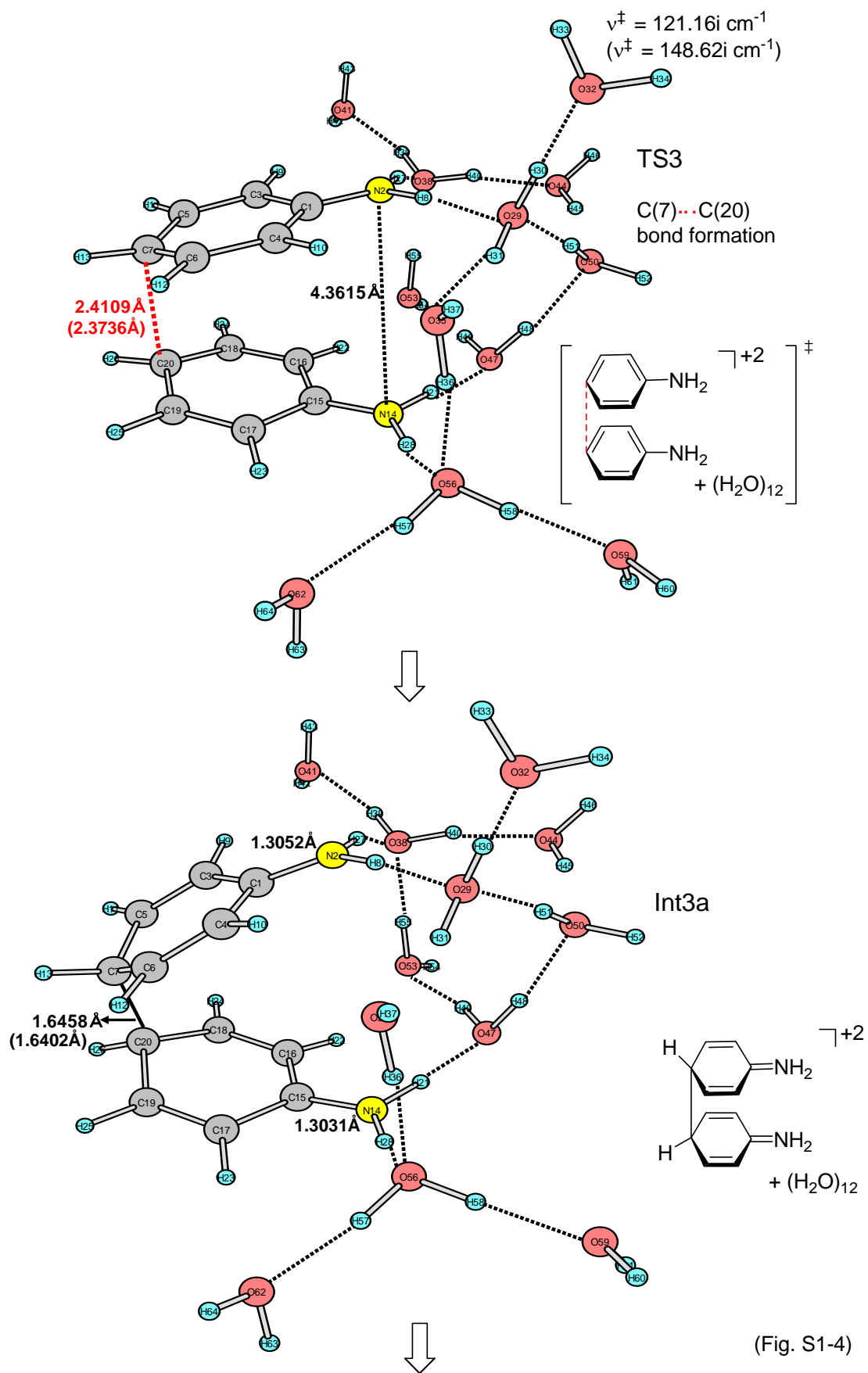


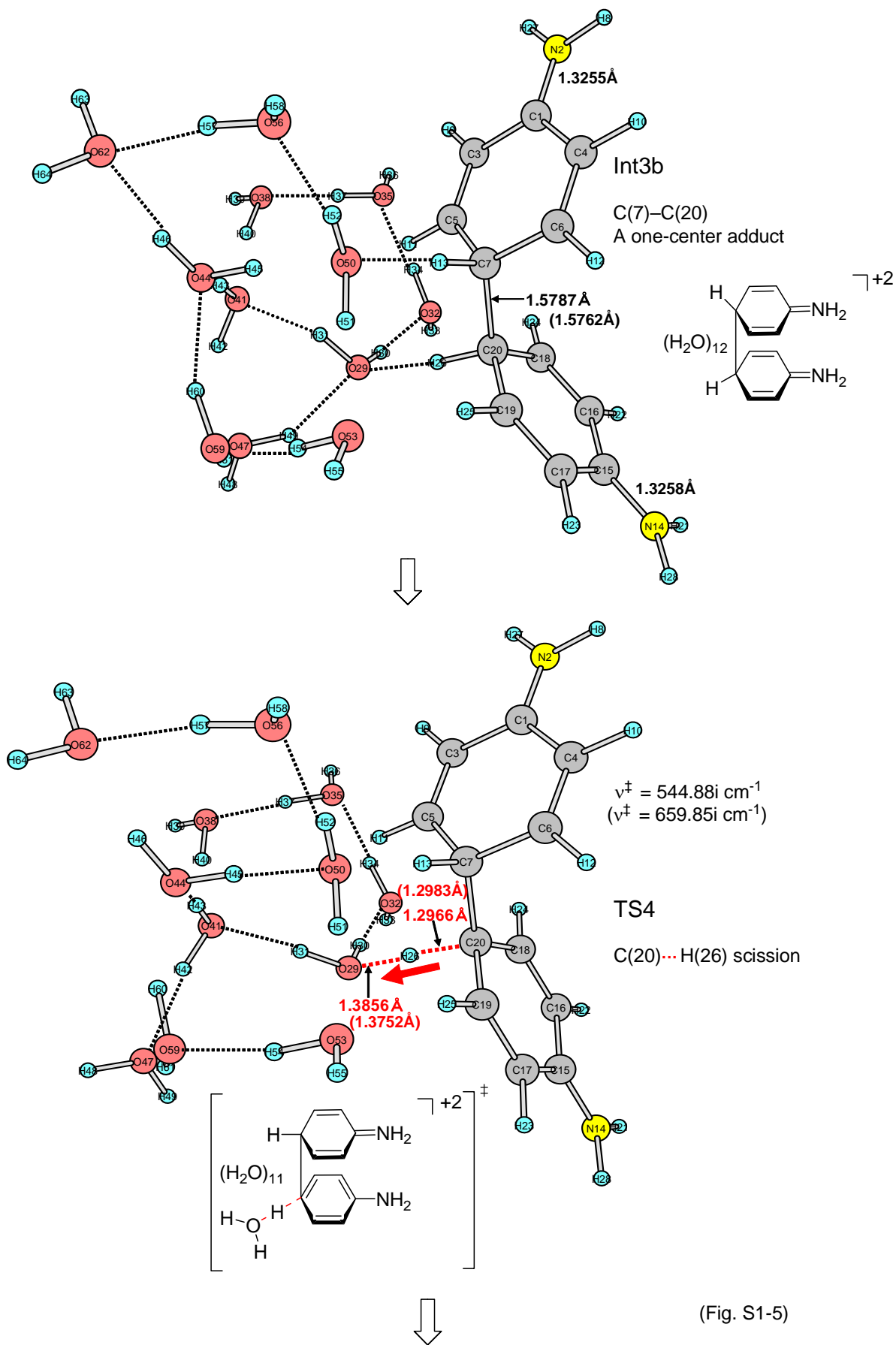
S6

(Fig. S1-2)

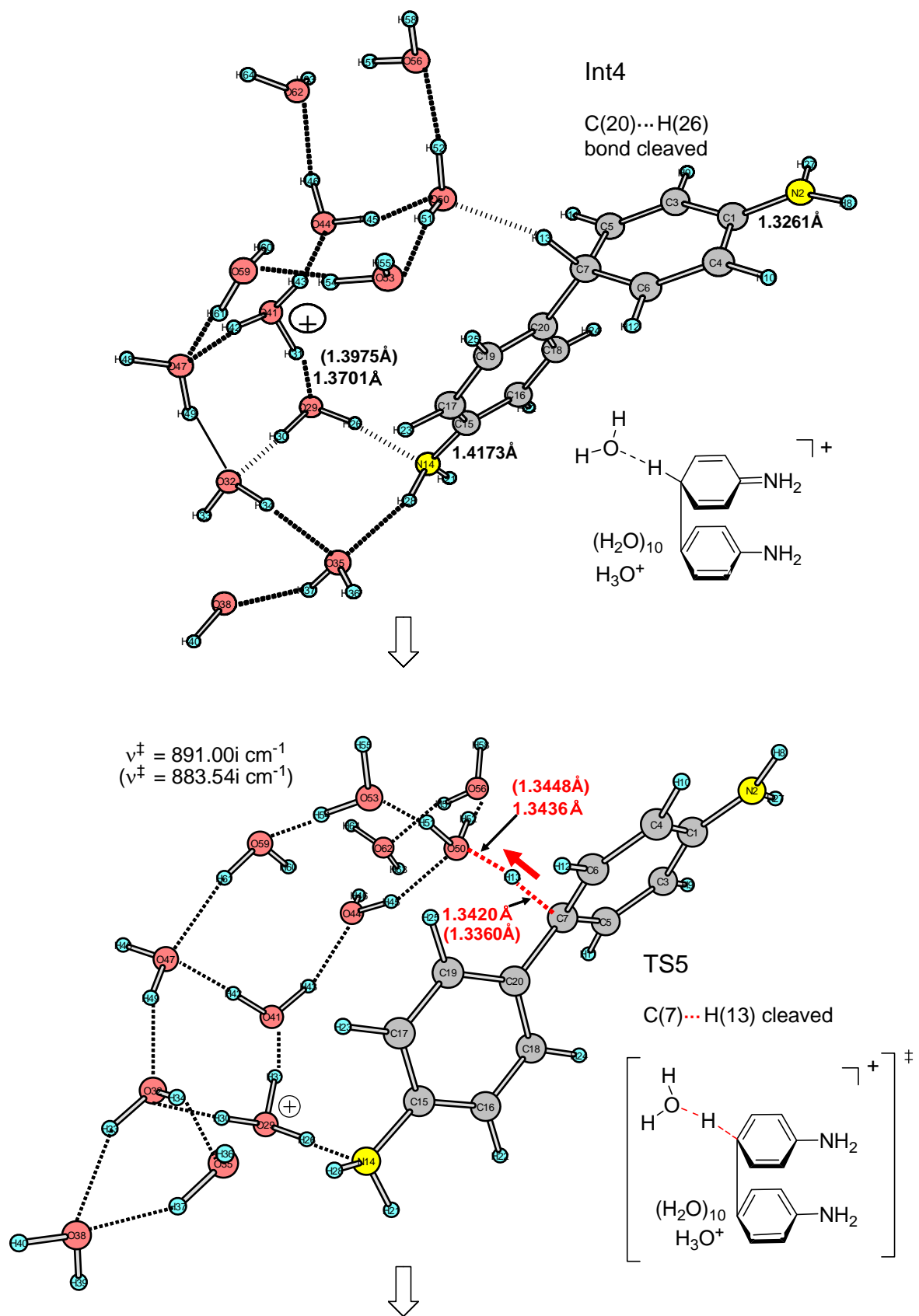


(Fig. S1-3)





(Fig. S1-5)



(Fig. S1-6)

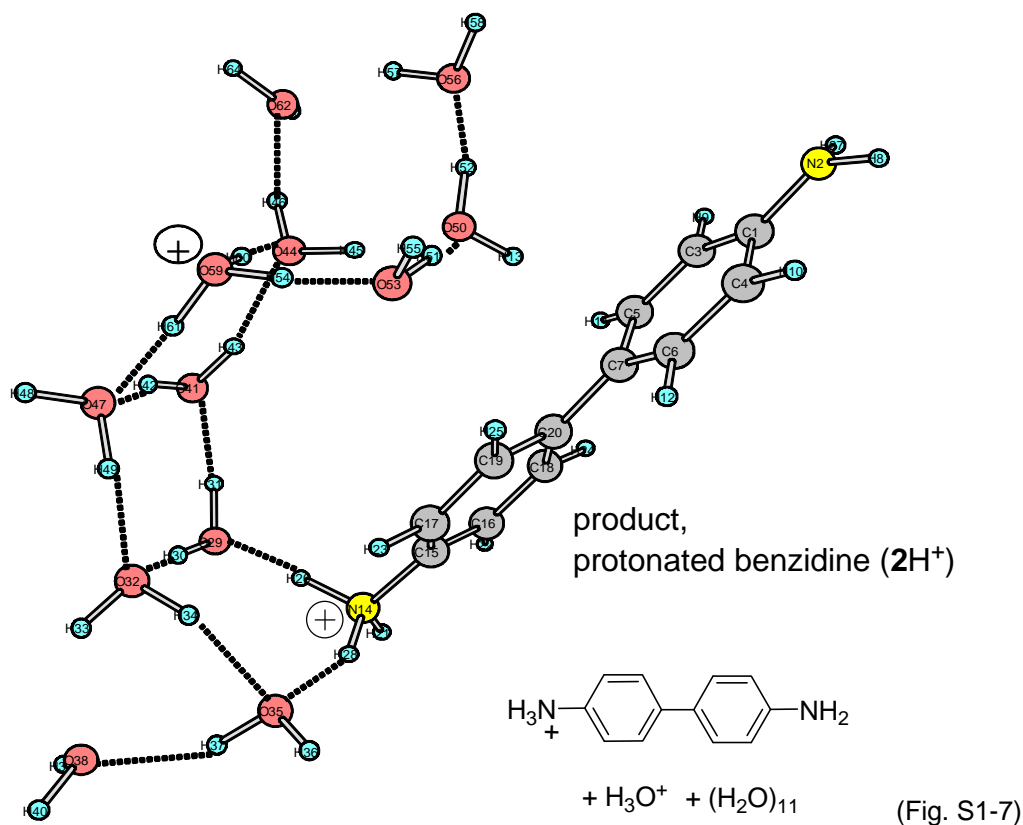


Figure S1. Geometric changes along the path from the protonated parent hydrazobenzene (1H^+) to the protonated benzidine (2H^+). TS denotes transition state, and Int does intermediate. RB3LYP/6-31G* and RB3LYP/6-311+G** distances are shown without and with parentheses, respectively.

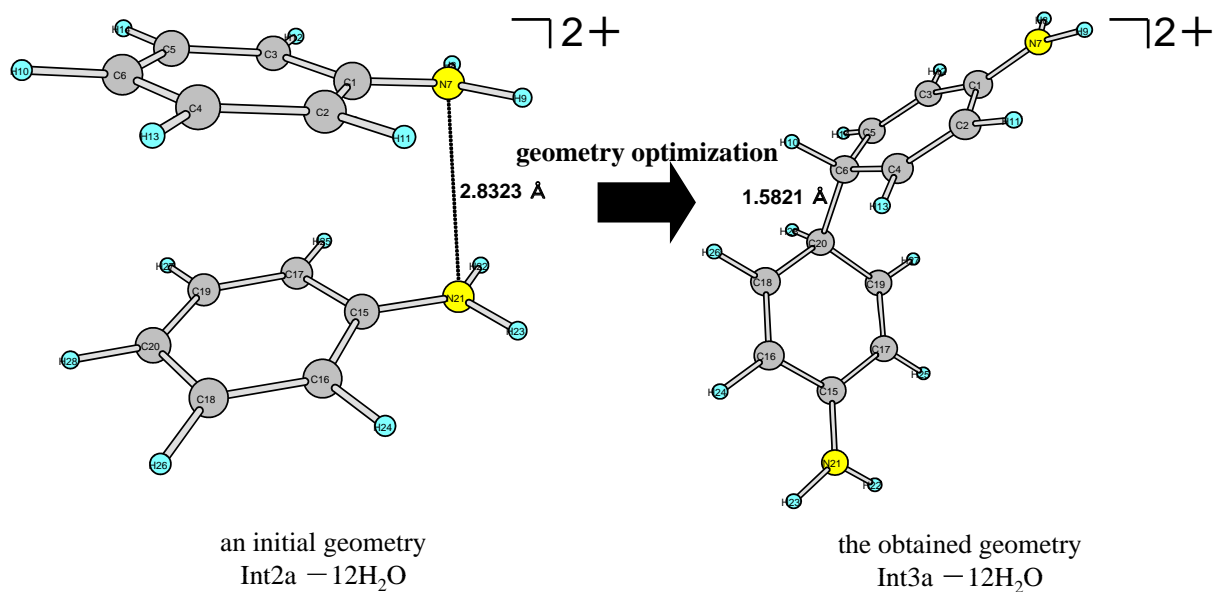
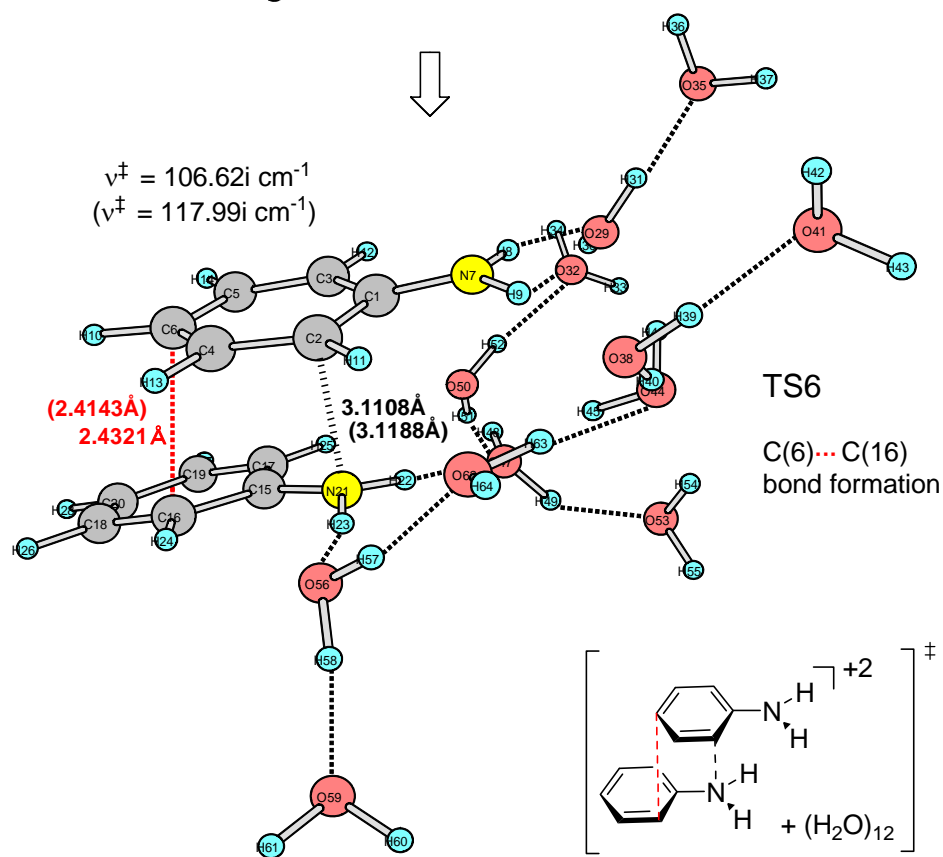
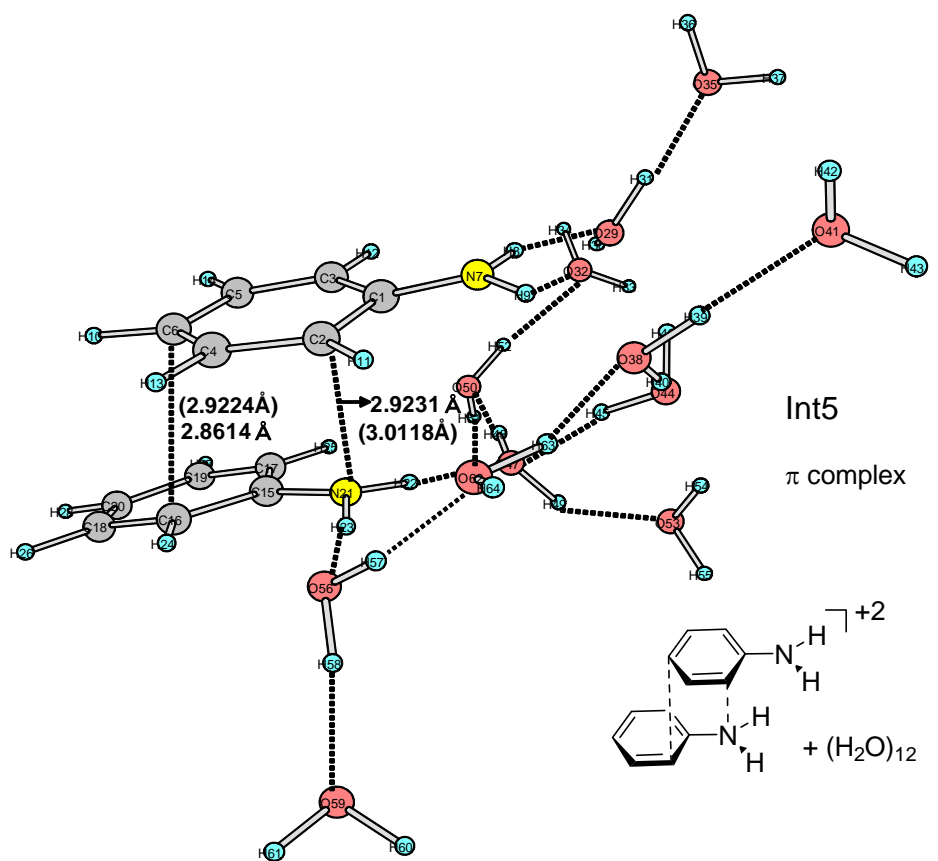
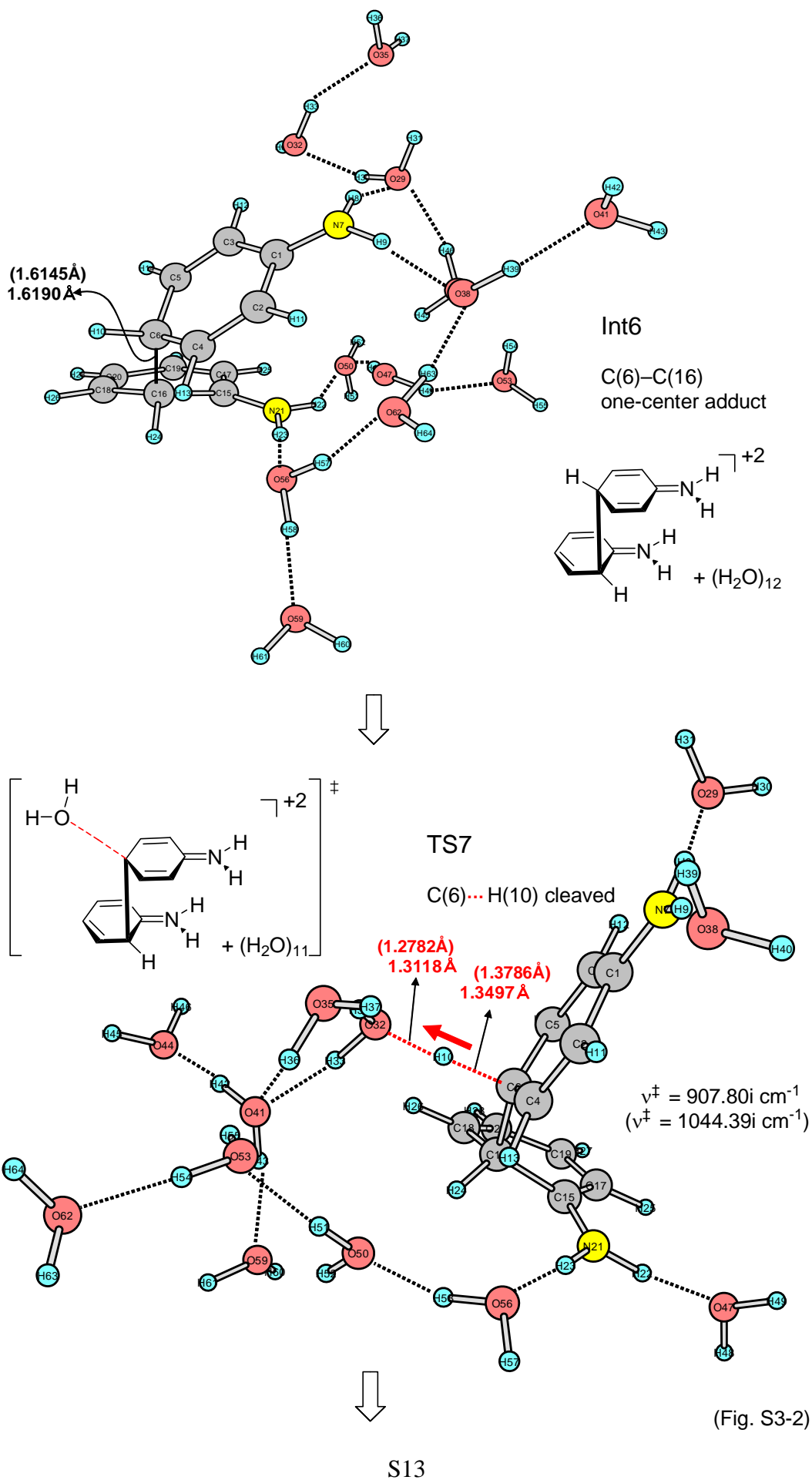
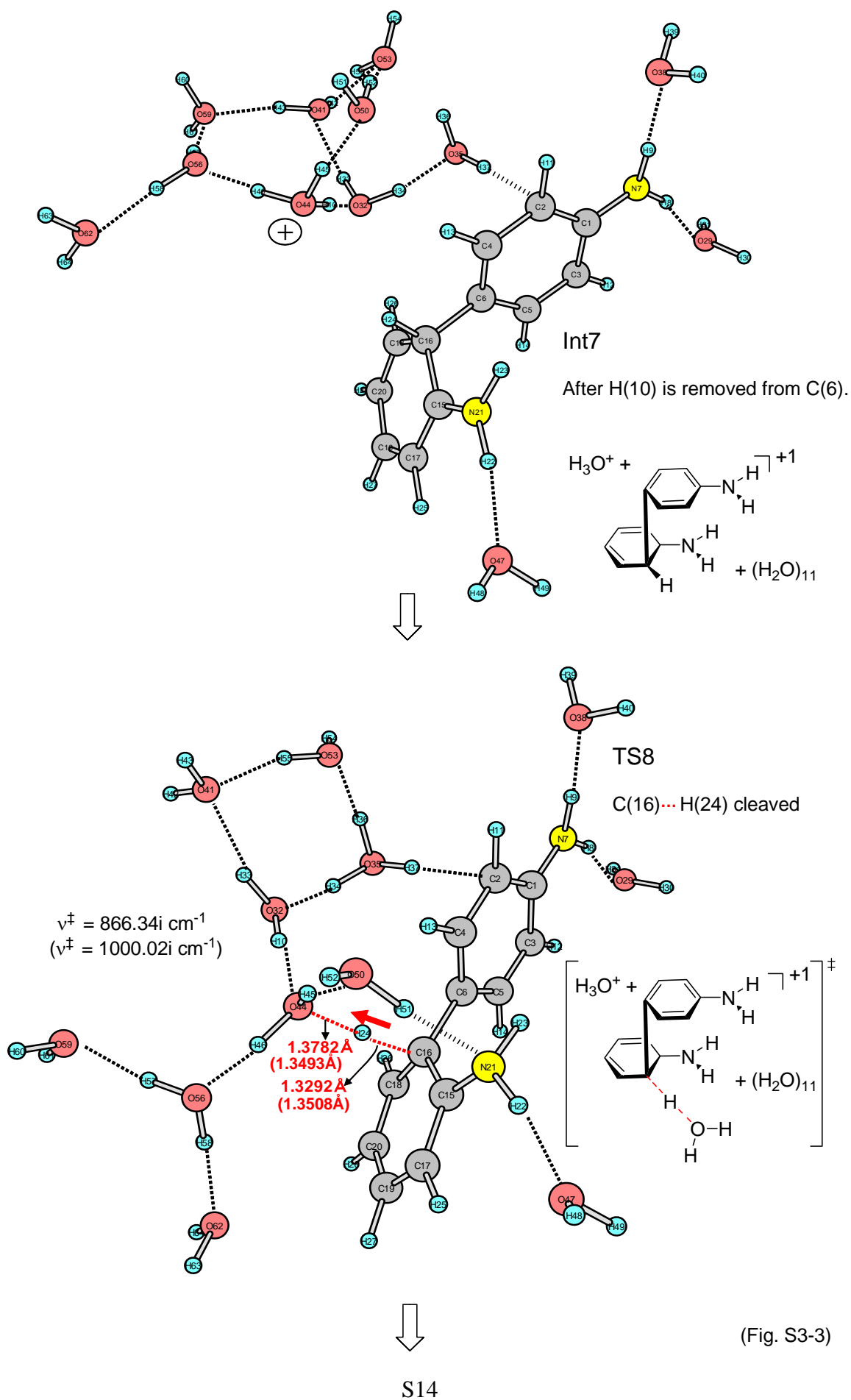


Figure S2. The water-free geometry of the π complex int2a is converted to the other one with the C-C covalent bond.



(Fig. S3-1)





(Fig. S3-3)

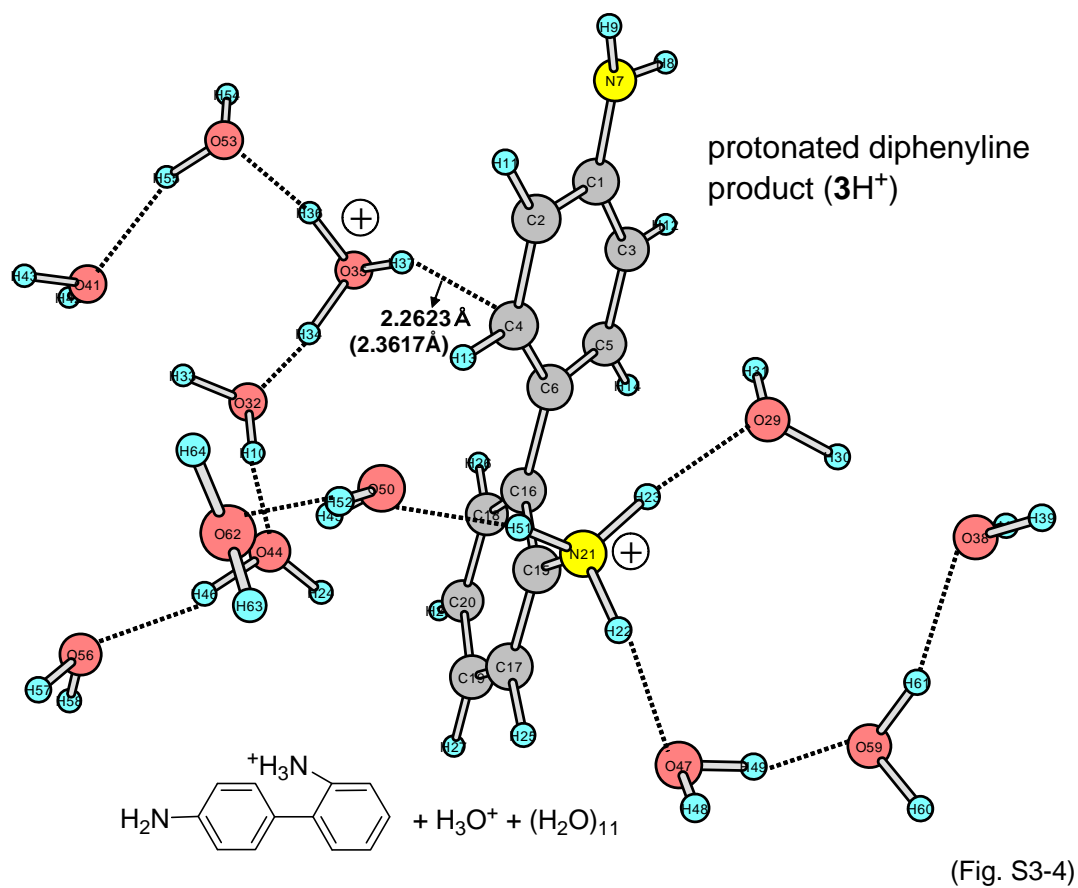
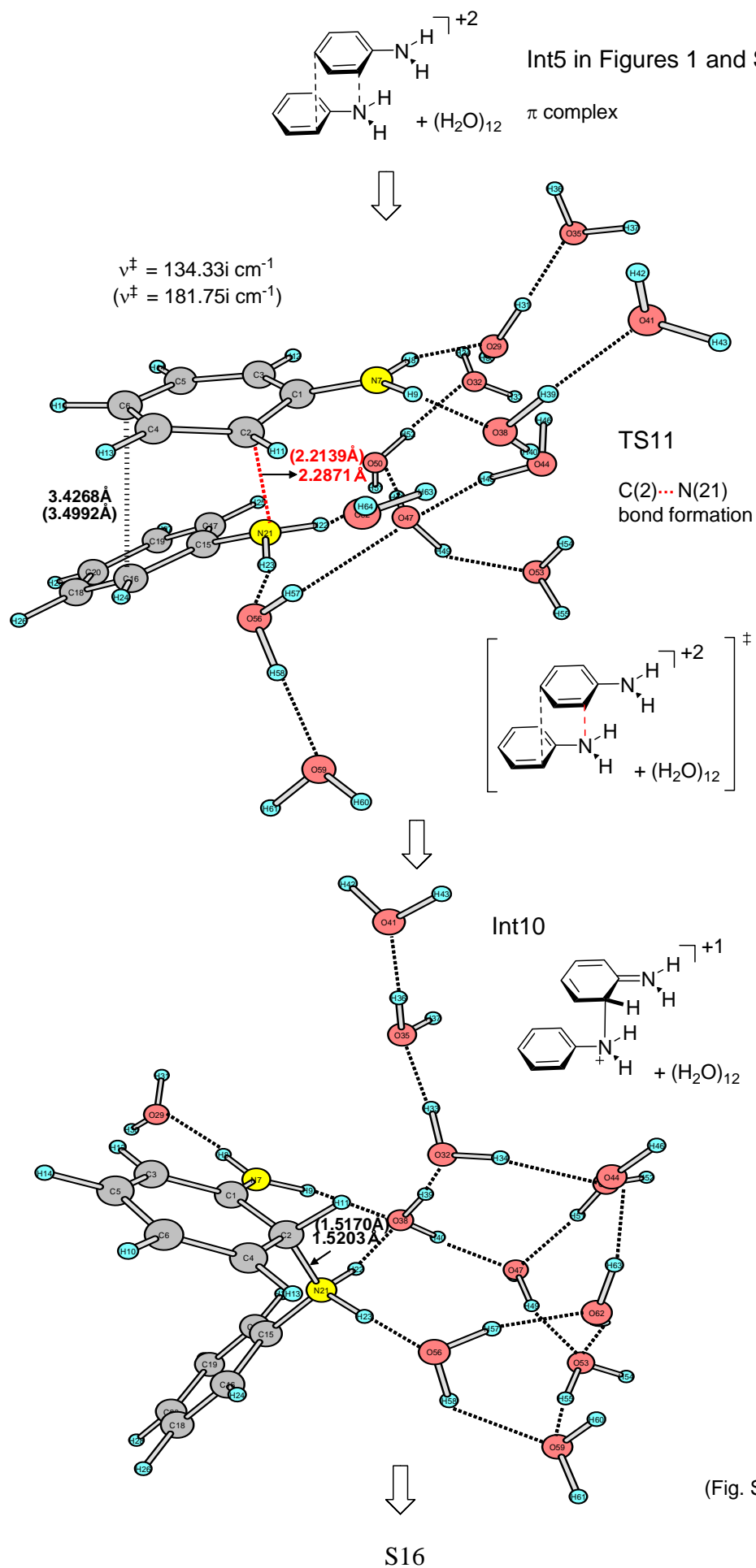


Figure S3. Geometric changes along the path from the intermediate Int5 to the protonated diphenylene (3H^+), which corresponds to Scheme 10.



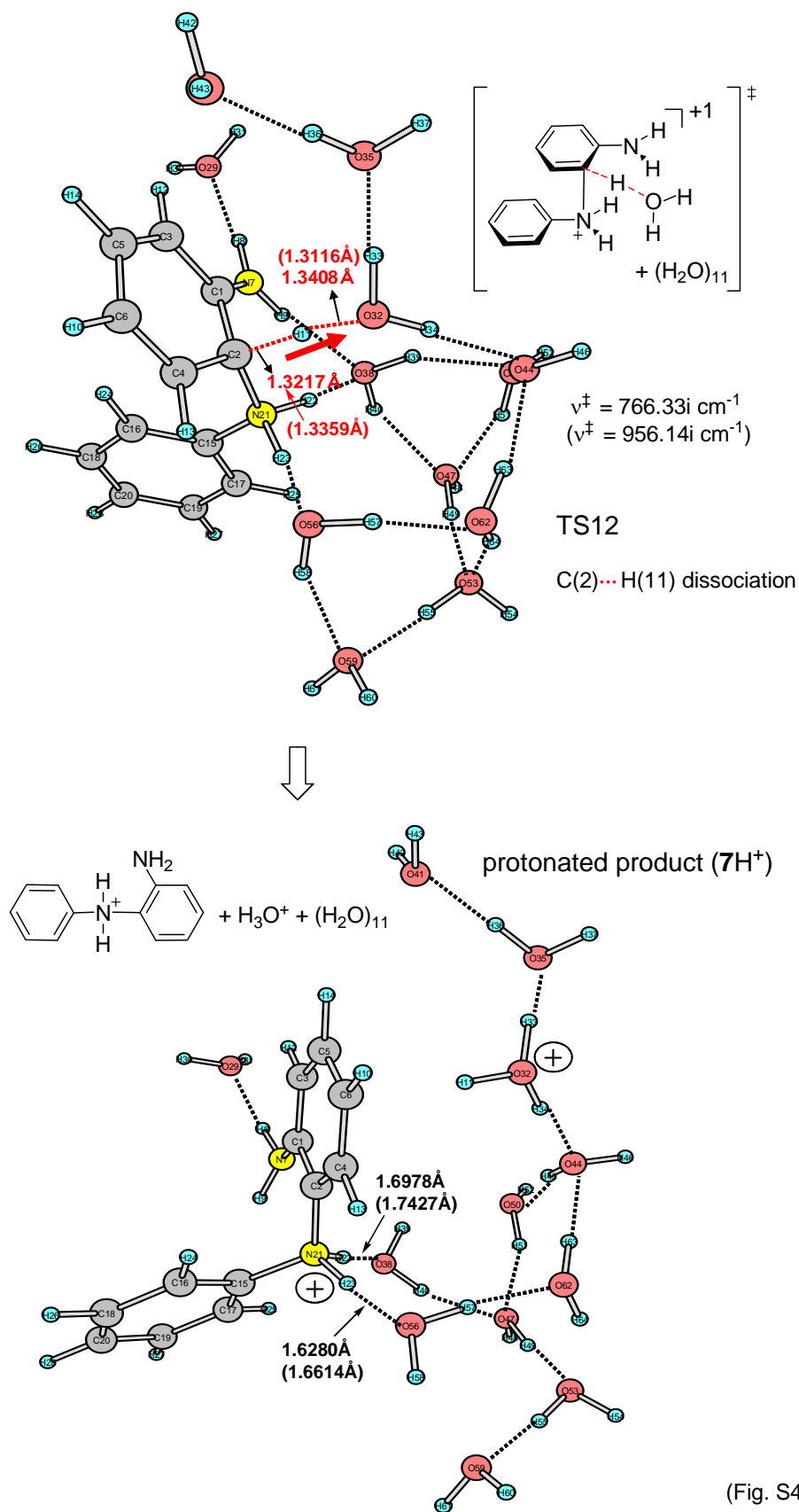
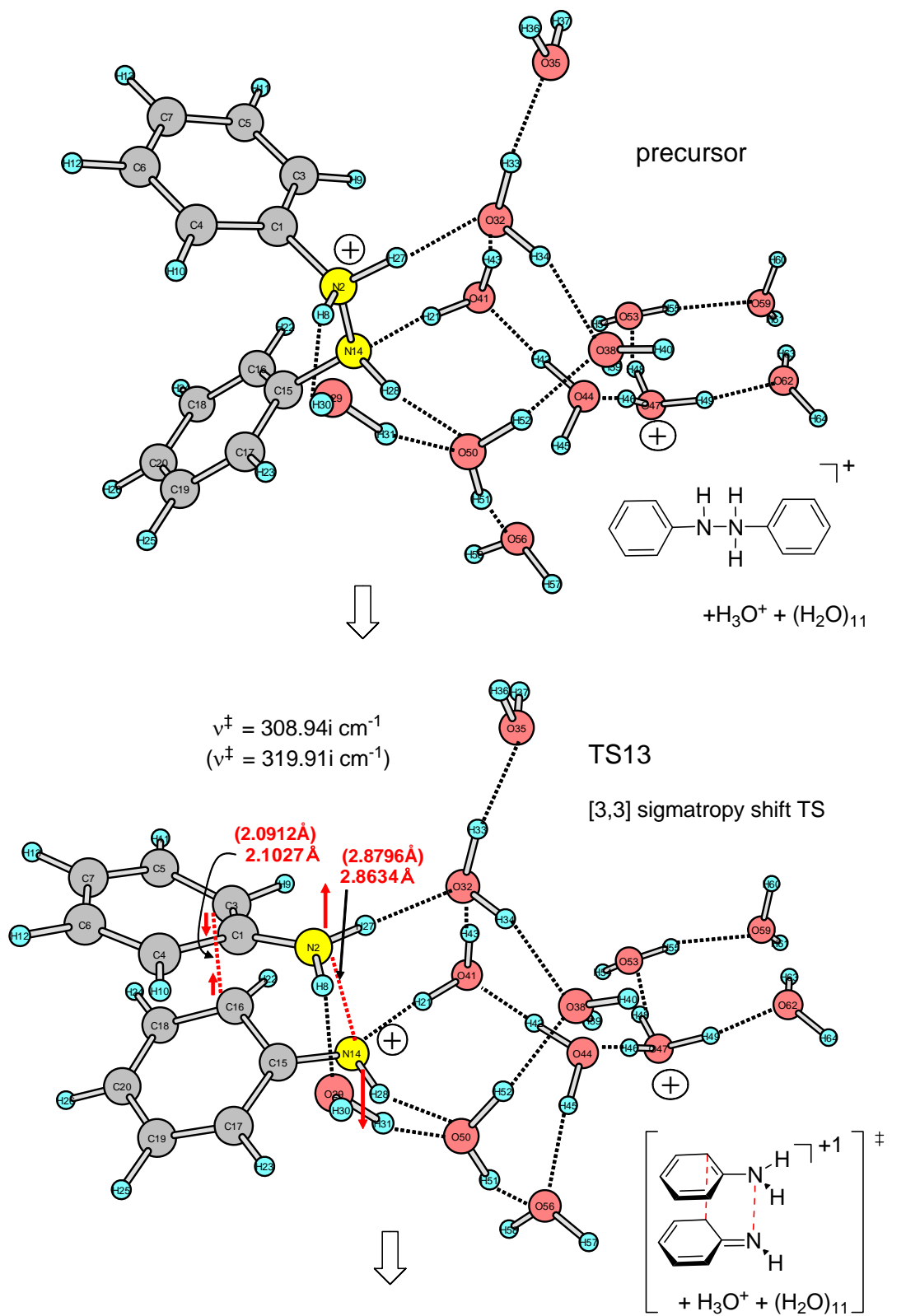
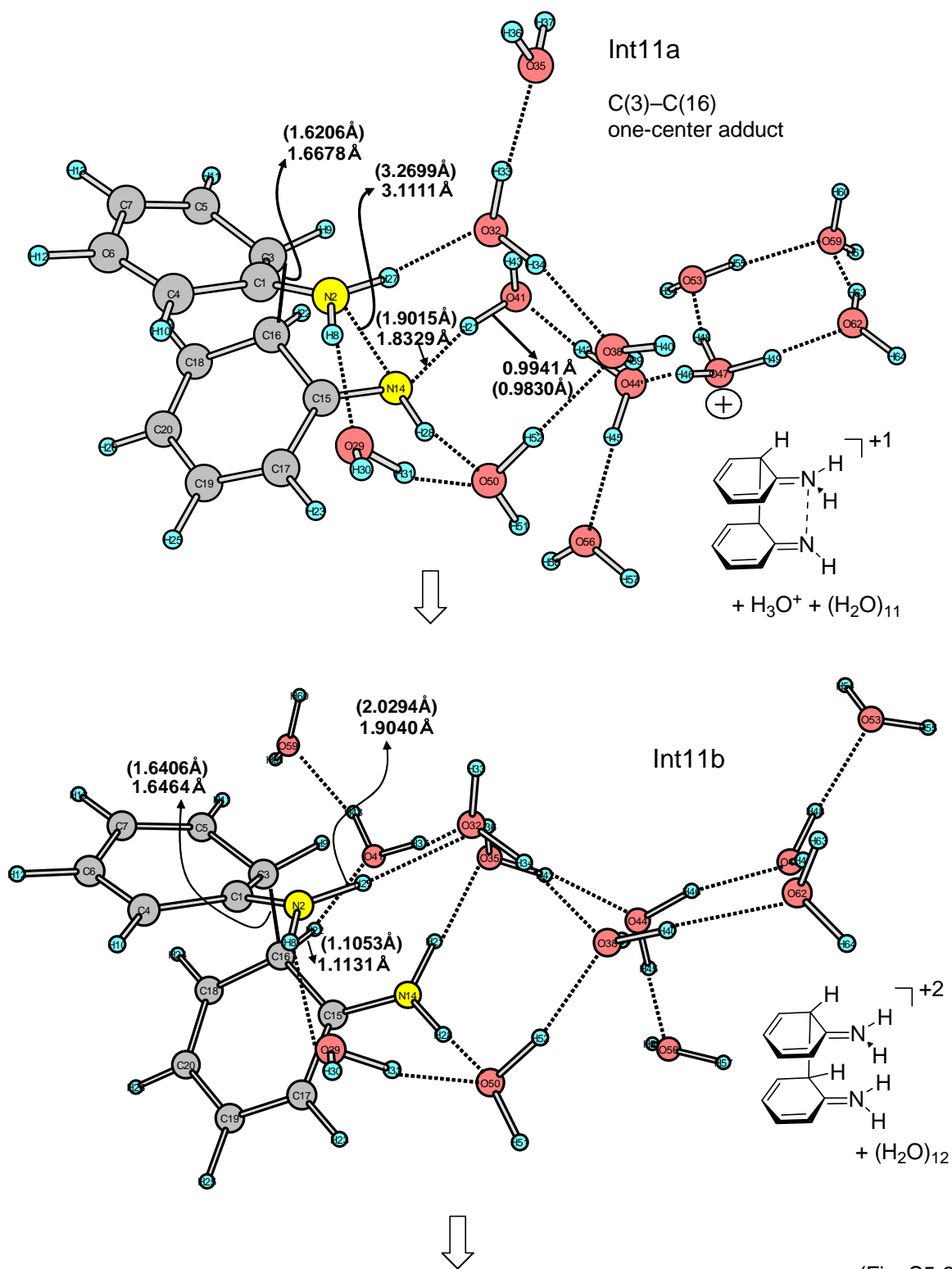


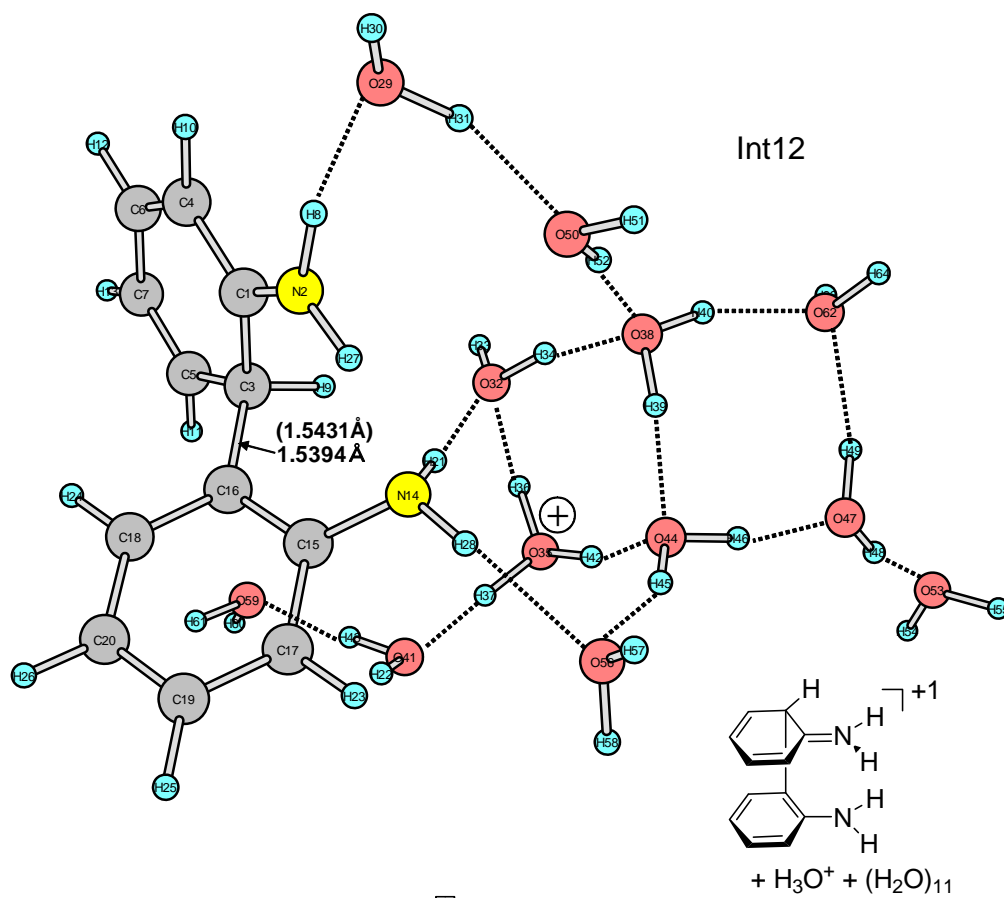
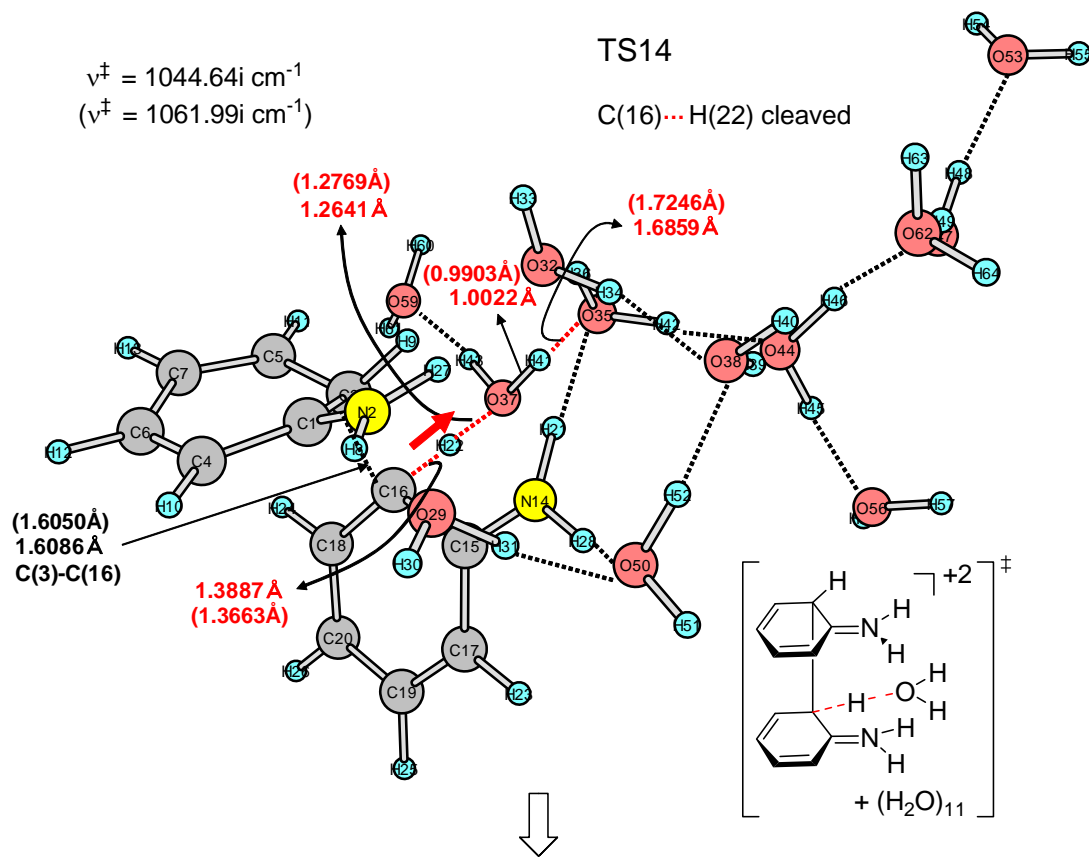
Figure S4. Geometric changes along the path from the intermediate Int5 to the protonated *o*-semidine (7H^+ X=H), which corresponds to Scheme 11.



(Fig. S5-1)

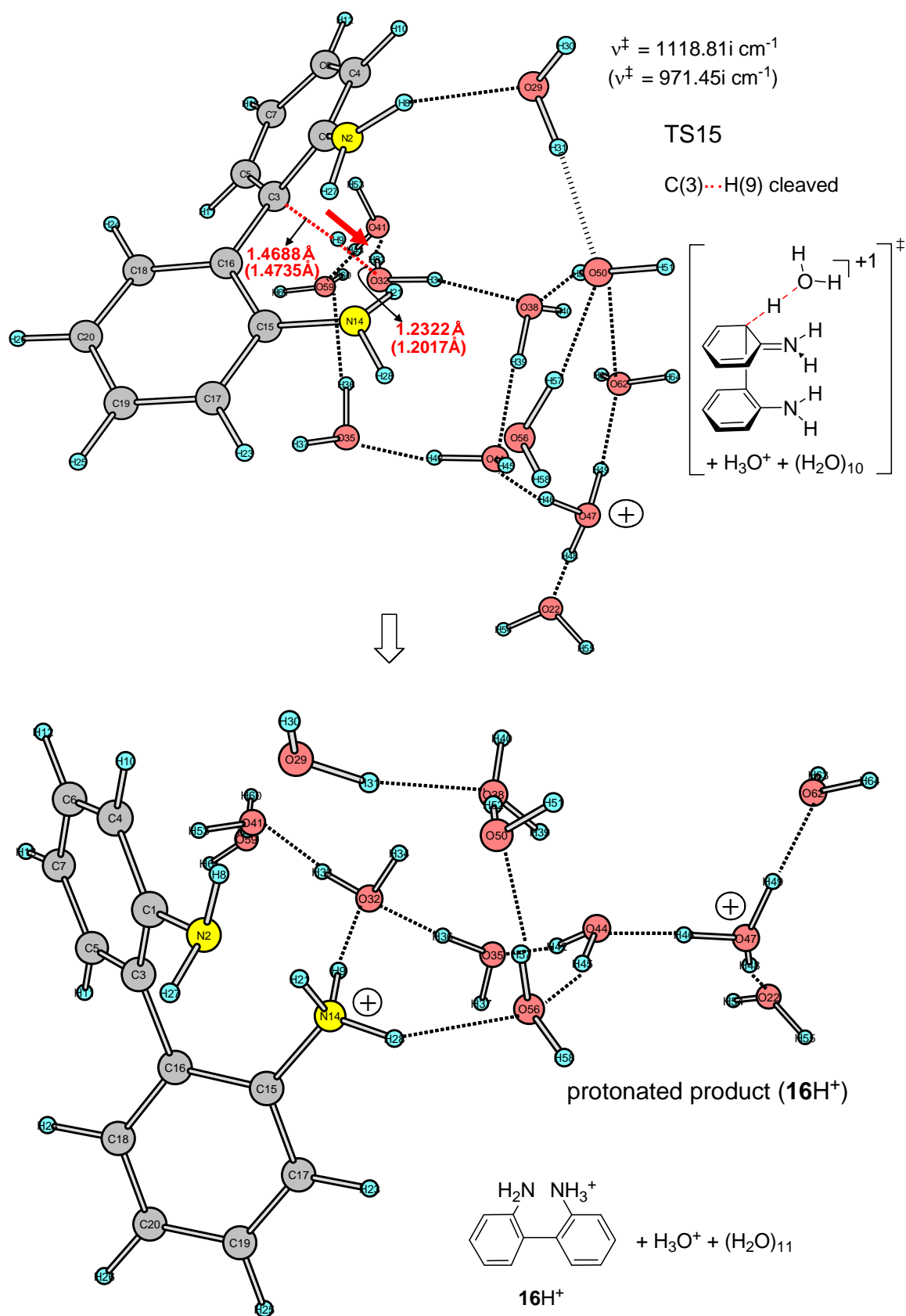


(Fig. S5-2)



↓
 S20

(Fig. S5-3)



(Fig. S5-4)

Figure S5. Geometric changes along the path from the protonated parent hydrazobenzene (**1H⁺**) to the protonated 2,2'-diamino-biphenyl (**16H⁺**), which corresponds to Scheme 12.

Type1 Rotation

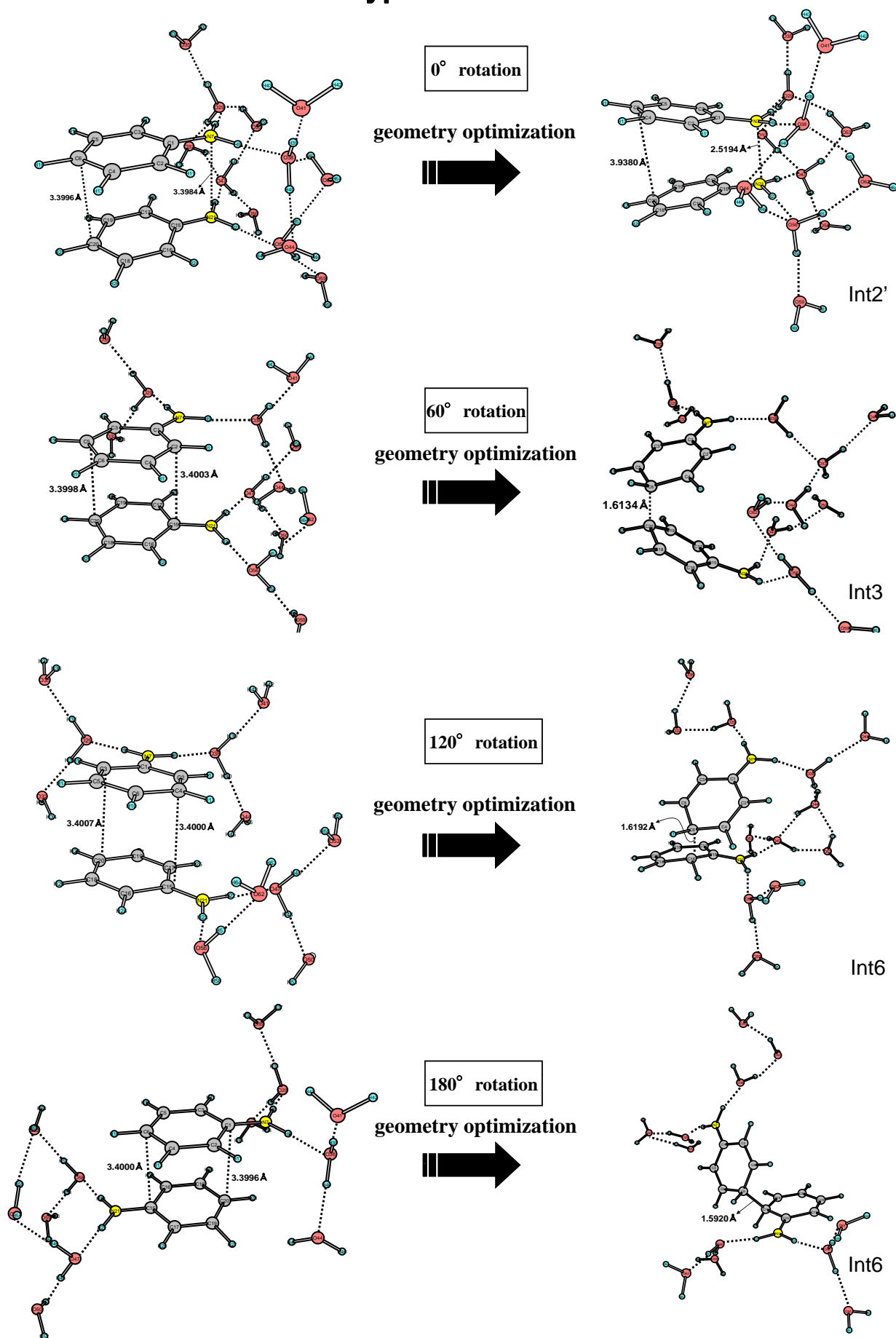


Figure S6. Optimization results of initial geometries rotated along the way shown in Scheme S1.

Type2 Shift

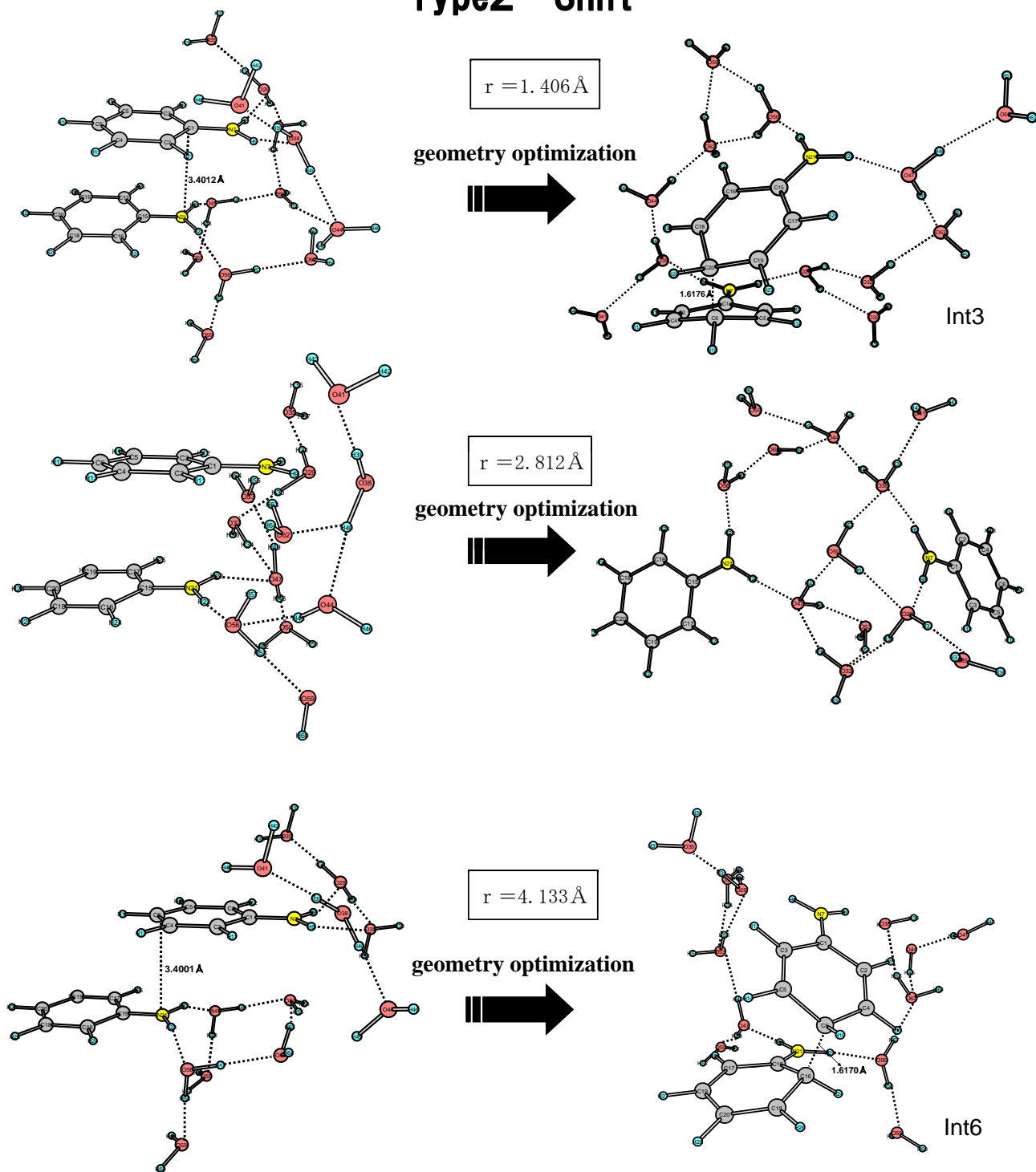


Figure S7. Optimization results of initial geometries shifted along the way shown in Scheme S1.

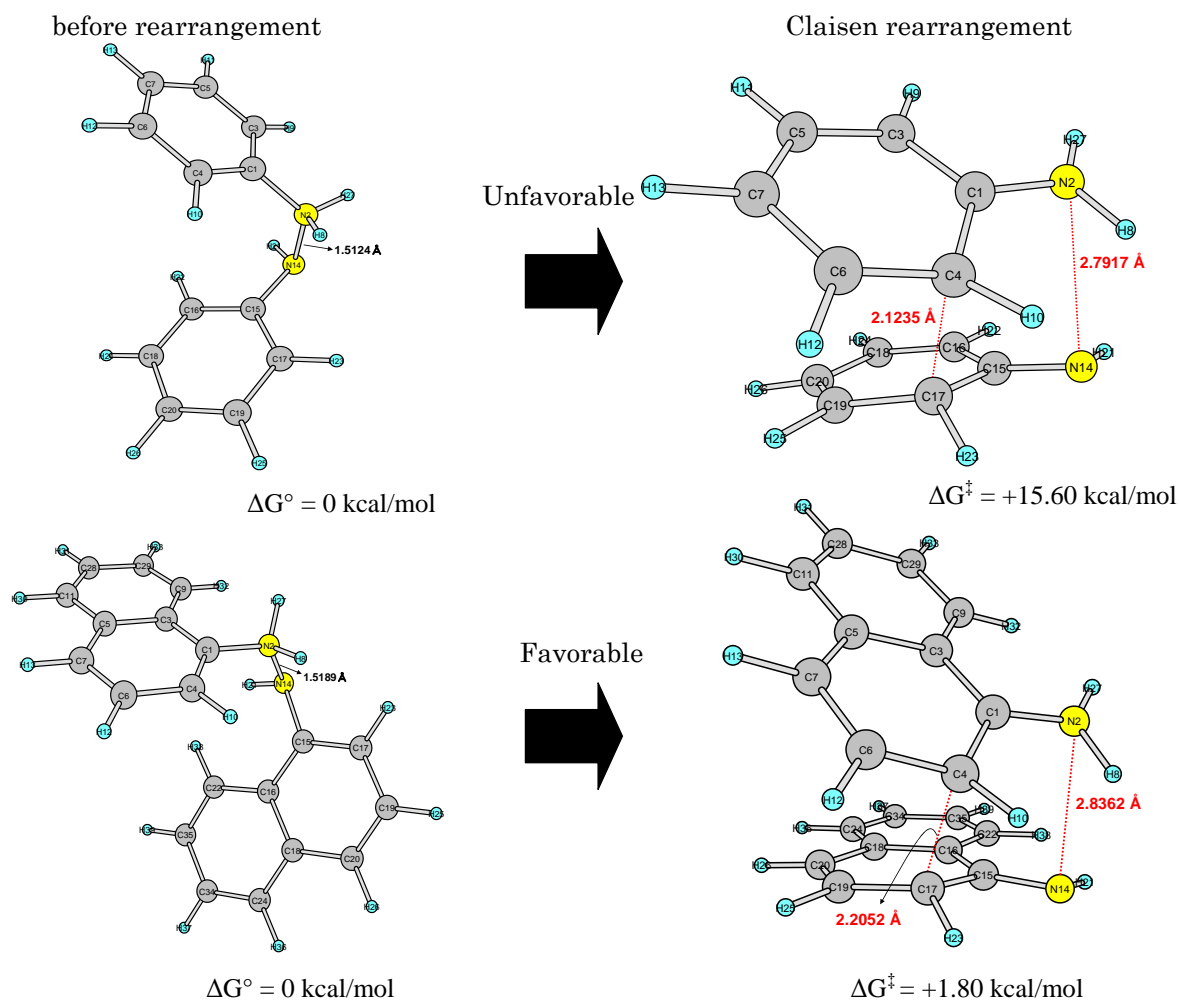


Figure S8. Two Claisen rearrangements in the mono-protonated form.

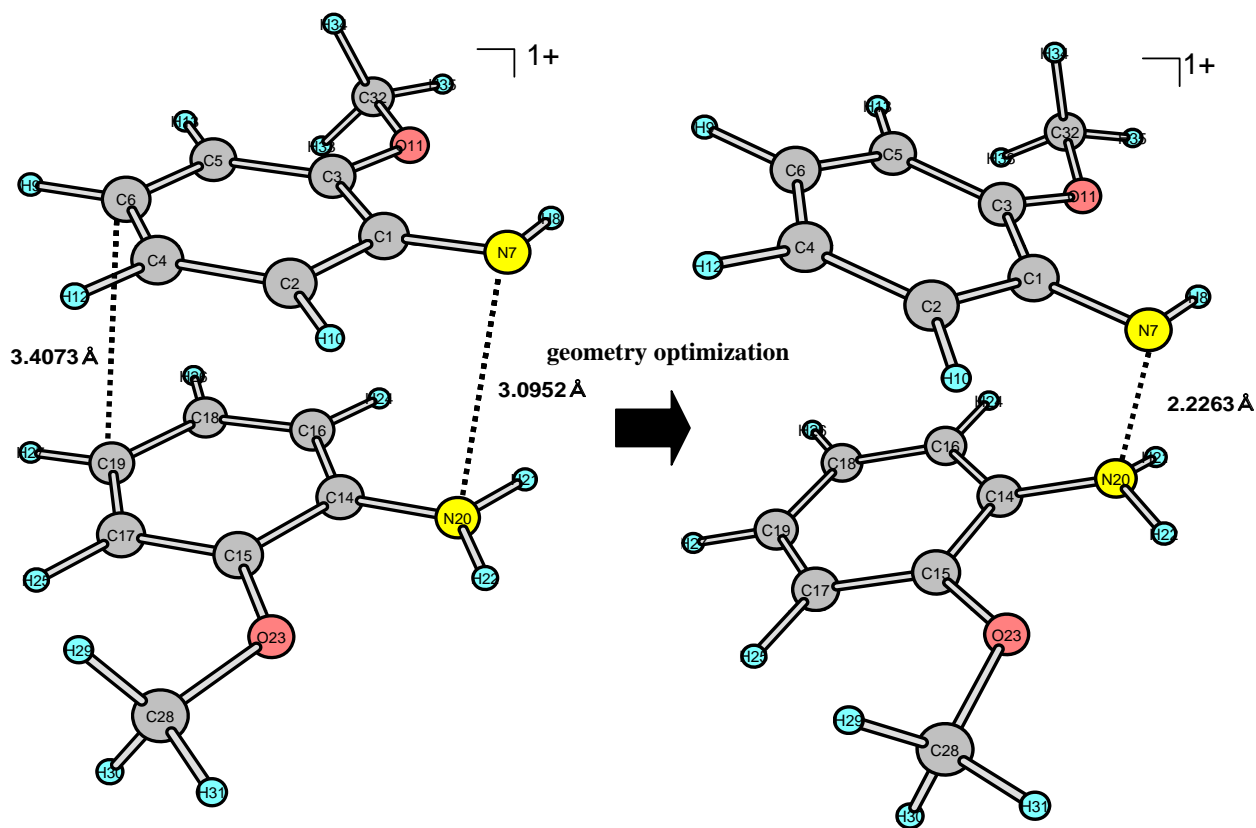


Figure S9. The gas-phase π complex of the mono-protonated 2,2'-dimethoxy-hydrazobenzene. The left geometry is an assumed one which is taken from that of the π complex one in Figure 3.

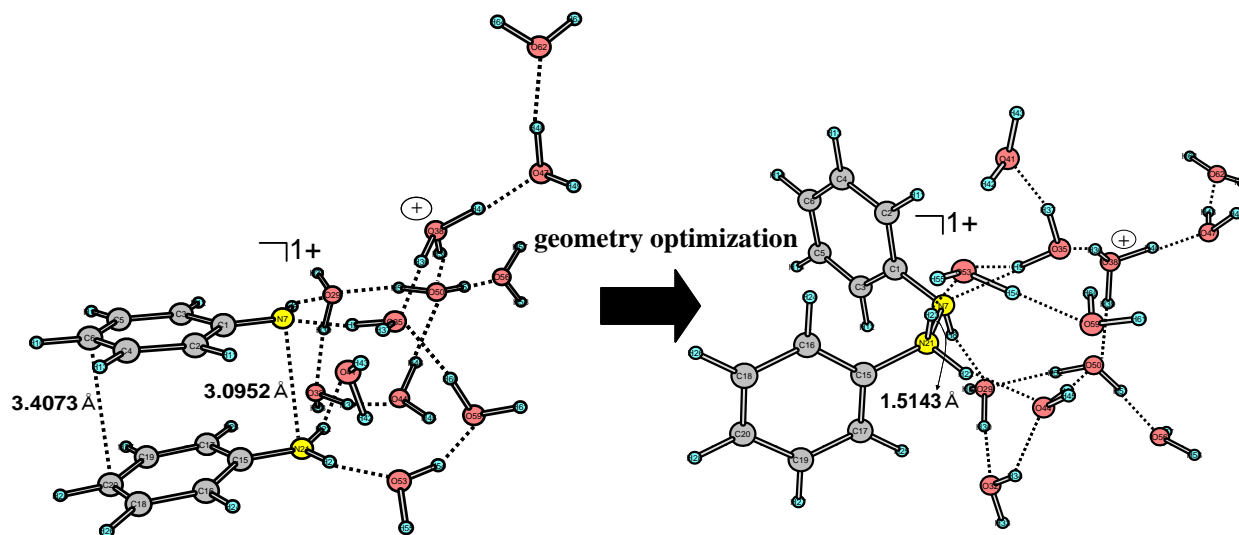
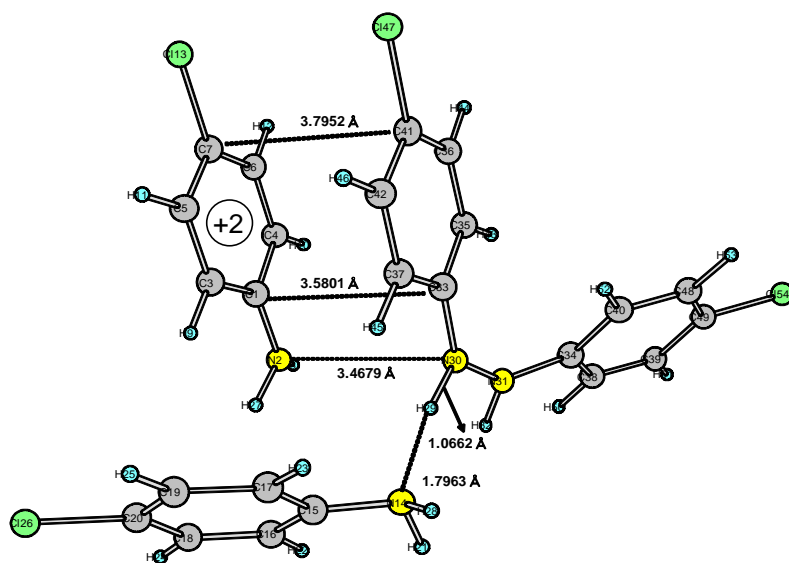
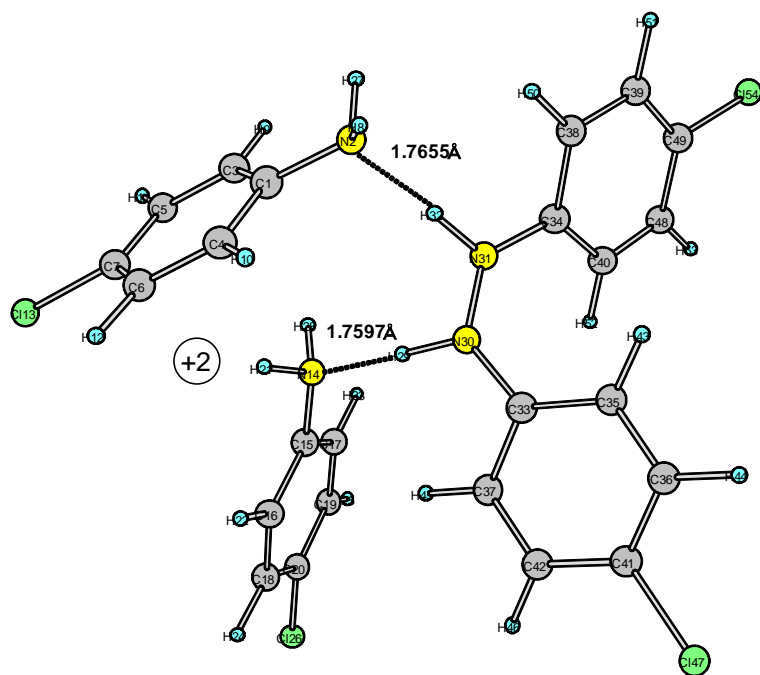


Figure S10. A π complex intermediate of the mono-protonated hydrazobenzene is absent. The left geometry is an assumed one which is taken from that of the π complex one in Figure 3.



(Fig. S11-1)

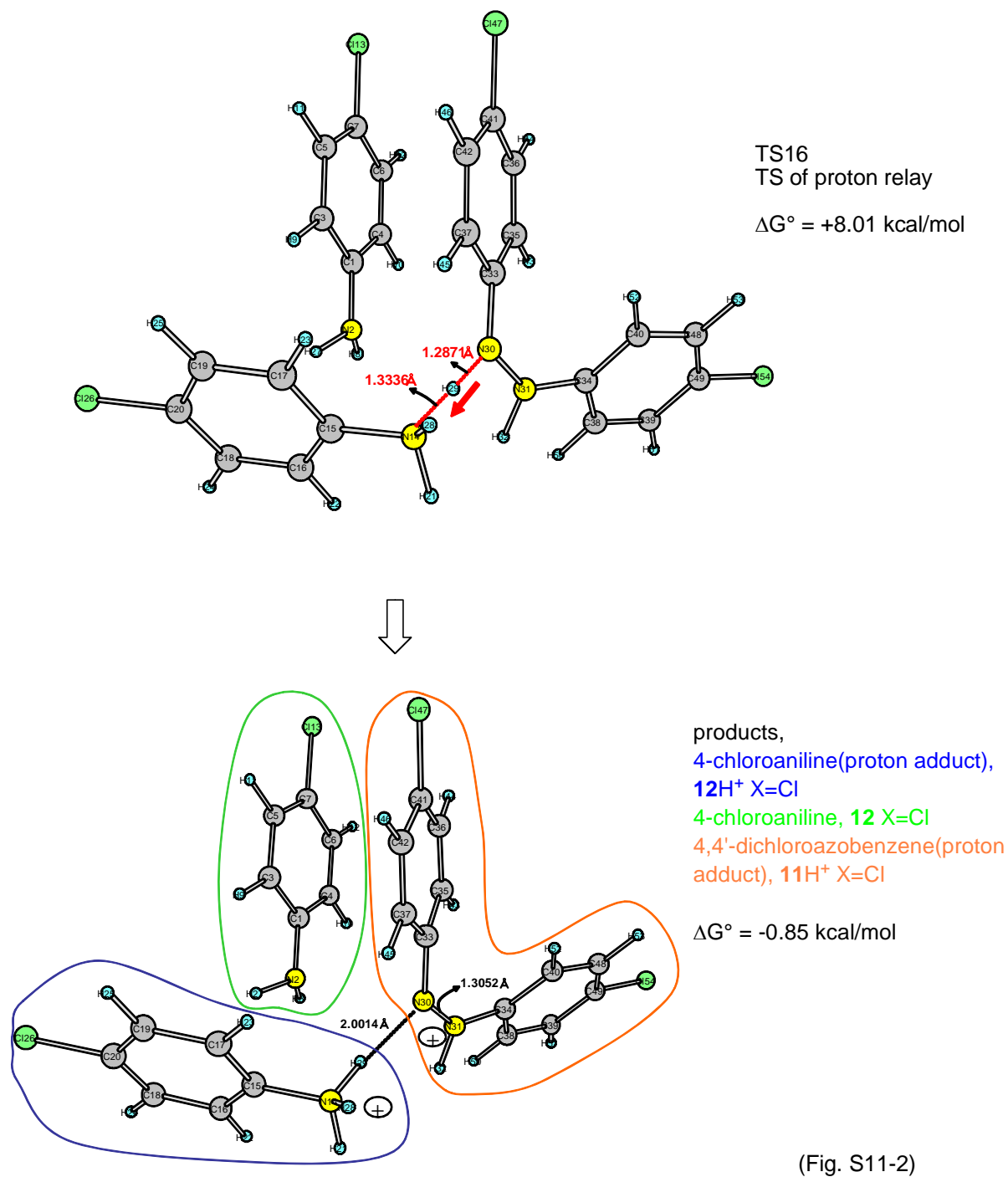


Figure S11. Geometric changes via disproportionation (Scheme 5) in a system composed of the π complex of the di-protonated 4,4'-dichlorohydrazobenzene and a neutral one.

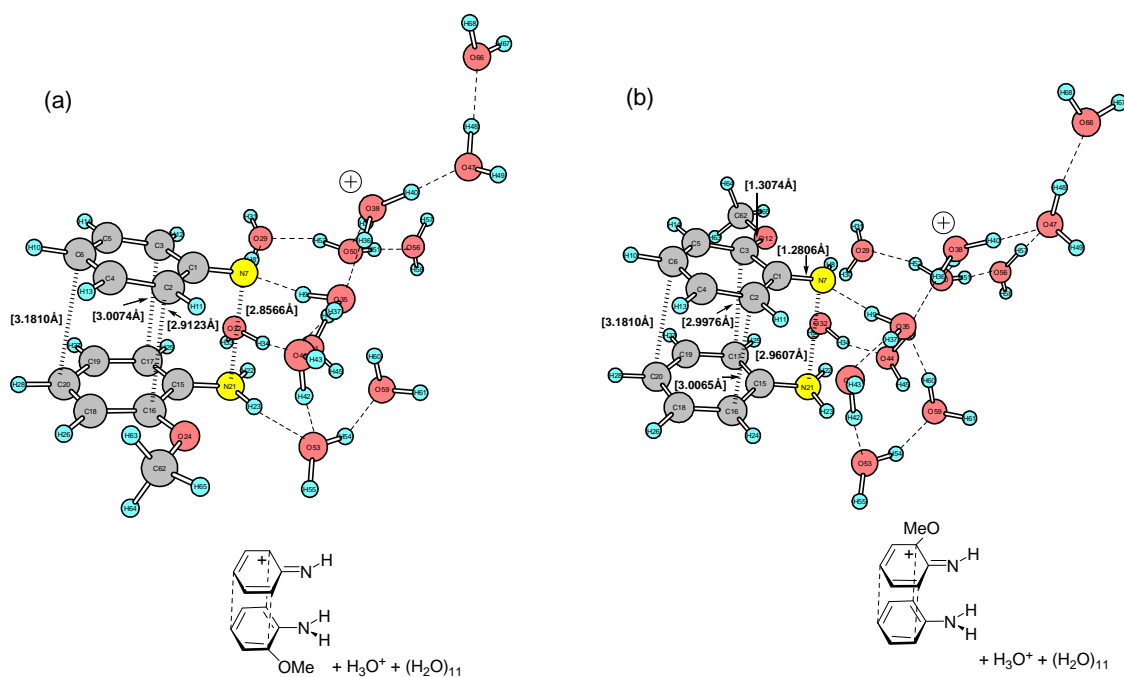


Figure S12. Geometries of two mono-protonated π complexes in the system of 2-methoxyhydrazobenzene and $(\text{H}_3\text{O}^+)_2(\text{H}_2\text{O})_{10}$. Total energies of MPWB1K/6-31G* are -1605.535863 a.u. (a) and -1605.540736 a.u. (b), respectively. The isomer (b) is slightly more stable than (a). That is, the methoxy group works slightly more effective for stabilization of the cation than for enhancement of the donor ability of aniline.