Supporting Information

Concerted One-Electron Two-Proton Transfer Processes in Models

Inspired by the Tyr-His Couple of Photosystem II

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# Table of Contents

## Experimental Results

1. Synthesis and Structural Characterization ................................................................. S3
   Figure S1
2. Nuclear Magnetic Resonance Spectra ................................................................. S10
   Figures S2 – S22
3. Electrochemical Measurements .................................................................................. S31
   Figures S23 – S25
4. IRSEC and IR data ..................................................................................................... S32
   Figures S26 – S33
5. Kinetic Isotope Effect (KIE) and Electrochemical Measurements ......................... S38
   Figures S34

## Computational Results

6. Electronic Structure Calculations ............................................................................... S39
   Figures S35 – S36 and Table S1
7. Thermodynamics of PCET ......................................................................................... S41
   Figures S37 – S38 and Table S2
8. Generating Average Structures .................................................................................. S45
9. Generating Proton Potentials ..................................................................................... S45
   Figures S39 – S41
10. Determining $P(R)$ .................................................................................................... S50
    Table S3
11. Calculating Heterogeneous Rate Constants $k(R)$ .................................................. S51
    Table S4
12. Summary of Calculations ......................................................................................... S54
13. Analysis of Rate Constants ...................................................................................... S55
    Figures S42 – S47 and Tables S5 – S6
14. References .................................................................................................................. S63
15. Optimized Cartesian Coordinates of Species Studied .............................................. S66
    Tables S7 – S28
Experimental Results

Synthesis and Structural Characterization

The $^1$H NMR spectra were recorded on Varian and Bruker spectrometers at 400 or 500 MHz, at 25 °C employing standard pulse techniques. Mass spectra of all compounds were obtained with a Voyager DE STR matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometer in positive ion mode, employing trans,trans-1,4-diphenyl-1,3-butadiene as matrix. All chemicals were purchased from Aldrich, Acros or Alfa Aesar. Solvents were obtained from EM Science. Dichloromethane (DCM) was distilled from calcium hydride. Tetrahydrofuran was distilled from sodium metal and benzophenone in an argon atmosphere immediately prior to use. All solvents were stored over the appropriate molecular sieves prior to use. Thin layer chromatography (TLC) was performed with silica gel coated glass plates from Analtech. Column chromatography was carried out using Silicycle silica gel 60 with 230–400 mesh.

2-(3',5'-Di-tert-butyl-2'-hydroxyphenyl)benzimidazole, BIP (1). A similar method was previously reported.$^{1,2}$ A portion of 3,5-di-tert-butyl-2-hydroxybenzaldehyde (351 mg, 1.50 mmol) in nitrobenzene (10 mL) was added drop-wise to a solution of $o$-phenylenediamine (162 mg, 1.50 mmol) in nitrobenzene (10 mL), the mixture was stirred under argon. Then, the reaction
was refluxed for 12 h under argon. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using hexanes and dichloromethane as the eluent. The product was recrystallized from hexanes to give 450 mg of BIP (1) (93% yield). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.38 (9H, s, C(CH$_3$)$_3$), 1.51 (9H, s, C(CH$_3$)$_3$), 7.26-7.32 (2H, m, ArH), 7.40 (1H, d, $J=2.2$ Hz, ArH), 7.45 (1H, d, $J=2.2$ Hz, ArH), 7.47–7.53 (1H, m, ArH), 7.71–7.76 (1H, m, ArH), 9.34 (1H, s, NH), 13.46 (1H, s, OH). MALDI-TOF-MS m/z. calcd. for C$_{21}$H$_{26}$N$_2$O+(H) 323.212, obsd. 323.214.

2-(3’,5’-Di-tert-butyl-2’-hydroxyphenyl)benzimidazole-4-carboxylic acid, BIP-COOH (2). The hydrolysis of BIP-COOMe (3) (200 mg, 0.525 mmol) was realized in a mixture of THF (15 mL), methanol (7.5 mL) and a solution of KOH 10% (5 mL), by stirring the solution under argon at 35 ºC overnight. The purification was performed by silica gel chromatography using dichloromethane/methanol (1–10%) as eluent, and then recrystallized with isopropanol and hexanes. The final product, BIP-COOH (2) (183 mg), was obtained in 95% yield. $^1$HNMR (400 MHz, (CD$_3$)$_2$CO): $\delta$ 1.37 (9H, s, C(CH$_3$)$_3$), 1.51 (9H, s, C(CH$_3$)$_3$), 7.41 (1H, t, $J=7.8$ Hz, ArH), 7.50 (1H, d, $J=2.3$ Hz, ArH), 7.96 (1H, d, $J=7.6$ Hz, ArH), 8.00 (1H, d, $J=8$ Hz, ArH), 8.13 (1H, s, ArH), 11.79 (1H, s, NH), 12.75 (1H, s, OH). MALDI-TOF-MS m/z. calcd. for C$_{22}$H$_{26}$N$_2$O$_3$+(H) 367.202, obsd. 367.203.
Methyl 2-(3’,5’-di-tert-butyl-2’-hydroxyphenyl)benzimidazole-4-carboxylate, BIP-COOME (3). The same procedure used in the synthesis of BIP (1) was followed, using methyl 2,3-diaminobenzoate. The purification was performed by column chromatography on silica using hexanes and dichloromethane as the eluent and then, the sample was recrystallized in hexanes and isopropanol (80% yield). $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 1.39 (9H, s, C(CH$_3$)$_3$), 1.51 (9H, s, C(CH$_3$)$_3$), 4.04 (3H, s, OCH$_3$), 7.32 (1H, t, $J=7.9$ Hz, ArH), 7.46-7.49 (2H, m, ArH), 7.88-7.94 (2H, m, ArH), 10.70 (1H, s, NH), 13.28 (1H, s, OH). MALDI-TOF-MS m/z. calcd. for C$_{23}$H$_{28}$N$_2$O$_3$+(H) 381.218, obsd. 381.214.

4-Amide-2-(3’,5’-di-tert-butyl-2’-hydroxyphenyl)benzimidazole, BIP-COONH$_2$ (4). The ester BIP-COOME (3) (500 mg, 1.31 mmol) and 20 mL of anhydrous methanol was added to a heavy-walled glass tube. The solution was kept under a positive nitrogen pressure as the tube was
cooled in liquid nitrogen; ammonia gas was added until approximately 10 g of solid ammonia had collected. The glass tube was then flame sealed. The reaction was stirred and heated at 70 °C for 72 h. After cooling to room temperature, the tube was again cooled in liquid nitrogen and the glass seal broken. The organic solvent was removed under reduced pressure. The solid was purified by column chromatography on silica gel using dichloromethane/methanol (1–5%) to give 440 mg (91% yield) of BIP-CONH$_2$ (4). $^1$HNMR (400 MHz, (CD$_3$)$_2$CO): δ 1.38 (9H, d, $J$ = 8.7 Hz, C(CH$_3$)$_3$), 1.51 (9H, s, C(CH$_3$)$_3$), 6.96 (1H, s, NH$_2$), 7.07 (1H, s, NH$_2$), 7.38 (1H, t, $J$ = 7.8 Hz, ArH), 7.43 (1H, t, $J$ = 7.8 Hz, ArH), 7.53 (1H, d, $J$ = 2.3 Hz, ArH), 7.56 (1H, d, $J$ = 2.3 Hz, ArH), 7.77 (1H, d, $J$ = 7.9 Hz, ArH), 7.87 (1H, d, $J$ = 7.5 Hz, ArH), 7.93 (1H, d, $J$ = 8 Hz, ArH), 7.96 (1H, d, $J$ = 2.0 Hz, ArH), 8.04 (1H, d, $J$ = 7.6 Hz, ArH), 8.12 (1H, d, $J$ = 2.3 Hz, ArH), 11.86 (0.5H, s, N-H), 12.63 (1.5H, s, OH, N-H), 13.74 (1H, s, OH). MALDI-TOF-MS m/z. calcd. for C$_{22}$H$_{27}$N$_3$O$_2$+(H) 366.218, obsd. 366.213.

2-(3’,5’-Di-tert-butyl-2’-hydroxyphenyl)-4-diethylamidebenzimidazole, BIP-CONEt$_2$ (5). The carboxylic acid BIP-COOH (2) (400 mg, 1.09 mmol) was dissolved in 50 mL of dry dichloromethane. Then 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDCI, 847 mg, 5.46 mmol), 4-(dimethylamino)pyridine (DMAP, 266 mg, 2.18 mmol), and 1-hydroxybenzotriazole (BtOH, 294 mg, 2.18 mmol) were added. After 30 min of stirring and under argon, dry
diethylamine (225 µL, 2.18 mmol) was added. The reaction mixture was stirred for 12 h at room temperature and the ensuing solution was treated with water (10 mL). The reaction mixture was extracted three times using dichloromethane/methanol. The organic solvent was removed under reduced pressure. The solid was purified by column chromatography on silica gel using dichloromethane/methanol (0.5–10%) and finally recrystallized with hexanes and isopropanol to afford 332 mg of pure BIP-CONEt₂ (5) (72% yield). ¹H NMR (400 MHz, CDCl₃): δ 1.03 (1H, t, J = 7.1, NCH₂CH₃), 1.23-1.33 (15H, m, C(CH₃)₃, NCH₂CH₃), 1.39 (4H, s, C(CH₃)₃), 1.41-1.46 (2H, m, C(CH₃)₃, NCH₂CH₃), 1.49 (13H, s, C(CH₃)₃), 3.29 (1H, q, NCH₂CH₃), 3.58 (4H, qb, NCH₂CH₃), 3.78 (1H, qb, NCH₂CH₃), 6.61 (0.5H, t, J = 7.7 Hz, ArH), 6.91 (0.5H, d, J = 8.0 Hz, ArH), 6.96 (0.5H, d, J = 7.4, ArH), 7.15-7.08 (2H, m, ArH), 7.39 (1H, d, J = 2.3 Hz, ArH), 7.40 (0.5H, d, J = 2.3 Hz, ArH), 7.62 (1H, d, J = 2.3, ArH), 7.68 (1H, dd, J = 7.2, 1.7 Hz, ArH), 7.74 (0.5H, d, J = 2.3, ArH), 11.52 (0.5H, s, NH), 11.88 (1H, s, NH), 13.34 (0.5H, s, OH), 13.46 (1H, s, OH). MALDI-TOF-MS m/z. calcd. for C₂₆H₃₅N₃O₂⁺(H) 422.281, obsd. 422.285.

2-(3',5'-Di-tert-butyl-2'-hydroxyphenyl)-4-methyleneaminebenzimidazole, BIP-CH₂NH₂ (6). In a Schlenk flask, BIP-CONH₂ (4) (100 mg, 0.273 mmol) dissolved in dry THF (25 mL) was added drop-wise to a cooled solution (0 ºC) of LiAlH₄ (103.6 mg, 2.73 mmol) in freshly distilled THF (25 mL). The solution was stirred under argon. The reaction was monitored by
TLC using ninhydrin reagent. After 24 h, the mixture was cooled and water (5 mL) was added carefully. Then, the reaction mixture was filtered through a celite pad and the solvent was removed under reduced pressure. The solid was purified by column chromatography using dichloromethane and methanol (0.5–10%); 46 mg of BIP-CH$_2$NH$_2$ (6) were obtained (yield 48%). $^1$HNMR (400 MHz, (CD$_3$)$_2$CO): $\delta$ 1.36 (9H, s, C(CH$_3$)$_3$), 1.50 (9H, s, C(CH$_3$)$_3$), 4.66 (1H, s, CH$_2$N), 4.78 (1H, s, CH$_2$N), 7.20-7.26 (1.5H, m, ArH), 7.33 (0.5H, d, $J$=7.3 Hz, ArH), 7.40 (0.5H, d, $J$=8.0 Hz, ArH), 7.47 (1H, d, $J$=2.2 Hz, ArH), 7.57-7.62 (0.5H, m, ArH), 7.82 (0.5H, d, $J$=2.2 Hz, ArH), 7.90 (0.5H, d, $J$=2.2 Hz, ArH), 12.25 (0.5H, s, NH), 13.80 (1H, s, OH). MALDI-TOF-MS m/z. calcd. for C$_{22}$H$_{29}$N$_3$O+(H) 352.239, obsd. 352.237.

2-(3',5'-Di-tert-butyl-2'-hydroxyphenyl)-4-diethylmethyleneaminebenzimidazole, BIP-CH$_2$NEt$_2$ (7). The same procedure for the preparation of BIP-CH$_2$NH$_2$ (6) was followed (yield 61%). $^1$HNMR (400 MHz, CDCl$_3$): $\delta$ 1.16 (6H, t, NCH$_2$CH$_3$), 1.38 (9H, s, C(CH$_3$)$_3$), 1.52 (9H, s, C(CH$_3$)$_3$), 2.63 (4H, q, NCH$_2$CH$_3$), 3.97 (2H, s, CH$_2$N), 7.05 (1H, d, $J$=7.3 Hz, ArH), 7.18 (1H, t, $J$=7.7 Hz, ArH), 7.40 (1H, d, $J$=2.3 Hz, ArH), 7.44 (1H, d, $J$=2.3 Hz, ArH), 7.61 (1H, d, $J$=8.0 Hz, ArH), 11.17 (1H, brs, NH), 13.45 (1H, s, OH). MALDI-TOF-MS m/z. calcd. for C$_{26}$H$_{37}$N$_3$O+(H) 408.301, obsd. 408.300.
Figure S1. Structures of compounds 9–11.
Nuclear Magnetic Resonance Spectra

A. BIP-COOH (2)

Figure S2. $^1$H NMR of BIP-COOH (2) in (CD$_3$)$_2$CO.
Figure S3. $^{13}$C NMR of BIP-COOH (2) in (CD$_3$)$_2$CO.
Figure S4. COSY of BIP-COOH (2) in (CD$_3$)$_2$CO.
B. BIP-COOMe (3)

Figure S5. $^1$H NMR of BIP-COOMe (3) in CDCl$_3$. 
Figure S6. $^{13}$C NMR of BIP-COOMe (3) in CDCl$_3$. 
**Figure S7.** COSY of BIP-COOMe (3) in CDCl$_3$. 
Figure S8. HMBC of BIP-COOMe (3) in CDCl$_3$. 
C. BIP-CONH$_2$ (4)

Figure S9. $^1$H NMR of BIP-CONH$_2$ (4) in (CD$_3$)$_2$CO.
Figure S10. COSY of BIP-CONH$_2$ (4) in (CD$_2$)$_2$CO.
D. BIP-CONEt$_2$ (5)

**Figure S11.** $^1$H NMR of BIP-CONEt$_2$ (5) in CDCl$_3$. 
Figure S 12. $^{13}$C NMR of BIP-CONEt$_2$ (5) in CDCl$_3$. 
Figure S13. COSY of BIP-CONEt₂ (5) in CDCl₃.
E. BIP-CH$_2$NH$_2$ (6)

Figure S14. $^1$H NMR of BIP-CH$_2$NH$_2$ (6) in (CD$_3$)$_2$CO.
Figure S15. COSY of BIP-CH$_2$NH$_2$ (6) in (CD$_3$)$_2$CO.
Figure S16. HMBC of BIP-CH$_2$NH$_2$ (6) in (CD$_3$)$_2$CO.
F. BIP-CH$_2$NEt$_2$ (7)

Figure S17. $^1$H NMR of BIP-CH$_2$NEt$_2$ (7) in CDCl$_3$. 

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Page | S25
Figure S18. $^{13}$C NMR of BIP-CH$_2$NEt$_2$ (7) in CDCl$_3$. 
Figure S19. COSY of BIP-CH$_2$NEt$_2$ (7) in CDCl$_3$. 
Figure S20. HMBC of BIP-CH$_2$NEt$_2$ (7) in CDCl$_3$. 
**Figure S21.** HSQC of BIP-CH₂NEt₂ (7) in CDCl₃.
Figure S22. $^1$H NMR of BIP-CH$_2$NEt$_2$ (7) tautomers (ratio 1:1.5) in ACN. In compound BIP-CH$_2$NEt$_2$ (6) the presence of tautomers cannot be detected in this solvent.
Electrochemical Measurements

Figure S23. Cyclic voltammetry of (A) BIP-CH$_2$NH$_2$ (6), (B) BIP-CH$_2$NEt$_2$ (7) (both in black) and the benzylic exocyclic amines references, benzylamine and $N,N$-diethylbenzylamine (both in red). Concentration of all electroactive compounds 1 mM, 0.5 M TBAPF$_6$ in dried acetonitrile. WE: glassy carbon, RE: Ag/AgCl (Fc as internal reference), CE: Pt, and scan rate of 100 mV s$^{-1}$.

Figure S24. Cyclic voltammetry of BIP (1) (blue), BIP-CH$_2$NEt$_2$ (7) (red) and $N,N$-diethylbenzylamine reference (black). Concentration of all electroactive compounds 1 mM, 0.5 M TBAPF$_6$ in dried dichloromethane (DCM). WE: glassy carbon, RE: Ag/AgCl (Fc as internal reference), CE: Pt, and scan rate of 100 mV s$^{-1}$. 
**Figure S25.** Cyclic voltammetry of (A) BIP-CH$_2$NH$_2$ (6) and (B) BIP-CH$_2$NEt$_2$ (7) at different concentrations of trifluoroacetic acid (TFA). Concentration of each electroactive compound was 1 mM; 0.5 M TBAPF$_6$ supporting electrolyte in dry DCM. WE: glassy carbon, RE: Ag/AgCl (Fc as internal reference), CE: Pt, and scan rate of 100 mV s$^{-1}$.  

**IRSEC and IR data**

**Figure S26.** (A) Time course in the IRSEC spectra of BIP (1) (19 mM) at a potential of 1.0 V vs. SCE. IRSEC spectrum of BIP (1) was obtained at resting potential (black). (B) IR spectra of BIP (1) (black) and BIP (1) protonated (red) by treatment with excess gaseous HCl. Solutions in DCM, 0.1 M TBAPF$_6$.

To avoid water in the IR samples, gaseous hydrogen chloride was generated by the reaction of sulfuric acid and sodium chloride and bubbled into the BIP (1) solutions. The protonation of benzimidazole matches the changes in the IRSEC, which, in this region, shows the protonation of the benzimidazole that accompany the oxidation of the phenol at 1 V vs. SCE.
BIP (1) shows two peaks (3453 and 3415 cm$^{-1}$, Figure S26A and B) for the band assigned to N–H stretching of the benzimidazole moiety. As shown in Figure S27A, there is only one band with a maximum at 3454 cm$^{-1}$ when BIP (1) was dissolved in dry dichloromethane in the absence of TBAPF$_6$. On the other hand, the bands in the region between 1575 and 1510 cm$^{-1}$ do not show any shift or splitting by the addition of TBAPF$_6$ (Figure S27B).

**Figure S27.** (A) IR of BIP (1) (19 mM) (black) and 1 BIP (1) protonated (blue) by treatment with excess gaseous HCl. Solution in DCM. (B) IR of BIP (1) (19 mM) (black) and protonated with HCl (blue). Solution in DCM and 0.1 M TBAPF$_6$.

**Figure S28.** (A) Time course in the IRSEC spectra of BIP-CH$_2$NEt$_2$ (7) (17 mM) obtained at a potential of 0.7 V vs. SCE in the 3550–3100 cm$^{-1}$ region. IRSEC spectrum of BIP-CH$_2$NEt$_2$ (7) obtained at resting potential (black); DCM, 0.1M TBAPF$_6$. (B) IR spectra showing the change on the NH stretching mode by titration of BIP-CH$_2$NEt$_2$ (7) in DCM with TFA (0.5–2 equivalents). When the tertiary amine is protonated, its hydrogen bond to the benzimidazole is disrupted and a shift from ~3353 to 3445 cm$^{-1}$ is observed, suggesting that the benzimidazole has undergone a similar reaction to that proposed for BIP (1).
Figure S29. (A) IRSEC spectra of BIP (1) in the 3550–3200 cm$^{-1}$ region at 0 V vs. SCE (black) and at 0.7 V vs. SCE for 5 min (red). (B) IRSEC spectra of BIP (1) in the 1700–1300 cm$^{-1}$ region at 0 V vs. SCE (black) and at 0.7 V vs. SCE for 5 min (red). Analyte: solution of BIP (1) (19 mM) in DCM and 0.1 M TBAPF$_6$. Essentially no changes were detected at this potential in both regions.
**Figure S30.** IR spectra of BIP (1) (19 mM) in DCM. (A) The neutral compound has a band at 1526 cm\(^{-1}\) that is primarily due to an NH bending vibration. (B) Protonated BIP (1) with excess gaseous HCl. This spectrum shows a band at 1556 cm\(^{-1}\) that includes an NH bending vibration of the benzimidazolium ion. (C) IRSEC spectrum of BIP (1) (19 mM) in DCM and 0.1 M TBAPF\(_6\) at 1 V vs. SCE (7 min). This spectrum shows a band at 1556 cm\(^{-1}\) that matches that of the NH bending vibration of the benzimidazolium ion and a band at 1526 cm\(^{-1}\) that is not present in panel B. The phenoxy radical has a component of a C–O bending in this region.
Figure S31. IR spectra of BIP-CH$_2$NEt$_2$ (7) (18 mM) in DCM. (A) The band at 1515 cm$^{-1}$ of the neutral compound is primarily due to an NH bending vibration. The shift to lower wavenumbers with respect to the related band in BIP (1) (1526 cm$^{-1}$) can be explained by the presence of the internal hydrogen bond with the exocyclic amine. (B) The protonation of the exocyclic amine (with 2 equivalents of TFA) disrupts the hydrogen bond between the benzimidazole NH and the –NEt$_2$. The band appears now at 1529 cm$^{-1}$ and matches the band primarily due to the NH bending of the neutral benzimidazole in BIP (1). (C) Protonation with excess gaseous HCl results in formation of the benzimidazolium ion at ~1560 cm$^{-1}$ (similar band was observed upon protonation of BIP (1)). (D) IRSEC spectrum of 7 (0.7 V vs. SCE, 5 min). The band that is formed at 1529 cm$^{-1}$ matches that obtained upon protonation of –NEt$_2$ (panel B). The absence of the band at ~1560 cm$^{-1}$ is the most important evidence that there is no protonation of the benzimidazole moiety upon oxidation of the phenol.
Figure S32. IR of BIP (1) (19 mM) in DCM. Shift of the NH bending vibration of BIP (1) upon deuteration. (A) Neutral BIP (1) (1526 cm$^{-1}$, black line) and BIP (1) after the addition of D$_2$O (1512 cm$^{-1}$, green line). (B) Benzimidazolium ion of BIP (1), generated with excess HCl (1556 cm$^{-1}$, blue line) and after addition of D$_2$O (1524 cm$^{-1}$, green line).

Figure S33. (A) IR spectra showing the titration of TFA (0.5–2 equivalents) to a solution of 7 in DCM. The band at 1515 cm$^{-1}$ decreases in intensity, and at the same time a new band appears at 1529 cm$^{-1}$. (B) Shifts in the band at 1515 cm$^{-1}$ after the addition of D$_2$O (green line).
Kinetic Isotope Effect (KIE) and Electrochemical Measurements

An example of one of the measurements is shown below. Cyclic voltammetry of BIP-COO\text{Me} (3) in acetonitrile exhibits a first reversible wave assigned to the phenoxyl/phenol couple at an apparent standard potential of 0.93 V vs. SCE (Figure S34A; black trace includes the phenol oxidation and the reference ferrocene; red and blue traces illustrate the irreversibility of the process(es) after reaching higher potentials).

**Figure S34.** (A) CV of BIP-COO\text{Me} (3), with ferrocene as an internal standard. (B) “Trumpet plot”: anodic (upper symbols) and cathodic (lower symbols) peak potentials as a function of the log of scan rate. Simulations of the “trumpet plot” (solid lines) leads to the determination of the apparent standard rate constant. Solvent: acetonitrile + 2% MeOH, experimental peak potential (black squares) and corresponding simulation (black solid lines). Solvent acetonitrile + 2% MeOD, experimental peak potential (red circles) and corresponding simulation (red solid lines). Electrode: glassy carbon.

To measure the apparent rate constant of the redox process, the electron transfer (ET) rate must be separated from the rate of diffusion processes, accomplished by increasing the scan rate until ET becomes rate determining. The peak potential separation increased from 80 mV at 2 V/s to more than 150 mV at 500 V/s. This peak separation is used to construct the “trumpet plot” (Figure S34B), and from the simulations the apparent standard rate constants for the electrochemical oxidation of the phenol were determined to be $0.128 \pm 0.005$ cm/s in the 2% MeOH solution and $0.071 \pm 0.007$ cm/s in the 2% MeOD solution, leading to a KIE of $1.8 \pm 0.3$. 
Computational Results

A. Electronic Structure Calculations

The geometries were optimized using density functional theory (DFT) with the B3LYP density functional\(^3,4\) and the 6-31G\(^*\) basis set\(^5-8\) for all atoms. The structures were optimized in acetonitrile using the conductor-like polarizable continuum model (C-PCM)\(^9,10\) with the Bondi atomic radii\(^11\) and including the nonelectrostatic contribution of dispersion,\(^12,13\) repulsion,\(^12,13\) and cavitation energies.\(^14\) For the simple BIP (1) and dyad BIP-PF\(_{10}\) (8), the starting geometries for the optimizations were the crystal structures for the respective compounds.\(^15-18\) The starting geometries for BIP compounds 2–7 and 9–11 were obtained by modifying the crystal structure of 1 prior to full optimizations. For computational tractability, the C\(_6\)F\(_5\) groups were replaced with Cl groups for the dyad BIP-PF\(_{10}\) (8) based on the similarity between their Hammett constants (\(\sigma_p = 27\) and 23,\(^19\) respectively), which represent their electron-withdrawing characters.

Thermochemical data were calculated at \(T = 298.15\) K. All calculated free energies included zero-point energy, entropic contributions, and solvation effects. The solution phase free energies are calculated using the standard Gibbs relation \(\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ\). The zero-point energy and entropic contributions for the molecules are calculated from the vibrational frequencies of the normal modes using the harmonic model, and the solvation free energies are calculated with C-PCM. The relative redox potentials were calculated from the corresponding reaction free energies (\(\Delta G^\circ\)) using methodology described elsewhere.\(^20-23\) The redox potentials were also calculated with five different functionals (BLYP,\(^3,24\) M06-2X,\(^25\) B3P86,\(^4,26\) BP86,\(^24,26\) and \(\omega B97XD^{27-30}\)) and gave qualitatively similar results (Table S1). The anharmonic frequencies were calculated within the framework of vibrational second-order perturbation theory (VPT2),\(^31,32\) which does not require the use of scaling factors typically applied to frequencies.
calculated within the harmonic model. The calculated IR spectra are shown in Figures S35 and S36 and are in qualitative agreement with the experimental IRSEC spectra. All calculations were performed using the Gaussian 09 electronic structure program. The structures and energies of the systems studied are provided in Tables S7–S28.

**Table S1.** Redox Potentials Calculated with Different Functionals

| Compound | Expt. $E_{1/2}$ (V vs. SCE) | Calc. $E_{1/2}$ (V vs. SCE) |
|----------|----------------------------|---------------------------|
|          |                            | B3LYP | BLYP | M06-2X | B3P86 | BP86 | B97XD |
| (1) BIP  | 1.04$^a$                   | 1.04$^b$ | 1.04$^b$ | 1.04$^b$ | 1.04$^b$ | 1.04$^b$ | 1.04$^b$ |
| (2) BIP-COOH | 0.90                | 0.98      | 0.99      | 0.99      | 0.98      | 1.00      | 0.98      |
| (3) BIP-COOMe | 0.93                | 0.96      | 0.98      | 0.97      | 0.96      | 0.99      | 0.96      |
| (4) BIP-CONH$_2$ | 0.92              | 0.94      | 0.97      | 0.93      | 0.94      | 0.95      | 0.93      |
| (5) BIP-CONEt$_2$ | 0.92            | 0.95      | 0.94      | 0.94      | 0.96      | 0.95      | 0.94      |
| (6) BIP-CH$_2$NH$_2$ | 0.56           | 0.66      | 0.71      | 0.58      | 0.64      | 0.64      | 0.66      |
| (7) BIP-CH$_2$NET$_2$ | 0.54         | 0.57      | 0.59      | 0.47      | 0.49      | 0.53      | 0.52      |
| (8) BIP-PF$_{10}$ | 1.00$^a$      | 0.94      | 1.03      | 1.00      | 1.05      | 0.98      | 0.98      |

$^a$Data from Ref. 18.  
$^b$This couple was used as the reference reaction for all other calculated potentials, so the experimental and calculated values agree by construction. Because the experimental reference is $E_{1/2}$, the calculated potentials are also assumed to be $E_{1/2}$.

**Figure S35.** Experimental IRSEC and calculated IR spectra for BIP-CH$_2$NET$_2$ (7) (A) and BIP (1) (B) in the 3550–3100 cm$^{-1}$ region. As mentioned previously, the two bands at 3453 and 3415 cm$^{-1}$ in the IRSEC spectra for BIP (1) appear as one band at 3454 cm$^{-1}$ when BIP (1) is dissolved in dry dichloromethane in the absence of TBAPF$_6$ (Figure 27A). For the calculated spectra, a Lorentzian function with a full-width at half maximum value of 100 cm$^{-1}$ was applied.
Figure S36. Experimental IRSEC and calculated IR spectra for BIP-CH$_2$NEt$_2$ (7) (A) and BIP (1) (B) in the ~1700–1300 cm$^{-1}$ region. For the calculated spectra, a Lorentzian function with a full-width at half maximum value of 8 cm$^{-1}$ was applied.

B. Thermodynamics of PCET

The diabatic states and corresponding electron transfer (ET) and proton transfer (PT) reactions are depicted in Figure S37 for BIP (1) and for BIP-CH$_2$NEt$_2$ (7). The analogous schemes for the other BIP system are similar, and the results are summarized in Figure S38 and Table S2. The ET steps correspond to an ET between the phenol and the electrode (e.g., $1a \rightarrow 2a$, $1aa \rightarrow 2aa$), while the PT steps correspond to an intramolecular PT between the phenol and the proximal N of the imidazole (e.g., $1a \rightarrow 1b$, $1aa \rightarrow 1ba$) or between the distal N of the imidazole and the exocyclic N of an amine group (e.g., $1ab \rightarrow 1bb$). For the concerted electron-proton transfer (EPT), the ET and PT occur concurrently without a stable intermediate. For BIP (1), the concerted EPT process corresponds to the process $1a \rightarrow 2b$. A concerted one-electron, two-proton transfer (E2PT) may also occur for certain systems and would correspond to the process $1aa \rightarrow 2bb$, as for BIP-CH$_2$NEt$_2$ (7).
Figure S37. Schematic depiction of the ET, PT, and EPT (or E2PT) reactions involved in the PCET processes for BIP (1) (A) and BIP-CH₂NEt₂ (7) (B). Similar schemes can be drawn for the other BIP systems.
Figure S38. The thermodynamic square/cube schemes with the relative free energies of the different oxidized states drawn for BIP compounds 1–11 (A–K). The free energies (ΔG°) are reported in units of kcal/mol and are calculated relative to either the 2a or 2aa states for the oxidized states. The states are labelled according to the representative structures shown in Figure S37.
In all systems 1–11, no minima were located with the proton(s) localized on the acceptor(s) in the reduced state, indicating that PT is not predicted to occur prior to ET (oxidation). For BIP (1) and BIP-PF₁₀ (8), the 2b state (the oxidized state with a PT to the proximal imidazole) is more thermodynamically stable than the 2a state, in which no PT occurs (Figure S37A and S38A for 1). For 2–5, the 2ba state (the oxidized state with only PT to the proximal imidazole) is more thermodynamically stable than the 2bb state (the oxidized state with PT to the proximal imidazole and PT to the exocyclic amine) and the 2aa state, in which neither PT step occurs. This 2ba state is favored over the 2bb state by ~14 kcal/mol in the case of BIP-COOMe (3) (Figure S38C). These results predict that only the first PT step will occur for 2–5.

In contrast, for BIP-CH₂NH₂ (6), BIP-CH₂NEt₂ (7), BIP-imineHM (9), BIP-imineMe (10), and BIP-imineCl (11), the 2bb state (the oxidized state with both PT reactions) is more thermodynamically stable than the 2ba state (the oxidized state with only PT to the proximal imidazole), predicting that both PT steps will occur for these systems. In the case of BIP-CH₂NEt₂ (7), this 2bb state is favored over the 2ba state by ~6 kcal/mol (Figure S38G). The calculated free energy differences between the states 2bb and 2ba are reproducible across different functionals as well (Table S2).

**Table S2.** $\Delta G^\circ$ Between the Double Proton Transfer and Single Proton Transfer Products in Oxidized State Calculated with Different Functionals

| Compound       | B3LYP | BLYP | M06-2X | B3P86 | BP86 | ωB97XD |
|----------------|-------|------|--------|-------|------|--------|
| (2) BIP-COOH** | 15.2  | 14.3 | 14.6   | 13.5  | N.D. | 16.1   |
| (3) BIP-COOMe**| 14.9  | 13.8 | 13.5   | 13.2  | N.D. | 15.6   |
| (4) BIP-CONH₂**| 7.1   | 6.5  | 5.9    | 5.7   | 5.2  | 7.9    |
| (5) BIP-CONEt₂**| 5.6  | 5.4  | 5.3    | 4.3   | 3.0  | 7.6    |
| (6) BIP-CH₂NH₂**| −4.2 | −4.3 | −6.6   | −4.4  | −5.0 | −4.7   |
| (7) BIP-CH₂NEt₂**| −6.5 | −7.4 | −8.6   | −8.0  | −8.5 | −7.0   |

*a* All $\Delta G^\circ$ values are reported in units of kcal/mol for the molecules in acetonitrile. The double proton transfer corresponds to PT from the phenol to the proximal imidazole N and PT from the distal imidazole NH to the R group, while the single proton transfer corresponds to only PT to the proximal imidazole. Negative values for $\Delta G^\circ$ indicate that the double proton transfer is more thermodynamically favorable than the single proton transfer. No values are reported for BIP (1) and BIP-PF₁₀ (8) since only the first PT is possible for these systems.

*b* Not determined since a minimum energy structure corresponding to the double proton transfer product was not found.
C. Generating Average Structures

We used average structures generated by averaging the optimized reduced (1a or 1aa), and oxidized (2b or 2bb) structures to calculate both the anodic and cathodic rate constants. The physical motivation for this procedure is that the electron transfer between the compound and the electrode is expected to occur when thermal fluctuations of the complex lead to a structure that is in between the equilibrium reduced and oxidized structures. This approach is consistent with Marcus theory and the golden rule formulation, in which the nonadiabatic transition occurs at the crossing point between the initial and final states. To obtain the structures, a series of geometry optimizations was performed for the reduced and oxidized species with the donor-acceptor distance(s) constrained to values displaced incrementally (by 0.05 Å) from the equilibrium distance(s). For each of the donor-acceptor distances, the resulting reduced and oxidized structures were then aligned along the donor-acceptor axis in the same plane and averaged together to generate an average structure at that donor-acceptor distance.

D. Generating Proton Potentials

For each of the average structures associated with a specific donor-acceptor distance, the position of the hydrogen was optimized for the reduced state (with the hydrogen on the donor) and the oxidized state (with hydrogen on the acceptor), while all other atoms were held fixed. A line connecting the positions of the hydrogens obtained from these constrained optimizations was then used to define the one-dimensional proton coordinate axis for each donor-acceptor distance. The proton potentials were generated on a one-dimensional grid along this axis for each donor-acceptor distance. Specifically, the hydrogen was moved along a grid of 24 points spanning this axis, a single point DFT calculation was performed at each position, and the resulting energies were then interpolated to generate a smooth potential energy curve. For the double proton
transfer system, the two-dimensional proton potential energy surfaces were generated analogously, where each hydrogen moved along a one-dimensional grid.

The shape of the proton potential energy surfaces depends strongly on the proton donor-acceptor distance(s). Figure S39 depicts the one-dimensional proton potentials for 1–5 and 8. Figures S40 and S41 depict the two-dimensional proton potential energy surfaces and contour plots for BIP-CH₂NH₂ (6) and BIP-CH₂NEt₂ (7), respectively, at the equilibrium geometries, as well as the one-dimensional slice along the diagonal of the two-dimensional proton potentials, which corresponds to the two protons moving simultaneously by the same amount. The proton vibrational wavefunctions and all input quantities for the rate constant calculations were determined from the proton potentials shown in Figures S39 and the full two-dimensional surfaces shown in Figures S40 and S41.
Figure S39. Proton potential energy curves for the reduced and oxidized states of BIP (1), BIP-CONH$_2$ (5), BIP-PF$_{10}$ (8), BIP-COOH (2), BIP-COOMe (3), and BIP-CONEt$_2$ (4) for the average structures at fixed donor-acceptor distances ($R_{ON}$) given in the legend.
Figure S40. Two-dimensional proton potential energy surfaces and contour plots for the reduced and oxidized states of BIP-CH$_2$NH$_2$ (6) at the average geometry at $R_{ON} = 2.57$ Å and $R_{NN} = 2.65$ Å, which are the equilibrium donor-acceptor distances for the reduced state (top). Diagonal slices of the proton potential energy surfaces for the reduced and oxidized states of BIP-CH$_2$NH$_2$ (6) for the average structures at fixed donor-acceptor distances ($R_{ON}$ and $R_{NN}$) given in the legend (bottom).
Figure S41. Two-dimensional proton potential energy surfaces and contour plots for the reduced and oxidized states of BIP-CH$_2$NEt$_2$ (7) at the average geometry at $R_{ON} = 2.57 \, \text{Å}$ and $R_{NN} = 2.65 \, \text{Å}$, which are the equilibrium donor-acceptor distances for the reduced state (top). Diagonal slices of the proton potential energy surfaces for the reduced and oxidized states of BIP-CH$_2$NEt$_2$ (7) for the average structures at fixed donor-acceptor distances ($R_{ON}$ and $R_{NN}$) given in the legend (bottom).
E. Determining $P(R)$

The Boltzmann probability for sampling each donor-acceptor distance is given by $P(R)$, which is the classical harmonic probability distribution function:

$$
P(R) = \frac{\exp\left[-k_{\text{eff}}(R - \bar{R})^2 / (2k_B T)\right]}{\int_{-\infty}^{\infty} \exp\left[-k_{\text{eff}}(R - \bar{R})^2 / (2k_B T)\right] dR}.
$$

(S1)

In our approach, the anodic and cathodic probability distribution functions were assumed to be the same, i.e., $P_a(R) \equiv P_c(R)$. We chose $\bar{R}$ to be the average of the donor-acceptor distance in the reduced and oxidized equilibrium structures. The effective force constant ($k_{\text{eff}}$) is obtained by projecting all of the normal modes onto the donor-acceptor axis and summing up the appropriately weighted force constants using methodology described elsewhere.$^{34,35}$ For the double proton transfer system, we include only the symmetric mode, in which both donor-acceptor distances, $R_1$ and $R_2$, increase or decrease concurrently by the same amount. The symmetric motion is expected to exert the greatest effect on the rate constant since both donor-acceptor distances should decrease for the protons to transfer simultaneously. In our approach, we used an average $\bar{k}_{\text{eff}}$ value obtained from the $k_{\text{eff}}$ values for the reduced and oxidized equilibrium structures. The equilibrium donor-acceptor distances and $k_{\text{eff}}$ values are given in Table S3.
Table S3. Proton Donor-Acceptor Distances and Effective Force Constants for Optimized Reduced and Oxidized Structures

| Compound | State | \( R_{\text{on}} \) (Å) | \( R_{\text{nn}} \) (Å) | \( \overline{R}_{\text{on}} \) (Å) | \( \overline{R}_{\text{nn}} \) (Å) | \( k_{\text{eff}} \) (au) | \( \overline{k}_{\text{eff}} \) (au) |
|----------|-------|-----------------|-----------------|-----------------|-----------------|----------------|----------------|
| (1) BIP  | Red   | 2.57            | —               | 2.58            | —               | 0.0451         | 0.0443         |
|          | Ox    | 2.59            | —               | —               | —               | 0.0435         |                |
| (2) BIP-COOH | Red | 2.58            | —               | 2.59            | —               | 0.0488         | 0.0457         |
|          | Ox    | 2.59            | —               | —               | —               | 0.0426         |                |
| (3) BIP-COOMe | Red | 2.58            | —               | 2.59            | —               | 0.0463         | 0.0440         |
|          | Ox    | 2.60            | —               | —               | —               | 0.0440         |                |
| (4) BIP-CONH2 | Red | 2.57            | —               | 2.59            | —               | 0.0488         | 0.0459         |
|          | Ox    | 2.63            | —               | —               | —               | 0.0430         |                |
| (5) BIP-CONEt2 | Red | 2.58            | —               | 2.59            | —               | 0.0458         | 0.0447         |
|          | Ox    | 2.60            | —               | —               | —               | 0.0435         |                |
| (6) BIP-CH2NH2 | Red | 2.57            | 2.86            | 2.61            | 2.85            | 0.0115         | 0.0115         |
|          | Ox    | 2.65            | 2.83            | —               | —               | 0.0115         |                |
| (7) BIP-CH2NEt2 | Red | 2.57            | 2.94            | 2.61            | 2.93            | 0.0139         | 0.0129         |
|          | Ox    | 2.65            | 2.91            | —               | —               | 0.0119         |                |
| (8) BIP-PF10 | Red  | 2.57            | —               | 2.56            | —               | 0.0460         | 0.0446         |
|          | Ox    | 2.55            | —               | —               | —               | 0.0433         |                |

*These values are averages of the values for the reduced and oxidized equilibrium geometries and are used to generate the probability distribution functions \( P(R) \).

F. Calculating Heterogeneous Rate Constants \( k(R) \)

The rate constant expression in Eq. 1 in the main text can be expanded to include the definition of the free energy barriers (\( \Delta G^\ddagger \)). For a fixed proton donor-acceptor distance \( R \), the anodic and cathodic nonadiabatic rate constants are:

\[
k_a^\text{EPT} (\eta; R) = \sum_{\mu,\nu} P_{\mu} \frac{(V^{el} S_{\mu\nu})^2}{\beta' h} \sqrt{\frac{\pi}{k_B T \lambda}} \rho_M \int d\epsilon [1 - f(\epsilon)] \exp \left[ -\frac{(\Delta \tilde{U}_{\mu\nu} + \epsilon - e\eta + \lambda)^2}{4\lambda k_B T} \right]
\]

\[
k_c^\text{EPT} (\eta; R) = \sum_{\mu,\nu} P_{\nu} \frac{(V^{el} S_{\mu\nu})^2}{\beta' h} \sqrt{\frac{\pi}{k_B T \lambda}} \rho_M \int d\epsilon f(\epsilon) \exp \left[ -\frac{(-\Delta \tilde{U}_{\mu\nu} - \epsilon + e\eta + \lambda)^2}{4\lambda k_B T} \right]
\]

where the double summations are over all pairs of reactant (\( \mu \)) and product (\( \nu \)) electron-proton vibronic states (i.e., proton vibrational states within the reactant and product ET states). The density of states \( \rho_M \) at the Fermi level, electronic coupling \( V^{el} \), and \( \beta' \) parameter representing the distance dependence of the electronic coupling are not required for the calculation of KIEs but would be required for the calculation of absolute rate constants.
The total reorganization energy $\lambda$ is the sum of the outer-sphere (solvent) reorganization energy $\lambda_s$ and the inner-sphere (solute) reorganization energy $\lambda_i$. We calculated $\lambda_s$ using a model in which the solute complex is placed in a spherical cavity of radius $a$ on the surface of the electrode, where the distance $d$ from the electrode is the cavity radius ($d = a$):

$$\lambda_s = \frac{(\Delta q)^2}{2} \left( \frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_0} \right) \left( \frac{1}{a} - \frac{1}{2d} \right). \quad (S4)$$

In this model, $\varepsilon_0$ and $\varepsilon_{\infty}$ are the static and optical dielectric constants of the solvent, respectively, $\Delta q$ is the change in charge upon oxidation/reduction ($\pm 1$), and the radius of the cavity $a$ can be estimated from the volume of the molecular cavity from the C-PCM calculation. In addition, we calculated $\lambda_i$ using the standard expression:

$$\lambda_i = \frac{1}{2} \left[ E_{\text{ox}} \left( R_{\text{eq}}^{\text{red}} \right) - E_{\text{ox}} \left( R_{\text{eq}}^{\text{ox}} \right) + E_{\text{red}} \left( R_{\text{eq}}^{\text{ox}} \right) - E_{\text{red}} \left( R_{\text{eq}}^{\text{red}} \right) \right]. \quad (S5)$$

The second and fourth terms are the energies at the optimized equilibrium geometry of the oxidized and reduced species, respectively. The first (third) term was calculated at the optimized reduced (oxidized) geometry with the transferring hydrogen(s) optimized for the oxidized (reduced) state. As shown previously, the KIEs are relatively insensitive to the reorganization energy. The calculated reorganization energies are given in Table S4 for all the BIP systems.

**Table S4. Inner-Sphere ($\lambda_i$), Outer-Sphere ($\lambda_s$), and Total ($\lambda$) Reorganization Energies**

| Compound | $\lambda_i$ | $\lambda_s$ | $\lambda$ |
|----------|-------------|-------------|-----------|
| (1) BIP  | 11.6        | 9.8         | 21.4      |
| (2) BIP-COOH | 12.5        | 9.5         | 22.0      |
| (3) BIP-COOMe | 12.5       | 9.4         | 21.9      |
| (4) BIP-CONH$_2$ | 9.9        | 9.5         | 19.4      |
| (5) BIP-CONEt | 9.8        | 9.0         | 18.8      |
| (6) BIP-CH$_2$NH$_2$ | 12.6       | 9.5         | 22.1      |
| (7) BIP-CH$_2$NEt$_2$ | 14.2       | 9.0         | 23.1      |
| (8) BIP-PF$_{10}$ | 9.8        | 7.1         | 16.9      |

*Units of kcal/mol.*
In Eqs. S2 and S3, the quantity $\Delta \tilde{U}_{\mu \nu}$ is defined to be $\Delta \tilde{U}_{\mu \nu} = \Delta U_{\mu \nu} + k_B T \ln(Q^{\text{II}} / Q^I)$, where $\Delta U_{\mu \nu}$ is the energy difference between the vibronic states $\mu$ and $\nu$, and $Q^I$ and $Q^{\text{II}}$ are the total partition functions of the reduced and oxidized solute compounds, respectively, in bulk solution. In this definition, the vibronic energies are calculated relative to their respective ground states. Moreover, $P_\mu$, $S_\mu$, and $\Delta \tilde{U}_{\mu \nu}$ depend on $R$, and we assume all other quantities are independent of $R$. The total rate constant can then be calculated using the results from Eqs. S2 and S3, along with the probability distribution function $P(R)$, by numerically integrating Eq. 2 in the main text. The numerical integration was done over the coordinate $\delta R$ for the single proton transfer systems and over the coordinate $2\delta R$ for the double proton transfer systems.
G. Summary of Calculations

- Step 1: Optimize the reduced and oxidized structures and determine $P(R)$.
- Step 2: Generate a set of average reduced/oxidized structures for a series of $R$ values.
- Step 3: Determine proton coordinate axes by optimizing the hydrogen position for the reduced and oxidized states on the donor and acceptor, respectively, of the average structures.
- Step 4: Generate the proton potentials for the reduced and oxidized states.
- Step 5: Calculate the proton vibrational wavefunctions corresponding to the proton potentials in Step 4, and determine $P_{\mu}$, $S_{\mu}$, and $\Delta \tilde{U}_{\mu}$.
- Step 6: Calculate the anodic and cathodic rate constants using Eqs. S2 and S3 for each $R$ value.
- Step 7: Calculate the standard rate constant using the results from Step 6, along with the probability distribution function, by numerically integrating Eq. 2 in the main text. The standard rate constant is approximated as $k_a^{\text{EPT}}(\eta = 0)$ because $k_a^{\text{EPT}}(\eta = 0) \approx k_c^{\text{EPT}}(\eta = 0)$ within this formulation for this system.
H. Analysis of Rate Constants

As illustrated in Figure S39, the proton potentials are asymmetric double well potentials, where the donor (left) well is lower in energy for the reduced state, and the acceptor (right) well is lower in energy for the oxidized state. The presence of higher energy minima on the opposite side allows for excited proton vibrational wavefunctions to become localized on the opposite side. Moreover, the separation between the two minima and the potential energy barrier decrease as the donor-acceptor distance decreases. Thus, the overlap integrals between the vibrational wave functions and the relative energies among the vibronic states will also depend on the donor-acceptor distance(s). It is also apparent from Figure S39 that the double well proton potentials for dyad BIP-PF$_{10}$ (8) are more symmetric than for the other systems, which will be discussed below.

The dominant proton donor-acceptor distance in the EPT process is determined by a balance between the probability distribution function $P(R)$ and the electrochemical rate constant $k_a^{\text{EPT}}(\eta; R)$. $P(R)$ has a maximum at the equilibrium donor-acceptor distance $\bar{R}$, and the rate constant typically increases as the donor-acceptor distance decreases relative to its equilibrium value. Figure S42 depicts the probability distribution function $P(R)$, the rate constant $k_a^{\text{EPT}}(\eta; R)$ calculated from Eq. S2, and the product of these two quantities (i.e., the integrand of Eq. 2 in the main text). The dominant donor-acceptor distance, which has the greatest contribution to the total anodic rate constant, is smaller than the equilibrium donor-acceptor distance due to the significant increase in the rate constant as $R$ decreases.
Figure S42. Harmonic probability distribution function $P(R)$, electrochemical rate constant $k_a^{\text{EPT}}(\eta = 0; R)$, and the product of the two quantities for all systems. The quantities are depicted as functions of $\delta R$ or $2\delta R$, the deviations of the proton donor-acceptor distances from their equilibrium values. The vertical line depicts the dominant proton donor-acceptor distance $s$: for 1–5 and 8 the values correspond to the dominant $R_{\text{ON}}$ distance, and for BIP-CH$_2$NH$_2$ (6) and BIP-CH$_2$NEt$_2$ (7) the first and second values correspond to the dominant $R_{\text{ON}}$ and $R_{\text{NN}}$ distances, respectively.

Tables S5 and S6 provide the main contributions to the rate constants at the dominant proton donor-acceptor distance(s). The contribution of each pair of reduced/oxidized ($\mu/\nu$) vibronic states is predominantly determined by a balance among the Boltzmann probability of the reactant state $P_\mu$, the free energy barrier $\Delta G^4$, and the overlap integral $S_{\mu\nu}$ between the reduced and oxidized proton vibrational wavefunctions.
Table S5. Main Contributions to the Rate Constant with Hydrogen$^a$

| Compound | $R_{on}^b$ | $R_{NN}^b$ | $\mu/\nu$ | $P_\mu$ | $\Delta\tilde{U}_{\mu\nu}$ | $\Delta G^2_{\mu\nu}$ | $S^2_{\mu\nu}$ | % contrib$^d$ |
|----------|-----------|-----------|------------|--------|-----------------|-----------------|------------|------------|
| (1) BIP  | 2.47      | —         | 1/0        | 1.07e-3 | -4.05           | 3.52            | 0.537      | 63         |
| (2) BIP-COOH | 2.47     | —         | 1/0        | 4.67e-4 | -4.54           | 3.47            | 0.447      | 51         |
| (3) BIP-COOMe | 2.48     | —         | 1/0        | 5.25e-4 | -4.47           | 3.47            | 0.459      | 53         |
| (4) BIP-CONH$_2$ | 2.52    | —         | 1/0        | 1.87e-4 | -5.09           | 2.63            | 0.524      | 70         |
| (5) BIP-CONEt$_2$ | 2.48   | —         | 1/0        | 7.12e-4 | -4.29           | 2.79            | 0.496      | 61         |
| (6) BIP-CH$_2$NH$_2$ | 2.42  | 2.71      | 1/0        | 7.17e-2 | -1.47           | 4.80            | 0.511      | 96         |
| (7) BIP-CH$_2$NET$_2$ | 2.47 | 2.84      | 1/0        | 1.61e-1 | -0.98           | 5.24            | 0.410      | 92         |
| (8) BIP-PF$_{10}$ | 2.52   | —         | 0/1        | 1.00    | 1.51            | 5.04            | 0.967      | 75         |

$^a$Distances given in Å and energies in kcal/mol.
$^b$These are the dominant donor-acceptor distances, which have the greatest contribution to the overall standard rate constant.

$^c \Delta G^2_{\mu\nu} = (\Delta\tilde{U}_{\mu\nu} + \lambda)^2 / 4\lambda$ and is the effective free energy barrier at $\eta = \epsilon = 0$.

$^d$This is the percentage contribution to the overall standard rate constant at the dominant donor-acceptor distance, $k^{\mu\nu}_\eta (\eta = 0; R)$, excluding contributions less than 10%.

Table S6. Main Contributions to the Rate Constant with Deuterium$^a$

| Compound | $R_{on}^b$ | $R_{NN}^b$ | $\mu/\nu$ | $P_\mu$ | $\Delta\tilde{U}_{\mu\nu}$ | $\Delta G^2_{\mu\nu}$ | $S^2_{\mu\nu}$ | % contrib$^d$ |
|----------|-----------|-----------|------------|--------|-----------------|-----------------|------------|------------|
| (1) BIP  | 2.52      | 2/0       | 1/0        | 1.07e-2 | -5.41           | 2.99            | 0.815      | 89         |
| (2) BIP-COOH | 2.52   | —         | 2/0        | 3.17e-5 | -6.14           | 2.87            | 0.818      | 82         |
| (3) BIP-COOMe | 2.48   | —         | 2/0        | 1.02e-4 | -5.44           | 3.09            | 0.682      | 63         |
| (4) BIP-CONH$_2$ | 2.57  | 2/0       | 2/0        | 2.46e-5 | -6.29           | 2.21            | 0.891      | 94         |
| (5) BIP-CONEt$_2$ | 2.53 | 2/0       | 2/0        | 6.14e-5 | -5.75           | 2.26            | 0.819      | 89         |
| (6) BIP-CH$_2$NH$_2$ | 2.42 | 2.71     | 1/0        | 8.64e-2 | -1.40           | 4.83            | 0.215      | 81         |
| (7) BIP-CH$_2$NET$_2$ | 2.52 | 2.89     | 2/0        | 3.17e-3 | -3.40           | 4.19            | 0.678      | 59         |
| (8) BIP-PF$_{10}$ | 2.52   | —         | 0/1        | 1.00    | 1.44            | 5.00            | 0.988      | 84         |

$^a$Distances given in Å and energies in kcal/mol.
$^b$These are the dominant donor-acceptor distances, which have the greatest contribution to the overall standard rate constant.

$^c \Delta G^2_{\mu\nu} = (\Delta\tilde{U}_{\mu\nu} + \lambda)^2 / 4\lambda$ and is the effective free energy barrier at $\eta = \epsilon = 0$.

$^d$This is the percentage contribution to the overall standard rate constant at the dominant donor-acceptor distance, $k^{\mu\nu}_\eta (\eta = 0; R)$, excluding contributions less than 10%.
A KIE of ~2 is predicted for 1–5. An analysis of these systems illustrates how the different factors contribute to the overall EPT process. Herein, we will focus on BIP-COOOMe (3), but the results for the other systems are presented in Tables S5 and S6. At the dominant donor-acceptor distance ($R_{ON} = 2.48 \text{ Å}$), the main contributions to the standard rate constant arise from the 1/0, 0/0, and the 0/1 pairs of states. As depicted in Figure S43, the first excited reactant state has substantial delocalization onto the acceptor side (near the nitrogen), resulting in significant overlap with the ground product state, which is localized on the acceptor side (near the nitrogen). This relatively large value of ~0.5 for the square of the overlap for the dominant contribution leads to a moderate KIE of ~2.

**Figure S43.** Proton potential energy curves and corresponding hydrogen vibrational wavefunctions for the reduced (blue) and oxidized (red) states of BIP-COOOMe (3). The data are depicted for the main contributing pairs of reduced/oxidized vibronic states at the dominant proton donor-acceptor distance ($R_{ON} = 2.48 \text{ Å}$), with the percentage contribution shown in the pie charts for the 1/0, 0/0, and 0/1 pairs.

In contrast, a KIE of unity is experimentally measured and calculated for the dyad BIP-PF$_{10}$ (8) compound. At the dominant donor-acceptor distance ($R_{ON} = 2.52 \text{ Å}$), the main contribution to the standard rate constant arises from the 0/1 and 1/0 pairs of state. The hydrogen vibrational wavefunctions for these states are depicted in Figure S44. Perhaps most significant is
that for the dyad BiP-PF$_{10}$ (8), the square of the overlap integral for the dominant contribution is much larger ($S_{\mu\nu}^2 = 0.967$) than it is for the systems mentioned previously. For comparison, the square of the overlap integral for the 1/0 pair in BIP-COOMe (3) is 0.459. The large overlap is presumably a result of the more symmetric double well proton potential (Figure S39). An overlap of nearly unity for the dominant contribution leads to the KIE of unity.

![Proton potential energy curves and corresponding hydrogen vibrational wavefunctions](image)  

**Figure S44.** Proton potential energy curves and corresponding hydrogen vibrational wavefunctions for the reduced (blue) and oxidized (red) states of BIP-PF$_{10}$ (8). The data are depicted for the main contributing pairs of reduced/oxidized vibronic states at the dominant proton donor-acceptor distance ($R_{ON} = 2.52$ Å), with the percentage contribution shown in the pie charts for the 0/1 and 1/0 pairs.

As discussed elsewhere,$^{18}$ the porphyrin ring is expected to play a large role in the structural and electronic properties of the compound. Figure S45 depicts the spin density, which represents the localization of the unpaired electron upon oxidation. This figure illustrates that the porphyrin ring can be considered a non-innocent ligand due to the significant delocalization of the spin density onto the porphyrin ring in the oxidized state.
Figure S45. Isocontour plots (isovalue 0.005) of the spin density of BIP-COOME (3) and BIP-PF$_{10}$ (8) at the equilibrium geometries of the oxidized state, showing delocalization of the unpaired spin density onto the porphyrin ring of BIP-PF$_{10}$ (8). The spin density is plotted in the cyan (positive values) and magenta (negative values) wireframe. Color key: carbon, gray; hydrogen, white; oxygen, red; nitrogen, blue; chlorine, green.

Further analysis of the spin density shows that the non-innocence of the porphyrin ring contributes to the more symmetric double well proton potential seen in Figure S39. Figure S46 depicts the proton potential at the dominant donor-acceptor distance ($R_{ON} = 2.52$ Å) for the oxidized state, along with the ratio of spin density on the phenol/phenoxyl and porphyrin ring. The right minimum corresponds to the oxidized state in which the proton is localized on the nitrogen (i.e., the proton has transferred). In this state, the spin density is delocalized over the phenoxy1 and porphyrin in a 55:45 ratio. The left minimum corresponds to the oxidized state in which the proton is localized on the oxygen (i.e., the proton has not transferred). In this state, the spin density is mainly localized on the porphyrin ring, with a 17:83 ratio. The predominant localization of the spin density on the porphyrin ring indicates that the phenol moiety is effectively neutral in this state (left minimum). In contrast, for the other BIP compounds, the left well in the oxidized state would feature a less stable phenol radical. Thus, the extensive delocalization of the spin density onto the porphyrin stabilizes the left well for the dyad BIP-PF$_{10}$ (8), leading to more symmetric proton potentials, greater wavefunction overlaps, and, ultimately, a smaller KIE of unity.
Figure S46. Proton potential energy curve for oxidized state of BIP-PF$_{10}$ (8) at the dominant proton donor-acceptor distance ($R_{ON} = 2.52$ Å) and the relative spin density on the phenol/phenoxyl and porphyrin moieties along the proton transfer coordinate (left). The isocontour plots (isovalue 0.002) of the spin density for [BIP-PF$_{10}$]$^+$ at the two minima along the potential energy curve are shown on the right. The spin density is plotted in the cyan (positive values) and magenta (negative values) wireframe. The left minimum corresponds to the oxidized state in which the proton has not transferred (i.e., on the oxygen), and the right minimum corresponds to the oxidized state in which the proton has transferred (i.e., on the nitrogen). In both cases the spin is delocalized onto the porphyrin ring; however, the predominant localization of the spin onto the porphyrin ring for the oxidized state with the proton localized on the donor stabilizes this state, which features an effectively neutral phenol moiety. Color key: carbon, gray; hydrogen, white; oxygen, red; nitrogen, blue; chlorine, green.

An intermediate KIE of ~1.5 is predicted for BIP-CH$_2$NH$_2$ (6) and BIP-CH$_2$NEt$_2$ (7). We will focus the analysis on BIP-CH$_2$NEt$_2$ (7), but the results for BIP-CH$_2$NH$_2$ (6) are shown in Tables S5 and S6. At the dominant donor-acceptor distances ($R_{ON} = 2.47$ Å and $R_{NN} = 2.84$ Å), the dominant contribution (92%) to the standard rate constant arises from the 1/0 pair of states, i.e., the first excited reactant state with the ground product state. As depicted in Figure S47, the first excited reactant state has substantial delocalization onto the acceptor sides (near the proximal imidazole nitrogen and the exocyclic nitrogen), resulting in significant overlap with the ground product state, which is localized on the acceptor side (near both nitrogen atoms). The square of the overlap integral ($S_{\mu\nu}^2 = 0.410$) is similar to that of the 1/0 pair for BIP-COOMe (3) ($S_{\mu\nu}^2 = 0.459$). However, BIP-COOMe (3) features greater participation from other vibronic...
states (i.e., the $1/0$, $0/0$, and $0/1$ pairs contribute to the total rate constant), leading to smaller rate constants and a larger KIE for BIP-COOMe (3) than BIP-CH$_2$NEt$_2$ (7).

**Figure S47.** Two-dimensional proton potential energy surfaces and contour plots (top) and corresponding hydrogen vibrational wavefunctions (bottom) for the reduced and oxidized states of BIP-CH$_2$NEt$_2$ (7). The data are depicted for the main contributing pair of reduced/oxidized vibronic states at the dominant proton donor-acceptor distances ($R_{ON} = 2.47$ Å and $R_{NN} = 2.84$ Å), the $1/0$ pair, which contributes 92% to the total rate constant.
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Optimized Cartesian Coordinates of Species Studied

The following tables provide the optimized Cartesian coordinates of all species studied. The geometries were optimized in the solution phase (acetonitrile) using the B3LYP functional with the 6-31G** basis set for all atoms.

Table S7. Cartesian coordinates for BIP (1, −1000.696497700 $E_n$)

| atom | x     | y     | z     |
|------|-------|-------|-------|
| O    | 7.865313 | 4.076487 | -3.037846 |
| H    | 8.184733 | 3.923043 | -2.098921 |
| N    | 6.232934 | 4.659070 | 0.779601 |
| H    | 5.329822 | 5.031961 | 1.028924 |
| N    | 7.944949 | 3.967393 | -0.474756 |
| C    | 5.970843 | 4.761719 | -1.714846 |
| C    | 4.655662 | 5.248690 | -1.669256 |
| H    | 4.182550 | 5.405950 | -0.705676 |
| C    | 6.598624 | 4.549008 | -2.972607 |
| C    | 6.710608 | 4.470705 | -0.490649 |
| C    | 6.555672 | 4.604213 | -5.548531 |
| C    | 9.453049 | 3.315568 | 1.449037 |
| H    | 10.284259 | 2.978799 | 0.840345 |
| C    | 5.897370 | 4.825246 | -4.170525 |
| C    | 4.590566 | 5.312435 | -4.054535 |
| H    | 4.051029 | 5.534220 | -4.963822 |
| C    | 8.284491 | 3.812449 | 0.858378 |
| C    | 7.254232 | 4.200720 | 3.061637 |
| H    | 6.421195 | 4.537161 | 3.667425 |
| C    | 7.207491 | 4.245298 | 1.667316 |
| C    | 3.940058 | 5.533816 | -2.828977 |
| C    | 2.508859 | 6.090868 | -2.728715 |
| C    | 9.504329 | 3.266596 | 2.839285 |
|   | H    | C    | H    | H    |
|---|------|------|------|------|
|   | 10.394609 | 8.422465 | 8.503047 | 5.610103 |
|   | 2.887888   | 3.699917 | 3.643357 | 4.973381 |
|   | 3.328939   | 3.632432 | 4.712206 | -6.705611 |
|   | H    | C    | H    | C    |
|   | 4.698554 | 6.120771 | 5.320806 | 6.937253 |
|   | 4.369103 | 4.789985 | 6.027522 | 3.115740 |
|   | -6.697215 | -7.654845 | -6.679429 | -5.722440 |
|   | H    | C    | H    | C    |
|   | 7.620698 | 7.817251 | 7.419865 | 6.044754 |
|   | 2.782054 | 5.488166 | 2.966720 | 2.483590 |
|   | -4.942069 | -5.683544 | -6.693474 | -5.693401 |
|   | H    | C    | H    | C    |
|   | 6.044754 | 7.552916 | 8.286870 | 8.546080 |
|   | 2.483590 | 6.547759 | 5.314042 | 5.267855 |
|   | -5.693474 | -5.620791 | -6.656866 | -4.904163 |
|   | C    | H    | H    | H    |
|   | 1.871575 | 2.437491 | 0.858963 | 1.802086 |
|   | 6.320767 | 7.043652 | 6.712461 | 5.391915 |
|   | -4.108858 | -4.703124 | -3.981614 | -4.681843 |
|   | H    | C    | H    | C    |
|   | 0.552916 | 1.623413 | 0.609618 | 2.019332 |
|   | 5.999179 | 5.496839 | 5.491915 | 4.915696 |
|   | -1.944226 | -1.838430 | -1.944226 | -0.942271 |
|   | C    | H    | H    | H    |
|   | 1.524825 | 2.957338 | 1.531914 | 3.156150 |
|   | 7.438932 | 7.321666 | 7.846677 | 8.169583 |
|   | -1.975980 | -0.971421 | -1.879595 | -2.510876 |
|   | H    | H    | H    | H    |
|   | 1.558472 | 4.138413 | 2.462745 | 2.462745 |
Table S8. Cartesian coordinates for BIP\textsuperscript{+} (1\textsuperscript{+}, −1000.51328386 \(E_h\))

| atom | x       | y       | z       |
|------|---------|---------|---------|
| C    | -2.793941 | -1.031696 | 0.019324 |
| C    | -1.360420  | -1.350364 | 0.045852 |
| C    | -0.409297  | -0.222324 | 0.043581 |
| C    | -0.860335  | 1.085521  | 0.042801 |
| C    | -2.236539  | 1.381856  | 0.028767 |
| C    | -3.151952  | 0.303707  | 0.014639 |
| H    | -0.150761  | 1.902224  | 0.055025 |
| H    | -4.206513  | 0.548123  | -0.001818 |
| C    | -2.764312  | 2.816379  | 0.018520 |
| C    | -3.582896  | 3.033643  | -1.277349 |
| C    | -3.685437  | 3.026516  | 1.244348 |
| C    | -1.634295  | 3.856491  | 0.065391 |
| H    | -2.950754  | 2.921493  | -2.161795 |
| H    | -4.411738  | 2.326457  | -1.355148 |
| H    | -3.997226  | 4.045508  | -1.279464 |
| H    | -3.140745  | 2.863387  | 2.177826 |
| H    | -4.064387  | 4.051941  | 1.241797 |
| H    | -4.543339  | 2.350543  | 1.227413 |
| H    | -2.067216  | 4.859327  | 0.048657 |
| H    | -1.037374  | 3.767588  | 0.977192 |
| H    | -0.965222  | 3.769394  | -0.794629 |
| C    | -3.917935  | -2.083735 | -0.002558 |
| C    | -4.815053  | -1.869397 | 1.242611 |
| C    | -4.767408  | -1.862609 | -1.279913 |
| C    | -3.466575  | -3.555618 | 0.000125 |
| H    | -4.250596  | -2.033547 | 2.164297 |
| H    | -5.240157  | -0.863822 | 1.275229 |
| H    | -5.641684  | -2.585176 | 1.218900 |
| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| H    | -4.166343 | -2.012998 | -2.180366 |
| H    | -5.588958 | -2.584298 | -1.295466 |
| H    | -5.197622 | -0.859529 | -1.319375 |
| H    | -4.366590 | -4.177105 | -0.024323 |
| H    | -2.858474 | -3.802302 | -0.870567 |
| H    | -2.899346 | -3.812092 | 0.895065  |
| O    | -0.931747 | -2.530749 | 0.069774  |
| H    | 0.975144  | -2.548872 | 0.134443  |
| C    | 1.012370  | -0.501248 | 0.033847  |
| N    | 1.570568  | -1.723597 | 0.089973  |
| N    | 2.013169  | 0.403641  | -0.048477 |
| H    | 1.890518  | 1.405329  | -0.106417 |
| C    | 3.959276  | -2.584951 | 0.062407  |
| C    | 2.947596  | -1.622935 | 0.043115  |
| C    | 3.235372  | -0.247251 | -0.046144 |
| C    | 4.546180  | 0.226011  | -0.123799 |
| C    | 5.551849  | -0.733527 | -0.107861 |
| C    | 5.263898  | -2.112868 | -0.016489 |
| H    | 6.585347  | -0.413480 | -0.165971 |
| H    | 6.082891  | -2.822429 | -0.006498 |
| H    | 3.733581  | -3.641006 | 0.134373  |
| H    | 4.760658  | 1.284508  | -0.195984 |
Table S9. Cartesian coordinates for BIP-COOH (2, −1189.27615936 $E_h$)

\[
\begin{array}{cccc}
\text{atom} & x & y & z \\
C & -2.741108 & -1.045421 & -0.009014 \\
C & -1.351897 & -1.323392 & -0.015808 \\
C & -0.419245 & -0.247382 & -0.021577 \\
C & -0.869671 & 1.083851 & -0.025082 \\
C & -2.224484 & 1.387069 & -0.018443 \\
C & -3.116697 & 0.301984 & -0.010154 \\
H & -0.137789 & 1.881744 & -0.032529 \\
H & -4.177621 & 0.523280 & -0.003669 \\
C & -2.766991 & 2.825246 & -0.011436 \\
C & -3.678218 & 3.041913 & -1.240119 \\
C & -3.593413 & 3.052025 & 1.274272 \\
C & -1.636987 & 3.865814 & -0.052361 \\
H & -3.127013 & 2.881534 & -2.171050 \\
H & -4.530961 & 2.358058 & -1.231822 \\
H & -4.068116 & 4.064240 & -1.245687 \\
H & -2.967639 & 2.944361 & 2.164695 \\
H & -4.018427 & 4.060487 & 1.278332 \\
H & -4.416878 & 2.337223 & 1.350385 \\
H & -2.063988 & 4.872020 & -0.031296 \\
H & -0.966687 & 3.770801 & 0.806233 \\
H & -1.037744 & 3.778429 & -0.963108 \\
C & -3.885266 & -2.091028 & -0.000646 \\
C & -4.751582 & -1.871694 & 1.262772 \\
C & -4.765678 & -1.876716 & 1.255197 \\
C & -3.450675 & -3.569062 & 0.000144 \\
H & -4.166657 & -2.037534 & 2.171921 \\
H & -5.166551 & -0.861999 & 1.306072 \\
\end{array}
\]
|  | x       | y       | z         |
|---|---------|---------|-----------|
| H | -5.587030 | -2.578662 | 1.265867  |
| H | -4.190120 | -2.043635 | -2.170152 |
| H | -5.599508 | -2.585582 | -1.247412 |
| H | -5.183802 | -0.868219 | -1.296666 |
| H | -4.355478 | -4.184764 | 0.006078  |
| H | -2.869988 | -3.828802 | -0.885485 |
| H | -2.860929 | -3.825164 | 0.880845  |
| O | -0.911897 | -2.600584 | -0.015469 |
| H | 0.088469  | -2.585708 | -0.019861 |
| C | 1.008442  | -0.535485 | -0.018278 |
| N | 1.523566  | -1.764108 | -0.023786 |
| N | 1.997089  | 0.419182  | -0.002112 |
| H | 1.902586  | 1.425434  | 0.005625  |
| C | 3.925812  | -2.555894 | -0.008774 |
| C | 2.898404  | -1.608653 | -0.010460 |
| C | 3.206433  | -0.228775 | 0.002900  |
| C | 4.527839  | 0.242349  | 0.018152  |
| C | 5.542488  | -0.725615 | 0.021049  |
| C | 5.244040  | -2.095407 | 0.008308  |
| H | 6.574058  | -0.397526 | 0.032275  |
| H | 6.056845  | -2.812285 | 0.010558  |
| H | 3.702584  | -3.616168 | -0.019889 |
| C | 4.775306  | 1.692831  | 0.025383  |
| O | 3.883584  | 2.534269  | 0.019206  |
| O | 6.077986  | 2.023518  | 0.038328  |
| H | 6.133847  | 2.994841  | 0.040059  |
Table S10. Cartesian coordinates for BIP-COOH$^\ddagger$ (2$^\ddagger$, $-1189.09494001 \ E_h$

| atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | -2.790721 | -1.036610 | 0.013820 |
| C    | -1.357210  | -1.357025  | 0.023061  |
| C    | -0.406363  | -0.229390  | 0.027893  |
| C    | -0.854203  | 1.078856   | 0.034942  |
| C    | -2.230930  | 1.377062   | 0.023031  |
| C    | -3.146926  | 0.299957   | 0.013519  |
| H    | -0.140924  | 1.892137   | 0.049979  |
| H    | -4.201323  | 0.545253   | 0.004622  |
| C    | -2.756468  | 2.812047   | 0.008899  |
| C    | -3.577238  | 3.024548   | -1.286575 |
| C    | -3.674870  | 3.028997   | 1.235567  |
| C    | -1.624638  | 3.850354   | 0.048846  |
| H    | -2.947388  | 2.905946   | -2.171778 |
| H    | -4.408102  | 2.319148   | -1.359100 |
| H    | -3.988816  | 4.037484   | -1.292881 |
| H    | -3.128744  | 2.868753   | 2.168655  |
| H    | -4.051275  | 4.055329   | 1.229136  |
| H    | -4.534471  | 2.355148   | 1.229900  |
| H    | -2.056177  | 4.853676   | 0.028378  |
| H    | -1.026105  | 3.764685   | 0.959820  |
| H    | -0.957387  | 3.758296   | -0.812080 |
| C    | -3.915691  | -2.087049  | 0.003661  |
| C    | -4.800039  | -1.869308  | 1.257655  |
| C    | -4.778351  | -1.866671  | -1.264966 |
| C    | -3.465860  | -3.559345  | 0.005430  |
| H    | -4.226214  | -2.029756  | 2.174126  |
| H    | -5.226128  | -0.864233  | 1.291340  |
| Element | X    | Y    | Z    |
|---------|------|------|------|
| H       | -5.625836 | -2.586223 | 1.244233 |
| H       | -4.188226  | -2.022404 | -2.171755 |
| H       | -5.602694  | -2.585335 | -1.268598 |
| H       | -5.205550  | -0.862231 | -1.302515 |
| H       | -4.366923  | -4.179684 | -0.003111 |
| H       | -2.871220  | -3.810517 | -0.873184 |
| H       | -2.886158  | -3.813051 | 0.893234 |
| O       | -0.928259  | -2.537175 | 0.027317 |
| H       | 0.981016   | -2.558031 | 0.049385 |
| C       | 1.014162   | -0.507250 | 0.021156 |
| N       | 1.574460   | -1.729812 | 0.035337 |
| N       | 2.015157   | 0.402965  | -0.008048 |
| H       | 1.939043   | 1.413973  | -0.027877 |
| C       | 3.971807   | -2.575543 | 0.018256 |
| C       | 2.951800   | -1.623171 | 0.015727 |
| C       | 3.229398   | -0.246301 | -0.011201 |
| C       | 4.544975   | 0.239321  | -0.035712 |
| C       | 5.562163   | -0.717775 | -0.035389 |
| C       | 5.278224   | -2.095312 | -0.009875 |
| H       | 6.591107   | -0.382688 | -0.052981 |
| H       | 6.099892   | -2.800813 | -0.009655 |
| H       | 3.754009   | -3.635373 | 0.040741 |
| C       | 4.767790   | 1.698749  | -0.051278 |
| O       | 3.852639   | 2.512562  | -0.046257 |
| O       | 6.059542   | 2.047064  | -0.069430 |
| H       | 6.109555   | 3.019308  | -0.074411 |
Table S11. Cartesian coordinates for BIP-COOMe (3, $-1228.5771037 \text{ } E_h$)

\[
\begin{array}{cccc}
\text{atom} & x & y & z \\
C & -2.743276 & -1.045734 & 0.008791 \\
C & -1.353609 & -1.321342 & 0.016245 \\
C & -0.422731 & -0.243768 & 0.021989 \\
C & -0.875419 & 1.086629 & 0.023389 \\
C & -2.230815 & 1.387592 & 0.015767 \\
C & -3.121214 & 0.301038 & 0.008575 \\
H & -0.144559 & 1.885500 & 0.029389 \\
H & -4.182526 & 0.520533 & 0.001522 \\
C & -2.775834 & 2.824824 & 0.006521 \\
C & -3.601755 & 3.048553 & -1.280062 \\
C & -3.688156 & 3.041561 & 1.234393 \\
C & -1.647682 & 3.867411 & 0.046806 \\
H & -2.975116 & 2.940749 & -2.169861 \\
H & -4.423963 & 2.332273 & -1.355914 \\
H & -4.028434 & 4.056309 & -1.285771 \\
H & -3.137132 & 2.883440 & 2.165813 \\
H & -4.079793 & 4.063233 & 1.238402 \\
H & -4.539692 & 2.356208 & 1.226604 \\
H & -2.076417 & 4.872852 & 0.024219 \\
H & -1.048808 & 3.782186 & 0.957985 \\
H & -0.976727 & 3.772445 & -0.811275 \\
C & -3.885579 & -2.093389 & 0.001012 \\
C & -4.766054 & -1.880206 & 1.255702 \\
C & -4.752588 & -1.876104 & -1.262278 \\
C & -3.448440 & -3.570680 & 0.000620 \\
H & -4.189890 & -2.045551 & 2.170560 \\
H & -5.186071 & -0.872482 & 1.296796 \\
\end{array}
\]
| Atoms | X       | Y       | Z       | Other         |
|-------|---------|---------|---------|---------------|
| H     | -5.598539 | -2.590669 | 1.248529 |
| H     | -4.167540 | -2.041179 | -2.171487 |
| H     | -5.586755 | -2.584596 | -1.264965 |
| H     | -5.169405 | -0.867194 | -1.305861 |
| H     | -4.352194 | -4.187939 | 0.005147  |
| H     | -2.858277 | -3.826026 | 0.880016  |
| H     | -2.867309 | -3.829243 | 0.886296  |
| O     | -0.911504 | -2.597821 | 0.016583  |
| H     | 0.089069  | -2.580987 | 0.020077  |
| C     | 1.005573  | -0.529672 | 0.020622  |
| N     | 1.521598  | -1.757986 | 0.023313  |
| N     | 1.993240  | 0.425583  | 0.009755  |
| H     | 1.898026  | 1.431784  | 0.005681  |
| C     | 3.923454  | -2.549317 | 0.009063  |
| C     | 2.896314  | -1.601714 | 0.012745  |
| C     | 3.203873  | -0.221526 | 0.004369  |
| C     | 4.524948  | 0.250724  | -0.010048 |
| C     | 5.538820  | -0.717644 | -0.015280 |
| C     | 5.241013  | -2.087899 | -0.005929 |
| H     | 6.570063  | -0.389165 | -0.025304 |
| H     | 6.054528  | -2.804051 | -0.009564 |
| H     | 3.700192  | -3.609613 | 0.016630  |
| C     | 4.770933  | 1.705000  | -0.014443 |
| O     | 3.874726  | 2.542236  | 0.006374  |
| O     | 6.072759  | 2.023939  | -0.044323 |
| C     | 6.380081  | 3.432672  | -0.050919 |
| H     | 7.458746  | 3.494831  | -0.171622 |
| H     | 5.872504  | 3.927972  | -0.878337 |
| H     | 6.077917  | 3.892426  | 0.890916  |
Table S12. Cartesian coordinates for BIP-COOME$^{+*}$ (3$^{+*}$, $-1228.39619985 \ E_{\text{h}}$)

| atom | x       | y       | z       |
|------|---------|---------|---------|
| C    | -2.798293 | -1.034345 | 0.007204 |
| C    | -1.364673 | -1.353938 | 0.016521 |
| C    | -0.414068 | -0.225867 | 0.026797 |
| C    | -0.862835 | 1.082119  | 0.035909 |
| C    | -2.239709 | 1.379431  | 0.023001 |
| C    | -3.155206 | 0.301904  | 0.010002 |
| H    | -0.150228 | 1.895936  | 0.052813 |
| H    | -4.209693 | 0.546787  | 0.001020 |
| C    | -2.766494 | 2.813984  | 0.013613 |
| C    | -3.592048 | 3.029469  | -1.278252|
| C    | -3.681381 | 3.026475  | 1.243759 |
| C    | -1.635485 | 3.853147  | 0.052731 |
| H    | -2.965778 | 2.912811  | -2.166243|
| H    | -4.423337 | 2.324418  | -1.349116|
| H    | -4.003617 | 4.042423  | -1.280667|
| H    | -3.132490 | 2.864076  | 2.174846 |
| H    | -4.059021 | 4.052374  | 1.241380 |
| H    | -4.540202 | 2.351563  | 1.231530 |
| H    | -2.067866 | 4.856169  | 0.035278 |
| H    | -1.034563 | 3.766252  | 0.962001 |
| H    | -0.970354 | 3.763156  | -0.810048|
| C    | -3.922724 | -2.085436 | -0.005052|
| C    | -4.806806 | -1.870538 | 1.249618 |
| C    | -4.785826 | -1.863095 | -1.273002|
| C    | -3.472334 | -3.557580 | -0.006110|
| H    | -4.232704 | -2.032741 | 2.165614 |
| H    | -5.233110 | -0.865634 | 1.285497 |
|   |   |   |   |
|---|---|---|---|
| H | -5.632428 | -2.587634 | 1.234989 |
| H | -4.195848 | -2.016908 | -2.180222 |
| H | -5.609883 | -2.582087 | -1.277768 |
| H | -5.213432 | -0.858745 | -1.308612 |
| H | -4.373189 | -4.178229 | -0.015098 |
| H | -2.878203 | -3.807081 | -0.885533 |
| H | -2.891961 | -3.812602 | 0.880879 |
| O | -0.935753 | -2.534150 | 0.016436 |
| H | 0.970715 | -2.554521 | 0.037787 |
| C | 1.006686 | -0.503684 | 0.024577 |
| N | 1.565436 | -1.727104 | 0.032176 |
| N | 2.008914 | 0.405301 | 0.008589 |
| H | 1.935089 | 1.416641 | -0.003021 |
| C | 3.960588 | -2.577146 | 0.020972 |
| C | 2.942850 | -1.622455 | 0.020850 |
| C | 3.222904 | -0.245614 | 0.006220 |
| C | 4.539156 | 0.238526 | -0.010652 |
| C | 5.553702 | -0.721122 | -0.012261 |
| C | 5.267535 | -2.098514 | 0.003157 |
| H | 6.583008 | -0.387480 | -0.023835 |
| H | 6.088389 | -2.805040 | 0.002286 |
| H | 3.740504 | -3.636652 | 0.033681 |
| C | 4.764298 | 1.700718 | -0.020718 |
| O | 3.847633 | 2.514125 | -0.00653 |
| O | 6.055569 | 2.034841 | -0.053178 |
| C | 6.347393 | 3.449497 | -0.068564 |
| H | 7.424235 | 3.521756 | -0.196075 |
| H | 5.827565 | 3.931507 | -0.895772 |
| H | 6.044750 | 3.906846 | 0.873846 |
Table S13. Cartesian coordinates for BIP-CONH₂ (4, -1169.41174561 $E_h$)

![Diagram](image)

| atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | -2.735804 | -1.046215 | 0.075487 |
| C    | -1.348675  | -1.334714  | 0.079882  |
| C    | -0.407124  | -0.266559  | 0.048604  |
| C    | -0.848013  | 1.067486  | 0.024223  |
| C    | -2.200791  | 1.381265  | 0.025750  |
| C    | -3.101586  | 0.303744  | 0.049154  |
| H    | -0.110634  | 1.860113  | 0.007483  |
| H    | -4.160831  | 0.533245  | 0.045440  |
| C    | -2.732045  | 2.823224  | -0.014611 |
| C    | -3.546488  | 3.026942  | -1.311972 |
| C    | -3.649346  | 3.075177  | 1.202643  |
| C    | -1.595071  | 3.856698  | 0.012388  |
| H    | -2.914545  | 2.891902  | -2.194309 |
| H    | -4.375259  | 2.317101  | -1.377615 |
| H    | -3.962663  | 4.038579  | -1.343776 |
| H    | -3.102755  | 2.937834  | 2.139904  |
| H    | -4.034404  | 4.099159  | 1.179782  |
| H    | -4.505091  | 2.395302  | 1.208501  |
| H    | -2.015238  | 4.865002  | -0.031939 |
| H    | -1.002399  | 3.783906  | 0.928692  |
| H    | -0.919579  | 3.740218  | -0.839501 |
| C    | -3.887553  | -2.083595  | 0.089476  |
| C    | -4.759217  | -1.846499  | 1.345850  |
| C    | -4.759929  | -1.875001  | -1.171749 |
| C    | -3.464088  | -3.564859  | 0.104808  |
| H    | -4.179411  | -2.004090  | 2.259774  |
| H    | -5.170851  | -0.834879  | 1.375357  |
|   |      |      |      |      |
|---|------|------|------|------|
| H | -5.597354 | -2.550293 | 1.352787 |
| H | -4.181828 | -2.057728 | -2.082086 |
| H | -5.600479 | -2.575808 | -1.160202 |
| H | -5.168037 | -0.863182 | -1.226589 |
| H | -4.373538 | -4.173716 | 0.106714 |
| H | -2.877314 | -3.834781 | -0.773787 |
| H | -2.884041 | -3.819315 | 0.992349 |
| O | -0.918986 | -2.615204 | 0.110072 |
| H | 0.082431 | -2.606877 | 0.112463 |
| C | 1.018580 | -0.568320 | 0.019203 |
| N | 1.519731 | -1.802095 | 0.088361 |
| N | 2.014900 | 0.366442 | -0.104866 |
| H | 1.952228 | 1.371896 | -0.194471 |
| C | 3.907491 | -2.630080 | 0.012509 |
| C | 2.893981 | -1.668101 | 0.001795 |
| C | 3.218286 | -0.296862 | -0.118802 |
| C | 4.539328 | 0.165871 | -0.226111 |
| C | 5.534799 | -0.821737 | -0.218648 |
| C | 5.224173 | -2.185801 | -0.102817 |
| H | 6.578075 | -0.542276 | -0.308339 |
| H | 6.031478 | -2.909171 | -0.102946 |
| H | 3.675440 | -3.684386 | 0.105864 |
| C | 4.773446 | 1.633641 | -0.338117 |
| O | 3.812834 | 2.421960 | -0.409282 |
| N | 6.048354 | 2.074485 | -0.370145 |
| H | 6.843751 | 1.473746 | -0.227751 |
| H | 6.206895 | 3.070386 | -0.395305 |
Table S14. Cartesian coordinates for BIP-CONH$_2^{+\ast}$ (4$^{+\ast}$, $-1169.23216765$ $E_h$)

| atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | -2.794227 | -1.037283 | 0.081037 |
| C    | -1.363958 | -1.372309 | 0.082522 |
| C    | -0.401022 | -0.255290 | 0.039500 |
| C    | -0.836357 | 1.057206  | 0.024416 |
| C    | -2.209896 | 1.369588  | 0.029769 |
| C    | -3.137372 | 0.302303  | 0.055631 |
| H    | -0.115908 | 1.864021  | 0.010259 |
| H    | -4.189467 | 0.557896  | 0.053739 |
| C    | -2.719851 | 2.809760  | -0.016182 |
| C    | -3.525299 | 3.001924  | -1.324702 |
| C    | -3.645199 | 3.065683  | 1.197257 |
| C    | -1.577972 | 3.837523  | 0.012161 |
| H    | -2.886755 | 2.859074  | -2.200025 |
| H    | -4.360812 | 2.301324  | -1.391145 |
| H    | -3.928258 | 4.017822  | -1.357123 |
| H    | -3.105950 | 2.925152  | 2.137475 |
| H    | -4.011405 | 4.095165  | 1.162389 |
| H    | -4.511438 | 2.400611  | 1.197156 |
| H    | -2.000038 | 4.844261  | -0.027947 |
| H    | -0.985556 | 3.761814  | 0.928003 |
| H    | -0.906585 | 3.725323  | -0.843158 |
| C    | -3.929574 | -2.076839 | 0.097570 |
| C    | -4.802850 | -1.830842 | 1.353934 |
| C    | -4.799705 | -1.868339 | -1.168009 |
| C    | -3.494463 | -3.553457 | 0.118946 |
| H    | -4.223295 | -1.978971 | 2.268862 |
| H    | -5.221401 | -0.822188 | 1.372671 |
|  | X       | Y       | Z       |
|---|---------|---------|---------|
| H | -5.633741 | -2.541949 | 1.359309 |
| H | -4.219124 | -2.047023 | -2.076832 |
| H | -5.632382 | -2.577201 | -1.152696 |
| H | -5.215756 | -0.859929 | -1.219586 |
| H | -4.401718 | -4.164787 | 0.121479  |
| H | -2.904798 | -3.822536 | -0.757791 |
| H | -2.914544 | -3.800517 | 1.008416  |
| O | -0.948206 | -2.556796 | 0.119826  |
| H | 0.961424 | -2.596879 | 0.122611  |
| C | 1.016693 | -0.548797 | -0.000552 |
| N | 1.563166 | -1.777955 | 0.051983  |
| N | 2.025394 | 0.343394  | -0.111252 |
| H | 1.986813 | 1.355320  | -0.191037 |
| C | 3.946536 | -2.656286 | -0.022696 |
| C | 2.939542 | -1.690990 | -0.026551 |
| C | 3.232941 | -0.320293 | -0.127906 |
| C | 4.548031 | 0.160568  | -0.224394 |
| C | 5.547420 | -0.815521 | -0.226227 |
| C | 5.252098 | -2.188813 | -0.129340 |
| H | 6.587892 | -0.524879 | -0.305415 |
| H | 6.068899 | -2.900178 | -0.135210 |
| H | 3.721106 | -3.711602 | 0.058313  |
| C | 4.753295 | 1.638744  | -0.305274 |
| O | 3.769372 | 2.399305  | -0.346279 |
| N | 6.014874 | 2.102026  | -0.335047 |
| H | 6.824906 | 1.510862  | -0.241040 |
| H | 6.157236 | 3.100689  | -0.355987 |
Table S15. Cartesian coordinates for BIP-CONEt₂ (5, −1326.6482539 $E_h$)

| atom | x      | y      | z      |
|------|--------|--------|--------|
| C    | -2.731157 | -1.045328 | 0.070538 |
| C    | -1.342375 | -1.325534 | 0.078152 |
| C    | -0.406408 | -0.251867 | 0.049644 |
| C    | -0.855750 | 1.079649  | 0.032898 |
| C    | -2.210702 | 1.385042  | 0.034952 |
| C    | -3.105130 | 0.302369  | 0.049992 |
| H    | -0.124429 | 1.877932  | 0.026850 |
| H    | -4.165733 | 0.525475  | 0.046969 |
| C    | -2.751214 | 2.823963  | 0.009407 |
| C    | -3.573787 | 3.034921  | -1.281600 |
| C    | -3.664528 | 3.058792  | 1.233206 |
| C    | -1.620575 | 3.864070  | 0.040426 |
| H    | -2.945793 | 2.912905  | -2.168629 |
| H    | -4.398444 | 2.320609  | -1.350063 |
| H    | -3.996639 | 4.044130  | -1.301096 |
| H    | -3.114267 | 2.912480  | 2.166982 |
| H    | -4.053589 | 4.081457  | 1.223376 |
| H    | -4.517733 | 2.375636  | 1.234318 |
| H    | -2.046823 | 4.870213  | 0.005642 |
| H    | -1.024436 | 3.787461  | 0.954105 |
| H    | -0.947533 | 3.758100  | -0.814687 |
| C    | -3.876890 | -2.089446 | 0.079660 |
| C    | -4.749098 | -1.863923 | 1.337786 |
| C    | -4.751156 | -1.879127 | -1.180005 |
| C    | -3.445237 | -3.568380 | 0.086679 |
| H    | -4.167829 | -2.023067 | 2.250496 |
| H    | -5.166169 | -0.854721 | 1.372863 |
| H    | -5.583444 | -2.572267 | 1.341653 |
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| H       | -4.172244 | -2.053219 | -2.091512 |
| H       | -5.587462 | -2.585054 | -1.172001 |
| H       | -5.165353 | -0.869482 | -1.229204 |
| H       | -4.351343 | -4.182245 | 0.083471  |
| H       | -2.855782 | -3.829886 | -0.792690 |
| H       | -2.865144 | -3.825033 | 0.973495  |
| O       | -0.906304 | -2.603756 | 0.110520  |
| H       | 0.095400  | -2.589501 | 0.124781  |
| C       | 1.021305  | -0.547855 | 0.022671  |
| N       | 1.525204  | -1.778881 | 0.114820  |
| N       | 2.016208  | 0.386564  | -0.115302 |
| H       | 1.933423  | 1.373156  | -0.318448 |
| C       | 3.910217  | -2.610856 | 0.016992  |
| C       | 2.898681  | -1.645266 | 0.017884  |
| C       | 3.222541  | -0.276828 | -0.122480 |
| C       | 4.544266  | 0.187890  | -0.225317 |
| C       | 5.534398  | -0.803590 | -0.251739 |
| C       | 5.222229  | -2.169298 | -0.133877 |
| H       | 6.569760  | -0.519295 | -0.388775 |
| H       | 6.027743  | -2.894233 | -0.163757 |
| H       | 3.676640  | -3.664122 | 0.117707  |
| C       | 4.754860  | 1.660356  | -0.400019 |
| O       | 3.866774  | 2.312862  | -0.987999 |
| N       | 5.87738   | 2.273418  | 0.060156  |
| C       | 6.808264  | 1.718767  | 1.054695  |
| C       | 8.226546  | 1.518765  | 0.5259    |
| H       | 6.402539  | 0.781129  | 1.42696   |
| H       | 6.827928  | 2.414561  | 1.899868  |
| H       | 8.858524  | 1.118105  | 1.322939  |
| H       | 8.245485  | 0.816883  | -0.312006 |
| H       | 8.666452  | 2.461879  | 0.192974  |
| C       | 6.015805  | 3.711628  | -0.236204 |
| C       | 6.421893  | 3.993335  | -1.681311 |
| H       | 6.764399  | 4.106805  | 0.451900  |
| H       | 5.064306  | 4.201593  | -0.014489 |
| H       | 6.521088  | 5.071167  | -1.835201 |
| H       | 7.378914  | 3.522554  | -1.919288 |
| H       | 5.665001  | 3.614270  | -2.369778 |
Table S16. Cartesian coordinates for BIP-CONEt$_2$•$^*$ (5$^*$, $^{1326.46901768}$ E$_h$)

| atom | x       | y       | z       |
|------|---------|---------|---------|
| C    | -2.786229 | -1.033117 | 0.081435 |
| C    | -1.356274 | -1.369079 | 0.094061 |
| C    | -0.391754 | -0.253132 | 0.049106 |
| C    | -0.826467 | 1.059652  | 0.028273 |
| C    | -2.199822 | 1.372871  | 0.028015 |
| C    | -3.128311 | 0.306477  | 0.051513 |
| H    | -0.106683 | 1.867041  | 0.016516 |
| H    | -4.180175 | 0.562915  | 0.044756 |
| C    | -2.709114 | 2.813361  | -0.017699|
| C    | -3.513952 | 3.007648  | -1.326162|
| C    | -3.634806 | 3.068282  | 1.195786 |
| C    | -1.566882 | 3.840534  | 0.012439 |
| H    | -2.875054 | 2.866075  | -2.201430|
| H    | -4.349709 | 2.307508  | -1.394142|
| H    | -3.916603 | 4.023718  | -1.357168|
| H    | -3.096080 | 2.925852  | 2.136035 |
| H    | -4.000295 | 4.098071  | 1.162367 |
| H    | -4.501453 | 2.403725  | 1.194294 |
| H    | -1.988311 | 4.847552  | -0.027200|
| H    | -0.975587 | 3.763628  | 0.928844 |
| H    | -0.894701 | 3.728515  | -0.842268|
| C    | -3.922651 | -2.071654 | 0.094465 |
| C    | -4.798502 | -1.825716 | 1.349010 |
| C    | -4.789773 | -1.861331 | -1.172904|
| C    | -3.489084 | -3.548713 | 0.115028 |
| H    | -4.221478 | -1.976336 | 2.265142 |
| H    | -5.214747 | -0.816099 | 1.367903 |
| H    | -5.631015 | -2.534965 | 1.351511 |
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | -4.207066 | -2.038834 | -2.080587 |
| H    | -5.622461 | -2.570215 | -1.160447 |
| H    | -5.205824 | -0.852919 | -1.224357 |
| H    | -4.396885 | -4.159226 | 0.110377  |
| H    | -2.894232 | -3.816137 | -0.758776 |
| H    | -2.914840 | -3.798463 | 1.007348  |
| O    | -0.942197 | -2.553753 | 0.143694  |
| H    | 0.964945  | -2.594494 | 0.180957  |
| C    | 1.025944  | -0.549726 | 0.018358  |
| N    | 1.569163  | -1.778408 | 0.099010  |
| N    | 2.037483  | 0.337015  | -0.109250 |
| H    | 1.979216  | 1.334061  | -0.286453 |
| C    | 3.944883  | -2.671240 | 0.004893  |
| C    | 2.945179  | -1.697635 | 0.011588  |
| C    | 3.245423  | -0.330535 | -0.112920 |
| C    | 4.564133  | 0.146290  | -0.210125 |
| C    | 5.552383  | -0.840188 | -0.247503 |
| C    | 5.247873  | -2.212772 | -0.142233 |
| H    | 6.587398  | -0.555772 | -0.380749 |
| H    | 6.059299  | -2.929582 | -0.177804 |
| H    | 3.712899  | -3.724190 | 0.096939  |
| C    | 4.742566  | 1.628854  | -0.361121 |
| O    | 3.825652  | 2.258146  | -0.930989 |
| N    | 5.840904  | 2.265026  | 0.10871   |
| C    | 6.842986  | 1.70167   | 1.027159  |
| C    | 8.232682  | 1.575483  | 0.407088  |
| H    | 6.490369  | 0.737617  | 1.385998  |
| H    | 6.886806  | 2.365482  | 1.895975  |
| H    | 8.923911  | 1.155506  | 1.142155  |
| H    | 8.22261   | 0.922251  | -0.469037 |
| H    | 8.619929  | 2.549957  | 0.101097  |
| C    | 5.925738  | 3.715788  | -0.148469 |
| C    | 6.318956  | 4.050270  | -1.586054 |
| H    | 6.659099  | 4.117738  | 0.551611  |
| H    | 4.956328  | 4.161931  | 0.085634  |
| H    | 6.374572  | 5.134598  | -1.711825 |
| H    | 7.293326  | 3.624569  | -1.836675 |
| H    | 5.576361  | 3.659371  | -2.283417 |
Table S17. Cartesian coordinates for BIP-CH$_2$NH$_2$ (6, $-1095.3608991\ E_h$)

![BLM2 molecular structure diagram]

| atom | x       | y       | z      |
|------|---------|---------|--------|
| C    | -2.736093 | -1.029761 | 0.015781 |
| C    | -1.346959 | -1.303509 | 0.065879 |
| C    | -0.417462 | -0.225613 | 0.111751 |
| C    | -0.874128 | 1.102642  | 0.141136 |
| C    | -2.230477 | 1.402175  | 0.104537 |
| C    | -3.118211 | 0.316158  | 0.038100 |
| H    | -0.146748 | 1.902696  | 0.199462 |
| H    | -4.179531 | 0.534207  | 0.002329 |
| C    | -2.776746 | 2.839034  | 0.136352 |
| C    | -3.609060 | 3.101942  | -1.138196 |
| C    | -3.684523 | 3.019578  | 1.373605 |
| C    | -1.648581 | 3.880413  | 0.201195 |
| H    | -2.988229 | 3.019845  | -2.034745 |
| H    | -4.433862 | 2.390988  | -1.230068 |
| H    | -4.033354 | 4.110369  | -1.111691 |
| H    | -3.128444 | 2.841634  | 2.298508 |
| H    | -4.083413 | 4.038026  | 1.405172 |
| H    | -4.530958 | 2.327866  | 1.352247 |
| H    | -2.076287 | 4.886596  | 0.206480 |
| H    | -1.047301 | 3.770364  | 1.108098 |
| H    | -0.979801 | 3.806643  | -0.660621 |
| C    | -3.874756 | -2.079082 | -0.064336 |
| C    | -4.821268 | -1.887444 | 1.144449 |
| C    | -4.669671 | -1.847019 | -1.371626 |
| C    | -3.434430 | -3.555641 | -0.061856 |
| H    | -4.294639 | -2.080105 | 2.083688 |
| H    | -5.236310 | -0.877974 | 1.188933 |
| H    | -5.656370 | -2.591624 | 1.077093 |
|   |       |       |       |
|---|-------|-------|-------|
| H | -4.027133 | -1.984137 | -2.245857 |
| H | -5.491434 | -2.566549 | -1.439014 |
| H | -5.096016 | -0.842365 | -1.420747 |
| H | -4.335262 | -4.174914 | -0.115016 |
| H | -2.803301 | -3.799003 | -0.916932 |
| H | -2.891867 | -3.821841 | 0.845735  |
| O | -0.902172 | -2.579767 | 0.065985  |
| H | 0.099729  | -2.557675 | 0.115459  |
| C | 1.013854  | -0.511380 | 0.120047  |
| N | 1.523160  | -1.745031 | 0.173489  |
| N | 2.002002  | 0.432824  | 0.060506  |
| H | 1.945133  | 1.432289  | -0.107533 |
| C | 3.923250  | -2.557668 | 0.148953  |
| C | 2.899821  | -1.601020 | 0.132475  |
| C | 3.216021  | -0.225872 | 0.058134  |
| C | 4.528501  | 0.260136  | -0.000209 |
| C | 5.527349  | -0.715873 | -0.001008 |
| C | 5.233223  | -2.092485 | 0.076132  |
| H | 6.563623  | -0.398075 | -0.056516 |
| H | 6.051212  | -2.804880 | 0.076960  |
| H | 3.700026  | -3.616383 | 0.210529  |
| C | 4.836840  | 1.739761  | -0.006166 |
| N | 3.802995  | 2.512474  | -0.718101 |
| H | 4.020155  | 3.501891  | -0.631139 |
| H | 3.863352  | 2.305482  | -1.712750 |
| H | 4.854209  | 2.103752  | 1.028068  |
| H | 5.849936  | 1.887718  | -0.403809 |
Table S18. Cartesian coordinates for BIP-CH$_2$NH$_2^+\cdot$ (6$^{+}$, $-1095.19483452$ $E_h$)

| atom | x        | y        | z        |
|------|----------|----------|----------|
| C    | -2.789202| -1.035986| 0.032813 |
| C    | -1.358310| -1.365822| 0.064968 |
| C    | -0.395968| -0.249487| 0.037160 |
| C    | -0.840070| 1.064603 | 0.002857 |
| C    | -2.207432| 1.372258 | -0.009714|
| C    | -3.136139| 0.299147 | 0.002436 |
| H    | -0.100169| 1.853169 | -0.016667|
| H    | -4.189089| 0.552552 | -0.018074|
| C    | -2.729027| 2.809825 | -0.055118|
| C    | -3.526701| 3.007034 | -1.366798|
| C    | -3.663882| 3.054667 | 1.153020 |
| C    | -1.594439| 3.844985 | -0.012845|
| H    | -2.880253| 2.877119 | -2.238624|
| H    | -4.355184| 2.299240 | -1.446103|
| H    | -3.939505| 4.019377 | -1.396160|
| H    | -3.130068| 2.911175 | 2.096178 |
| H    | -4.038121| 4.081722 | 1.124097 |
| H    | -4.525015| 2.382781 | 1.143994 |
| H    | -2.020576| 4.850150 | -0.058546|
| H    | -1.013026| 3.771841 | 0.910231 |
| H    | -0.910899| 3.734381 | -0.858518|
| C    | -3.924709| -2.079941| 0.026693 |
| C    | -4.815654| -1.848118| 1.272189 |
| C    | -4.779326| -1.868114| -1.248080|
| C    | -3.486784| -3.556257| 0.041654 |
| H    | -4.248996| -2.007101| 2.193687 |
| H    | -5.230846| -0.838017| 1.296123 |
| H    | -5.649428| -2.556324| 1.261024 |
| Atom | x       | y       | z       |
|------|---------|---------|---------|
| H    | -4.184277 | -2.032918 | -2.150323 |
| H    | -5.607427 | -2.582859 | -1.253653 |
| H    | -5.201595 | -0.862024 | -1.297128 |
| H    | -4.392137 | -4.170780 | 0.022275  |
| H    | -2.880445 | -3.815305 | -0.826760 |
| H    | -2.920848 | -3.810560 | 0.937933  |
| O    | -0.943060 | -2.553994 | 0.112064  |
| H    | 0.994120  | -2.587725 | 0.133422  |
| C    | 1.036552  | -0.505981 | 0.022904  |
| N    | 1.580180  | -1.760907 | 0.079639  |
| N    | 1.979728  | 0.438439  | -0.070181 |
| H    | 2.830133  | 2.167557  | 0.403598  |
| C    | 3.990664  | -2.569101 | 0.038844  |
| C    | 2.946037  | -1.640365 | 0.021943  |
| C    | 3.175419  | -0.246698 | -0.077636 |
| C    | 4.487549  | 0.260226  | -0.163518 |
| C    | 5.524792  | -0.664836 | -0.137864 |
| C    | 5.279409  | -2.053212 | -0.043676 |
| H    | 6.548841  | -0.312399 | -0.195501 |
| H    | 6.123738  | -2.732805 | -0.029600 |
| H    | 3.808057  | -3.633804 | 0.115936  |
| C    | 4.725177  | 1.733409  | -0.342606 |
| N    | 3.792995  | 2.531742  | 0.529041  |
| H    | 4.036913  | 2.446502  | 1.517255  |
| H    | 3.813216  | 3.523166  | 0.285558  |
| H    | 5.745003  | 2.018830  | -0.091987 |
| H    | 4.513797  | 2.048855  | -1.366048 |
**Table S19.** Cartesian coordinates for BIP-CH$_2$NEt$_2$ (7, –1252.60581068 $E_h$)

![Structure Diagram]

| atom | x       | y       | z       |
|------|---------|---------|---------|
| C    | -2.699071| -1.046978| -0.237453 |
| C    | -1.305923| -1.296643| -0.212080 |
| C    | -0.389745| -0.211769| -0.153509 |
| C    | -0.872763| 1.105049 | -0.123051 |
| C    | -2.236229| 1.384840 | -0.152335 |
| C    | -3.114080| 0.289341 | -0.205155 |
| H    | -0.160791| 1.922313 | -0.086455 |
| H    | -4.175123| 0.489109 | -0.226834 |
| O    | -0.857635| -2.573799| -0.244948 |
| H    | 0.146095 | -2.548101| -0.235035 |
| C    | 1.043287 | -0.484428| -0.113857 |
| N    | 1.562048 | -1.712021| -0.193437 |
| N    | 2.022166 | 0.463092 | 0.014331  |
| H    | 1.945095 | 1.454774 | 0.211677  |
| C    | 3.966019 | -2.511230| -0.106845 |
| C    | 2.935447 | -1.561877| -0.096690 |
| C    | 3.239239 | -0.188818| 0.031902  |
| C    | 4.544854 | 0.305441 | 0.142907  |
| C    | 5.550541 | -0.663281| 0.146728  |
| C    | 5.268854 | -2.039533| 0.023146  |
| H    | 6.582651 | -0.340338| 0.236284  |
| H    | 6.092038 | -2.745850| 0.027950  |
| H    | 3.753373 | -3.568928| -0.209373 |
| C    | 4.839830 | 1.788018 | 0.153447  |
| N    | 3.859799 | 2.577143 | 0.920838  |
| H    | 5.867157 | 1.953705 | 0.518885  |
| H    | 4.816567 | 2.145420 | -0.880177 |
| C    | 3.985871 | 4.013595 | 0.609136  |
| C    | 3.485561 | 4.394141 | -0.781674 |
|   |   |   |   |
|---|---|---|---|
| H | 3.537247 | 5.479289 | -0.903831 |
| H | 4.083638 | 3.949203 | -1.580532 |
| H | 2.445975 | 4.083914 | -0.919063 |
| C | 4.046912 | 2.334722 | 2.365926 |
| C | 2.865981 | 2.780084 | 3.223066 |
| H | 4.972423 | 2.825715 | 2.713256 |
| H | 4.194361 | 1.259297 | 2.495242 |
| H | 3.058361 | 2.562454 | 4.271335 |
| H | 2.694878 | 3.857665 | 3.164343 |
| H | 1.948224 | 2.270828 | 2.916779 |
| H | 3.395476 | 4.559656 | 1.347229 |
| H | 5.031689 | 4.343975 | 0.735171 |
| C | -2.725830 | 2.843116 | -0.100809 |
| C | -2.326208 | 3.457399 | 1.258823 |
| C | -2.064362 | 3.657918 | -1.234310 |
| C | -4.251371 | 2.949433 | -0.261175 |
| H | -2.794703 | 2.914848 | 2.084926 |
| H | -1.242959 | 3.419710 | 1.402373 |
| H | -2.642766 | 4.503428 | 1.314635 |
| H | -2.315478 | 3.240854 | -2.213643 |
| H | -2.412822 | 4.694680 | -1.205578 |
| H | -0.975439 | 3.668488 | -1.139574 |
| H | -4.551546 | 4.000147 | -0.233129 |
| H | -4.583007 | 2.530047 | -1.215175 |
| H | -4.783095 | 2.430806 | 0.541330 |
| C | -3.719408 | -2.202215 | -0.289235 |
| C | -3.505858 | -3.043764 | -1.569394 |
| C | -3.563530 | -3.100942 | 0.960301 |
| C | -5.171150 | -1.691312 | -0.311925 |
| H | -3.657246 | -2.431708 | -2.463421 |
| H | -2.502248 | -3.465905 | -1.607347 |
| H | -4.230107 | -3.864155 | -1.598277 |
| H | -3.758513 | -2.538027 | 1.871878 |
| H | -4.267520 | -3.937519 | 0.900560 |
| H | -2.554321 | -3.503594 | 1.040168 |
| H | -5.847573 | -2.549597 | -0.344781 |
| H | -5.417287 | -1.110605 | 0.581385 |
| H | -5.377304 | -1.074228 | -1.190880 |
Table S20. Cartesian coordinates for BIP-CH$_2$NEt$_2$** ($7^*$, $-1252.44311635$ $E_h$)

| atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | -2.739617 | -1.034844 | -0.258100 |
| C    | -1.304344 | -1.352171 | -0.237048 |
| C    | -0.351857 | -0.232358 | -0.174572 |
| C    | -0.815471 | 1.070954  | -0.147709 |
| C    | -2.190076 | 1.369728  | -0.187296 |
| C    | -3.113132 | 0.294365  | -0.234783 |
| H    | -0.087465 | 1.871401  | -0.100134 |
| H    | -4.164935 | 0.536477  | -0.254817 |
| O    | -0.892148 | -2.543301 | -0.269574 |
| H    | 1.052264  | -2.559777 | -0.242209 |
| C    | 1.082911  | -0.477023 | -0.127674 |
| N    | 1.632235  | -1.729658 | -0.172260 |
| N    | 2.018432  | 0.472952  | -0.026453 |
| H    | 2.870323  | 2.177540  | 0.719979 |
| C    | 4.042911  | -2.528372 | -0.076769 |
| C    | 2.996227  | -1.602203 | -0.089180 |
| C    | 3.217934  | -0.205754 | -0.005518 |
| C    | 4.526221  | 0.306761  | 0.105478 |
| C    | 5.564068  | -0.619152 | 0.137062 |
| C    | 5.327007  | -2.008527 | 0.041806 |
| H    | 6.584765  | -0.263383 | 0.223734 |
| H    | 6.173294  | -2.685440 | 0.063594 |
| H    | 3.864492  | -3.593959 | -0.151478 |
| C    | 4.785744  | 1.789060  | 0.092062 |
| N    | 3.806200  | 2.554888  | 0.955798 |
| H    | 5.786858  | 2.026955  | 0.450933 |
| H    | 4.675839  | 2.183720  | -0.918346 |
| C    | 3.821506  | 4.033912  | 0.641473 |
| C    | 3.209996  | 4.368042  | -0.710021 |
|    |    |    |    |    |
|----|----|----|----|----|
| H  | 3.192040 | 5.454717 | -0.814004 |
| H  | 3.786932 | 3.967700 | -1.545339 |
| H  | 2.181844 | 4.005586 | -0.782588 |
| C  | 4.056334 | 2.287055 | 2.423848 |
| C  | 2.891594 | 2.698310 | 3.307986 |
| H  | 4.975308 | 2.817455 | 2.678542 |
| H  | 4.242252 | 1.216429 | 2.505205 |
| H  | 3.125965 | 2.411303 | 4.335048 |
| H  | 2.181844 | 4.005586 | 0.782588 |
| C  | 4.056334 | 2.287055 | 2.423848 |
| C  | 2.891594 | 2.698310 | 3.307986 |
| H  | 4.975308 | 2.817455 | 2.678542 |
| H  | 4.242252 | 1.216429 | 2.505205 |
| H  | 3.125965 | 2.411303 | 4.335048 |
| H  | 2.181844 | 4.005586 | 0.782588 |
| H  | 4.863940 | 4.347707 | 0.709884 |
| C  | -2.642447 | 2.831449 | -0.147610 |
| C  | -2.227379 | 3.431746 | 1.216555 |
| C  | -1.945457 | 3.620826 | -1.280811 |
| C  | -4.162180 | 2.984851 | -0.317403 |
| H  | -2.719351 | 2.907853 | 2.040262 |
| H  | -1.146806 | 3.365292 | 1.365953 |
| H  | -2.516614 | 4.485481 | 1.259618 |
| H  | -2.191607 | 3.200697 | -2.259492 |
| H  | -2.284419 | 4.660117 | -1.259737 |
| H  | -0.858589 | 3.618842 | -1.170617 |
| H  | -4.420666 | 4.046254 | -0.301593 |
| H  | -4.503320 | 2.569762 | -1.269498 |
| H  | -4.715698 | 2.496520 | 0.488763 |
| C  | -3.769985 | -2.169380 | -0.298572 |
| C  | -3.566793 | -3.019415 | -1.576984 |
| C  | -3.610654 | -3.065366 | 0.954610 |
| C  | -5.213382 | -1.636766 | -0.314769 |
| H  | -3.702039 | -2.409054 | -2.474347 |
| H  | -2.571755 | -3.461241 | -1.604107 |
| H  | -4.309743 | -3.822337 | -1.600717 |
| H  | -3.804887 | -2.495473 | 1.867850 |
| H  | -4.335997 | -3.883433 | 0.910201 |
| H  | -2.609211 | -3.489383 | 1.014014 |
| H  | -5.901735 | -2.485186 | -0.343410 |
| H  | -5.446552 | -1.052406 | 0.579525 |
| H  | -5.413777 | -1.018626 | -1.194116 |
Table S21. Cartesian coordinates for BIP-PF$_{10}$ (8, $-3209.91104577$ $E_h$)

![Diagram of BIP-PF$_{10}$ molecule]

| atom | x    | y    | z      |
|------|------|------|--------|
| C    | 17.120935 | 10.380269 | 0.107454 |
| H    | 18.123442 | 10.741096 | 0.268168 |
| O    | 4.770553  | 5.155192  | -1.618706 |
| O    | 3.832134  | 7.185063  | -1.326434 |
| N    | 12.342266 | 8.731343  | -0.246899 |
| N    | 11.244869 | 9.269457  | 2.398649 |
| H    | 12.127101 | 9.428252  | 1.924881 |
| N    | 13.893754 | 10.315149 | 3.175561 |
| N    | 14.968737 | 9.849414  | 0.509628 |
| H    | 14.082950 | 9.705412  | 0.981650 |
| H    | 17.123952 | 9.661447  | -1.970317 |
| N    | 18.912811 | 15.241831 | 1.123569 |
| C    | 12.980493 | 8.583853  | -1.448749 |
| C    | 12.078494 | 8.075875  | -2.469929 |
| H    | 12.333912 | 7.885963  | -3.500547 |
| C    | 10.876739 | 7.919150  | -1.864542 |
| H    | 9.953962  | 7.582882  | -2.310217 |
| C    | 11.056653 | 8.320965  | -0.474769 |
| C    | 10.013155 | 8.301041  | 0.475862 |
| C    | 10.126699 | 8.729409  | 1.807925 |
| C    | 9.113567  | 8.672640  | 2.820338 |
| H    | 8.119991  | 8.283946  | 2.668760 |
| C    | 9.636755  | 9.179435  | 3.979426 |
| H    | 9.144332  | 9.278399  | 4.932958 |
| C    | 10.990362 | 9.564360  | 3.718148 |
| C    | 11.904290 | 10.149328 | 4.598538 |
| C    | 13.234641 | 10.531909 | 4.354859 |
| C    | 14.076891 | 11.224932 | 5.316052 |
| H    | 13.788413 | 11.519881 | 6.312517 |
|   | X   | Y   | Z   |
|---|-----|-----|-----|
| C | 15.263531 | 11.429557 | 4.694057 |
| H | 16.136539 | 11.932775 | 5.078648 |
| C | 15.140502 | 10.850514 | 3.362837 |
| C | 16.183156 | 10.885990 | 2.411526 |
| C | 16.083935 | 10.402934 | 1.095830 |
| O | 21.154661 | 13.126235 | 3.951898 |
| H | 21.302800 | 13.958113 | 3.405046 |
| C | 16.611153 | 9.466631  | -0.787932 |
| C | 14.327723 | 8.909330  | -1.672787 |
| C | 8.671503  | 7.802934  | 0.041516  |
| C | 7.56402   | 8.668024  | 0.020702  |
| H | 7.686733  | 9.700215  | 0.326420  |
| C | 6.321487  | 8.217474  | -0.410042 |
| H | 5.471247  | 8.888041  | -0.439152 |
| C | 6.155595  | 6.888695  | -0.819021 |
| C | 7.250952  | 6.015501  | -0.792545 |
| H | 7.123804  | 4.986594  | -1.102794 |
| C | 4.895325  | 6.470897  | -0.367366 |
| H | 9.337002  | 5.789081  | -0.345835 |
| C | 4.808274  | 6.452465  | -1.271592 |
| C | 3.492762  | 4.662815  | -2.072421 |
| H | 2.732338  | 4.818832  | -1.307215 |
| H | 3.638605  | 3.601039  | -2.255153 |
| H | 3.197381  | 5.172089  | -2.990477 |
| C | 17.490104 | 11.491537 | 2.812232 |
| C | 18.275843 | 10.906330 | 3.823018 |
| H | 17.903695 | 10.005529 | 4.291125 |
| C | 19.504332 | 11.421894 | 4.237558 |
| C | 19.966327 | 12.599492 | 3.593160 |
| C | 19.178309 | 13.223997 | 2.587689 |
| C | 17.956001 | 12.652481 | 2.204728 |
| H | 17.358043 | 13.127805 | 1.435497 |
| C | 20.320771 | 10.747328 | 5.357542 |
| C | 19.607966 | 9.503418  | 5.919066 |
| H | 19.462872 | 8.732992  | 5.156624 |
| H | 18.633668 | 9.749899  | 6.350070 |
| H | 20.223419 | 9.073776  | 6.713791 |
| C | 20.517440 | 11.733451 | 6.533309 |

Page | S95
|   |   |   |   |
|---|---|---|---|
| H | 21.111388 | 11.255604 | 7.318456 |
| H | 19.552977 | 12.012771 | 6.967549 |
| H | 21.032296 | 12.640433 | 6.218385 |
| C | 21.695061 | 10.292187 | 4.815359 |
| H | 22.276727 | 9.836263 | 5.622573 |
| H | 22.264776 | 11.129467 | 4.413330 |
| H | 21.571000 | 9.545029 | 4.026177 |
| C | 19.636047 | 14.478323 | 1.999830 |
| C | 19.653047 | 16.372660 | 0.834636 |
| C | 19.397936 | 17.487337 | 0.034295 |
| H | 18.473663 | 17.587820 | -0.522077 |
| C | 20.387090 | 18.467760 | -0.005773 |
| H | 20.228971 | 19.354422 | -0.609074 |
| C | 21.588440 | 18.334991 | 0.719875 |
| H | 22.332369 | 19.121744 | 0.657840 |
| C | 21.837980 | 17.220775 | 1.515759 |
| H | 22.759606 | 17.120301 | 2.076875 |
| C | 20.851259 | 16.228829 | 1.573736 |
| H | 17.985981 | 15.035053 | 0.782779 |
| Cl | 11.275882 | 10.465185 | 6.219442 |
| Cl | 14.967874 | 8.561406 | -3.282919 |
Table S22. Cartesian coordinates for BIP-PF$^{10}$* (8$^{*}$, $-3209.72797191 E_h$)

| atom | x         | y         | z         |
|------|-----------|-----------|-----------|
| C    | 16.988306 | 10.679901 | 0.080131  |
| H    | 18.023206 | 10.923577 | 0.250170  |
| O    | 4.860546  | 5.137324  | -1.857358 |
| O    | 3.777855  | 6.845525  | -0.857698 |
| N    | 12.207829 | 9.038024  | -0.306369 |
| N    | 11.307265 | 9.022356  | 2.447551  |
| H    | 12.125798 | 9.346212  | 1.942321  |
| N    | 13.939433 | 10.16994  | 3.245878  |
| N    | 14.818010 | 10.242427 | 0.482282  |
| H    | 13.937313 | 10.097642 | 0.964531  |
| H    | 16.900391 | 10.192898 | -2.064126 |
| N    | 19.186879 | 15.019992 | 0.784415  |
| C    | 12.749719 | 9.182091  | -1.552625 |
| C    | 11.803388 | 8.826081  | -2.594568 |
| H    | 11.984500 | 8.872482  | -3.656275 |
| C    | 10.667920 | 8.456363  | -1.955134 |
| H    | 9.734704  | 8.145238  | -2.396233 |
| C    | 10.939738 | 8.578418  | -0.530294 |
| C    | 9.999020  | 8.268063  | 0.476915  |
| C    | 10.204407 | 8.453354  | 1.862472  |
| C    | 9.309110  | 8.091427  | 2.913885  |
| H    | 8.358643  | 7.604582  | 2.771008  |
| C    | 9.878907  | 8.470934  | 4.103481  |
| H    | 9.471566  | 8.351377  | 5.093487  |
| C    | 11.141452 | 9.061432  | 3.806337  |
| C    | 12.053926 | 9.634390  | 4.718024  |
| C    | 13.312658 | 10.196552 | 4.468302  |
| C    | 14.116915 | 10.880971 | 5.461352  |
| H    | 13.840302 | 11.057159 | 6.488319  |
| Atom | X Position | Y Position | Z Position |
|------|------------|------------|------------|
| C    | 15.247480  | 11.266789  | 4.822451   |
| H    | 16.068156  | 11.836531  | 5.226827   |
| C    | 15.131131  | 10.790455  | 3.450734   |
| C    | 16.134485  | 10.991231  | 2.458940   |
| C    | 15.974454  | 10.664465  | 1.085315   |
| O    | 21.003623  | 13.272156  | 4.108714   |
| H    | 21.201080  | 14.071399  | 3.508920   |
| C    | 16.416862  | 10.295395  | -1.106850  |
| N    | 20.827670  | 15.023711  | 2.294448   |
| C    | 15.044132  | 10.015237  | -0.852283  |
| C    | 14.075190  | 9.589557   | -1.783189  |
| C    | 8.672246   | 7.734107   | 0.061740   |
| C    | 7.497676   | 8.442142   | 0.369198   |
| H    | 7.559117   | 9.379939   | 0.907366   |
| C    | 6.260287   | 7.959376   | -0.039840  |
| H    | 5.352738   | 8.504895   | 0.188039   |
| C    | 6.170274   | 6.754903   | -0.747712  |
| C    | 7.336191   | 6.038584   | -1.048304  |
| H    | 7.270195   | 5.102748   | -1.587331  |
| C    | 8.576389   | 6.527719   | -0.651683  |
| H    | 9.475283   | 5.970169   | -0.885009  |
| C    | 4.817753   | 6.274271   | -1.146711  |
| C    | 3.584949   | 4.581131   | -2.238186  |
| H    | 2.995081   | 4.350968   | -1.350598  |
| H    | 3.819056   | 3.670859   | -2.784741  |
| H    | 3.039736   | 5.280367   | -2.872274  |
| C    | 17.420420  | 11.578643  | 2.862583   |
| C    | 18.132369  | 11.074496  | 3.978479   |
| H    | 17.719656  | 10.217556  | 4.490703   |
| C    | 19.347895  | 11.588259  | 4.406364   |
| C    | 19.862268  | 12.716812  | 3.701999   |
| C    | 19.164384  | 13.247038  | 2.571338   |
| C    | 17.970881  | 12.658291  | 2.158910   |
| H    | 17.430650  | 13.069610  | 1.315438   |
| C    | 20.114204  | 10.967431  | 5.590360   |
| C    | 19.378989  | 9.745230   | 6.169390   |
| H    | 19.260221  | 8.950123   | 5.428038   |
| H    | 18.390750  | 10.004362  | 6.559221   |
| H    | 19.966699  | 9.342615   | 6.998160   |
| C    | 20.261106  | 12.004670  | 6.728682   |
|     |       |       |       |
|-----|-------|-------|-------|
| H   | 20.818157 | 11.559051 | 7.558128 |
| H   | 19.278534 | 12.303116 | 7.104986 |
| H   | 20.791679 | 12.896789 | 6.398249 |
| C   | 21.509517 | 10.491341 | 5.122979 |
| H   | 22.051611 | 10.058216 | 5.968875 |
| H   | 22.102810 | 11.312562 | 4.722274 |
| H   | 21.416834 | 9.721148  | 4.352078 |
| C   | 19.716001 | 14.413353 | 1.890019 |
| C   | 20.004026 | 16.086094 | 0.456707 |
| C   | 19.949247 | 17.040538 | -0.560994|
| H   | 19.157560 | 17.037636 | -1.300836|
| C   | 20.960598 | 17.997954 | -0.576926|
| H   | 20.955549 | 18.759516 | -1.349180|
| C   | 21.990894 | 18.002962 | 0.387180 |
| H   | 22.756602 | 18.769456 | 0.338798 |
| C   | 22.044361 | 17.047119 | 1.395540 |
| H   | 22.834083 | 17.046801 | 2.137798 |
| C   | 21.035561 | 16.076372 | 1.425068 |
| H   | 18.348700 | 14.745475 | 0.294366 |
| Cl  | 11.505882 | 9.650600  | 6.378288 |
| Cl  | 14.617141 | 9.559776  | -3.443935|
Table S23. Cartesian coordinates for BIP-Ph$^H$imine (9, –1325.20249562 $E_h$)

| atom | x       | y       | z        |
|------|---------|---------|----------|
| C    | -2.752890 | -1.062183 | 0.074790 |
| C    | -1.363087 | -1.337214 | 0.070406 |
| C    | -0.431439 | -0.259738 | 0.039446 |
| C    | -0.885838 | 1.069997  | 0.025089 |
| C    | -2.241765 | 1.370251  | 0.036584 |
| C    | -3.131960 | 0.284080  | 0.058438 |
| H    | -0.156613 | 1.870240  | 0.008633 |
| H    | -4.193408 | 0.503186  | 0.061941 |
| C    | -2.787926 | 2.806847  | 0.009281 |
| C    | -3.615845 | 3.010790  | -1.279567|
| C    | -3.698155 | 3.041868  | 1.235312 |
| C    | -1.661251 | 3.851449  | 0.033092 |
| H    | -2.990933 | 2.887050  | -2.168516|
| H    | -4.438643 | 2.293793  | -1.342304|
| H    | -4.041708 | 4.018677  | -1.301239|
| H    | -3.144212 | 2.901600  | 2.167783 |
| H    | -4.091627 | 4.062815  | 1.222972 |
| H    | -4.548436 | 2.355121  | 1.241696 |
| H    | -2.092233 | 4.855592  | -0.000426|
| H    | -1.059009 | 3.778471  | 0.943169 |
| H    | -0.992765 | 3.747544  | -0.825821|
| C    | -3.894601 | -2.110680 | 0.087256 |
| C    | -4.766189 | -1.886854 | 1.346120 |
| C    | -4.770989 | -1.905179 | -1.171696|
| C    | -3.457424 | -3.587981 | 0.096457 |
| H    | -4.183082 | -2.041969 | 2.258335 |
| H    | -5.187946 | -0.879598 | 1.380343 |
|   |   |   |   |
|---|---|---|---|
| H | -5.597274 | -2.598983 | 1.352027 |
| H | -4.192460 | -2.078475 | -2.083601 |
| H | -5.605039 | -2.613776 | -1.161972 |
| H | -5.188325 | -0.896841 | -1.221498 |
| H | -4.361298 | -4.205138 | 0.099574 |
| H | -2.871314 | -3.850115 | -0.784879 |
| H | -2.872248 | -3.839903 | 0.981351 |
| O | -0.922306 | -2.613879 | 0.091773 |
| H | 0.079358  | -2.596559 | 0.091419 |
| C | 0.996686  | -0.549822 | 0.000893 |
| N | 1.505442  | -1.780570 | 0.065570 |
| N | 1.989923  | 0.390689  | -0.129463 |
| H | 1.917280  | 1.398009  | -0.197262 |
| C | 3.898047  | -2.600381 | -0.021128 |
| C | 2.878616  | -1.641135 | -0.027433 |
| C | 3.193321  | -0.270775 | -0.149146 |
| C | 4.514265  | 0.195511  | -0.270094 |
| C | 5.515973  | -0.788896 | -0.262731 |
| C | 5.214186  | -2.153538 | -0.141764 |
| H | 6.549479  | -0.472751 | -0.353838 |
| H | 6.022551  | -2.875821 | -0.141491 |
| H | 3.668935  | -3.655144 | 0.074453 |
| C | 4.848610  | 1.603822  | -0.400793 |
| H | 5.915859  | 1.831956  | -0.492479 |
| N | 3.950934  | 2.529312  | -0.397345 |
| C | 4.348542  | 3.871199  | -0.582892 |
| C | 3.608902  | 4.868873  | 0.073039 |
| C | 5.414772  | 4.250468  | -1.418142 |
| C | 3.955937  | 6.211240  | -0.064961 |
| H | 2.771658  | 4.571039  | 0.694638 |
| C | 5.749082  | 5.596000  | -1.561181 |
| H | 5.958983  | 3.494827  | -1.973029 |
| C | 5.029034  | 6.580880  | -0.880325 |
| H | 3.381797  | 6.969864  | 0.455748 |
| H | 6.569275  | 5.877684  | -2.212810 |
| H | 5.289955  | 7.626740  | -0.998077 |
\textbf{Table S24.} Cartesian coordinates for BIP-Ph$^\text{imine}^{\text{*}}$ (9$^\text{**}$, –1325.02838212 $E_h$)

\begin{table}[h]
\centering
\begin{tabular}{llll}
\hline
atom & x & y & z \\
\hline
C & -2.760272 & -1.001250 & 0.150020 \\
C & -1.337977 & -1.369406 & 0.148761 \\
C & -0.348087 & -0.279019 & 0.072531 \\
C & -0.755040 & 1.044380 & 0.032598 \\
C & -2.116299 & 1.389784 & 0.054514 \\
C & -3.071696 & 0.343402 & 0.105798 \\
H & 0.004431 & 1.812729 & -0.017706 \\
H & -4.117675 & 0.624544 & 0.110286 \\
C & -2.597503 & 2.839931 & -0.006548 \\
C & -3.395909 & 3.036411 & -1.318265 \\
C & -3.519351 & 3.131026 & 1.201105 \\
C & -1.435682 & 3.845172 & 0.015618 \\
H & -2.758156 & 2.875156 & -2.191118 \\
H & -4.241927 & 2.348143 & -1.380493 \\
H & -3.783455 & 4.058057 & -1.361695 \\
H & -2.984303 & 2.992176 & 2.144151 \\
H & -3.865730 & 4.167007 & 1.153395 \\
H & -4.398873 & 2.483729 & 1.209108 \\
H & -1.837386 & 4.859434 & -0.043180 \\
H & -0.853313 & 3.770966 & 0.938193 \\
H & -0.758726 & 3.705858 & -0.831248 \\
C & -3.921993 & -2.013634 & 0.190557 \\
C & -4.775072 & -1.736195 & 1.453236 \\
C & -4.802946 & -1.799524 & -1.065962 \\
C & -3.523267 & -3.500666 & 0.221752 \\
H & -4.188451 & -1.886449 & 2.363466 \\
H & -5.170318 & -0.717989 & 1.464928 \\
\hline
\end{tabular}
\end{table}
|   |   |   |   |
|---|---|---|---|
| H | -5.621625 | -2.428349 | 1.477528 |
| H | -4.238430 | -2.003161 | -1.979930 |
| H | -5.652930 | -2.487196 | -1.033553 |
| H | -5.195074 | -0.781911 | -1.125002 |
| H | -4.444994 | -4.090249 | 0.233065 |
| H | -2.943621 | -3.790082 | -0.655264 |
| H | -2.944362 | -3.754682 | 1.109862 |
| O | -0.953030 | -2.565770 | 0.211761 |
| H | 0.973600 | -2.685867 | 0.192615 |
| C | 1.073955 | -0.577464 | 0.014557 |
| N | 1.581566 | -1.840888 | 0.090103 |
| N | 2.045022 | 0.340662 | -0.138204 |
| H | 3.007344 | 2.099897 | -0.348428 |
| C | 3.960908 | -2.715697 | -0.016320 |
| C | 2.946540 | -1.759843 | -0.019995 |
| C | 3.206999 | -0.375493 | -0.161897 |
| C | 4.544484 | 0.076625 | -0.313781 |
| C | 5.563131 | -0.897643 | -0.309278 |
| C | 5.274360 | -2.258005 | -0.163391 |
| H | 6.591116 | -0.574338 | -0.423129 |
| H | 6.085845 | -2.975363 | -0.165566 |
| H | 3.744526 | -3.770923 | 0.096418 |
| C | 4.877444 | 1.451096 | -0.479884 |
| H | 5.917187 | 1.728691 | -0.605584 |
| N | 3.979955 | 2.404480 | -0.490005 |
| C | 4.194429 | 3.793984 | -0.671622 |
| C | 3.104833 | 4.640300 | -0.437631 |
| C | 5.430630 | 4.311376 | -1.077816 |
| C | 3.258626 | 6.015498 | -0.595701 |
| H | 2.152546 | 4.219167 | -0.134829 |
| C | 5.568956 | 5.687580 | -1.231680 |
| H | 6.271356 | 3.660151 | -1.281157 |
| C | 4.488748 | 6.541952 | -0.991908 |
| H | 2.417009 | 6.672658 | -0.412983 |
| H | 6.524217 | 6.094073 | -1.542218 |
| H | 4.607483 | 7.611966 | -1.118057 |
**Table S25.** Cartesian coordinates for BIP-Ph<sup>Me</sup>imine (10, -1364.52096527 $E_h$)
|   |   |   |   |   |
|---|---|---|---|---|
| H | -5.599684 | -2.605283 | 1.347595 |
| H | -4.194411 | -2.080542 | -2.087085 |
| H | -5.607329 | -2.616502 | -1.166319 |
| H | -5.189655 | -0.899668 | -1.223205 |
| H | -4.364070 | -4.210383 | 0.094875 |
| H | -2.875046 | -3.855123 | -0.791116 |
| H | -2.873810 | -3.846293 | 0.975121 |
| O | -0.923947 | -2.620599 | 0.081081 |
| H | 0.077660  | -2.603381 | 0.078409  |
| C | 0.995296  | -0.556383 | -0.003631 |
| N | 1.505068  | -1.787249 | 0.052381  |
| N | 1.987291  | 0.385708  | -0.128528 |
| H | 1.914949  | 1.393772  | -0.185711 |
| C | 3.899221  | -2.603647 | -0.041911 |
| C | 2.878255  | -1.645818 | -0.041150 |
| C | 3.191368  | -0.274389 | -0.153990 |
| C | 4.511083  | 0.195403  | -0.275015 |
| C | 5.513989  | -0.787649 | -0.276536 |
| C | 5.214279  | -2.153627 | -0.162540 |
| H | 6.546945  | -0.469830 | -0.368122 |
| H | 6.023884  | -2.874545 | -0.167883 |
| H | 3.672143  | -3.659370 | 0.047880  |
| C | 4.840384  | 1.606333  | -0.394083 |
| H | 5.905601  | 1.839128  | -0.497452 |
| N | 3.938754  | 2.527712  | -0.365973 |
| C | 4.321607  | 3.874918  | -0.540340 |
| C | 3.569692  | 4.861007  | 0.116941  |
| C | 5.387866  | 4.281120  | -1.361800 |
| C | 3.902739  | 6.207252  | -0.006965 |
| H | 2.733999  | 4.552590  | 0.735773  |
| C | 5.702586  | 5.631655  | -1.489181 |
| H | 5.953527  | 3.541687  | -1.917417 |
| C | 4.973125  | 6.620345  | -0.812901 |
| H | 3.316522  | 6.950628  | 0.524034  |
| H | 6.527597  | 5.927241  | -2.130252 |
| C | 5.302502  | 8.082710  | -0.980294 |
| H | 6.371044  | 8.232286  | -1.152096 |
| H | 4.770579  | 8.509727  | -1.837841 |
| H | 5.008875  | 8.656003  | -0.097942 |
Table S26. Cartesian coordinates for BIP-PhMe-imine\(^{**}\) (10\(^{*}\), –1364.34786079 \(E_{h}\))

| atom | x       | y       | z       |
|------|---------|---------|---------|
| C    | -2.768132 | -0.983038 | 0.093939 |
| C    | -1.349306 | -1.362758 | 0.065083 |
| C    | -0.350396 | -0.279118 | 0.008235 |
| C    | -0.746416 | 1.048498  | 0.012807 |
| C    | -2.103915 | 1.403705  | 0.064423 |
| C    | -3.068031 | 0.364629  | 0.094624 |
| H    | 0.017787  | 1.813013  | -0.021281 |
| H    | -4.111091 | 0.654646  | 0.122956 |
| C    | -2.573084 | 2.858776  | 0.092729 |
| C    | -3.511959 | 3.115632  | -1.109842|
| C    | -3.350118 | 3.103046  | 1.408484 |
| C    | -1.402636 | 3.851799  | 0.021359 |
| H    | -2.992384 | 2.941589  | -2.055770|
| H    | -4.392943 | 2.470492  | -1.082085|
| H    | -3.854503 | 4.153811  | -1.091489|
| H    | -2.700012 | 2.965564  | 2.276329 |
| H    | -3.730167 | 4.128256  | 1.424710 |
| H    | -4.200398 | 2.424450  | 1.506351 |
| H    | -1.792037 | 4.871905  | 0.057381 |
| H    | -0.712243 | 3.728261  | 0.859823 |
| H    | -0.837079 | 3.743601  | -0.908427|
| C    | -3.938331 | -1.986018 | 0.120205 |
| C    | -4.785174 | -1.726789 | 1.391044 |
| C    | -4.820922 | -1.738348 | -1.128804|
| C    | -3.552507 | -3.476746 | 0.122351 |
| H    | -4.195524 | -1.894049 | 2.296272 |
| H    | -5.178759 | -0.708344 | 1.422259 |
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | -5.633239 | -2.417280 | 1.407059 |
| H    | -4.261337 | -1.930819 | -2.048229 |
| H    | -5.679132 | -2.416166 | -1.106963 |
| H    | -5.199678 | -0.714479 | -1.166072 |
| H    | -4.479229 | -4.058426 | 0.133231 |
| H    | -2.983758 | -3.756568 | -0.764748 |
| H    | -2.967116 | -3.749961 | 1.000591 |
| O    | -0.974255 | -2.563654 | 0.091367 |
| H    | 0.949150  | -2.662520 | 0.071533 |
| C    | 1.068736  | -0.588694 | -0.061209 |
| N    | 1.564610  | -1.858456 | -0.012521 |
| N    | 2.048545  | 0.323611  | -0.189772 |
| H    | 3.037741  | 2.090979  | -0.367532 |
| C    | 3.936256  | -2.752739 | -0.119704 |
| C    | 2.930605  | -1.787356 | -0.113252 |
| C    | 3.204366  | -0.402502 | -0.223637 |
| C    | 4.547128  | 0.040023  | -0.354665 |
| C    | 5.556257  | -0.943755 | -0.364661 |
| C    | 5.254446  | -2.304432 | -0.248376 |
| H    | 6.588057  | -0.627255 | -0.462645 |
| H    | 6.059694  | -3.028772 | -0.257987 |
| H    | 3.709060  | -3.807698 | -0.027983 |
| C    | 4.899454  | 1.414220  | -0.481920 |
| H    | 5.943991  | 1.677100  | -0.597695 |
| N    | 4.018306  | 2.382714  | -0.473069 |
| C    | 4.257231  | 3.772023  | -0.605647 |
| C    | 3.143324  | 4.618168  | -0.615944 |
| C    | 5.544774  | 4.306198  | -0.731947 |
| C    | 3.319965  | 5.990686  | -0.754433 |
| H    | 2.146983  | 4.200283  | -0.522395 |
| C    | 5.700356  | 5.680566  | -0.870032 |
| H    | 6.420257  | 3.669257  | -0.724065 |
| C    | 4.598797  | 6.550080  | -0.883074 |
| H    | 2.448900  | 6.636364  | -0.765900 |
| H    | 6.701199  | 6.086231  | -0.970636 |
| C    | 4.784625  | 8.039110  | -1.007081 |
| H    | 5.732087  | 8.281842  | -1.492077 |
| H    | 3.972874  | 8.491354  | -1.581378 |
| H    | 4.788187  | 8.512489  | -0.019286 |
Table S27. Cartesian coordinates for BIP-PhClimine (11, -1784.79719641 $E_h$)

![Diagram of BIP-PhClimine](image)

| atom | x          | y          | z          |
|------|------------|------------|------------|
| C    | -2.749097  | -1.058704  | 0.075920   |
| C    | -1.359962  | -1.337177  | 0.069226   |
| C    | -0.425831  | -0.262019  | 0.036896   |
| C    | -0.876946  | 1.068841   | 0.022827   |
| C    | -2.232008  | 1.372474   | 0.036100   |
| C    | -3.124840  | 0.288506   | 0.059672   |
| H    | -0.146009  | 1.867442   | 0.004996   |
| H    | -4.185722  | 0.510241   | 0.064727   |
| C    | -2.774237  | 2.810492   | 0.008271   |
| C    | -3.602404  | 3.015687   | -1.280213  |
| C    | -3.683092  | 3.048914   | 1.234626   |
| C    | -1.644617  | 3.851979   | 0.030745   |
| H    | -2.978703  | 2.888631   | -2.169546  |
| H    | -4.427658  | 2.301367   | -1.341280  |
| H    | -4.024921  | 4.024953   | -1.302795  |
| H    | -3.128884  | 2.908383   | 2.166898   |
| H    | -4.074205  | 4.070756   | 1.221430   |
| H    | -4.534972  | 2.364177   | 1.242224   |
| H    | -2.072945  | 4.857254   | -0.002361  |
| H    | -1.041607  | 3.777398   | 0.940209   |
| H    | -0.977372  | 3.746301   | -0.828950  |
| C    | -3.893483  | -2.104238  | 0.090248   |
| C    | -4.763333  | -1.877298  | 1.349768   |
| C    | -4.770576  | -1.897333  | -1.167988  |
| C    | -3.459934  | -3.582588  | 0.100159   |
| H    | -4.179819  | -2.033195  | 2.261583   |
| H    | -5.182616  | -0.868995  | 1.383657   |
| Atom | X     | Y     | Z     | Coordinates |
|------|-------|-------|-------|-------------|
| H    | -5.596133 | -2.587391 | 1.356907 |
| H    | -4.193514  | -2.073089 | -2.080357 |
| H    | -5.606623  | -2.603544 | -1.156772 |
| H    | -5.185131  | -0.887862 | -1.218205 |
| H    | -4.365286  | -4.197540 | 0.104950  |
| H    | -2.875538  | -3.846829 | -0.781687 |
| H    | -2.874233  | -3.835121 | 0.984546  |
| O    | -0.922022  | -2.614878 | 0.089822  |
| H    | 0.079418   | -2.600110 | 0.087836  |
| C    | 1.001522   | -0.555009 | -0.003346 |
| N    | 1.509034   | -1.786261 | 0.060051  |
| N    | 1.995619   | 0.384698  | -0.133947 |
| H    | 1.923684   | 1.392110  | -0.200793 |
| C    | 3.901398   | -2.607313 | -0.028257 |
| C    | 2.882348   | -1.647807 | -0.033832 |
| C    | 3.198101   | -0.277587 | -0.154823 |
| C    | 4.519667   | 0.187816  | -0.274989 |
| C    | 5.521190   | -0.797131 | -0.268098 |
| C    | 5.218129   | -2.161366 | -0.148477 |
| H    | 6.554921   | -0.481631 | -0.358319 |
| H    | 6.025753   | -2.884431 | -0.148575 |
| H    | 3.671849   | -3.662033 | 0.066752  |
| C    | 4.853166   | 1.595721  | -0.402508 |
| H    | 5.920212   | 1.826637  | -0.488127 |
| N    | 3.951697   | 2.518278  | -0.401199 |
| C    | 4.338335   | 3.861407  | -0.580485 |
| C    | 3.569483   | 4.850135  | 0.054029  |
| C    | 5.417361   | 4.257448  | -1.390654 |
| C    | 3.890100   | 6.198365  | -0.074403 |
| H    | 2.720973   | 4.546841  | 0.656359  |
| C    | 5.740386   | 5.604461  | -1.535283 |
| H    | 5.992453   | 3.514424  | -1.930155 |
| C    | 4.977370   | 6.560833  | -0.867962 |
| H    | 3.297525   | 6.955021  | 0.423864  |
| H    | 6.569188   | 5.906754  | -2.163278 |
| Cl   | 5.377190   | 8.269163  | -1.053549 |
Table S28. Cartesian coordinates for BIP-PhClimine$^{+}$(11$^{+}$, -1784.62138900 $E_h$)

```
| atom | x     | y     | z     |
|------|-------|-------|-------|
| C    | -2.760445 | -1.009054 | 0.111904 |
| C    | -1.338194  | -1.377165  | 0.094444  |
| C    | -0.348692  | -0.285659  | 0.033605  |
| C    | -0.755560  | 1.038264  | 0.019408  |
| C    | -2.116626  | 1.383025  | 0.052412  |
| C    | -3.071964  | 0.336247  | 0.092550  |
| H    | 0.003010  | 1.807994  | -0.020820 |
| H    | -4.117813  | 0.617358  | 0.107866  |
| C    | -2.596684  | 2.834270  | 0.014679  |
| C    | -3.402231  | 3.049575  | -1.289686 |
| C    | -3.512155  | 3.108807  | 1.231003  |
| C    | -1.433033  | 3.837313  | 0.043716  |
| H    | -2.770047  | 2.898072  | -2.168383 |
| H    | -4.250014  | 2.363877  | -1.355759 |
| H    | -3.788012  | 4.072444  | -1.317580 |
| H    | -2.974331  | 2.951994  | 2.169664  |
| H    | -3.855459  | 4.146472  | 1.201766  |
| H    | -4.393891  | 2.464346  | 1.231526  |
| H    | -1.833104  | 4.853108  | 0.002884  |
| H    | -0.843788  | 3.748353  | 0.960603  |
| H    | -0.762473  | 3.709459  | -0.809893 |
| C    | -3.921845  | -2.021988  | 0.143002  |
| C    | -4.770866  | -1.761289  | 1.412002  |
| C    | -4.806645  | -1.791391  | -1.107901 |
| C    | -3.522672  | -3.509148  | 0.154032  |
| H    | -4.181365  | -1.923124  | 2.318337  |
| H    | -5.166823  | -0.743652  | 1.438518  |
```
| Element | X | Y | Z | Coordinates |
|---------|---|---|---|-------------|
| H       | -5.616940 | -2.454211 | 1.429944 |
| H       | -4.244087 | -1.981038 | -2.026068 |
| H       | -5.199840 | -0.773321 | -1.151098 |
| H       | -4.444232 | -4.098957 | 0.165718 |
| H       | -2.949866 | -3.788434 | -0.730680 |
| H       | -2.936904 | -3.773009 | 1.034785 |
| O       | 0.952402  | -2.574289 | 0.130936 |
| H       | 0.975942  | -2.657141 | 0.100366 |
| C       | 1.073007  | -0.582580 | -0.033153 |
| N       | 1.582357  | -1.846512 | 0.013334 |
| N       | 2.043033  | 0.340036  | -0.165913 |
| H       | 2.998925  | 2.102692  | -0.308222 |
| C       | 3.964125  | -2.713943 | -0.109179 |
| C       | 2.947397  | -1.760986 | -0.095328 |
| C       | 3.205397  | -0.373410 | -0.206499 |
| C       | 4.542341  | 0.085228  | -0.345169 |
| C       | 5.563573  | -0.887030 | -0.361427 |
| C       | 5.277265  | -2.250363 | -0.245378 |
| H       | 6.591017  | -0.558855 | -0.465545 |
| H       | 6.090047  | -2.965997 | -0.261150 |
| H       | 3.750321  | -3.771748 | -0.017637 |
| C       | 4.871450  | 1.463688  | -0.470139 |
| H       | 5.910292  | 1.748617  | -0.589137 |
| N       | 3.969897  | 2.414815  | -0.445306 |
| C       | 4.183748  | 3.806533  | -0.591547 |
| C       | 3.120969  | 4.659250  | -0.273840 |
| C       | 5.400652  | 4.326559  | -1.047980 |
| C       | 3.274278  | 6.036804  | -0.396606 |
| H       | 2.178900  | 4.248577  | 0.070671 |
| C       | 5.556370  | 5.702277  | -1.170184 |
| H       | 6.221523  | 3.677905  | -1.324959 |
| C       | 4.492961  | 6.543992  | -0.843008 |
| H       | 2.457838  | 6.701921  | -0.148572 |
| H       | 6.493517  | 6.114615  | -1.520247 |
| Cl      | 4.696697  | 8.281502  | -1.005676 |