Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Proton-Coupled Electron Transfer Oxidation of O-H Bond by the N-Radical Cation of Wurster's Blue Salt ($TMPDA^{\bullet+}$)

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1. Materials and Instrumentation

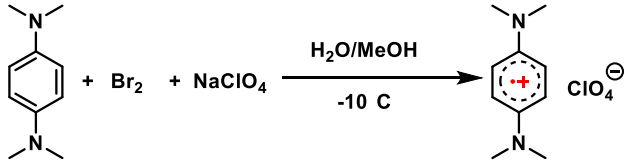
1.1 Materials

N, N, N', N'-Tetramethyl-1, 4-phenylenediamine was purchased from Energy Chemical. 1-Hydroxy-2, 2, 6, 6-tetramethylpiperidine was purchased from 3A Chemicals. Purification by sublimation at room temperature to a cold finger cooled with dry ice/acetone gave orange crystalline TEMPO-H.[1] Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was purchased from J&K, and recrystallized from anhydrous EtOH.[2] And commercial solvents were used in this work were used as received and further purified by the standard methods, if necessary. Distilled water was further purified using a Milli-Q Ultrapure water purification system.

1.2 Instrumentation

UV-Vis measurements were recorded by Agilent Cary 8454 spectrometer. Electrochemical experiments were performed on a CHI-660E electrochemical workstation. UV-vis stopped-flow kinetic measurements of the reaction between $TMPDA^{\bullet+}$ and TEMPOH were examined using a Hi-Tech Scientific SF-51 stopped-flow set-up equipped with a halogen light source, a monochromator, a 0.2 cm quartz cell and a photomultiplier detector connected to an oscilloscope. To determine the kinetic isotope effects, MeCN solutions of TEMPOH were prepared with 0.72 mM CD_3OD and the kinetics performed otherwise as above. The large molar excess of CD_3OD provided high isotopic enrichment at the exchangeable OH positions.

2. Synthesis and characterisation of N, N, N', N'-Tetramethyl-p-phenylenediamine radical cation perchlorate ($TMPDA^{\bullet+}ClO_4^-$)



N,N,N',N'-Tetramethyl-p-phenylenediamine radical cation perchlorate ($TMPDA^{\bullet+}ClO_4^-$) was prepared according to the reported procedure.[3] 0.5 g of tetramethyl-p-phenylenediamine hydrochloride was dissolved in a solution of 8.75 mL of water/ 15 mL of methanol containing 6.25 g of sodium perchlorate. It was cooled to —10°C; 15.88 mL of 51 μL aqueous bromine solution was added drop wise. The crystals were filtered, washed several times with small portions of ice-cold methanol, then abundantly with dry ether; yield 3.4 g. The crystals have a brown metallic luster. Very thin needles, observed under the polarizing microscope when the long axis is parallel to blue; when perpendicular to the vector they are indigo blue. The solutions show the characteristic bands of the Wurster's blue free radical. The crystals are not hygroscopic and did not change in any of their observed properties over months. And the EPR spectra was similar with the reference.[4]

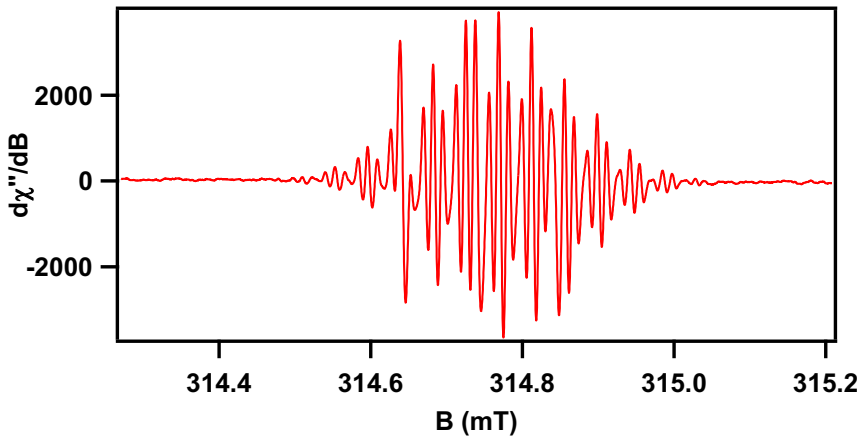
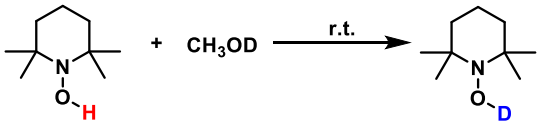


Figure S1. ESR spectra of $TMPDA^{\bullet+}$ recorded in acetonitrile solution at 25 °C.

3. Synthesis and characterization of TEMPOD



Anhydrous TEMPOD was synthesized by stirring purified TEMPOH with CH_3OD for 1h then removing volatiles under vacuum. And repeated the process for three times. The ^1H NMR should the chemical shift at 5.21 ppm was disappeared.

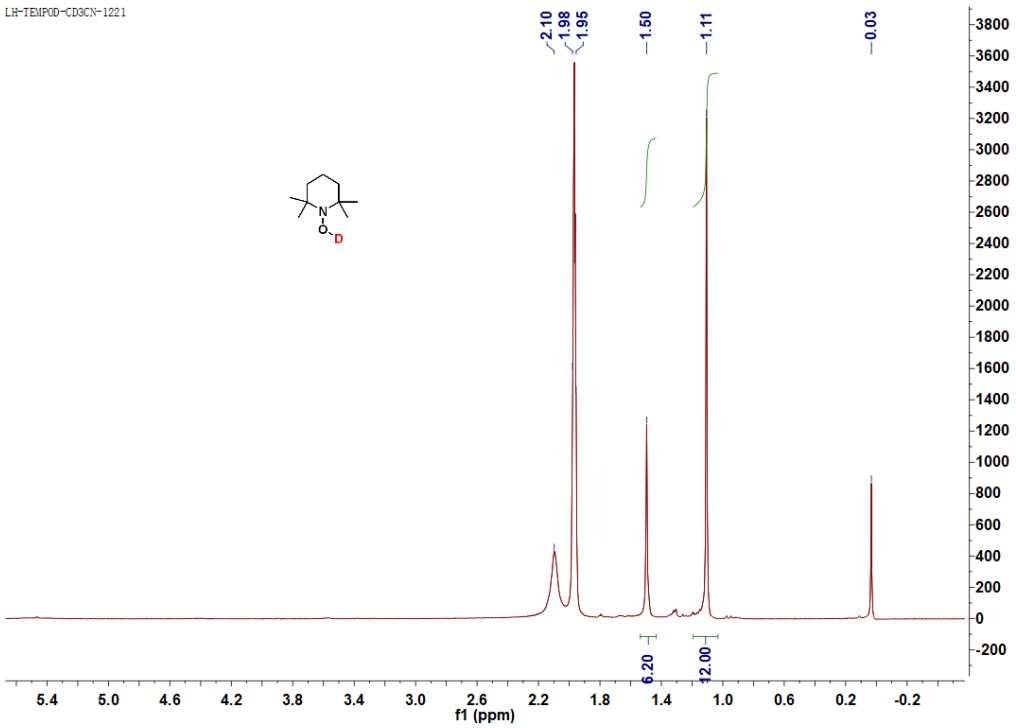


Figure S2. The ^1H NMR of TEMPOD in CD_3CN.

4. The electrochemical behavior of $TMPDA^{\bullet+}$

The CV of TMPD radical cation was measured in 0.1 M $TBAPF_6$ acetonitrile solution. The working electrode was used GC. Pt wire was used as counter electrode, and $Ag/AgNO_3$ was used as reference electrode.

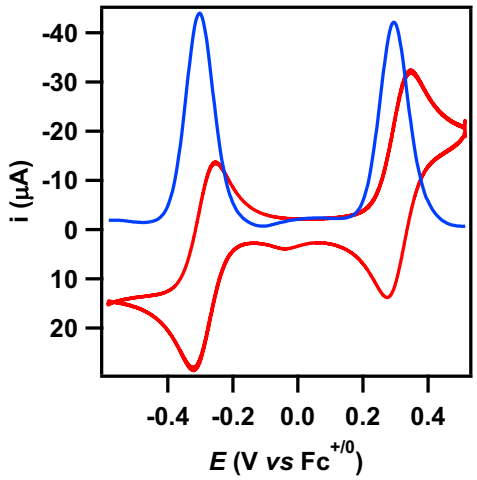


Figure S3. The Cyclic voltalmmetry (CV) and Differential pulse polarograms (DPV) of $TMPDA^{\bullet+}$ in acetonitrile. The reversible peaks are at potential E_a = -0.26, 0.35 V (vs. $Fc^{+/0}$), E_c = -0.32, 0.27 V (vs. $Fc^{+/0}$). DPV of $TMPDA^{\bullet+}$ (Blue line) showed the peaks at potential -0.30, 0.29 V (vs. $Fc^{+/0}$).

5. The UV-vis spectra of $TMPDA^{\bullet+}$

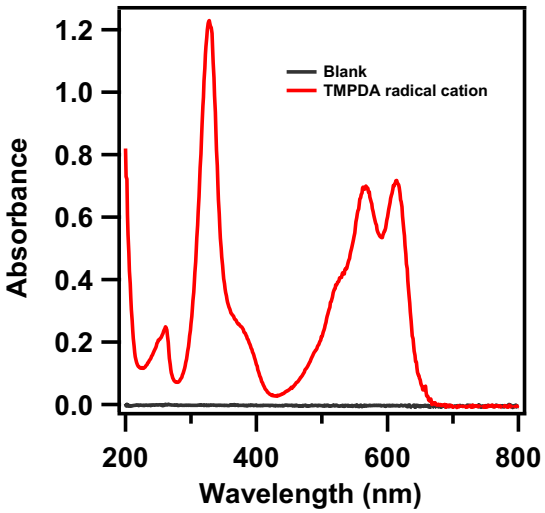
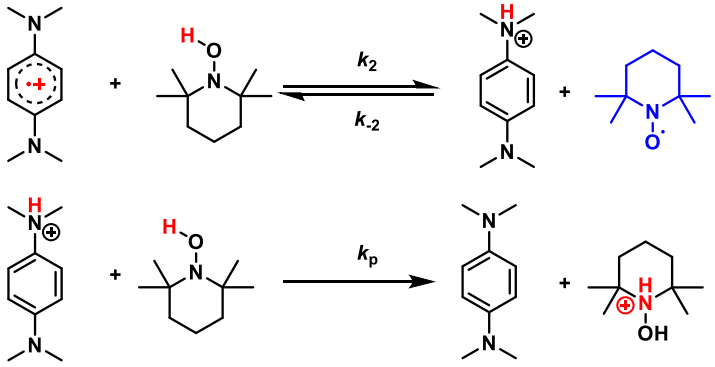


Figure S4. The UV-vis spectra of $TMPDA^{\bullet+}$ in acetonitrile.

6. The kinetic analysis

The possible reaction between $TMPDA^{\bullet+}$ and TEMPOH is anylyzed as the follows:



The rate equation for the proposed mechanism is derived from the rate limiting step being the bimolecular reaction between $TMPDA^{\bullet+}$ and TEMPOH.

$$\frac{d[TMPD^{\cdot+}]}{dt} = -k_2[TEMPOH][TMPD^{\cdot+}] + k_{-2}[TEMPO^{\cdot}][TMPDH^{+}] \quad \text{(S1)}$$

$$\frac{d[TMPDH^{+}]}{dt} = -k_{-2}[TEMPO^{\cdot}][TMPDH^{+}] - k_p[TEMPOH][TMPDH^{+}] + k_1[TEMPOH][TMPD^{\cdot+}] = 0 \quad \text{(S2)}$$

$$[TMPDH^{+}] = \frac{k_2[TEMPOH][TMPD^{\cdot+}]}{k_{-2}[TEMPO^{\cdot}]+k_p[TEMPOH]} \quad \text{(S3)}$$

$$\frac{d[TMPD^{\cdot+}]}{dt} = -k_2[TEMPOH][TMPD^{\cdot+}] + \frac{k_{-2}k_2[TEMPOH][TMPD^{\cdot+}][TEMPO^{\cdot}]}{k_{-2}[TEMPO^{\cdot}] + k_p[TEMPOH]}$$

$$\boldsymbol{\frac{d[TMPD^{\cdot+}]}{dt} = -\frac{k_2k_p[TEMPOH]^2[TMPD^{\cdot+}]}{k_{-2}[TEMPO^{\cdot}]+k_p[TEMPOH]}} \quad \textbf{(S4)}$$

$$\boldsymbol{k_{obs} = \frac{k_2k_p[TEMPOH]^2}{k_{-2}[TEMPO^{\cdot}]+k_p[TEMPOH]}} \quad \textbf{(S5)}$$

If the k_{-2}[TEMPO$^{\bullet}$]<<k_p[TEMPOH], so the

$$\boldsymbol{k_{obs} = k_2[TEMPOH]}$$

Pseudo first order rate constants k_{obs} were extracted using a global fit the absorption at 563 nm over time using Igor Pro analysis software. The observed rate constants (k_{obs}) at individual concentrations or temperatures are reported on Table S1, S2 and plotted in Figures 2, S5 and S6. Second order rate constants were extracted as described in the text. KIE measurements were performed with TEMPOD in MeCN.

Table S1 Observed pseudo-first order rate constants for $TMPDA^{\bullet+}$ with TEMPO-H(D) in MeCN at 298 K

[TEMPOD] [a]	k_{obs}^{D} [b]	SD^{D}	[TEMPOH] [a]	k_{obs}^{H} [b]	SD^{H}
1.78×10^{-2}	9.5×10^{-3}	2.45×10^{-4}	1.54×10^{-2}	3.11×10^{-2}	6.94×10^{-4}
2.03×10^{-2}	1.06×10^{-2}	3.09×10^{-4}	1.76×10^{-2}	4.18×10^{-2}	1.31×10^{-3}
2.27×10^{-2}	1.28×10^{-2}	2.05×10^{-4}	2.05×10^{-2}	6.20×10^{-2}	1.55×10^{-3}
2.51×10^{-2}	1.60×10^{-2}	1.25×10^{-4}	2.33×10^{-2}	7.48×10^{-2}	6.68×10^{-4}
2.78×10^{-2}	1.73×10^{-2}	1.25×10^{-4}	2.54×10^{-2}	9.12×10^{-2}	1.11×10^{-3}

[a] M; [b] s^{-1}

Table S2 Observed pseudo-first order rate constants for $TMPDA^{\bullet+}$ with TEMPO-H(D) in MeCN at different temperatures

T [a]	k_{obs}^{H} [b]	SD^{H}	k_2^{H} [c]	k_{obs}^{D} [b]	SD^{D}	k_2^{D} [c]
293	0.0585	3.55×10^{-3}	2.29	0.92×10^{-2}	8.34×10^{-4}	0.372
298	0.113	2.57×10^{-3}	4.40	1.56×10^{-2}	3.27×10^{-4}	0.630
303	0.155	3.03×10^{-3}	6.05	1.80×10^{-2}	1.18×10^{-3}	0.727
308	0.202	4.51×10^{-3}	7.92	2.22×10^{-2}	4.97×10^{-4}	0.897
313	0.262	6.86×10^{-3}	10.3	2.82×10^{-2}	5.73×10^{-4}	1.14
318	0.327	3.35×10^{-3}	12. 8	3.60×10^{-2}	5.72×10^{-4}	1.46

[a] K; [b] s^{-1}; [c] $M^{-1}s^{-1}$

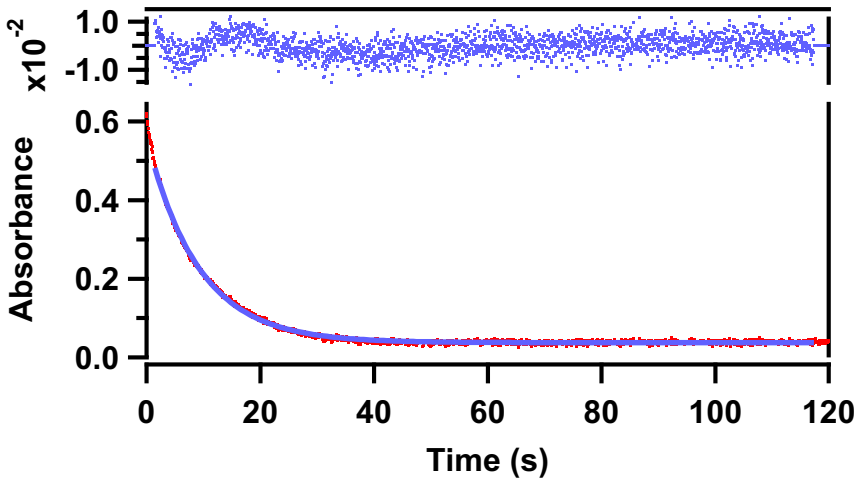


Figure S5. Kinetic trace of the $TMPDA^{\bullet+}$ (0.1 mM) absorption at 563 nm over time in the presence of 51.1 mM TEMPOH at 298 K in MeCN. The blue line is a fit to a single exponential.

7. The Eyring equation anaglysis

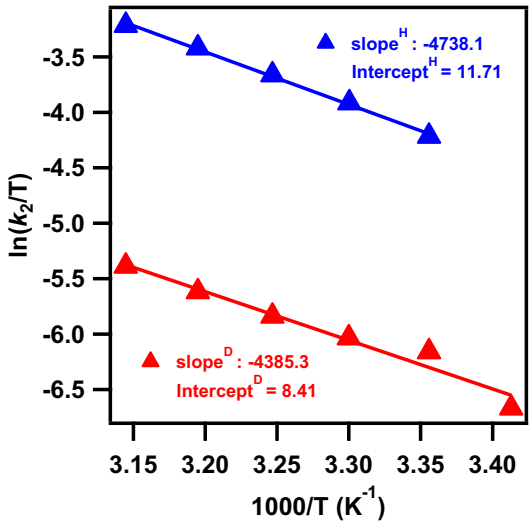


Figure S6. Plots of k_2 versus T for the reactions of TMPDA$^{\bullet+}$ with TEMPOH (Blue points) and TEMPOD (Red points). Fits are to the Eyring equation: $\ln\frac{k}{T} = -\frac{\Delta H^{\neq}}{RT} + ln\frac{k_B}{h} + \frac{\Delta S^{\neq}}{R}$. The slope $-\frac{\Delta H^{\neq}}{RT}$ of the Eyring plot was used in the equation below to calculate $\Delta H^{\ddagger}$; The intercept $ln\frac{k_B}{h} + \frac{\Delta S^{\neq}}{R}$ of the Eyring plot was used in the equation below to calculate $\Delta S^{\ddagger}$.

8. The DFT Calculation

8.1 Computational Methods

All calculations were carried out with the Gaussian 09 software package[5]. Geometry optimizations were conducted under the ωB97X-D[6, 7]/def2-SVP[8] level of theory. Frequency calculations were carried out at the same level of theory as the geometry optimization to obtain the Gibbs free energy corrections and to identify all the stationary points as minima (no imaginary frequency) or transition states (one imaginary frequency). Single-point electronic energies were computed under the ωB97X-D/def2-TZVP[7] level of theory. The Gibbs free energies at the higher level were calculated from the single-point electronic energies and the corresponding zero-point vibrational energies obtained from the frequency calculation. The solvation effect of acetonitrile was taken into consideration by using SMD continuum solvation model[9] in all the geometry optimization, frequency calculations and single point calculations.

To calculated the pK_a value of [TMPDAH$^{\bullet}$]$^{2+}$ is -24. The calculation was performed as below and experimental pK_a value of TMPDAH^{+} 13.98[10] was used.:

$$\mathrm{TMPDAH^+ \rightarrow TMPDA + H^+}, \mathrm{p}K_a = 13.98$$

$$[\mathrm{TMPDAH^{\bullet}}]^{2+} \rightarrow \mathrm{TMPDA^{\bullet+} + H^+}, \mathrm{p}K_a$$

$$[\mathrm{TMPDAH^{\bullet}}]^{2+} + \mathrm{TMPDA} \rightarrow \mathrm{TMPDA^{\bullet+} + TMPDAH^+}, \Delta G = -RT\ln K, K = 10^{13.98-\mathrm{p}K_a}$$

The correction factor Q_t is calculated using the following formula[11a], in which $v^{\ddagger}$ is imaginary frequency of TS (H: -1941.41 cm^{-1}, D: -1778.92 cm^{-1}), h is Planck constant, k is Boltzmann constant, T is 298.15 K.

$$\ln Q_t = \frac{u^{\ddagger 2}}{24} + \frac{u^{\ddagger 4}}{2880} + \cdots, u^{\ddagger} = \frac{h\nu^{\ddagger}}{kT}$$

The tunnel corrected KIE is obtained by the following formula[11b]:

$$\left(\frac{k_H}{k_D}\right)_{tunneling} = \left(\frac{Q_{t,H}}{Q_{t,D}}\right)\left(\frac{k_H}{k_D}\right)_{no\ tunneling}$$

8.2 Cartesian Coordinates

TMPDA$^{\bullet+}$, charge: 1, spin multiplicity: 2.

C	-0.68304400	1.21975800	-0.00009800
C	-1.43071000	0.00000200	-0.00004300
C	-0.68304300	-1.21975400	0.00006000
C	0.68304400	-1.21975400	0.00009800
C	1.43071000	0.00000200	0.00002800
C	0.68304400	1.21975900	-0.00006500
H	-1.19631400	2.17959600	-0.00016200
H	-1.19631300	-2.17959300	0.00011700
H	1.19631400	-2.17959200	0.00017300
H	1.19631300	2.17959700	-0.00009100
N	2.77707100	0.00000000	0.00005500
N	-2.77707100	0.00000000	-0.00007700
C	-3.51955300	1.25308000	-0.00015700
H	-3.29233300	1.84878000	-0.89698200
H	-4.59219300	1.03744700	-0.00015200
H	-3.29234700	1.84888500	0.89660100
C	-3.51954700	-1.25308400	-0.00001300
H	-3.29228200	-1.84891000	-0.89674200
H	-3.29238000	-1.84876000	0.89684100
H	-4.59218900	-1.03745600	-0.00009300
C	3.51954600	-1.25308400	0.00030200
H	3.29245800	-1.84893500	-0.89645700
H	4.59218800	-1.03745800	0.00044400

H	3.29220100	-1.84873600	0.89712700
C	3.51955400	1.25308000	-0.00011100
H	3.29217900	1.84880900	-0.89687400
H	3.29250500	1.84885600	0.89670900
H	4.59219400	1.03744600	-0.00032000

TMPDAH^{+}, charge: 1, spin multiplicity: 1.

C	0.63513600	-1.14543400	-0.00003600
C	1.45457900	0.01432300	-0.00014500
C	0.79791100	1.27109300	-0.00003100
C	-0.58451000	1.35622000	-0.00007100
C	-1.35572400	0.19935600	-0.00011800
C	-0.74533400	-1.05199900	-0.00005200
H	1.08066000	-2.13800800	0.00005400
H	1.36840100	2.19769500	0.00011800
H	-1.05300700	2.34483800	-0.00002000
H	-1.32996700	-1.97473900	0.00000900
N	2.81283600	-0.07714500	-0.00030600
H	-3.02085000	1.32335500	-0.00036800
N	-2.82749500	0.31648300	-0.00013700
C	3.45604700	-1.37379700	0.00050400
H	4.54329700	-1.23972200	0.00008600
H	3.19625400	-1.96371000	0.89594700
H	3.19579500	-1.96494600	-0.89397200
C	3.61842500	1.12544500	0.00008000
H	3.43342100	1.74439500	-0.89414900
H	3.43486100	1.74302200	0.89558100
H	4.67998400	0.85442000	-0.00106000
C	-3.45559700	-0.23163200	1.23806800
H	-4.53170800	-0.01962400	1.22072400

H	-3.29143000	-1.31449200	1.27169800
H	-2.98587600	0.24004800	2.10828400
C	-3.45562000	-0.23219600	-1.23808000
H	-4.53172300	-0.02014100	-1.22083100
H	-2.98588400	0.23905300	-2.10852000
H	-3.29150300	-1.31507900	-1.27119700

TEMPOH, charge: 0, spin multiplicity: 1.

C	0.00000100	2.15883100	-0.00369700
C	1.24547800	1.42123800	-0.47677200
C	1.28454300	-0.05006300	-0.03109900
C	-1.28454300	-0.05006100	-0.03109900
C	-1.24547600	1.42123900	-0.47677200
H	1.27784900	1.45090800	-1.57892200
H	2.15983000	1.91945300	-0.11699500
H	0.00000100	2.25339200	1.09448700
H	0.00000200	3.18765000	-0.39611000
H	-1.27784700	1.45090900	-1.57892200
H	-2.15982700	1.91945500	-0.11699500
N	0.00000000	-0.66532100	-0.42173800
C	2.38016200	-0.77396600	-0.82319100
H	3.34751700	-0.26324600	-0.70062900
H	2.50024200	-1.81035200	-0.47724100
H	2.13044600	-0.78985500	-1.89506600
C	1.61357700	-0.17014000	1.46786800
H	1.42867600	-1.19675600	1.81304600
H	2.67571700	0.06116200	1.64101700
H	1.02573000	0.51314300	2.09390900
C	-2.38016300	-0.77396400	-0.82319100
H	-2.50024200	-1.81035100	-0.47724200

H	-3.34751700	-0.26324500	-0.70062800
H	-2.13044700	-0.78985200	-1.89506600
C	-1.61357700	-0.17013800	1.46786800
H	-2.67571700	0.06116400	1.64101700
H	-1.42867700	-1.19675500	1.81304500
H	-1.02572900	0.51314400	2.09390900
O	-0.00000200	-2.01533100	-0.01084900
H	-0.00000400	-2.50793300	-0.83713800

TEMPO, charge: 0, spin multiplicity: 2.

C	0.00000000	2.12014200	-0.02198000
C	1.24086000	1.38366400	-0.50463400
C	1.31649200	-0.07272300	-0.02256100
C	-1.31649200	-0.07272300	-0.02256100
C	-1.24086000	1.38366300	-0.50463400
H	1.24776300	1.39089700	-1.60785100
H	2.15935000	1.89931300	-0.18301700
H	0.00000000	2.20884400	1.07669000
H	-0.00000100	3.14992600	-0.41026700
H	-1.24776400	1.39089700	-1.60785100
H	-2.15935000	1.89931300	-0.18301600
N	0.00000000	-0.74447400	-0.20957500
C	2.33944700	-0.83694700	-0.86500500
H	3.31347000	-0.32737700	-0.81683400
H	2.45886000	-1.86560300	-0.50321100
H	2.02254700	-0.87945200	-1.91765600
C	1.71538100	-0.15442300	1.45888100
H	1.60576800	-1.18908400	1.81377200
H	2.76517000	0.14861400	1.58867100
H	1.10014000	0.49483800	2.09727100

C	-2.33944800	-0.83694700	-0.86500500
H	-2.45886000	-1.86560400	-0.50321100
H	-3.31347000	-0.32737800	-0.81683400
H	-2.02254700	-0.87945300	-1.91765600
C	-1.71538100	-0.15442300	1.45888200
H	-2.76517000	0.14861300	1.58867100
H	-1.60576700	-1.18908400	1.81377200
H	-1.10014000	0.49483800	2.09727100
O	0.00000100	-2.00593000	-0.10124800

TS, charge: 1, spin multiplicity: 2.

C	3.59708500	-2.28270300	0.77916700
C	4.16525700	-1.29492500	-0.22796600
C	3.08883000	-0.47656000	-0.95602200
C	1.62543500	-0.71172600	1.21366900
C	2.77944100	-1.52829300	1.81573800
H	4.84296000	-0.60089000	0.29561700
H	4.76853600	-1.80763700	-0.99170600
H	2.98597900	-3.04994300	0.27755400
H	4.41622600	-2.82327700	1.27501400
H	3.44560600	-0.84465000	2.36720800
H	2.34860800	-2.21431900	2.56034700
N	2.13459300	0.04178000	0.04771400
O	1.22346500	0.83035800	-0.53997200
H	0.86369200	1.51868100	0.07589400
C	-2.97974400	0.17853900	0.99563200
C	-3.15005400	-0.52758900	-0.22666500
C	-2.44820900	-0.02627300	-1.35342300
C	-1.61709300	1.06940000	-1.25658500
C	-1.42051100	1.74775800	-0.02919000

C	-2.15304700	1.27751000	1.08452500
H	-3.51899900	-0.12868300	1.89004100
H	-2.55197000	-0.50294900	-2.32633400
H	-1.10739000	1.39991700	-2.15915000
H	-2.08505900	1.78162300	2.04719600
N	-0.49070600	2.78354100	0.09119900
N	-3.95106000	-1.62216000	-0.30835000
C	3.74483000	0.72876600	-1.63833100
H	4.55914400	0.38109800	-2.28994000
H	3.03041000	1.28645300	-2.25783500
H	4.17235100	1.41515200	-0.89288300
C	2.35586100	-1.32687200	-2.00949400
H	1.49896400	-0.77891300	-2.42448300
H	3.04519000	-1.55846500	-2.83393800
H	1.99158000	-2.27916000	-1.60219500
C	0.44336300	-1.60985800	0.79913200
H	0.76915300	-2.48092300	0.21597800
H	-0.06801600	-1.98033100	1.69977900
H	-0.28065200	-1.04150800	0.19986800
C	1.14646200	0.30773300	2.25558300
H	0.95966400	-0.20281500	3.21054500
H	1.90706300	1.08351800	2.43076500
H	0.19875800	0.77629200	1.95932500
C	-0.12793700	3.52188700	-1.11769000
H	0.65247400	4.25000900	-0.86804900
H	0.28636800	2.85114200	-1.87950500
H	-0.99235700	4.05906100	-1.54320500
C	-0.50975700	3.59237800	1.30447100
H	-1.45576600	4.14951600	1.41516600
H	-0.35920300	2.97322500	2.19810500

H	0.31459600	4.31394400	1.26534600
C	-4.13652800	-2.29622700	-1.57710200
H	-4.84967200	-3.11817200	-1.45270800
H	-4.54454300	-1.61556700	-2.34173700
H	-3.19287100	-2.72314700	-1.95687000
C	-4.61751400	-2.12967500	0.87387400
H	-3.89621600	-2.38507700	1.66725500
H	-5.34285200	-1.40502300	1.27968100
H	-5.16626700	-3.04279200	0.61975800

TMPDA, charge: 0, spin multiplicity: 1.

C	-0.00331300	0.69535000	-1.19601700
C	0.00288000	1.43972500	-0.00196900
C	-0.00288000	0.69563100	1.19173200
C	0.00288000	-0.69563100	1.19173200
C	-0.00288000	-1.43972500	-0.00196900
C	0.00331300	-0.69535000	-1.19601700
H	-0.00497900	1.20005900	-2.16205900
H	-0.00676000	1.19941600	2.15814500
H	0.00676000	-1.19941600	2.15814500
H	0.00497900	-1.20005900	-2.16205900
N	-0.01932200	-2.83163800	-0.00388500
N	0.01932200	2.83163800	-0.00388500
C	-0.13856600	3.53459200	1.24145000
H	0.66044600	3.27476400	1.95605700
H	-0.06730100	4.61570700	1.06466100
H	-1.10987900	3.33772600	1.73934000
C	-0.24013200	3.53051100	-1.23511400
H	0.53010500	3.31925900	-1.99646000
H	-1.22510500	3.28147900	-1.67859200

H	-0.21991900	4.61297900	-1.05438900
C	0.13856600	-3.53459200	1.24145000
H	-0.66044600	-3.27476400	1.95605700
H	0.06730100	-4.61570700	1.06466100
H	1.10987900	-3.33772600	1.73934000
C	0.24013200	-3.53051100	-1.23511400
H	-0.53010500	-3.31925900	-1.99646000
H	1.22510500	-3.28147900	-1.67859200
H	0.21991900	-4.61297900	-1.05438900

TEMPOH$^{\bullet+}$, charge: 1, spin multiplicity: 2.

C	-0.02546000	2.13937200	-0.08543800
C	1.22524300	1.40714100	-0.54859600
C	1.33310800	-0.02644900	-0.00769200
C	-1.34557900	-0.06148800	-0.01096100
C	-1.26497700	1.38120900	-0.53640400
H	1.24084200	1.37185300	-1.64979100
H	2.13691100	1.93768400	-0.23837800
H	-0.02043000	2.28181300	1.00640200
H	-0.03633300	3.14833600	-0.51968300
H	-1.29490100	1.35632100	-1.63755900
H	-2.18255900	1.89183400	-0.21137700
N	0.00013900	-0.68184300	-0.16008200
C	2.35448500	-0.82541900	-0.82468900
H	3.29502600	-0.25890900	-0.84577500
H	2.61863700	-1.79860300	-0.37499600
H	2.03311700	-0.96958400	-1.86646200
C	1.70510100	-0.05606900	1.48560400
H	1.62605700	-1.06867400	1.90698900
H	2.74922000	0.27008400	1.58770100

H	1.08255200	0.61726500	2.08656000
C	-2.34343900	-0.87471500	-0.83956700
H	-2.52427900	-1.87038200	-0.41582500
H	-3.29760900	-0.33054700	-0.84888900
H	-2.00848300	-0.98459900	-1.88066800
C	-1.72202900	-0.11526000	1.48088500
H	-2.77258700	0.19044100	1.57882900
H	-1.62838700	-1.13503000	1.87910500
H	-1.11734200	0.56300300	2.09565500
O	-0.03442300	-1.99043400	-0.12324000
H	0.87624000	-2.32586500	-0.22420300

[TMPDAH$^{\bullet}$]$^{2+}$, charge: 2, spin multiplicity: 2.

C	0.78975600	-1.28428700	-0.11461500
C	1.42861300	-0.01691800	0.00232900
C	0.61882600	1.15125300	0.11528500
C	-0.75678400	1.05125300	0.11197100
C	-1.35394600	-0.20689300	-0.01553600
C	-0.58953900	-1.36897800	-0.12923600
H	1.36664200	-2.20070400	-0.22809400
H	1.06778300	2.13508300	0.23980900
H	-1.34882400	1.96172600	0.21450700
H	-1.05997500	-2.34889300	-0.23742800
N	-2.82010000	-0.31863500	-0.03219700
N	2.78535100	0.07716200	0.00482400
C	3.63969500	-1.09691600	0.12184000
H	3.78995600	-1.54684200	-0.87380700
H	4.61468100	-0.78342800	0.51159500
H	3.20933800	-1.83495700	0.80725500
C	3.47256300	1.35578600	-0.11065200

H	2.91074000	2.05542400	-0.73730200
H	3.62528000	1.78513900	0.89388300
H	4.45410800	1.18557700	-0.56830600
C	-3.44827200	0.11830500	1.26015400
H	-3.30309200	1.19702200	1.38498000
H	-4.51997500	-0.10762100	1.21488700
H	-2.97943400	-0.42693200	2.08723500
C	-3.43448800	0.36059700	-1.22248500
H	-3.27954200	1.44201900	-1.13847700
H	-2.96172700	-0.02266900	-2.13377500
H	-4.50821400	0.13946800	-1.22924300
H	-3.03304700	-1.31830700	-0.13043900

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