Electronic Supplementary Information (ESI) for

Deoxygenation of nitrosoarene by N-heterocyclic carbene (NHC): an elusive Breslow-type intermediate bridging carbene and nitrene

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1. General Instrumentation and Physical Methods

The preparation and handling of air-sensitive chemicals were performed under dry argon/ nitrogen atmosphere by utilizing standard Schlenk techniques and/or a MBraun Glovebox with <0.1 ppm O_2 and H_2O. More specifically, apart from the preparations of the carbene precursors and nitrosoarenes, all the reactions and NMR sample preparations were exclusively carried out in the glovebox.

***NMR Spectroscopic Studies*:** ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance III 500 MHz and Bruker Avance III 700 MHz NMR spectrometers at room temperature unless otherwise noted. The chemical shift (δ) values are expressed in ppm relative to tetramethylsilane, whereas the residual ^{1}H, ^{13}C signals of the deuterated solvent served as an internal standard.

***CHNS Analyses*:** Elemental analyses were performed on an Elementar Vario Micro Cube CHNS analyzer.

***UV–vis Spectroscopic Studies*:** UV-vis spectra were recorded on an Agilent 8454 Diode Array spectrometer equipped with stirrer and Unisoku USP-203 cryostats for variable temperature (-105 °C to 90 °C) experiments. Solutions for UV-vis analysis were prepared freshly by dissolving analytically pure compounds in anhydrous solvents.

***Infrared (IR) Spectroscopic Studies*:** IR spectra (with the spectral resolution of 4 cm^{-1}) were collected on a Shimadzu IRPrestige-21 FTIR spectrometer by using KBr pellet method. The intensities of the vibrational bands are abbreviated as follows: s = strong, m = medium, w = weak, and br = broad.

Electrospray Ionization – Mass Spectrometric (ESI–MS) Analyses: High resolution mass spectra (HRMS) were recorded on Thermo Scientific™ Q Exactive™ Hybrid Quadrupole-Orbitrap Mass Spectrometer using electrospray ionization (ESI) technique. Low resolution mass spectra (LRMS) were recorded using Thermo Scientific™ LCQ Fleet™ ion trap mass spectrometer. For the preparations of samples, the crude reaction mixtures were diluted with precooled acetonitrile. The instruments were set with capillary temperatures 320 °C and 280 °C for HRMS and LRMS, respectively.

***Melting Point Analyses*:** Melting point analyses were carried out using Stuart SMP50 automatic melting point analyzer. Melting points were recorded in sealed capillaries and are uncorrected.

***Single Crystal X-ray Diffraction (SCXRD) Analysis*:** Single crystal of compound **3-Br_3Ar** (CCDC 1976500) were mounted under mineral oil on a glass capillary. Data for compound **3-Br_3Ar** was collected at 150 K on a Bruker Kappa diffractometer equipped with an APEXII CCD detector and Mo fine focus sealed tube source employing graphite monochromated Mo K_α radiation ($\lambda = 0.7107$ Å). The data sets were processed using APEX II software. Integration of the data sets were carried out with the Bruker SAINT program. Structure solutions were performed using the SHELXTL/PC suite.[S1] Intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using Blessing's method as incorporated into the program SADABS.[S2] Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in idealized positions. The molecular structures were rendered using MERCURY 3.10.3 software.[S3]

***Computational Details*:** Gaussian 09[S4] was used to optimize the structures, calculate single point geometries, and also find the vibrational frequencies and reaction free energies. All calculations were carried out employing M062X[S5,S6] functional and 6-31G(d,p)[S7] basis set unless otherwise mentioned. B3LYP[S8]/6-31G(d,p) was used for TDDFT to calculate the excited state energies. All the ground state minima were confirmed by the absence of imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were further carried out to confirm the transition states connecting the correct reactants and product.

2. Materials

All chemicals were purchased from standard vendors (e.g. Sigma-Aldrich, Spectrochem, Strem Chemicals, TCI) and used without further purification unless otherwise mentioned. Molecular sieves (4Å, 4-8 mesh beads) were activated in *vacuo* at 220 °C for 24 h. Anhydrous solvents were sparged with nitrogen and stored over activated molecular sieves under nitrogen atmosphere.

1,3-dimesitylimidazol-2-ylidene (**IMes**),[S9] 2-phenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ylidene,[S10] 1,3,4-triphenyl-4,5-dihydro-*1H*-l,2,4-triazol-5-ylidene,[S11] PhNO,[S12] MesNO[S12] were synthesized and characterized according to the literature procedures. Section 8 describes the synthesis and characterization of 2,4,6-tribromonitrosobenzene (**Br_3ArNO**).

3. Reactions of N-Heterocyclic Carbenes (NHCs) with PhNO

(a) Reaction of 1,3-dimesitylimidazol-2-ylidene (IMes) with PhNO

In a N_2 filled glovebox, tetrahydrofuran (~4 mL) was added to **IMes** (0.100 g, 0.328 mmol) in a 20 mL vial and kept at −35 °C for ½ h. To the resultant clear solution, a chilled solution of PhNO (0.035 g, 0.328 mmol) in ~2 mL tetrahydrofuran was added slowly at −35 °C with vigorous stirring and the color of the solution immediate turned dark brown color. After stirring for 1 h at room temperature, volatiles were removed and subsequently the resultant solid was dried *in vacuo* to afford brown colored powder. NMR and mass spectroscopic analyses on the crude material indicates the presence of **IMes**=O (**1)** and azoxybenzene (~5% NMR yield) (Figures S1, S2). These were identified by comparing the respective spectroscopic signatures as reported previously.[S13,S14]

^{1}H NMR (500 MHz, $CDCl_3$) of **IMes**=O (**1**): δ 6.95 (s, 4H), 6.32 (s, 2H), 2.30 (s, 6H), 2.20 (s, 12H).

^{1}H NMR (500 MHz, $CDCl_3$) of azoxybenzene: δ 8.31 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 7.6 Hz, 1H), 7.58 – 7.46 (m, 3H), 7.41 – 7.38 (m, 1H).

ESI–MS(+): *m/z* calculated for $[C_{21}H_{25}N_2O]^+$, $[MH]^+$:321.19, found: 321.15 (Figure S2).

Crystals suitable for single crystal X-ray diffraction analysis were grown from slow evaporation of a crude reaction mixture in ethyl acetate. The unit cell parameters of the colorless crystals obtained from the reaction mixture are comparable to that of the previously reported cell matrices (CCDC 892936),[S15] thereby confirming the presence of **IMes**=O (**1**).

(b) Reaction of 2-Phenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ylidene with PhNO

In a N_2 filled glovebox, tetrahydrofuran (~4 mL) was added to the triazolium carbene (0.060 g, 0.324 mmol) in a 20 mL vial and kept at –35 °C for ½ h. To the resultant clear solution, a chilled solution of PhNO (0.035 g, 0.324 mmol) in ~2 mL tetrahydrofuran was added slowly at –35 °C with vigorous stirring and the colour of the solution immediately turned dark orange. After stirring for 15 h at room temperature, volatiles were removed and subsequently the resultant solid was dried *in vacuo* to afford a brown sticky compound. NMR and mass spectroscopic analyses of the crude material indicated the presence of azoxybenzene and corresponding urea derivative, namely, 2-phenyl-6,7-dihydro-2H-pyrrolo[2,1-c][1,2,4]triazol-3(5H)-one. Products were purified by column chromatography employing hexane/ethyl acetate to obtain 9% isolated yield of azoxybenzene and 63% isolated yield of the urea derivative (both the yields are reported with respect to the carbene as the limiting reagent).

^{1}H NMR (700 MHz, $CDCl_3$) of 2-phenyl-6,7-dihydro-2H-pyrrolo[2,1-c][1,2,4]triazol-3(5H)-one: δ 7.89 (d, 2H), 7.39 (t, 2H), 7.17 (t, 1H), 3.83 (t, 2H), 2.88 (t, 2H), 2.58 (m, 2H). The ^{1}H resonances are similar to those reported in the previous literature.[S16] High-resolution ESI–MS(+): *m/z* calculated for $[C_{11}H_{12}N_3O]^+$, $[MH]^+$: 202.0975, found: 202.0974.

Reaction of PhNO with in situ generated triazolium NHC: In a N_2 filled glovebox, to a 20 mL vial containing the carbene precursor salt 2-Phenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ium chloride (0.040 g, 0.180 mmol), PhNO (0.097 g, 0.902 mmol), KO^{t}Bu (0.020 g, 0.180 mmol) tetrahydrofuran (~4 mL) were added. The resultant turbid dark red solution was stirred at room temperature for 16 h and volatiles were removed *in vacuo* to afford dark brown sticky compound. Mass spectrometric analyses on the crude material indicated the presence of 2-phenyl-6,7-dihydro-2H-pyrrolo[2,1-c][1,2,4]triazol-3(5H)-one and azoxybenzene. Products were purified by column chromatography employing hexane/ethyl acetate to obtain 69% isolated yield of 2-phenyl-6,7-dihydro-2H-pyrrolo[2,1-c][1,2,4]triazol-3(5H)-one and 95% yield of isolated azoxybenzene.

(c) Reaction of 1,3,4-triphenyl-l,2,4-triazol-5-ylidene with PhNO

In a N_2 filled glovebox, tetrahydrofuran (~2 mL) was added to 1,3,4-triphenyl-l,2,4-triazol-5-ylidene (0.020 g, 0.067 mmol) in a 20 mL vial and kept at −35 °C for ½ h. To the resultant clear yellow solution, a chilled solution of PhNO (0.007 g, 0.067 mmol) in ~1 mL tetrahydrofuran was added slowly at −35 °C with vigorous stirring and the color of the solution immediately turned orange. After stirring for 15 h at room temperature the clear solution became brown. Volatiles were removed and subsequently the resultant solid was dried *in vacuo* to afford brown compound. Comparison of NMR and mass spectroscopic features of the crude material with that of previously reported compounds indicated the presence of 1,3,4-triphenyl-1H-1,2,4-triazol-5-one and azoxybenzene.[S16] High-resolution ESI–MS(+): *m/z* calculated for $[C_{20}H_{16}N_3O]^+$, $[MH]^+$: 314.1288, found: 314.1281.

4. Trapping of *in situ* generated Phenyl Nitrene (PhN) by PhNO

In a N_2 filled glovebox, the freshly generated **IMes** (0.200 g, 0.656 mmol) was dissolved in tetrahydrofuran (~4 mL) in a 20 mL vial and kept at −35 °C for ½ h. To the resultant clear solution, a chilled solution of PhNO (0.352 g, 3.284 mmol) in ~2 mL tetrahydrofuran was added slowly at −35 °C with vigorous stirring. The resultant brown solution was stirred at room temperature for 1 h and volatiles were removed. The resulting solid was dried *in vacuo* to afford brown colored powder. NMR and mass spectroscopic analyses on the crude material indicates the presence of **IMes**=O and azoxybenzene (Figure S4). Products were purified by column chromatography employing hexane/ethyl acetate to obtain 71% isolated yield of azoxybenzene and 62% isolated yield of **IMes**=O (both the yields are calculated with respect to **IMes** as the limiting reagent).

^{1}H NMR (500 MHz, $CDCl_3$) of **IMes**=O (**1**): δ 6.95 (s, 4H), 6.32 (s, 2H), 2.30 (s, 6H), 2.20 (s, 12H).

^{1}H NMR (500 MHz, $CDCl_3$) of azoxybenzene: δ 8.31 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 7.6 Hz, 1H), 7.58 – 7.46 (m, 3H), 7.41 – 7.38 (m, 1H).

5. Trapping of *in situ* generated Phenyl Nitrene (PhN) by Et_2NH

To a solution of **IMes** (0.050 g, 0.164 mmol) in diethylamine (~1 mL), chilled solution of PhNO (0.017 g, 0.164 mmol) in diethylamine (~2 mL) was added slowly at −35 °C. The resultant brown solution was stirred for 1 h. Subsequently, excess diethylamine was removed under reduced pressure and dried under vacuum. ^{1}H NMR analysis on the crude material indicates the presence of azoxybenzene, **IMes**=O and 2-diethylamino-3H-azepine. The yield of the desired product 2-diethylamino-3H-azepine was estimated to be 52% (with respect to **IMes** as the limiting reagent).

^{1}H NMR (500 MHz, $CDCl_3$) of 2-diethylamino-3H-azepine: δ 7.13 (d, 1H), 5.75 (d, 1H), 5.11 (d, 1H), 3.37 (q, 4H), 2.31 (brs, 2H), 1.15 (t, 6H). The observed chemical shifts agree well with that of the previous report.[S17]

^{1}H NMR (500 MHz, $CDCl_3$) of **IMes**=O (**1**): δ 6.95 (s, 4H), 6.32 (s, 2H), 2.30 (s, 6H), 2.20 (s, 12H).

^{1}H NMR (500 MHz, $CDCl_3$) of azoxybenzene: δ 8.31 (d, J = 8.0 Hz, 1H), 8.16 (d, J = 7.6 Hz, 1H), 7.58 – 7.46 (m, 3H), 7.41 – 7.38 (m, 1H).

ESI–MS(+): *m/z* calculated for $\{C_{10}H_{16}N_2+H\}^+$, $[MH]^+$: 165.1386, found: 165.1388 (Figure S6).

Trapping of PhN generated from the reaction of triazolium based carbenes and PhNO in the presence of diethylamine were carried out following a similar procedure as described for **IMes**. High-resolution ESI-MS(+) spectrometric analyses confirm the formation of 2-diethylamino-3H-azepine (Figure S7).

6. UV-Vis monitoring of the reaction of IMes with PhNO

A stock solution of **IMes** in tetrahydrofuran with 10.0 mM concentration was further diluted with tetrahydrofuran to achieve a 2.0 mM solution of **IMes**. Inside a N_2 filled glovebox, a solution of **IMes** (2.0 mL, 2.0 mM, 4.0 μmol) in tetrahydrofuran was taken in a quartz cuvette capped with a rubber septum. The sealed cuvette was then placed in a precooled cryostat (at –40 °C) connected to a UV-vis spectrometer. After injecting a PhNO solution in tetrahydrofuran (200 μL, 20.0 mM, 4.0 μmol) to the cuvette, UV-vis absorption spectra were collected at a time interval of 2 s (Figure S8).

UV-Vis monitoring of the reaction of **IMes** with Br_3ArNO was performed by following a similar procedure as described for PhNO (Figure S12).

Comment: While the UV-vis spectroscopic studies at –40 °C show the generation of intermediate, the absorption features associated with the generated intermediate change rapidly even at –40 °C (Figures S8 and S12). Hence, monitoring of the reaction intermediates by NMR spectroscopic studies was hampered.

7. Preparation and Analyses of ESI-MS samples

In a N_2 filled glovebox, tetrahydrofuran (~4 mL) was added to the fine powder of **IMes** (0.100 g, 0.328 mmol) in a 20 mL vial and kept at –35 °C for ½ h. To the clear solution of **IMes**, a chilled solution of PhNO (0.035 g, 0.328 mmol) in ~2 mL tetrahydrofuran was added slowly at –35 °C with vigorous stirring. Then an aliquot of the resultant crude sample was diluted with precooled acetonitrile for the mass spectrometric analysis.

ESI-MS sample preparations for the reactions of **IMes** with Br_3ArNO and MesNO were performed by following the similar procedure as described for PhNO.

High-resolution ESI–MS(+): *m/z* calculated for [{**IMes**(PhNO)}H]$^+$, [MH]$^+$: 412.2383, found: 412.2382 and *m/z* calculated for [{**IMes**(PhNO)}H–O]$^+$, [MH–O]$^+$: 396.2434, found: 396.2440. (Figure S9).

High-resolution ESI–MS(+): *m/z* calculated for [{**IMes**(Br_3ArNO)}H]$^+$, [MH]$^+$: 647.9678 (for ^{79}Br isotope), found: 647.9676 and *m/z* calculated for [{**IMes**(Br_3ArNO)}H–O]$^+$, [MH–O]$^+$: 631.9729 (for ^{79}Br isotope), found: 631.9721. (Figure S14)

High-resolution ESI–MS(+): *m/z* calculated for [{**IMes**(MesNO)}H]$^+$, [MH]$^+$: 454.2853, found: 452.2842 and *m/z* calculated for [{**IMes**(MesNO)}H–O]$^+$, [MH–O]$^+$: 438.2904, found: 438.2894 (Figure S15).

8. Synthesis and Characterization of 2,4,6-tribromonitrosobenzene (Br_3ArNO).

2,4,6-tribromonitrosobenzene (**Br_3ArNO**) was synthesized by a slight modification of an analogous literature procedure.[S18]

To a mixture of 2,4,6-tribromoaniline (2.000 g, 6.064 mmol) in glacial acetic acid (~40 mL), 30% aqueous hydrogen peroxide (5.00 mL) was added. To the resultant suspension 1.5 mL of concentrated sulfuric acid was added slowly. The mixture was warmed gently in order to bring all the amine into the solution and was kept at 40-45 °C for 10 hours. The warm solution was diluted with an equal volume of water. After stirring for 10 minutes, the reaction mixture was filtered to isolate off-white coloured residue, which was washed with glacial acetic acid and dried under vacuum to yield off-white coloured powder. Recrystallisation from dichloromethane at −35 °C resulted in the formation of colourless crystals of **Br_3ArNO** (1.770 g, 5.17 mmol) in 85% yield.

Anal. *calcd* for 2,4,6-tribromonitrosobenzene (**Br_3ArNO**), $C_6H_2Br_3NO$: C, 20.96; H, 0.59; N, 4.07. Found: C, 21.17; H, 0.50; N, 3.81. Melting point 153 °C (decom.).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 136.82, 136.10, 128.94, 120.16, 117.71. (Figures S10, S11)

FTIR (KBr pellet): 3111 (s), 3072 (s), 2727 (m),1718 (m), 1602 (m), 1554 (s), 1406 (s), 1371 (s), 1348 (w), 1290 (s), 1263 (s, ONNO),[S19] 1201 (s),1166 (m), 1116(m), 1097(s), 1062(m), 941 (w), 875 (m), 858 (s), 792 (m), 744 (s), 671 (s), 557 (s), 472 (s).

9. Reactions of 1,3-dimesitylimidazol-2-ylidene (IMes) with Br_3ArNO

In a N_2 filled glovebox, tetrahydrofuran (~4 mL) was added to the fine powder of **IMes** (0.100 g, 0.328 mmol) in a 20 mL vial and kept at –35 °C for ½ h. To the above-mentioned solution, a chilled solution of Br_3ArNO (0.113 g, 0.328 mmol) in ~2 mL tetrahydrofuran was added slowly at –35 °C with vigorous stirring. The resultant solution immediately turned orange and additional stirring at room temperature lead to the change in color to pale yellow-brown. After stirring for 1 h, volatiles were removed and dried *in vacuo* to afford brown colored powder. ^{1}H NMR and ESI-MS analyses on the crude material confirmed the presence of **IMes**=O (**1**) and **IMes**=NBr_3Ar (**3-Br_3Ar**) (Figures S32-S35).

Products were purified by column chromatography employing petroleum ether/ethyl acetate (20:1) to obtain 49% isolated yield of **3-Br_3Ar**. Melting point: 194 °C. Anal. *calcd* for **3-Br_3Ar**, $C_{27}H_{26}Br_3N_3$: C, 51.29; H, 4.15; N, 6.65. Found: C, 51.74; H, 4.25; N, 6.64.

^{1}H NMR (500 MHz, $CDCl_3$) of **3-Br_3Ar**: δ 7.15 (s, 1H), 6.83 (s, 2H), 6.32 (s, 1H), 2.35 (s, 6H), 2.25 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) of **3-Br_3Ar**: δ 147.05, 144.84, 138.43, 136.79, 132.69, 129.02, 119.59, 114.60, 110.89, 20.95, 19.09 (Figures S33-S34).

ESI–MS(+): *m/z* calculated for $[C_{27}H_{27}Br_3N_3]^+$, $[M+H]^+$: 631.9729 (for ^{79}Br isotope), found: 631.9705 (Figure S35).

Crystals suitable for single crystal X-ray diffraction were grown from slow evaporation of a solution of **3-Br_3Ar** in ethyl acetate (Figure S36).

10. Reactions of 1,3-dimesitylimidazol-2-ylidene (IMes) with MesNO

In a N_2 filled glovebox, tetrahydrofuran (~4 mL) was added to the fine powder of **IMes** (0.100 g, 0.328 mmol) in a 20 mL vial and kept at −35 °C for ½ h. To the above-mentioned solution, a chilled solution of MesNO (0.489 mg, 0.328 mmol) in ~2 mL tetrahydrofuran was added slowly at −35 °C with vigorous stirring. The resultant reaction mixture immediately turned dark brown color. After stirring for 1 h, volatiles were removed from the reaction mixture and dried *in vacuo* to afford brown colored powder. NMR and mass spectroscopic analyses on the crude material suggest the presence of **IMes**=O (**1**).

^{1}H NMR (500 MHz, $CDCl_3$) of **IMes**=O (**1**): δ 6.95 (s, 4H), 6.32 (s, 2H), 2.30 (s, 6H), 2.20 (s, 12H) (Figure S31).

ESI–MS(+): *m/z* calculated for $[C_{21}H_{25}N_2O]^+$, $[MH]^+$: 321.19, found: 321.18 (Figure S16).

11. Trapping of Oxygen-atom During the Reaction of Br_3ArNO with IMes

In a N_2 filled glovebox, a solution of **IMes** (0.050 mg, 0.168 mmol) in tetrahydrofuran (~2 mL) loaded in a sealed 20 mL vial and taken out of the glovebox. The solution was cooled to −78 °C. Then a chilled solution consisting of Br_3ArNO (0.577 mg, 0.168 mmol) and thioanisole (1.947 mL, 16.8 mmol) in ~0.5 mL tetrahydrofuran was added to the precooled solution of **IMes**. The reaction mixture was stirred for 5 h at room temperature and analyzed by high resolution mass spectrometric method. While the yield of desired methyl phenyl sulfoxide was found to be low, high resolution ESI-MS spectrum confirms the formation of methyl phenyl sulfoxide.

ESI–MS(+): *m/z* calculated for $\{C_7H_9SO\}^+$, $[MH]^+$: 141.0369, found: 141.0369 (Figure S37).

12. Figures and Tables

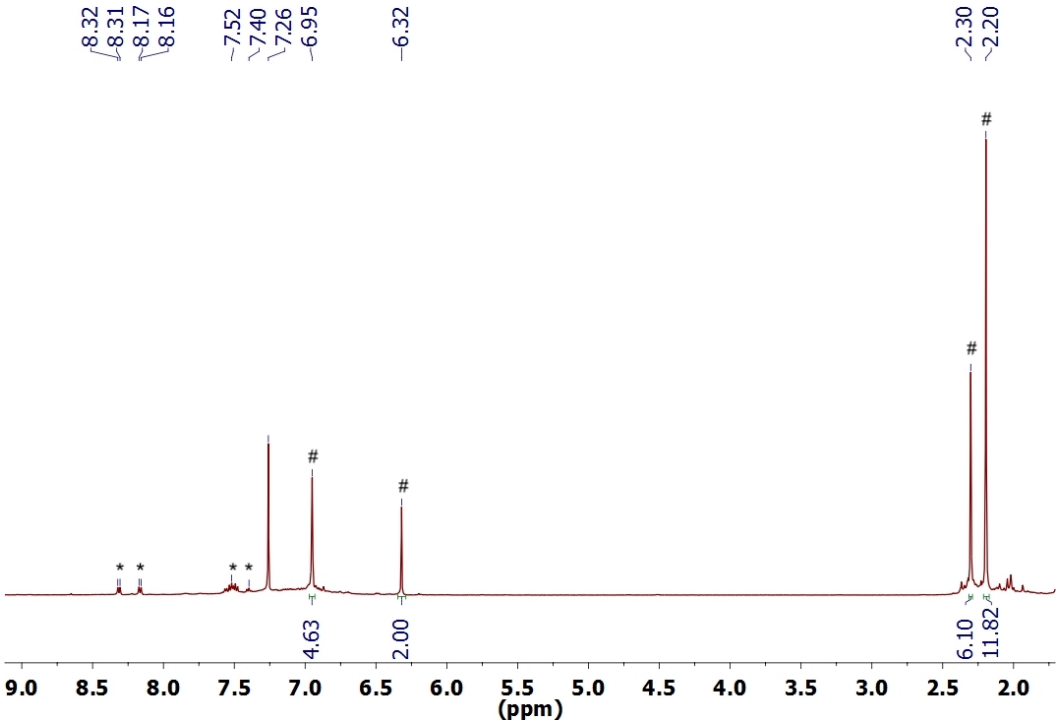


Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the crude reaction mixture obtained from the reaction of **IMes** with one equivalent of PhNO. The resonances marked with *, # correspond to the azoxybenzene and **IMes**=O (**1**), respectively.

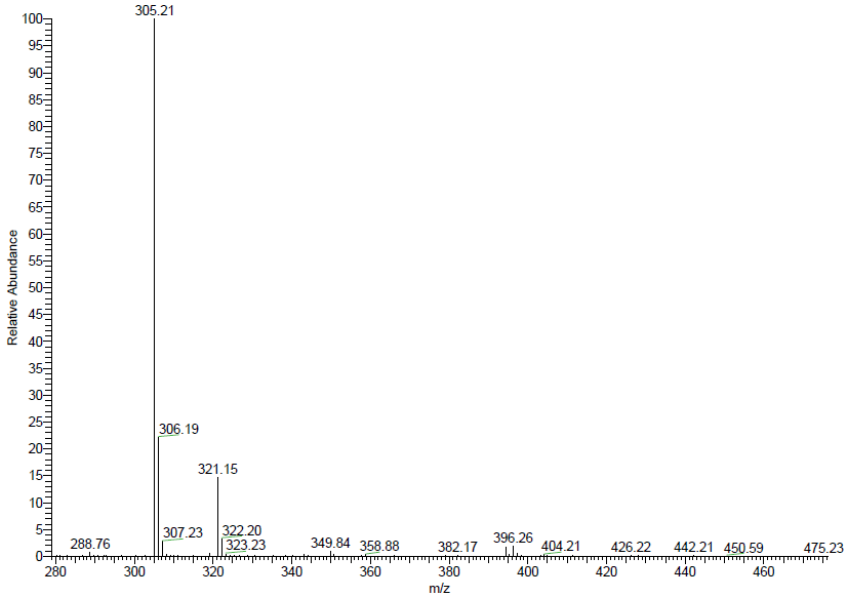


Figure S2. ESI–MS(+) spectrum of the crude reaction mixture obtained from the reaction of **IMes** with one equivalent of PhNO. The *m/z* peaks at 321.15 and 305.21 originate from [{**IMes**=O}+H]$^+$ and [{**IMes**}+H]$^+$, respectively.

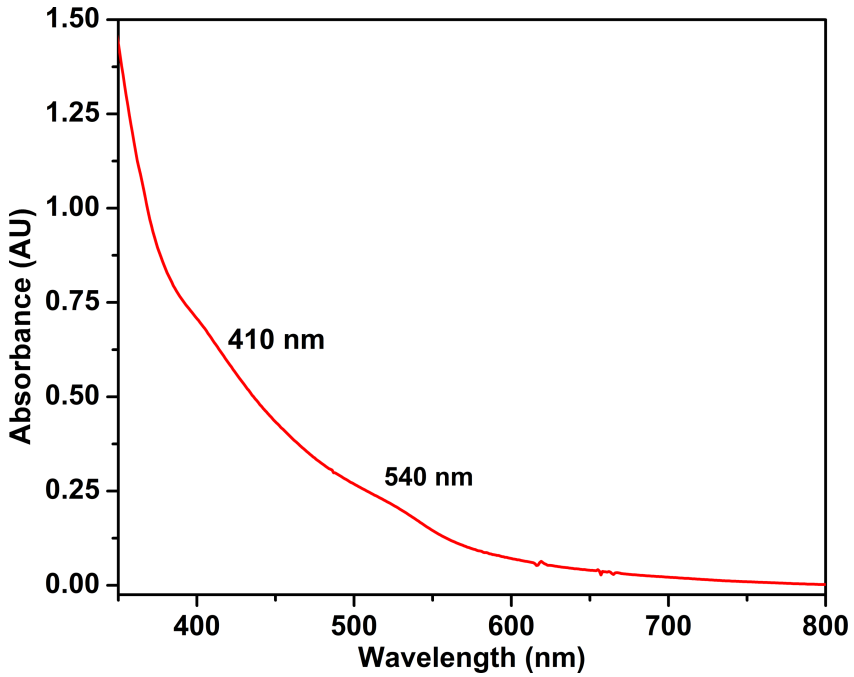


Figure S3. Qualitative UV-vis spectrum of the crude reaction mixture obtained from the reaction of **IMes** with one equivalent of PhNO.

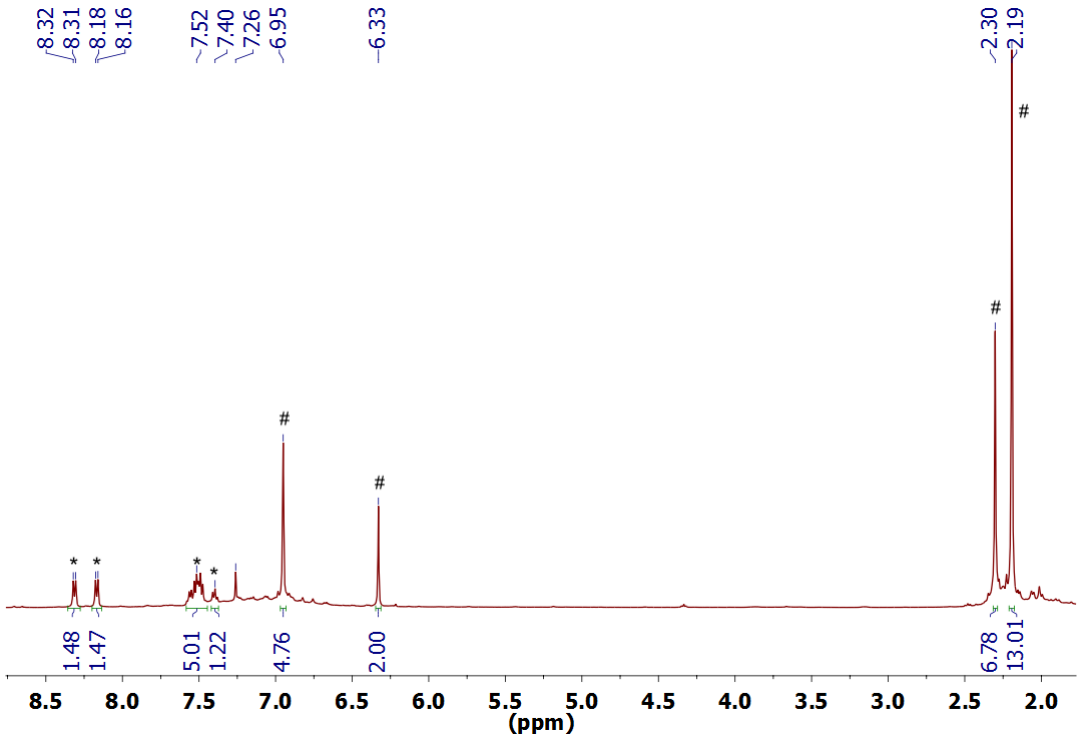


Figure S4. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the crude reaction mixture obtained from the reaction of **IMes** and five equivalents of PhNO. The resonances marked with *, # correspond to the azoxybenzene and **IMes**=O (**1**), respectively.

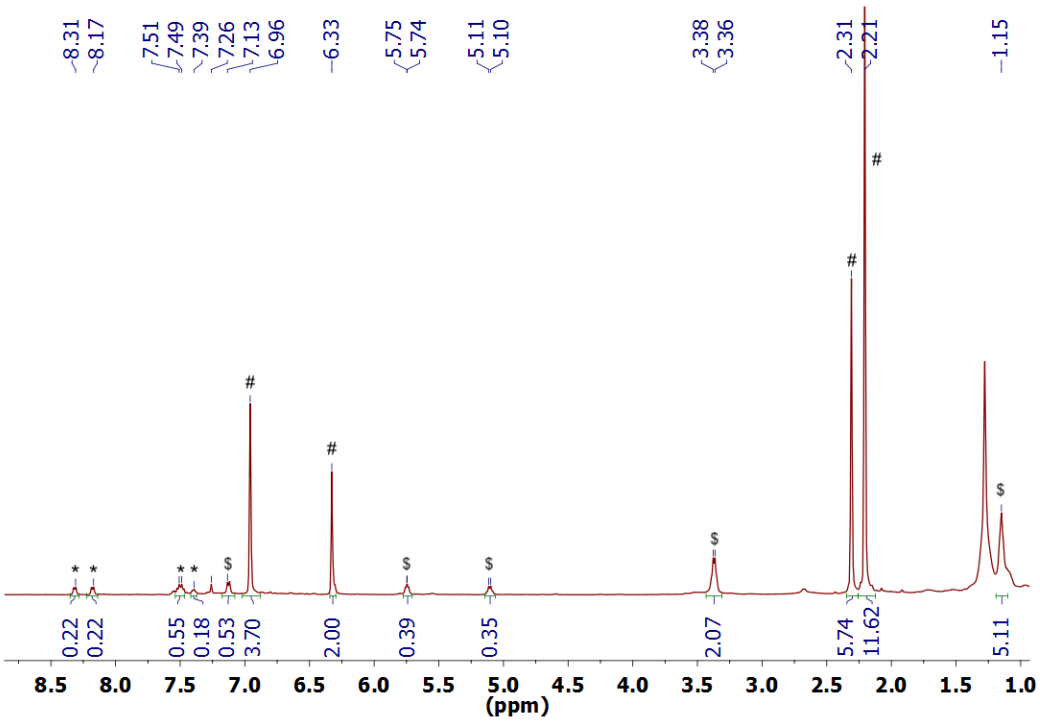


Figure S5. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the crude reaction mixture obtained from the reaction of **IMes** and PhNO in the presence of $HNEt_2$. The resonances marked with *, #, $ correspond to the azoxybenzene, **IMes**=O (**1**) and 2-diethylamino-3H-azepine, respectively.

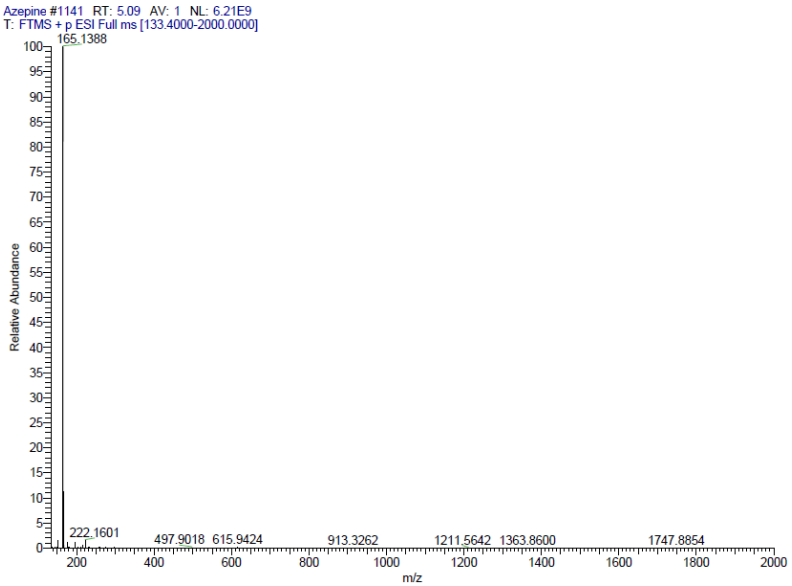


Figure S6. High resolution ESI–MS(+) spectrum of 2-diethylamino-3H-azepine obtained from the reaction of **IMes** with one equivalent of PhNO in the presence of $HNEt_2$. The *m/z* peak at 165.1388 corresponds to the formulation of $[\{C_{10}H_{16}N_2\}+H]^+$ (*calc. m/z* 165.1386).

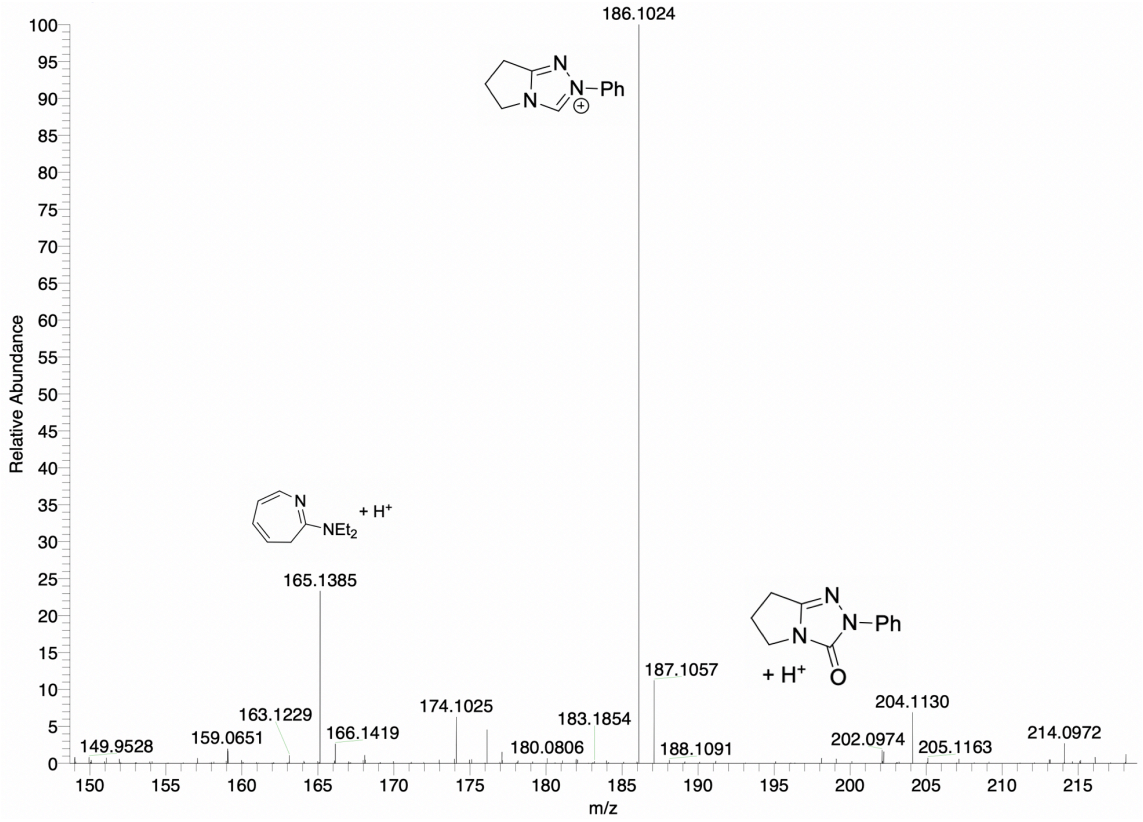


Figure S7. High resolution ESI–MS(+) spectrum of the crude reaction mixture obtained from the reaction of 2-Phenyl-6,7-dihydro-5*H*-pyrrolo[2,1-*c*][1,2,4]triazol-2-ylidene with one equivalent of PhNO in the presence of $HNEt_2$. The *m/z* peaks at 165.1385 and 202.0974 correspond to the respective formulations of 2-diethylamino-3H-azepine $[\{C_{10}H_{16}N_2\}+H]^+$ (*calc. m/z* 165.1386) and 2-phenyl-6,7-dihydro-2H-pyrrolo[2,1-c][1,2,4]triazol-3(5H)-one $+H]^+$ (*calc. m/z* 202.0975).

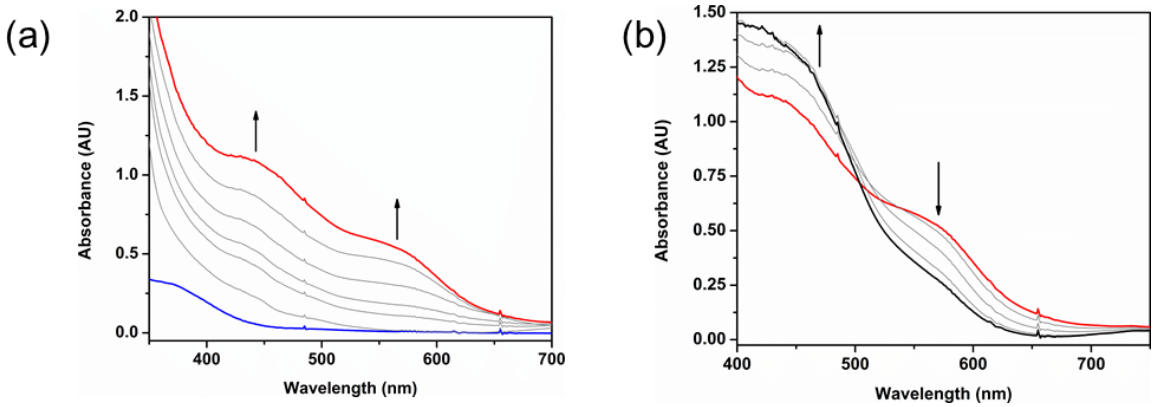


Figure S8. Changes in the UV-Vis spectra of **IMes** in tetrahydrofuran (2.0 mL 2.0 mM in tetrahydrofuran at –40 °C) upon injecting PhNO (200.0 µL, 20.0 mM, 4.0 µmol) demonstrates (a) the formation of the intermediate, (b) the decomposition of the intermediate at –40 °C. Blue trace indicates the absorption features of **IMes** and gradual changes in the absorption features upon addition of PhNO are shown in grey traces. The red trace indicates the absorption features of the resultant intermediate prior to the decomposition. Black trace indicates the absorption features of the decomposed species.

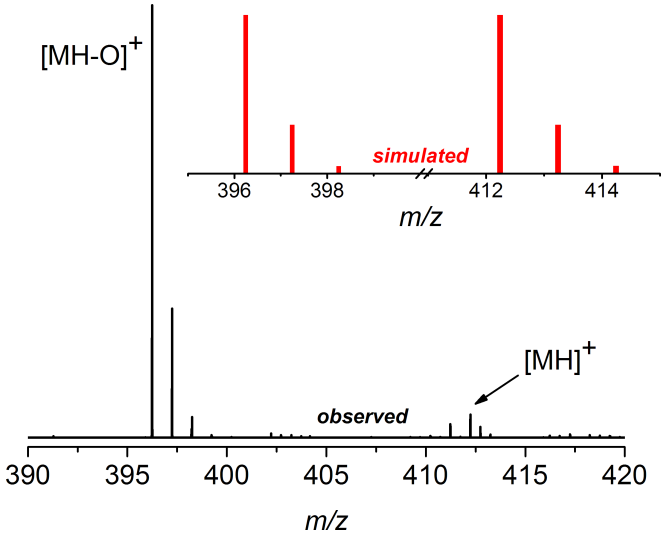


Figure S9. High resolution ESI–MS(+) spectrum of the crude reaction mixture obtained immediately after the reaction of **IMes** with one equivalent of PhNO at –35 °C. The *m/z* peaks at 412.2382 and 396.2440 correspond to the respective formulations of [{**IMes**(PhNO)}H]$^+$ and [{**IMes**(PhNO)}H-O]$^+$. Inset shows the simulated spectral patterns for [{$C_{27}H_{29}N_3O$}+H]$^+$ (*calc. m/z* 412.2383) and [{$C_{27}H_{29}N_3$}+H]$^+$ (*calc. m/z* 396.2434).

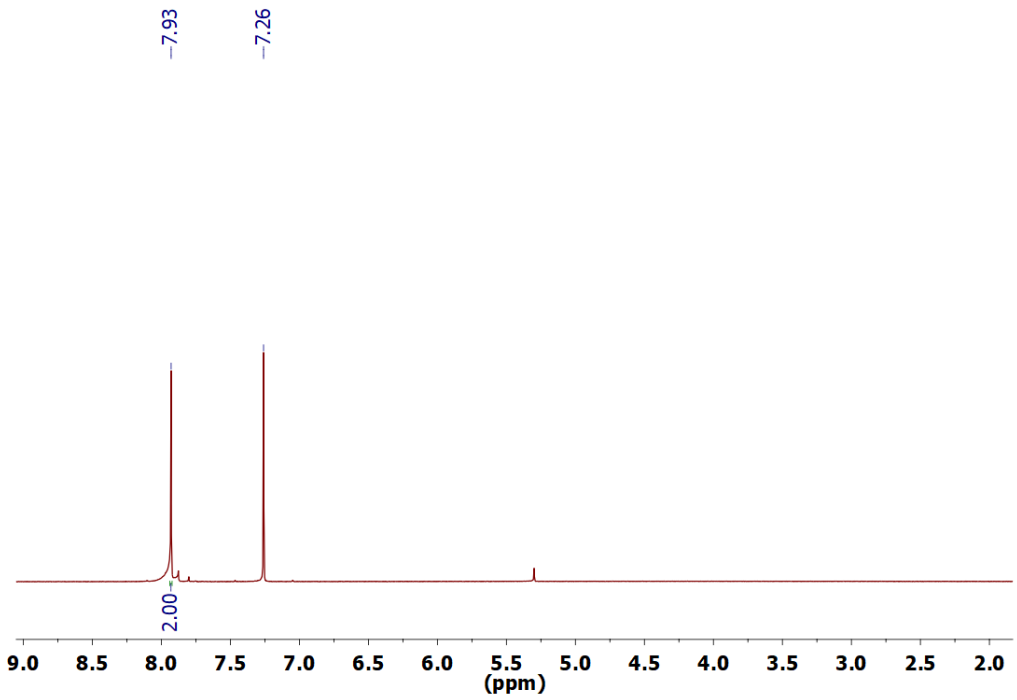


Figure S10. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Br_3ArNO.

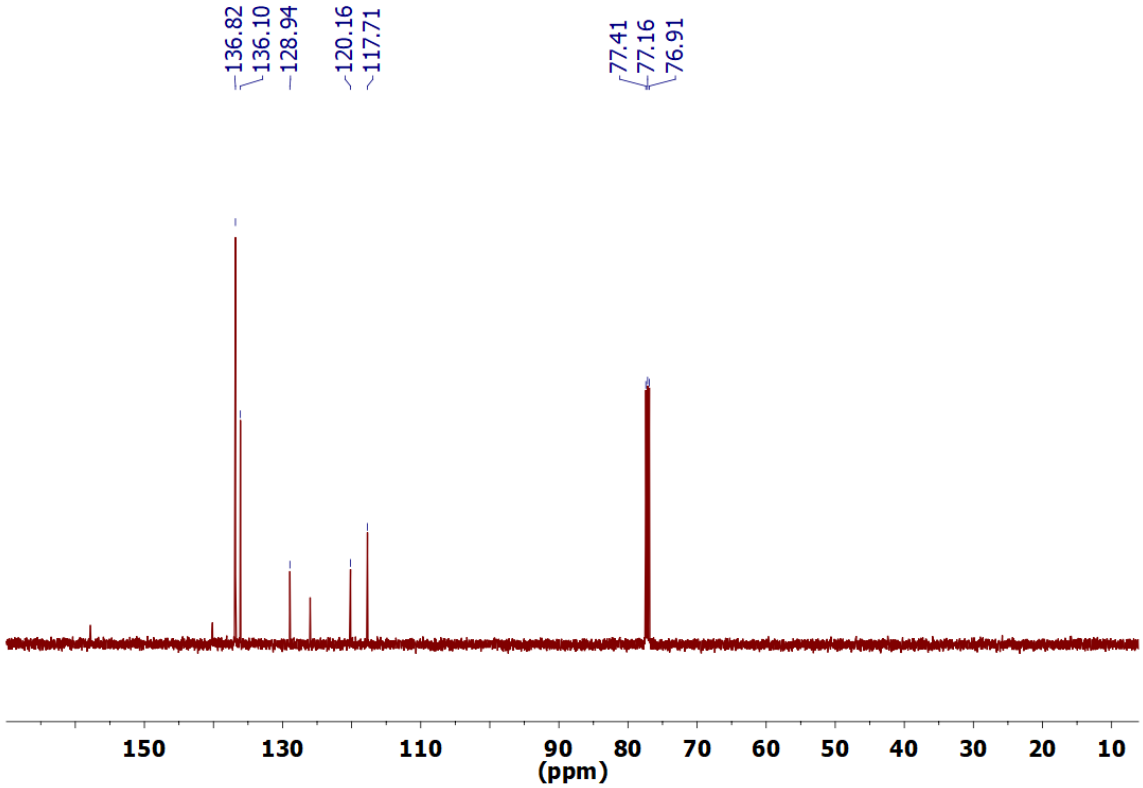


Figure S11. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of Br_3ArNO.

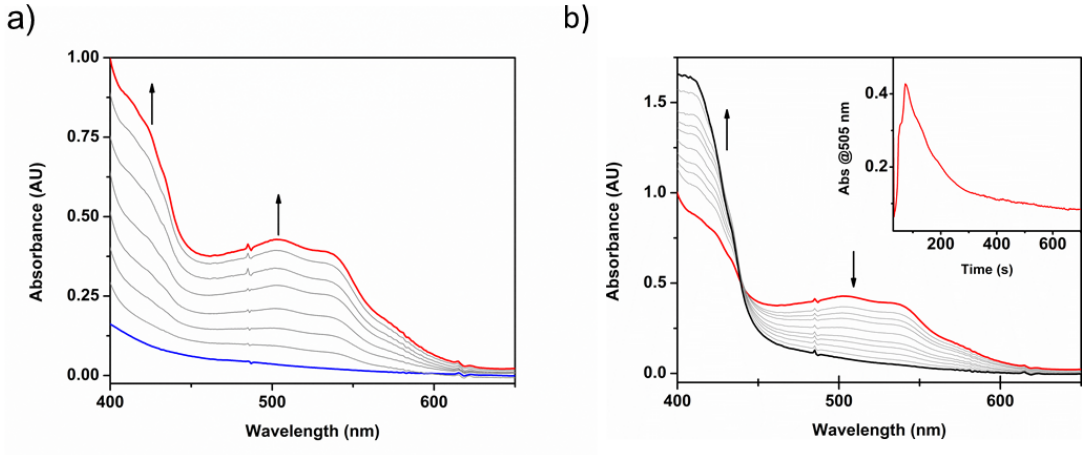


Figure S12. Changes in the UV-Vis spectra of **IMes** in tetrahydrofuran (2.0 mL 2.0 mM in tetrahydrofuran at –40 °C) upon injecting Br_3ArNO (200.0 µL, 20.0 Mm, 4.0 µmol) demonstrates (a) the formation of the intermediate, (b) the decomposition of the intermediate. Blue trace indicates the absorption features of **IMes** and gradual changes in the absorption features upon addition of Br_3ArNO are shown in grey traces. The red trace indicates the absorption features of the resultant intermediate prior to the decomposition. Black trace indicates the absorption features of the decomposed species. The inset displays a plot of time trace showing the changes at the 505 nm absorption feature indicating very fast decomposition of the transient species at –40 °C.

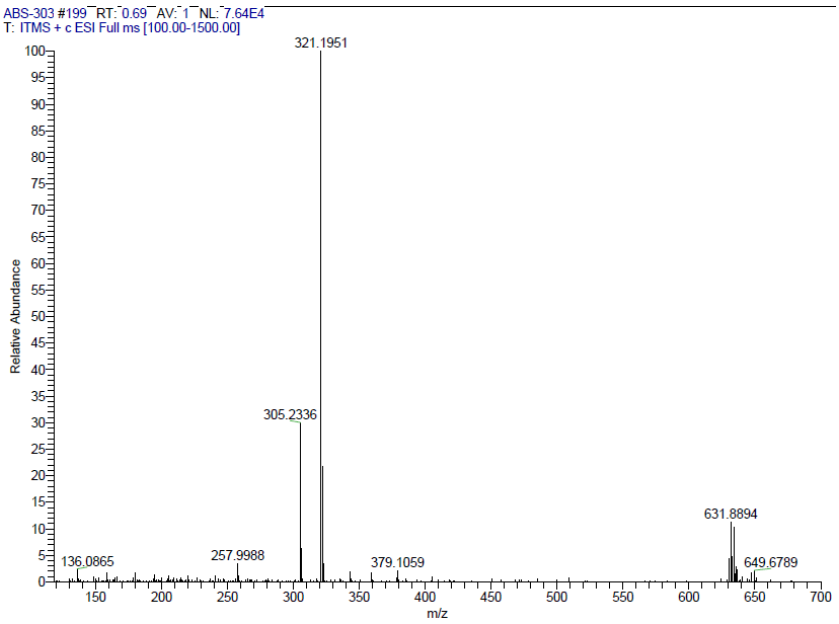


Figure S13. ESI–MS(+) spectrum of the crude reaction mixture obtained after the reaction of **IMes** with one equivalent of Br_3ArNO at –35 °C. The *m/z* peaks at 649.67, 631.88 and 321.19 correspond to $[\{\textbf{IMes}(Br_3ArNO)\}+H]^+$, $[\{\textbf{IMes}(Br_3ArNO)\}+H\text{-}O]^+$, and $[\{\textbf{IMes}{=}O\}+H]^+$.

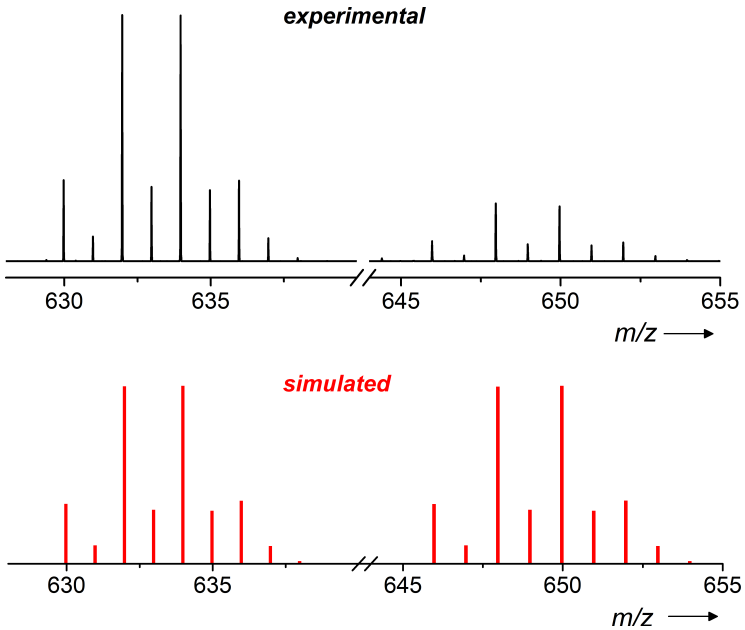


Figure S14. High resolution ESI–MS(+) spectrum of the crude reaction mixture obtained after the reaction of **IMes** with one equivalent of Br_3ArNO at –35 °C. **Top:** ESI-MS(+) plot showing the isotopic distribution patterns of $\{\textbf{IMes}(Br_3ArNO)H\}^+$ and $[\{\textbf{IMes}(Br_3ArNO)H\}\text{-}O]^+$ at 647.9676 and 631.9721 (for ^{79}Br isotope), respectively. **Bottom:** simulated spectral patterns for $\{C_{27}H_{27}Br_3N_3O\}^+$ (calc. *m/z* 647.9678) and $\{C_{27}H_{27}Br_3N_3\}^+$ (calc. *m/z* 631.9729).

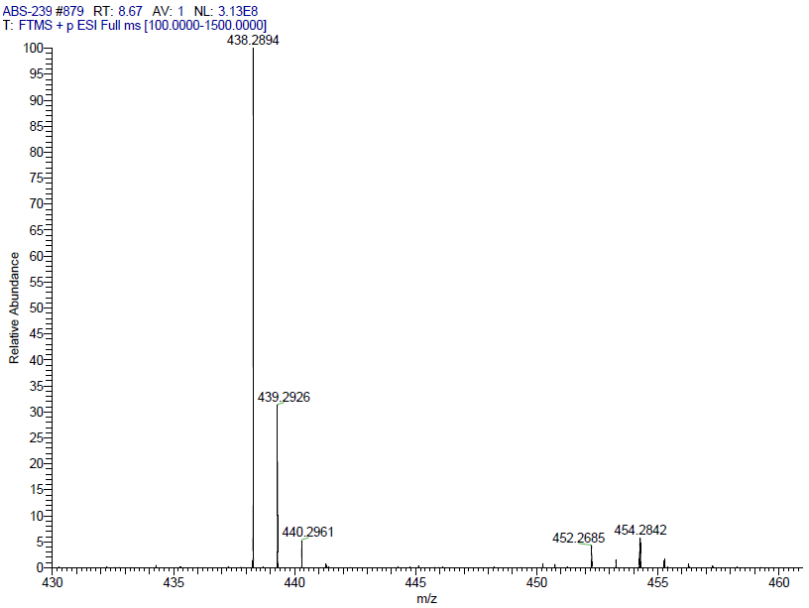


Figure S15. High resolution ESI–MS(+) spectrum of the crude reaction mixture obtained immediately after the reaction of **IMes** with one equivalent of MesNO at –35 °C. The *m/z* peak at 454.2842 and 438.2894 correspond to the respective formulation of [{**IMes**(MesNO)}H]$^+$ and [{**IMes**(MesNO)}H-O]$^+$. (*calc. m/z* for [{$C_{30}H_{35}N_3O$}+H]$^+$ 454.2853) and *calc. m/z* for [{$C_{30}H_{35}N_3$}+H]$^+$ 438.2904).

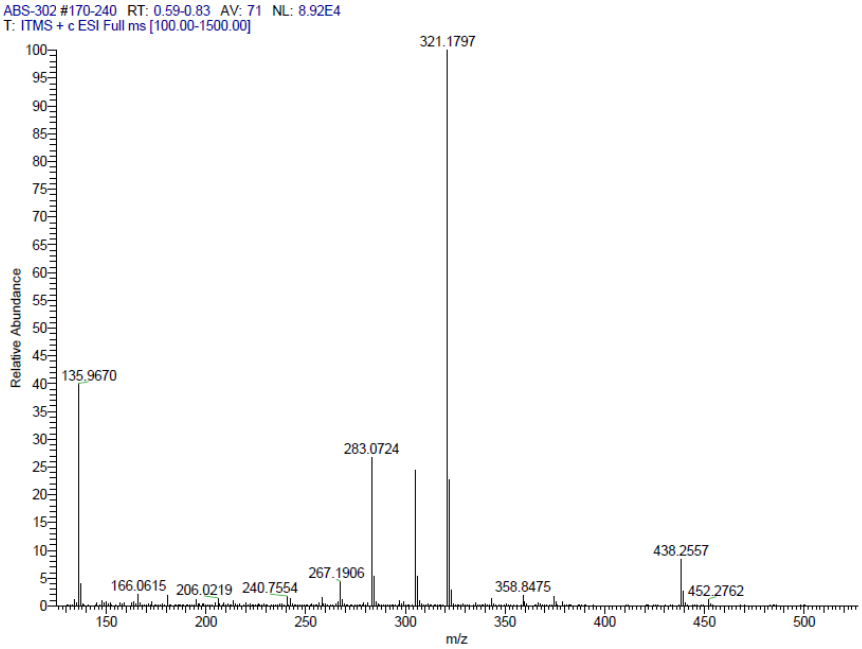


Figure S16. ESI–MS(+) spectrum of the crude reaction mixture obtained immediately after the reaction of **IMes** with one equivalent of MesNO at –35 °C. The *m/z* peaks at 452.27 and 438.25 correspond to the respective formulation of [{**IMes**(MesNO)}H$^+$] and [{**IMes**(MesNO)}H-O}]$^+$. Additionally, the *m/z* peaks at 321.18 and 283.07 originate from [{**IMes**=O}+H]$^+$and the corresponding azoxybenzene derivative of MesNO, respectively.

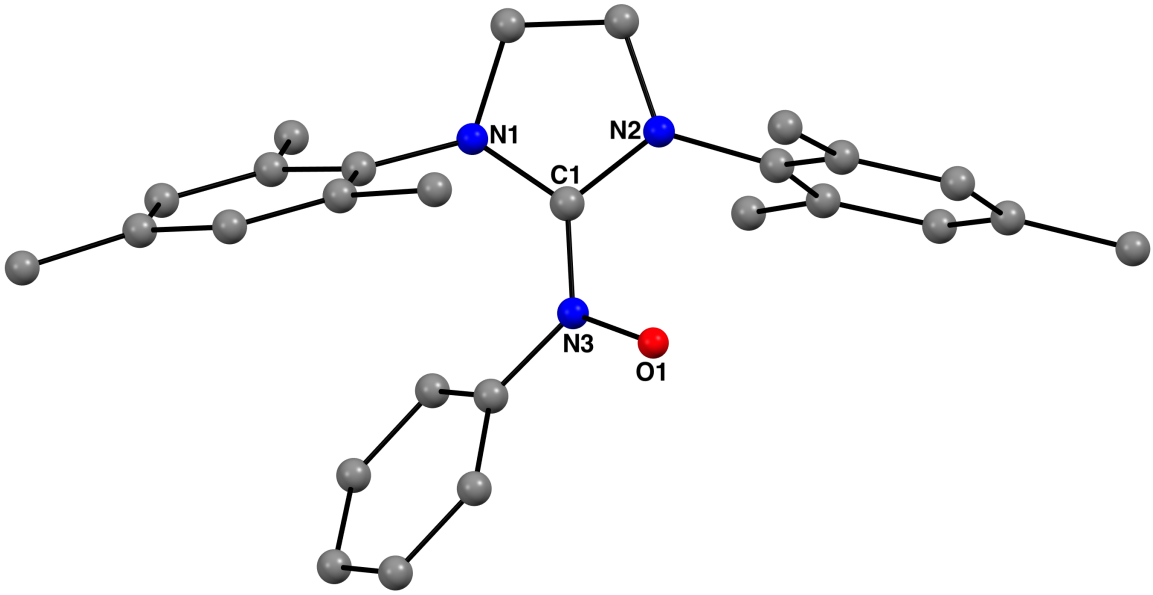


Figure S17. Geometry optimized structure of **2a-Ph** at M062X/6-31G(d,p) level of theory with charge = 0, multiplicity =1. Selected bond distances (in Å) for **2a-Ph**: C1–N1 1.376, C1–N2 1.365, C1–N3 1.324, N3–O1 1.347, C1•••O1 2.278. H-atoms are omitted for clarity.

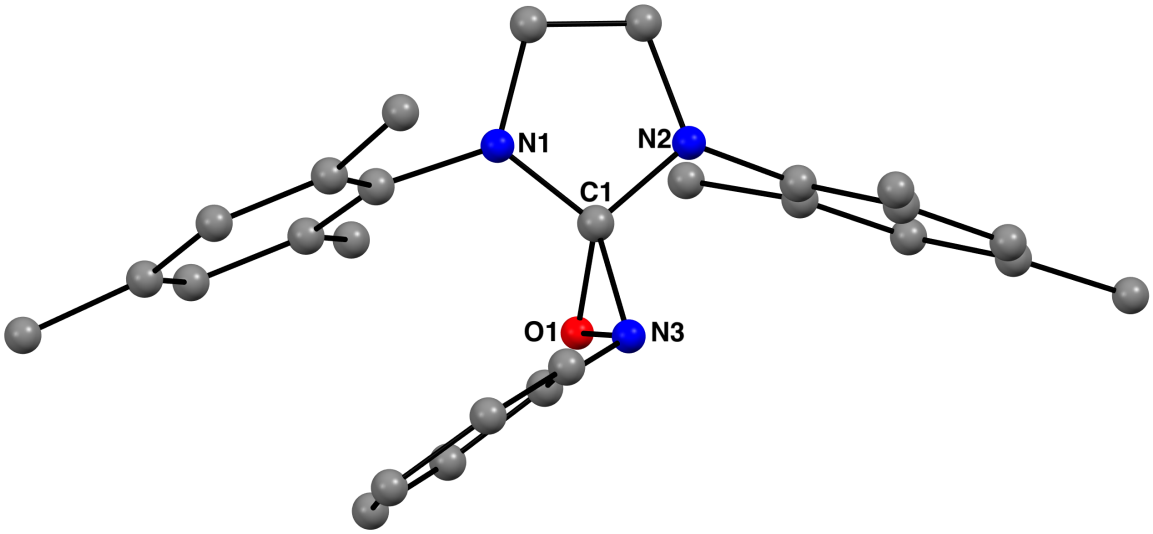


Figure S18. Geometry optimized structure of **2b-Ph** at M062X/6-31G(d,p) level of theory with charge = 0, multiplicity =1. Selected bond distances (in Å) for **2b-Ph**: C1–N1 1.413, C1–N2 1.409, C1–N3 1.452, N3–O1 1.484, C1–O1 1.402. H-atoms are omitted for clarity.

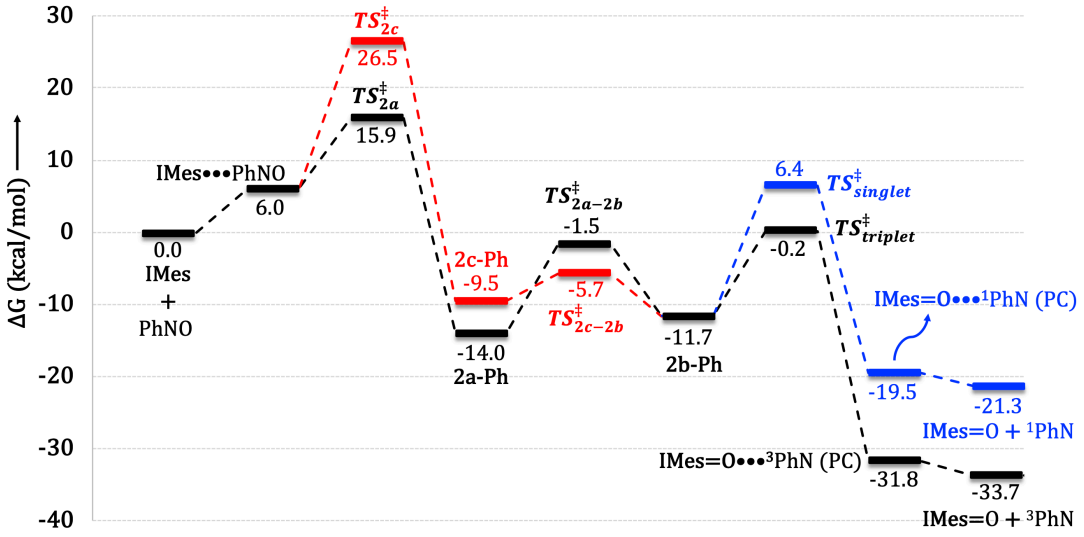


Figure S19. DFT calculated (M062X/6-31G(d,p) in gas phase) Gibbs free energy profiles for the interconversion of intermediates and generation of phenylnitrene (PhN) from **IMes** and PhNO (all values at 298.15 K). For drawing of intermediates and transition structures see Figure S20. Color Code: Black and red colored pathways denote two different paths from RC to **2b-Ph** via intermediate **2a-Ph** and **2c-Ph**, respectively. The black and blue steps generated after **2b-Ph** indicates the reaction paths for the formation of triplet and open-shell singlet nitrene, respectively.

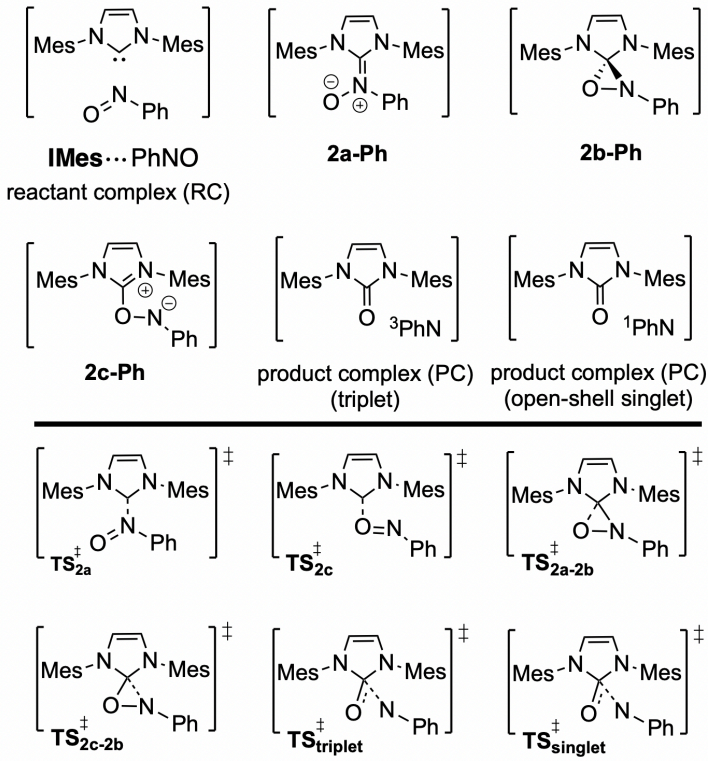


Figure S20. Structural drawings of the intermediates (top) and transition states (bottom) involved in the generation of phenyl nitrene (PhN) from **IMes** and PhNO.

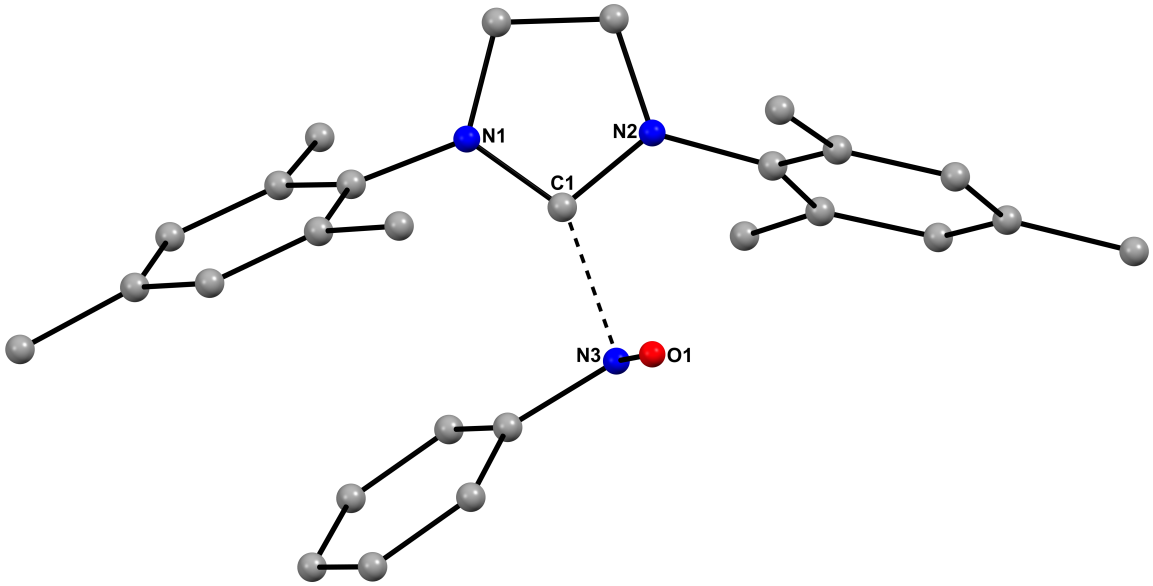


Figure S21. Predicted transition state $\mathbf{TS^{‡}_{2a}}$ at M062X/6-31G(d,p) level of theory with charge = 0, multiplicity = 1. Selected bond distances (in Å) for $\mathbf{TS^{‡}_{2a}}$: C1-N1, 1.352; C1-N2, 1.346; C1•••N3, 1.937; N3-O1, 1.257; C1•••O1, 2.589. H-atoms are omitted for clarity.

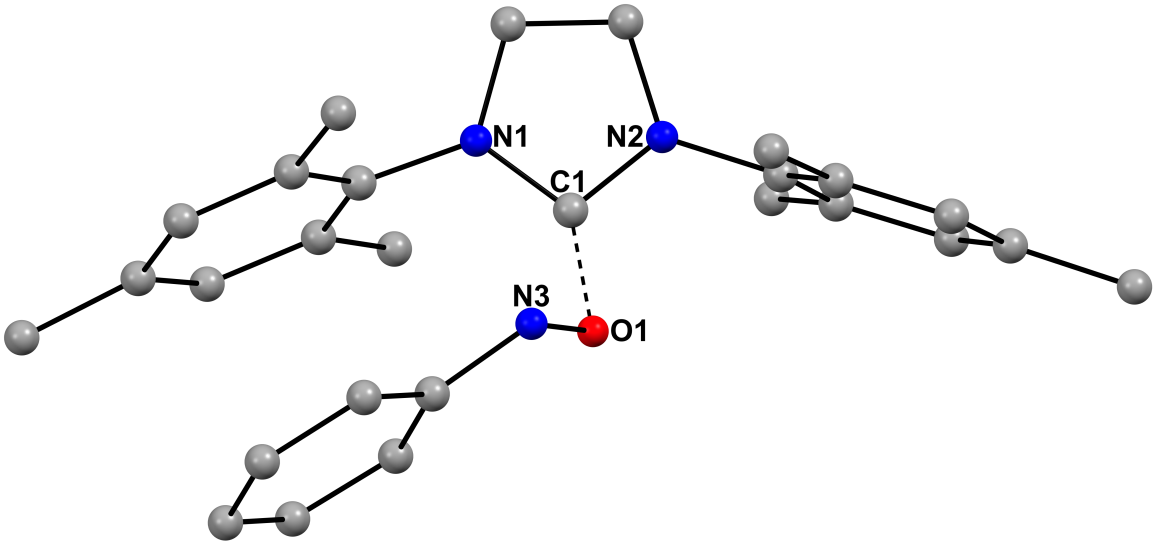


Figure S22. Predicted transition state $\mathbf{TS^{‡}_{2c}}$ at M062X/6-31G(d,p) level of theory with charge = 0, multiplicity = 1. Selected bond distances (in Å) for $\mathbf{TS^{‡}_{2c}}$: C1-N1, 1.353; C1-N2, 1.350; C1•••N3, 2.537; N3-O1, 1.296; C1•••O1, 1.760. H-atoms are omitted for clarity.

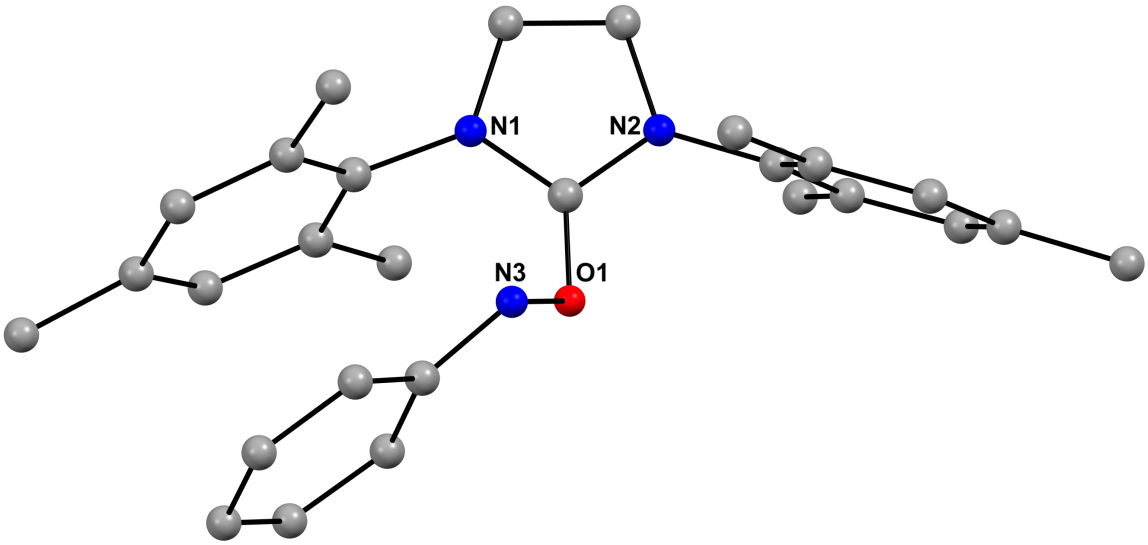


Figure S23. Geometry optimized structure of **2c-Ph** at M062X/6-31G(d,p) level of theory with charge = 0, multiplicity =1. Selected bond distances (in Å) for **2c-Ph**: C1-N1, 1.351; C1-N2, 1.350; C1•••N3, 2.274; N3-O1, 1.539; C1-O1, 1.290. H-atoms are omitted for clarity

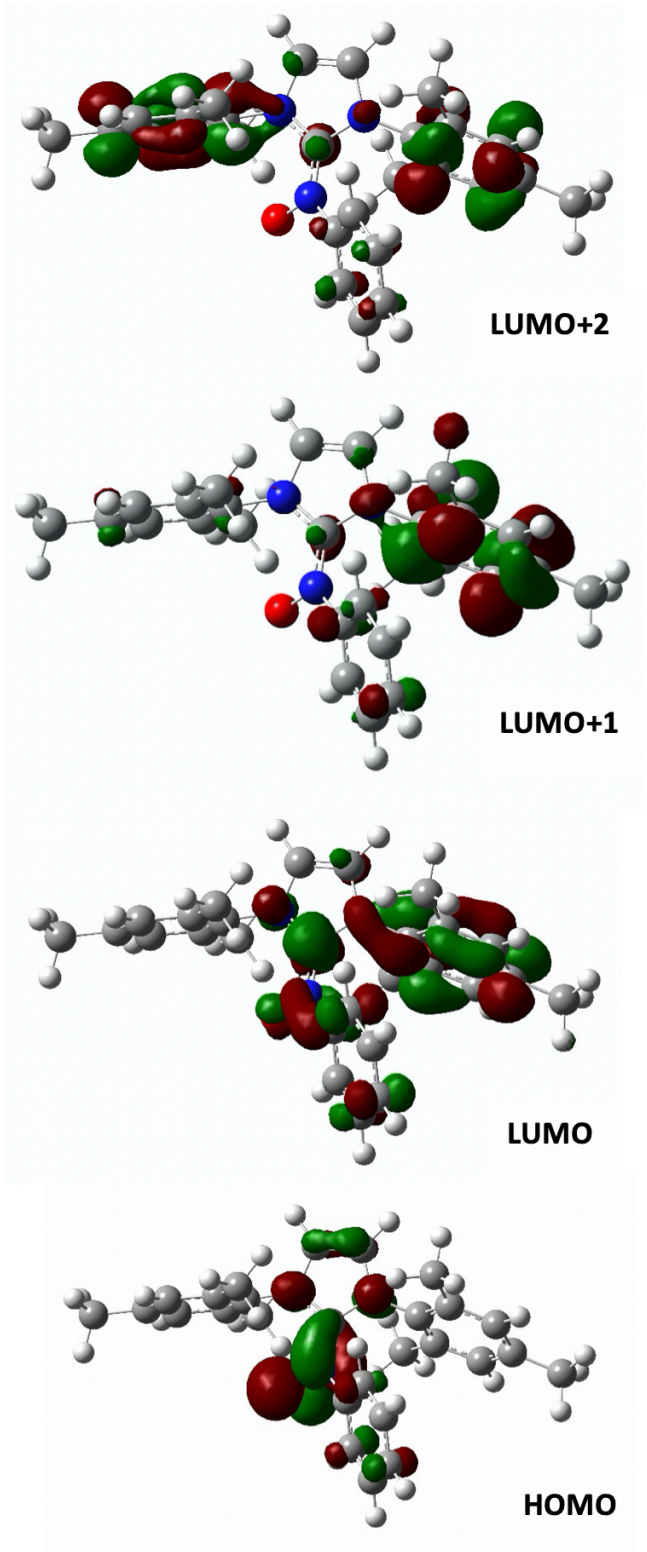


Figure S24. HOMO, LUMO, LUMO+1 and LUMO+2 orbital plots for **2a-Ph**.

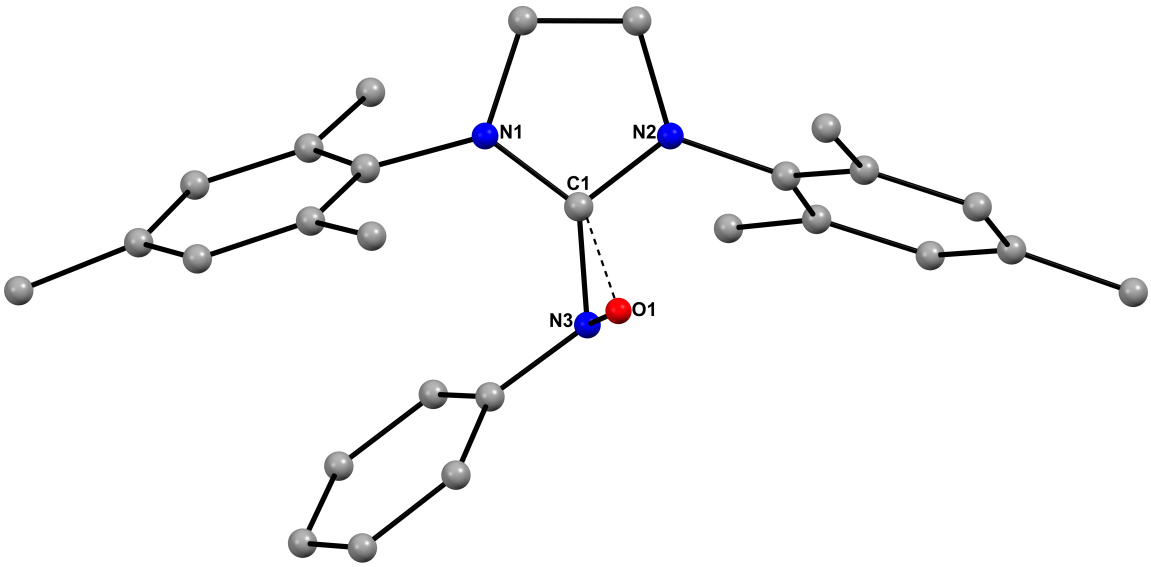


Figure S25. Predicted transition state $\mathbf{TS^{‡}_{2a\text{-}2b}}$ at M062X/6-31G(d,p) level of theory with charge = 0, multiplicity = 1. Selected bond distances (in Å) for $\mathbf{TS^{‡}_{2a\text{-}2b}}$: C1-N1, 1.369; C1-N2, 1.367; C1-N3,1.370; N3-O1, 1.439; C1•••O1, 1.836. H-atoms are omitted for clarity

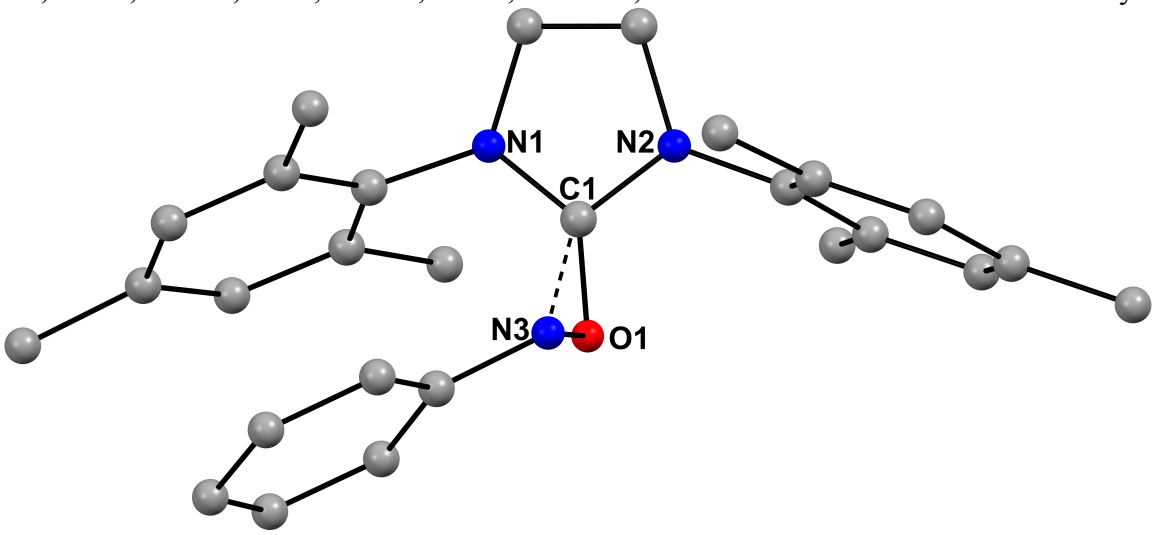


Figure S26. Predicted transition state $\mathbf{TS^{‡}_{2c\text{-}2b}}$ at M062X/6-31G(d,p) level of theory with charge = 0, multiplicity = 1. Selected bond distances (in Å) for $\mathbf{TS^{‡}_{2c\text{-}2b}}$: C1-N1, 1.371; C1–N2, 1.366; C1•••N3, 1.834; N3–O1, 1.526; C1–O1, 1.316. H-atoms are omitted for clarity

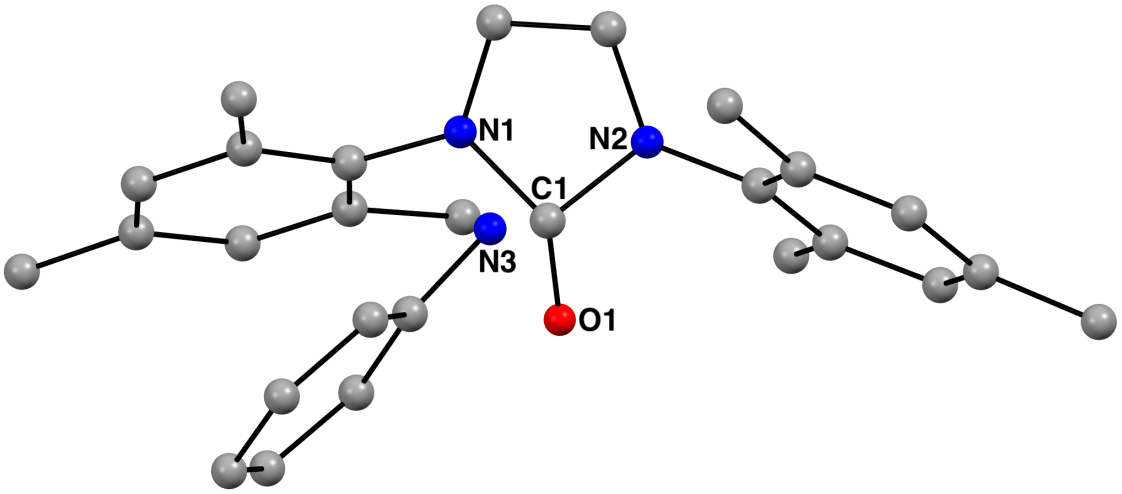


Figure S27. Predicted transition state $\mathbf{TS^{\ddagger}_{triplet}}$ at M062X/6-31G(d,p) level of theory with charge = 0, multiplicity = 3. Selected bond distances (in Å) for $\mathbf{TS^{\ddagger}_{triplet}}$: C1-N1, 1.479; C1–N2, 1.468; C1•••N3, 1.824; N3•••O1, 2.555; C1–O1, 1.234. H-atoms are omitted for clarity

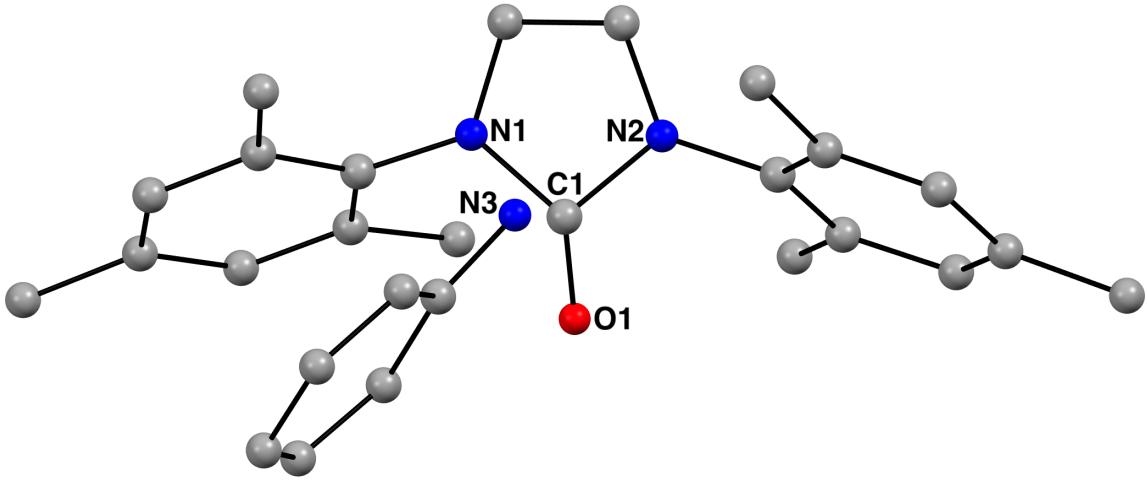


Figure S28. Predicted transition state $\mathbf{TS^{\ddagger}_{singlet}}$ at M062X/6-31G(d,p) level of theory with charge = 0, multiplicity = 1 (open-shell singlet). Selected bond distances (in Å) for $\mathbf{TS^{\ddagger}_{singlet}}$: C1-N1, 1.464; C1–N2, 1.450; C1•••N3, 1.919; N3•••O1, 2.618; C1–O1, 1.230. H-atoms are omitted for clarity

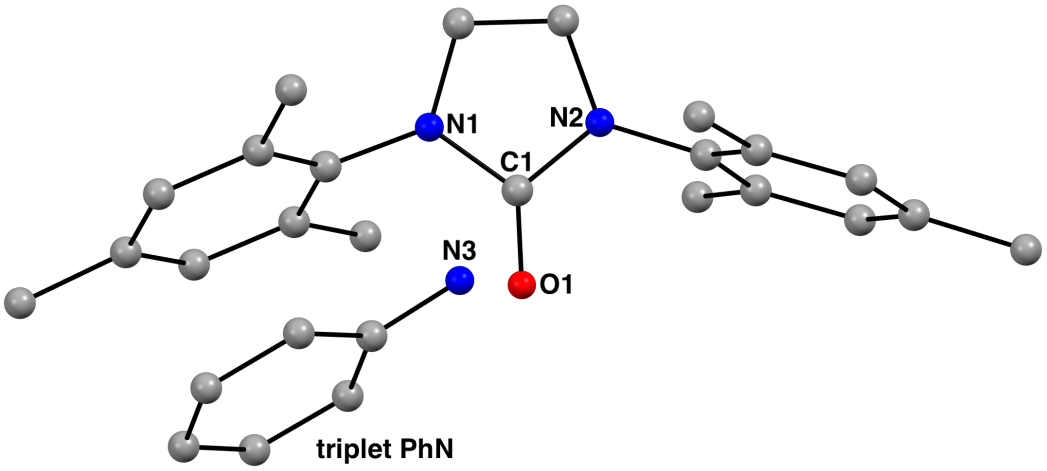


Figure S29. Predicted product complex **IMes=O•••**^{3}PhN at M062X/6-31G(d,p) level of theory with charge = 0, multiplicity = 3. Selected bond distances (in Å) for product complex **IMes=O•••**^{3}PhN: C1-N1, 1.391; C1–N2, 1.383; C1–O1, 1.224. H-atoms are omitted for clarity.

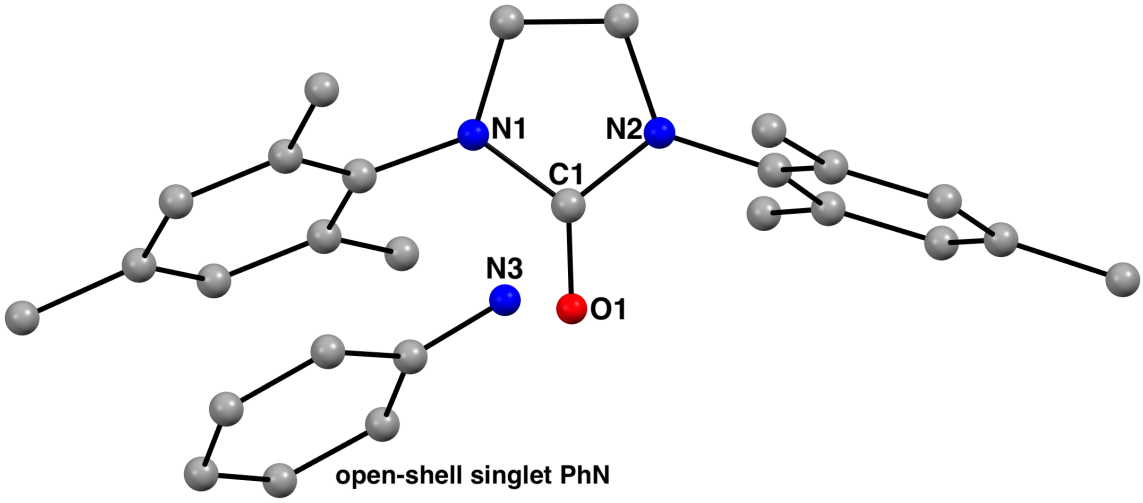


Figure S30. Predicted product complex **IMes=O•••**^{1}PhN at M062X/6-31G(d,p) level of theory with charge = 0, multiplicity = 1 (open-shell singlet). Selected bond distances (in Å) for product complex **IMes=O•••**^{1}PhN: C1-N1, 1.391; C1–N2, 1.383; C1–O1, 1.224. H-atoms are omitted for clarity.

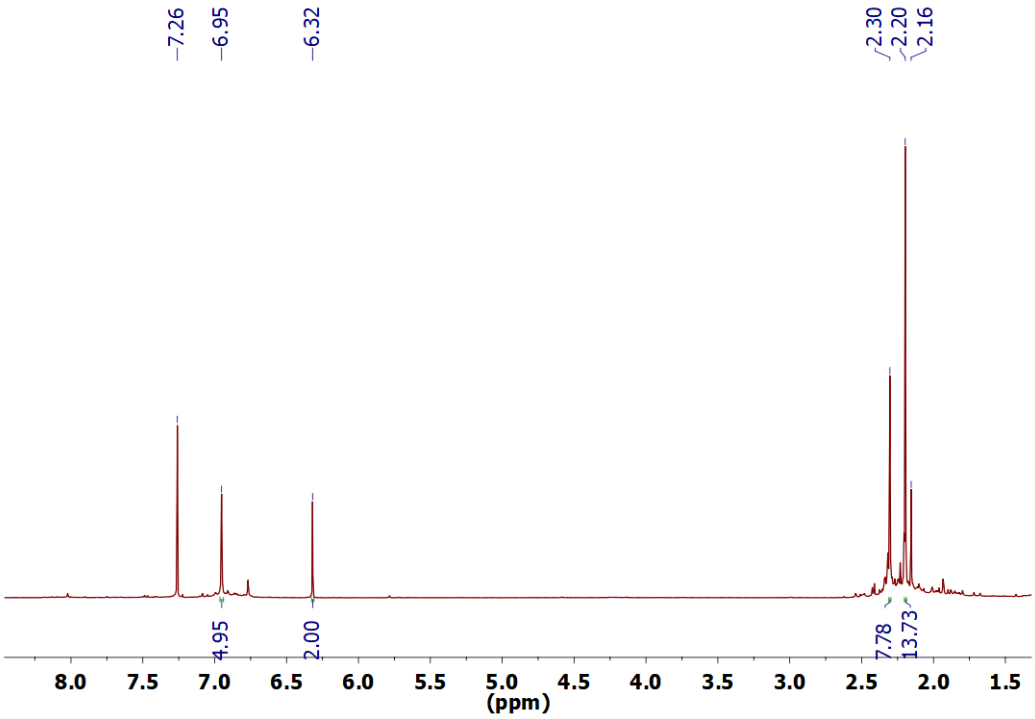


Figure S31. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the crude reaction mixture obtained from the reaction of **IMes** with one equivalent of MesNO.

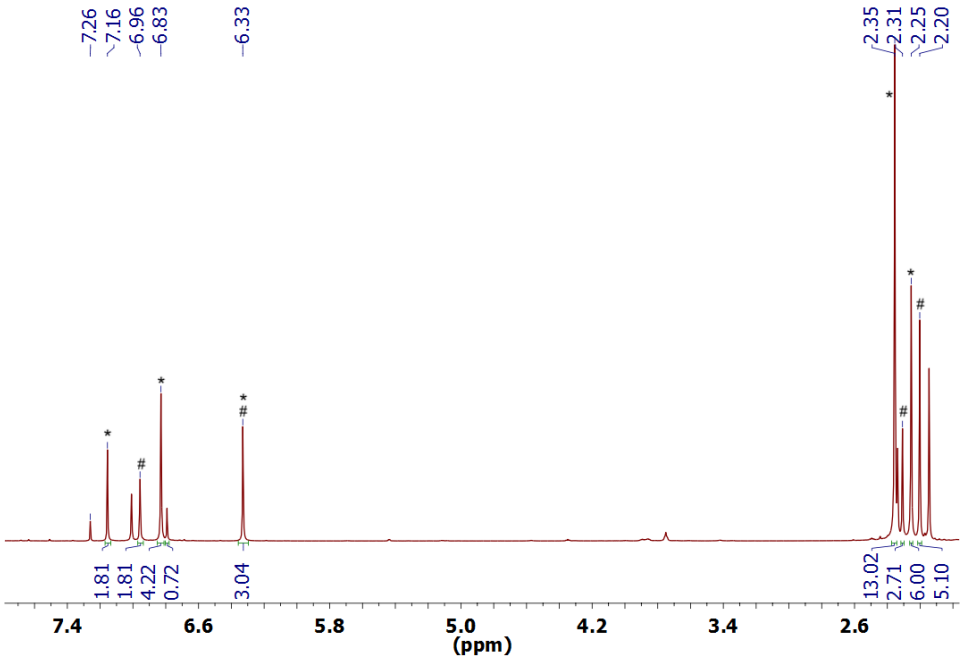


Figure S32. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of the crude reaction mixture obtained from the reaction of **IMes** with one equivalent of Br_3ArNO. The resonances marked with *, # correspond to the **3-Br$_3$Ar** and **IMes**=O (**1**), respectively.

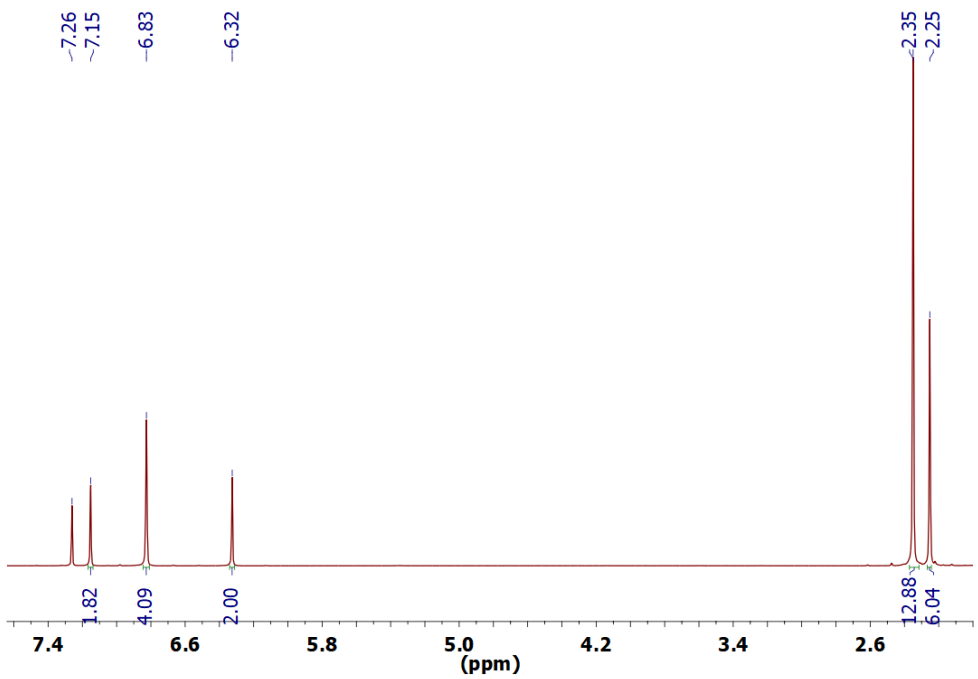


Figure S33. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of **3-Br$_3$Ar**.

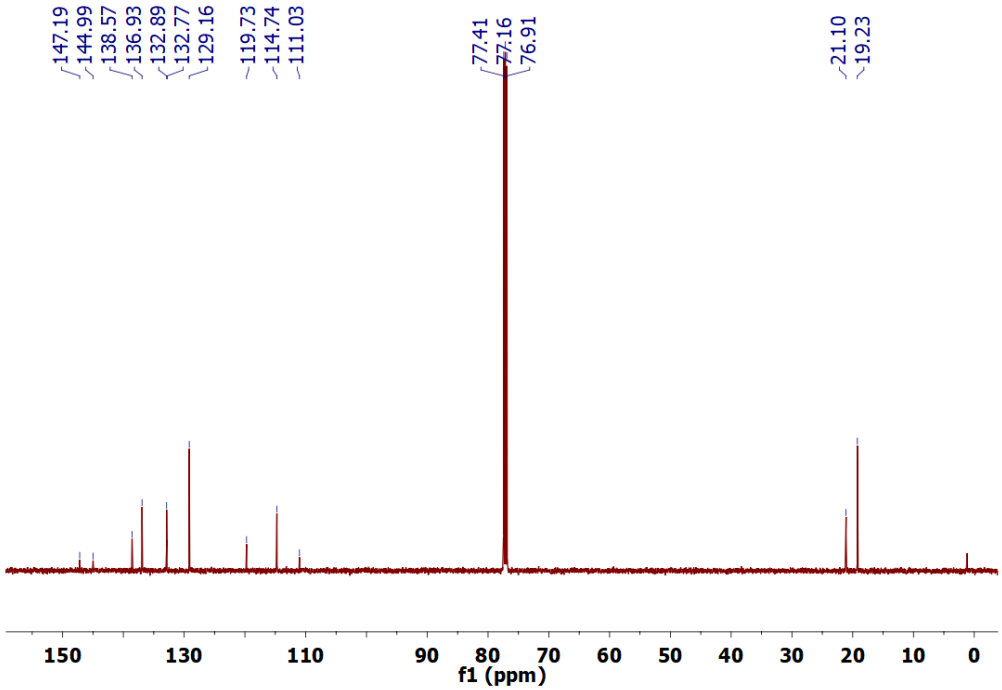


Figure S34. ^{13}C NMR spectrum (125 MHz, $CDCl_3$) of **3-Br$_3$Ar**.

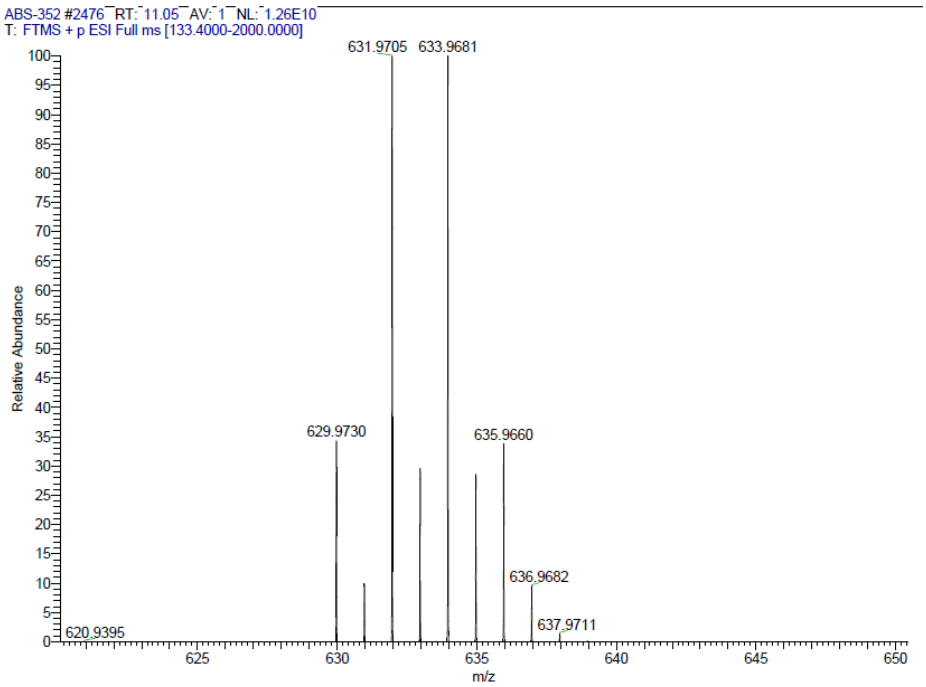


Figure S35. High resolution ESI–MS(+) spectrum of **3-Br$_3$Ar** form the reaction of **IMes** and Br$_3$ArNO. at –35 °C. The *m/z* peak at 631.9705 corresponds to [{**IMes**=N^{79}Br$_3$Ar}+H]$^+$ (*calc. m/z* for [{$C_{27}H_{26}Br_3N_3$}+H]$^+$ = 631.9729 for ^{79}Br isotope).

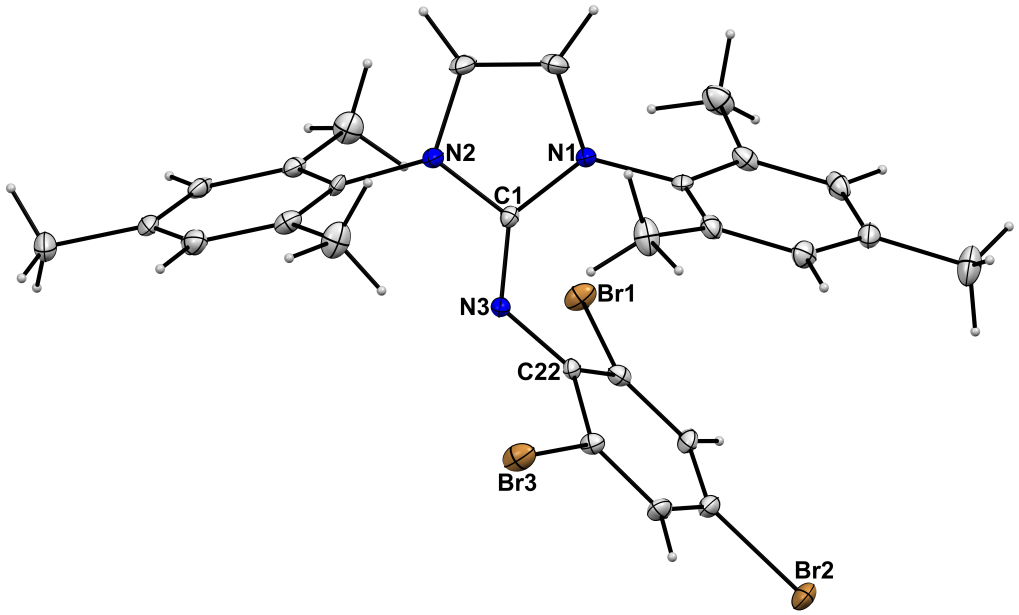


Figure S36. X-ray crystal structure of **IMes**=NArBr$_3$ (**3-Br$_3$Ar**) (CCDC 1976500) with the thermal ellipsoids set at 30% probability. Selected bond lengths (Å) and angles (°): C1–N1 1.380(5), C1–N2 1.375(5), C1–N3 1.304(5), C22–N3 1.375(5), N1–C1–N2 104.8(3), N1–C1–N3 133.2(4), N2–C1–N3 121.8(4), C1–N3–C22 123.8(3).

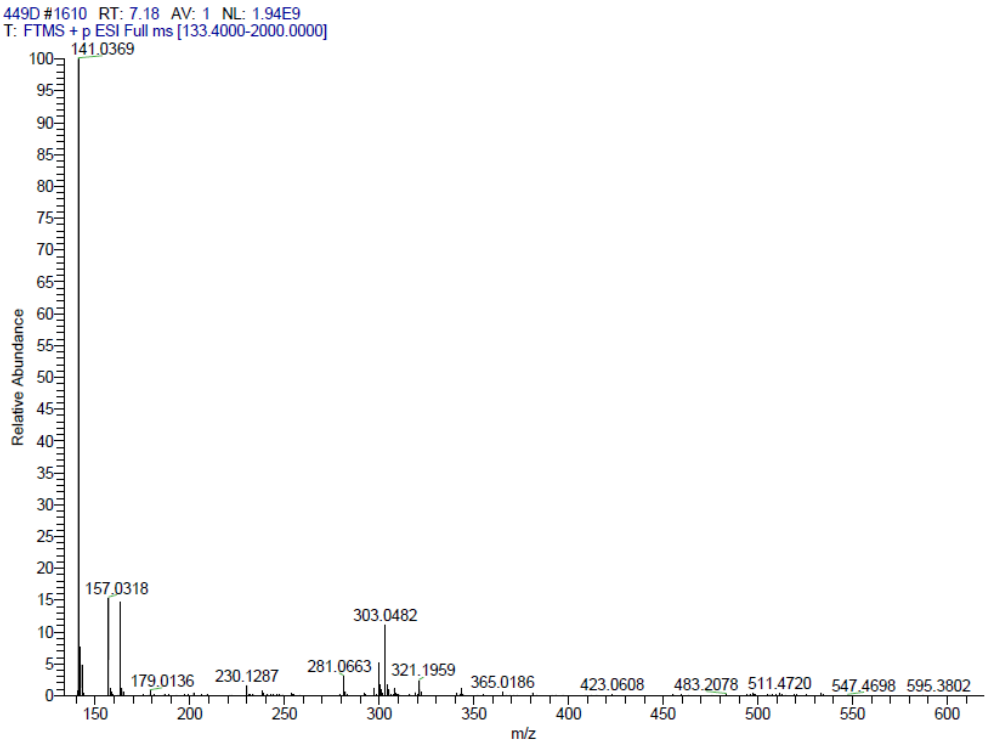


Figure S37. High resolution ESI–MS(+) spectrum of PhS(O)Me from the reaction of **IMes** and Br_3ArNO in the presence of PhSMe at –78 °C. The *m/z* peak at 141.0369 corresponds to the isotope distribution pattern $[\{C_7H_8SO\}+H]^+$ (*calc. m/z* 141.0369).

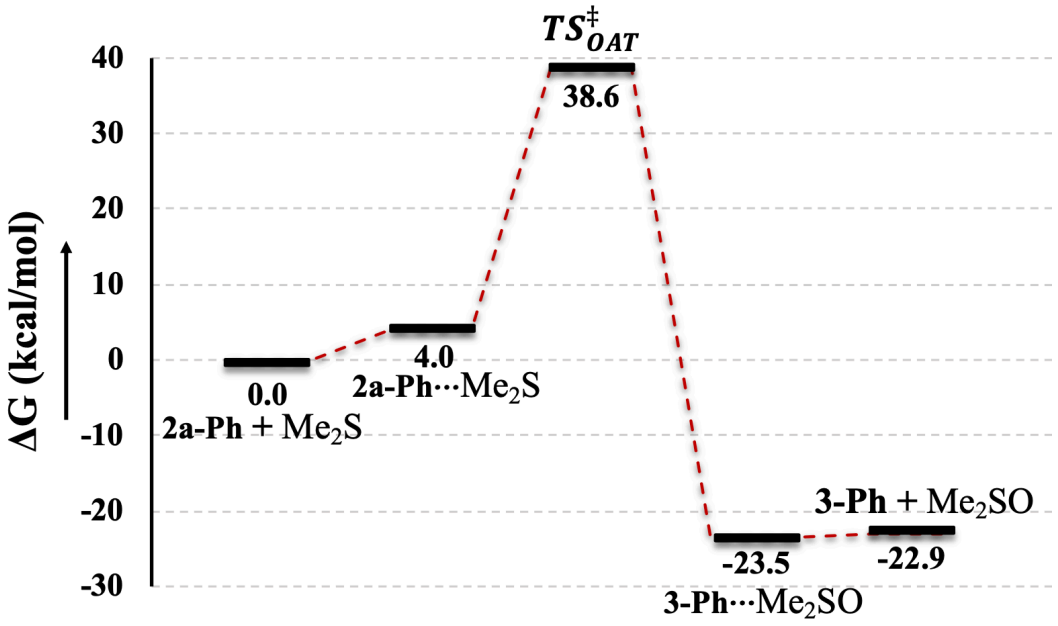


Figure S38. DFT calculated (M062X/6-31G(d,p) in gas phase) Gibbs free energy profiles for the oxygen-atom-transfer (OAT) reaction by **2a-Ph**. (all values at 298.15 K). For drawing of intermediates and transition structures see Figure S39.

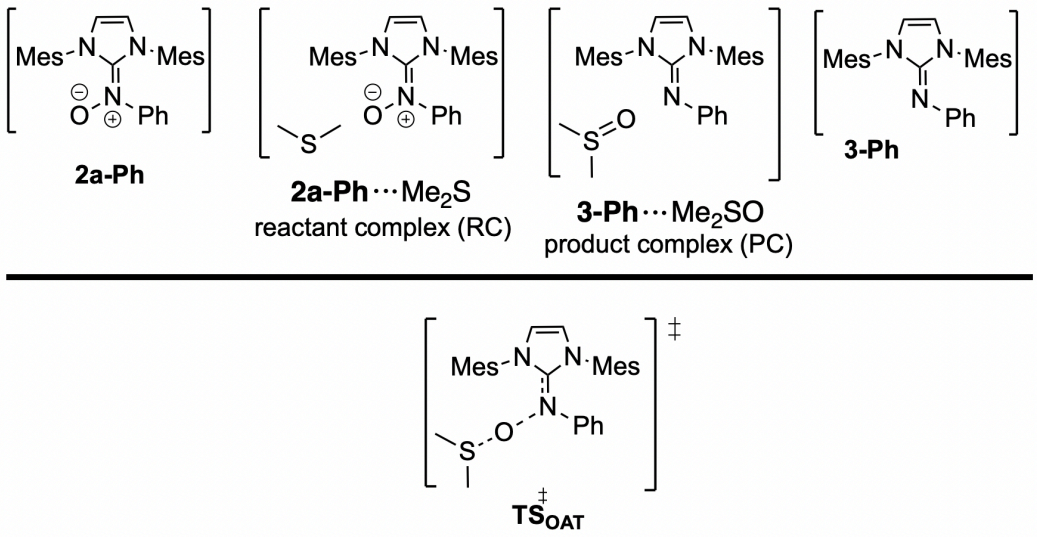


Figure S39. Structural drawings of the intermediates (top) and transition states (bottom) involved in the oxygen-atom-transfer reaction mediated by **2a-Ph**.

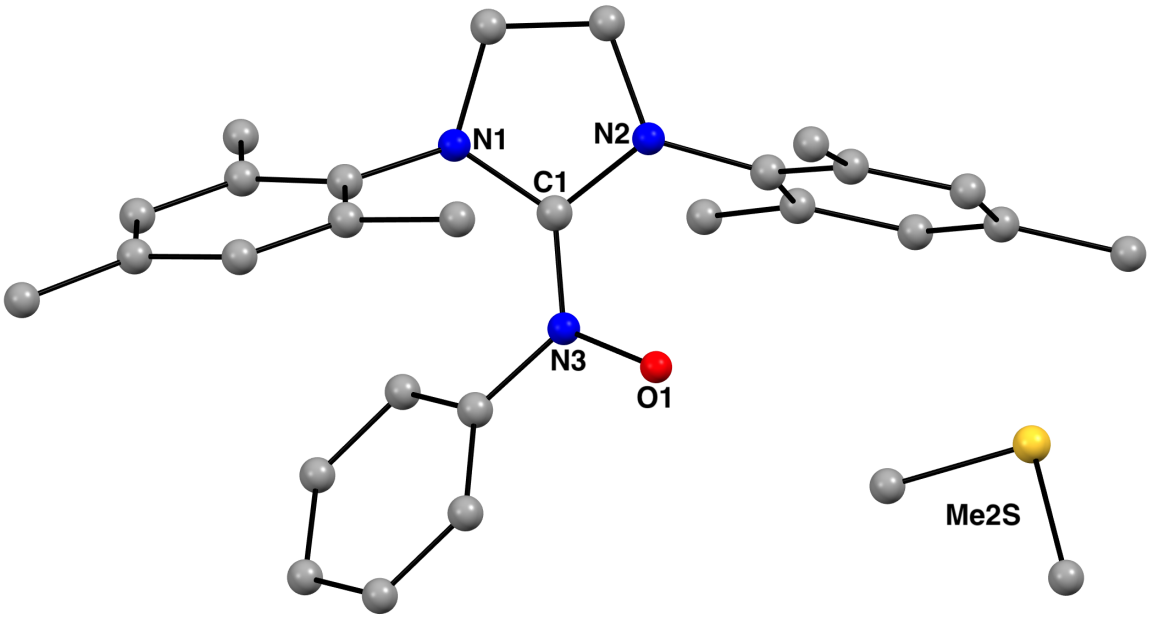


Figure S40. Predicted structure of reactant complex **2a-Ph•••Me$_2$S** at M062X/6-31G(d,p) level of theory with charge = 0, multiplicity = 1. Selected bond distances (in Å) for **2a-Ph•••Me$_2$S**: C1–N1, 1.374; C1–N2, 1.361; C1–N3, 1.325; N3–O1, 1.352. H-atoms are omitted for clarity.

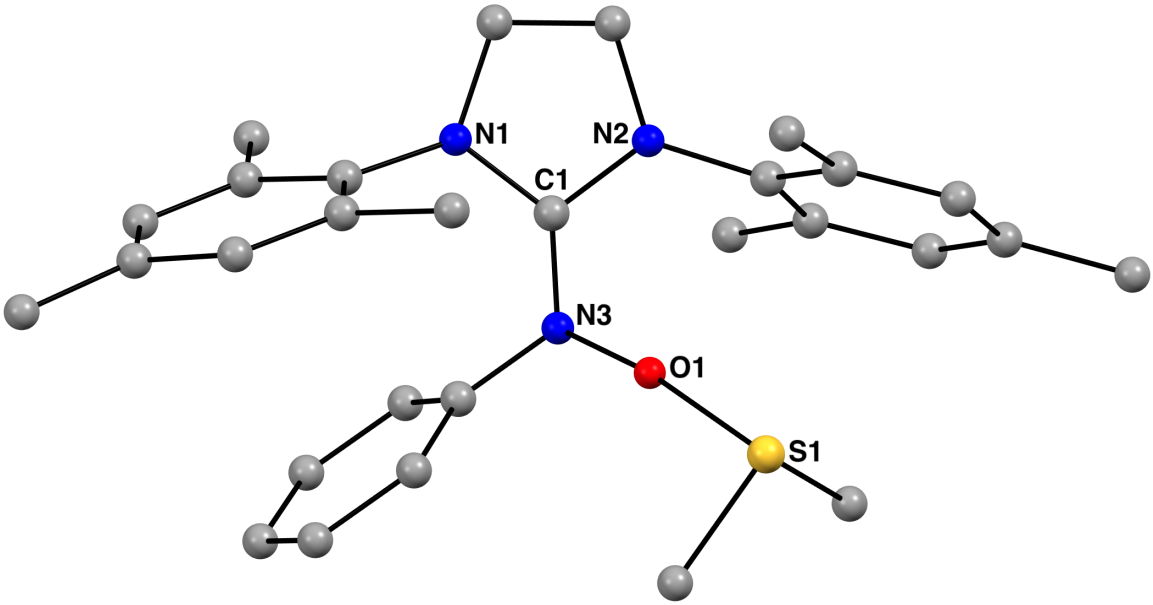


Figure S41. Predicted transition state **TS$^{‡}_{OAT}$** at M062X/6-31G(d,p) level of theory with charge = 0, multiplicity = 1. Selected bond distances (in Å) for **TS$^{‡}_{OAT}$**: C1–N1, 1.382; C1–N2, 1.371; C1–N3, 1.303; N3–O1, 1.772; S1–O1, 2.059. H-atoms are omitted for clarity.

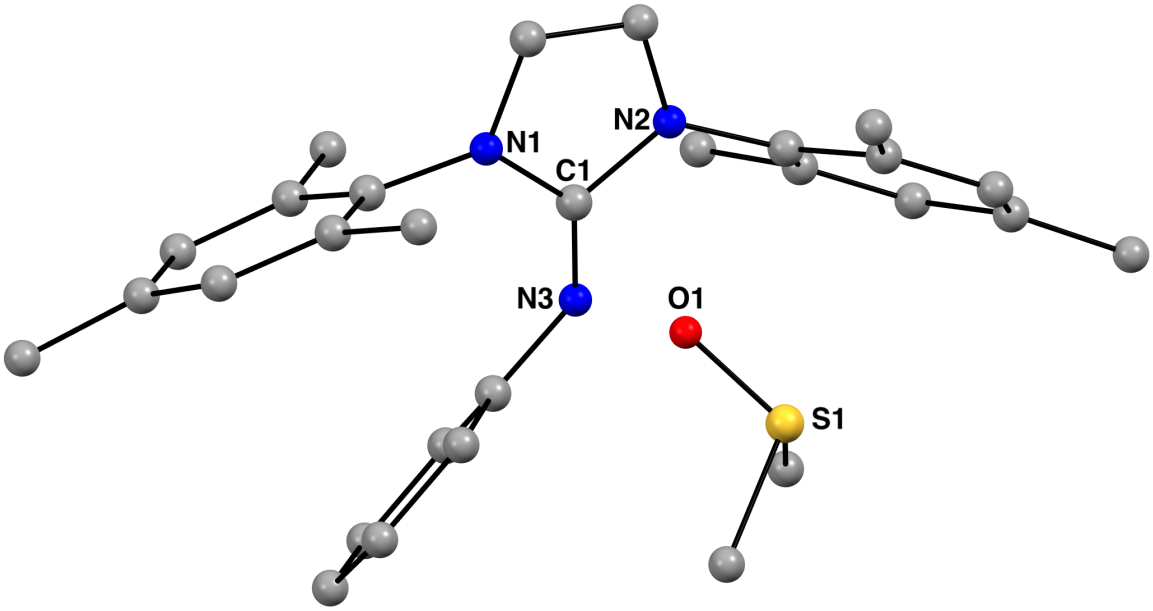
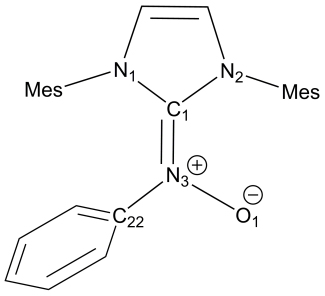
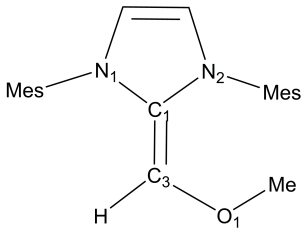


Figure S42. Predicted structure of reactant complex **3-Ph•••Me$_2$SO** at M062X/6-31G(d,p) level of theory with charge = 0, multiplicity = 1. Selected bond distances (in Å) for **3-Ph•••Me$_2$SO**: C1–N1, 1.387; C1–N2, 1.391; C1–N3, 1.292; S1–O1, 1.517. H-atoms are omitted for clarity.

Table S1. Selected bond distances (in Å) and angles (in °) for **2a-Ph** (DFT optimized) and structurally characterized[S15] diamino enol (**CCDC 892934**) structures.



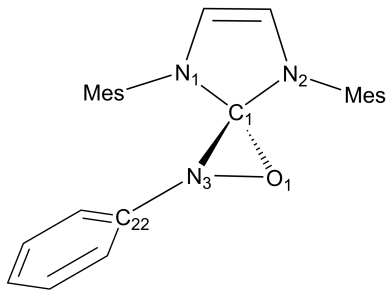
2a-Ph



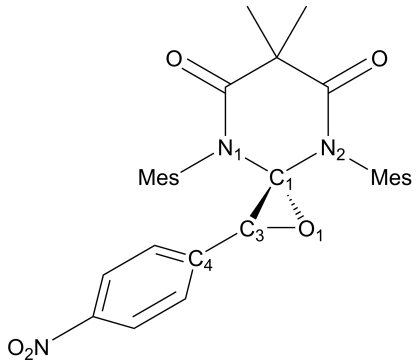
CCDC 892934

2a-Ph (DFT)		**CCDC 892934**	
C1–N1	1.376	C1–N1	1.395(3)
C1-N2	1.365	C1-N2	1.398(3)
C1-N3	1.324	C1-C3	1.349(3)
N3-O1	1.347	C3-O1	1.397(3)
N3-C22	1.413	-	-
N1-C1-N2	107.38	N1-C1-N2	104.00(2)
N1-C1-N3	128.85	N1-C1-C3	125.20(2)
N2-C1-N3	125.58	N2-C1-C3	130.80(2)
C1-N3-C22	123.88	-	-
C1-N3-O1	119.06	C1-C3-O1	122.00(2)
C22-N3-O1	118.41	-	-

Table S2. Selected bond distances (in Å) and angles (in °) for **2b-Ph** (DFT optimized) and structurally characterized[S20] spiro-epoxide (**CCDC 831418**)



2b-Ph



CCDC 831418

2b-Ph		**CCDC 831418**	
C1–N1	1.413	C1–N1	1.437(3)
C1-N2	1.409	C1-N2	1.448(3)
C1-N3	1.452	C1-C3	1.481(3)
N3-O1	1.484	C3-O1	1.451(3)
N3-C22	1.426	C3-C4	1.489(3)
C1-O1	1.402	C1-O1	1.444(3)
N1-C1-N2	104.19	N1-C1-N2	112.66(18)
N1-C1-N3	126.27	N1-C1-C3	124.90(19)
N2-C1-N3	118.85	N2-C1-C3	117.74(18)
C1-N3-C22	118.58	C1-C3-C4	129.99(19)
C1-N3-O1	57.06	C1-C3-O1	59.02(13)
C22-N3-O1	111.40	C4-C3-O1	117.76(18)
C1-O1-N3	60.31	C1-O1-C3	61.55(14)
N2-C1-O1	119.94	N2-C1-O1	114.13(17)

13. Cartesian Coordinates of the DFT Optimized Structures

IMes•••PhNO reactant complex			
O	0.08453100	2.84729000	-1.17141800
N	-0.49126100	-1.38189900	-0.45467300
N	1.61116500	-1.18703200	-0.32351100
C	0.47481900	-0.42991100	-0.29287900
C	0.02117400	-2.66844300	-0.59333900
C	1.36390400	-2.54326400	-0.51002900
N	0.28583100	2.48839400	-0.03512000
C	-0.91810500	2.17639300	0.71008400
C	-0.71337100	1.67665300	1.99201100
H	0.30802500	1.52698800	2.32765200
C	-1.81163600	1.35762000	2.78202400
H	-1.66938000	0.95756200	3.78081500
C	-3.09943900	1.54932700	2.28180100
C	-3.29289700	2.06048600	0.99758700
H	-4.29964900	2.19725600	0.61546100
C	-2.19907700	2.37502800	0.20176500
C	-1.89036800	-1.08523800	-0.50211700
C	-2.40742000	-0.41960700	-1.62014900
C	-3.78143400	-0.19419900	-1.66683000
H	-4.19897700	0.32162800	-2.52903200
C	-4.63112800	-0.60852600	-0.63953900
C	-4.07361700	-1.23694800	0.47124000
H	-4.71633500	-1.53293400	1.29761800
C	-2.70217800	-1.47848000	0.56450100
C	-1.49645500	0.07469000	-2.71158400
C	-2.10227300	-2.10406600	1.79623300
C	2.91988000	-0.62836000	-0.17471600
C	3.41287100	0.22637900	-1.16857700
C	4.69754500	0.73935800	-1.00417200
H	5.09753600	1.40167000	-1.76880000
C	5.48128800	0.42902100	0.10797400
C	4.94979600	-0.41483700	1.08006600
H	5.54105600	-0.65570800	1.96058400
C	3.66705800	-0.95079500	0.96182500
C	2.57969500	0.59694800	-2.36616800
C	3.09357500	-1.82556500	2.04751200
H	3.20755200	1.03509400	-3.14495000
H	1.81020400	1.32308800	-2.08623500
H	2.06735100	-0.27704900	-2.77878800
H	3.67641500	-1.72412700	2.96514600
H	3.09500900	-2.88366600	1.76673400
H	2.05584500	-1.55053000	2.25845100
H	-2.31133500	2.76345500	-0.80512400
H	-3.95976800	1.29505800	2.89368200
H	-0.80667900	-0.70927700	-3.03852400
H	-0.88620200	0.90772300	-2.34602700
H	-2.07593000	0.41378200	-3.57269000
H	-1.20930700	-1.55095100	2.10333400
H	-1.80097200	-3.14249700	1.62443300
H	-2.82070300	-2.09146200	2.61882200
H	2.15469100	-3.27340500	-0.58121500
H	-0.60852400	-3.52991000	-0.75182500
C	-6.11692400	-0.37072300	-0.73236000
H	-6.59062700	-0.43421400	0.25010200
H	-6.59356500	-1.11403800	-1.37966100
H	-6.33384700	0.61475500	-1.15380900
C	6.85860600	1.02220800	0.26105000
H	7.42083400	0.96020100	-0.67463300
H	7.42894400	0.50626500	1.03661000

2a-Ph			
O	1.09564500	1.08520700	-1.40263700
N	-0.64524100	-1.23805800	0.62153600
N	1.52190300	-1.10826000	0.21365000
C	0.34744900	-0.41644600	0.13862000
C	-0.05358700	-2.44547000	1.02399800
C	1.26509400	-2.35855500	0.77876800
N	0.23882900	0.78454000	-0.40725100
C	-0.82591100	1.67614500	-0.14426200
C	-1.45775100	1.73709000	1.10128100
H	-1.13161700	1.08652100	1.90761300
C	-2.48930300	2.64482300	1.30305600
H	-2.97988100	2.68695700	2.27100100
C	-2.87991100	3.50924300	0.28190600
C	-2.21690900	3.46636400	-0.94277100
H	-2.50118600	4.15024500	-1.73668700
C	-1.18666700	2.55970200	-1.16192200
C	-2.01961500	-1.13073700	0.22589600
C	-2.32073400	-1.07901200	-1.14542000
C	-3.65879200	-0.94688500	-1.50156000
H	-3.91574700	-0.90525800	-2.55757600
C	-4.67762300	-0.87824700	-0.54788200
C	-4.33568000	-0.96600800	0.79748400
H	-5.11739200	-0.92456000	1.55279200
C	-3.00780700	-1.08859500	1.20965100
C	-1.24789500	-1.18795500	-2.20078200
C	-2.67774800	-1.18106000	2.67717400
C	2.83983500	-0.54640500	0.10632700
C	3.56618300	-0.74563100	-1.06901200
C	4.87188200	-0.26658600	-1.10666600
H	5.45687700	-0.40761600	-2.01270000
C	5.44087000	0.40245300	-0.02086600
C	4.67320300	0.59349400	1.12571200
H	5.10242000	1.11824000	1.97619700
C	3.36063000	0.12832100	1.20992800
C	2.91191500	-1.38877400	-2.25735900
C	2.51637200	0.37049300	2.43399800
H	3.61273100	-1.47711300	-3.08973200
H	2.06463200	-0.75699300	-2.54664900
H	2.52730800	-2.38656300	-2.02045700
H	3.12159300	0.77568000	3.24717400
H	2.03972700	-0.55060000	2.78669100
H	1.72009200	1.09027900	2.21260800
H	-0.62574300	2.51404200	-2.08704100
H	-3.68076500	4.22233900	0.44682200
H	-0.52112900	-1.96620400	-1.93920800
H	-0.68166400	-0.25654600	-2.33017300
H	-1.69712100	-1.45455500	-3.15959000
H	-1.64253000	-0.89932500	2.88100500
H	-2.81904100	-2.20249100	3.04789200
H	-3.33609900	-0.52982300	3.25741200
H	2.06922700	-3.05442800	0.95565100
H	-0.65550900	-3.24513300	1.42359400
C	-6.11041200	-0.69245900	-0.97461500
H	-6.31107800	0.35997100	-1.19958800
H	-6.80283000	-1.00345300	-0.18913200
H	-6.33274700	-1.26895000	-1.87629100
C	6.84549100	0.94237700	-0.10669400
H	7.48892000	0.28167900	-0.69312500
H	7.28749400	1.06059900	0.88538800

H	6.79860800	2.07979800	0.53704700	H	6.85198900	1.92377000	-0.59228700
2b-Ph				**2c-Ph**			
N	-1.65615000	-0.38868900	0.96624300	N	-1.88936400	-0.99490900	0.50631800
N	0.54408400	-0.71495900	1.07028900	N	0.24241200	-1.35655000	0.76686800
O	-0.44533600	-0.32897900	-1.14434000	O	-0.43919900	0.48492300	-0.57034600
C	-0.46486600	-0.16405500	0.24827500	C	-0.66020700	-0.53739200	0.18478000
C	-1.38151900	-1.17658000	2.09613700	C	-1.75772200	-2.12496200	1.30525800
C	-0.05901100	-1.36693600	2.16534300	C	-0.43255400	-2.34576700	1.46535500
C	1.89638000	-0.91981200	0.66217900	C	1.66214500	-1.27685200	0.54431900
C	2.90313800	-0.15034800	1.26662700	C	2.46126800	-0.60003700	1.46718900
C	4.20793600	-0.28831800	0.80251300	C	3.80994800	-0.46187700	1.15412500
H	4.99076900	0.32360600	1.24589200	H	4.44735000	0.10240100	1.83008600
C	4.53114100	-1.17514300	-0.22469600	C	4.35282600	-0.98567400	-0.01975600
C	3.52029500	-1.97346600	-0.75423100	C	3.52136400	-1.68917900	-0.88950700
H	3.76378000	-2.70137600	-1.52577900	H	3.93185100	-2.09843200	-1.80941200
C	2.19803600	-1.87214500	-0.31999900	C	2.16026000	-1.83267600	-0.63495000
C	1.14303000	-2.77487400	-0.90597300	C	1.23834700	-2.49300700	-1.62575900
H	1.57012300	-3.75593200	-1.12893200	H	1.80861500	-2.97858800	-2.41933000
H	0.73783900	-2.35898300	-1.83306200	H	0.58459800	-1.74462200	-2.09001100
H	0.30687000	-2.90979800	-0.21440700	H	0.59727600	-3.24507200	-1.15403300
C	5.93930000	-1.25248500	-0.75518800	C	5.79474300	-0.73036600	-0.36635500
H	6.12085800	-0.45155700	-1.48023100	H	5.88313800	0.26891500	-0.80570300
H	6.12326300	-2.20431700	-1.25881700	H	6.16942600	-1.45767500	-1.09027400
H	6.67357700	-1.14035800	0.04658600	H	6.43132800	-0.76387200	0.52144800
C	2.59414200	0.78354800	2.40648900	C	1.86673300	0.01790100	2.70057300
H	2.63802600	0.25093700	3.36357800	H	1.37132100	-0.73083800	3.32840300
H	1.59426100	1.20925000	2.31173100	H	1.11806900	0.75797400	2.39482200
H	3.31922100	1.60000500	2.44121500	H	2.63980800	0.50711900	3.29527600
C	-2.94941100	-0.18966400	0.39752500	C	-3.11869600	-0.33062900	0.16984400
C	-3.59300800	1.03592600	0.59791500	C	-3.45195700	0.83100300	0.87011900
C	-4.86699000	1.20863600	0.05791800	C	-4.65981600	1.44526500	0.54106100
H	-5.37736600	2.15771500	0.20525300	H	-4.94641100	2.34978400	1.07140100
C	-5.49824100	0.19704700	-0.66420000	C	-5.50200800	0.93300100	-0.44476900
C	-4.82364800	-1.00940000	-0.85424500	C	-5.12187500	-0.22932900	-1.11830700
H	-5.29982400	-1.80253000	-1.42670400	H	-5.76988200	-0.63560100	-1.89123100
C	-3.54786200	-1.22182300	-0.33654300	C	-3.92389600	-0.87831500	-0.83100100
C	-2.80948800	-2.51030100	-0.58376200	C	-3.49445300	-2.11480000	-1.57653100
H	-1.93923600	-2.32502700	-1.22210100	H	-2.49842100	-1.98074100	-2.01040600
H	-3.45433300	-3.23892600	-1.07921900	H	-4.19336400	-2.33788900	-2.38406400
H	-2.44067500	-2.94969600	0.34851400	H	-3.44578100	-2.98912700	-0.91943800
C	-6.89066700	0.39034400	-1.20821400	C	-6.78672200	1.63449800	-0.80253400
H	-7.11271000	1.44920200	-1.35964400	H	-6.64236800	2.27900600	-1.67573600
H	-7.63839100	-0.01001900	-0.51554600	H	-7.13785200	2.26225800	0.01907600
H	-7.01728000	-0.12567000	-2.16319500	H	-7.57364600	0.91725000	-1.04851700
C	-2.91119200	2.13855000	1.36203200	C	-2.53372000	1.39788700	1.91765500
H	-2.52543100	1.77434200	2.31832100	H	-2.22663300	0.62689700	2.63301400
H	-3.60013900	2.96432500	1.55099700	H	-3.03349800	2.19663800	2.46863800
H	-2.05853100	2.51463100	0.78827600	H	-1.62102900	1.79850300	1.45739400
N	-0.35191800	1.03365500	-0.56425300	N	0.31893300	1.51266100	0.28837700
C	0.94053700	1.59898300	-0.76984500	C	1.50015900	1.78828700	-0.32378900
C	1.28356800	2.69592500	0.02020200	C	2.35345200	2.65969300	0.41113500
H	0.57771200	3.06222300	0.76017200	H	1.99307100	3.05090700	1.35857100
C	2.52885500	3.29539300	-0.14088300	C	3.60637600	2.99876000	-0.06186300
H	2.80012100	4.13989600	0.48512200	H	4.22789600	3.66593600	0.53041400
C	3.41924500	2.82247400	-1.10155300	C	4.08412300	2.49751000	-1.27844000
C	3.05027700	1.74968300	-1.91127600	C	3.25036000	1.65760800	-2.01188100
H	3.73536100	1.37725500	-2.66687600	H	3.59225800	1.25854500	-2.96464800
C	1.81308900	1.13672400	-1.75445700	C	1.98139500	1.30938100	-1.56315100
H	1.52246500	0.28702400	-2.36090900	H	1.35432800	0.65214200	-2.15502100
H	4.38940500	3.29227300	-1.22538100	H	5.06673600	2.77183500	-1.64760900
H	-2.17614400	-1.47849500	2.75935400	H	-2.62234300	-2.64164100	1.68815400
H	0.54858900	-1.87553300	2.89602400	H	0.10463700	-3.10942600	2.00365500

3-Ph			
N	-0.54233100	-1.37864800	0.19383200
N	1.63294800	-1.08789900	0.15693400
C	0.43690300	-0.39626500	0.05142700
C	0.06371100	-2.62925500	0.36589600
C	1.39440900	-2.44792100	0.34196100
N	0.39276000	0.87150700	-0.18137300
C	-0.76826200	1.63333800	-0.04792500
C	-1.58168200	1.59317100	1.09676600
H	-1.30465900	0.92955300	1.91233000
C	-2.72877100	2.37136900	1.18408200
H	-3.35213600	2.30350100	2.07109500
C	-3.07952500	3.23477300	0.14769500
C	-2.25195600	3.32181500	-0.96938900
H	-2.49927000	4.00552300	-1.77618300
C	-1.10586100	2.54067800	-1.06335100
C	-1.94155700	-1.18839400	-0.00500000
C	-2.39930200	-0.79315700	-1.26775100
C	-3.75348900	-0.49908800	-1.40577900
H	-4.12111500	-0.16363000	-2.37276800
C	-4.64441000	-0.62170000	-0.33990400
C	-4.16135300	-1.08406800	0.88353900
H	-4.84782900	-1.19970500	1.71921200
C	-2.81092300	-1.36664700	1.07637500
C	-1.45314500	-0.68863500	-2.43289400
C	-2.29639300	-1.80636700	2.42214600
C	2.91810700	-0.47395700	0.09633400
C	3.70927700	-0.68219800	-1.03669400
C	4.98177800	-0.11243900	-1.06336900
H	5.61030400	-0.26728100	-1.93726800
C	5.45713300	0.66122100	-0.00589000
C	4.63006900	0.86131600	1.10039800
H	4.98776000	1.46611500	1.93075500
C	3.35549300	0.30480100	1.17391000
C	3.18042900	-1.47517800	-2.20313700
C	2.46189800	0.54355600	2.35967300
H	3.84968300	-1.38966700	-3.06121100
H	2.19035600	-1.11055300	-2.49407500
H	3.07346800	-2.53764000	-1.96191200
H	3.02507800	0.97109200	3.19139500
H	1.99346500	-0.38709700	2.69543000
H	1.65821400	1.23392000	2.08317800
H	-0.45264400	2.60736100	-1.92811200
H	-3.97539200	3.84282600	0.21817800
H	-0.80199900	-1.56761000	-2.48318500
H	-0.80732200	0.19062300	-2.33980600
H	-2.00795500	-0.61221400	-3.36988900
H	-3.03583000	-1.60567200	3.19981300
H	-1.36776200	-1.28742500	2.67881000
H	-2.07553200	-2.87895600	2.44118500
H	2.20770300	-3.14612300	0.45539500
H	-0.53067300	-3.52171400	0.47395800
C	-6.08959700	-0.22904800	-0.50234600
H	-6.72328100	-0.72223300	0.23825900
H	-6.46162200	-0.48368400	-1.49788400
H	-6.20416200	0.85249100	-0.37411500
C	6.82128900	1.29962000	-0.06575200
H	6.74581600	2.34809500	-0.37174500
H	7.46713900	0.78950800	-0.78390000
H	7.31093000	1.27783400	0.91120000

IMes=O•••^{1}PhN product complex (open-shell singlet)			
N	-1.89716500	-0.58601200	0.84543300
N	0.24286700	-1.03233500	1.02301300
O	-0.60785500	-0.47864100	-1.10075600
C	-0.73409200	-0.66712700	0.10240000
C	-1.63892800	-0.89128200	2.18113100
C	-0.32661100	-1.16524800	2.29098500
C	1.62565600	-1.13407100	0.70205000
C	2.54824300	-0.30040000	1.35759200
C	3.88628500	-0.38264300	0.98282500
H	4.60510100	0.27602200	1.46595400
C	4.32154200	-1.25606400	-0.01387400
C	3.38395800	-2.08665300	-0.62085000
H	3.70874300	-2.78957200	-1.38488700
C	2.03194400	-2.05202900	-0.27538900
C	1.05301000	-2.98170300	-0.94025400
H	1.57544700	-3.83198900	-1.38342400
H	0.49347300	-2.45531500	-1.71853600
H	0.32063800	-3.35893000	-0.21987900
C	5.76581600	-1.26525200	-0.44088000
H	6.43684500	-1.24711300	0.42206400
H	5.98833100	-0.37970300	-1.04689700
H	5.99989100	-2.14865900	-1.03903900
C	2.12592800	0.67528400	2.42663800
H	2.87307000	1.46702300	2.52051900
H	2.03544500	0.18810700	3.40346700
H	1.16246300	1.13281200	2.18763300
C	-3.15731300	-0.20221900	0.29983100
C	-3.69290500	1.04294300	0.64575500
C	-4.94081000	1.38199700	0.12511300
H	-5.37368400	2.34546000	0.38445800
C	-5.63492700	0.52808000	-0.73166600
C	-5.05727300	-0.69627300	-1.06732500
H	-5.58574100	-1.37033400	-1.73763700
C	-3.81746500	-1.08339300	-0.56270900
C	-3.19030500	-2.39842000	-0.93781600
H	-2.30458900	-2.22448100	-1.55723700
H	-3.89506500	-3.02076200	-1.49248200
H	-2.86535600	-2.94746100	-0.04815800
C	-6.96407400	0.93644800	-1.31387000
H	-6.82560600	1.47152200	-2.25908400
H	-7.50679900	1.59958000	-0.63601100
H	-7.59174700	0.06545100	-1.51714000
C	-2.92334800	1.99341700	1.52511200
H	-2.86072500	1.63135900	2.55663200
H	-3.40746400	2.97183000	1.54228100
H	-1.89913900	2.11256600	1.15745600
N	0.42916200	2.15899500	0.00611400
C	1.61589300	2.12022000	-0.52074800
C	2.66048800	2.98621400	-0.01494700
H	2.40704600	3.67140300	0.78671100
C	3.92552100	2.92533000	-0.54515500
H	4.70294400	3.57787300	-0.16024400
C	4.22226300	2.02813800	-1.58724500
C	3.22564700	1.17997000	-2.09735500
H	3.47070900	0.48291600	-2.89264700
C	1.94583900	1.20804800	-1.59583000
H	1.15893600	0.54844500	-1.94409400
H	5.22431700	1.99792900	-2.00225500
H	-2.42848800	-0.90946300	2.91450800
H	0.25989400	-1.47177600	3.14098400

IMes=O•••^{3}PhN product complex (triplet)

N	-1.90991300	-0.61604800	0.83167400
N	0.22852800	-1.06708700	1.01181100
O	-0.60378500	-0.44712900	-1.10011300
C	-0.74081100	-0.67461200	0.09522900
C	-1.66145300	-0.96132000	2.15971100
C	-0.34978400	-1.23835800	2.27090300
C	1.61364800	-1.16047400	0.69630600
C	2.52914300	-0.33249100	1.36695300
C	3.86870800	-0.40170500	0.99522200
H	4.58255100	0.25475700	1.48839300
C	4.31063100	-1.25734500	-0.01385800
C	3.37895600	-2.08261100	-0.63736500
H	3.70920400	-2.77009000	-1.41299300
C	2.02590200	-2.05937600	-0.29551600
C	1.04982100	-2.97626600	-0.98186900
H	1.57463000	-3.81193100	-1.44929500
H	0.48647600	-2.43153000	-1.74483000
H	0.32111100	-3.37604900	-0.26997700
C	5.75486300	-1.24956200	-0.44025700
H	5.96517000	-0.36141000	-1.04689900
H	5.99990200	-2.13037400	-1.03789900
H	6.42547200	-1.22210400	0.42268400
C	2.09576900	0.62873500	2.44453300
H	1.99766700	0.12954200	3.41458200
H	1.13204300	1.08646900	2.20568400
H	2.83908800	1.42193700	2.55385800
C	-3.16475100	-0.20876200	0.29087800
C	-3.69781800	1.02581700	0.67591300
C	-4.94122500	1.38790600	0.15979900
H	-5.37197200	2.34357000	0.44964200
C	-5.63314800	0.56697000	-0.73008900
C	-5.05766000	-0.64722200	-1.10467600
H	-5.58434700	-1.29543000	-1.80138800
C	-3.82260400	-1.05667400	-0.60627100
C	-3.19746100	-2.35992600	-1.02332800
H	-2.30566900	-2.16729700	-1.62834000
H	-3.89978700	-2.95867000	-1.60629700
H	-2.88251000	-2.94221500	-0.15142800
C	-6.95732800	0.99939300	-1.30617600
H	-6.81298100	1.53936800	-2.24770200
H	-7.48895200	1.66491200	-0.62201000
H	-7.59801500	0.13916200	-1.51495400
C	-2.93029100	1.94337700	1.59141700
H	-2.87432300	1.54721500	2.61062300
H	-3.41053800	2.92269300	1.63818400
H	-1.90368600	2.07103100	1.23345400
N	0.44049800	2.14391400	0.03477900
C	1.66548100	2.12390100	-0.50778800
C	2.67429600	2.98587600	0.01020800
H	2.41358600	3.65915600	0.82043500
C	3.95118800	2.94986800	-0.51718500
H	4.71734000	3.60854000	-0.12072900
C	4.25766400	2.07215100	-1.56319500
C	3.27509100	1.22157900	-2.08053800
H	3.52472500	0.53370200	-2.88236600
C	1.98875700	1.23515400	-1.57295000
H	1.21067200	0.56839100	-1.92862600
H	5.26131900	2.05549300	-1.97638600
H	-2.45654600	-1.00163400	2.88620300
H	0.23133900	-1.56975200	3.11536800

$TS^{\ddagger}_{2a}$

O	-1.02629300	1.67779000	1.13716700
N	0.54897700	-1.52752500	0.26307700
N	-1.55992200	-1.19877800	0.14472400
C	-0.37571700	-0.56974300	0.02991600
C	-0.05133100	-2.75307400	0.52162300
C	-1.38675300	-2.54300400	0.44272900
N	-0.63076100	1.34969900	-0.01024000
C	0.74334400	1.79295600	-0.28991500
C	1.38630500	1.35428500	-1.44781000
H	0.90195000	0.60223600	-2.06734000
C	2.64423600	1.84123100	-1.76871200
H	3.15300800	1.47696200	-2.65629300
C	3.26043700	2.79025100	-0.94760400
C	2.60107800	3.24728700	0.18753000
H	3.06703700	3.99623300	0.82133900
C	1.33839600	2.75460700	0.51789500
C	1.95877800	-1.25987700	0.28976700
C	2.45745000	-0.48595100	1.34219500
C	3.80645300	-0.14597300	1.29841000
H	4.21606800	0.47555800	2.09127300
C	4.63850100	-0.56552200	0.25865300
C	4.10274400	-1.36243500	-0.75089600
H	4.74057200	-1.69398500	-1.56684200
C	2.75308200	-1.71328100	-0.76274200
C	1.56143600	-0.04218800	2.46875600
C	2.15752100	-2.50370900	-1.89811700
C	-2.84729300	-0.57463800	-0.01264500
C	-3.58885700	-0.28728000	1.13382000
C	-4.86070200	0.25461500	0.95685800
H	-5.45843100	0.48745500	1.83484500
C	-5.37278800	0.52471900	-0.31146300
C	-4.58053100	0.25175100	-1.42658300
H	-4.96114200	0.47539600	-2.42058300
C	-3.30464600	-0.29346500	-1.30015100
C	-3.00057900	-0.50174900	2.50140800
C	-2.42121200	-0.52021200	-2.49598800
H	-3.69822000	-0.17408700	3.27429000
H	-2.08148200	0.08885000	2.58094000
H	-2.75358300	-1.55195600	2.68680800
H	-2.98584500	-0.40943800	-3.42362100
H	-1.96593000	-1.51570200	-2.48195800
H	-1.61117100	0.21766100	-2.48889600
H	0.79449300	3.09220800	1.39278100
H	4.24388800	3.17337400	-1.20238300
H	1.07160000	-0.90499000	2.93394500
H	0.77047600	0.63952700	2.13059300
H	2.14595200	0.47193000	3.23434600
H	1.28420700	-1.98937900	-2.31392800
H	1.82115900	-3.49405300	-1.57549400
H	2.88979700	-2.64054000	-2.69577400
H	-2.22519000	-3.21029300	0.56485200
H	0.52322200	-3.63807600	0.74583200
C	6.07626500	-0.11926400	0.21463600
H	6.65668400	-0.70765100	-0.49937200
H	6.54954000	-0.20555000	1.19636300
H	6.13426500	0.93187700	-0.08742300
C	-6.73740100	1.14401300	-0.47437800
H	-7.38882100	0.89368000	0.36614600
H	-7.21874500	0.80530900	-1.39517200
H	-6.66236700	2.23525700	-0.52268000

$TS^{‡}_{2a\text{-}2b}$			
O	0.70724600	0.46025200	-1.75362100
N	-0.53149200	-1.44331600	-0.14489600
N	1.61319200	-1.11169600	0.16263800
C	0.45095400	-0.49242700	-0.20465900
C	0.06480700	-2.68482600	0.11222500
C	1.38249000	-2.47913400	0.28660100
N	0.38719200	0.86099500	-0.40917500
C	-0.82291300	1.58945300	-0.27493800
C	-1.42005500	1.74094400	0.97856600
H	-0.97647400	1.26518700	1.84997300
C	-2.59682700	2.46930800	1.09516200
H	-3.07366900	2.55937100	2.06663400
C	-3.16130900	3.08479300	-0.02164100
C	-2.53049800	2.96760900	-1.25711000
H	-2.95503700	3.45400000	-2.13026500
C	-1.36345200	2.22230000	-1.39256300
C	-1.94636500	-1.21340600	-0.03612700
C	-2.69359100	-0.91647700	-1.17938300
C	-4.03896700	-0.60021600	-1.00053600
H	-4.63016300	-0.33024600	-1.87239700
C	-4.64131100	-0.61107900	0.25671600
C	-3.87376300	-0.97323000	1.36252200
H	-4.33057300	-0.99085900	2.34942600
C	-2.51804500	-1.26667700	1.24043800
C	-2.06690300	-0.93740200	-2.54607900
C	-1.68434600	-1.57669400	2.45713100
C	2.89321800	-0.47070400	0.18102700
C	3.75631000	-0.65376800	-0.90273700
C	5.00977000	-0.04793500	-0.83931800
H	5.69798400	-0.17819500	-1.67125700
C	5.39489300	0.73231200	0.25075000
C	4.49564200	0.90246000	1.30308300
H	4.78064700	1.51252400	2.15702700
C	3.23463800	0.31091600	1.28744800
C	3.32341300	-1.45208900	-2.10226400
C	2.25552900	0.52464200	2.40969600
H	4.05729100	-1.36269300	-2.90540000
H	2.35715900	-1.07697400	-2.45097300
H	3.21025000	-2.51518900	-1.86443200
H	2.73637000	1.01699300	3.25701000
H	1.83053900	-0.42366500	2.75400600
H	1.43051000	1.15746000	2.06513400
H	-0.86129600	2.09383900	-2.34363700
H	-4.07781700	3.65774700	0.07510300
H	-1.87300900	-1.97082400	-2.85577600
H	-1.11100600	-0.40394800	-2.54777400
H	-2.73881000	-0.48495300	-3.27860000
H	-0.71721000	-1.06368900	2.41605200
H	-1.47081100	-2.64721700	2.54151700
H	-2.20345400	-1.26475200	3.36557600
H	2.18903700	-3.16217900	0.49724200
H	-0.53162200	-3.58140300	0.15071000
C	-6.07744600	-0.18870600	0.41990400
H	-6.14121900	0.90224700	0.49771200
H	-6.51927100	-0.61403400	1.32404200
H	-6.68268300	-0.49360700	-0.43723400
C	6.74051600	1.41044600	0.27212700
H	7.47860400	0.84428200	-0.30098700
H	7.11207500	1.52399300	1.29340100
H	6.67511600	2.41042000	-0.16907800

$TS^{‡}_{2c}$			
N	-1.85276700	-0.86340800	0.68707200
N	0.25502400	-1.21658800	0.86936900
O	-0.55107800	1.04981700	-0.51232300
C	-0.66769600	-0.59681700	0.09830400
C	-1.68308300	-1.66161000	1.81143700
C	-0.35284900	-1.88235300	1.92717100
C	1.65989000	-1.23424200	0.57723400
C	2.52593900	-0.48983000	1.38375600
C	3.86866500	-0.45501300	1.01868500
H	4.55468200	0.15227100	1.60415500
C	4.34453000	-1.13787000	-0.10091500
C	3.45168900	-1.90064400	-0.85150000
H	3.81258300	-2.44507300	-1.72096400
C	2.09627800	-1.95908600	-0.53382700
C	1.12973100	-2.73405600	-1.39009000
H	1.66587600	-3.41975800	-2.04891300
H	0.53570900	-2.05311600	-2.00868100
H	0.42715500	-3.31234900	-0.78204300
C	5.78295500	-0.99445700	-0.51905200
H	5.92216600	-0.02930200	-1.01896400
H	6.08028600	-1.78314900	-1.21373100
H	6.45482900	-1.02011900	0.34267100
C	2.01510300	0.28571600	2.56878000
H	1.73873400	-0.37818400	3.39524200
H	1.13332800	0.87143400	2.28743100
H	2.78604000	0.96970200	2.92911000
C	-3.10607200	-0.33476800	0.22959000
C	-3.57332000	0.85561000	0.79425600
C	-4.79965300	1.33812800	0.34158300
H	-5.18769100	2.26162300	0.76476800
C	-5.53458300	0.67438200	-0.64236500
C	-5.02377000	-0.50599100	-1.18102400
H	-5.58625300	-1.03160600	-1.94881600
C	-3.80208200	-1.02947100	-0.76015500
C	-3.23473400	-2.29159300	-1.35456200
H	-2.28901800	-2.08556700	-1.86552300
H	-3.92977800	-2.72623000	-2.07490400
H	-3.02625100	-3.03831400	-0.58180100
C	-6.84123700	1.24408700	-1.13200300
H	-6.66554900	2.04208700	-1.86047800
H	-7.41855300	1.67253300	-0.30890600
H	-7.45111400	0.47890800	-1.61721200
C	-2.76529000	1.58510400	1.83311700
H	-2.55512200	0.94342500	2.69521500
H	-3.30597300	2.46434900	2.18825900
H	-1.80110100	1.90324100	1.42058000
N	0.24666700	1.76717100	0.21434200
C	1.50405500	1.92929000	-0.37997400
C	2.40968000	2.76829700	0.29250600
H	2.07348000	3.25790400	1.20203000
C	3.69183600	2.95794700	-0.19944200
H	4.37836600	3.61602100	0.32535000
C	4.10481300	2.30343500	-1.36274300
C	3.21149400	1.46491500	-2.02850000
H	3.52736600	0.94819400	-2.93100200
C	1.91672600	1.28206900	-1.55593000
H	1.21231400	0.63857200	-2.07167000
H	5.10782800	2.45435900	-1.74999100
H	-2.51983300	-1.98903400	2.40779400
H	0.21754400	-2.45865200	2.63808100

$TS^{‡}_{2c\text{-}2b}$			
N	-1.71565700	-0.82684200	0.76671200
N	0.42670100	-1.27557500	0.87620800
O	-0.41295700	-0.23280600	-1.11532200
C	-0.52065100	-0.61148700	0.14049000
C	-1.48666800	-1.49393900	1.97173100
C	-0.16969000	-1.76383400	2.04092100
C	1.83101000	-1.18016200	0.61932900
C	2.58001900	-0.25033800	1.35186700
C	3.91652100	-0.08791500	1.00839700
H	4.50641500	0.66175200	1.53060700
C	4.50078700	-0.82086400	-0.02639900
C	3.72761500	-1.75739400	-0.70825400
H	4.17440000	-2.33440000	-1.51467100
C	2.38007100	-1.95100000	-0.40448300
C	1.52413400	-2.90432300	-1.19485000
H	2.14250900	-3.55886600	-1.81199600
H	0.84690900	-2.34874400	-1.85312300
H	0.90499400	-3.52368500	-0.53941600
C	5.92505900	-0.54520500	-0.42822100
H	5.99113300	0.44356100	-0.89592100
H	6.29178900	-1.28500100	-1.14306400
H	6.59137300	-0.54358600	0.43882100
C	1.94518500	0.57162800	2.44200400
H	1.86190500	0.00162900	3.37433500
H	0.93895600	0.88876100	2.15223500
H	2.54235500	1.46405000	2.63740800
C	-2.97437100	-0.33803200	0.29488200
C	-3.50364900	0.81970000	0.86811200
C	-4.74765700	1.25640300	0.41273300
H	-5.17771400	2.15704000	0.84380500
C	-5.43965300	0.57917300	-0.58955600
C	-4.86411200	-0.56375100	-1.14879700
H	-5.39025600	-1.09486500	-1.93891700
C	-3.62867600	-1.04164700	-0.72137500
C	-2.99415400	-2.25958300	-1.33772500
H	-2.11531400	-1.97249800	-1.92431400
H	-3.69725400	-2.77129000	-1.99750400
H	-2.66015000	-2.96498100	-0.57044300
C	-6.78069400	1.06758700	-1.07427200
H	-6.74710100	1.30502700	-2.14162500
H	-7.09260300	1.96586400	-0.53757800
H	-7.55066100	0.30315800	-0.93328800
C	-2.72924000	1.58007200	1.91033800
H	-2.56351200	0.98120200	2.81190100
H	-3.26053600	2.48913500	2.19795300
H	-1.74870400	1.84819300	1.50407000
N	-0.24857300	1.11414100	-0.41620400
C	1.02843300	1.58996200	-0.69109700
C	1.42933800	2.72219100	0.04931700
H	0.74245000	3.13106400	0.78551600
C	2.67672400	3.29256400	-0.14945000
H	2.96289800	4.15849200	0.44130400
C	3.55992500	2.77197200	-1.09780100
C	3.15397500	1.67552000	-1.85481100
H	3.82090700	1.25953600	-2.60625200
C	1.90829400	1.08832600	-1.66606900
H	1.61352000	0.22654500	-2.25289500
H	4.53495900	3.22242500	-1.25186700
H	-2.29886500	-1.72825200	2.64005700
H	0.41431300	-2.27461600	2.78866400

$TS^{‡}_{singlet}$			
N	-1.55998000	-0.65361200	0.83562700
N	0.66463800	-0.91927700	0.96385500
O	-0.33684100	-0.67239400	-1.19743900
C	-0.37133100	-0.49759000	0.01967500
C	-1.21007000	-0.79617300	2.13944800
C	0.14775800	-0.96181300	2.22174800
C	2.03250100	-1.07237800	0.60334000
C	3.00411700	-0.18109600	1.07456200
C	4.32220600	-0.36791400	0.64635900
H	5.08287700	0.32668000	0.99614100
C	4.68116500	-1.39538200	-0.21673400
C	3.68817700	-2.28272500	-0.64236400
H	3.95699100	-3.11065700	-1.29466100
C	2.36446800	-2.14888100	-0.24240300
C	1.32481200	-3.15141800	-0.66639400
H	1.79744700	-4.01301900	-1.14196500
H	0.61425300	-2.69281700	-1.35862700
H	0.75379000	-3.50330700	0.19913600
C	6.10322800	-1.56396900	-0.68552300
H	6.77267700	-0.86220200	-0.18384700
H	6.18070700	-1.39284300	-1.76362800
H	6.46348600	-2.57814600	-0.49024400
C	2.70716700	0.96956100	2.00484700
H	3.09375600	1.89857500	1.57388200
H	3.20668600	0.81638600	2.96730500
H	1.64061400	1.10961700	2.17815600
C	-2.87449300	-0.42920300	0.33550600
C	-3.62445300	0.66633800	0.78951900
C	-4.91006100	0.83525700	0.27503600
H	-5.49847400	1.68453000	0.61498400
C	-5.45327000	-0.03973400	-0.66221500
C	-4.68463400	-1.12713000	-1.07474600
H	-5.10106900	-1.83453500	-1.78847800
C	-3.39744300	-1.34697500	-0.59014100
C	-2.61777500	-2.55431200	-1.03657400
H	-1.91502900	-2.27808800	-1.82561200
H	-3.29483500	-3.32854200	-1.40410900
H	-2.02586700	-2.96643000	-0.21410300
C	-6.82889400	0.19011800	-1.23273800
H	-6.76740400	0.70718600	-2.19586800
H	-7.43817400	0.80371000	-0.56521100
H	-7.35009000	-0.75573300	-1.40102000
C	-3.09594800	1.64322300	1.81072100
H	-3.27897300	1.28694400	2.83131700
H	-3.61231800	2.60034500	1.70815200
H	-2.02305700	1.80341500	1.68704100
N	-0.11413700	1.35613900	0.44307000
C	0.75050400	2.02812600	-0.29720700
C	0.93232700	3.41435100	0.06263700
H	0.31311200	3.80053600	0.86554400
C	1.86082800	4.20483500	-0.57472400
H	1.97995600	5.24318900	-0.28128900
C	2.65931100	3.66937800	-1.59669600
C	2.49814800	2.33221200	-1.97946700
H	3.11453500	1.92585600	-2.77537000
C	1.56598100	1.51721200	-1.36999500
H	1.42670700	0.49064900	-1.68065300
H	3.39632100	4.29209800	-2.09282100
H	-1.94162900	-0.78927400	2.93266600
H	0.76813000	-1.11123900	3.09194800

$TS^{\ddagger}_{triplet}$			
N	-1.54319100	-0.69184700	0.82898400
N	0.69242000	-0.93952000	0.95246500
O	-0.31193900	-0.63540600	-1.20778500
C	-0.34484500	-0.46111400	0.01368100
C	-1.18988000	-0.85505500	2.12509900
C	0.17355500	-1.00451800	2.20485000
C	2.06417300	-1.06777100	0.59600400
C	3.02302600	-0.16564500	1.07116400
C	4.34496300	-0.33659400	0.64741600
H	5.09651000	0.36601200	1.00101500
C	4.71823400	-1.35726100	-0.21765400
C	3.73590000	-2.25177300	-0.65377300
H	4.01523600	-3.07097300	-1.31261700
C	2.40978700	-2.13347700	-0.25762300
C	1.37568800	-3.13574500	-0.69511900
H	1.84585800	-3.95961000	-1.23553500
H	0.63007100	-2.65416700	-1.33329800
H	0.84770300	-3.54684600	0.17180200
C	6.14426000	-1.51006800	-0.67990200
H	6.22308800	-1.35018400	-1.75959300
H	6.51854400	-2.51664800	-0.47182800
H	6.80167800	-0.79318600	-0.18373400
C	2.70683600	0.98743500	1.99200600
H	3.23170700	0.86631600	2.94528400
H	1.64012000	1.09382400	2.18793800
H	3.05090300	1.92286100	1.53911700
C	-2.85980600	-0.46482000	0.33716300
C	-3.62491700	0.60572000	0.82658700
C	-4.91079000	0.77674200	0.31469800
H	-5.51058800	1.60649300	0.68211400
C	-5.44103400	-0.07202000	-0.65417400
C	-4.65807000	-1.13446500	-1.10202500
H	-5.06377500	-1.82154500	-1.84122400
C	-3.36891600	-1.35524400	-0.62206000
C	-2.57356100	-2.53648600	-1.10876800
H	-1.87537500	-2.22372700	-1.88800500
H	-3.24074000	-3.30727500	-1.50096800
H	-1.97443100	-2.96662400	-0.30099500
C	-6.81761200	0.16376400	-1.21986600
H	-6.76514800	0.78496500	-2.11999200
H	-7.45975200	0.67756500	-0.50061800
H	-7.29765100	-0.77776100	-1.49772900
C	-3.11169500	1.55484300	1.88152900
H	-3.29657500	1.16521400	2.88948800
H	-3.63669300	2.50978200	1.80604000
H	-2.04005500	1.72986700	1.76887000
N	-0.14483900	1.29703000	0.45588200
C	0.70126200	2.01867800	-0.30070500
C	0.78889600	3.40225500	0.05396500
H	0.13058600	3.75716300	0.84037700
C	1.68890500	4.24577800	-0.56531300
H	1.74167900	5.28989200	-0.27350100
C	2.53498000	3.75279600	-1.56503200
C	2.45633200	2.40929400	-1.94318700
H	3.10933000	2.03262100	-2.72420900
C	1.55767600	1.54546700	-1.34290100
H	1.48313200	0.51186100	-1.65175900
H	3.24634700	4.41355000	-2.04974700
H	-1.91769600	-0.87444500	2.92201900
H	0.79070100	-1.16567500	3.07588700

2a-Ph···Me_2S (reactant complex)			
O	0.76270600	1.02021700	-0.14356400
N	-1.68647800	-1.51379600	-0.37071600
N	0.50820500	-1.72069500	-0.45532700
C	-0.49976200	-0.88024000	-0.09328400
C	-1.39031200	-2.77954600	-0.89811200
C	-0.05166700	-2.90227700	-0.94272200
N	-0.30819400	0.35571100	0.34535500
C	-1.24846400	1.06200800	1.12538200
C	-2.07615800	0.41373800	2.04693900
H	-2.00336300	-0.66243000	2.17808500
C	-2.97706700	1.15540900	2.79970200
H	-3.61925400	0.64851300	3.51396700
C	-3.04337000	2.54048200	2.65891300
C	-2.18686100	3.17985800	1.76530800
H	-2.21929500	4.26036300	1.66394700
C	-1.28280200	2.45131700	1.00110800
C	-2.90171900	-0.80376100	-0.65603600
C	-2.86787400	0.19528700	-1.64482600
C	-4.04632300	0.88920300	-1.89277300
H	-4.04485200	1.66610700	-2.65418000
C	-5.23066800	0.61138400	-1.20298500
C	-5.22390300	-0.40292300	-0.25310200
H	-6.13810200	-0.63788600	0.28742400
C	-4.06413700	-1.12374600	0.04341200
C	-1.61236100	0.49817300	-2.42491700
C	-4.10144200	-2.20203100	1.09553300
C	1.88961300	-1.58829000	-0.08463000
C	2.81612300	-1.22187000	-1.06420200
C	4.15904200	-1.19614400	-0.70286900
H	4.89816900	-0.90950400	-1.44679900
C	4.57464100	-1.48288700	0.60138900
C	3.61146600	-1.80777100	1.55344900
H	3.91872500	-2.02007200	2.57475100
C	2.25454200	-1.87185800	1.23036800
C	2.34113800	-0.76831400	-2.41496700
C	1.21462500	-2.19411100	2.27155900
H	3.18327100	-0.46941500	-3.04141800
H	1.67886100	0.09131700	-2.25691500
H	1.77227900	-1.54557800	-2.93664600
H	1.67862200	-2.61899600	3.16369400
H	0.47432400	-2.90887800	1.89595900
H	0.67719300	-1.28633300	2.56861500
H	-0.58234100	2.91100600	0.31483400
H	-3.74382400	3.11687800	3.25397800
H	-1.11029400	-0.42738700	-2.73114200
H	-0.88251000	1.07951500	-1.84527900
H	-1.86248600	1.05945200	-3.32733100
H	-3.10172400	-2.55332300	1.35699100
H	-4.68101300	-3.06453400	0.75013000
H	-4.58318200	-1.82715900	2.00315900
H	0.57937500	-3.71853900	-1.25492900
H	-2.18058900	-3.44690200	-1.20080000
C	-6.47660900	1.41076000	-1.48277900
H	-6.39062800	2.41700100	-1.06073400
H	-7.35916400	0.93837200	-1.04627800
H	-6.64205500	1.51979100	-2.55810800
C	6.03529300	-1.40474400	0.95978600
H	6.63260200	-2.05768400	0.31644400
H	6.20668400	-1.69870100	1.99770500
H	6.40064900	-0.38201000	0.82367800
S	5.06876900	1.97021700	-0.69871100

C	5.55459100	3.71176100	-0.83523400
H	6.51979800	3.75245500	-1.34243200
H	4.82221900	4.27139200	-1.42191700
H	5.65424700	4.16899800	0.15218000
C	3.47122200	2.19595600	0.12803100
H	2.79630300	2.78998200	-0.49134400
H	3.00000700	1.22213100	0.27081400
H	3.60987200	2.67939200	1.09795100

$TS^{‡}_{OAT}$

O	0.97789500	1.25851800	-0.24711900
N	-1.08323700	-1.72477900	-0.45610300
N	1.11000700	-1.69012300	-0.34439900
C	-0.01338700	-1.00547900	0.04063200
C	-0.60104700	-2.83666500	-1.15351400
C	0.74241900	-2.81269800	-1.08275900
N	0.01835400	0.11429500	0.70671500
C	-1.12447600	0.65630800	1.30920000
C	-1.66308900	0.05497500	2.45458200
H	-1.17652300	-0.82873100	2.85956600
C	-2.80015600	0.58160400	3.05774500
H	-3.21423000	0.09626900	3.93670800
C	-3.39794100	1.73117000	2.54656000
C	-2.83722700	2.35488000	1.43289900
H	-3.29165400	3.25656800	1.03235600
C	-1.70370000	1.83276100	0.82072300
C	-2.37917500	-1.14896400	-0.68314800
C	-2.49027800	-0.15206500	-1.65916700
C	-3.74081600	0.43579300	-1.84030200
H	-3.84840200	1.22084500	-2.58520300
C	-4.84656000	0.05664600	-1.08021900
C	-4.69699600	-0.96242500	-0.13958600
H	-5.55411400	-1.27328700	0.45305100
C	-3.46859000	-1.58332500	0.07464500
C	-1.28650200	0.29230200	-2.44533200
C	-3.31092800	-2.68049900	1.09181700
C	2.46037300	-1.29193000	-0.09015100
C	3.21720800	-0.79676700	-1.15963100
C	4.55426400	-0.49194400	-0.92309300
H	5.15853500	-0.10658400	-1.74164800
C	5.12856000	-0.64342600	0.34286800
C	4.32994400	-1.10522800	1.38620200
H	4.75971500	-1.21753200	2.37880800
C	2.98742800	-1.43923700	1.19191300
C	2.56690400	-0.53920000	-2.49055500
C	2.12834700	-1.91800100	2.32997600
H	3.26194900	-0.04138500	-3.16964600
H	1.70309700	0.11167700	-2.31681400
H	2.21745300	-1.45973400	-2.96966200
H	2.73942300	-2.17961000	3.19593600
H	1.53857400	-2.79362500	2.04158400
H	1.42584100	-1.12909500	2.61792500
H	-1.25157300	2.29130100	-0.05144100
H	-4.28369700	2.14383700	3.01836300
H	-0.76564700	-0.56802000	-2.88242900
H	-0.56058000	0.81598400	-1.80278500
H	-1.58627300	0.95794800	-3.25758700
H	-4.21396700	-2.77599100	1.69768100
H	-2.46762500	-2.47449100	1.75563000
H	-3.12007700	-3.64585000	0.61111700
H	1.48699300	-3.49569500	-1.45817500
H	-1.27748300	-3.53072700	-1.62503500
C	-6.16833100	0.76179500	-1.23893200

3-Ph···Me_2SO (product complex)

O	0.73433800	1.49613400	-1.53630100
N	-0.86872000	-1.35449600	-0.99426900
N	1.29563400	-1.49562500	-0.65422600
C	0.13260600	-0.94288900	-0.12739500
C	-0.32226800	-2.12721300	-2.02270800
C	1.00062200	-2.21136500	-1.81368500
N	0.11077500	-0.27909300	0.98034900
C	-0.96144800	0.49707700	1.41231700
C	-1.35338900	0.41168100	2.75855000
H	-0.82614400	-0.28548900	3.40390400
C	-2.40176800	1.18136500	3.25094500
H	-2.69419700	1.08033200	4.29213100
C	-3.07495100	2.07522300	2.42178400
C	-2.66507600	2.20318000	1.09521700
H	-3.17036700	2.90385200	0.43537100
C	-1.61474800	1.44099000	0.59637300
C	-2.26423600	-1.12713600	-0.81585200
C	-2.93115500	-0.28752100	-1.71468100
C	-4.27386200	-0.00819700	-1.46786100
H	-4.80513600	0.65650800	-2.14544500
C	-4.93811400	-0.52462300	-0.35580900
C	-4.24727300	-1.38702500	0.49507400
H	-4.75958600	-1.81392500	1.35426200
C	-2.91200500	-1.71669300	0.27593400
C	-2.20073600	0.34118000	-2.87295000
C	-2.17940900	-2.66537000	1.18562400
C	2.60122400	-1.16941500	-0.19238800
C	3.49322800	-0.49550400	-1.04549900
C	4.73476900	-0.12063600	-0.52969500
H	5.42590500	0.41303900	-1.17839300
C	5.11030800	-0.40345900	0.78233600
C	4.22209100	-1.12245300	1.57971300
H	4.51172000	-1.39004500	2.59365100
C	2.97175800	-1.52872200	1.11367300
C	3.16740200	-0.18819200	-2.48655300
C	2.07074400	-2.34795400	1.99643200
H	3.79336900	0.63563700	-2.83867900
H	2.12041900	0.09506300	-2.60680100
H	3.37601200	-1.05204500	-3.12742800
H	2.66030600	-2.89626400	2.73465100
H	1.49070000	-3.06328400	1.40645900
H	1.35320900	-1.70059300	2.50633100
H	-1.27599000	1.55198800	-0.42907400
H	-3.89638000	2.67139100	2.80554600
H	-1.99745000	-0.38898300	-3.66387300
H	-1.23475900	0.75126000	-2.55701100
H	-2.80188000	1.14167800	-3.30974000
H	-2.88202400	-3.19834100	1.82911600
H	-1.46545800	-2.12982400	1.82048900
H	-1.61043700	-3.39885300	0.60530800
H	1.76964200	-2.73077000	-2.36049300
H	-0.95177600	-2.56590900	-2.77931400
C	-6.36150100	-0.13290400	-0.05483100

H	-7.00631200	0.08299300	-1.06260000	H	-6.92378800	-0.96923400	0.36822100
H	-6.27495300	1.18836400	-2.23895400	H	-6.87961900	0.20999900	-0.95338900
H	-6.24925100	1.58133400	-0.51679400	H	-6.38373900	0.68238900	0.67612400
C	6.56981600	-0.26667200	0.57420200	C	6.43767500	0.05839600	1.32671200
H	6.68812800	0.82201000	0.59368700	H	6.33372500	1.01544500	1.84870900
H	7.21184900	-0.65019500	-0.22325200	H	7.16832200	0.19603800	0.52628600
H	6.93478400	-0.65851200	1.52603600	H	6.84390700	-0.66177200	2.04130500
S	2.20131800	2.75313400	-0.95928500	S	1.69629300	2.53406100	-0.99011900
C	3.20253700	2.60413200	0.52861600	C	1.94225900	2.25683300	0.78181000
H	3.85488100	1.74116900	0.38672500	H	2.42333400	1.28570700	0.90513700
H	3.79640500	3.50274300	0.71113400	H	2.59094400	3.05774500	1.14657700
H	2.51645900	2.38999400	1.35006000	H	0.97956800	2.25326900	1.29653600
C	1.11475100	4.08179700	-0.41756900	C	0.71361100	4.04717400	-0.81575700
H	1.66908800	4.99853800	-0.20420700	H	1.31855200	4.83328500	-0.35928500
H	0.39718300	4.27033600	-1.21795400	H	0.40323800	4.34654200	-1.81716000
H	0.58178400	3.72527400	0.46813400	H	-0.16150000	3.81965300	-0.20168200

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