Supporting Information for the Paper Entitled **"Intermolecular C−H bond activation of benzene and pyridines by a vanadium(III) alkylidene including a stepwise conversion of benzene to a vanadium-benzyne complex."**

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## Experimental Details

**General Considerations.** Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified nitrogen or using high vacuum standard Schlenk techniques under an argon atmosphere. Anhydrous *n*-hexane, pentane, toluene, and benzene were purchased from Aldrich in sure-sealed reservoirs (18 L) and dried by passage through two columns of activated alumina and a Q-5 column. Diethyl ether and $CH_2Cl_2$ were dried by passage through two columns of activated alumina.[S1] THF was distilled, under nitrogen, from purple sodium benzophenone ketyl and stored under sodium metal (thin cuts). Distilled THF was transferred under vacuum into glass bombs before being brought into a dry box. 2-Picoline was distilled from $CaH_2$, and then passed through a column of activated alumina. Celite, alumina, and 4 Å

molecular sieves were activated under vacuum overnight at 200 °C. (PNP)V($CH_2tBu$)$_2$ and (PNP)V=O(CH*t*Bu) were prepared according to the literature procedures.[S2] All other chemicals were used as received. CHN analyses were performed by Desert Analytics, Tucson, AZ or Midwest Microlabs, Indianapolis. $^{31}$P-NMR chemical shifts are reported with respect to external $H_3PO_4$ (0.0 ppm). $^{51}$V-NMR chemical shifts are reported with respect to neat $VOCl_3$ (0.0 ppm). $^1$H, $^{13}$C, $^{51}$V, $^{15}$N and $^{31}$P-NMR spectra were recorded on Varian 500, 400 or 300 MHz NMR spectrometers. $^1$H and $^{13}$C-NMR are reported with reference to residual solvent resonances: for $^1$H-NMR residual $C_6H_6$ in $C_6D_6$ at 7.16 ppm, for $^{13}$C-NMR $C_6D_6$ at 128 ppm. $^{51}$V NMR chemical shifts are reported with respect to $VOCl_3$ (0.0 ppm) and $\nu_{1/2}$ values in the $^{51}$V spectra are reported with the line broadening parameter set to 20. $^{15}$N-NMR chemical shifts are reported with respect to $MeNO_2$ (0.0 ppm). $C_6D_6$ was purchased from Cambridge Isotope Laboratory (CIL), degassed and then vacuum transferred to 4 Å molecular sieves. Solution magnetic moments measurements were obtained by the method of Evans.[S3, S4] X-ray diffraction data were collected on a SMART6000 (Bruker) system or a Bruker APEX Kappa DUO using Mo radiation under a stream of $N_2$ (g) at low temperatures except for compound **4** which was collected on a Bruker APEX II detector on a D8 platform at ChemMatCARS, APS, Chicago. CI mass spectra were collected with a MAT-95 XP mass spectrometer. Peak matching was done with CMASS and LIST subroutines of XCalibur.

**Preparation of the oxo-benzyne complex (PNP)V=O($\eta^2$-$C_6H_4$) (2)**

Under an atmosphere of argon, a side arm reaction vessel was charged with a $C_6H_6$ solution of **2** (100 mg, 0.159 mmol). The solution was heated to 110 °C for 6 hours;

rapidly the green solution became brown. Monitoring of this solution by $^{1}$H-NMR clearly shows a change from **2** into an unidentified intermediate we propose to be (PNP)V($C_6H_5$)$_2$ (**4**) (*vide infra*). At this point, the headspace of this mixture was then evacuated *in vacuo* and $N_2O$ was added. This mixture was then heated to 110 °C for 4-6 hours. The solution was then dried in vacuo. This residue was extracted with hexanes. Concentration and storage of this solution allows for isolation of **2** as a brown powder in 24% yield. (22 mg, 0.038 mmol). Examination of the crude solution revealed almost quantitative formation of **2** (>95% yield based on an internal integration standard, 5 µl 1,4-dioxane).

$^{1}$H-NMR (25 °C, 400.1 MHz, $C_6D_6$): 8.04 (m, 2H, Ar*H of benzyne*); 7.64 (m, 2H, Ar*H of benzyne*); 7.29 (d, 1H, Ar*H*); 7.11 (m, 2H, Ar*H*); 6.98 (d, 1H, Ar*H*); 6.87 (d, 1H, Ar*H*); 6.64 (d, 1H, Ar*H*); 3.05 (septet, 1H, C*H*($CH_3$)$_2$); 2.85 (septet, 1H, C*H*($CH_3$)$_2$); 2.64 (m, 2H, C*H*($CH_3$)$_2$); 2.19 (s, 3H, ArC*H$_3$*); 2.10 (s, 3H, ArC*H$_3$*); 1.62 (doublet of doublets, 3H, CH(C*H$_3$*)$_2$); 1.47 (doublet of doublets, 6H, CH(C*H$_3$*)$_2$); 1.28 (m, 6H, CH(C*H$_3$*)$_2$); 1.13 (m, 3H, CH(C*H$_3$*)$_2$); 1.09 (m, 3H, CH(C*H$_3$*)$_2$); 0.62 (doublet of doublets, 3H, CH(C*H$_3$*)$_2$). $^{13}$C{$^{1}$H}-NMR (25 $^{o}$C, 100.6 MHz, $C_6D_6$): δ 163.3 (Ar), 160.7 (Ar), 157.6 (V-*C*$_6$H$_4$), 156.6 (V-*C*$_6$H$_4$), 132.9 (Ar), 132.4 (Ar), 132.2 (Ar), 131.2 (Ar), 130.0 (Ar), 129.3 (Ar), 129.0 (Ar), 127.2 (Ar), 127.0 (Ar), 125.5(Ar), 122.5 (Ar), 121.5 (Ar), 118.2 (Ar), 116.2 (Ar), 27.0 (CMe$_2$), 25.5 (CMe$_2$), 23.0 (CMe$_2$), 21.0 (CMe$_2$), 20.6 (CMe$_2$), 20.3 (CMe$_2$), 19.7 (CMe$_2$), 19.3 (Ar*Me*), 19.0 (Ar*Me*), 18.4 (CMe$_2$), 18.0 (CMe$_2$), 16.0 (CMe$_2$). $^{31}$P-NMR (25 °C, 161.97 MHz, $C_6D_6$): δ 62. MS-CI for formula $C_{32}H_{44}NOP_2V$: Theoretical [M]$^{+}$: 571.2338; Experimental [M]$^{+}$, 571.2311. Analysis of the volatiles by GC-MS revealed peaks consistent with formation of neopentane.

**Preparation of the oxo-benzyne complex (PNP)V=O($\eta^2$-$C_6H_4$) (2-$D_4$).**

Under an atmosphere of argon, an NMR tube with a J. Young screw top valve was charged with a $C_6D_6$ solution of **1** (50 mg, 0.80 mmol). This solution was heated to 110 °C for 6 hours; rapidly the green solution became brown. This headspace of this mixture was then evacuated *in vacuo* and $N_2O$ was added (1 atm). This mixture was then heated to 110 °C for 6 hours. Monitoring of this solution by $^1$H-NMR spectroscopy clearly shows transformation of the contents into the diamagnetic oxo-benzyne **2-$D_4$**.

$^1$H-NMR (25 °C, 400.1 MHz, $C_6D_6$): 7.29 (d, 1H, Ar*H*); 7.11 (m, 2H, Ar*H*); 6.98 (d, 1H, Ar*H*); 6.87 (d, 1H, Ar*H*); 6.64 (d, 1H, Ar*H*); 3.05 (septet, 1H, C*H*($CH_3$)$_2$); 2.85 (septet, 1H, C*H*($CH_3$)$_2$); 2.64 (m, 2H, C*H*($CH_3$)$_2$); 2.19 (s, 3H, ArC*H*$_3$); 2.10 (s, 3H, ArC*H*$_3$); 1.62 (doublet of doublets, 3H, CH(C*H*$_3$)$_2$); 1.47 (doublet of doublets, 6H, CH(C*H*$_3$)$_2$); 1.28 (m, 6H, CH(C*H*$_3$)$_2$); 1.13 (m, 3H, CH(C*H*$_3$)$_2$); 1.09 (m, 3H, CH(C*H*$_3$)$_2$); 0.62 (doublet of doublets, 3H, CH(C*H*$_3$)$_2$). $^{31}$P-NMR (25 °C, 161.97 MHz, $C_6D_6$): δ 62. MS-CI for formula $C_{32}H_{40}D_4NOP_2V$: Theoretical $[M]^+$: 575.2589; Experimental $[M]^+$, 575.2564. Analysis of the volatiles by GC-MS revealed peaks consistent with neopentane and neopentane-*d*$_2$.

**Preparation of Complex (PNP)V($C_6H_5$)$_2$ (4).**

(PNP)$VCl_2$ (0.183 g, 0.28 mmol) was dissolved in 10 mL of THF giving a purple solution. The solution was cooled down to –36 ˚C and a 3M solution of PhMgBr (0.25 mL, 0.60 mmol) in diethyl ether (from a Sure-Seal bottle without further purification) was added and the mixture was allowed to warm up to room temperature while stirring.

The mixture was stirred for 2 h and the solvent was evaporated to dryness. The product was extracted with hexane and crystallized at –36 ˚C from 10 mL of 1:1 solution of hexane/pentane for a 79% yield.

$^1$H-NMR (25 °C, 400.1 MHz, $C_6D_6$): 22.98 ($\Delta\nu_{1/2}$ = 501.0 Hz), 18.88 ($\Delta\nu_{1/2}$ = 2277 Hz), 16.17 ($\Delta\nu_{1/2}$ = 235 Hz), 4.65 ($\Delta\nu_{1/2}$ = 1010 Hz), 3.66 ($\Delta\nu_{1/2}$ = 153 Hz), 3.38 ($\Delta\nu_{1/2}$ = 900 Hz), –11.81 ($\Delta\nu_{1/2}$ = 1788 Hz) ppm. Evans' Magnetic Moment: (25 °C, 400.00 MHz, $C_6D_6$) $\mu_{eff}$ = 2.78 ± 0.2 $\mu_B$. MS-CI: Theoretical $[M]^+$, 633.2853; Experimental $[M]^+$, 633.2845.

**Synthesis of (PNP)V($CH_2$*t*Bu)($\eta^2$-$NC_5MeH_4$) (5)**

To a stirring hexane solution of **2** (100 mg, 0. 159 mmol) was added 1 mL of 2-picoline at room temperature. The solution was stirred for 5 days over which time the green solution took on a red-brown color. The volatiles were removed in vacuo and the red residue was taken up into hexanes (≈ 5 mL), concentrated, then filtered. X-ray diffraction quality crystals were grown by concentration and storage of this solution at room temperature. Storage of a concentrated hexane solution at −36 °C allows for isolation of the complex as brown-red crystals of **5** in 19.7% yield (20.1 mg, 0.031 mmol).

$^1$H-NMR (25 °C, 400.1 MHz, $C_6D_6$): δ 17.28 ($\Delta\nu_{1/2}$ = 255.4), 13.92 ($\Delta\nu_{1/2}$ = 143.9), 11.92 ($\Delta\nu_{1/2}$ = 4800.9), 5.95 ($\Delta\nu_{1/2}$ = 2254.5), 4.70 ($\Delta\nu_{1/2}$ = 1830.7), 3.45 ($\Delta\nu_{1/2}$ = 1913.5), –14.5 ($\Delta\nu_{1/2}$ = 599.9). Evans' Magnetic Moment: (25 °C, 300.06 MHz, $C_6D_6$) $\mu_{eff}$ = 2.7 ± 0.3 $\mu_B$. MS-CI: Theoretical $[M]^+$, 642.3437; Experimental $[M]^+$, 642.3386.

**Synthesis of (PNP)V($CH_2tBu$)($\eta^2$-$NC_5PhH_4$) (6)**

To a stirring hexane solution of (PNP)V($CH_2tBu$)$_2$ (**1**) (100 mg, 0.159 mmol) was added 0.5 mL of 2-phenylpyridine at room temperature. The solution was stirred for 5 days over which time the green solution took on a red-brown color. The volatiles were removed in vacuo and the red residue was taken up into hexanes (≈ 5 mL), concentrated, then filtered. X-ray diffraction quality crystals of **6** were grown by concentration and storage of this solution at room temperature. Storage of a concentrated hexane solution at −36 °C allows for isolation of the complex as brown-red crystals in 21.9% yield (24.5 mg, 0.035 mmol). $^1$H-NMR (25 °C, 400.1 MHz, $C_6D_6$): δ 17.74 ($\Delta\nu_{1/2}$ = 245.5), 11.42 ($\Delta\nu_{1/2}$ = 118.5), 8.54 ($\Delta\nu_{1/2}$ = 40.7), 8.11 ($\Delta\nu_{1/2}$ = 39.8), 7.20 ($\Delta\nu_{1/2}$ = 74.7), 2.12 ($\Delta\nu_{1/2}$ = 80.9), -11.02 ($\Delta\nu_{1/2}$ = 399.9), -24.9 ($\Delta\nu_{1/2}$ = 231.1) . Evans' Magnetic Moment: (25 °C, 300.06 MHz, $C_6D_6$) $\mu_{eff}$ = 2.8 ± 0.2 $\mu_B$. MS-CI: Theoretical $[M]^+$, 704.3593; Experimental $[M]^+$, 704.3587.

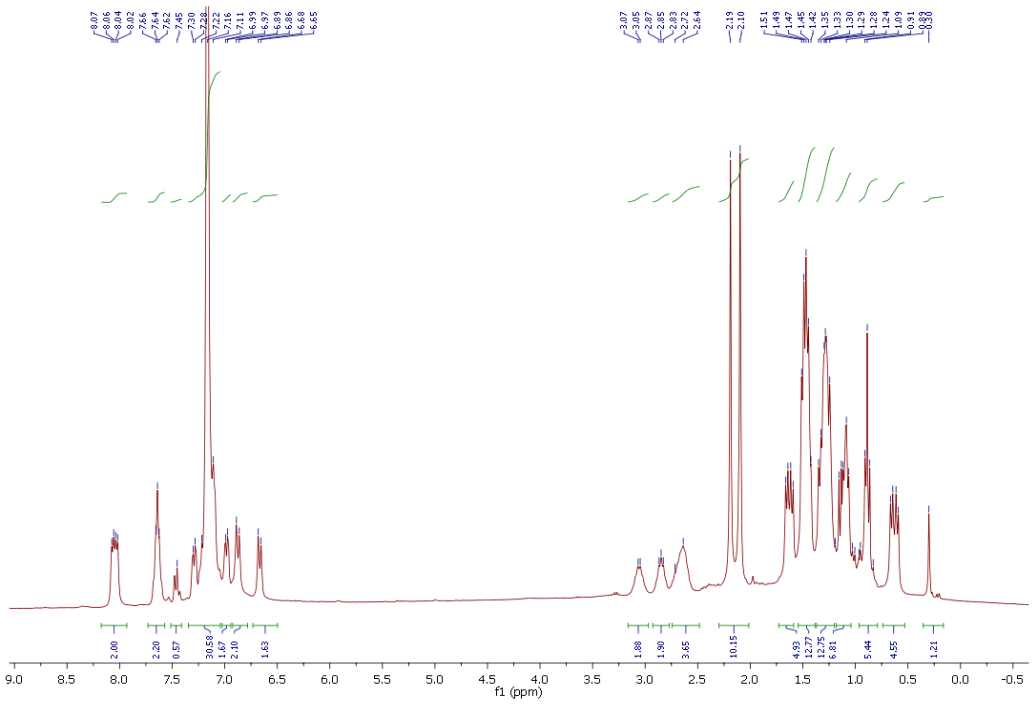
**Oxidation of alkyl-pyridyl complexes 5 or 6 by $N_2O$.**

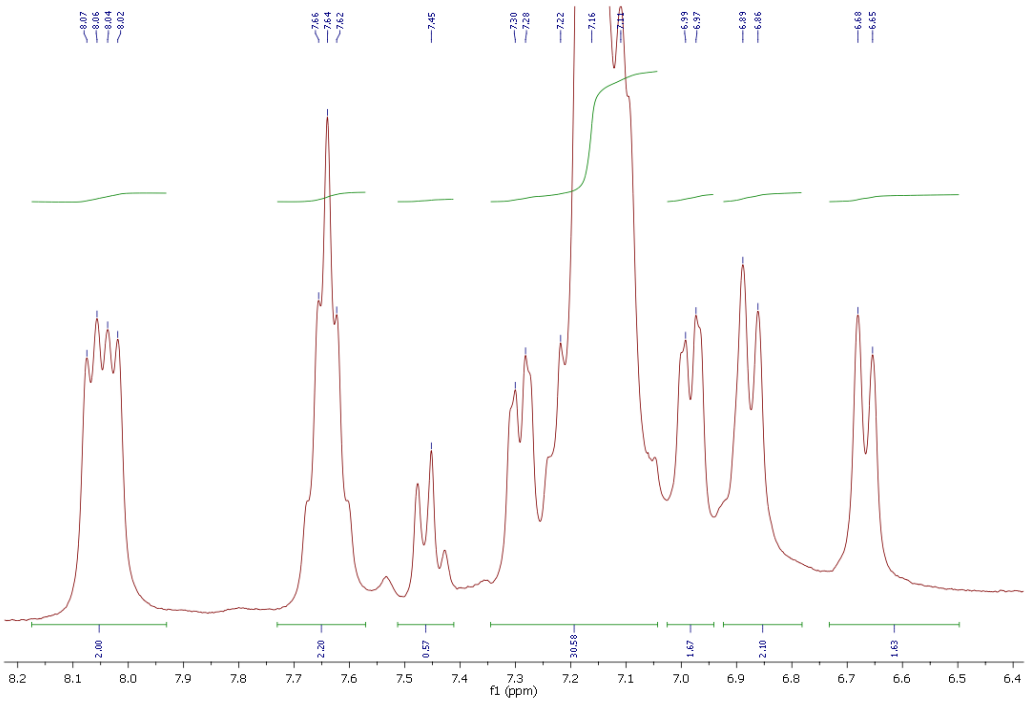
In a typical experiment: to an NMR tube with a J. Young screw top valve was added a $C_6D_6$ solution of **5** or **6** (≈ 20 mg in ≈ 1 mL of deuterated solvent). This solution was then frozen and degassed under two freeze pump thaw cycles. To this solution was added $N_2O$ (1 atm). The solutions were heated to 80 °C overnight with continuous shaking of the NMR tube (using an NMR tube rotator). The resulting reaction mixture was found to contain a mixture of the oxo-alkylidene, **3**, and the corresponding *ortho*-substituted pyridine by $^1$H-NMR spectroscopy. The yield of **3** as found by use of a $^1$H-NMR spectroscopic internal integration standard (5 μl 1,4-dioxane) was > 80%.

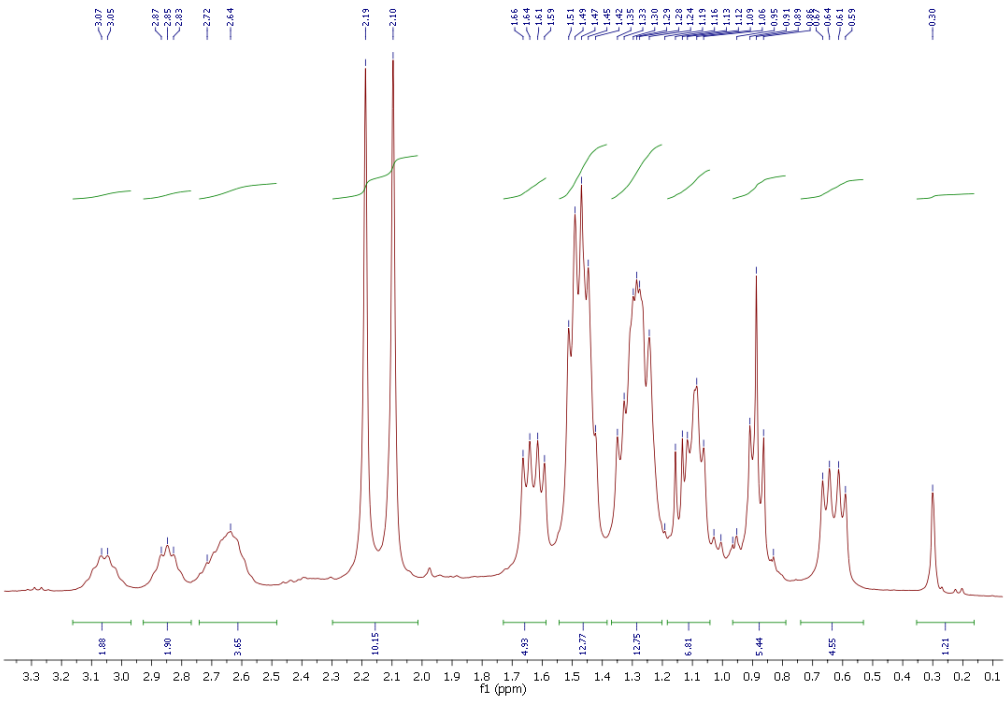
**Thermolysis of 1 in $C_6H_6$, followed by oxidation with $N_2O$ in THF-$d_8$.**

In a typical experiment complex **1** (20-40 mg) was thermolyzed in a J-Young NMR tube $C_6H_6$ (1-2 mL) at 110 $^oC$ for 3 h and the volatiles then removed under reduced pressure (over several hours). To the residue, was added THF-$D_8$ (~1 mL), the solution was evacuated and the atmosphere replaced with $N_2O$ in THF-$D_8$. Thermolysis of the solution (110 $^oC$, 6 h) revealed formation of **2** as well as $C_6H_6$.

$^1H$ NMR of (PNP)V(=O)($C_6H_4$) (**3**)




8.07
8.06
8.04
8.02
7.66
7.64
7.62
7.45
7.30
7.28
7.22
7.16
7.11
6.99
6.97
6.89
6.86
6.68
6.65
2.00
2.20
0.57
30.58
1.67
2.10
1.63
f1 (ppm)


3.07
3.05
2.87
2.85
2.83
2.72
2.64
2.19
2.10
1.66
1.64
1.61
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1.51
1.49
1.47
1.45
1.42
1.35
1.33
1.30
1.29
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1.24
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1.16
1.13
1.12
1.09
1.06
0.95
0.91
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0.64
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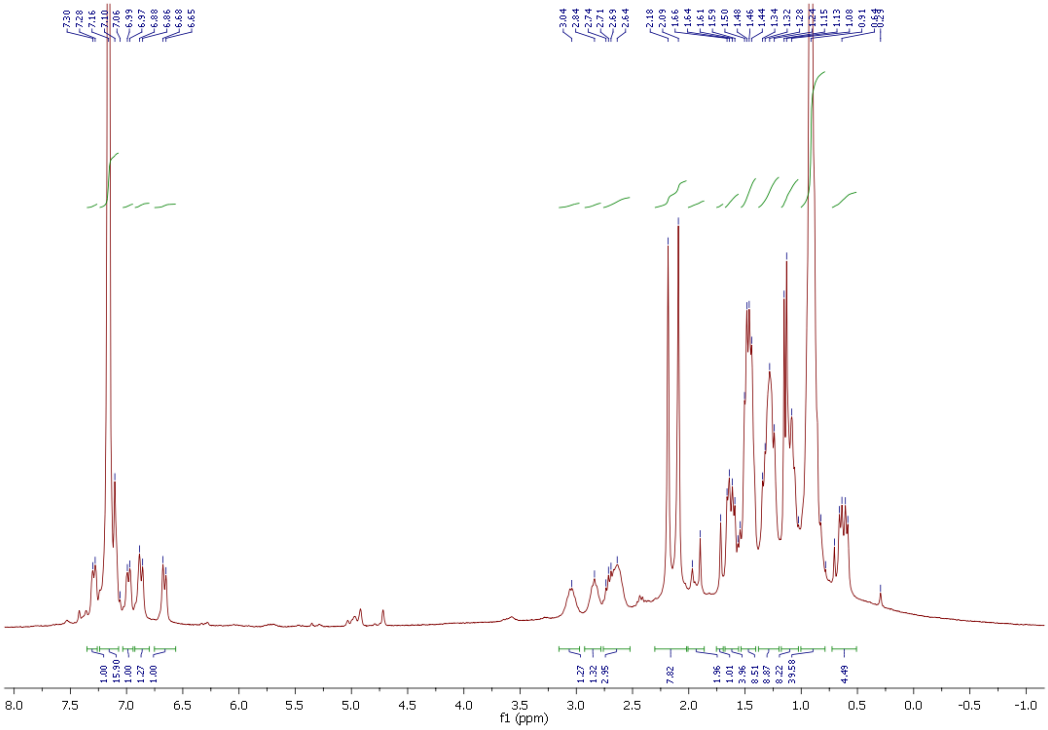
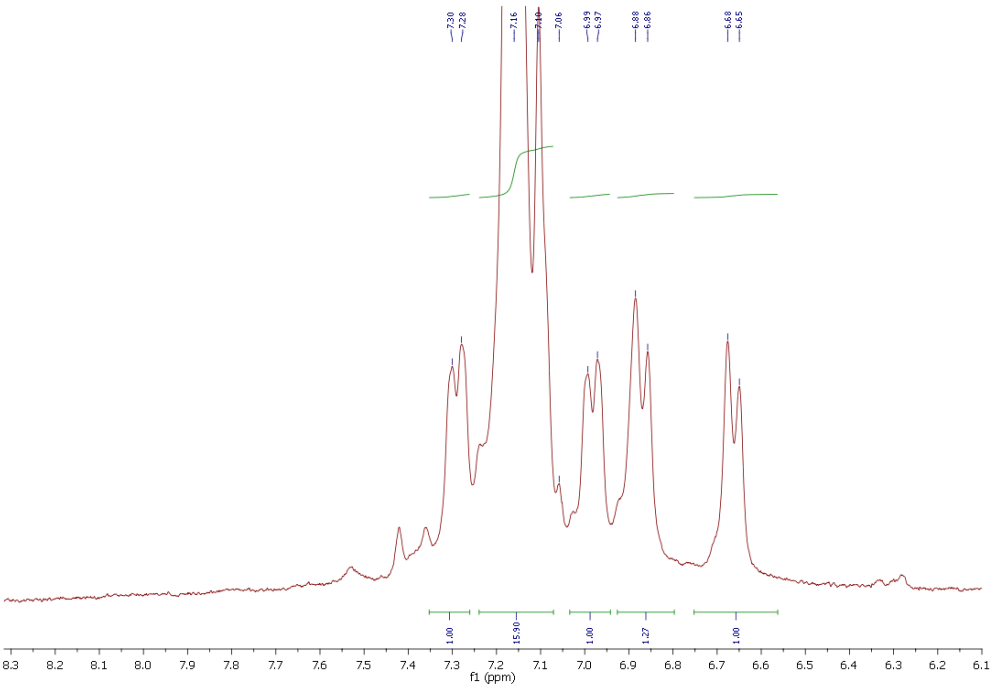
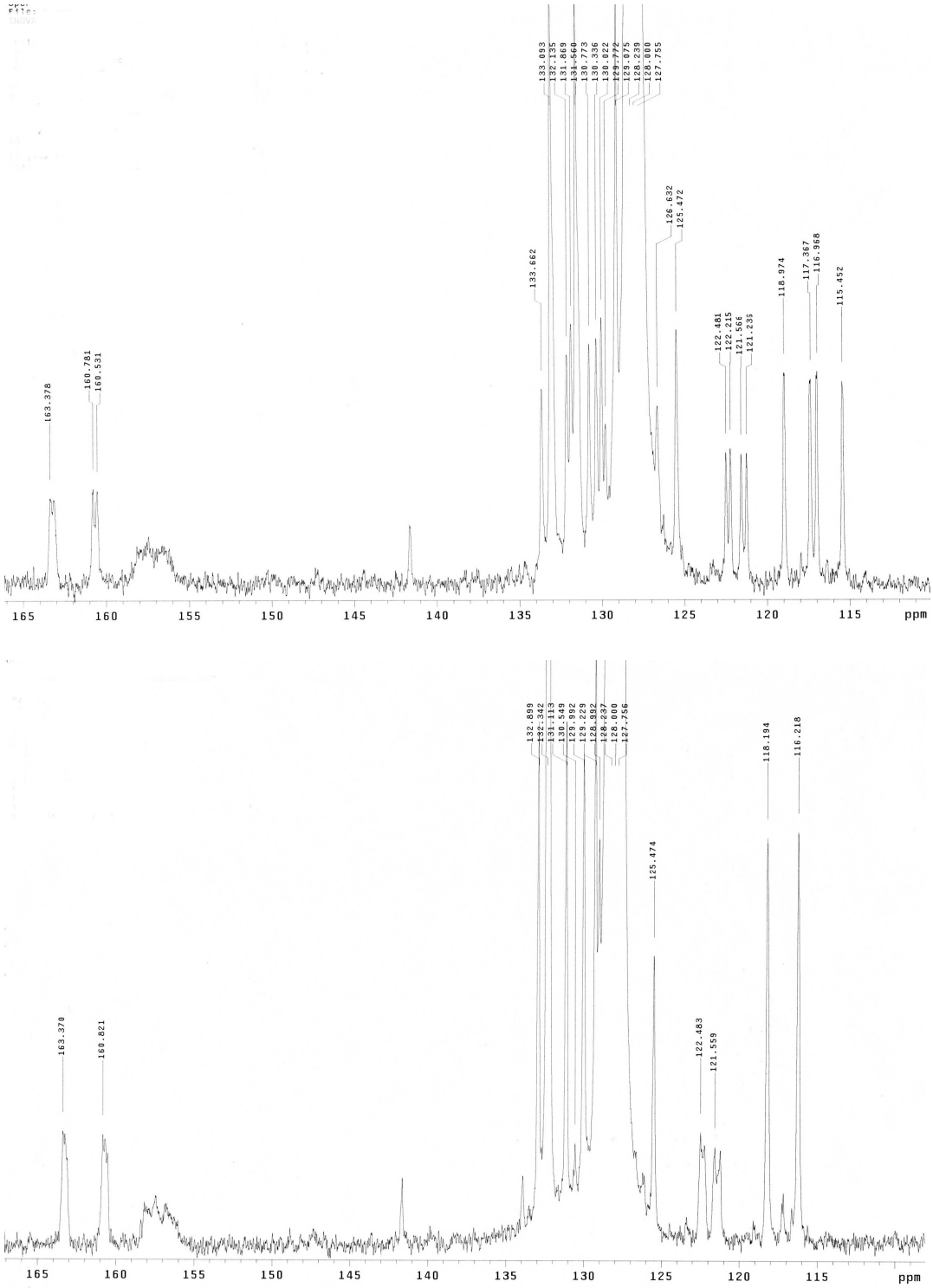
0.53
0.30
1.88
1.90
3.65
10.15
4.93
12.77
12.75
6.81
5.44
4.55
1.21
f1 (ppm)

$^1$H NMR of (PNP)V(=O)($C_6D_4$) (**3-D**)

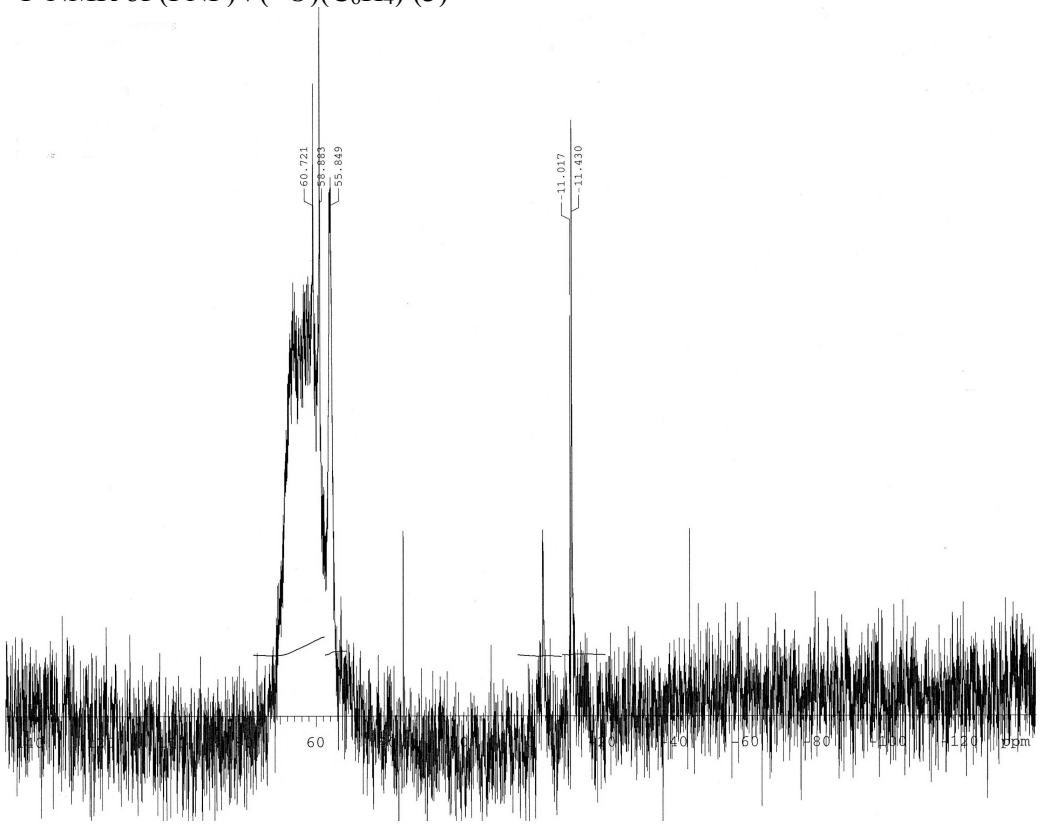


$^{13}C$ NMR of (PNP)V(=O)($C_6H_4$) (**3**)



$^{31}$P NMR of (PNP)V(=O)($C_6H_4$) (**3**)




**HFEPR Data Acquisition.** High-frequency and -field electron paramagnetic resonance (HFEPR) spectra were recorded using the Electron Magnetic Resonance (EMR) Facility at the National High Magnetic Field Laboratory (NHMFL, Tallahassee, FL).[S5] The spectrometer employs a Virginia Diodes (Charlottesville, VA) source operating at a base frequency of 12 – 14 GHz and multiplied by a cascade of multipliers in conjunction with a 15/17 T superconducting magnet. Detection was provided with an InSb hot-electron bolometer (QMC Ltd., Cardiff, UK). The magnetic field was modulated at 50 kHz. A Stanford Research Systems SR830 lock-in amplifier converted the modulated signal to DC voltage. Low temperature was provided by an Oxford Instruments (Oxford, UK) continuous flow cryostat and a temperature controller from the same source. Solid

powder materials (typically, 30 – 50 mg) were loaded into sample holders under argon atmosphere.

**Analysis of HFEPR Data.** The multi-frequency HFEPR data were fitted using a spin Hamiltonian for $S = 1$ systems comprised of Zeeman and zfs terms:[S6,S7]

$$\mathcal{H} = \beta\, B \bullet \mathbf{g} \bullet S + D(S_z^2 - S(S+1)/3) + E(S_x^2 - S_y^2). \qquad \text{(eqn 1)}$$

Individual powder-pattern spectra at multiple frequencies were simulated using this spin Hamiltonian, which allows direct extraction of the zero-field splitting (zfs) parameters $D$ and $E$, along with the $g$ values.[S8,S9] Further details of the HFEPR methodology are given elsewhere.[5]

**HFEPR Results and Discussion.** HFEPR investigation of (PNP)V($CH_2tBu$)$_2$ (**1**) gave well-defined spectra at low temperatures (5 – 60 K) and at frequencies ranging from 50 to 300 GHz. An exemplary spectrum recorded at 10 K and 224 GHz is shown in Figure EPR-1. The spectrum can be immediately identified as one originating from a spin triplet ($S = 1$) state, with a strong "half-field" transition corresponding to an off-axis turning point of the $\Delta M_S = \pm 2$ transition, and a set of $\Delta M_S = \pm 1$ turning points. Additional spectra at lower and higher frequencies are shown in Fig. S1 and Fig. 2, respectively. At each frequency, spectra are accompanied by their simulations assuming a perfect powder distribution. The resonant fields provide the spin Hamiltonian (eqn 1) parameters and the relative intensities of the two branches further allows determination of the sign of $D$, which is positive (see Figure 1). The parameter $E$ is given the same sign, by convention.

The parameters are as follows: $S = 1$; $D = +3.93$ cm$^{-1}$, $E = +0.145$ cm$^{-1}$; $g_x = g_y = 1.955$, $g_z = 1.99$. These parameters do not change upon raising the temperature up to 60 K.

Note: A signal from a V(IV) ($3d^1$, $S = 1/2$) impurity is also seen at $g = 2.00$. It should be noted that the integrated intensity of this impurity relative to that of the V(III) species of interest is very low, as the latter covers the entire field range from 3 – 12 T, while the former is essentially a "spike" at 8 T.

Qualitatively, our spectroscopic results demonstrate again that use of sufficiently high frequencies combined with high resonant magnetic fields allows observation of EPR resonances from systems traditionally regarded as "EPR-silent". The quantitative significance of the spin Hamiltonian parameters for **1** will require both additional experimental and theoretical work. We plan to study a wider range of V(III) pincer complexes, in which the ancillary ligands are systematically varied, so that coordination environment and electronic structure can be correlated. Equally important, detailed quantum chemical analysis is needed to understand the multiple factors that contribute to zfs. Such work has been done on a series of V(III) complexes of phosphinethiolato ligands (PS3),[S10] and these methods will eventually be applied to the systems described herein. At present, however, we note only that the relatively large magnitude of $D$ for (PNP)V($CH_2{}^tBu$)$_2$ (nearly 4 cm$^{-1}$) is consistent with a system that is best described as V(III), rather than as an organic (ligand-centered) (di)radical, which would exhibit zfs much below 1 cm$^{-1}$. Indeed, (PNP)V($CH_2{}^tBu$)$_2$ exhibits zfs that is significantly larger than that found for any of the previously studied five-coordinate $[V^{III}(PS3)L]^{0,-}$ (L = 1-methylimidazole, $Cl^-$, $N_3^-$) complexes, for which $1.0 < |D| < 2.0$ cm$^{-1}$.[S10] However, other V(III) complexes that are six-coordinate with oxygen and halogen donor ligands exhibit

zfs much larger than that seen here (e.g., for $VCl_3(thf)_3$, $|D| = 11.85$ $cm^{-1}$ by HFEPR; ~10 $cm^{-1}$ by MCD).[S11] Clearly, the correlation of zfs of V(III) complexes with coordination environment is a challenging problem, but one that we plan on tackling both experimentally and computationally in future studies.

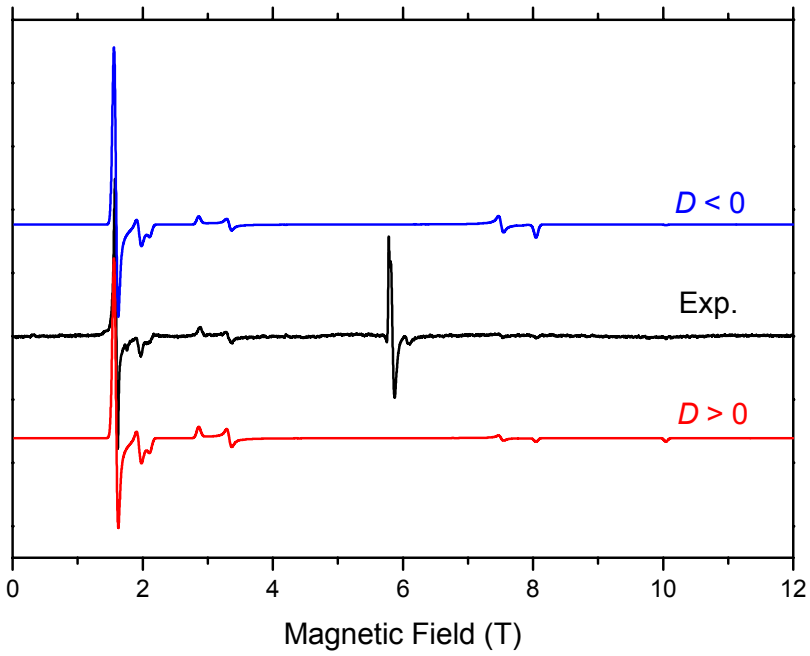



**Fig. S1.** EPR spectrum of polycrystalline (PNP)V($CH_2{}^tBu)_2$ at 10 K and 162 GHz (black trace) accompanied using simulations assuming a powder pattern and using the same absolute values of the spin Hamiltonian parameters as in the main text. The top, blue trace was simulated using a negative value for *D*, while the bottom, red trace used a positive value for the same parameter. Single-crystal linewidth used: 300 G, isotropic. The group of resonances at ca. 6 T originating from V(IV) and other impurities was not simulated.

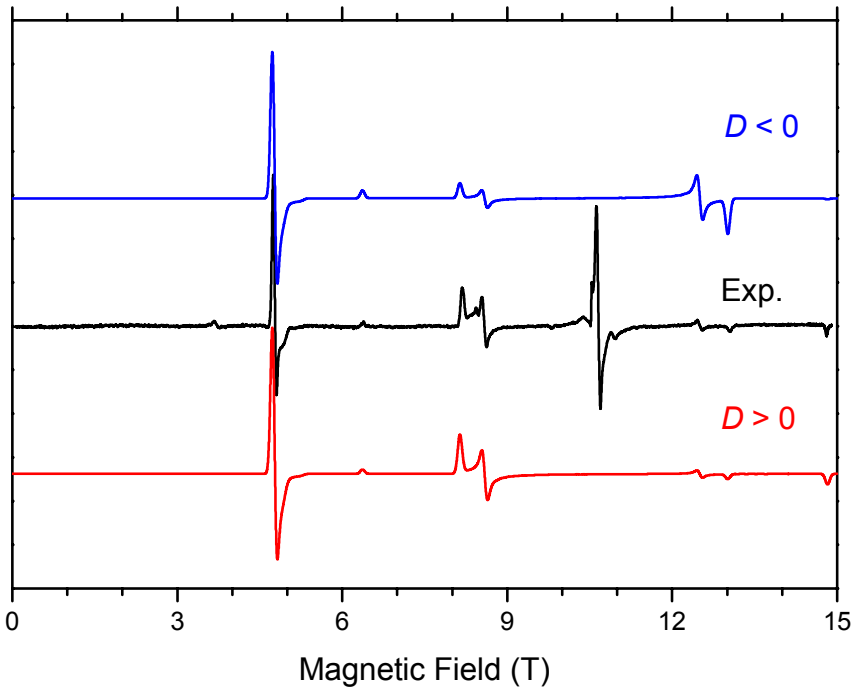


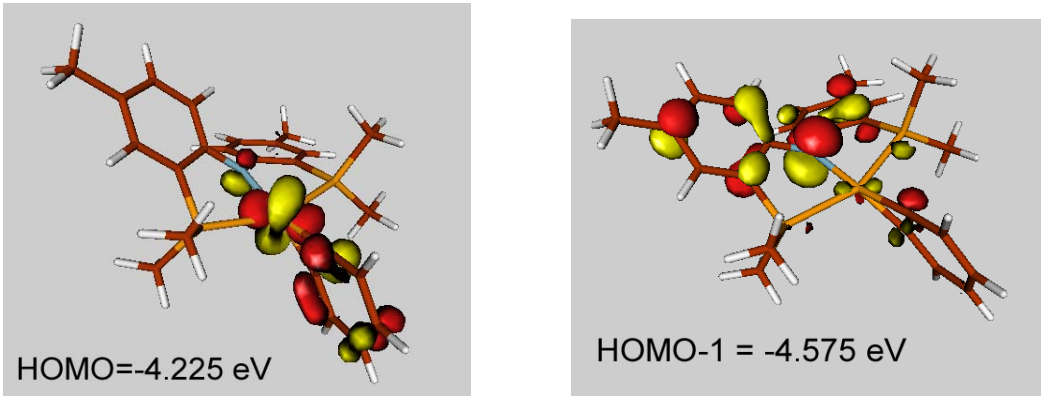

Fig. S2. EPR spectrum of polycrystalline complex (PNP)V($CH_2{}^tBu)_2$ at 10 K and 295.2 GHz (black trace) accompanied using simulations assuming a powder pattern and using the same absolute values of the spin Hamiltonian parameters as in the main text. The top, blue trace was simulated using a negative value for *D*, while the bottom, red trace used a positive value for the same parameter. Single-crystal linewidth used: 400 G, isotropic. The group of resonances at ca. 10.6 T originating from V(IV) and other impurities was not simulated.

**Theoretical Studies**

The electronic structure of reactant complex **1** consists of a triplet state and the activation of benzene proceeds on the triplet potential energy surface. The HOMO of **1** is metal-based with considerable spin density on the aryl rings of the PNP ligand backbone. Loss of neopentane from **1** leaves coordinatively unsaturated neopentylidene complex **A**, which has a metal-based HOMO also with some pincer ligand character. After activation of benzene by **A**, the new phenyl ligand in **B** contributes moderately to HOMO-1, while

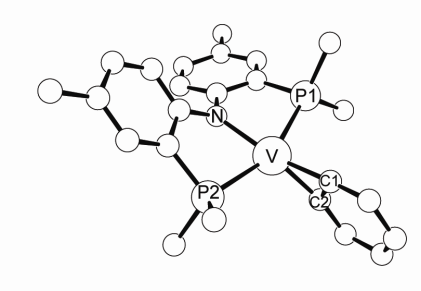
the HOMO consistently displays considerable character on the terdentate ligand backbone. However, upon liberation of a second neopentane molecule and once no alkyl ligands are present in benzyne complex **C**, while the HOMO is mostly composed of metal character, some benzyne character is also present and no aryl groups from the PNP ligand backbone appear to contribute. Nevertheless, HOMO-1 is located mostly on the ligand backbone. This different distribution of HOMO's in benzyne complex **C** may be the result of a more efficient delocalization of spin by the presence of an additional aromatic group in the system that can act as a π-acid. The HOMO and HOMO-1 of benzyne complex **C** are separated by 8 kcal $mol^{-1}$ and are shown below.

**Fig. S1.** HOMO and HOMO-1 of benzyne complex **C**.

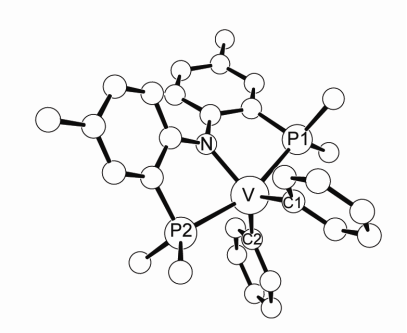



Benzyne complex **C** is capable of activating a second benzene molecule to form diphenyl complex **4**. The stability of **4** can be partially attributed to the ability of the phenyl rings to interact as π–acids, but the HOMO is located on the PNP ligand as observed for the precursor alkyl containing intermediates. However HOMO-1 of **4** is only 6 kcal $mol^{-1}$ below the HOMO and is partially located on the phenyl rings.

**Fig. S2**. Comparison of geometrical parameters of benzyne complex **C** and diphenyl complex **4.**




V–N: 2.075
V–P1: 2.507
V–P2: 2.525
V–C1: 1.982
V–C2: 1.968




V–N: 1.995
V–P1: 2.511
V–P2: 2.511
V–C1: 2.052
V–C2: 2.052

**Fig. S3.** Comparison of **TS-3** and **TS-4.** Superimposition of complex fragment of **TS-3** and **TS-4**.

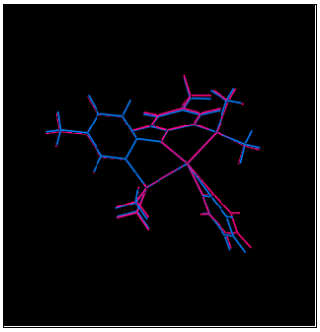
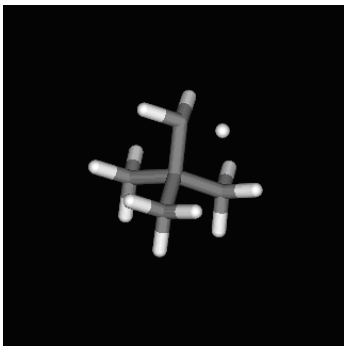
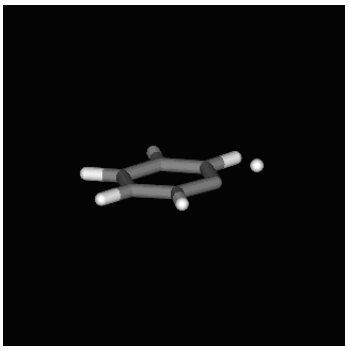


**Fig. S4.** Comparison of electronic energy of activated neopentane with activated benzene.



(A)



(B)

Activated neopentane substrate in **TS-3**

Activated benzene substrate in **TS-4**

(A) is 7.93 kcal mol$^{-1}$ higher in electronic energy than (B).

Transition states **TS-3** and **TS-4** are compared to provide a rationale for the difference in energy between the activation of C–H in benzene compared to the backward reaction corresponding to C–H activation in neopentane. Since the complex fragments of **TS-3** and **TS-4** are nearly superimposable as seen above, we consider that the main difference in energy between these two transition states can be attributed to the structural distortions associated with the activated substrate and its interactions with the complex fragment. The difference in electronic energy between the two activated fragments is approximately 8 kcal mol$^{-1}$ which is within 1 kcal mol$^{-1}$ with respect to the difference in free energy of the two transition states.

**Figure S5 Comparison of the PES with full model and small model**

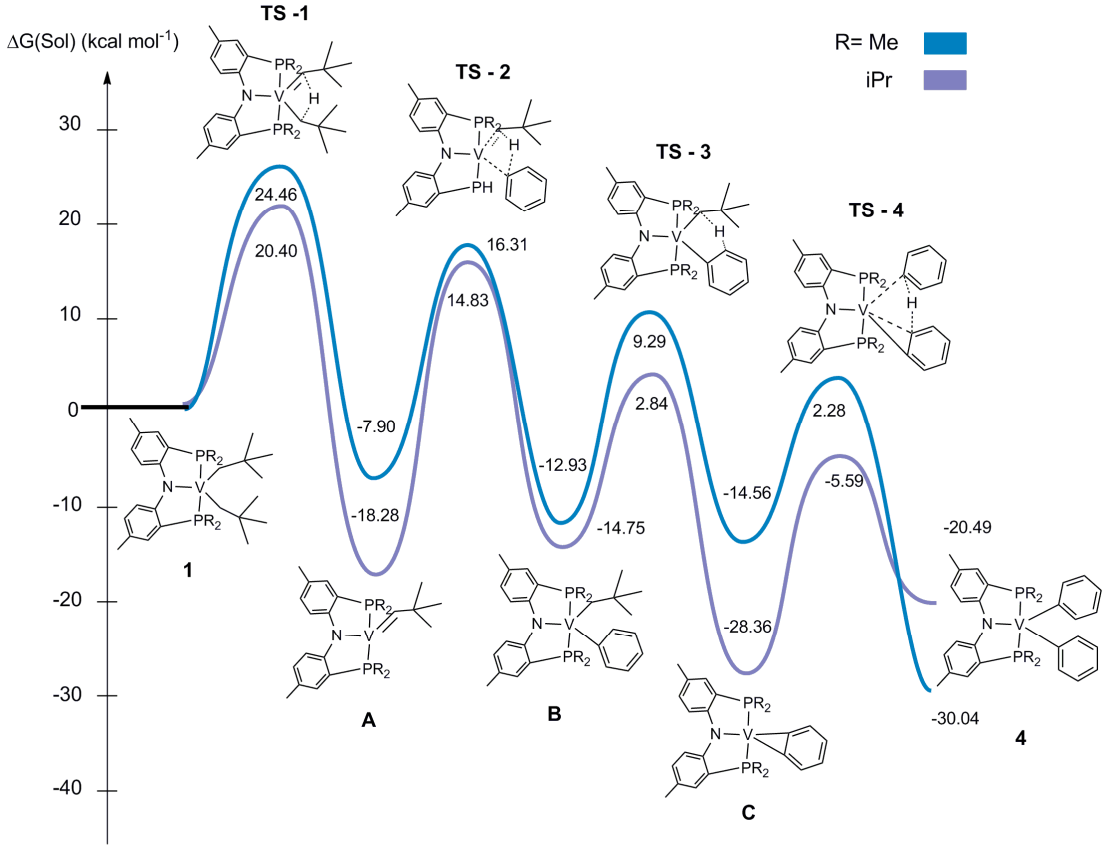
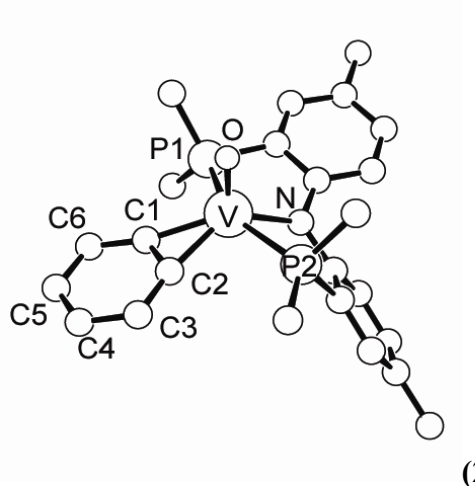


**Figure S6 Geometrical parameters of modeled (PNP)V=O($\eta^2$-$C_6H_4$) (2) and (PNP)V($\kappa^2$-O-$C_6H_4$) (2t)**

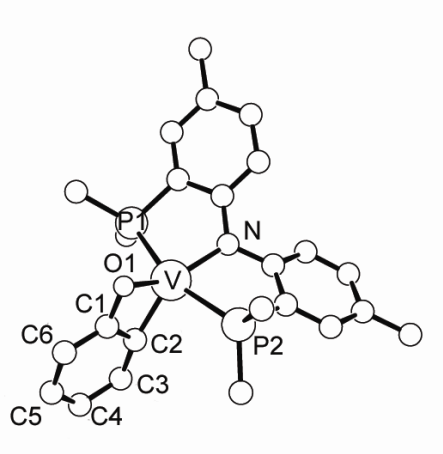
In order to provide theoretical support to our assignment of **2** based on spectral data and DFT-optimized structure, we have made a comparison with its isomer, **2t**, which has an inserted O-atom into the formal benzyne V-C carbon**.** Complex **2t** has a different geometry as the oxygen atom becomes part of the ortho-activated phenoxy fragment. The high spin character of **2t** is the result of the trivalent V in this complex. The difference in energy between the two compounds is 15.19 kcal $mol^{-1}$ in favor of **2**, which is consistent with its isolation and its NMR spectroscopic data.




**(2)**

| Selected Bond Distances (Å) and Angles (°) | | Computed NMR Shieldings (calibrated) | |
|---|---|---|---|
| **V-C1** | **2.033** | **δ(ppm)** | **$^1$H(from above)** |
| **V-C2** | **2.031** | **8.08** | **6** |
| **V-P1** | **2.451** | **7.99** | **5** |
| **V-P2** | **2.458** | **7.71** | **4** |
| **V-N** | **2.100** | **7.66** | **3** |
| **V-O** | **1.592** | | |
| **C1-C2** | **1.338** | | |
| **C1-C6** | **1.400** | | |
| **C2-C3** | **1.401** | | |
| **C3-C4** | **1.396** | | |
| **C4-C5** | **1.411** | | |
| **C5-C6** | **1.396** | | |
| **P1-V-P2** | **149.78** | | |

| | | | |
|---|---|---|---|
| **C1-V-C2** | **38.43** | | |
| **N-V-C1** | **131.41** | | |
| **N-V-C2** | **131.99** | | |
| **O-V-N** | **115.48** | | |
| **O-V-C1** | **108.06** | | |
| **O-V-C2** | **109.06** | | |




**(2t)**

| **Selected Bond Distances (Å) and Angles (°)** | |
|---|---|
| **V-C1** | **2.290** |
| **V-C2** | **1.988** |
| **V-P1** | **2.516** |
| **V-P2** | **2.516** |
| **V-N** | **2.013** |
| **V-O** | **1.916** |
| **C1-C2** | **1.436** |
| **C1-C6** | **1.400** |
| **C2-C3** | **1.393** |
| **C3-C4** | **1.402** |
| **C4-C5** | **1.399** |
| **C5-C6** | **1.398** |
| **P1-V-P2** | **159.56** |
| **O1-V-C2** | **74.89** |
| **N-V-C2** | **139.76** |
| **N-V-O1** | **144.72** |

**Computational Details**

All calculations were carried out using Density Functional Theory as implemented in the Jaguar 7 suite[S12] of ab initio quantum chemistry programs. Geometry optimizations were

performed with the B3LYP[S13-S16] functional and the 6-31G** basis set with no symmetry restrictions. Vanadium was represented using the Los Alamos LACVP basis[S17, S18]. The energies of the optimized structures were reevaluated by additional single-point calculations on each optimized geometry using PBE[S26] and Dunning's correlation-consistent triple-ζ basis set[S19] cc-pVTZ(-f). For all transition metals, we used a modified version of LACVP, designated as LACV3P, in which the exponents were decontracted to match the effective core potential with the triple-ζ quality basis and used PBE. Vibrational frequency calculations based on analytical second derivatives at the B3LYP/6-31G** (LACVP) level of theory were carried out to derive the zero-point-energy (ZPE) and entropy corrections at room temperature utilizing unscaled frequencies. Note that by entropy here we refer specifically to the vibrational/rotational/translational entropy of the solute(s); the entropy of the solvent is implicitly included in the dielectric continuum model. We used a truncated model for the geometries and vibrational frequency calculations by replacing i-propyl groups with methyl groups.

Solvation energies were evaluated by a self-consistent reaction field (SCRF)[S20-S22] approach based on accurate numerical solutions of the Poisson-Boltzmann equation.[S23] In the results reported, solvation calculations were carried out at the optimized gas-phase geometry employing the dielectric constant of $\epsilon = 2.287$ for benzene. As is the case for all continuum models, the solvation energies are subject to empirical parameterization of the atomic radii that are used to generate the solute surface. We employ the standard set of optimized radii in Jaguar for H (1.150 Å), C (1.900 Å), N (1.600 Å), P (2.150Å). We make use of the metallic van der Waals radius 1.572 Å for V.

The energy components have been computed following the protocol of our previous work.[S24] The free energy in solution phase G(sol) was calculated as follows:

$$G(\text{sol}) = G(\text{gas}) + G_{\text{solv}} \quad (1)$$
$$G(\text{gas}) = H(\text{gas}) - TS(\text{gas}) \quad (2)$$
$$H(\text{gas}) = H(\text{SCF}) + ZPE \quad (3)$$

G(gas) = free energy in gas phase; Gsolv = free energy of solvation as computed using the continuum solvation model; H(gas) = enthalpy in gas phase; T = temperature (383.15K); S(gas) = entropy in gas phase; H(SCF) = Self consistent field energy, i.e. "raw" electronic energy as computed from the SCF procedure; ZPE = zero point energy. The models used in this study consist of ~80 atoms, which represent the truncated substrates. We found that a smaller model is also able to reproduce the most important features of the studied reaction.

**Additional comments**

Probing for σ-bond metathesis using a constrained geometry approach generated energies in the order of >50 kcal $mol^{-1}$ above the reactant, which is consistent with our previous findings pursuing this route. The reader is encouraged to look at our previous work where we have evaluated in detail a variety of alternatives for the possible pathways in related reactions.[S25] In the present work we limit our mechanistic evaluations to the most favorable pathway found in our previous studies.

**Table S1: Selected computed bond distances in Å**

| Bond | 1 | TS-1 | A | TS-2 | B |
|---|---|---|---|---|---|
| V–N | 2.011 | 2.087 | 2.049 | 2.083 | 2.004 |
| V–P1 | 2.584 | 2.608 | 2.493 | 2.611 | 2.528 |
| V–P2 | 2.581 | 2.571 | 2.497 | 2.602 | 2.547 |
| V–C1 | 2.123 | 1.916 | 1.882 | 1.924 | 2.111 |
| V–C2 | 2.123 | 2.258 | - | 2.231 | 2.073 |
| C1–C2 | 3.941 | 3.040 | - | 2.954 | 3.777 |

| | | | | | |
|---|---|---|---|---|---|
| C1–H1 | 1.104 | 1.629 | - | 1.651 | 1.104 |
| C2–H1 | 4.478 | 1.466 | - | 1.354 | 4.391 |

**Table S2: Selected computed bond distances in Å**

| Bond | TS-3 | C | TS-4 | 4 | |
|---|---|---|---|---|---|
| V–N | 2.031 | 2.075 | 2.032 | 1.995 | |
| V–P1 | 2.530 | 2.507 | 2.528 | 2.511 | |
| V–P2 | 2.542 | 2.525 | 2.541 | 2.511 | |
| V–C1 | 2.271 | 1.982 | 2.135 | 2.052 | |
| V–C2 | 2.140 | 1.968 | 2.258 | 2.052 | |
| C1–C2 | 2.974 | 1.407 | 2.901 | 3.584 | |
| C1–H1 | 1.438 | - | 1.603 | - | |
| C2–H1 | 1.548 | - | 1.325 | - | |

**Table S3.** Coordinates for Geometry Optimized Structures

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**1**

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| | | | |
|---|---|---|---|
| V | -0.098859286 | 0.790377679 | -0.249333060 |
| P | -1.204734723 | 3.075318940 | 0.233071699 |
| N | -2.022697777 | 0.267146102 | 0.015984633 |
| P | -0.002932137 | -1.765634249 | -0.597973111 |
| C | -2.345024143 | -0.968059438 | 0.610060379 |
| C | -1.471510932 | -2.076992456 | 0.448409052 |
| C | -1.742563806 | -3.291377479 | 1.085158617 |
| H | -1.059201380 | -4.127379641 | 0.949861525 |
| C | -2.868087154 | -3.472696330 | 1.895690842 |
| C | -3.158871658 | -4.803770486 | 2.549331969 |
| C | -3.717341041 | -2.370671575 | 2.061112215 |
| H | -4.591801950 | -2.464847114 | 2.702106489 |
| C | -3.468344462 | -1.149855827 | 1.442590448 |
| H | -4.143419096 | -0.317325110 | 1.611758414 |
| C | -3.053379908 | 1.133103926 | -0.396928523 |
| C | -2.840545720 | 2.537929036 | -0.386243891 |
| C | -3.830489181 | 3.408493659 | -0.851485904 |
| H | -3.646141507 | 4.480823128 | -0.835910505 |
| C | -5.057486435 | 2.948744400 | -1.340480959 |
| C | -6.126805304 | 3.908741528 | -1.807858674 |
| C | -5.253648040 | 1.561549830 | -1.362857656 |
| H | -6.185966355 | 1.162789308 | -1.758119781 |
| C | -4.284172515 | 0.673328348 | -0.909054342 |
| H | -4.471768597 | -0.394228760 | -0.959644856 |
| C | -0.471307124 | -2.514799936 | -2.229396550 |
| H | -1.310619586 | -1.953796580 | -2.648562194 |
| C | 1.293228241 | -2.938608099 | 0.005745835 |
| H | 1.554857892 | -2.697057706 | 1.039056704 |
| C | -1.559993375 | 3.610111188 | 1.973854994 |
| H | -1.862261395 | 2.737055601 | 2.558012878 |
| C | -0.864989484 | 4.689237972 | -0.603631168 |
| H | -0.785690819 | 4.533564752 | -1.682551662 |
| C | 1.007680085 | 0.672224080 | 1.558507855 |
| C | 2.353734099 | 1.314545768 | 1.968390839 |
| C | 0.313067543 | 1.292853696 | -2.270703278 |
| H | -6.839163759 | 3.416018145 | -2.476911593 |
| H | -5.696931057 | 4.760127673 | -2.346780840 |
| H | -6.701432156 | 4.317394125 | -0.965953287 |
| H | -3.852571167 | -4.691689903 | 3.388318950 |
| H | -2.246062461 | -5.273639823 | 2.931804519 |
| H | -3.613756902 | -5.511529541 | 1.843663923 |
| C | 2.622858652 | 1.051680072 | 3.469257096 |
| H | 1.830448638 | 1.483815034 | 4.091674842 |
| H | 2.658239458 | -0.023902270 | 3.678124195 |
| H | 3.578296428 | 1.487879238 | 3.790651835 |
| C | 3.508624126 | 0.694070918 | 1.156941155 |
| H | 3.544210195 | -0.393258460 | 1.296414764 |
| H | 3.395031975 | 0.888612521 | 0.086142807 |
| H | 4.478915022 | 1.100628014 | 1.469173192 |
| C | 2.337870811 | 2.839423146 | 1.743552811 |
| H | 3.294164000 | 3.293489177 | 2.032726165 |
| H | 2.152021523 | 3.088593663 | 0.693520391 |
| H | 1.554627181 | 3.314412849 | 2.346336732 |
| C | 1.662271299 | 1.411709172 | -3.017822234 |
| C | 2.465841179 | 2.610729221 | -2.475258381 |
| H | 3.411484711 | 2.735954836 | -3.017695479 |
| H | 1.896433526 | 3.542093122 | -2.581974140 |
| H | 2.704348317 | 2.486632754 | -1.414342733 |
| C | 1.406544097 | 1.645541582 | -4.526222164 |
| H | 2.347119090 | 1.746806514 | -5.084430654 |
| H | 0.845109663 | 0.811382942 | -4.963463870 |
| H | 0.821339285 | 2.558485526 | -4.687261064 |
| C | 2.499474211 | 0.125807597 | -2.866327557 |
| H | 1.970820708 | -0.736144246 | -3.290953748 |
| H | 3.458989771 | 0.212606455 | -3.391808335 |
| H | 2.711121584 | -0.094630899 | -1.814931374 |
| H | -0.285646729 | 0.501519147 | -2.758767710 |
| H | -0.248611284 | 2.226086690 | -2.448836071 |
| H | 0.218939752 | 1.058817837 | 2.231657418 |
| H | 1.073456409 | -0.405005131 | 1.787000159 |
| H | -0.765169919 | -3.562838644 | -2.112125867 |
| H | 0.370123076 | -2.450722226 | -2.925697053 |
| H | 2.187401102 | -2.818576813 | -0.613569944 |
| H | 0.970545853 | -3.983172271 | -0.048252689 |
| H | -2.363199755 | 4.353505238 | 2.000645495 |
| H | -0.659056144 | 4.034809066 | 2.426263119 |
| H | 0.091786881 | 5.076101088 | -0.239770894 |
| H | -1.640304805 | 5.435736833 | -0.404245584 |

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**TS -1**

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| | | | |
|---|---|---|---|
| H | 0.028963775 | -0.114400229 | 0.149013703 |
| C | 0.041030460 | -0.229641651 | 1.610058525 |
| V | 1.759994971 | 0.024373597 | 0.168893529 |
| P | 2.263184946 | 2.482929685 | 0.727821041 |
| N | 3.825825134 | 0.043437207 | 0.464709827 |
| P | 2.449779323 | -2.470687486 | -0.148805395 |
| C | 4.660405669 | -0.838212803 | -0.240238866 |
| C | 4.166973337 | -2.104001997 | -0.650569704 |
| C | 4.968462986 | -2.976889316 | -1.397103741 |
| H | 4.567453055 | -3.943051151 | -1.697001729 |
| C | 6.272638159 | -2.650888920 | -1.774301746 |
| C | 7.135084601 | -3.603251342 | -2.569096856 |
| C | 6.751383928 | -1.390854649 | -1.379916681 |
| H | 7.755663042 | -1.088696505 | -1.672105376 |
| C | 5.976334460 | -0.508258644 | -0.638980940 |
| H | 6.381258703 | 0.461704779 | -0.368185827 |
| C | 4.381704112 | 0.890127322 | 1.433798179 |
| C | 3.741863760 | 2.122536462 | 1.736786082 |
| C | 4.223876611 | 2.948696276 | 2.758902870 |
| H | 3.712057669 | 3.884661340 | 2.973019494 |
| C | 5.343550602 | 2.611477700 | 3.522386910 |
| C | 5.859212566 | 3.510813006 | 4.621751610 |
| C | 5.971759220 | 1.392184968 | 3.222720954 |
| H | 6.837349413 | 1.083343869 | 3.806547163 |
| C | 5.513240436 | 0.553667415 | 2.215035370 |
| H | 6.020094927 | -0.388531459 | 2.034170240 |
| C | 2.661907154 | -3.640653368 | 1.279033939 |
| H | 1.688073239 | -4.010763615 | 1.613085190 |
| C | 1.784371997 | -3.592987701 | -1.461410011 |
| H | 1.755335530 | -3.058849449 | -2.414376773 |
| H | 0.763108570 | -3.881184416 | -1.195110622 |
| H | 2.382992608 | -4.501433139 | -1.578678039 |
| H | 3.134366761 | -3.106742234 | 2.107856366 |
| H | 3.292909195 | -4.490429938 | 1.000815057 |
| C | 2.914990627 | 3.614898073 | -0.591310379 |
| H | 2.100030084 | 3.981050097 | -1.221685448 |
| C | 1.243644762 | 3.636025825 | 1.758807833 |
| H | 0.334742255 | 3.894469717 | 1.207949816 |
| H | 3.611645524 | 3.051672756 | -1.217110790 |
| H | 3.439736580 | 4.465974787 | -0.145856597 |
| H | 1.776784752 | 4.560048914 | 2.003115394 |
| H | 0.954069146 | 3.137820623 | 2.688050195 |
| C | 0.606114563 | 0.094001986 | -1.359631763 |
| C | -0.202889465 | 1.047880196 | -2.247843197 |
| H | 6.001535881 | 2.961126400 | 5.559987927 |
| H | 5.165149952 | 4.332856231 | 4.822913536 |
| H | 6.828679279 | 3.955946309 | 4.363107442 |
| H | 7.557784456 | -3.119623920 | -3.457840648 |
| H | 6.562885296 | -4.473001291 | -2.906470181 |
| H | 7.980376697 | -3.975786225 | -1.976239144 |

| | | | |
|---|---|---|---|
| C | -1.425195021 | 0.318603810 | -2.857008536 |
| H | -1.107893451 | -0.555008207 | -3.438378889 |
| H | -2.111645407 | -0.032064110 | -2.078695263 |
| H | -1.990521513 | 0.978887653 | -3.527342844 |
| C | -0.708224032 | 2.295127895 | -1.497982674 |
| H | -1.366539344 | 2.022039931 | -0.666537216 |
| H | 0.123038408 | 2.874580431 | -1.089324852 |
| H | -1.273144772 | 2.953164128 | -2.170128526 |
| C | 0.713220345 | 1.498080404 | -3.413384522 |
| H | 0.170225144 | 2.146276779 | -4.114784034 |
| H | 1.581902815 | 2.046226556 | -3.036567473 |
| H | 1.085678342 | 0.633426045 | -3.974011724 |
| C | -1.291691218 | -1.008474993 | 1.786953197 |
| C | -2.460907204 | -0.202312957 | 1.190833951 |
| H | -3.410854991 | -0.732076382 | 1.327981640 |
| H | -2.552342792 | 0.776941187 | 1.675793189 |
| H | -2.325350627 | -0.034894508 | 0.118221359 |
| C | -1.554357272 | -1.218524083 | 3.293723833 |
| H | -2.501737398 | -1.746571726 | 3.460532983 |
| H | -0.755428033 | -1.810161901 | 3.756111001 |
| H | -1.607674648 | -0.259546599 | 3.821923429 |
| C | -1.218614903 | -2.382693360 | 1.095774194 |
| H | -0.415942165 | -2.995044163 | 1.522711850 |
| H | -2.157649857 | -2.934736459 | 1.221660936 |
| H | -1.030942480 | -2.274376264 | 0.022375466 |
| H | 0.801318348 | -0.743163555 | 2.225095751 |
| H | -0.084010645 | 0.776867400 | 2.027924304 |
| H | 0.571498215 | -0.911359314 | -1.815137194 |

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**A**

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| | | | |
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| V | -0.199555559 | 0.822565667 | 0.107923301 |
| P | -1.314714322 | 3.055686010 | 0.158345557 |
| N | -2.155633367 | 0.212336759 | 0.117673963 |
| P | 0.022586195 | -1.497040932 | -0.777193520 |
| C | -2.372221243 | -1.113437278 | 0.532707865 |
| C | -1.413714664 | -2.105170287 | 0.181718244 |
| C | -1.552771989 | -3.422105172 | 0.628692776 |
| H | -0.804666186 | -4.161967064 | 0.352039324 |
| C | -2.626882621 | -3.825682476 | 1.428336890 |
| C | -2.784805315 | -5.263436704 | 1.865877811 |
| C | -3.552762121 | -2.839966298 | 1.795092851 |
| H | -4.383140104 | -3.107313182 | 2.445849701 |
| C | -3.432945665 | -1.520906345 | 1.369134119 |
| H | -4.156840353 | -0.785594877 | 1.703286918 |
| C | -3.226095104 | 1.070924701 | -0.147716038 |
| C | -3.023005346 | 2.481977435 | -0.141861764 |
| C | -4.079552720 | 3.358613376 | -0.411793773 |
| H | -3.894424371 | 4.431695449 | -0.387722908 |
| C | -5.364410301 | 2.911250349 | -0.727229799 |
| C | -6.501048771 | 3.872735455 | -0.984151866 |
| C | -5.546371792 | 1.522137693 | -0.790111031 |
| H | -6.520995689 | 1.127107030 | -1.071424959 |
| C | -4.520352827 | 0.627469062 | -0.513712387 |
| H | -4.712254955 | -0.436337450 | -0.596272948 |
| C | -0.404537936 | -1.899964402 | -2.540593772 |
| H | 0.434266893 | -1.639943521 | -3.194407575 |
| C | 1.392087085 | -2.690975385 | -0.441586503 |
| H | 1.141138359 | -3.714233152 | -0.738454904 |
| H | 2.277748584 | -2.375853790 | -1.001712948 |
| H | 1.631863514 | -2.668100712 | 0.623556443 |
| H | -0.635573750 | -2.963126824 | -2.660185415 |
| H | -1.275372667 | -1.311351937 | -2.840259574 |
| C | -1.403383372 | 4.060146479 | 1.710894923 |
| H | -2.172393532 | 4.836500278 | 1.643353234 |
| C | -1.026643894 | 4.364149996 | -1.124125755 |
| H | -1.769422048 | 5.166095151 | -1.075163711 |
| H | -1.632888883 | 3.395908124 | 2.546988479 |
| H | -0.432053438 | 4.526724673 | 1.899937482 |
| H | -0.032184123 | 4.797191665 | -0.976617031 |
| H | -1.061133586 | 3.912169452 | -2.119124415 |
| C | 0.858517043 | 0.771368084 | 1.663348486 |
| C | 2.302939734 | 1.136474218 | 1.978300103 |
| H | -7.233666507 | 3.448242737 | -1.678738153 |
| H | -6.142645867 | 4.814612307 | -1.413208755 |
| H | -7.040879819 | 4.123428396 | -0.060905750 |
| H | -3.339583438 | -5.335624585 | 2.806907675 |
| H | -1.813654902 | -5.748126356 | 2.012701598 |
| H | -3.332461874 | -5.857370560 | 1.121660885 |
| C | 2.339895939 | 2.257332753 | 3.045430611 |
| H | 1.833492312 | 3.158427773 | 2.682561717 |
| H | 1.836159371 | 1.938465586 | 3.964798258 |
| H | 3.372942889 | 2.527406326 | 3.303011497 |
| C | 3.053193653 | -0.096867923 | 2.536791579 |
| H | 2.563706029 | -0.476104170 | 3.440943931 |
| H | 3.072978559 | -0.907720081 | 1.800933250 |
| H | 4.091306928 | 0.151992130 | 2.795062937 |
| C | 3.030334859 | 1.631278520 | 0.708594274 |
| H | 4.073092095 | 1.903921512 | 0.916203268 |
| H | 3.040886009 | 0.852320342 | -0.064553285 |
| H | 2.533011257 | 2.517248692 | 0.293891724 |
| H | 0.333079735 | 0.386046236 | 2.555699091 |

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**TS-2**

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| | | | |
|---|---|---|---|
| H | -0.032362554 | -0.007650018 | 0.025739910 |
| C | -0.134672240 | 0.009438944 | 1.376011245 |
| V | 1.727273404 | 0.022096474 | 0.146754521 |
| P | 2.236669102 | 2.565111829 | -0.062136232 |
| N | 3.801315808 | 0.142445178 | 0.300813360 |
| P | 2.534614267 | -2.340286710 | 0.912687782 |
| C | 4.580126054 | -0.925650529 | -0.181687464 |
| C | 4.112510689 | -2.250745874 | 0.002669675 |
| C | 4.801142817 | -3.335033721 | -0.548638144 |
| H | 4.416602408 | -4.342951387 | -0.410153130 |
| C | 5.980660052 | -3.161367337 | -1.279708436 |
| C | 6.727389193 | -4.337884203 | -1.864032685 |
| C | 6.449835019 | -1.849344531 | -1.442087232 |
| H | 7.359470516 | -1.677802191 | -2.014726178 |
| C | 5.773727744 | -0.755838272 | -0.910919279 |
| H | 6.156105616 | 0.247257458 | -1.074058943 |
| C | 4.445723474 | 1.246341041 | 0.871377596 |
| C | 3.820429246 | 2.521528009 | 0.841263262 |
| C | 4.395373136 | 3.615529044 | 1.498519573 |
| H | 3.890441564 | 4.578631509 | 1.473728115 |
| C | 5.602251801 | 3.514046258 | 2.194397273 |
| C | 6.213218095 | 4.697231790 | 2.908520900 |
| C | 6.226772153 | 2.257013569 | 2.204833643 |
| H | 7.164144297 | 2.133884585 | 2.744724406 |
| C | 5.674829385 | 1.154461141 | 1.565876097 |
| H | 6.181843764 | 0.196344202 | 1.618221826 |
| C | 3.033605146 | -2.259561907 | 2.700980050 |
| H | 2.139068694 | -2.304431325 | 3.329777392 |
| C | 1.990144544 | -4.106237071 | 0.785499143 |
| H | 2.756865022 | -4.787782326 | 1.167125399 |
| H | 1.759646260 | -4.365440396 | -0.249439429 |
| H | 1.083586149 | -4.239621496 | 1.383232679 |
| H | 3.539139875 | -1.308547702 | 2.884072910 |
| H | 3.706649403 | -3.081401111 | 2.964436593 |
| C | 2.705329217 | 3.046278433 | -1.789906370 |
| H | 3.272319478 | 3.982110732 | -1.802824794 |
| C | 1.381088496 | 4.095300215 | 0.536880971 |
| H | 0.416242453 | 4.186357823 | 0.029103007 |
| H | 1.803287728 | 3.156701351 | -2.399825450 |
| H | 3.313018003 | 2.245840462 | -2.217668049 |
| H | 1.201656048 | 4.024983555 | 1.612775404 |
| H | 1.964700712 | 4.998505963 | 0.333429827 |
| C | 0.677589197 | -0.083054639 | -1.462618913 |

| | | | |
|---|---|---|---|
| C | -0.037809050 | -1.078552992 | -2.373365623 |
| H | 6.439115549 | 4.462941878 | 3.955942272 |
| H | 5.538675422 | 5.559039403 | 2.901947006 |
| H | 7.155189334 | 5.013212322 | 2.442212495 |
| H | 6.995392980 | -4.164034472 | -2.912552485 |
| H | 6.126441256 | -5.251548220 | -1.822724008 |
| H | 7.661984243 | -4.535134995 | -1.323227511 |
| C | 0.535591311 | -0.918115481 | -3.802345151 |
| H | 0.386259802 | 0.102015428 | -4.174443007 |
| H | 1.610370530 | -1.127796556 | -3.816774519 |
| H | 0.042531564 | -1.605847252 | -4.501724428 |
| C | 0.157822164 | -2.538225061 | -1.930271363 |
| H | 1.220872957 | -2.799641260 | -1.933450006 |
| H | -0.234039702 | -2.703163211 | -0.921092686 |
| H | -0.363345853 | -3.226927205 | -2.606990531 |
| C | -1.553474556 | -0.761991105 | -2.408533769 |
| H | -2.081556223 | -1.429625075 | -3.101901922 |
| H | -2.004622619 | -0.882178013 | -1.417110468 |
| H | -1.731703601 | 0.269023460 | -2.735123054 |
| C | -0.619356946 | -1.193777847 | 1.935095052 |
| H | -0.370246396 | -2.138527578 | 1.458916753 |
| C | -1.417580073 | -1.202346974 | 3.078466365 |
| H | -1.763600880 | -2.146701536 | 3.492741400 |
| C | -1.780271340 | 0.001308775 | 3.688425425 |
| H | -2.403671036 | -0.001510981 | 4.578730230 |
| C | -1.356365062 | 1.208510370 | 3.129397206 |
| H | -1.651268554 | 2.150535336 | 3.586058424 |
| C | -0.562730875 | 1.209788850 | 1.981445065 |
| H | -0.270747164 | 2.160718740 | 1.547396432 |
| H | 0.517277950 | 0.929841900 | -1.874062490 |

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**B**

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| | | | |
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| P | -1.138562565 | 3.081859092 | 0.229834640 |
| N | -2.010084427 | 0.262029133 | 0.145406974 |
| P | 0.068394872 | -1.706026740 | -0.483379137 |
| C | -2.343774129 | -1.015986609 | 0.646838423 |
| C | -1.468636385 | -2.112539769 | 0.420850947 |
| C | -1.769377137 | -3.376763560 | 0.936420895 |
| H | -1.086024703 | -4.202748176 | 0.749707048 |
| C | -2.922330759 | -3.619134169 | 1.689621840 |
| C | -3.253193282 | -5.003479954 | 2.196754823 |
| C | -3.761263794 | -2.524971429 | 1.939179321 |
| H | -4.651360453 | -2.665534886 | 2.549258526 |
| C | -3.483415562 | -1.256079959 | 1.440475414 |
| H | -4.152073888 | -0.433276253 | 1.670535964 |
| C | -3.032480113 | 1.135268499 | -0.277533291 |
| C | -2.801411732 | 2.539039785 | -0.305217651 |
| C | -3.785231635 | 3.412606122 | -0.780975843 |
| H | -3.580887515 | 4.481332096 | -0.795871556 |
| C | -5.021292522 | 2.962105108 | -1.252092082 |
| C | -6.082861491 | 3.922729788 | -1.735226531 |
| C | -5.231661278 | 1.576532954 | -1.249365899 |
| H | -6.167642000 | 1.180530338 | -1.638832891 |
| C | -4.272400118 | 0.685184413 | -0.782142600 |
| H | -4.474802533 | -0.379365952 | -0.822138467 |
| C | -0.209287497 | -2.295665200 | -2.215762782 |
| H | 0.694305474 | -2.113840247 | -2.805971022 |
| C | 1.339021811 | -2.894670839 | 0.139937706 |
| H | 1.496159207 | -2.737057613 | 1.210086325 |
| H | 1.056262552 | -3.938131351 | -0.033483712 |
| H | 2.282914703 | -2.699581089 | -0.378581207 |
| H | -0.460950565 | -3.360974831 | -2.244155630 |
| H | -1.022514658 | -1.717257716 | -2.661409462 |
| C | -1.415178212 | 3.814539761 | 1.910431866 |
| H | -1.761791356 | 3.029366827 | 2.587891314 |
| C | -0.737518169 | 4.560610313 | -0.799725698 |
| H | -0.664300772 | 4.253355692 | -1.846103156 |
| H | -0.474087171 | 4.216273862 | 2.299448768 |
| H | -2.162594477 | 4.614284479 | 1.879046269 |
| H | -1.479398927 | 5.359247699 | -0.700120291 |
| H | 0.237806703 | 4.947209713 | -0.487668437 |
| C | 0.993454540 | 0.746039558 | 1.757808224 |
| C | 2.445266315 | 1.253809331 | 1.937928427 |
| H | -6.720684637 | 3.462147436 | -2.496799179 |
| H | -5.640278817 | 4.824473916 | -2.171209624 |
| H | -6.739969966 | 4.247572753 | -0.917378761 |
| H | -3.876273756 | -4.961574796 | 3.095747641 |
| H | -2.348072332 | -5.568924015 | 2.442450120 |
| H | -3.804715249 | -5.586987996 | 1.447391513 |
| C | 2.785945521 | 1.350727686 | 3.443313903 |
| H | 2.121344141 | 2.059127527 | 3.951621606 |
| H | 2.670846988 | 0.377248404 | 3.933906574 |
| H | 3.819445223 | 1.687376655 | 3.601627182 |
| C | 3.439756170 | 0.272475072 | 1.284632116 |
| H | 3.375825413 | -0.716558183 | 1.753731271 |
| H | 3.238699601 | 0.145054050 | 0.216013355 |
| H | 4.473708973 | 0.624039358 | 1.390326595 |
| C | 2.621370309 | 2.651581067 | 1.308215819 |
| H | 3.638567757 | 3.032265334 | 1.465983738 |
| H | 2.434841923 | 2.636128889 | 0.228692472 |
| H | 1.928490586 | 3.372630140 | 1.759201050 |
| H | 0.329421373 | 1.344256779 | 2.406726432 |
| C | 0.591039491 | 1.209578033 | -1.968978405 |
| C | 1.940085889 | 1.192975157 | -2.379835907 |
| H | 2.725550544 | 0.954480566 | -1.664373896 |
| C | 2.318841695 | 1.476890737 | -3.695839759 |
| H | 3.370742258 | 1.458830038 | -3.974572966 |
| C | 1.349932576 | 1.777295577 | -4.655366801 |
| H | 1.640588068 | 1.994771218 | -5.680205338 |
| C | 0.003587029 | 1.793207194 | -4.285033115 |
| H | -0.760712947 | 2.022665933 | -5.025187593 |
| C | -0.363739766 | 1.517823562 | -2.963901327 |
| H | -1.423917359 | 1.545486536 | -2.710728920 |
| H | 0.933792283 | -0.284646822 | 2.145996054 |

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**TS-3**

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| | | | |
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| H | 0.057382265 | -0.087249636 | 0.116108823 |
| C | -0.009380393 | -0.235132825 | 1.544524911 |
| H | 0.889145385 | -0.444579686 | 2.144066292 |
| V | 1.284561978 | 1.172023539 | 0.318656943 |
| P | 3.413932893 | -0.216404600 | 0.295736862 |
| N | 2.537383530 | 2.416040784 | 1.323659815 |
| P | -0.157135945 | 3.233713641 | 0.583398257 |
| C | 2.021735825 | 3.356435369 | 2.240893647 |
| C | 0.725387605 | 3.898424704 | 2.037709692 |
| C | 0.177315514 | 4.801109222 | 2.955770294 |
| H | -0.817166336 | 5.204457066 | 2.775709563 |
| C | 0.863078367 | 5.200226602 | 4.105507509 |
| C | 0.276490127 | 6.199712096 | 5.074381421 |
| C | 2.127947294 | 4.633081090 | 4.320420447 |
| H | 2.680830622 | 4.892305964 | 5.221489135 |
| C | 2.694498876 | 3.735913356 | 3.422716792 |
| H | 3.668961627 | 3.310307830 | 3.638106464 |
| C | 3.926126465 | 2.380306202 | 1.088140652 |
| C | 4.535281910 | 1.191126607 | 0.608192796 |
| C | 5.908897950 | 1.150831734 | 0.340469744 |
| H | 6.350495415 | 0.224018610 | -0.021468242 |
| C | 6.736186813 | 2.262243283 | 0.509888243 |
| C | 8.221016683 | 2.202039635 | 0.239447793 |
| C | 6.121843394 | 3.446835497 | 0.943224967 |
| H | 6.722538033 | 4.347789045 | 1.055108825 |
| C | 4.762986989 | 3.511804600 | 1.222399829 |
| H | 4.332523212 | 4.455890481 | 1.537861066 |
| C | 0.003450280 | 4.522484594 | -0.733830161 |
| H | -0.407132966 | 5.483130948 | -0.407530294 |

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| C | -1.954774440 | 3.319526334 | 1.008714821 |
| H | -2.288083348 | 4.340954597 | 1.217298040 |
| H | -2.159073794 | 2.693359155 | 1.881060778 |
| H | -2.530112788 | 2.930708899 | 0.163306216 |
| H | -0.515877302 | 4.184939054 | -1.635330265 |
| H | 1.061877966 | 4.642911895 | -0.976082935 |
| C | 3.910861117 | -1.489960116 | 1.551051151 |
| H | 3.346028934 | -2.412511465 | 1.385355075 |
| C | 3.996349875 | -0.971995564 | -1.284485053 |
| H | 5.055146970 | -1.245403936 | -1.254380735 |
| H | 4.981276615 | -1.710748957 | 1.491197872 |
| H | 3.683068509 | -1.118341390 | 2.553734453 |
| H | 3.403164286 | -1.869482047 | -1.483300226 |
| H | 3.820185809 | -0.262630988 | -2.095791330 |
| C | -0.882621896 | -1.519091240 | 1.549664388 |
| H | 8.556708153 | 3.059299407 | -0.355412982 |
| H | 8.491556457 | 1.292794960 | -0.306047508 |
| H | 8.803018907 | 2.211447937 | 1.170189644 |
| H | 0.403013097 | 5.875918853 | 6.113700086 |
| H | -0.793751383 | 6.345708868 | 4.898874999 |
| H | 0.759780181 | 7.181224308 | 4.983986167 |
| C | -1.124048221 | -1.952894859 | 3.011620975 |
| H | -0.178672701 | -2.180934475 | 3.517709027 |
| H | -1.624363319 | -1.160832519 | 3.580790419 |
| H | -1.754539612 | -2.849694636 | 3.058631216 |
| C | -2.246673610 | -1.237544181 | 0.889217666 |
| H | -2.791677983 | -0.460338358 | 1.438328586 |
| H | -2.135406115 | -0.897525397 | -0.144408863 |
| H | -2.871243522 | -2.138668077 | 0.882155073 |
| C | -0.163669392 | -2.661503387 | 0.804571381 |
| H | -0.764081170 | -3.578917004 | 0.822810548 |
| H | 0.027855330 | -2.403984409 | -0.241746053 |
| H | 0.799949799 | -2.888542167 | 1.276824713 |
| C | 1.234214639 | 1.253340513 | -1.680187979 |
| C | 0.312245864 | 0.280308910 | -1.366484083 |
| C | -0.401484224 | -0.390908637 | -2.361271682 |
| H | -1.132429427 | -1.167995466 | -2.140584012 |
| C | -0.150526519 | -0.042097224 | -3.697890748 |
| H | -0.687271953 | -0.548100903 | -4.497648896 |
| C | 0.785113287 | 0.950325861 | -4.015129016 |
| H | 0.962913332 | 1.203213791 | -5.058755206 |
| C | 1.493869320 | 1.616177151 | -3.002754235 |
| H | 2.219121790 | 2.386017874 | -3.264609293 |
| H | -0.568047065 | 0.559476289 | 2.058557459 |

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**C**

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| | | | |
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| N | 2.657114340 | 2.520140141 | -0.314273528 |
| P | 0.166056710 | 3.402283672 | -1.485030638 |
| C | 1.974526537 | 3.384848674 | 0.562635206 |
| C | 0.736410817 | 3.948124091 | 0.158855754 |
| C | 0.013866953 | 4.784182761 | 1.017717330 |
| H | -0.931564131 | 5.204029499 | 0.678827448 |
| C | 0.463233553 | 5.091059771 | 2.303546693 |
| C | -0.307619834 | 6.011916127 | 3.219779936 |
| C | 1.670141612 | 4.501605890 | 2.712608451 |
| H | 2.038190287 | 4.690288181 | 3.719531902 |
| C | 2.406646541 | 3.671554804 | 1.877009220 |
| H | 3.325020228 | 3.225191096 | 2.244119981 |
| C | 4.063293917 | 2.507061058 | -0.310689341 |
| C | 4.766162961 | 1.368925621 | -0.794996916 |
| C | 6.167183430 | 1.350555051 | -0.822004994 |
| H | 6.676513657 | 0.463657497 | -1.194215297 |
| C | 6.937745919 | 2.432783616 | -0.395545857 |
| C | 8.447529318 | 2.392350463 | -0.405485153 |
| C | 6.241368398 | 3.570284409 | 0.044191590 |
| H | 6.801879687 | 4.451159973 | 0.351872369 |
| C | 4.854435288 | 3.614420651 | 0.082966255 |
| H | 4.364037505 | 4.523905798 | 0.411695819 |
| C | 0.348680921 | 4.869528195 | -2.601590689 |
| H | -0.197008863 | 5.736935035 | -2.216901674 |
| C | -1.664022571 | 3.217754010 | -1.349851487 |
| H | -2.161147882 | 4.156121968 | -1.084974372 |
| H | -1.890017748 | 2.461352331 | -0.594809398 |
| H | -2.049061765 | 2.864441977 | -2.310399977 |
| H | -0.028880468 | 4.616278981 | -3.596796151 |
| H | 1.408076085 | 5.124822224 | -2.688084876 |
| C | 3.842525925 | -1.347484514 | -0.178510940 |
| H | 3.287096735 | -2.221085682 | -0.532685895 |
| C | 4.655598425 | -0.695367424 | -2.874494569 |
| H | 5.635279258 | -1.093798790 | -2.593193549 |
| H | 4.882684821 | -1.630974223 | 0.010770774 |
| H | 3.389986565 | -1.003956347 | 0.755106930 |
| H | 4.056579686 | -1.498287872 | -3.313134917 |
| H | 4.787207410 | 0.083315541 | -3.629817794 |
| H | 8.871978143 | 3.301213119 | -0.847460015 |
| H | 8.820934144 | 1.538427673 | -0.978920573 |
| H | 8.857317926 | 2.309789974 | 0.609542591 |
| H | -0.430535968 | 5.577379563 | 4.218632718 |
| H | -1.305701821 | 6.224294156 | 2.824754673 |
| H | 0.204947706 | 6.973644464 | 3.350739994 |
| C | 0.893739605 | 0.666783144 | -3.415533507 |
| C | 0.157326059 | 0.234149274 | -2.297586298 |
| C | -0.862678850 | -0.715978944 | -2.422421822 |
| H | -1.474053581 | -1.025024673 | -1.574779679 |
| C | -1.103583853 | -1.269065005 | -3.685679722 |
| H | -1.876918729 | -2.025077561 | -3.808424574 |
| C | -0.363433274 | -0.850363543 | -4.804393054 |
| H | -0.578533424 | -1.285599006 | -5.778638539 |
| C | 0.629794717 | 0.128844825 | -4.681829795 |
| H | 1.155883664 | 0.471578787 | -5.573198797 |

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**TS-4**

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| | | | |
|---|---|---|---|
| H | 0.149482751 | -0.029232815 | -0.230378685 |
| C | 0.084983285 | -0.112279935 | 1.090858106 |
| V | 1.937589113 | 0.018827987 | -0.193164693 |
| P | 2.706942285 | -2.337288931 | 0.305874255 |
| N | 3.762342855 | 0.391053745 | 0.621516559 |
| P | 2.171336176 | 2.527162039 | -0.527687089 |
| C | 4.018506008 | 1.617169402 | 1.271945322 |
| C | 3.344833697 | 2.792450940 | 0.846198628 |
| C | 3.542987673 | 4.008753537 | 1.509033416 |
| H | 3.015240209 | 4.895333824 | 1.163464844 |
| C | 4.397579924 | 4.124150704 | 2.608617885 |
| C | 4.631592172 | 5.448097622 | 3.297488913 |
| C | 5.038357221 | 2.954256293 | 3.042377599 |
| H | 5.688897642 | 2.996414243 | 3.914077397 |
| C | 4.856930236 | 1.734244546 | 2.401142166 |
| H | 5.359160360 | 0.851200411 | 2.782116885 |
| C | 4.800726537 | -0.554559160 | 0.509348684 |
| C | 4.486994511 | -1.929540712 | 0.350759159 |
| C | 5.502439256 | -2.879267349 | 0.193827277 |
| H | 5.234302137 | -3.927681318 | 0.077501312 |
| C | 6.854133884 | -2.529051967 | 0.171589370 |
| C | 7.943713347 | -3.564622973 | 0.024182883 |
| C | 7.157025599 | -1.165073594 | 0.294796031 |
| H | 8.196497744 | -0.844787850 | 0.251331905 |
| C | 6.168076810 | -0.202988003 | 0.456921493 |
| H | 6.451818060 | 0.841347316 | 0.529355492 |
| C | 3.091212958 | 2.998004593 | -2.062294119 |
| C | 0.915174116 | 3.879000138 | -0.400450861 |
| C | 2.407660350 | -3.229076626 | 1.904006746 |
| C | 2.532061309 | -3.682381971 | -0.946991295 |
| C | -0.629194448 | -1.285549853 | 1.395086338 |
| H | -0.676044755 | -2.079534995 | 0.651677603 |

| | | | |
|---|---|---|---|
| C | -1.289364930 | -1.443632269 | 2.613562931 |
| H | -1.834363044 | -2.360519396 | 2.824854615 |
| C | -1.251910269 | -0.419042620 | 3.562511967 |
| H | -1.762485644 | -0.536735808 | 4.514785626 |
| C | -0.568066247 | 0.763505711 | 3.276046764 |
| H | -0.538034151 | 1.566051895 | 4.009063180 |
| C | 0.076127963 | 0.920104454 | 2.046353360 |
| H | 0.602706092 | 1.851341998 | 1.854232196 |
| C | 1.832405996 | -0.341884069 | -2.176280234 |
| C | 0.525801004 | -0.244975014 | -1.772696754 |
| C | -0.543388970 | -0.378973266 | -2.658360913 |
| H | -1.583453110 | -0.302267392 | -2.341999161 |
| C | -0.235701098 | -0.618105604 | -4.007538888 |
| H | -1.036561928 | -0.727024824 | -4.735880419 |
| C | 1.098297149 | -0.716599210 | -4.427422499 |
| H | 1.312770153 | -0.902142212 | -5.478362271 |
| C | 2.156823541 | -0.579178978 | -3.514275985 |
| H | 3.186189371 | -0.657439745 | -3.862680195 |
| H | 8.699478591 | -3.252221468 | -0.705498680 |
| H | 7.539160624 | -4.525914231 | -0.307151723 |
| H | 8.467854410 | -3.739092577 | 0.972863554 |
| H | 4.603745954 | 5.345747482 | 4.388233483 |
| H | 3.875744923 | 6.186400203 | 3.012604647 |
| H | 5.612575483 | 5.868807335 | 3.040793509 |
| H | 3.074611507 | -4.090837372 | 2.007145514 |
| H | 1.368109485 | -3.564814416 | 1.953603479 |
| H | 2.583235530 | -2.539478164 | 2.733617410 |
| H | 3.180238009 | -4.539125773 | -0.740292441 |
| H | 2.760949374 | -3.273287756 | -1.933441072 |
| H | 1.491787031 | -4.021849242 | -0.953139073 |
| H | 1.367580510 | 4.873777466 | -0.461163755 |
| H | 0.358840626 | 3.796074548 | 0.536407985 |
| H | 0.208587301 | 3.766621983 | -1.228135695 |
| H | 3.430390587 | 4.037738493 | -2.020436785 |
| H | 2.442476319 | 2.853227398 | -2.930789549 |
| H | 3.953818804 | 2.336462319 | -2.167905956 |

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| V | -0.077236282 | 0.820615685 | -0.333469277 |
| P | -1.037760950 | 3.102339400 | 0.087341840 |
| N | -1.991893878 | 0.323691775 | -0.071907598 |
| P | 0.104256844 | -1.664324388 | -0.644807457 |
| C | -2.320385480 | -0.942000512 | 0.460364030 |
| C | -1.434653682 | -2.040138417 | 0.270848445 |
| C | -1.718768175 | -3.287345654 | 0.834293158 |
| H | -1.023512684 | -4.109626259 | 0.675625836 |
| C | -2.859882793 | -3.513846749 | 1.610529479 |
| C | -3.149289663 | -4.873986275 | 2.201129071 |
| C | -3.709978694 | -2.420706876 | 1.819833246 |
| H | -4.593289306 | -2.545929088 | 2.442699964 |
| C | -3.453186251 | -1.169008708 | 1.268458035 |
| H | -4.131262024 | -0.348374750 | 1.475980100 |
| C | -3.011902494 | 1.239188828 | -0.410224647 |
| C | -2.746400890 | 2.637009408 | -0.374202535 |
| C | -3.730118813 | 3.557105690 | -0.748215785 |
| H | -3.500140313 | 4.620321257 | -0.711811550 |
| C | -4.998954314 | 3.159677548 | -1.183419927 |
| C | -6.050322884 | 4.173416361 | -1.568869634 |
| C | -5.240702263 | 1.781681003 | -1.250718553 |
| H | -6.203376070 | 1.428024615 | -1.614415904 |
| C | -4.280951152 | 0.843745172 | -0.880905449 |
| H | -4.510017335 | -0.212830411 | -0.968416639 |
| C | -0.117429062 | -2.410960284 | -2.323583488 |
| H | 0.796435112 | -2.258929914 | -2.905615256 |
| C | 1.412228329 | -2.725048438 | 0.111947379 |
| H | 1.169683598 | -3.791326622 | 0.071911215 |
| H | 1.559978430 | -2.418493921 | 1.150092067 |
| H | 2.348154044 | -2.559044462 | -0.430304329 |
| H | -0.934683493 | -1.897601362 | -2.835842530 |
| H | -0.340120493 | -3.480995420 | -2.264431619 |
| C | -1.147248997 | 3.751759837 | 1.816191393 |
| H | -0.157525391 | 4.093849618 | 2.133101549 |
| C | -0.641971672 | 4.610435280 | -0.901090413 |
| H | -1.347127280 | 5.428989708 | -0.727641823 |
| H | -1.453853437 | 2.940701935 | 2.481052161 |
| H | -1.862362945 | 4.576582065 | 1.894686168 |
| H | 0.361716274 | 4.949528015 | -0.626996889 |
| H | -0.635692439 | 4.347108833 | -1.961399187 |
| C | 1.169062048 | 0.866931835 | 1.295628916 |
| C | 2.392842078 | 1.567915906 | 1.260675711 |
| H | 2.686883385 | 2.104508338 | 0.358527406 |
| C | 3.254895776 | 1.596555878 | 2.361051721 |
| H | 4.195481931 | 2.141021421 | 2.302167185 |
| C | 2.907325259 | 0.933838925 | 3.540437103 |
| H | 3.573158087 | 0.959296045 | 4.399447797 |
| C | 1.696627594 | 0.240014079 | 3.607658263 |
| H | 1.417824637 | -0.275634570 | 4.524661549 |
| C | 0.844965980 | 0.205274496 | 2.499004597 |
| H | -0.087841684 | -0.353316580 | 2.577794339 |
| C | 0.597706976 | 1.260891110 | -2.220664603 |
| C | 1.968808462 | 1.214241450 | -2.548757507 |
| H | 2.700772422 | 0.937709056 | -1.789810435 |
| C | 2.427673033 | 1.516765303 | -3.834075276 |
| H | 3.492531911 | 1.478339932 | -4.055729704 |
| C | 1.520172980 | 1.860893115 | -4.838559078 |
| H | 1.873892247 | 2.090942505 | -5.840525271 |
| C | 0.154846424 | 1.904951705 | -4.545947913 |
| H | -0.558057749 | 2.169088710 | -5.324712175 |
| C | -0.295658377 | 1.612923737 | -3.254712139 |
| H | -1.365930305 | 1.666068310 | -3.054048785 |
| H | -6.894142968 | 3.696634529 | -2.076387397 |
| H | -5.645994345 | 4.937931758 | -2.242210267 |
| H | -6.449256946 | 4.697376913 | -0.690919494 |
| H | -3.980718456 | -4.829760428 | 2.910800195 |
| H | -2.279414265 | -5.276446531 | 2.733246726 |
| H | -3.417157378 | -5.603692433 | 1.426499794 |

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| | | | |
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| V | 1.991029636 | 0.020791206 | -0.414805693 |
| P | 2.826930365 | -2.159228671 | 0.370778172 |
| N | 3.848586356 | 0.429135842 | 0.482693849 |
| P | 2.138025371 | 2.460649452 | -0.417417810 |
| C | 4.011821094 | 1.570375953 | 1.284966084 |
| C | 3.237396501 | 2.721473321 | 0.999345724 |
| C | 3.341705632 | 3.878182835 | 1.775493126 |
| H | 2.731972870 | 4.745912774 | 1.528130349 |
| C | 4.200471779 | 3.947584240 | 2.876694538 |
| C | 4.321473161 | 5.197669232 | 3.716515211 |
| C | 4.950082254 | 2.798643160 | 3.171076313 |
| H | 5.611675642 | 2.806096151 | 4.035836870 |
| C | 4.867107742 | 1.639866582 | 2.406775569 |
| H | 5.458898906 | 0.774616621 | 2.686168620 |
| C | 4.913125558 | -0.486236626 | 0.390265184 |
| C | 4.612874238 | -1.864357143 | 0.295473534 |
| C | 5.619249728 | -2.818575041 | 0.125507861 |
| H | 5.354757598 | -3.871377090 | 0.048767803 |
| C | 6.965299483 | -2.449930195 | 0.052651495 |
| C | 8.061299457 | -3.476354663 | -0.111640373 |
| C | 7.261621142 | -1.080574916 | 0.147242292 |
| H | 8.298927337 | -0.758125422 | 0.075630920 |
| C | 6.272569087 | -0.116933112 | 0.309132435 |
| H | 6.545754590 | 0.932317003 | 0.357249598 |
| C | 2.895541769 | 3.417189909 | -1.803891258 |
| C | 0.565392688 | 3.343458473 | -0.063973929 |
| C | 2.438372162 | -2.424723678 | 2.157966993 |
| C | 2.519128335 | -3.810337231 | -0.379307432 |

| | | | |
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| C | 1.416900186 | -0.968960481 | -2.093396378 |
| C | 1.242645326 | 0.344213916 | -2.281447890 |
| C | 0.667215094 | 0.879381970 | -3.441121269 |
| H | 0.513807682 | 1.944620030 | -3.611608391 |
| C | 0.274733686 | -0.045656427 | -4.410022886 |
| H | -0.189037095 | 0.299748272 | -5.331994148 |
| C | 0.451853523 | -1.432328191 | -4.210788046 |
| H | 0.125357925 | -2.121044525 | -4.987093216 |
| C | 1.032953094 | -1.927056069 | -3.041119387 |
| H | 1.151656617 | -2.999911177 | -2.903665144 |
| H | 8.785013748 | -3.173878186 | -0.877158901 |
| H | 7.655944333 | -4.450173224 | -0.403184598 |
| H | 8.622618131 | -3.620531660 | 0.820635966 |
| H | 4.298918937 | 4.967475422 | 4.788027416 |
| H | 3.506557246 | 5.898637857 | 3.510565879 |
| H | 5.264260309 | 5.725876915 | 3.522979653 |
| H | 2.989808219 | -3.277293593 | 2.566958443 |
| H | 1.362790197 | -2.588937561 | 2.270294878 |
| H | 2.704432533 | -1.517209208 | 2.704460711 |
| H | 3.031246747 | -4.605458645 | 0.171963810 |
| H | 2.858602662 | -3.809649663 | -1.416928019 |
| H | 1.443749236 | -4.008708123 | -0.363616713 |
| H | 0.724714454 | 4.409170914 | 0.127771408 |
| H | 0.098094916 | 2.875481378 | 0.805041525 |
| H | -0.104774270 | 3.227664846 | -0.920171512 |
| H | 3.017011968 | 4.469697415 | -1.528673062 |
| H | 2.271832160 | 3.341892712 | -2.698250861 |
| H | 3.877294750 | 2.992601749 | -2.029130435 |
| O | 0.762762386 | 0.047487816 | 0.597669205 |

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| | | | |
|---|---|---|---|
| V | 2.225172954 | 0.075004315 | -0.417189412 |
| P | 3.034376090 | -2.259162150 | 0.056881147 |
| N | 3.971938435 | 0.467283178 | 0.504249080 |
| P | 2.203816942 | 2.589016591 | -0.511533375 |
| C | 4.056996418 | 1.634070400 | 1.294976218 |
| C | 3.286282180 | 2.778086384 | 0.950258433 |
| C | 3.327324065 | 3.929752892 | 1.744639518 |
| H | 2.728397056 | 4.792199576 | 1.458148665 |
| C | 4.102470125 | 4.009311096 | 2.903289618 |
| C | 4.155271154 | 5.264247250 | 3.741764758 |
| C | 4.832630015 | 2.865226329 | 3.257897947 |
| H | 5.425434970 | 2.874143871 | 4.171081424 |
| C | 4.812470178 | 1.710068214 | 2.486036955 |
| H | 5.376991157 | 0.843235882 | 2.812670856 |
| C | 5.048535433 | -0.443908589 | 0.482643234 |
| C | 4.794287443 | -1.824707102 | 0.278013666 |
| C | 5.849351532 | -2.742086762 | 0.217300479 |
| H | 5.626263617 | -3.796752872 | 0.064305028 |
| C | 7.183830407 | -2.349042437 | 0.340418745 |
| C | 8.315506873 | -3.348796760 | 0.304931135 |
| C | 7.429601827 | -0.977618836 | 0.506900501 |
| H | 8.457681067 | -0.626446090 | 0.577915235 |
| C | 6.400003083 | -0.047010050 | 0.574142421 |
| H | 6.640021974 | 1.005661090 | 0.683200709 |
| C | 3.031753988 | 3.535974556 | -1.869232200 |
| C | 0.694548870 | 3.591562283 | -0.161236980 |
| C | 2.560846627 | -3.196897775 | 1.583411116 |
| C | 2.988422333 | -3.559868616 | -1.249891549 |
| C | 0.291829078 | -0.493028795 | -1.504459197 |
| C | 1.532884334 | -0.397853479 | -2.219843138 |
| C | 1.524906406 | -0.558621540 | -3.603366629 |
| H | 2.454943971 | -0.493098706 | -4.167367861 |
| C | 0.323469428 | -0.798114721 | -4.286005796 |
| H | 0.325283232 | -0.926446625 | -5.365910204 |
| C | -0.879418365 | -0.877760851 | -3.575357153 |
| H | -1.808971414 | -1.064548235 | -4.108068670 |
| C | -0.910452209 | -0.716031227 | -2.186929582 |
| H | -1.838583607 | -0.782835128 | -1.624736316 |
| H | 9.141393383 | -3.000146581 | -0.325778132 |
| H | 7.983196881 | -4.315930187 | -0.084939781 |
| H | 8.729528413 | -3.523930185 | 1.306550194 |
| H | 4.048969019 | 5.038270062 | 4.808903655 |
| H | 3.358341852 | 5.962604008 | 3.468003368 |
| H | 5.110300184 | 5.791428550 | 3.619696995 |
| H | 3.200379891 | -4.073465905 | 1.730259001 |
| H | 1.517993771 | -3.517579060 | 1.498690141 |
| H | 2.649983674 | -2.539357625 | 2.452297650 |
| H | 3.585792128 | -4.439623016 | -0.990612413 |
| H | 3.346532922 | -3.132508984 | -2.188938591 |
| H | 1.947552448 | -3.864467018 | -1.393991829 |
| H | 0.918518380 | 4.649439401 | 0.007726358 |
| H | 0.186917066 | 3.180758886 | 0.715000134 |
| H | 0.018802683 | 3.505556252 | -1.017521744 |
| H | 3.192055150 | 4.580167482 | -1.582317885 |
| H | 2.414281154 | 3.495628564 | -2.771558173 |
| H | 3.996866198 | 3.071941955 | -2.088920880 |
| O | 0.373244241 | -0.334939821 | -0.149047878 |

**Full Model Optimized Structures**

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| | | | |
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| V | -0.032680790 | 0.809928523 | -0.272103729 |
| P | -1.276455645 | 3.166670648 | 0.331313020 |
| N | -1.959080692 | 0.287932713 | 0.014024893 |
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| C | -2.930210092 | -3.414201696 | 1.916757801 |
| C | -3.274930889 | -4.729224436 | 2.576741203 |
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| C | -3.400989577 | -1.062028794 | 1.489495131 |
| H | -4.022781054 | -0.193323902 | 1.677079046 |
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| H | -3.777663381 | 4.452555531 | -0.764839206 |
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| H | 1.865103193 | 1.578387979 | 4.047628120 |
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| H | 3.619133556 | 1.594195519 | 3.786529547 |
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| H | 3.589906013 | 0.180544929 | -3.382770089 |
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TS-1

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| P | 2.301892340 | -2.598679861 | 0.670358018 |
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| P | 2.379963152 | 2.621205824 | 1.190015933 |
| C | 4.606241322 | 0.989225116 | 0.969693343 |
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| H | -2.336117082 | -0.430810047 | 1.864695987 |
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| H | -0.512133954 | -3.796126796 | 1.007888384 |
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| P | -0.029717620 | -1.581293447 | -0.767279859 |
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| H | -3.841989974 | 4.401108591 | -0.504243244 |
| C | -5.325209015 | 2.881490201 | -0.755194445 |
| C | -6.441008381 | 3.842015581 | -1.095569599 |
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| H | -3.215339832 | 5.122616249 | 1.590572221 |
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| H | -2.061247065 | 5.878053996 | 2.692665717 |
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| H | 1.889023058 | 2.209933296 | 3.890310668 |
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| N | 3.544847902 | 0.320798526 | 1.247584884 |
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| H | 7.946523338 | -1.030242053 | 1.041912781 |

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| C | 3.330179995 | 2.775868484 | 1.365300557 |
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| H | 5.466674642 | 2.834912300 | 4.596801263 |
| C | 4.615278653 | 1.625619599 | 3.053479976 |
| H | 5.006245121 | 0.709617555 | 3.483792999 |
| C | 2.036841691 | -2.776513056 | 3.116358704 |
| H | 0.965068560 | -3.012606220 | 3.119926892 |
| C | 2.311005916 | -4.112649033 | 0.486901016 |
| H | 3.027226215 | -4.751689479 | 1.016794952 |
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| H | 3.770643653 | -3.699141237 | -1.090970065 |
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| H | 3.287654098 | -1.197846196 | 3.962173533 |
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| H | -1.937954427 | 0.338751796 | -1.827783331 |
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| P | -0.004135816 | -1.807983441 | -0.604757881 |
| C | -2.315089614 | -0.977497618 | 0.654723433 |
| C | -1.501953822 | -2.115963888 | 0.405761041 |
| C | -1.843162768 | -3.355424814 | 0.962018989 |
| H | -1.213937201 | -4.218870889 | 0.758419746 |
| C | -2.963692998 | -3.528079655 | 1.780836121 |
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| H | 2.072658917 | 2.175122298 | 3.882696571 |
| H | 2.657645964 | 0.505468824 | 3.922462433 |
| H | 3.793897582 | 1.835407484 | 3.626238620 |
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TS-3

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| N | 2.143461204 | 2.598518726 | 1.518673387 |
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| C | 1.406382144 | 3.370597931 | 2.444316801 |
| C | 0.137967921 | 3.894907771 | 2.081689076 |
| C | -0.606555232 | 4.639224524 | 3.006908365 |
| H | -1.574383090 | 5.038680160 | 2.712759284 |
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| C | 1.081464079 | 4.326631848 | 4.668055204 |
| H | 1.453272226 | 4.466020494 | 5.681553815 |
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| H | 2.791700818 | 3.171224032 | 4.086842225 |
| C | 3.543372978 | 2.750788977 | 1.494645502 |
| C | 4.368564999 | 1.706174180 | 0.999507003 |
| C | 5.758285181 | 1.874977281 | 0.926139732 |
| H | 6.369584829 | 1.064211483 | 0.536278514 |
| C | 6.392756567 | 3.054999158 | 1.321953064 |
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| H | 3.597361600 | 4.783172515 | 2.232550203 |
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| H | 5.997656304 | -0.857685009 | 2.015995782 |
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| H | 5.337846446 | -2.322030736 | 2.747661094 |
| C | 3.799050133 | -1.761751239 | -1.514006430 |
| H | 4.381340059 | -2.179364600 | -2.343766033 |
| H | 3.725878480 | -2.534766131 | -0.741390214 |
| H | 2.789440498 | -1.553270192 | -1.882192141 |
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| H | 3.641020854 | 0.839206554 | -2.532315541 |
| H | 5.110443884 | 1.472880749 | -1.773657749 |
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| C | -0.771984087 | -1.573071063 | 1.395936172 |
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| H | 8.351379842 | 2.442114622 | 0.631481643 |
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| H | -0.088586821 | -2.153122947 | 3.397380922 |
| H | -1.633206803 | -1.287911545 | 3.391900429 |
| H | -1.565561957 | -2.982890934 | 2.876556879 |
| C | -2.129576927 | -1.457762075 | 0.673529510 |
| H | -2.807185616 | -0.790336569 | 1.218295127 |
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| H | -0.584957757 | -0.618422817 | -4.586631255 |
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| H | 0.704846726 | 1.418217919 | -5.142541248 |
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| C | 3.230571747 | -2.652865875 | 3.085514820 |
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| H | 0.931090024 | -5.133430313 | 3.647190093 |
| C | 2.688197243 | -5.395723055 | 2.451751865 |
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**References**

S1. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* 1996, **15**, 1518–1520.

S2 U. J. Kilgore, C. A. Sengelaub, H. Fan, J. Tomaszewski, M. Pink, J. A. Karty, M.-H. Baik, D. J. Mindiola, *Organometallics* 2009, **28***,* 843. U. J. Kilgore, C. A. Sengelaub, M. Pink, A. R. Fout, D. J. Mindiola, *Angew. Chem.* 2008, **120**, 3829–3832; *Angew. Chem. Int. Ed.* 2008, **47***,* 3769–3772.

S3. D. F. Evans, *J. Chem. Soc.* 1959, 2003–2005.

S4. S. K. Sur, *J. Mag. Reson.* 1989, *82*, 169.

S5. A. K. Hassan, L. A. Pardi, J. Krzystek, S. Sienkiewicz, P. Goy, M. Rohrer, L.-C. Brunel, *J. Magn. Reson.* 2000, **142**, 300-312.

S6. E. Wasserman, L. C. Snyder, W. A. Yager, *J. Chem. Phys.* 1964, **41**, 1763-1772.

S7. A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*; Dover Publications, Inc.: New York, 1986.

S8. J. Baranowski, T. Cukierda, B. Jezowska-Trzebiatowska, H. Kozlowski, *Chem. Phys. Lett.* 1976, **39**, 606-608.

S9. J. Krzystek, S. A. Zvyagin, A. Ozarowski, S. Trofimenko, J. Telser, J. *J. Magn. Reson.* 2006, **178**, 174-183.

S10. S. Ye, F. Neese, A. Ozarowski, D. Smirnov, J. Krzystek, J. Telser, J.-H. Liao, C.-H. Hung, W.-C. Chu, Y.-F. Tsai, R.-C. Wang, K.-Y. Chen, H.-F. Hsu, *Inorg. Chem*. 2010, **49**, 977–988.

S11. J. Krzystek, A. T. Fiedler, J. J. Sokol, A. Ozarowski, S. A. Zvyagin, T. C. Brunold, J. R. Long, L.-C. Brunel, J. Telser, *Inorg. Chem.* 2004, **43**, 5645–5658.

S12. Jaguar, version 7.0, *Schrödinger, L.L.C, New York, NY,* **2007**.

S13. A. D. Becke, *Phys. Rev. A* 1988, **38**, 3098–3100.

S14. A. D. Becke, *J. Chem. Phys.* 1993, **98**, 5648–5652.

S15. C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* 1988, **37**, 785–789.

S16 S. H.Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* 1980, **58**, 1200–1211.

S17 P. J. Hay, W. R. Wadt, *J. Chem. Phys.* 1985, **82**, 270–283.

S18. W. R. Wadt, P. J. Hay, *J. Chem. Phys.* 1985, **82**, 284–298.

S19. T. H. Dunning, *J. Chem. Phys.* 1989, **90**, 1007–1023.

S20. B. Marten, K. Kim, C. Cortis, R. A. Friesner, R. B. Murphy, M. N. Ringnalda, D. Sitkoff, B. Honig, *J. Phys. Chem.* 1996, **100***,* 11775–11788.

S21. M. Friedrichs, R. H. Zhou, S. R. Edinger, R. A. Friesner, *J. Phys. Chem. B* 1999, **103**, 3057–3061.

S22. S. R.Edinger, C. Cortis, P. S. Shenkin, R. A. Friesner, *J. Phys. Chem. B* 1997, **101**, 1190–1197.

S23. A. A. Rashin, B. Honig, *J. Phys. Chem.* 1985, **89**, 5588–5593.

S24. M.-H. Baik, R. A. Friesner, *J. Phys. Chem. A* 2002, **106**, 7407–7412.

S25. B. C. Bailey, H. Fan, J. C. Huffman, M.-H. Baik, D. J. Mindiola, *J. Am. Chem. Soc*. 2007, **129**, 8781–8793.

S26. Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865-3868; Phys. Rev. Lett (Erratum) 1997, 78, 1386.