Supporting Information for:

*Finding a Soft Spot for Vanadium: A P-Bound OCP Ligand***

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Synthetic Details

General Procedures

Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified dinitrogen or using high vacuum standard Schlenk techniques under an argon or dinitrogen atmosphere. Hexanes, tetrahydrofuran (THF) and toluene were purchased from Fisher Scientific and Et_2O was purchased from Sigma Aldrich. Solvents were sparged with argon for 20 minutes and dried using a two-column solvent purification system where columns designated for hexanes and toluene were packed with Q5 and alumina respectively, and columns designated for Et_2O and THF were packed with alumina. Deuterated benzene was purchased from Cambridge Isotope Laboratories (CIL) and was sparged with nitrogen for 20 minutes, then was dried over a potassium mirror, vacuum transferred to a collection flask, and degassed by freeze–pump–thaw cycles. All solvents were transferred into a dry box and were stored over 4 Å sieves. All sieves were heated to 200 °C under vacuum overnight prior to use. Celite used for filtrations was heated to 200 °C under vacuum overnight prior to use. IR spectra were recorded on a JASCO FT/IR-4600LE Spectrometer using clear disks and mini KBr plates. Elemental analyses were measured by Midwest Microlab.

Synthesis of precursors

NaOAr was synthesized from HOAr (Ar = 2,6-$^{i}Pr_2C_6H_3$) and $NaN(SiMe_3)_2$ in toluene followed by filtration of the pale solid, and washed with copious amounts of toluene, and then dried under reduced pressure. [(nacnac)VCl_2] (nacnac$^-$ = [$ArNC(CH_3)]_2CH$; Ar = 2,6-$^{i}Pr_2C_6H_3$), [(nacnac)VCl(OAr)] and [Na(OCP)$(dioxane)_{2.5}$] were prepared according to published literature procedures.[1-3]

Synthesis of [(nacnac)V(OAr)(PCO)] (2)

To a dark green solution of [(nacnac)VCl(OAr)] (329.1 mg, 0.48 mmol, 1 equiv.) in 10 mL toluene in a 20 mL vial was added a 5 mL toluene slurry of [Na(OCP)$(dioxane)_{2.5}$] (154.8 mg, 0.48 mmol, 1 equiv). After stirring for 16 hours, the reaction mixture turned a lighter green color, and a noticeable precipitate had formed, NaCl. The solution was filtered over Celite for removal of alkaline side product. All volatiles were removed in vacuo, and the green residue was dissolved in a minimum (5 mL) of toluene, and was stored at −35 °C overnight, resulting in the deposition of large green crystals suitable for single crystal X-ray diffraction. These were decanted and dried over vacuum and isolated good yield. Yield: (303 mg, 0.43 mmol, 89%). Multiple attempts to obtain satisfactorily elemental analysis were unsuccessful most likely due to the thermal sensitivity of this complex.

Anal. Calcd. for $C_{42}H_{58}N_2O_2PV$: C, 71.57; H, 8.29; N, 3.97. Found: C, 69.99; H, 8.23; N, 3.76.

NMR Spectral Data

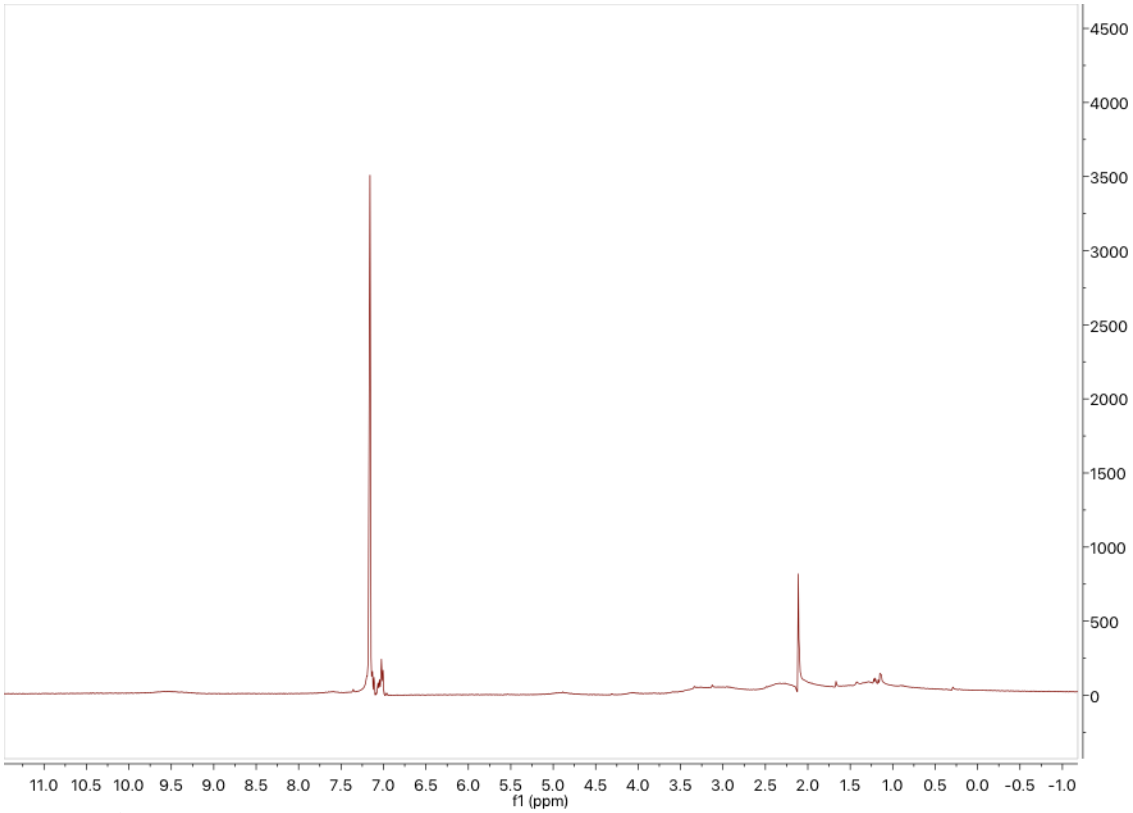

Fig. S1. ^{1}H NMR Spectrum of **2** in C_6D_6, 500 MHz, 298 K.

IR Spectral Data

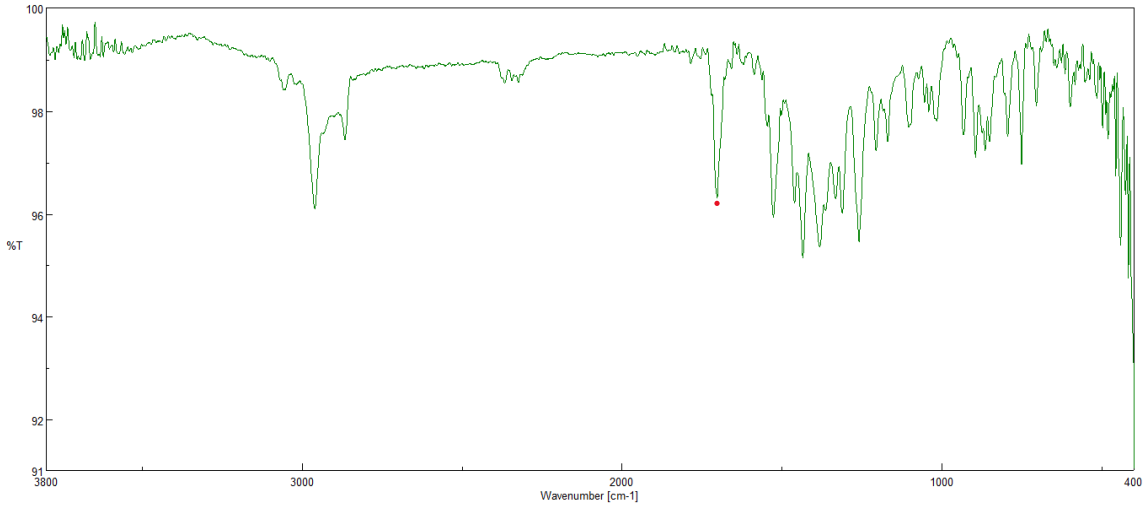

Fig. S2. IR Spectrum of **2**. The ν(C–O) of 1876 cm^{-1} has been annotated with a red dot. This spectrum was recorded on a JASCO FT/IR-4600LE Spectrometer using clear disks and mini KBr plates. The calculated ν(C–O) is 2000 cm^{-1}

Crystallographic Experimental Details

Crystallographic data are summarized Table S1. A suitable crystal for X-ray analysis of **2** was placed on the end of a Cryoloop coated in NVH oil. Data for single crystal structure determination of **2** were taken on a Bruker D8 with CMOS area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) at a temperature of 100(1) K. Rotation frames were integrated using SAINT,[4] producing a listing of non-averaged F^2 and σ(F^2) values. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.[5] The initial structure of **2** was solved by dual methods – SHELXT.[6] Refinement was by full-matrix least squares based on F^2 using SHELXL.[7] All reflections were used during refinement.

Molecular Structure and Crystallographic Table

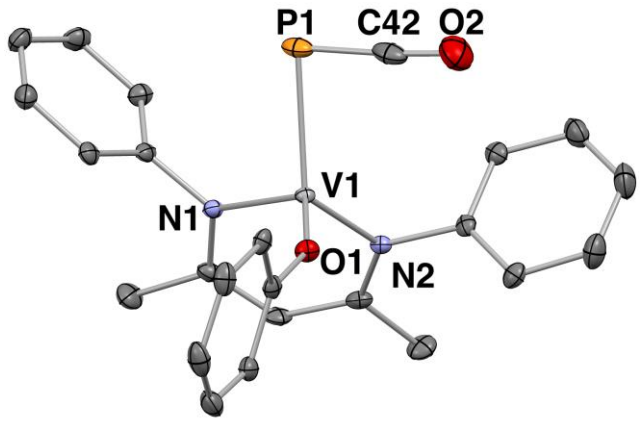

Fig. S3. Molecular structure of complex **2** showing thermal ellipsoids at the 50% probability level. The ^{i}Pr groups on the nacnac aryls and aryloxides have been omitted for clarity.

Table S1. Crystallographic Data for 2

Molecular formula	C42H58N2O2PV
Formula weight	704.81
Temperature (K)	100(1)
Crystal system	Monoclinic
Space group	P 1 2_1/n 1
Cell constants:	
a (Å)	11.7814(6)
b (Å)	21.2101(10)
c (Å)	17.8807(8)
Beta Angle	109.211(2)
Volume ($Å^3$)	4219.3(4)
Z	4
Density (calcd mg/m^3)	1.110
Abs coeff (mm^{-1})	0.307
F(000)	1512
Wavelength	0.71073
θ range for data collection (°)	3.084 to 27.565
h, *k*, *l* ranges collected	$-15 \leq h \leq 15$ $-23 \leq k \leq 27$ $-23 \leq l \leq 23$
# Reflns collected	9712
Refinement method	Full-matrix least-squares on F^2
R_1[a]	0.0358
wR_2[b]	0.0883
Goodness-of-fit on F^2[c]	1.025

SQUID Magnetometry Experimental Details:

Magnetic susceptibility data for **2** was collected on a Quantum Design Magnetic Property Measurement System (MPMS-7). Temperature-dependent data were collected under applied 1 T DC fields from 2 to 300 K. Corrections for the intrinsic diamagnetism of **2** was made using Pascal's constants.[8] Samples of microcrystalline **2** (10 – 20 mg) in the glove box were loaded into plastic drinking straws that had been evacuated overnight, and had been previously sealed at one end (~9.5 cm from the top) with heated forceps. Quartz wool (<10 mg, dried at 250 ^{o}C) was used to cap the sample, followed by sealing of the other end of the straw. The sample and quartz wool masses were weighed to the nearest 0.1 mg, and the value used was the average of four mass measurements. The data were fitted by use of the locally written program DSUSFITP,[9] which employs the Hamiltonian in eq. 1 assuming an isolated ground spin state and collinear ***D*** (axial component D, rhombic component E) and ***g*** matrixes, along with a temperature independent paramagnetism (TIP) term (not shown in eq. (1)) to account for contributions from excited spin states. True powder averages in three dimensions are calculated. A least-squares minimization using experimental data optimizes the spin Hamiltonian parameters. For simplicity, fits with only an isotropic g were employed, and the effect of E was not explored since rhombicity is best obtained from HFEPR spectroscopy (see main text). Error associated with these parameters was estimated using the standard deviations of several fits with very similar goodness-of-fit values.

$$H = \beta_e B \cdot \boldsymbol{g} \cdot \hat{S} + D\left[\hat{S}_z^{\,2} - S(S+1)/3\right] + E\left(\hat{S}_x^{\,2} - \hat{S}_y^{\,2}\right) \qquad (1)$$

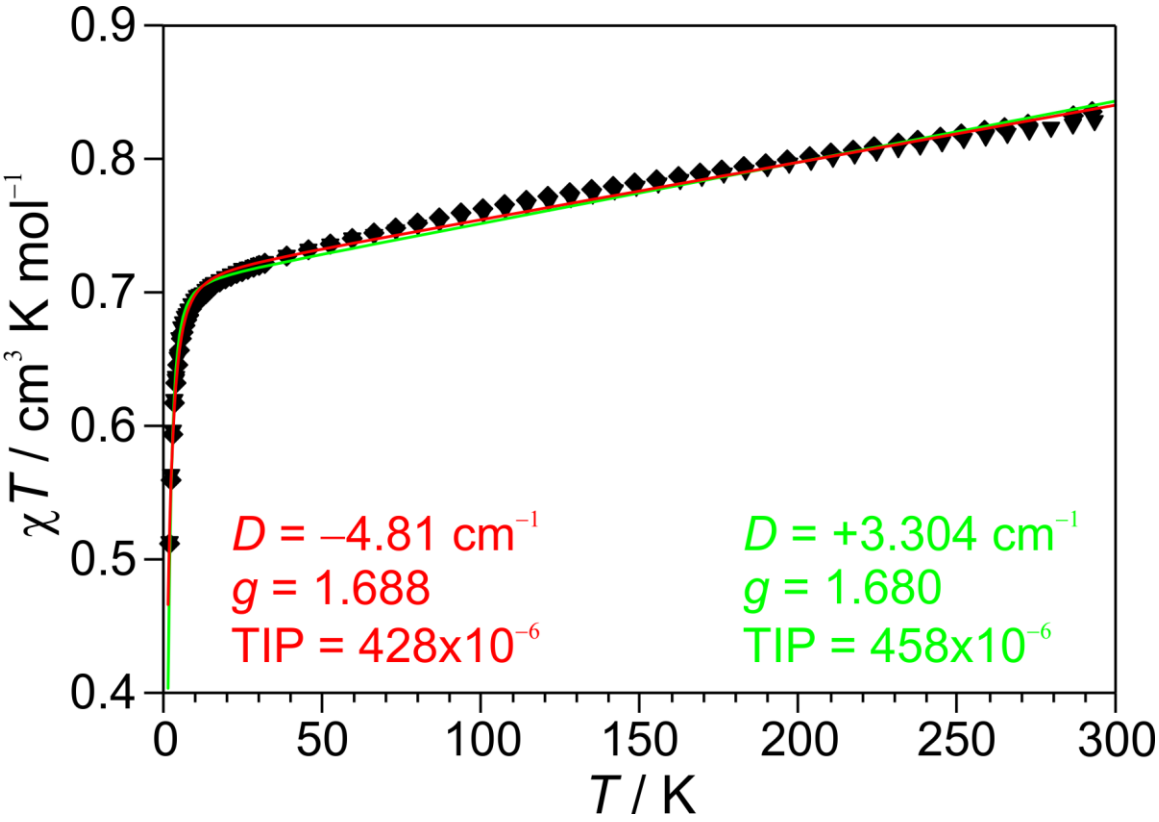

Fig. S4. Plot of experimental molar χT values (black triangles; two datasets are included: one as up triangles and one as down triangles). Fit lines using both positive (green line) and negative (red line) D values are shown with the fit parameters for each given on the plot.

HFEPR Experimental Details:

HFEPR spectra were recorded using a spectrometer that has been described previously,[10] with a difference of using a Virginia Diodes (Charlottesville, VA) source operating at 13 ± 1 GHz, amplified and multiplied by a cascade of frequency multipliers. Multifrequency HFEPR data were fitted using the spin Hamiltonian in eq. (1), as used with the magnetic susceptibility data.

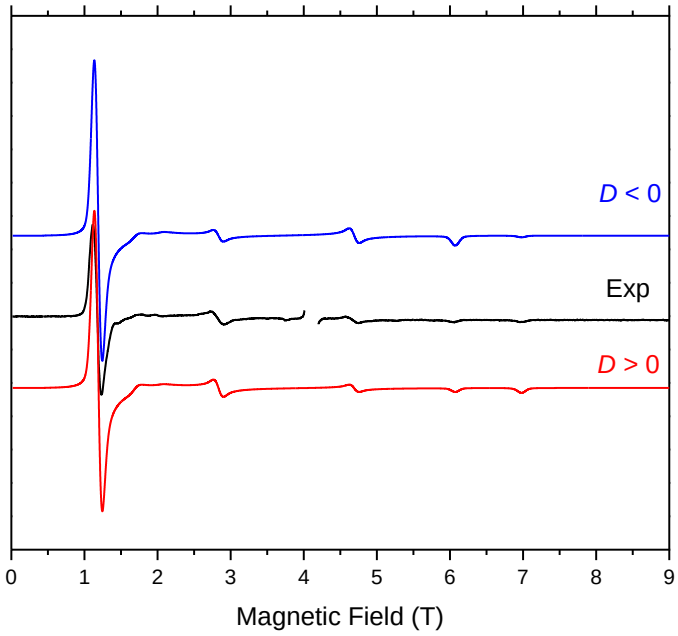

Fig. S5. An HFEPR spectrum of **2** at 10 K and 113 GHz. The black trace is experiment in which the V(IV) impurity signal at g = 1.98 was left out; the colored traces are simulations using following spin Hamiltonian (sH) parameters: S = 1, $|D|$ = 2.62 cm^{-1}, $|E|$ = 0.36 cm^{-1}, g_x = 1.96, g_y = 1.94, g_z = 1.95. Blue trace: negative D; red trace: positive D. These parameters represent the best fit at this particular frequency and thus differ slightly from those in the main text, which result from consensus fits of spectra recorded at multiple frequencies (see Figure 3).

Computational Details:

All calculations were carried out using DFT as implemented in the ORCA (version 4.0.1.2) program package.[11] Geometry optimizations were performed with B3LYP functional[12] and the all-electron def2-SV(P)[13] basis set in combination with the auxiliary basis set def2-SV(P)/J.[14] To accelerate geometry optimizations we used the resolution of the identity approximation for Coulomb and chain of spheres approximation for exchange interactions (RIJCOSX).[15] Already for optimizations a tight convergence of the wavefunction was demanded on grid quality of Grid4 and GridX4. Grimme's D3 method[16] was employed to take dispersion effects into account in all these calculations. We also carried out harmonic vibrational frequency calculations at the same level of theory that was for used for optimizations (B3LYP/def2-SV(P)) in order to confirm that the obtained structures indeed correspond to local minima of the potential energy surface.
Subsequent single point calculations for refined energies have been carried out using the B3LYP functional in combination with def2-TZVP basis set (without RI, on Grid5 and Grid5x). The electronic structure of **2** has been scrutinized, including QRO's, at the latter level of theory.

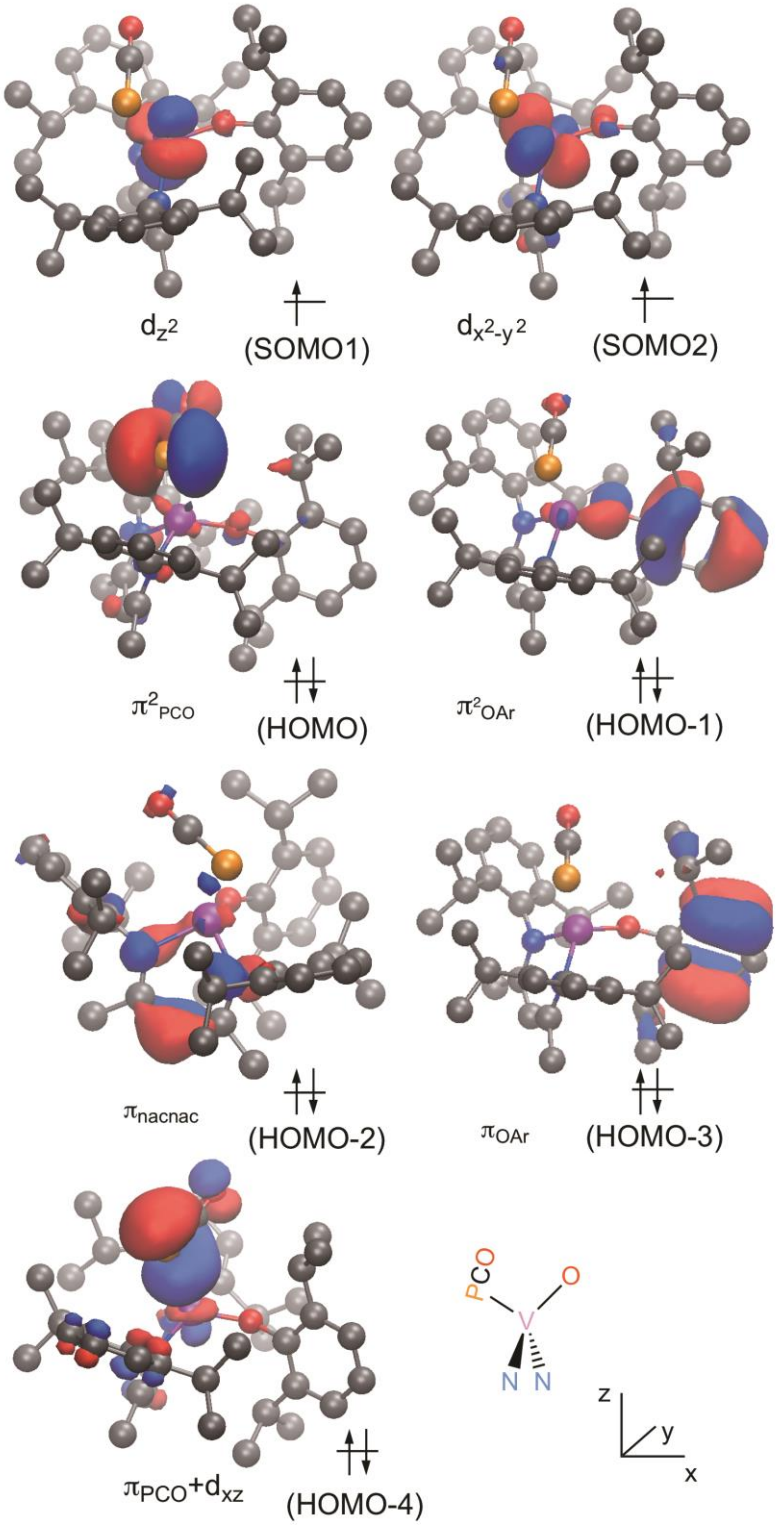

Fig. S6. Singly occupied and high lying doubly occupied QROs of **2**.

Table S2. Cartesian Coordinates of 2

V	3.57439330984635	16.23025120323968	6.76444867535986
P	3.06270226717931	15.68433714308601	4.44793998796593
O	2.56523213936315	17.54526712383274	7.46924242951389
O	3.92797233097161	18.34483674922165	4.02034180865791
N	3.52397813470715	14.42955268290680	7.57877846125215
N	5.44504420220315	16.47288488085663	7.35053783832300
C	4.22356956470245	14.11162338224807	8.68033253079637
C	5.32641924973298	14.84851320163938	9.11345202115401
H	5.80885243397315	14.50236356157173	10.01697803191927
C	5.96477255201269	15.89626607022371	8.43761954048123
C	2.70118306868659	13.39712259903077	6.99746030920254
C	1.31865289823651	13.35912733272071	7.22859001172615
C	0.58285112317208	12.31081679044940	6.67441223066886
H	-0.48596717401426	12.26815627731410	6.84939152938125
C	1.19198176470849	11.32942195525514	5.90990723309487
H	0.60508187799314	10.51841369095584	5.49493089074498
C	2.55611555977912	11.40002117266502	5.66378247591194
H	3.02709337745779	10.64251427799320	5.04846371348717
C	3.33252874933213	12.43093073996839	6.18737779519097
C	0.59714080329220	14.42350722660187	8.02655253858567
H	1.34023416834879	15.13384262150179	8.39502050386727
C	-0.37709930436764	15.18744476081150	7.12277598924763
H	0.14939792041738	15.63303174903146	6.27665859076506
H	-0.87101573927002	15.98188984258010	7.68309953886866
H	-1.14100187800312	14.51354690858235	6.72601252201115
C	-0.14428757161737	13.84105346728169	9.23629545399549
H	-0.94412124829812	13.16831069072909	8.91677166252658
H	-0.59403855627951	14.64694456301120	9.82072511605302
H	0.52505654270526	13.27423334750860	9.88775023601672
C	4.81754245957538	12.48414064661400	5.87230297196580
H	5.18744116357853	13.45809079741980	6.19523711809655
C	5.07342759920869	12.36021012717729	4.36582015573466
H	4.73899230307819	11.39345926767509	3.98218855351835
H	6.14383090749323	12.44003907349583	4.16313589206766
H	4.55611626493437	13.14717232655568	3.81493600910786
C	5.60523761336845	11.40526883717328	6.62997031520040
H	5.51936496415618	11.52350979004292	7.71070671895731
H	6.66532913982004	11.46208118824046	6.36961170718324
H	5.24423825678940	10.40705471472486	6.36769960025268
C	3.81657496254440	12.90889173418937	9.49146096250312
H	2.82545113701561	13.07620911984039	9.91952912586896
H	4.52381670709274	12.73417523335383	10.30038132311883
H	3.74543169084586	12.01435756335967	8.87336699904943
C	7.28318754459392	16.36932593639543	8.99029545910579
H	7.92949019128949	16.75552734008554	8.20354649509962
H	7.78716813082101	15.55901260299983	9.51587695722160
H	7.11004940304057	17.17966872445024	9.70286935785386
C	6.19107475685428	17.47413066517027	6.62917641533071
C	6.19587136586409	18.81076468730372	7.06344969560139
C	6.90997636877651	19.74471851532324	6.31200456912970
H	6.91947671190790	20.78030845000035	6.63147541520154
C	7.59587887516151	19.37535948708651	5.16796949686055
H	8.14131270137226	20.11692400006162	4.59622600295385

C	7.56894008706571	18.05364082125790	4.74570603490265
H	8.09248111823578	17.77437137347420	3.84073639695285
C	6.86845961120463	17.08260519750841	5.45597363863570
C	5.44434193024582	19.28497726756630	8.29219383921132
H	4.97829314959823	18.41764309008715	8.76160201589938
C	4.32959185256705	20.25880126108672	7.88981479949447
H	4.75101891914933	21.16190485663260	7.44142935424817
H	3.74247687589951	20.55617561280084	8.76200650133575
H	3.65912285283187	19.79547960137963	7.16997190426547
C	6.37929826309387	19.95119847356203	9.31132761278322
H	7.21294539009093	19.30316582969717	9.58751877881833
H	5.82660276787395	20.20730688545030	10.21840835543705
H	6.79933222082607	20.87488290470331	8.90580252180341
C	6.85629084611162	15.64152515906862	4.98229498137050
H	5.89142755392666	15.21952561882397	5.27346185334791
C	6.95963768787590	15.51627358629318	3.46108473801740
H	6.20132756335289	16.12454483023182	2.96553990131436
H	6.80671939720425	14.47705933063243	3.16631763068777
H	7.94379580544171	15.81876499196236	3.09361004701901
C	7.95696446920561	14.82159173150878	5.67077831678447
H	8.94289299576176	15.24146569168866	5.45420251939233
H	7.94053994371614	13.78888803394666	5.31295562994194
H	7.82484037216198	14.80276200793180	6.75345178156387
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H	2.61480311367840	18.62299743898981	11.97718851449233
C	2.30307560597584	16.00214757658772	11.17815801673797
H	1.59313652780103	16.26960232678423	11.96495501755538
H	3.20239013002678	15.60528349366313	11.65657845200855
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C	0.40455348368423	18.56823663272616	5.96437670679386
H	1.04365479558971	17.76327973628931	5.59157797686732
C	1.04742632669808	19.89896696584165	5.54497723349479
H	0.45042765204170	20.74019100058370	5.90816297590895
H	1.11194793927898	19.96350752891875	4.45604145837052
H	2.05501823737024	19.99517047095387	5.94677506822093
C	-0.96903441009955	18.41737063333048	5.30555658509984
H	-1.47226486862429	17.50389876976659	5.62848997206478
H	-0.85152283982650	18.37773617662487	4.22020522596221
H	-1.62105492734703	19.26515185179910	5.53306206573879
C	3.57668133583261	17.24556339333420	4.22037078090483

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