Electronic Supplementary Information for:

Dinitrogen Activation at Chromium by Photochemically Induced Cr^{II}–C Bond Homolysis

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I. General Methods

NMR Spectroscopy. NMR experiments were conducted in J. Young NMR tubes with a PTFE valve and recorded on a Bruker ASCEND AVANCE III HD 500 MHz spectrometer equipped with a Prodigy (liquid nitrogen cooled) cryoprobe. ^{1}H chemical shifts were referenced to the residual protonated resonances in the deuterated solvent.$^{31}P\{^{1}H\}$ NMR spectra were proton decoupled and referenced to 85% H_3PO_4 ($\delta = 0$) as the external reference. All NMR spectroscopy was performed at room temperature unless otherwise noted. 1,3,5-trimethoxybenzene (99%) was used as the internal standard for bibenzyl and TEMPO-CH_2Ph quantification. Magnetic moments were determined in solution via the Evans method.[1]

Infrared Spectroscopy. Infrared spectra were recorded on a Thermo Scientific Nicolet iS50 FT-IR spectrometer at ambient temperature (25 °C) and under a purge stream of nitrogen gas. Solid-state FT-IR samples were prepared as KBr pellets.

UV-Vis Spectroscopy. Electronic absorption spectra were acquired using a Cary 5000 spectrometer (Agilent) or an Ocean Optics Flame-S UV-vis spectrophotometer. Stock solutions (6-7000 μM) were prepared in a glove box and ~1-3 mL was transferred to an air-free quartz cuvette (1.00 cm path length) with a PTFE lined cap.

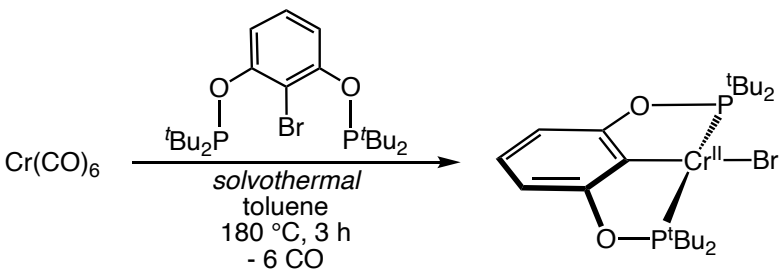
Raman Spectroscopy. Raman spectra were recorded using a HORIBA Scientific MacroRAM spectrometer with a back illuminated IR enhanced scientific grade CCD deep cooled detector and 785 nm integrated laser with adjustable power (0-450 mW). LabSpec software was utilized for data collection and analysis. Solutions (6-100 mM) were prepared in a glove box and ~1 mL was transferred to a low-volume, air-free quartz cuvette (1.00 cm path length).

Photolysis. Photochemical studies utilized three LED lamps purchased from Kessil. Wavelengths that were examined were 370, 390, 427, and 525 nm (PR160L-370nm; PR160L-390nm; PR160L-427nm; PR160L-525nm). Reactions were conducted at room temperature with the use of a standard fan and behind a protective black-out screen. Orange safety goggles were used as additional eye protection. Reaction vessels were placed in the center the beam path and positioned approximately 5 cm from each LED lamp. See **Figure S1** below for lamp configuration. Elemental analysis of **1** and **2** was performed by Atlantic Microlabs, Norcross, GA. Elemental analysis of **3** was performed by Midwest Microlab, Indianapolis, IN.

II. Synthetic Procedures and Materials

All synthetic reactions were conducted under an atmosphere of N_2 or argon using standard Schlenk and/or glovebox techniques. Unless specified, all solvents and compounds were used as received and stored under N_2 atmosphere. Protio solvents were sparged and stored under Ultra High Purity (UHP) argon gas before being dried via passage through activated alumina in a CHEMBLY solvent purification system (formerly JC Meyer Solvent Systems) using UHP argon as the working gas and stored under N_2 until use. Deuterated solvents were purchased from Acros Chemical or Cambridge Isotope Labs, degassed by three freeze-pump-thaw cycles and stored in an N_2 or Ar filled glovebox over activated molecular sieves (3 Å). 1,4-dioxane was refluxed over $NaBH_4$ then distilled under N_2 and degassed via three freeze-pump-thaw cycles and stored over 3 Å molecular sieves. Benzene was dried over sodium / benzophenone, then purified via distillation followed by three freeze-pump-thaw cycles. All glassware was heated to 160 °C overnight prior to use. Celite was heated to 160 °C overnight before being evacuated and then stored under nitrogen. $^{15}N_2$ gas ($^{15}N_2$, 98%+) was purchased from Cambridge Isotope Laboratories. Chromium hexacarbonyl, di-*tert*-butylchlorophosphine, 1,4-dioxane were purchased from ThermoScientific. Benzylmagnesium chloride, *p*-tolylmagnesium bromide, and 1,3,5-trimethoxybenzene were purchased from Acros Chemical. 2-bromobenzene-1,3-diol was purchased from AmBeed. 2,2,6,6-(tetramethylpiperidine-1-yl)oxyl (TEMPO) was purchased from Oakwood Chemical. Solvothermal synthesis was performed in a 25 mL stainless steel reaction vessel (Swagelok SS-4CS-TW-25) equipped with a metal ball valve (SS-43GS6). The (POCOP^{tBu}) ligand was prepared following published literature procedures.[2]

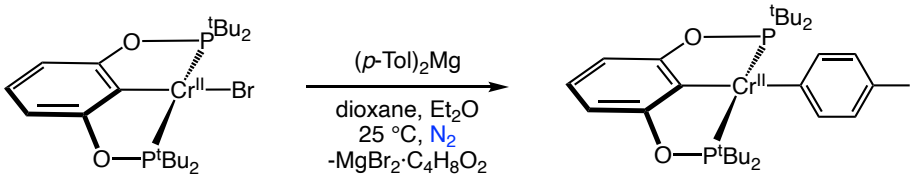
Modified (POCOP^{tBu})Cr^{II}Br synthesis[3]



$Cr(CO)_6$ (132 mg, 0.6 mmol) and POCOP^{tBu} ligand (295 mg, 0.62 mmol) were added to a 25 mL metal vessel with 4 mL of toluene. The temperature was gradually increased to 180 °C and the reaction was heated/stirred for 3 h. After the vessel cooled to room temperature, the headspace gas was evacuated. The resulting red crystals were collected, washed

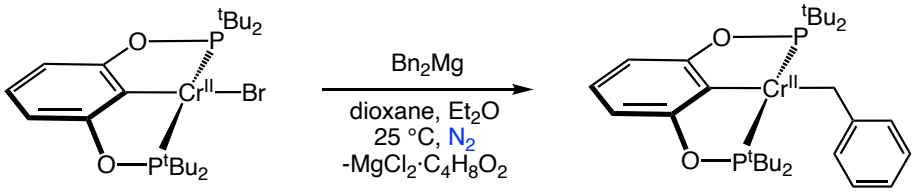
with pentane (2 × 2 mL), dried, and storied under an N_2 atmosphere. Crystalline yield: 207.4 mg (65%) Characterization matched reported literature values.[2] ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 15.7 (br s, 30H, ^{t}Bu), 19.0 (br s, 6H, ^{t}Bu). No $^{31}P\{^1H\}$ signal.

(POCOP^{tBu})Cr^{II}(*p*-Tol) synthesis (1)



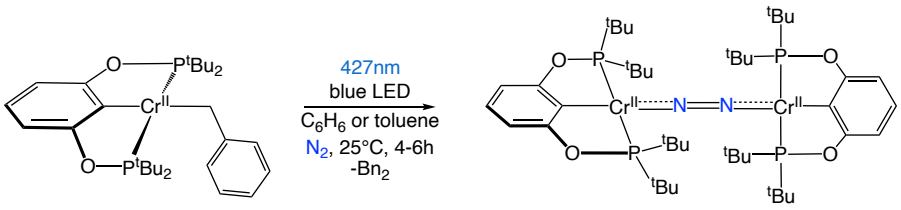
A cloudy solution of Et_2O (7 mL), 1,4-dioxane (2 mL), and 0.5 M *p*-tolylmagnesium bromide (0.45 mL, 0.23 mmol) was filtered through a plug of Celite while being added dropwise into a stirring solution of (POCOP^{tBu})CrBr (60.7 mg, 0.11 mmol) dissolved in Et_2O (40 mL). The solution stirred overnight, then solvent was removed under reduced pressure. The remaining orange solid was extracted with pentane and filtered through a Celite pad. The solution was concentrated and stored at -30 °C resulting in the formation of orange crystals which were isolated and dried. Crystalline yield: 47.5 mg (77%) ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 15.8 (br, 36 H, P^{t}Bu, $w_{1/2}$ = 2659 Hz), 30.8 (br, 3 H, C*H*$_3$), 34.8 (br, 4H, C$_6$*H*$_4$CH$_3$). No $^{31}P\{^1H\}$ signal. IR (KBr, cm^{-1}): 1597 (C=C), 2870 (C–H), 2903 (C–H), 2966 (C–H). UV-vis (toluene): λ_{max} (ε, M^{-1} cm^{-1}) 331 (2903), 361 (1668), 390 (1031), 464 (285). Magnetic moment (Evans, C_6D_6): μ_{eff} = 4.5 μ_B. Calcd. for $C_{29}H_{46}P_2O_2Cr$: C, 64.43%; H, 8.58%. Found: C, 64.61%; H, 8.58%.

(POCOP^{tBu})Cr^{II}Bn synthesis (2)



A turbid solution of Et_2O (10 mL), 1,4-dioxane (2 mL), and 1.4 M benzyl magnesium chloride in THF (0.3 mL, 0.42 mmol) was filtered through a plug of Celite and added dropwise into a stirring solution of (POCOP^{tBu})CrBr (112 mg, 0.21 mmol) dissolved in Et_2O (50 mL). The solution stirred overnight, then solvent was removed under reduced pressure. The remaining red solid was extracted with pentane and filtered through a Celite pad. The filtrate was concentrated and stored at -30 °C resulting in the formation of red crystals which were isolated and dried under vacuum. Crystalline yield: 107.2 mg (94%). ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 15.4 (br, 36 H, P^{t}Bu, $w_{1/2}$ = 2580 Hz), 24.9 (br, 2 H, CH$_2$C$_6$*H*$_5$), 28.7 (br, 3 H, CH$_2$C$_6$*H*$_5$). No $^{31}P\{^1H\}$ signal. IR (KBr, cm^{-1}): 1577 (C=C), 2871(C–H), 2923 (C–H), 2953(C–H). UV-vis (toluene): λ_{max} (ε, M^{-1} cm^{-1}) 320 (9258), 350 (3782), 393 (2041), 493 (525). Magnetic moment (Evans, C_6D_6): μ_{eff} = 4.5 μ_B. Calcd. for $C_{29}H_{46}P_2O_2Cr$: C, 64.43%; H, 8.58%. Found: C, 63.10%; H, 8.73%. *Analysis of crystalline material tested low in carbon with and without the use of combustion aid.*

[(POCOP$^{t\mathrm{Bu}}$)Cr$^{\mathrm{II}}$]$_2$(μ-N$_2$) synthesis (3)



In a 10 mL hydrolysis tube with PTFE valve (POCOP$^{t\mathrm{Bu}}$)CrBn (41.1 mg, 0.076 mmol) was dissolved in C_6H_6 (or toluene) (3 mL) and the red/orange solution was placed in front of three 427 nm Kessil lamps for ~4-6 h. Upon photolysis the solution became dark purple in color. The solvent was removed under reduced pressure. The remaining solid was extracted with pentane and filtered through a pad of Celite. A concentrated solution was stored at -30 °C for *ca.* two days resulting in purple crystals. Mother liquor was decanted and crystals were dried under vacuum. Crystalline yield: 25.8 mg (73%). ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 11.2 (br, 12 H, P^{t}Bu), 20.7 (br, 60 H, P^{t}Bu, $w_{1/2}$ = 2167 Hz). No ^{31}P{^{1}H} signal. UV-vis (toluene): λ_{max} (ε, M^{-1} cm^{-1}) 379 (8608), 495 (9568), 578 (10503). Raman (λ_{ex}= 785 nm, pentane solution at room temperature, cm^{-1}); $^{14}N_2$: 1639 (ν_{NN}); $^{15}N_2$: 1585 (ν_{NN}). Magnetic moment (Evans, C_6D_6): μ_{eff} = 6.87 μ_B. Elemental analysis was used to determine the total composition of the photolysis reaction in formation of **3** and bibenzyl. Using the procedure described above, after photolysis toluene was removed under reduced pressure and the solid residue was extracted with pentane, filtered through a plug of Celite and dried under vacuum. Calcd. for $C_{44}H_{78}P_4O_4N_2Cr_2$•$C_{14}H_{14}$: C, 62.80%; H, 8.36%; N, 2.53%. Found: C, 63.00%; H, 8.79%; N, 2.64%.

Attempted photolysis of 1

Under an N_2 atmosphere, a C_6D_6 solution of **1** was photolyzed in a Teflon-valved NMR tube using a 390 nm LED lamp for 6 h and monitored by ^{1}H and ^{31}P NMR spectroscopy. Solution maintained orange color and NMR spectra remained unchanged. The solution was then photolyzed using a 370 nm LED lamp for 22 h and no change was observed in the color of the sample and no changes were noted in the ^{1}H and ^{31}P NMR spectra, indicating no degradation of complex **1** or formation of **3** occurred during the photolysis experiments.

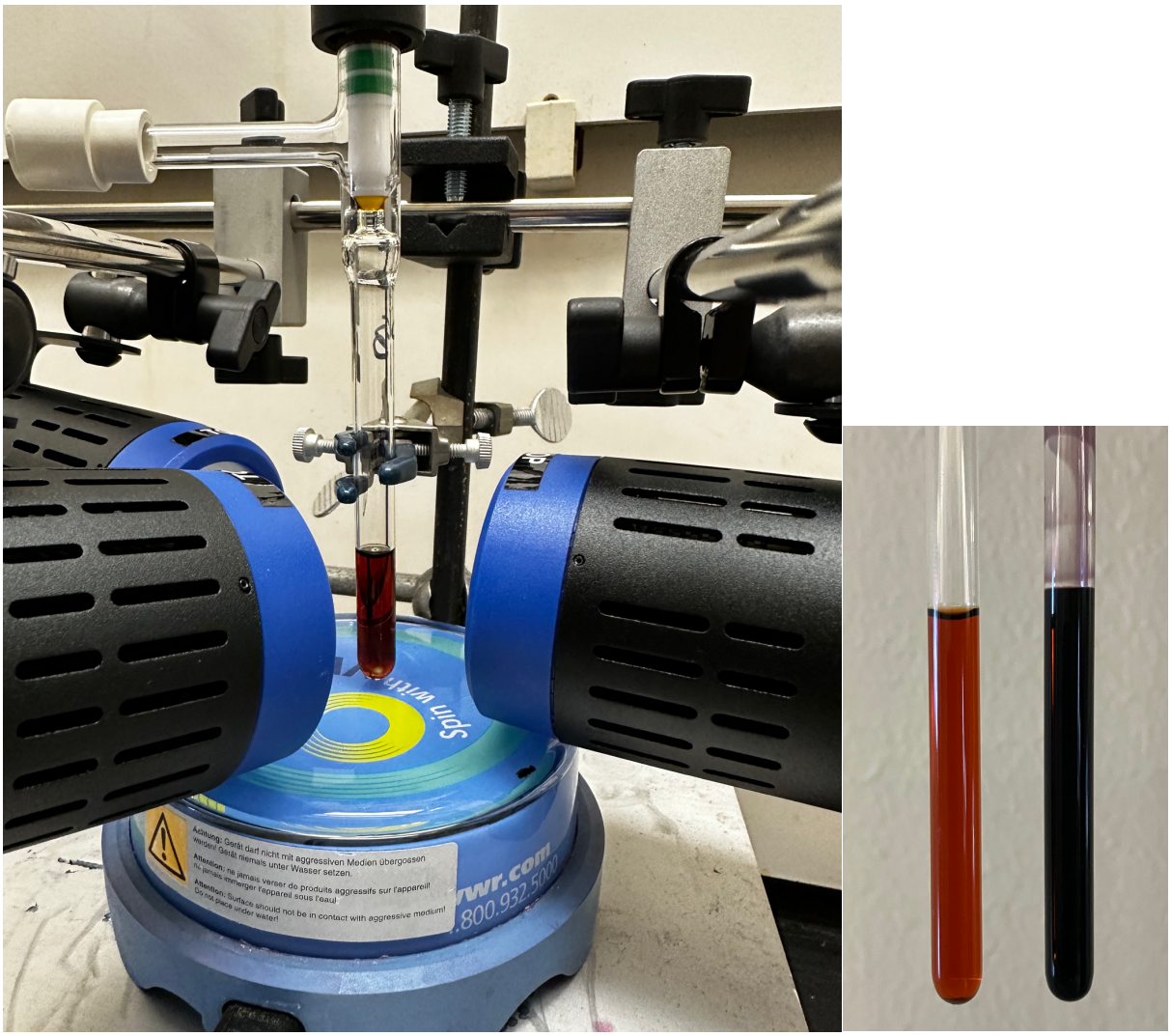


Figure S1. (Left) Apparatus assembly for photolysis of (POCOP$^{t\text{Bu}}$)CrBn utilizing three Kessil lamps. A fan (not shown) is directed down on the reaction vessel to mitigate heat generated by lamps. (Right) The color evolution of the photolysis reaction: (POCOP$^{t\text{Bu}}$)CrBn (left) and [(POCOP$^{t\text{Bu}}$)Cr]$_2$(μ-N$_2$) (right).

IV. NMR Spectra

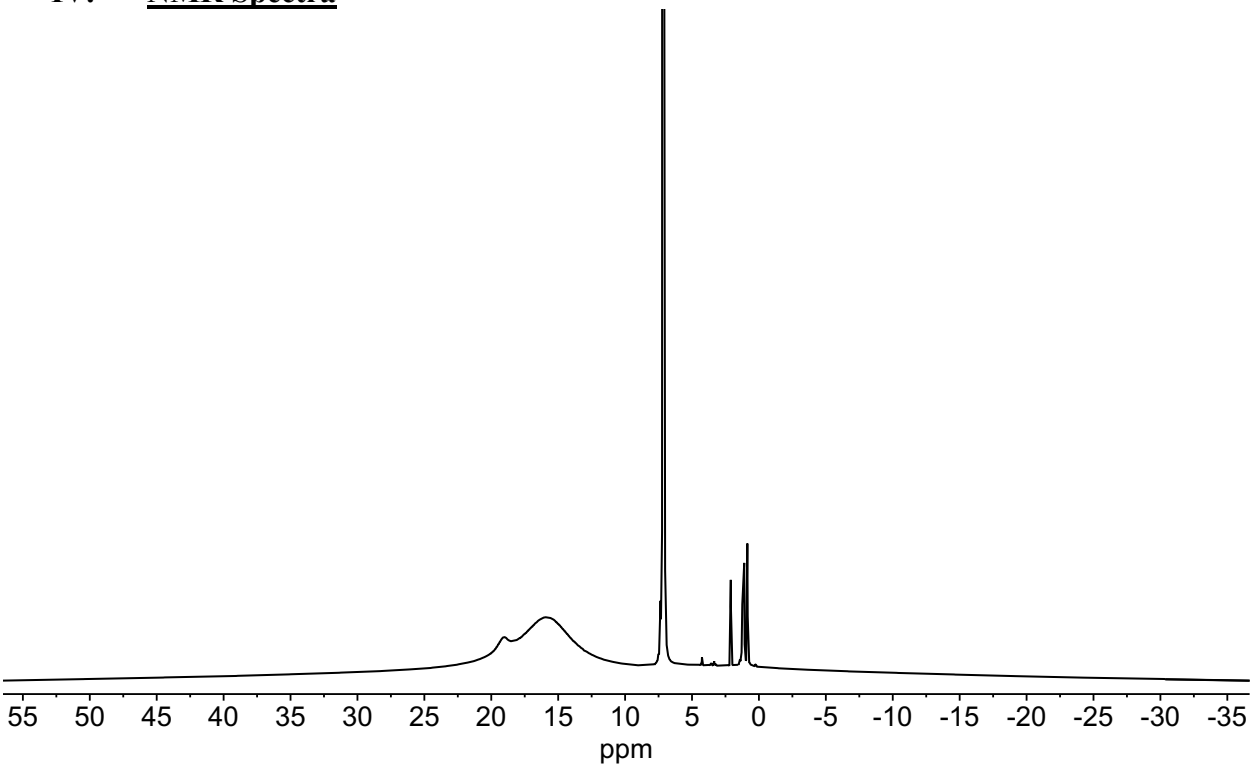


Figure S2. ^{1}H NMR spectrum of (POCOP$^{t\text{Bu}}$)CrBr in benzene-d_6.

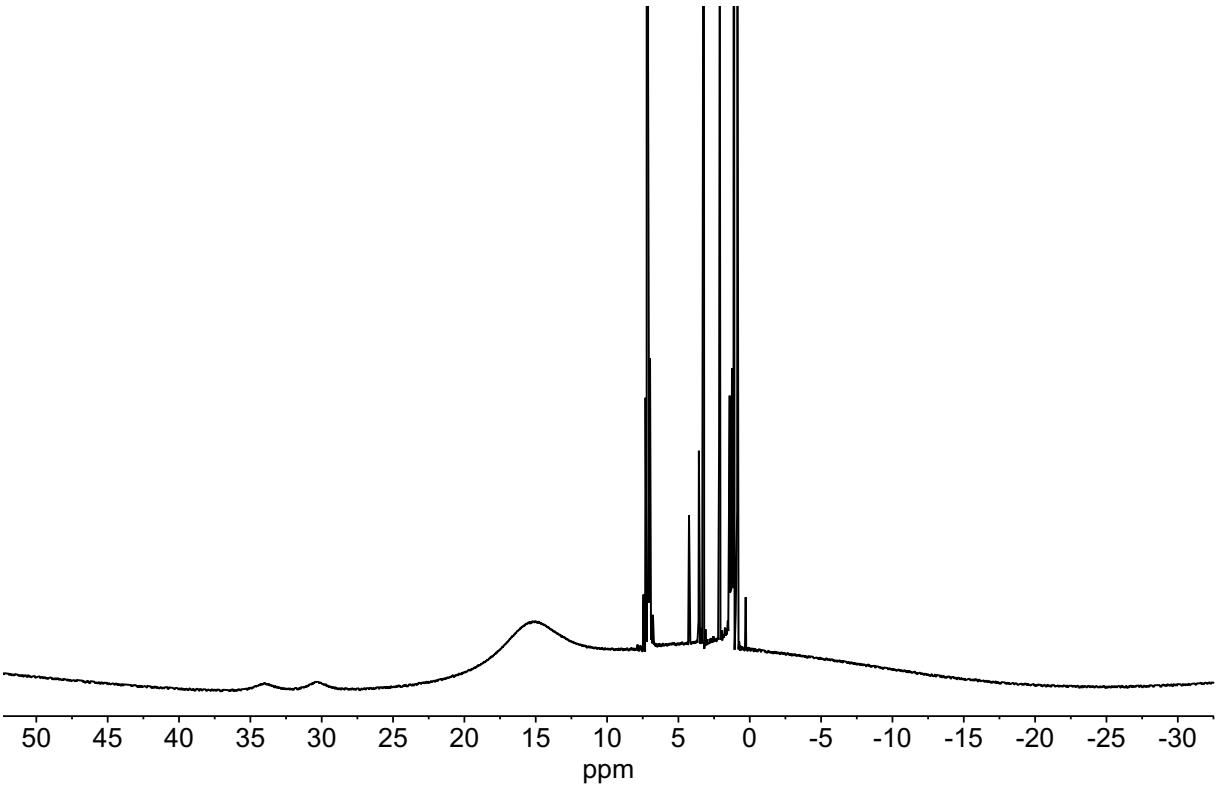


Figure S3. ^{1}H NMR spectrum of **1** in benzene-d_6. Residual solvent peaks in diamagnetic region.

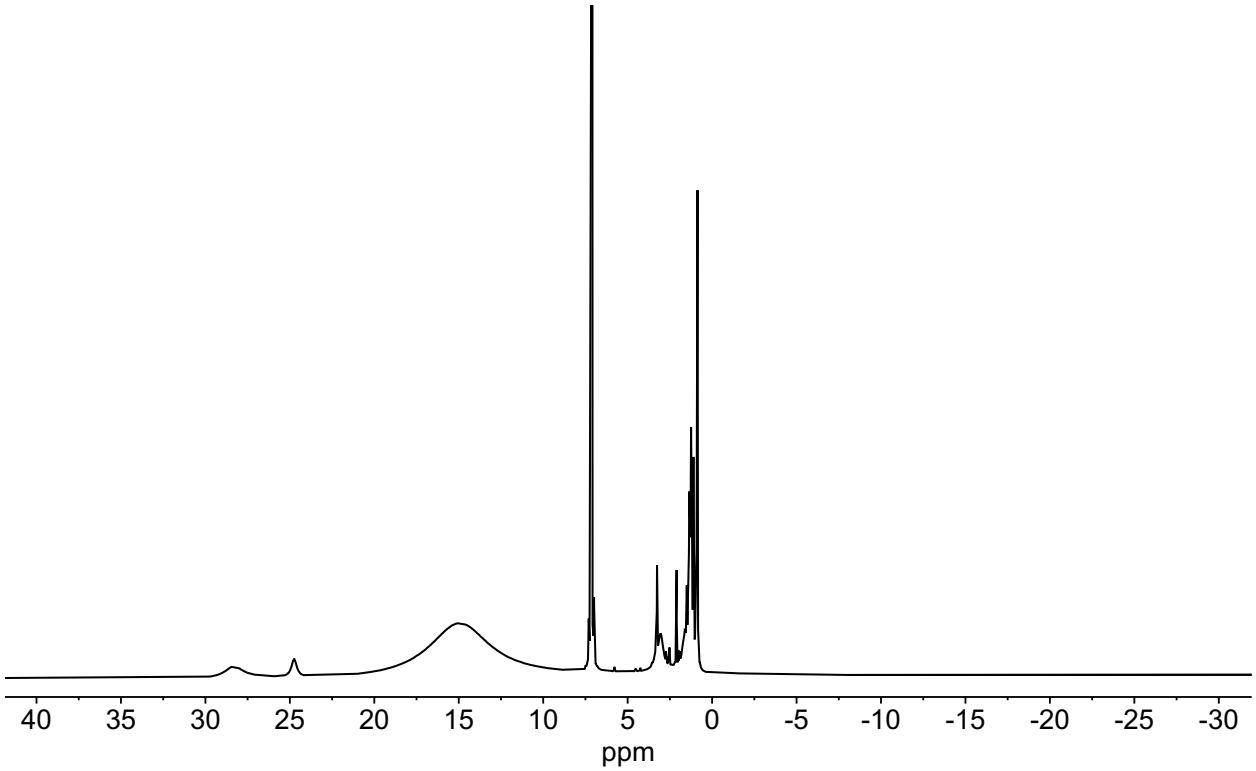


Figure S4. ^{1}H NMR spectrum of **2** in benzene-d_6. Residual solvent Et_2O peaks at 3.25 and 1.11 ppm.

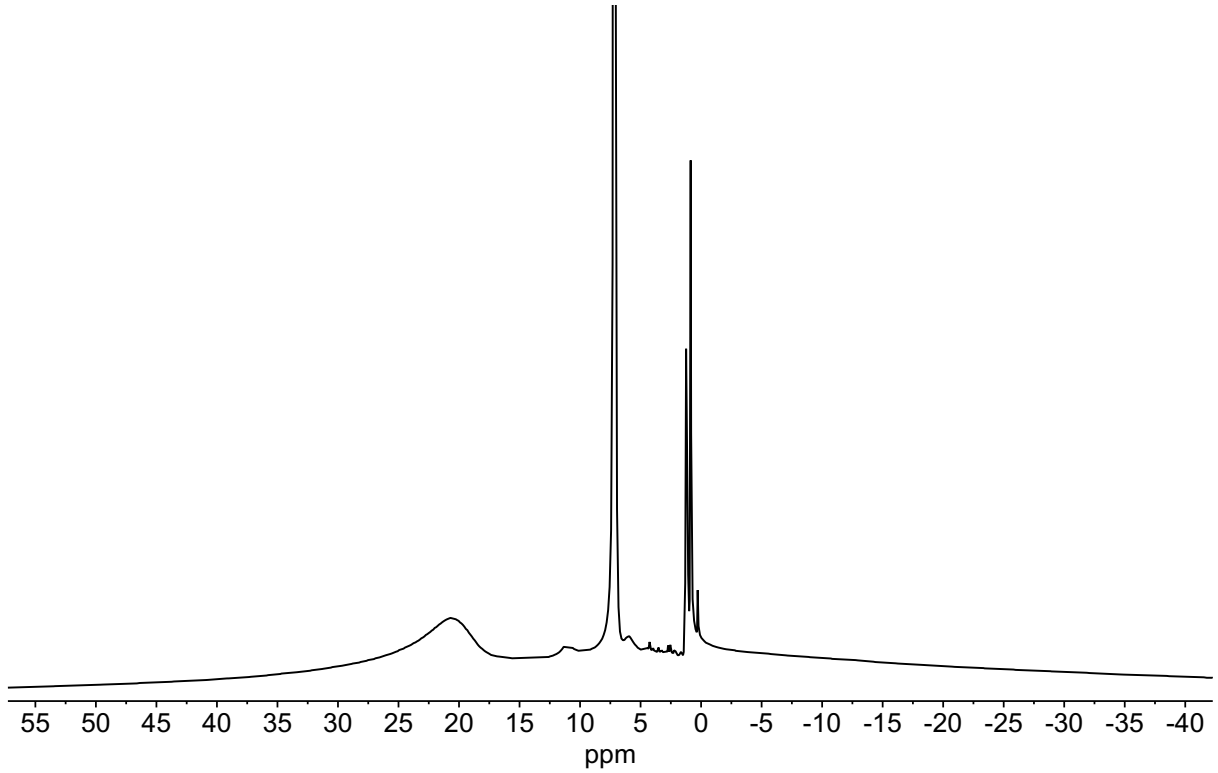


Figure S5. ^{1}H NMR spectrum of **3** recorded in benzene-d_6.

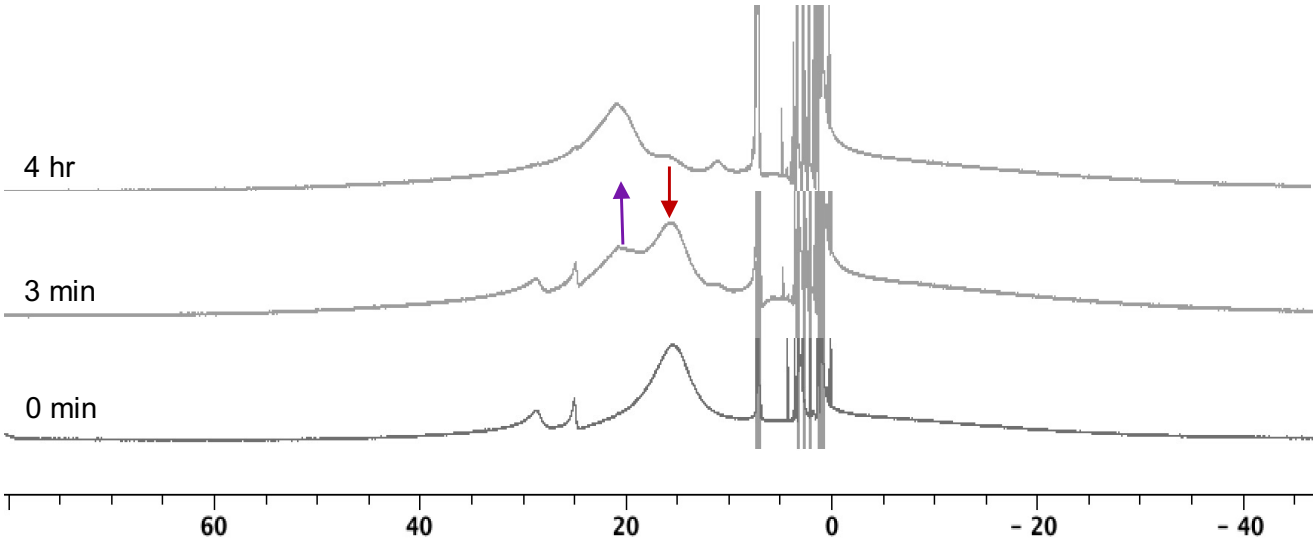


Figure S6. ^{1}H NMR spectra of the photolysis of **2** in benzene-d_6 under an N_2 atmosphere at time points: 0 min, 3 min, and 4 h. Increased exposure to blue light results in the decrease of the starting (POCOP$^{t\text{Bu}}$)CrBn complex (red arrow) and the formation of [(POCOP$^{t\text{Bu}}$)Cr]$_2$(μ-N_2) (purple arrow).

V. Infrared Spectra

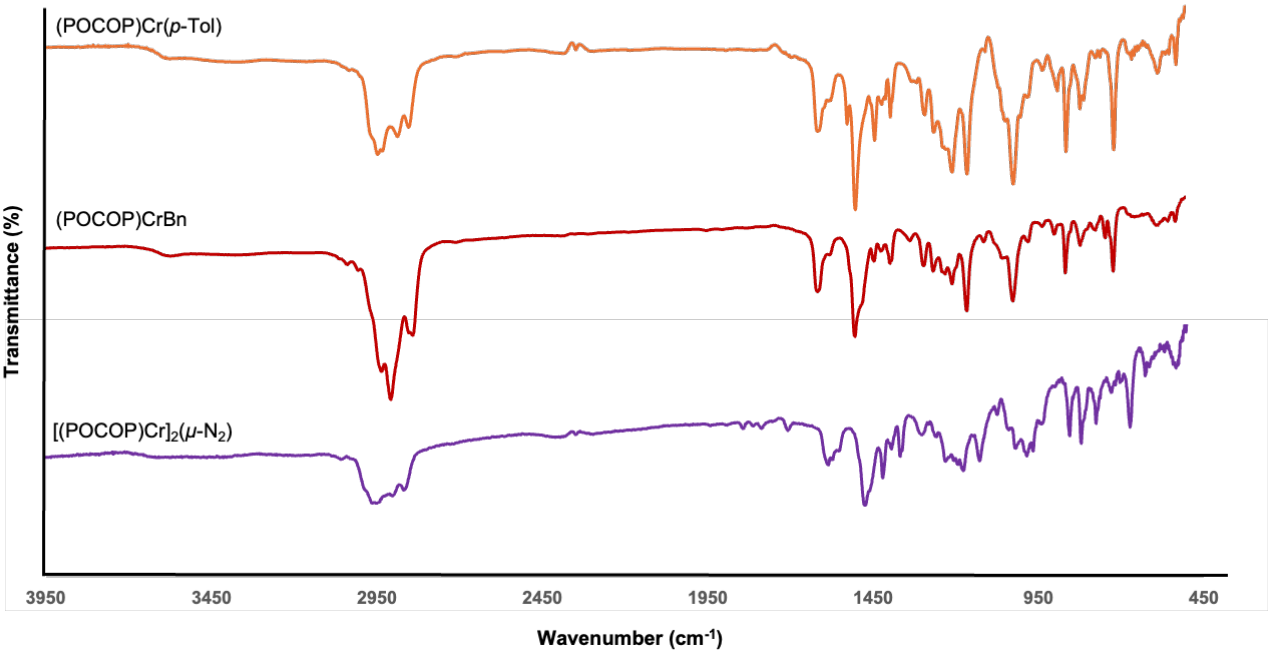


Figure S7. IR spectra of (POCOP$^{t\text{Bu}}$)Cr(p-Tol), (POCOP$^{t\text{Bu}}$)CrBn, and [(POCOP$^{t\text{Bu}}$)Cr]$_2$(μ-N_2) prepared as KBr pellets.

VI. UV-Visible Spectra

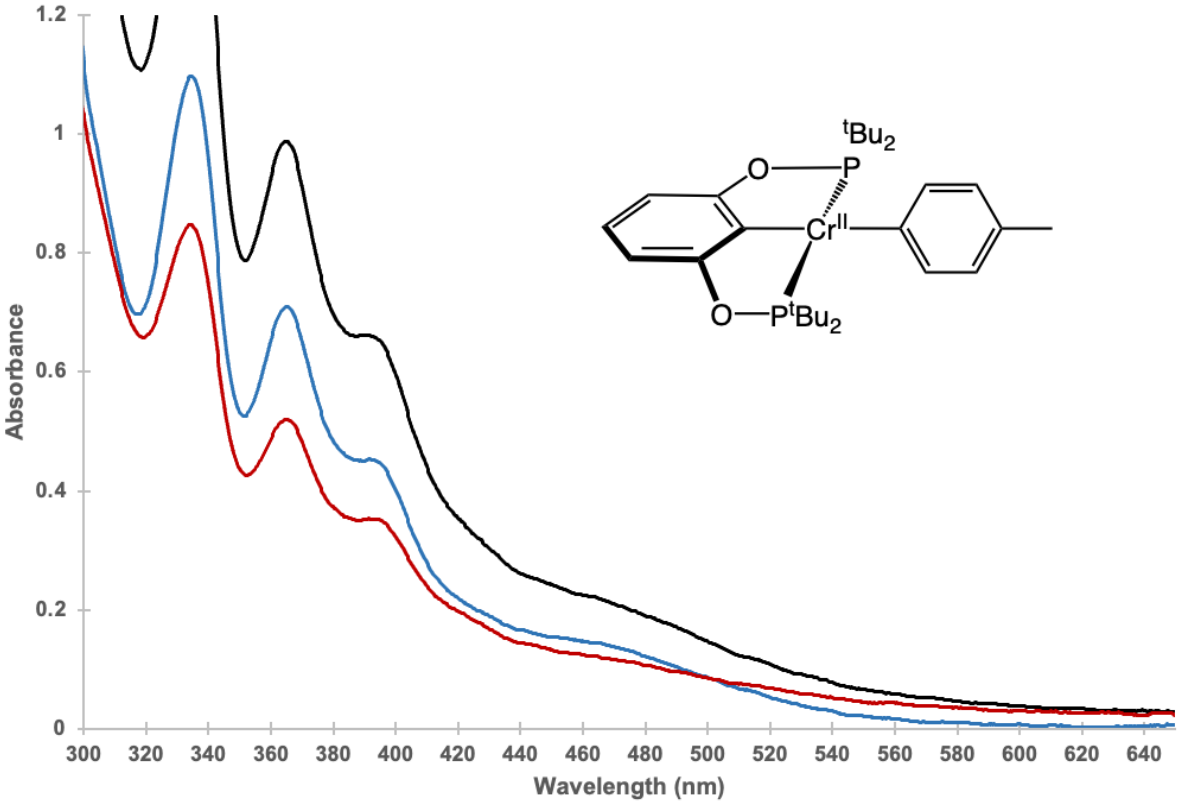


Figure S8. UV-vis spectra of **1** recorded in toluene. Sample concentrations of **1** are 9.99 x 10^{-4} M; 5.99 x 10^{-4} M; 3.00 x 10^{-4} M.

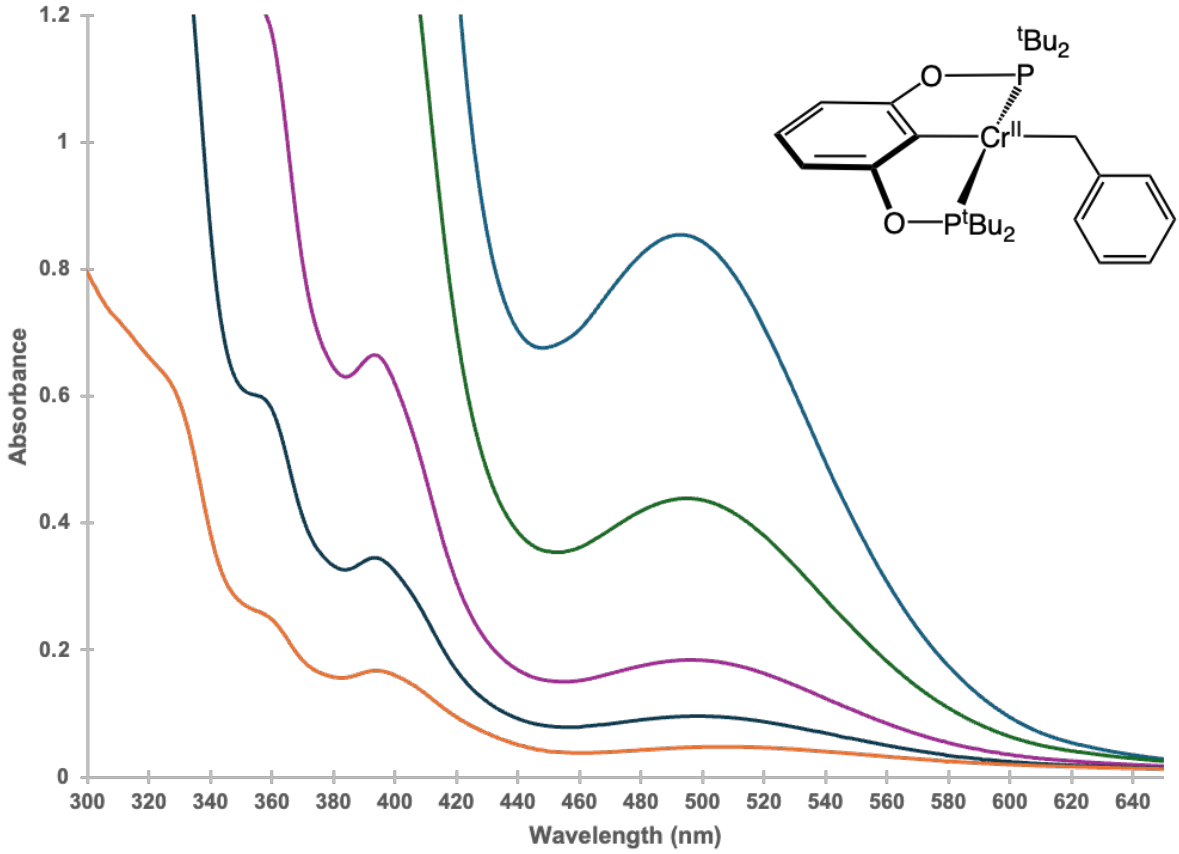


Figure S9. UV-vis spectra of **2** recorded in toluene. Sample concentrations of **2** are 1.63×10^{-3} M; 8.14×10^{-4} M; 3.26×10^{-4} M; 1.63×10^{-4} M; 8.14×10^{-4} M.

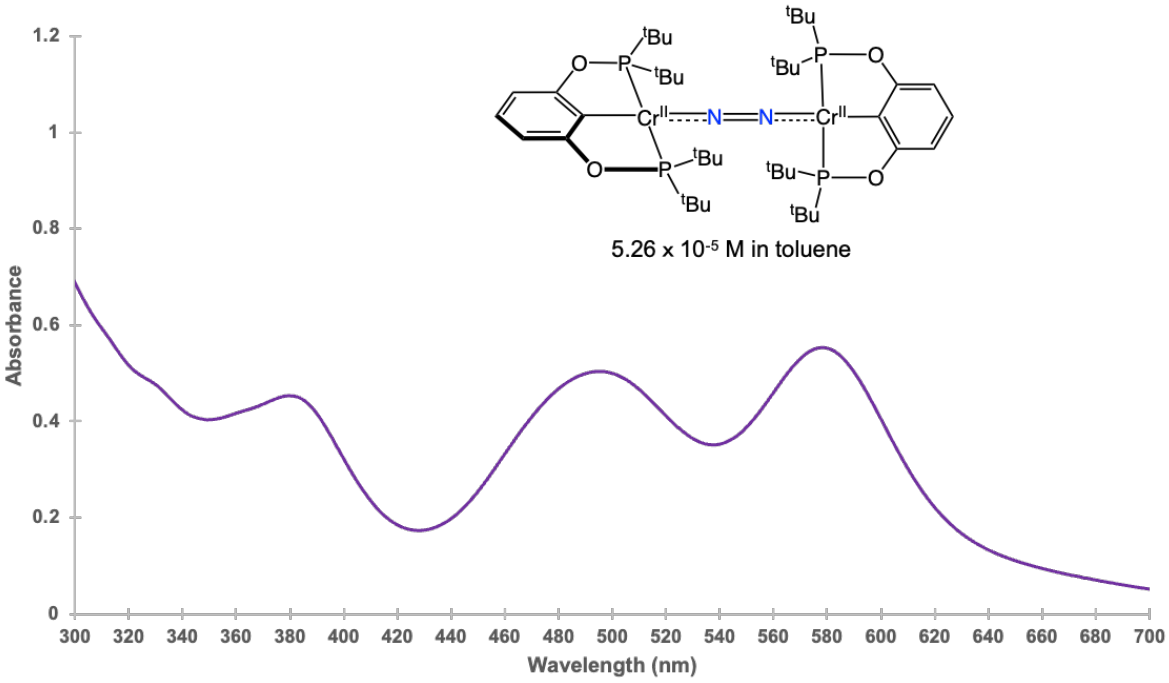


Figure S10. UV-vis spectrum of **3** recorded in toluene.

VII. Raman Spectra

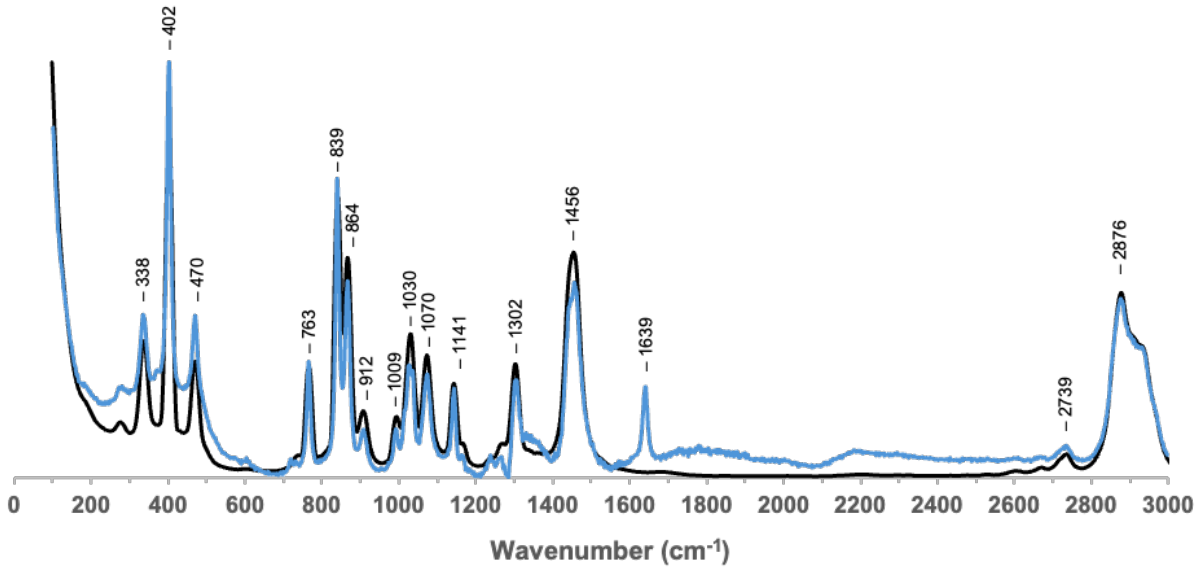


Figure S11. Raman spectra of **3** (blue trace) recorded in pentane at room temperature (λ = 785 nm). Raman spectrum of neat pentane (black trace).

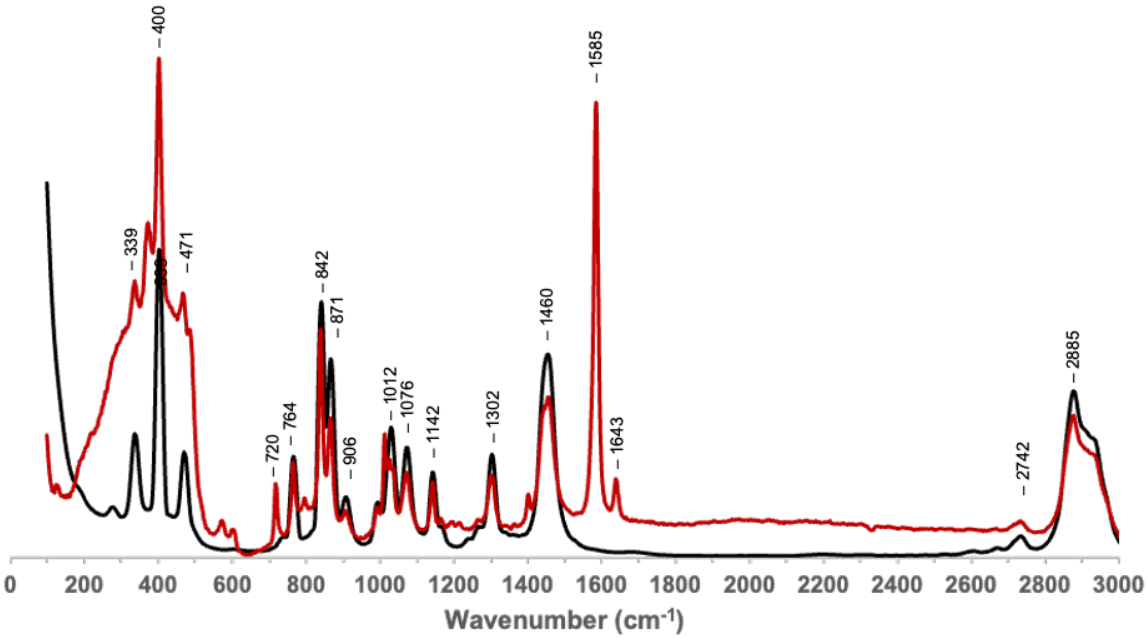


Figure S12. Raman spectra of $\mathbf{3}^{\mathbf{15N}}$ (red trace) recorded in pentane at room temperature (λ = 785 nm). Raman spectrum of neat pentane (black trace).

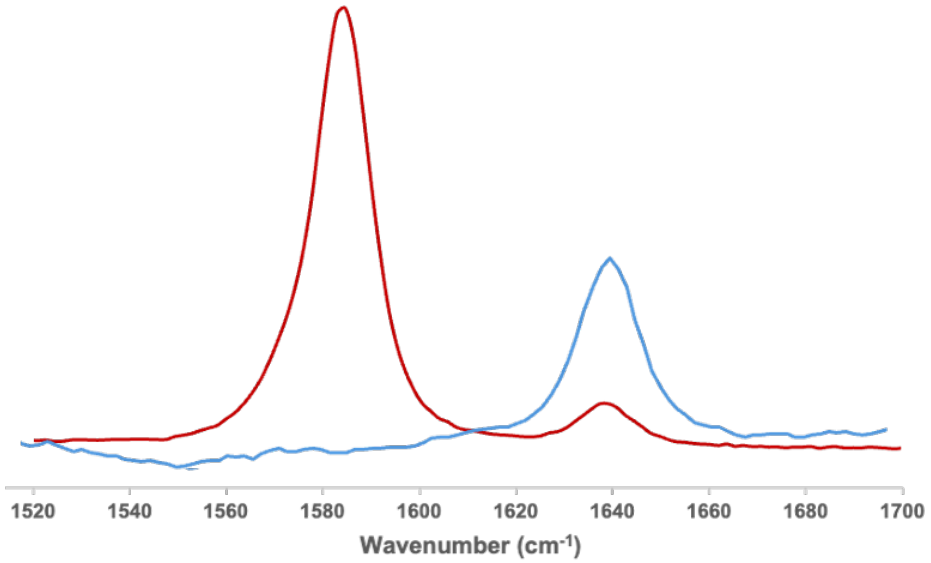


Figure S13. Overlayed Raman spectra of $\mathbf{3}^{\mathbf{15N}}$ (red) and **3** (blue) in pentane (λ = 785 nm) at room temperature.

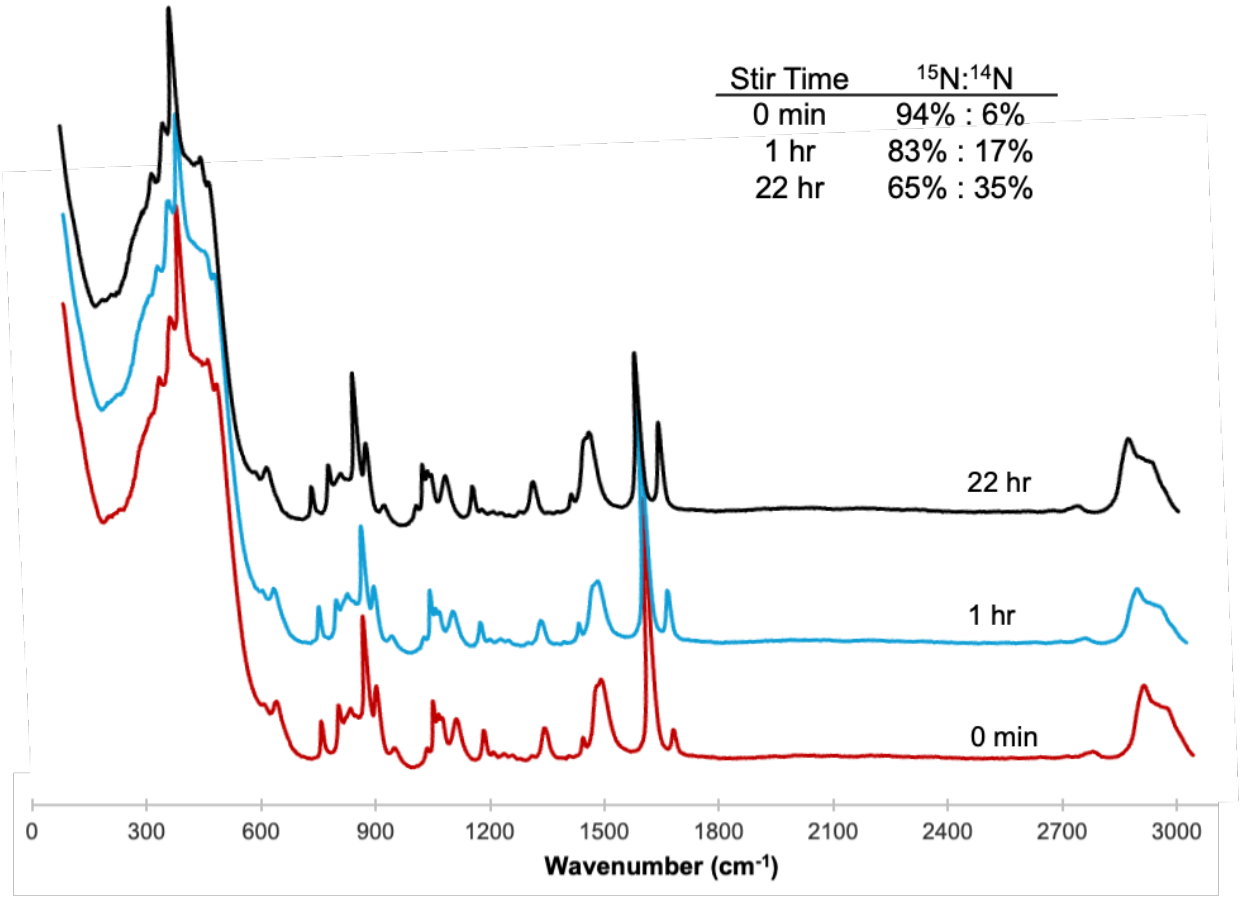


Figure S14. Raman spectra of $^{15}N_2/^{14}N_2$ exchange of $\mathbf{3}^{\mathbf{15N}}$ to **3**. A solution of [(POCOP$^{t\mathrm{Bu}}$)Cr]$_2$(μ-$^{15}N_2$) (14 mg, 0.015 mmol) in pentane (2 mL) was stirred under an $^{14}N_2$ atmosphere. Over time $^{15}N_2/^{14}N_2$ exchange occurred and the solution maintained a purple color.

IX. Radical Trap Experiments

Under an N_2 atmosphere, TEMPO (1.6 mg, 0.01 mmol, 1 equiv) was added to a red solution of **2** (5.3 mg, 0.01 mmol) in C_6D_6 (0.5 mL). No apparent color change was observed during 24 h of mixing. **2** was not fully consumed in the reaction (Figure S16), and the formation of TEMPO–CH_2Ph (Figure S15) was noted by ^{1}H NMR spectroscopy. Alternatively, the addition of two equiv of TEMPO (1.9 mg, 0.012 mmol) to a solution of **2** (3 mg, 0.006 mmol) in C_6D_6 (0.5 mL) resulted in an immediate color change from red to dark blue. ^{1}H NMR spectroscopy indicates the formation of TEMPO–CH_2Ph (77% NMR yield) and full consumption of **2**. **3** was not formed in this reaction. *TEMPO–CH_2Ph*: ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 4.89 (s, 2 H, C*H*$_2$Ph), 1.46 (m, 3 H, C*H*$_2$ TEMPO), 1.32 (m, 1 H, C*H*$_2$ TEMPO), 1.28 (s, 6 H, C*H*$_3$ TEMPO), 1.17 (s, 6 H, C*H*$_3$ TEMPO), 1.06 (m, 2 H, C*H*$_2$ TEMPO).

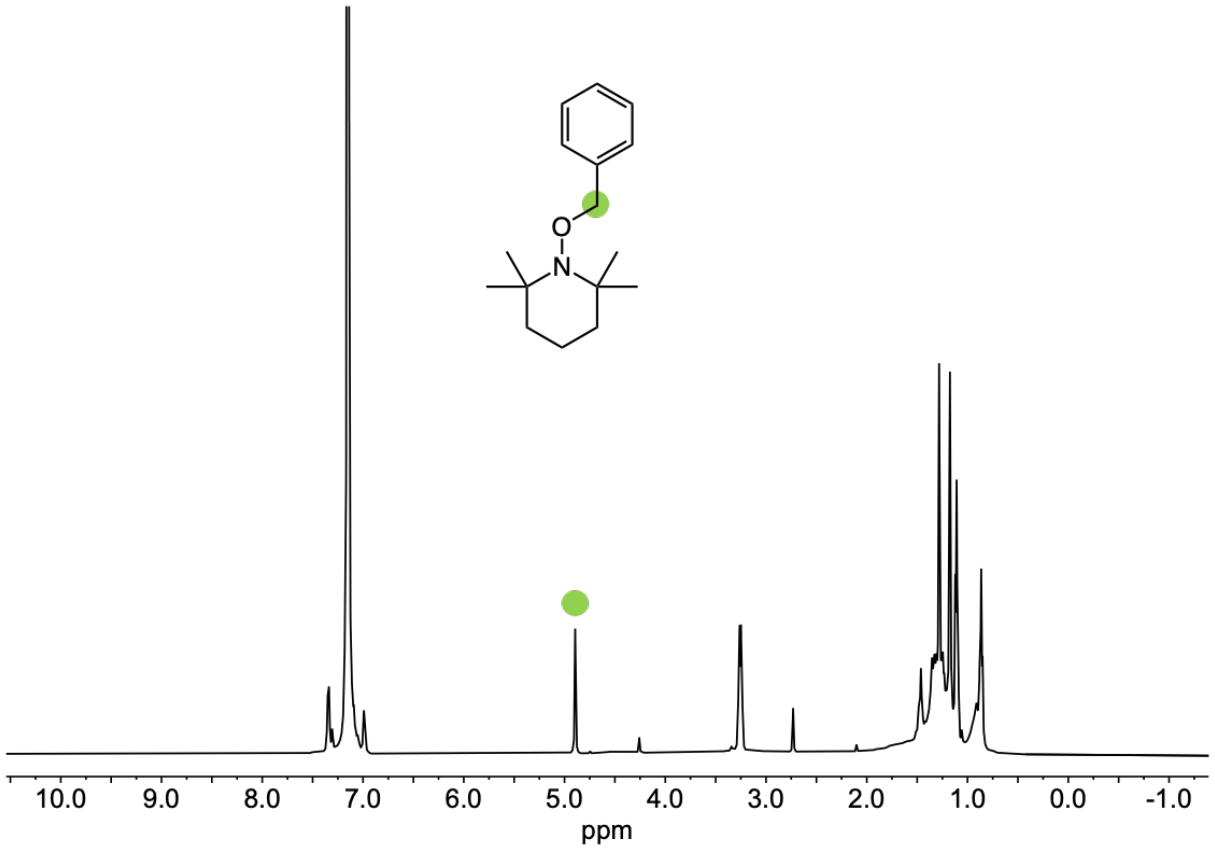


Figure S15. Diamagnetic region of ^{1}H NMR spectrum of **2** in the presence of TEMPO (1 equiv) under an N_2 atmosphere. Bibenzyl (PhC*H*$_2$)$_2$ formation at 2.73 ppm. Residual solvent Et_2O resonance at 3.26 ppm. TEMPO-C*H*$_2$Ph resonance at 4.9 ppm.

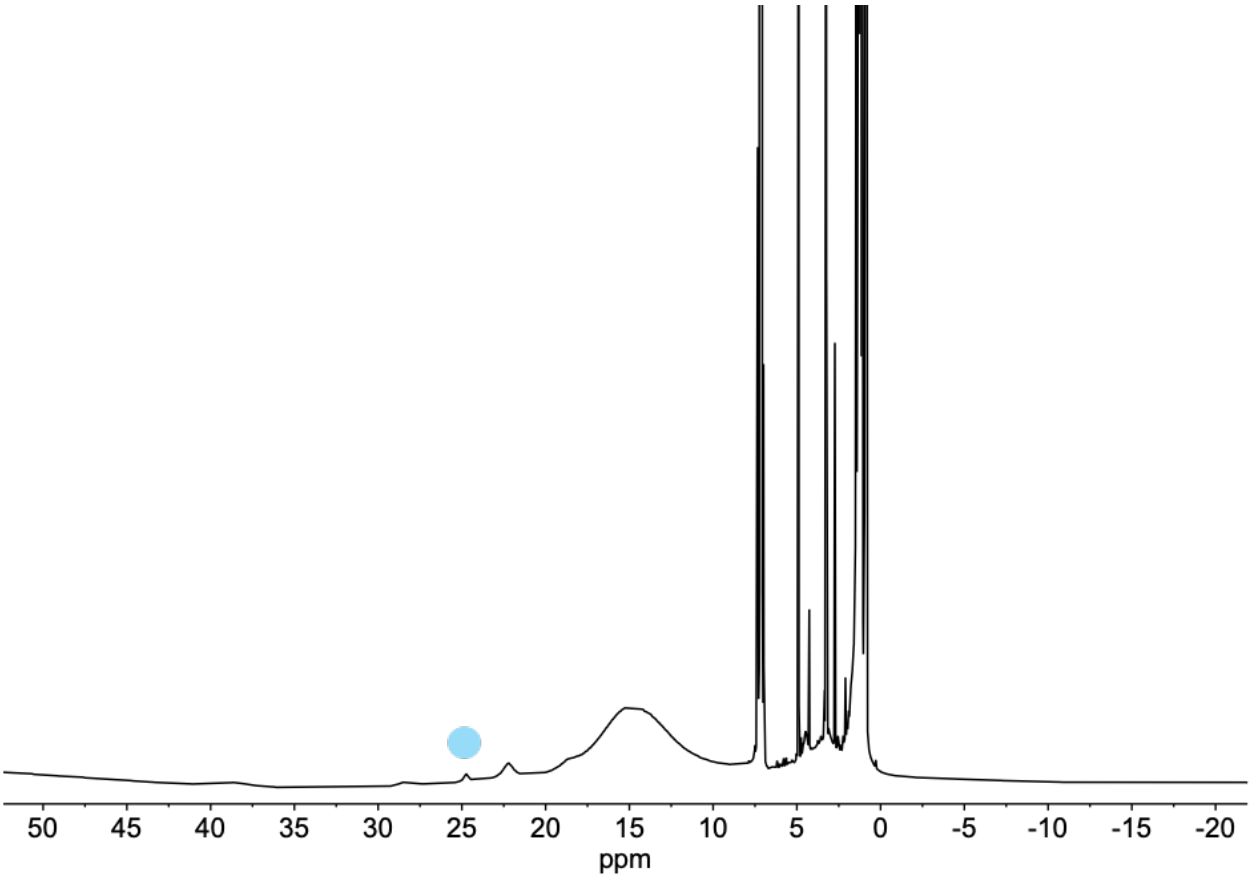


Figure S16. Wide sweep width of the ^{1}H NMR spectrum of **2** in the presence of TEMPO (1 equiv) under an N_2 atmosphere. **2** was not completely consumed (blue) after 24 h of mixing.

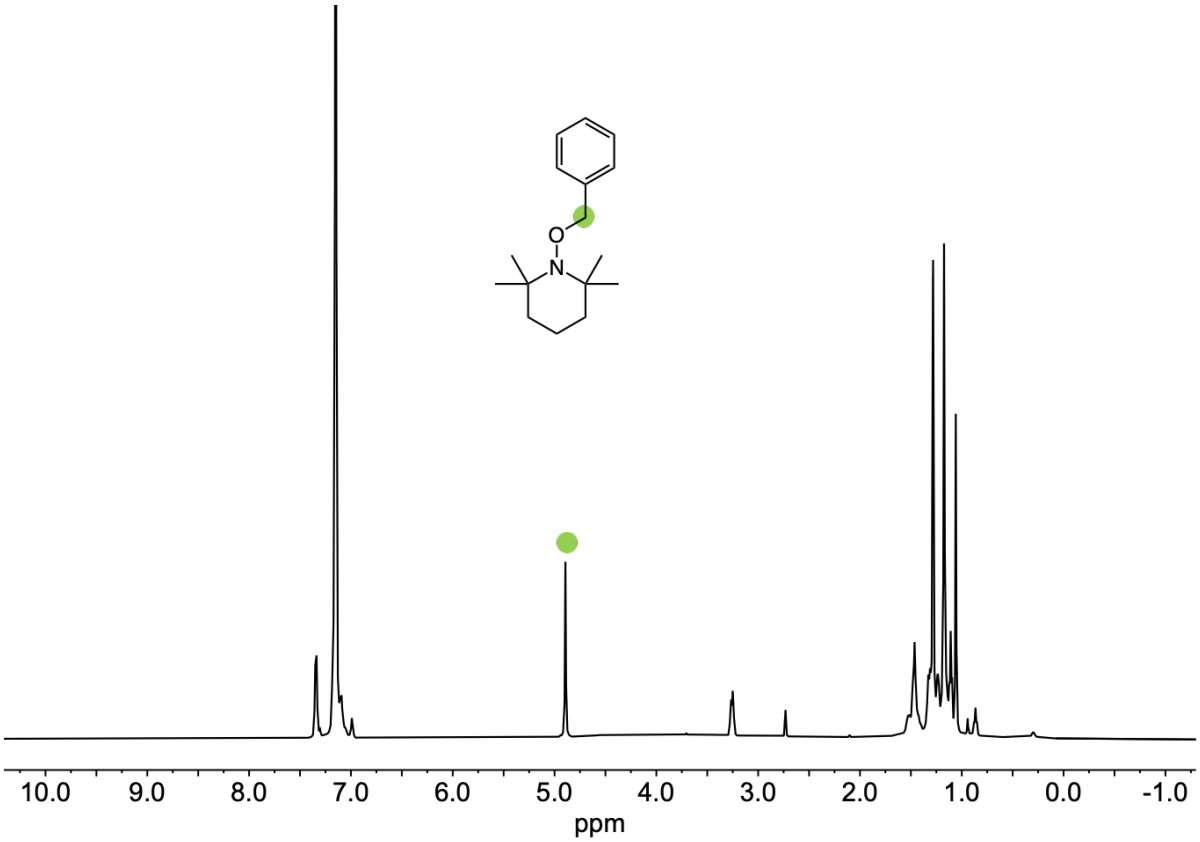


Figure S17. Diamagnetic region of ^{1}H NMR spectrum of **2** in the presence of TEMPO (2 equiv) under an N_2 atmosphere. Bibenzyl (PhCH_2)$_2$ resonance at 2.73 ppm. TEMPO-CH_2Ph resonance at 4.9 ppm.

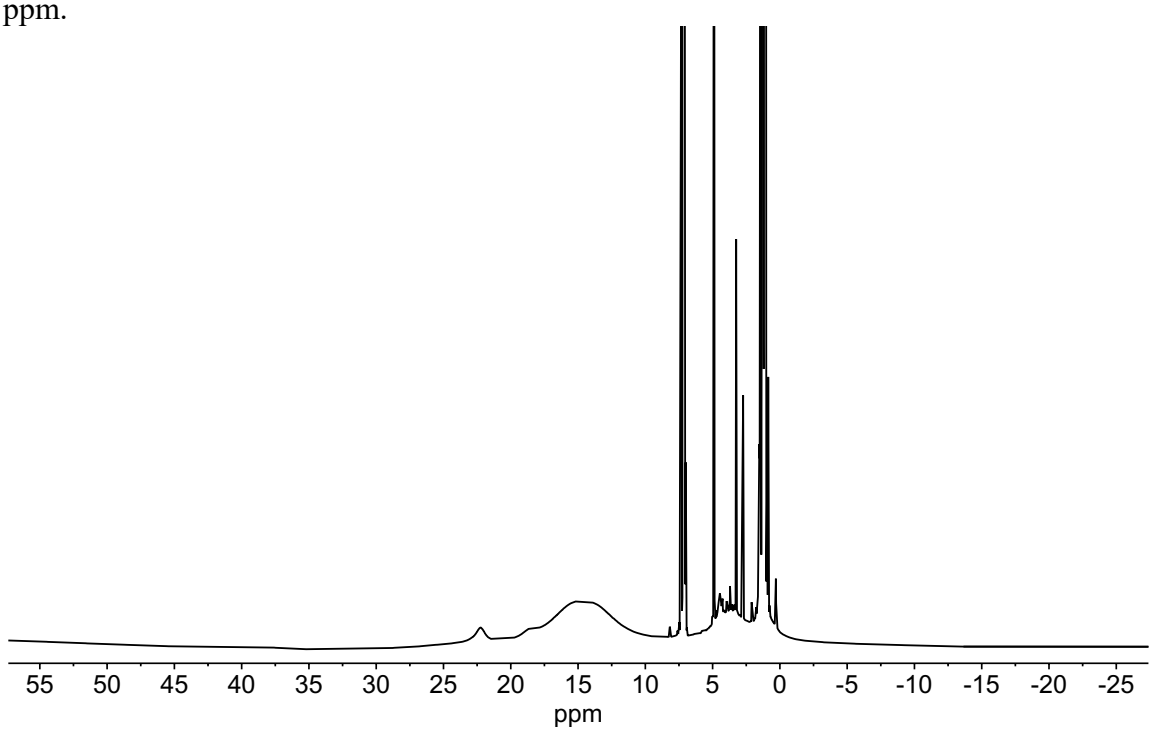


Figure S18. Wide sweep width of the ^{1}H NMR spectrum of **2** in the presence of TEMPO (2 equiv) under an N_2 atmosphere. **2** was completely consumed after 5 min of mixing.

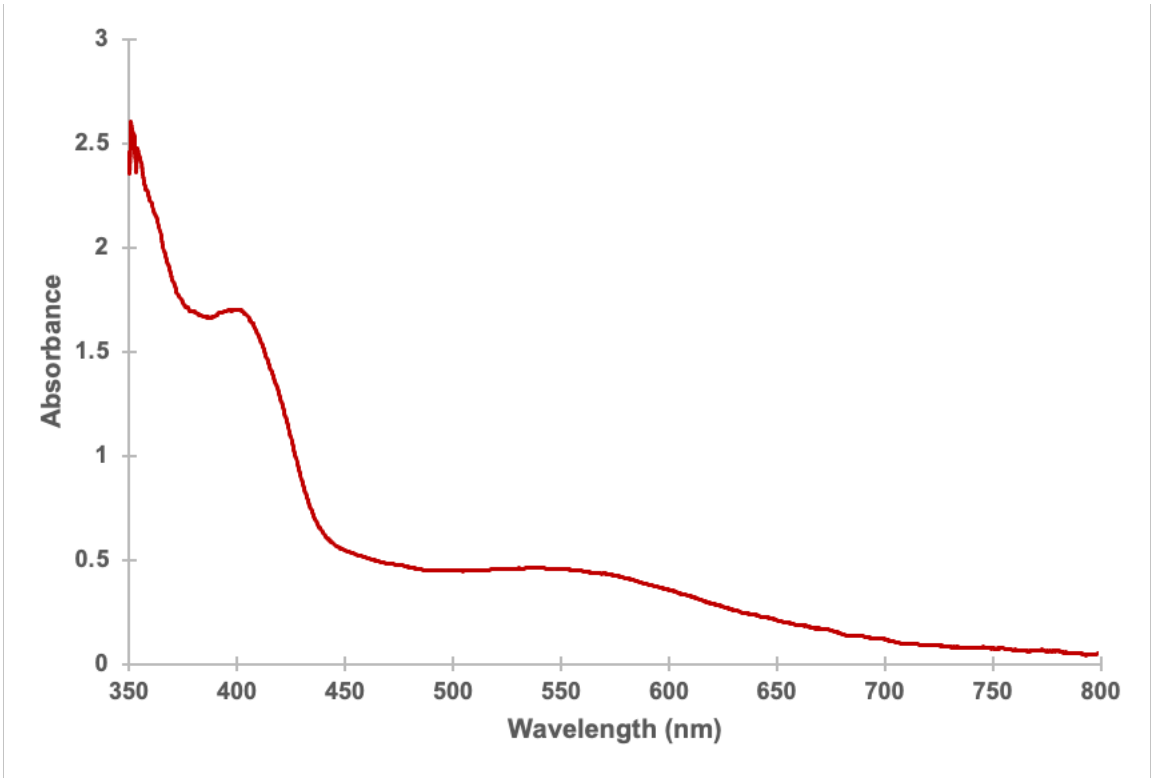


Figure S19. UV-vis spectrum of **2** recorded in pentane in the presence of TEMPO (1 equiv) under an N_2 atmosphere.

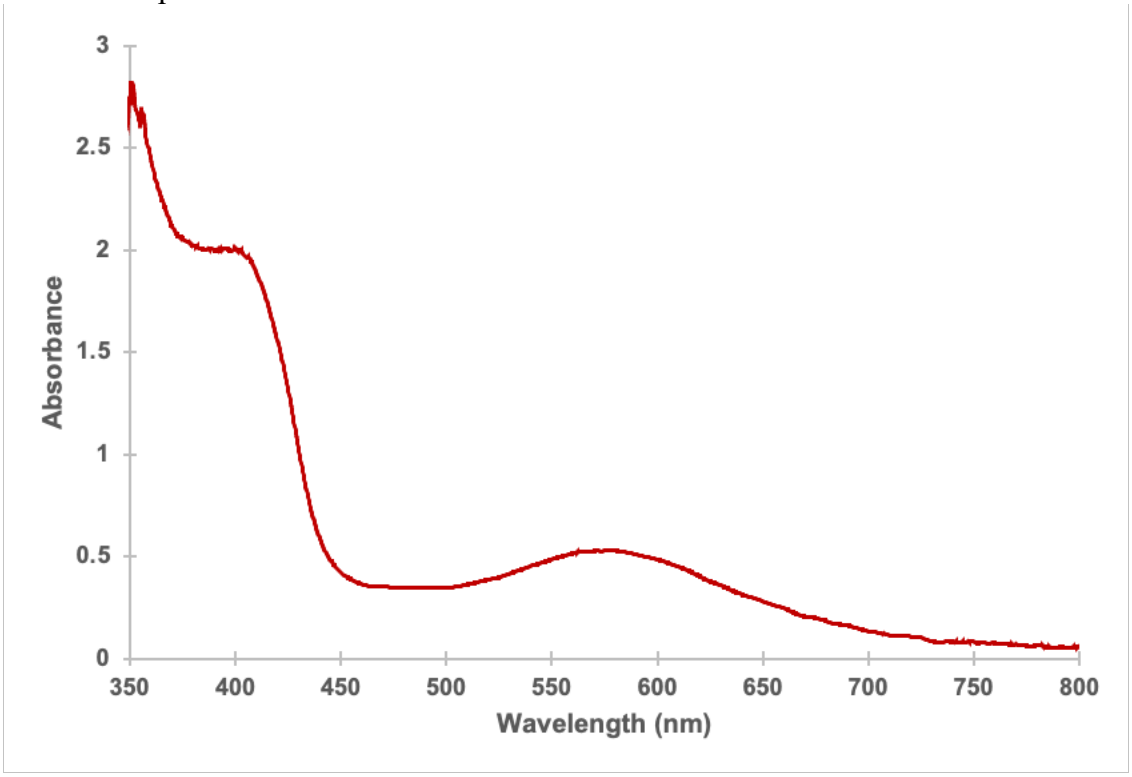


Figure S20. UV-vis spectrum of **2** recorded in pentane in the presence of TEMPO (2 equiv) under an N_2 atmosphere.

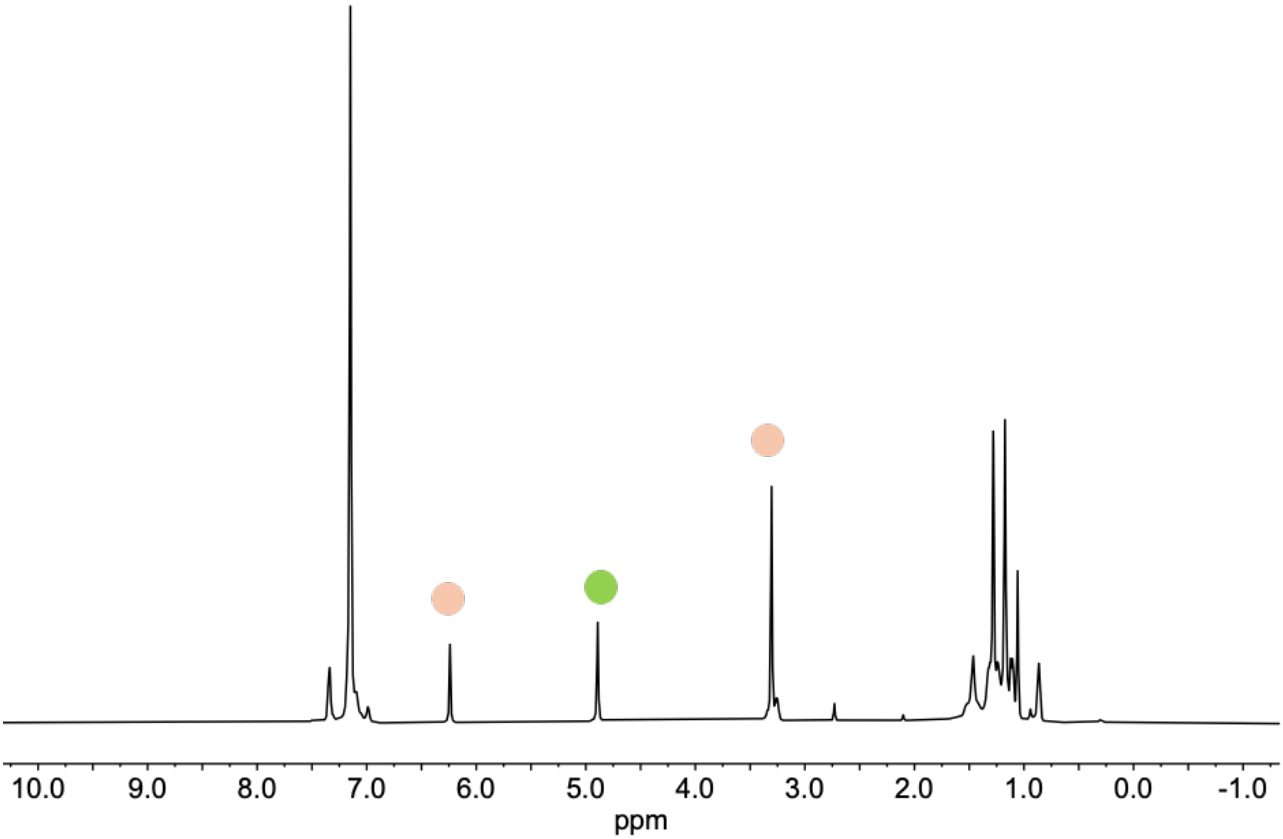


Figure S21. ^{1}H NMR spectrum (-1.0 to 10 ppm) of TEMPO-CH_2Ph quantification from TEMPO (2 equiv) addition to **2** under N_2 recorded in benzene-d_6. TEMPO-CH_2Ph (CH_2) [green] formation at 4.9 ppm. 1,3,5-trimethoxybenzene resonances at 6.2 (C_6H_3, 3 H) and 3.3 ppm (OCH_3, 9 H) [orange].

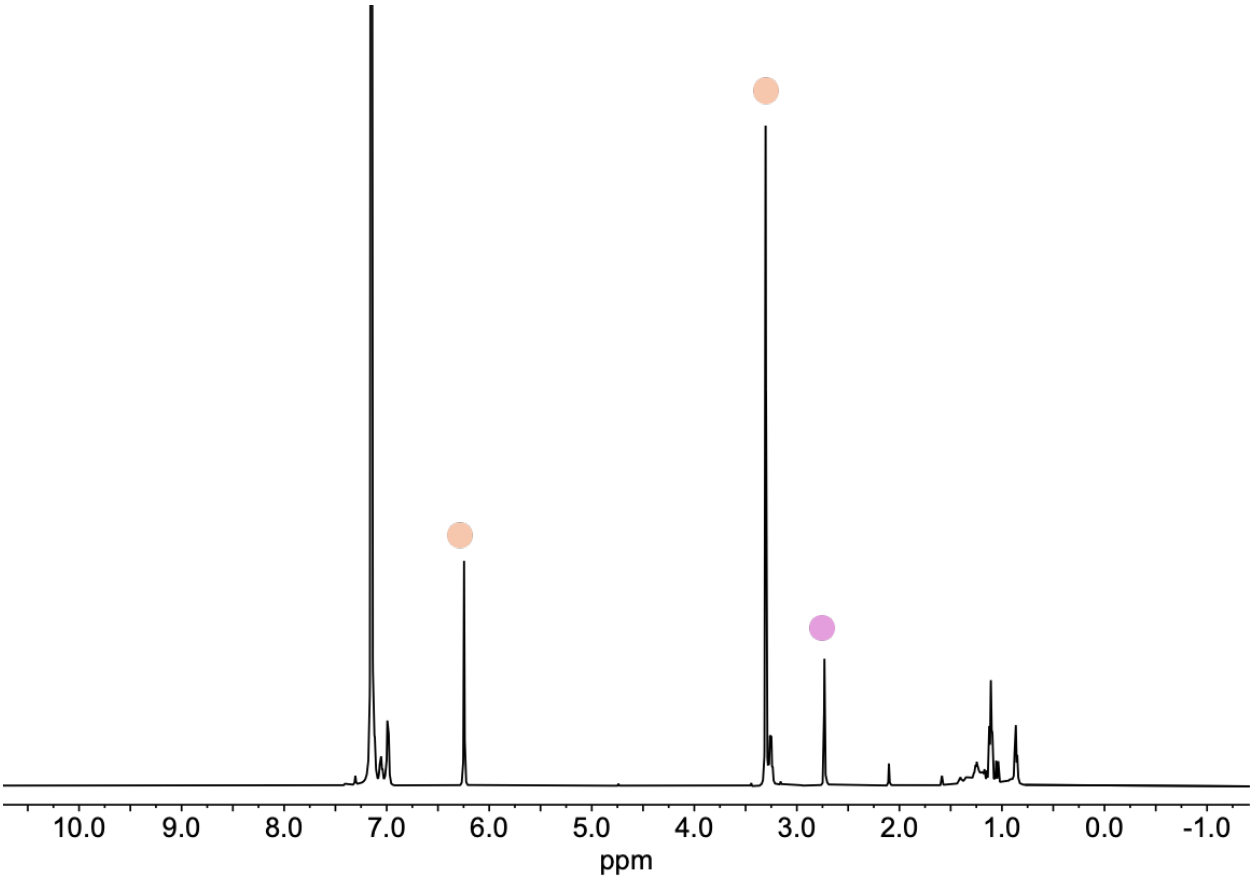


Figure S22. ^{1}H NMR spectrum (-1.0 to 10 ppm) of bibenzyl quantification from photolysis of **2** under N_2 recorded in benzene-d_6. Bibenzyl (PhCH_2)$_2$ [purple] formation (92% NMR yield) at 2.73 ppm. 1,3,5-trimethoxybenzene resonances at 6.2 (C_6H_3, 3 H) and 3.3 ppm (OCH_3, 9 H) [orange].

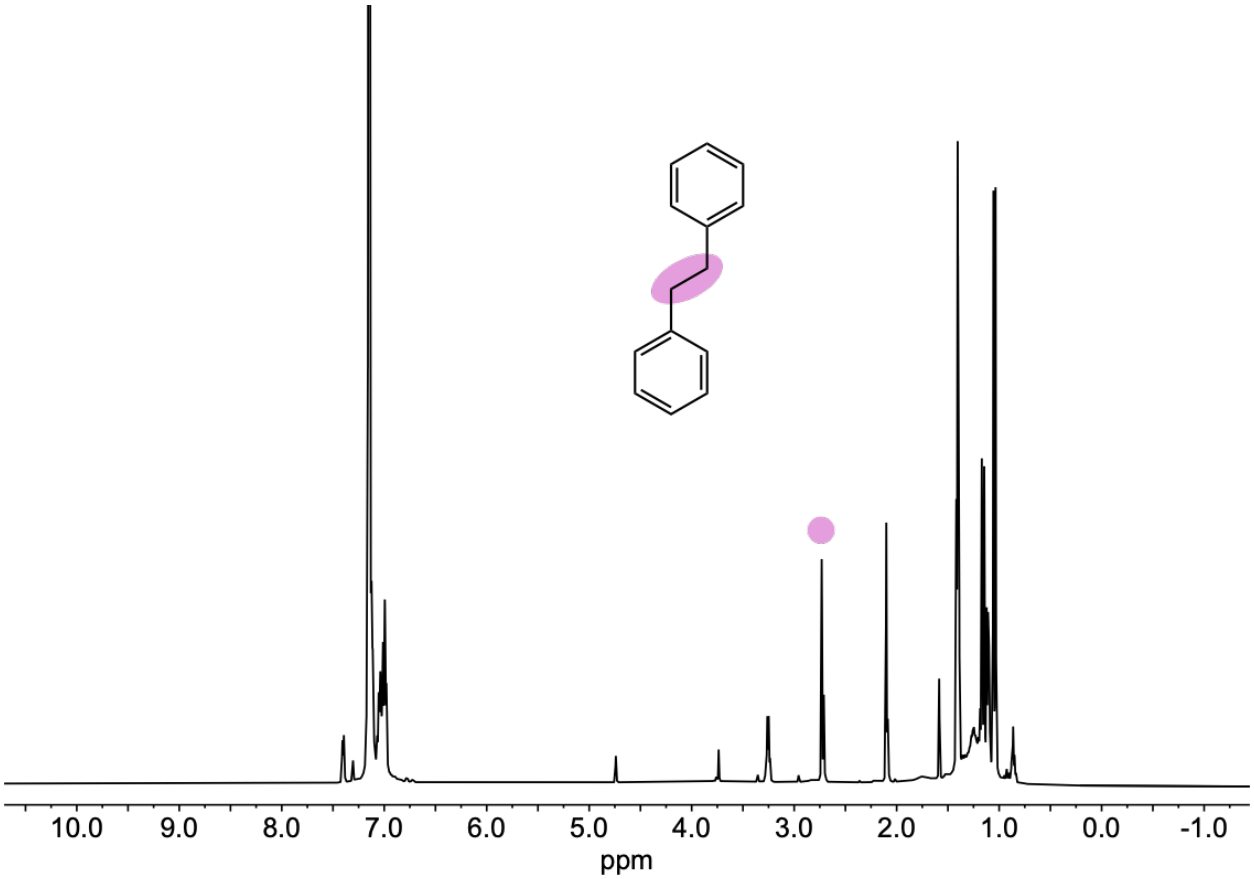


Figure S23. ^{1}H NMR spectrum (-1.0 to 10 ppm) of photolysis of **2** in the absence of N_2 recorded benzene-d_6. Bibenzyl (PhCH_2)$_2$ [purple] formation at 2.73 ppm.

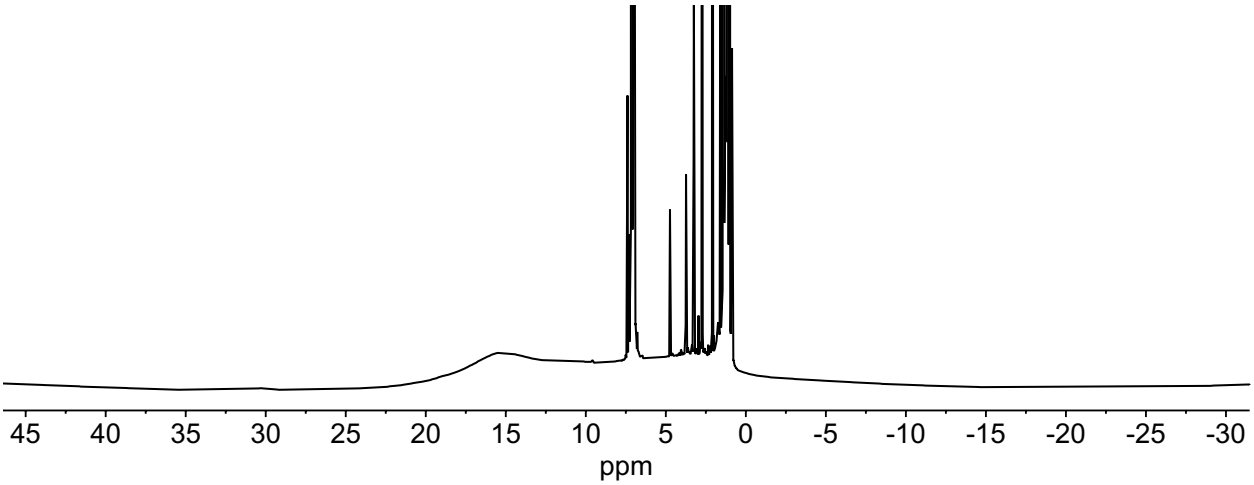


Figure S24. Wide sweep width ^{1}H NMR spectrum of photolysis of **2** in the absence of N_2 recorded benzene-d_6.

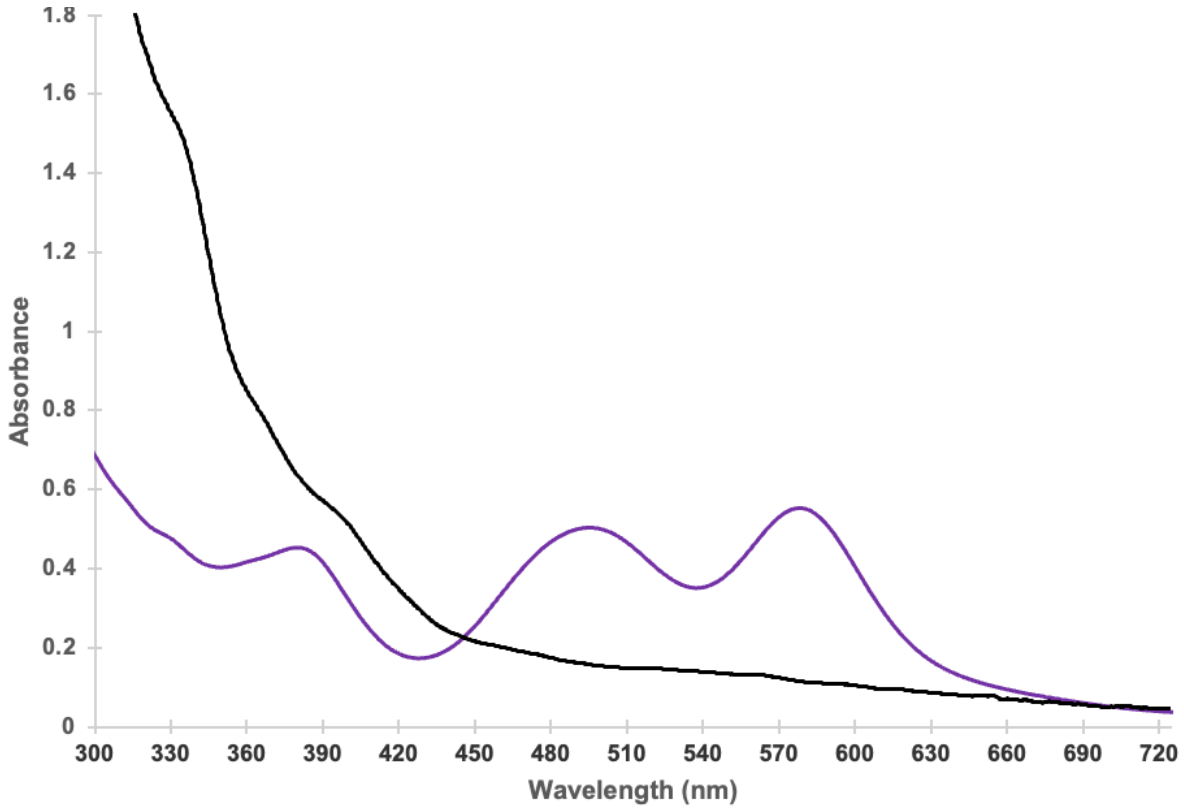
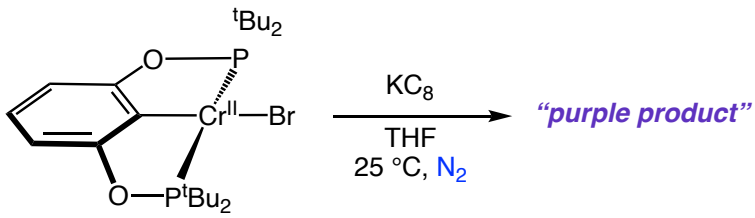


Figure S25. UV-Vis spectra recorded in toluene of **3** (purple trace) and the product generated from the photolysis of **2** in the absence of N_2 after being exposed to N_2 (black trace).

XII. KC_8 reduction of ($POCOP^{tBu}$)CrBr:



KC_8 (16.4 mg, 0.12 mmol) was added to a stirring solution of ($POCOP^{tBu}$)CrBr (58.4 mg, 0.11 mmol) in THF (9 mL). The solution stirred overnight, then was filtered through a pad of Celite. Volatiles were removed from the purple filtrate. The resulting solid was extracted with pentane (7 mL) and filtered through a Celite pad. The solution was concentrated and set up for recrystallization via slow evaporation. Yield: 16.9 mg. ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 15.5 (br s), 18.9 (br s), 20.7 (br s). No $^{31}P\{^1H\}$ signal. UV-vis (toluene): λ_{max}; 312, 330, 378, 392, and 519 nm. Elemental analysis indicated that nitrogen was not present in the bulk sample. Found: C, 52.96%; H, 8.36%; N, 0%. No (ν_{NN}) present via IR or Raman data.

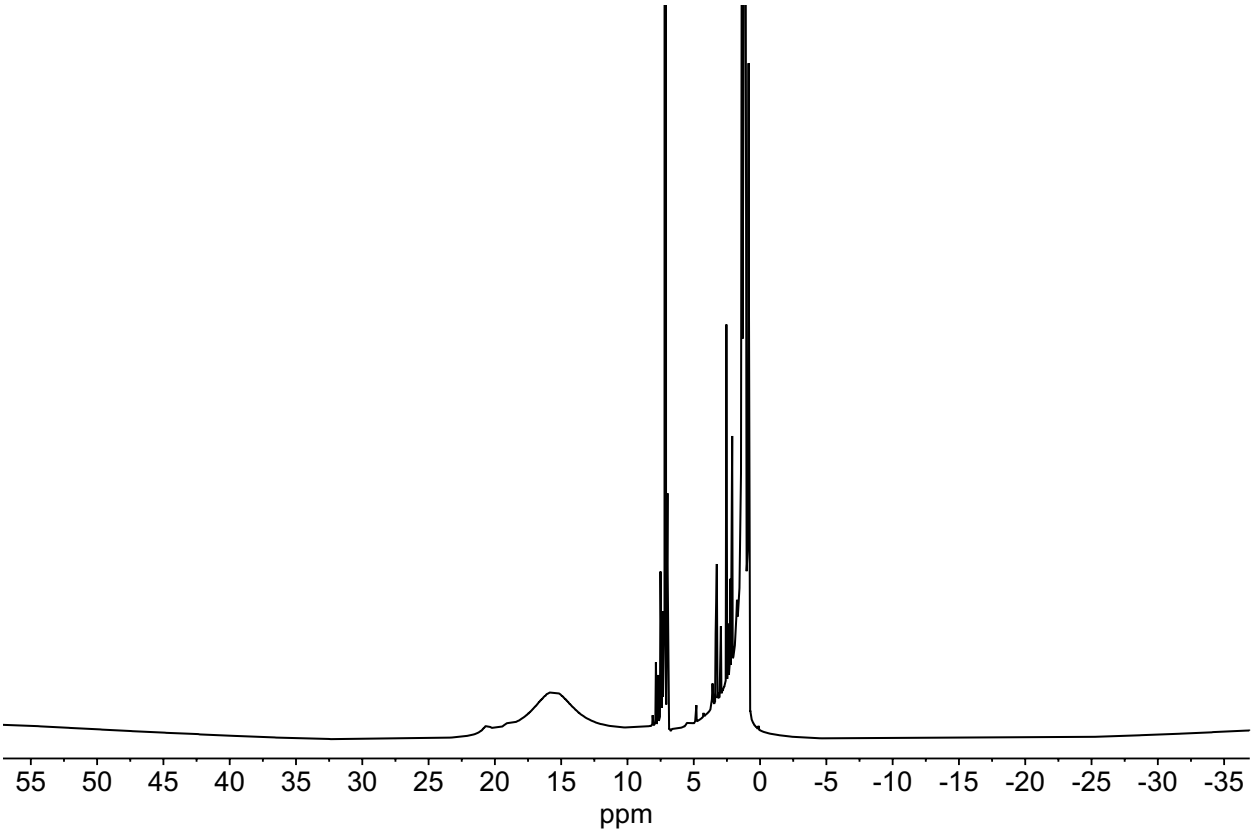


Figure S26. ^{1}H NMR spectrum recorded in benzene-d_6 of reduction product from the reaction of (POCOP$^{t\text{Bu}}$)CrBr with KC_8 under an N_2 atmosphere. $^{31}P\{^{1}H\}$ NMR displays free POCOP$^{t\text{Bu}}$ ligand.

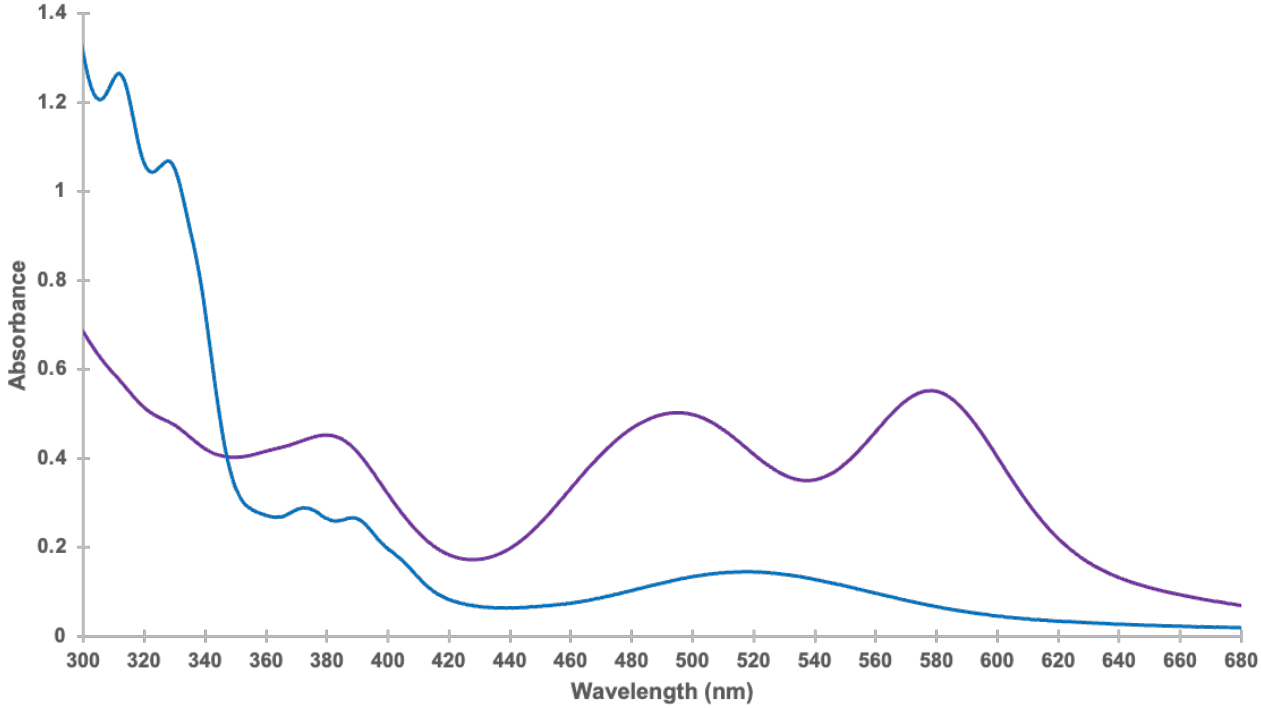


Figure S27. Comparison of the UV-Vis spectra recorded in toluene of [(POCOP$^{t\text{Bu}}$)Cr]$_2$(μ-N_2) (purple trace) and the "purple solid" (blue trace) from the reaction of (POCOP$^{t\text{Bu}}$)CrBr + KC_8.

XIII. X-Ray Crystallography Data

CCDC: 2353925 (**1**), 2353926 (**2**), and 2353927 (**3**) contains the supplementary crystallographic data for this work. The data can be obtained free of charge from the Cambridge Crystallography Data Center via http://www.ccdc.cam.ac.uk/data_request/cif.

An orange, prism-like specimen of (**1**), approximate dimensions 0.150 mm × 0.270 mm × 0.430 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å) on a *Bruker D8 Venture Duo* X-ray diffractometer equipped with a CMOS IμS 3.0 Mo source and a PHOTON detector. A total of 2328 frames were collected. The total exposure time was 1.74 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 120630 reflections to a maximum θ angle of 33.73° (0.64 Å resolution), of which 11782 were independent (average redundancy 10.238, completeness = 99.9%, R_{int} = 7.19%, R_{sig} = 3.76%) and 9969 (84.61%) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.4305(11) Å, b = 10.4775(9) Å, c = 14.5388(15) Å, α = 78.486(4)°, β = 83.946(4)°, γ = 71.492(3)°, volume = 1474.9(3) Å^3, are based upon the refinement of the XYZ-centroids of 9170 reflections above 2 $\sigma(I)$ with 4.882° < 2θ < 69.73°. Data was corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.910. The structure was solved and refined using the Bruker SHELXTL Software Package[4, 5], using the space group P -1, with Z = 2 for the formula unit, (POCOP$^{t\text{Bu}}$)Cr(*p*-Tol). The asymmetric unit consists of a well ordered (**1**). All nonhydrogen atoms were located in successive Fourier maps and refined isotropically. The H atoms were also located in the Fourier maps and were refined isotropically. Views of (**1**) and packing are shown in **Figures S28** and **S29**. The final anisotropic full-matrix least-squares refinement on F^2 with 480 variables converged at R_1 = 4.76%, for the observed data and wR_2 = 11.83% for all data. The goodness-of-fit was 1.083. The largest peak in the final difference electron density synthesis was 0.725 e$^-$/Å^3 and the largest hole was -0.527 e$^-$/Å^3 with an RMS deviation of 0.092 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.217 g/cm^3 and F(000), 580 e$^-$.

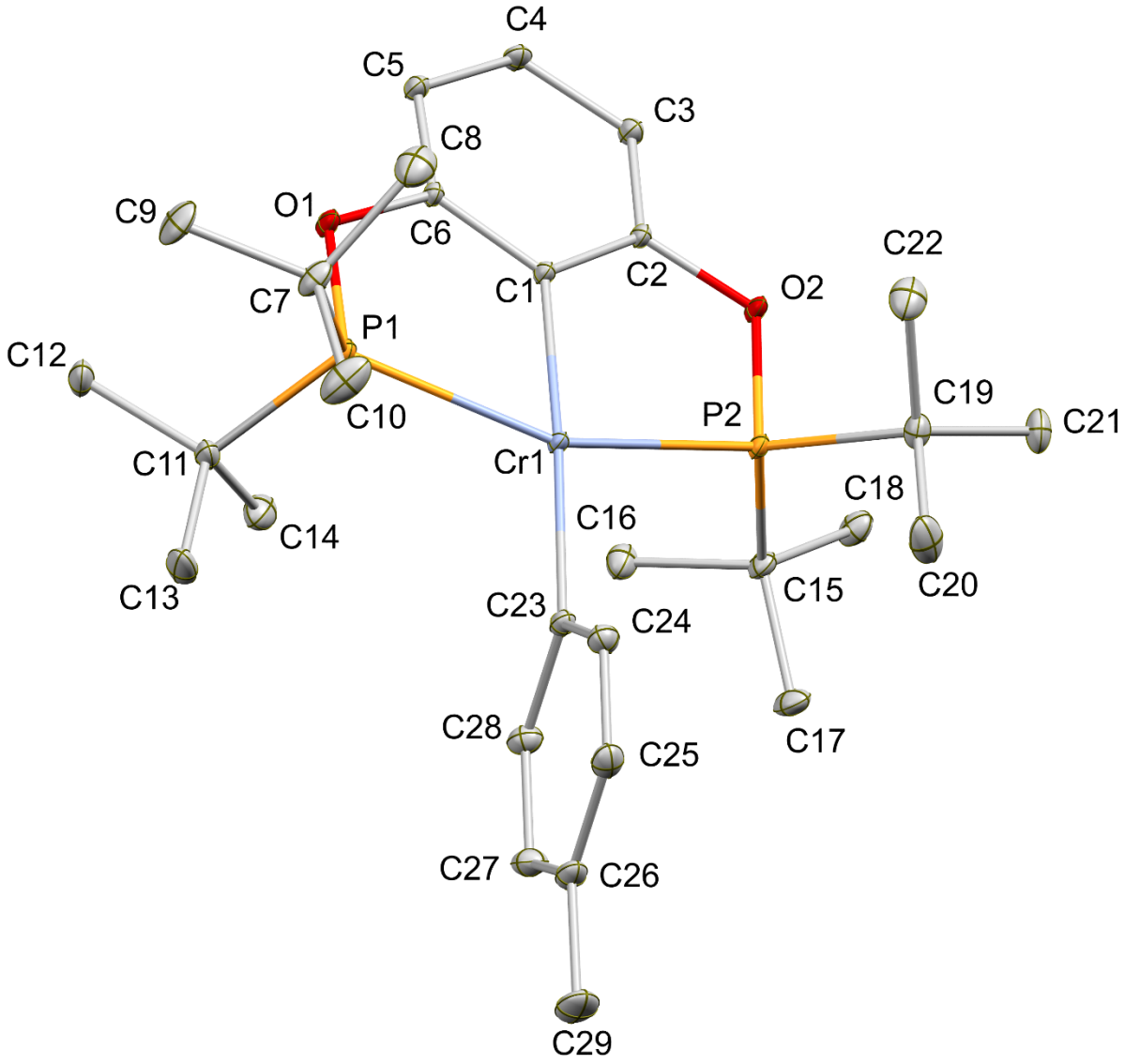


Figure S28. X-Ray crystal structure (POCOP$^{t\text{Bu}}$)Cr(*p*-Tol) (**1**) with atom labelling. Thermal parameters are drawn at 50% probability. All H atoms are omitted for clarity.

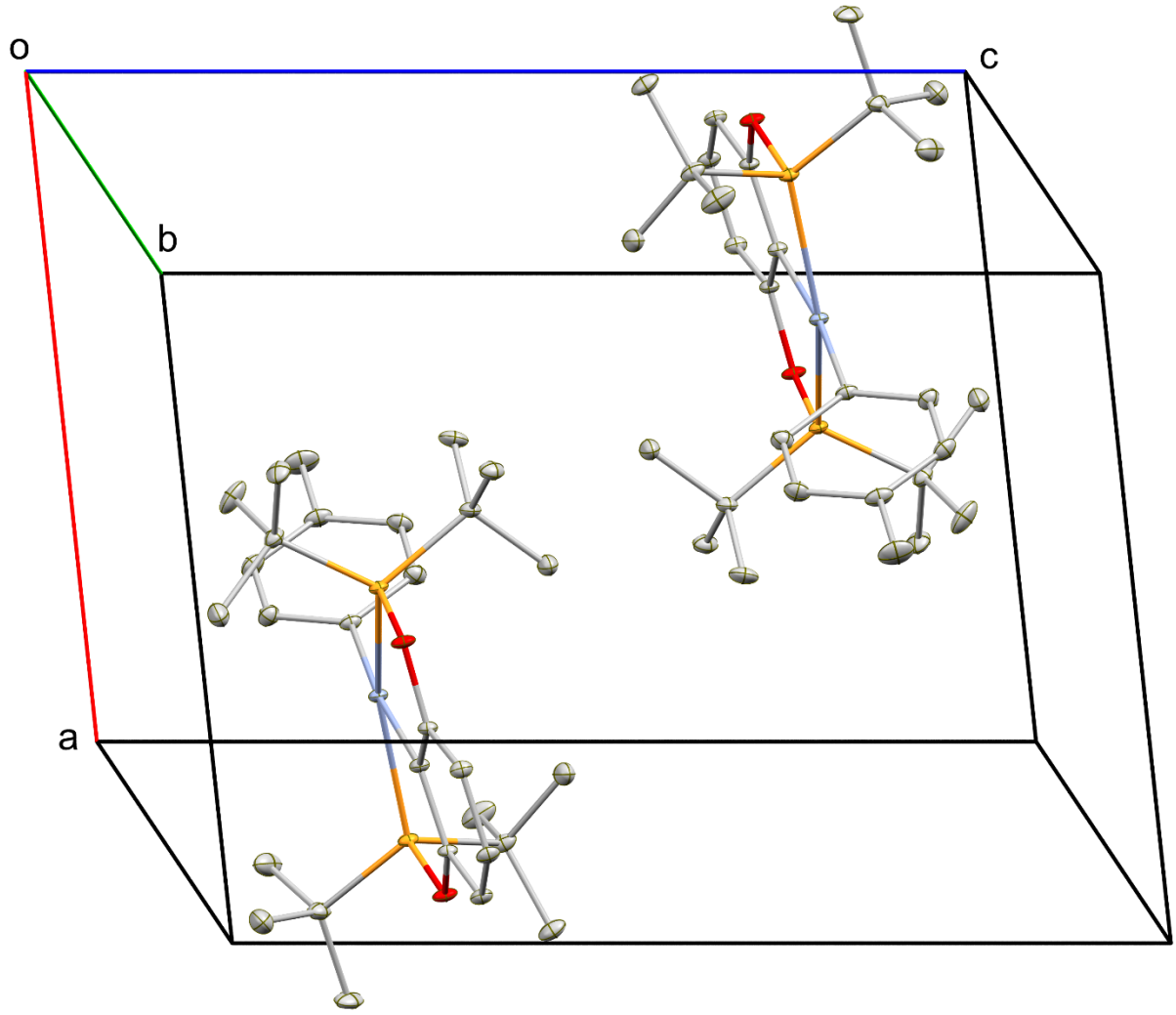


Figure S29. Crystal packing of **1**. All atoms are unlabeled and H atoms are omitted for clarity.

Table S1. Crystal data and structure refinement for **1**.

Chemical formula	$C_{29}H_{46}CrO_2P_2$	
Formula weight	540.60 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.150 × 0.270 × 0.430 mm	
Crystal habit	orange prism	
Crystal system	triclinic	
Space group	*P -1*	
Unit cell dimensions	a = 10.4305(11) Å	
	b = 10.4775(9) Å	α = 78.486(4)°
	c = 14.5388(15) Å	β = 83.946(4)°
Volume	1474.9(3) Å^3	γ = 71.492(3)°
Z	2	
Density (calculated)	1.217 g/cm^3	
Absorption coefficient	0.519 mm^{-1}	
F(000)	580	
Theta range for data collection	2.31 to 33.73°	
Index ranges	$-16 \le h \le 16$, $-16 \le k \le 16$, $-22 \le l \le 22$	
Reflections collected	120630	
Independent reflections	11782 [R_{int} = 0.0719]	
Coverage of independent reflections	99.9%	
Absorption correction	Multi-Scan	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2018/2	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	

Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)	
Function minimized	Σw(Fo2 - Fc2)2	
Data / restraints / parameters	11782 / 0 / 480	
Goodness-of-fit on F2	1.083	
Δ/σmax	0.001	
Final *R* indices	9969 data; $I > 2\sigma(I)$	$R_1 = 0.0476$, $wR_2 = 0.1135$
	all data	$R_1 = 0.0572$, $wR_2 = 0.1183$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0598P)^2 + 0.8006P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Largest diff. peak and hole	0.725 and -0.527 eÅ^{-3}	
R.M.S. deviation from mean	0.092 eÅ^{-3}	

Table S2. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for **1**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
Cr1	0.21304(2)	0.51968(2)	0.75353(2)	0.00992(5)
P1	0.02478(3)	0.43013(3)	0.74878(2)	0.01161(7)
P2	0.31973(3)	0.70217(3)	0.71872(2)	0.01092(7)
C1	0.05651(12)	0.69357(12)	0.69645(9)	0.0109(2)
C23	0.37581(13)	0.34164(13)	0.79628(10)	0.0137(2)
C2	0.07357(12)	0.82283(12)	0.66770(9)	0.0109(2)
O2	0.19659(9)	0.84152(9)	0.68174(7)	0.01367(17)
C3	0.97733(13)	0.93682(13)	0.62286(10)	0.0142(2)
C4	0.85441(13)	0.92256(13)	0.60566(10)	0.0151(2)
C5	0.82942(13)	0.79733(13)	0.63262(10)	0.0141(2)

	x/a	y/b	z/c	U(eq)
C6	0.93102(12)	0.68704(12)	0.67677(9)	0.0109(2)
O1	0.90279(9)	0.56232(9)	0.69981(7)	0.01438(17)
C7	0.93549(15)	0.37309(16)	0.85855(11)	0.0205(3)
C8	0.8816(2)	0.5001(2)	0.90596(13)	0.0312(4)
C9	0.81734(17)	0.3238(2)	0.84300(13)	0.0275(3)
C10	0.03861(19)	0.2610(2)	0.92183(14)	0.0337(4)
C11	0.05420(14)	0.31669(14)	0.66064(11)	0.0174(2)
C12	0.92475(16)	0.31499(16)	0.61962(13)	0.0223(3)
C13	0.13962(19)	0.17236(16)	0.70195(16)	0.0302(4)
C14	0.13842(17)	0.37887(19)	0.58163(12)	0.0252(3)
C15	0.43594(13)	0.70009(14)	0.61271(10)	0.0154(2)
C16	0.36720(16)	0.65421(18)	0.54211(11)	0.0220(3)
C17	0.57364(14)	0.59382(16)	0.63543(12)	0.0223(3)
C18	0.45256(16)	0.83986(16)	0.56841(11)	0.0206(3)
C19	0.37834(14)	0.75261(14)	0.81829(10)	0.0168(2)
C20	0.4771(2)	0.62571(18)	0.87310(14)	0.0315(4)
C21	0.44095(18)	0.86907(17)	0.79198(12)	0.0238(3)
C22	0.24985(19)	0.7980(2)	0.88085(12)	0.0286(3)
C24	0.40450(15)	0.28028(15)	0.89025(10)	0.0179(2)
C25	0.51460(15)	0.16472(15)	0.91546(11)	0.0201(3)
C26	0.60408(14)	0.10275(14)	0.84805(12)	0.0200(3)
C27	0.57857(15)	0.15995(16)	0.75447(12)	0.0213(3)
C28	0.46723(15)	0.27507(15)	0.73041(11)	0.0188(3)
C29	0.72432(18)	0.97871(18)	0.87489(16)	0.0326(4)

Table S3. Bond lengths (Å) and bond angles (°) for **1**.

Cr1-C1	2.1136(12)	C23-C24	1.4082(19)
Cr1-P1	2.4424(4)	C2-O2	1.3990(15)
P1-O1	1.6502(10)	C4-C5	1.3905(19)
P1-C11	1.8554(14)	C6-O1	1.3983(15)
P2-C19	1.8563(14)	C7-C10	1.535(2)
C1-C6	1.3940(17)	C11-C13	1.528(2)
C23-C28	1.402(2)	C11-C12	1.539(2)
C2-C3	1.3875(17)	C15-C18	1.533(2)
C3-C4	1.3903(18)	C19-C21	1.526(2)
C5-C6	1.3930(17)	C19-C22	1.537(2)
C7-C9	1.532(2)	C25-C26	1.389(2)
C7-C8	1.540(3)	C26-C29	1.510(2)
C11-C14	1.539(2)		
C15-C17	1.533(2)	C1-Cr1-C23	174.04(5)
C15-C16	1.539(2)	C23-Cr1-P1	103.41(4)
C19-C20	1.531(2)	C23-Cr1-P2	103.50(4)
C24-C25	1.396(2)	O1-P1-C7	100.65(6)
C26-C27	1.390(2)	C7-P1-C11	113.60(7)
C27-C28	1.398(2)	C7-P1-Cr1	120.78(5)
Cr1-C23	2.1208(13)	O2-P2-C19	101.12(6)
Cr1-P2	2.4487(4)	C19-P2-C15	113.71(6)
P1-C7	1.8522(15)	C19-P2-Cr1	118.26(5)
P2-O2	1.6469(10)	C6-C1-C2	113.99(11)
P2-C15	1.8568(14)	C2-C1-Cr1	122.92(9)
C1-C2	1.3971(17)	C28-C23-Cr1	121.33(10)

C3-C2-C1	124.69(11)	C3-C4-C5	120.68(12)
C1-C2-O2	119.32(10)	C5-C6-C1	124.43(11)
C2-C3-C4	118.07(12)	C1-C6-O1	119.54(11)
C4-C5-C6	118.13(12)	C9-C7-C10	110.68(14)
C5-C6-O1	116.01(11)	C10-C7-C8	108.82(15)
C6-O1-P1	116.23(8)	C10-C7-P1	108.83(11)
C9-C7-C8	109.47(14)	C13-C11-C14	108.78(14)
C9-C7-P1	114.12(11)	C14-C11-C12	108.77(13)
C8-C7-P1	104.65(11)	C14-C11-P1	103.15(10)
C13-C11-C12	111.31(12)	C17-C15-C18	110.93(12)
C13-C11-P1	109.81(11)	C18-C15-C16	108.15(12)
C12-C11-P1	114.59(10)	C17-C15-P2	109.88(10)
C17-C15-C16	109.39(12)	C16-C15-P2	103.79(9)
C1-Cr1-P1	76.35(3)	C21-C19-C22	108.93(13)
C1-Cr1-P2	76.27(3)	C21-C19-P2	115.60(10)
P1-Cr1-P2	152.448(14)	C22-C19-P2	104.29(10)
O1-P1-C11	100.27(6)	C26-C25-C24	121.40(14)
O1-P1-Cr1	104.88(4)	C25-C26-C29	121.66(15)
C11-P1-Cr1	112.99(5)	C26-C27-C28	120.71(14)
O2-P2-C15	99.34(6)	C18-C15-P2	114.38(10)
O2-P2-Cr1	104.70(4)	C21-C19-C20	110.61(13)
C15-P2-Cr1	115.87(5)	C20-C19-C22	108.50(15)
C6-C1-Cr1	122.88(9)	C20-C19-P2	108.54(10)
C28-C23-C24	113.77(12)	C25-C24-C23	123.10(13)
C24-C23-Cr1	124.90(10)	C25-C26-C27	117.16(13)
C3-C2-O2	115.96(11)	C27-C26-C29	121.18(15)
C2-O2-P2	116.25(8)	C27-C28-C23	123.85(14)

Table S4. Anisotropic atomic displacement parameters (Å^2) for **1**. The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr1	0.00706(8)	0.00847(9)	0.01435(9)	-0.00040(6)	-0.00196(6)	-0.00305(6)
P1	0.00976(13)	0.00977(13)	0.01621(15)	-0.00008(11)	-0.00235(10)	-0.00500(10)
P2	0.00818(13)	0.01076(13)	0.01490(14)	-0.00076(10)	-0.00235(10)	-0.00469(10)
C1	0.0082(5)	0.0094(5)	0.0153(5)	-0.0013(4)	-0.0017(4)	-0.0032(4)
C23	0.0111(5)	0.0106(5)	0.0190(6)	-0.0008(4)	-0.0036(4)	-0.0031(4)
C2	0.0080(5)	0.0105(5)	0.0151(5)	-0.0023(4)	-0.0009(4)	-0.0041(4)
O2	0.0085(4)	0.0096(4)	0.0238(5)	-0.0004(3)	-0.0042(3)	-0.0044(3)
C3	0.0127(5)	0.0098(5)	0.0197(6)	-0.0005(4)	-0.0027(4)	-0.0037(4)
C4	0.0113(5)	0.0104(5)	0.0219(6)	-0.0003(4)	-0.0050(4)	-0.0011(4)
C5	0.0096(5)	0.0126(5)	0.0202(6)	-0.0024(4)	-0.0033(4)	-0.0028(4)
C6	0.0086(5)	0.0096(5)	0.0156(5)	-0.0019(4)	-0.0010(4)	-0.0044(4)
O1	0.0097(4)	0.0098(4)	0.0246(5)	0.0000(3)	-0.0045(3)	-0.0048(3)
C7	0.0150(6)	0.0265(7)	0.0201(6)	0.0034(5)	-0.0014(5)	-0.0110(5)
C8	0.0266(8)	0.0459(11)	0.0242(8)	-0.0103(7)	0.0051(6)	-0.0148(8)
C9	0.0194(7)	0.0349(9)	0.0310(8)	0.0057(7)	-0.0013(6)	-0.0189(6)
C10	0.0240(8)	0.0452(11)	0.0262(8)	0.0163(8)	-0.0063(6)	-0.0144(8)
C11	0.0157(6)	0.0120(5)	0.0262(7)	-0.0054(5)	-0.0059(5)	-0.0037(4)
C12	0.0214(7)	0.0176(6)	0.0319(8)	-0.0056(6)	-0.0099(6)	-0.0078(5)
C13	0.0273(8)	0.0130(6)	0.0511(11)	-0.0092(7)	-0.0167(8)	-0.0005(6)
C14	0.0219(7)	0.0341(9)	0.0236(7)	-0.0128(6)	0.0021(6)	-0.0106(6)
C15	0.0103(5)	0.0178(6)	0.0190(6)	-0.0022(5)	0.0004(4)	-0.0064(4)
C16	0.0205(7)	0.0306(8)	0.0191(6)	-0.0090(6)	0.0023(5)	-0.0118(6)
C17	0.0106(5)	0.0206(7)	0.0334(8)	-0.0024(6)	0.0024(5)	-0.0037(5)
C18	0.0169(6)	0.0214(7)	0.0233(7)	0.0029(5)	-0.0009(5)	-0.0096(5)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C19	0.0188(6)	0.0168(6)	0.0170(6)	-0.0007(5)	-0.0046(5)	-0.0088(5)
C20	0.0416(10)	0.0224(7)	0.0315(9)	-0.0005(6)	-0.0236(8)	-0.0064(7)
C21	0.0290(8)	0.0254(7)	0.0248(7)	-0.0055(6)	-0.0030(6)	-0.0180(6)
C22	0.0302(8)	0.0419(10)	0.0195(7)	-0.0097(7)	0.0052(6)	-0.0183(8)
C24	0.0172(6)	0.0167(6)	0.0187(6)	-0.0029(5)	-0.0035(5)	-0.0030(5)
C25	0.0203(6)	0.0169(6)	0.0220(6)	0.0006(5)	-0.0092(5)	-0.0039(5)
C26	0.0137(6)	0.0126(5)	0.0320(7)	-0.0006(5)	-0.0073(5)	-0.0016(4)
C27	0.0152(6)	0.0184(6)	0.0274(7)	-0.0044(5)	0.0014(5)	-0.0014(5)
C28	0.0162(6)	0.0180(6)	0.0195(6)	-0.0006(5)	-0.0006(5)	-0.0031(5)
C29	0.0194(7)	0.0196(7)	0.0519(11)	-0.0001(7)	-0.0124(7)	0.0032(6)

Table S5. Hydrogen bond distances (Å) and angles (°) for **1**.

	Donor-H	**Acceptor-H**	**Donor-Acceptor**	**Angle**
C12-H12B···O1	0.90(2)	2.52(2)	2.9833(18)	112.3(15)

Table S6. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for **1**.

	x/a	**y/b**	**z/c**	**U(eq)**
H3	-0.001(2)	1.015(2)	0.6025(15)	0.022(5)
H4	-0.210(2)	0.994(2)	0.5763(16)	0.027(5)
H5	-0.252(2)	0.782(2)	0.6208(14)	0.019(5)
H8A	-0.155(3)	0.475(3)	0.9652(19)	0.043(7)
H8B	-0.183(3)	0.570(3)	0.8711(17)	0.035(6)
H8C	-0.052(3)	0.543(3)	0.9120(19)	0.047(7)
H9A	-0.230(3)	0.313(3)	0.9004(19)	0.045(7)
H9B	-0.157(2)	0.237(3)	0.8236(16)	0.031(6)

	x/a	y/b	z/c	U(eq)
H9C	-0.239(2)	0.391(2)	0.7988(17)	0.031(6)
H10A	-0.003(3)	0.242(3)	0.982(2)	0.050(8)
H10B	0.110(3)	0.290(3)	0.9333(18)	0.038(7)
H10C	0.078(3)	0.180(3)	0.8948(18)	0.043(7)
H12A	-0.059(3)	0.276(3)	0.5638(18)	0.036(6)
H12B	-0.131(2)	0.401(2)	0.6039(14)	0.019(5)
H12C	-0.119(2)	0.271(2)	0.6590(15)	0.022(5)
H13A	0.172(3)	0.122(3)	0.6528(18)	0.039(7)
H13B	0.087(2)	0.121(2)	0.7452(16)	0.030(6)
H13C	0.213(2)	0.177(2)	0.7325(16)	0.027(6)
H14A	0.151(3)	0.334(3)	0.5304(19)	0.044(7)
H14B	0.226(2)	0.370(2)	0.6017(16)	0.029(6)
H14C	0.098(2)	0.473(2)	0.5591(15)	0.024(5)
H16A	0.421(2)	0.651(2)	0.4821(15)	0.023(5)
H16B	0.280(3)	0.713(2)	0.5267(16)	0.032(6)
H16C	0.359(2)	0.563(2)	0.5652(14)	0.021(5)
H17A	0.626(2)	0.583(2)	0.5775(17)	0.033(6)
H17B	0.566(2)	0.507(2)	0.6637(16)	0.032(6)
H17C	0.622(2)	0.621(2)	0.6765(15)	0.023(5)
H18A	0.504(3)	0.832(3)	0.5077(19)	0.042(7)
H18B	0.500(2)	0.870(2)	0.6011(15)	0.025(5)
H18C	0.377(2)	0.900(2)	0.5571(16)	0.029(6)
H20A	0.499(3)	0.647(3)	0.9309(18)	0.038(6)
H20B	0.559(3)	0.604(3)	0.8361(17)	0.034(6)
H20C	0.437(2)	0.551(3)	0.8945(17)	0.035(6)
H21A	0.455(3)	0.895(3)	0.8507(18)	0.042(7)

	x/a	y/b	z/c	U(eq)
H21B	0.385(2)	0.943(3)	0.7502(17)	0.033(6)
H21C	0.532(3)	0.843(3)	0.7613(19)	0.043(7)
H22A	0.275(3)	0.811(3)	0.9388(19)	0.044(7)
H22B	0.206(3)	0.725(3)	0.9000(19)	0.048(7)
H22C	0.188(3)	0.878(3)	0.8527(18)	0.036(6)
H24	0.345(2)	0.324(2)	0.9427(16)	0.028(6)
H25	0.526(2)	0.123(2)	0.9802(16)	0.030(6)
H27	0.634(2)	0.119(2)	0.7057(16)	0.029(6)
H28	0.456(2)	0.312(2)	0.6641(16)	0.026(5)
H29A	0.7757	-0.0489	0.8179	0.049000
H29B	0.6927	-0.0964	0.9103	0.049000
H29C	0.7826	0.0010	0.9139	0.049000

X-ray diffraction data were measured at 100 K on a *Bruker SMART APEX II CCD* area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube operated at 1.2 kW power (40 kV, 30 mA). A red rectangular prism of **2** of approximate dimensions 0.394 × 0.248 × 0.126 mm^3 was glued to a MiTeGen micromount using Fomblin oil. The detector was placed at a distance of 5.12 cm from the crystal during the data collection. A series of narrow

frames of data were collected with an exposure time of 10 s per frame. The frames were integrated with the Bruker SAINT Software package[6] using a narrow-frame integration algorithm. The integration of the data using a monoclinic unit cell yielded a total of 59998 reflections in the θ range of 1.794 to 33.720º of which 11869 were independent with $I \geq 2\sigma(I)$ ($R_{int} = 0.0500$). The data were corrected for absorption effects by the multi-scan method (SADABS). The structure was solved and refined by the direct methods using the Bruker SHELXTL (V2017.3-0) Software Package.[5, 6] All non-hydrogen atoms were located in successive Fourier maps and refined anisotropically. The asymmetric unit consists of **2** and is well-ordered. All H atoms were also located in the Fourier maps, but were refined isotropically. A view of **2** is shown in **Figures S30,** and the packing of **2** is shown in **Figure S31**. The crystal belongs to the chiral $P2_1$ space group with the chirality arising from the packing of **2**. The handedness of the packing of the molecules is satisfactorily determined by refining the Flack parameter.[7] The final refinement parameters are $R_1 = 0.0318$ and $wR_2 = 0.0681$ for data with $F > 4\sigma(F)$ giving the data to parameter ratio of 24.1. The refinement data for all data are $R_1 = 0.0386$ and $wR_2 = 0.0715$.

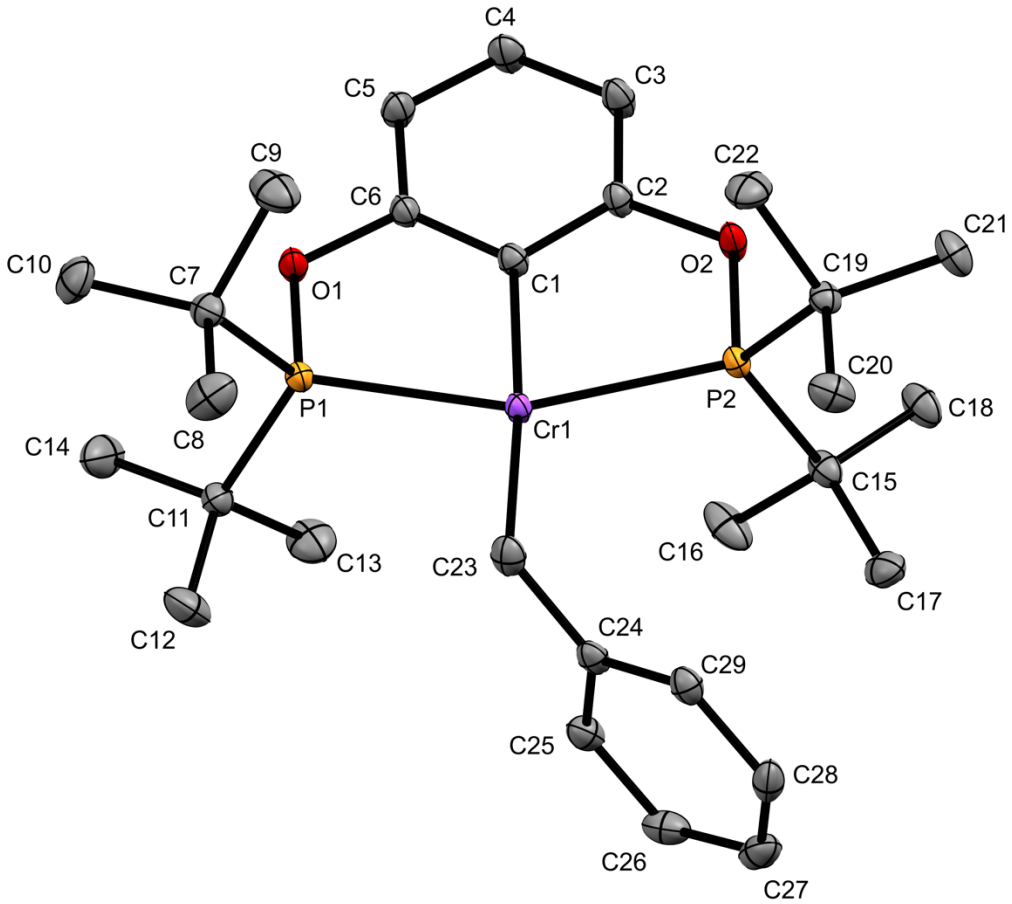


Figure S30. X-Ray crystal structure of (POCOP$^{t\text{Bu}}$)Cr(Bn) (**2**) with atom labelling. Thermal parameters are drawn at 50% probability. All H atoms are omitted for clarity.

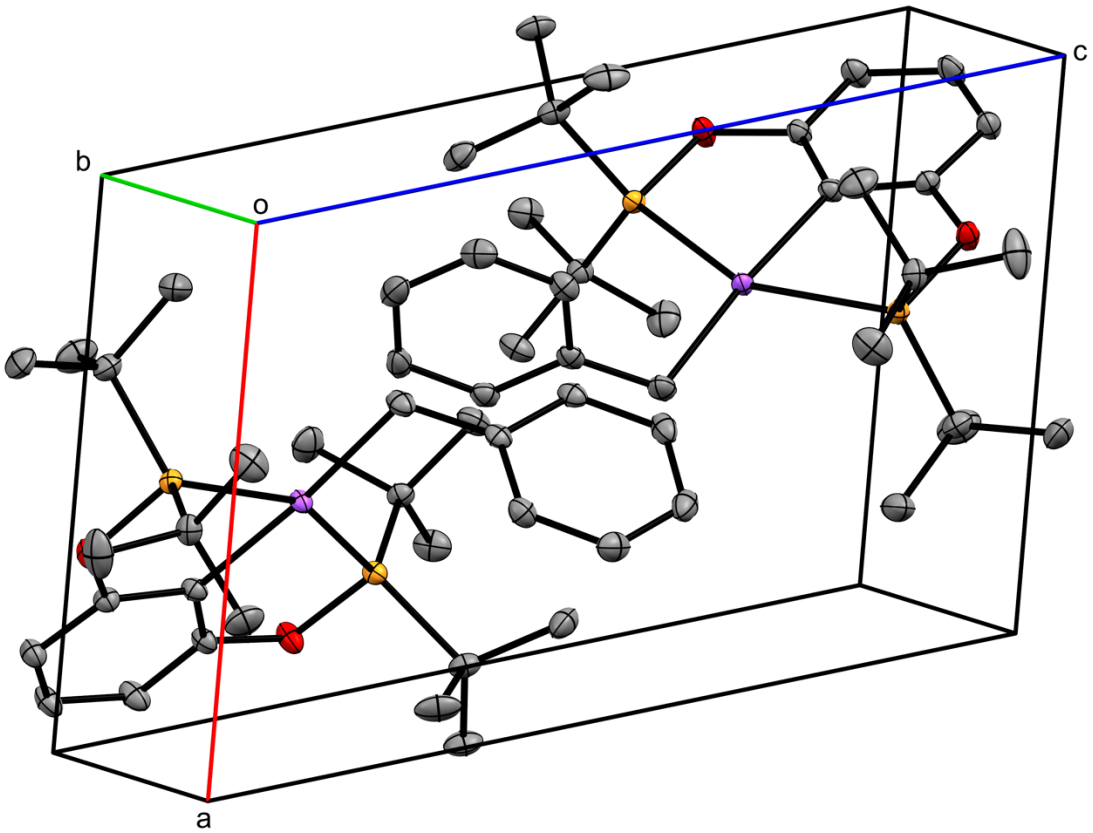


Figure S31. Packing of **2** crystals. All atoms are unlabeled and H atoms are omitted for clarity.

Table S7. Crystal data and structure refinement for **2**.

Empirical formula	C29 H46 Cr O2 P2	
Formula weight	540.60	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P2₁*	
Unit cell dimensions	a = 8.2502(2) Å	α = 90°.
	b = 15.8605(5) Å	β = 106.188(1)°.
	c = 11.8231(4) Å	γ = 90°.
Volume	1485.74(8) $Å^3$	
Z	2	
Density (calculated)	1.208 Mg/m^3	
Absorption coefficient	0.515 mm^{-1}	
F(000)	580	

Crystal size	0.394 × 0.248 × 0.126 mm^3
Theta range for data collection	1.794 to 33.720°.
Index ranges	$-12 \le h \le 12$, $-24 \le k \le 24$, $-18 \le l \le 18$
Reflections collected	59998
Independent reflections	11869 [R(int) = 0.0500]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7469 and 0.7016
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11869 / 1 / 491
Goodness-of-fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0318, wR2 = 0.0681
R indices (all data)	R1 = 0.0386, wR2 = 0.0715
Absolute structure parameter	0.012(5)
Extinction coefficient	n/a
Largest diff. peak and hole	1.115 and -0.269 e.$Å^{-3}$

Table S8. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cr(1)	3538(1)	4874(1)	7168(1)	11(1)
C(1)	2291(2)	5450(1)	8301(2)	13(1)
P(1)	4481(1)	4050(1)	8992(1)	11(1)
P(2)	1849(1)	5996(1)	5934(1)	11(1)
C(23)	4989(2)	4248(1)	6134(2)	17(1)
C(2)	1254(2)	6157(1)	7980(2)	13(1)
C(3)	476(3)	6579(1)	8716(2)	18(1)
C(4)	739(3)	6278(1)	9856(2)	18(1)
C(5)	1738(2)	5572(1)	10242(2)	16(1)
C(6)	2474(2)	5179(1)	9454(2)	13(1)
O(1)	3456(2)	4465(1)	9874(1)	15(1)
C(7)	6708(2)	4188(1)	9890(2)	16(1)
C(8)	7908(3)	3914(2)	9170(2)	26(1)
C(9)	6888(3)	5144(2)	10104(3)	29(1)

C(10)	7167(3)	3736(2)	11080(2)	24(1)
C(11)	3721(2)	2939(1)	8936(2)	16(1)
C(12)	4758(3)	2366(1)	8367(2)	26(1)
C(13)	1906(3)	2984(2)	8134(2)	27(1)
C(14)	3683(4)	2577(2)	10128(2)	31(1)
O(2)	945(2)	6479(1)	6839(1)	17(1)
C(15)	-68(2)	5675(1)	4763(2)	16(1)
C(16)	-604(3)	4843(2)	5224(2)	26(1)
C(17)	340(3)	5513(1)	3595(2)	21(1)
C(18)	-1525(3)	6306(1)	4574(2)	21(1)
C(19)	3000(2)	6891(1)	5511(2)	13(1)
C(20)	4076(3)	6571(1)	4732(2)	20(1)
C(21)	1888(3)	7627(1)	4910(2)	21(1)
C(22)	4189(3)	7192(2)	6677(2)	24(1)
C(24)	4083(2)	4052(1)	4912(2)	14(1)
C(25)	2729(3)	3475(1)	4640(2)	17(1)
C(26)	1818(3)	3297(1)	3496(2)	21(1)
C(27)	2228(3)	3689(1)	2555(2)	22(1)
C(28)	3581(3)	4243(1)	2792(2)	19(1)
C(29)	4484(2)	4421(1)	3945(2)	15(1)

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Table S9. Bond lengths [Å] and angles [°] for **2**.

Cr(1)-C(1)	2.1110(18)	C(10)-H(10B)	0.93(3)
Cr(1)-C(23)	2.1735(19)	C(10)-H(10C)	1.01(3)
Cr(1)-P(1)	2.4557(5)	C(11)-C(12)	1.527(3)
Cr(1)-P(2)	2.4705(5)	C(11)-C(14)	1.530(3)
C(1)-C(6)	1.397(3)	C(11)-C(13)	1.535(3)
C(1)-C(2)	1.398(2)	C(12)-H(12A)	0.94(3)
P(1)-O(1)	1.6504(14)	C(12)-H(12B)	0.93(3)
P(1)-C(7)	1.8615(19)	C(12)-H(12C)	0.98(3)
P(1)-C(11)	1.8662(19)	C(13)-H(13A)	0.84(3)
P(2)-O(2)	1.6530(14)	C(13)-H(13B)	1.05(3)
P(2)-C(19)	1.8526(18)	C(13)-H(13C)	0.99(4)
P(2)-C(15)	1.859(2)	C(14)-H(14A)	0.86(4)
C(23)-C(24)	1.464(3)	C(14)-H(14B)	0.97(3)
C(23)-H(23A)	0.95(3)	C(14)-H(14C)	0.91(4)
C(23)-H(23B)	0.97(3)	C(15)-C(17)	1.531(3)
C(2)-C(3)	1.388(3)	C(15)-C(18)	1.532(3)
C(2)-O(2)	1.398(2)	C(15)-C(16)	1.539(3)
C(3)-C(4)	1.389(3)	C(16)-H(16A)	0.98(3)
C(3)-H(3)	0.99(3)	C(16)-H(16B)	0.96(3)
C(4)-C(5)	1.390(3)	C(16)-H(16C)	0.93(3)
C(4)-H(4)	0.97(3)	C(17)-H(17A)	0.92(3)
C(5)-C(6)	1.394(3)	C(17)-H(17B)	0.91(3)
C(5)-H(5)	0.96(2)	C(17)-H(17C)	0.99(3)
C(6)-O(1)	1.400(2)	C(18)-H(18A)	0.96(3)
C(7)-C(10)	1.530(3)	C(18)-H(18B)	0.88(3)
C(7)-C(8)	1.538(3)	C(18)-H(18C)	1.00(3)
C(7)-C(9)	1.538(3)	C(19)-C(22)	1.529(3)
C(8)-H(8A)	0.98(3)	C(19)-C(21)	1.532(3)
C(8)-H(8B)	0.96(3)	C(19)-C(20)	1.533(3)
C(8)-H(8C)	0.99(3)	C(20)-H(20A)	0.90(3)
C(9)-H(9A)	0.89(4)	C(20)-H(20B)	0.98(3)
C(9)-H(9B)	0.92(4)	C(20)-H(20C)	0.96(3)
C(9)-H(9C)	1.04(4)	C(21)-H(21A)	0.97(3)
C(10)-H(10A)	0.96(3)	C(21)-H(21B)	1.01(3)
		C(21)-H(21C)	0.98(3)

C(22)-H(22A)	0.94(3)
C(22)-H(22B)	0.94(4)
C(22)-H(22C)	0.93(3)
C(24)-C(29)	1.404(3)
C(24)-C(25)	1.410(3)
C(25)-C(26)	1.381(3)
C(25)-H(25)	1.04(3)
C(26)-C(27)	1.395(3)
C(26)-H(26)	0.99(3)
C(27)-C(28)	1.386(3)
C(27)-H(27)	0.99(3)
C(28)-C(29)	1.388(3)
C(28)-H(28)	0.90(3)
C(29)-H(29)	1.00(3)

C(1)-Cr(1)-C(23)	175.10(8)
C(1)-Cr(1)-P(1)	76.31(5)
C(23)-Cr(1)-P(1)	99.30(5)
C(1)-Cr(1)-P(2)	76.63(5)
C(23)-Cr(1)-P(2)	107.79(5)
P(1)-Cr(1)-P(2)	152.907(19)
C(6)-C(1)-C(2)	113.79(16)
C(6)-C(1)-Cr(1)	123.18(13)
C(2)-C(1)-Cr(1)	122.99(13)
O(1)-P(1)-C(7)	101.00(8)
O(1)-P(1)-C(11)	99.96(8)
C(7)-P(1)-C(11)	113.56(9)
O(1)-P(1)-Cr(1)	104.51(5)
C(7)-P(1)-Cr(1)	117.32(6)
C(11)-P(1)-Cr(1)	116.78(6)
O(2)-P(2)-C(19)	100.22(8)
O(2)-P(2)-C(15)	99.53(8)
C(19)-P(2)-C(15)	113.77(8)
O(2)-P(2)-Cr(1)	103.50(5)
C(19)-P(2)-Cr(1)	117.63(6)
C(15)-P(2)-Cr(1)	117.70(6)
C(24)-C(23)-Cr(1)	116.28(13)
C(24)-C(23)-H(23A)	113.1(19)
Cr(1)-C(23)-H(23A)	106.7(19)
C(24)-C(23)-H(23B)	109.6(17)
Cr(1)-C(23)-H(23B)	107.0(17)
H(23A)-C(23)-H(23B)	103(3)
C(3)-C(2)-O(2)	115.93(15)
C(3)-C(2)-C(1)	124.86(17)
O(2)-C(2)-C(1)	119.21(16)
C(2)-C(3)-C(4)	117.92(17)
C(2)-C(3)-H(3)	119.5(16)
C(4)-C(3)-H(3)	122.5(16)
C(3)-C(4)-C(5)	120.89(17)
C(3)-C(4)-H(4)	121.1(17)
C(5)-C(4)-H(4)	118.0(17)
C(4)-C(5)-C(6)	118.04(17)
C(4)-C(5)-H(5)	123.5(15)
C(6)-C(5)-H(5)	118.5(15)
C(5)-C(6)-C(1)	124.49(16)
C(5)-C(6)-O(1)	116.20(16)
C(1)-C(6)-O(1)	119.30(16)
C(6)-O(1)-P(1)	116.46(11)
C(10)-C(7)-C(8)	110.09(17)
C(10)-C(7)-C(9)	108.90(19)
C(8)-C(7)-C(9)	108.85(19)
C(10)-C(7)-P(1)	114.91(15)
C(8)-C(7)-P(1)	109.65(14)
C(9)-C(7)-P(1)	104.15(14)
C(7)-C(8)-H(8A)	110.8(19)
C(7)-C(8)-H(8B)	109.8(18)
H(8A)-C(8)-H(8B)	107(3)
C(7)-C(8)-H(8C)	112.3(18)
H(8A)-C(8)-H(8C)	112(3)
H(8B)-C(8)-H(8C)	105(3)
C(7)-C(9)-H(9A)	112(2)
C(7)-C(9)-H(9B)	110(2)

H(9A)-C(9)-H(9B)	107(3)
C(7)-C(9)-H(9C)	109(2)
H(9A)-C(9)-H(9C)	105(3)
H(9B)-C(9)-H(9C)	112(3)
C(7)-C(10)-H(10A)	114.1(18)
C(7)-C(10)-H(10B)	107.2(19)
H(10A)-C(10)-H(10B)	111(3)
C(7)-C(10)-H(10C)	109.2(15)
H(10A)-C(10)-H(10C)	105(2)
H(10B)-C(10)-H(10C)	110(2)
C(12)-C(11)-C(14)	109.90(19)
C(12)-C(11)-C(13)	108.97(18)
C(14)-C(11)-C(13)	108.6(2)
C(12)-C(11)-P(1)	110.76(14)
C(14)-C(11)-P(1)	114.50(14)
C(13)-C(11)-P(1)	103.79(14)
C(11)-C(12)-H(12A)	116(2)
C(11)-C(12)-H(12B)	110.6(19)
H(12A)-C(12)-H(12B)	109(3)
C(11)-C(12)-H(12C)	102.8(17)
H(12A)-C(12)-H(12C)	112(3)
H(12B)-C(12)-H(12C)	107(3)
C(11)-C(13)-H(13A)	110(2)
C(11)-C(13)-H(13B)	111.2(18)
H(13A)-C(13)-H(13B)	117(3)
C(11)-C(13)-H(13C)	108(2)
H(13A)-C(13)-H(13C)	103(3)
H(13B)-C(13)-H(13C)	107(3)
C(11)-C(14)-H(14A)	112(3)
C(11)-C(14)-H(14B)	111.7(18)
H(14A)-C(14)-H(14B)	108(3)
C(11)-C(14)-H(14C)	106(2)
H(14A)-C(14)-H(14C)	115(4)
H(14B)-C(14)-H(14C)	103(3)
C(2)-O(2)-P(2)	117.52(11)
C(17)-C(15)-C(18)	109.80(17)
C(17)-C(15)-C(16)	109.46(17)
C(18)-C(15)-C(16)	108.68(16)
C(17)-C(15)-P(2)	111.22(14)
C(18)-C(15)-P(2)	113.54(14)
C(16)-C(15)-P(2)	103.91(14)
C(15)-C(16)-H(16A)	113(2)
C(15)-C(16)-H(16B)	109.3(19)
H(16A)-C(16)-H(16B)	109(3)
C(15)-C(16)-H(16C)	112.9(16)
H(16A)-C(16)-H(16C)	106(2)
H(16B)-C(16)-H(16C)	107(3)
C(15)-C(17)-H(17A)	115.7(18)
C(15)-C(17)-H(17B)	110.7(19)
H(17A)-C(17)-H(17B)	105(3)
C(15)-C(17)-H(17C)	113.3(16)
H(17A)-C(17)-H(17C)	109(2)
H(17B)-C(17)-H(17C)	102(2)
C(15)-C(18)-H(18A)	113.7(17)
C(15)-C(18)-H(18B)	112.7(17)
H(18A)-C(18)-H(18B)	104(2)
C(15)-C(18)-H(18C)	109.3(17)
H(18A)-C(18)-H(18C)	111(2)
H(18B)-C(18)-H(18C)	106(2)
C(22)-C(19)-C(21)	109.34(17)
C(22)-C(19)-C(20)	108.20(17)
C(21)-C(19)-C(20)	110.26(16)
C(22)-C(19)-P(2)	104.11(13)
C(21)-C(19)-P(2)	115.02(13)
C(20)-C(19)-P(2)	109.56(12)
C(19)-C(20)-H(20A)	109(2)
C(19)-C(20)-H(20B)	107.6(15)
H(20A)-C(20)-H(20B)	111(2)
C(19)-C(20)-H(20C)	111.2(17)
H(20A)-C(20)-H(20C)	109(3)
H(20B)-C(20)-H(20C)	109(2)
C(19)-C(21)-H(21A)	112.1(16)

C(19)-C(21)-H(21B)	108.4(18)
H(21A)-C(21)-H(21B)	110(2)
C(19)-C(21)-H(21C)	106.3(17)
H(21A)-C(21)-H(21C)	109(2)
H(21B)-C(21)-H(21C)	111(2)
C(19)-C(22)-H(22A)	108(2)
C(19)-C(22)-H(22B)	109(2)
H(22A)-C(22)-H(22B)	109(3)
C(19)-C(22)-H(22C)	113.3(16)
H(22A)-C(22)-H(22C)	108(3)
H(22B)-C(22)-H(22C)	109(3)
C(29)-C(24)-C(25)	115.91(17)
C(29)-C(24)-C(23)	122.93(17)
C(25)-C(24)-C(23)	121.15(17)
C(26)-C(25)-C(24)	122.37(18)
C(26)-C(25)-H(25)	119.4(15)
C(24)-C(25)-H(25)	118.3(15)
C(25)-C(26)-C(27)	120.25(19)
C(25)-C(26)-H(26)	120.7(16)
C(27)-C(26)-H(26)	119.1(16)
C(28)-C(27)-C(26)	118.77(19)
C(28)-C(27)-H(27)	122.6(16)
C(26)-C(27)-H(27)	118.6(16)
C(27)-C(28)-C(29)	120.61(18)
C(27)-C(28)-H(28)	120(2)
C(29)-C(28)-H(28)	119(2)
C(28)-C(29)-C(24)	122.05(18)
C(28)-C(29)-H(29)	120.3(15)
C(24)-C(29)-H(29)	117.6(15)

Table S10. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cr(1)	12(1)	11(1)	11(1)	1(1)	4(1)	3(1)
C(1)	13(1)	12(1)	14(1)	1(1)	5(1)	1(1)
P(1)	12(1)	11(1)	11(1)	1(1)	3(1)	2(1)
P(2)	12(1)	10(1)	13(1)	2(1)	4(1)	2(1)
C(23)	15(1)	19(1)	18(1)	3(1)	7(1)	5(1)
C(2)	15(1)	12(1)	14(1)	3(1)	6(1)	2(1)
C(3)	22(1)	16(1)	20(1)	4(1)	11(1)	6(1)
C(4)	22(1)	18(1)	18(1)	2(1)	12(1)	6(1)
C(5)	19(1)	17(1)	14(1)	2(1)	7(1)	4(1)
C(6)	14(1)	11(1)	14(1)	1(1)	4(1)	2(1)
O(1)	19(1)	15(1)	12(1)	3(1)	6(1)	6(1)
C(7)	14(1)	16(1)	18(1)	-1(1)	1(1)	1(1)
C(8)	17(1)	38(1)	24(1)	-4(1)	6(1)	0(1)
C(9)	24(1)	20(1)	38(1)	-4(1)	1(1)	-4(1)
C(10)	19(1)	32(1)	18(1)	2(1)	-1(1)	5(1)

C(11)	20(1)	12(1)	14(1)	1(1)	5(1)	-1(1)
C(12)	33(1)	14(1)	34(1)	-2(1)	15(1)	2(1)
C(13)	20(1)	25(1)	32(1)	-3(1)	2(1)	-6(1)
C(14)	54(2)	20(1)	20(1)	2(1)	13(1)	-9(1)
O(2)	22(1)	15(1)	15(1)	6(1)	10(1)	9(1)
C(15)	12(1)	13(1)	21(1)	0(1)	2(1)	0(1)
C(16)	16(1)	14(1)	46(1)	2(1)	7(1)	-4(1)
C(17)	18(1)	23(1)	19(1)	-6(1)	-2(1)	2(1)
C(18)	13(1)	17(1)	31(1)	2(1)	3(1)	4(1)
C(19)	13(1)	12(1)	15(1)	1(1)	4(1)	-2(1)
C(20)	20(1)	18(1)	26(1)	-2(1)	13(1)	-3(1)
C(21)	22(1)	13(1)	29(1)	6(1)	9(1)	2(1)
C(22)	27(1)	21(1)	22(1)	-4(1)	3(1)	-9(1)
C(24)	14(1)	12(1)	17(1)	0(1)	7(1)	4(1)
C(25)	21(1)	14(1)	19(1)	-1(1)	9(1)	0(1)
C(26)	18(1)	18(1)	27(1)	-8(1)	7(1)	-2(1)
C(27)	20(1)	26(1)	17(1)	-6(1)	2(1)	7(1)
C(28)	21(1)	22(1)	15(1)	5(1)	7(1)	8(1)
C(29)	14(1)	15(1)	19(1)	2(1)	6(1)	3(1)

Table S11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **2**.

	x	y	z	U(eq)
H(23A)	5970(40)	4580(20)	6200(30)	42(9)
H(23B)	5430(40)	3735(18)	6550(20)	26(7)
H(3)	-280(30)	7061(17)	8400(20)	21(6)
H(4)	240(40)	6553(19)	10410(30)	30(7)
H(5)	1940(30)	5340(16)	11020(20)	13(6)
H(8A)	7630(40)	4200(20)	8410(30)	39(8)
H(8B)	9040(40)	4070(20)	9580(30)	31(7)
H(8C)	7930(40)	3290(20)	9080(30)	34(8)
H(9A)	6620(50)	5440(20)	9430(30)	50(10)
H(9B)	6190(50)	5320(20)	10550(30)	56(11)

H(9C)	8150(50)	5290(20)	10510(30)	51(10)
H(10A)	6390(40)	3829(19)	11530(30)	30(7)
H(10B)	7260(40)	3170(20)	10930(30)	36(8)
H(10C)	8280(30)	3956(17)	11580(20)	21(6)
H(12A)	4900(40)	2560(20)	7650(30)	41(9)
H(12B)	5810(40)	2260(20)	8880(30)	33(8)
H(12C)	4130(40)	1831(19)	8270(20)	25(7)
H(13A)	1300(40)	3270(20)	8450(30)	30(8)
H(13B)	1880(40)	3150(20)	7270(30)	39(8)
H(13C)	1400(40)	2410(20)	8100(30)	53(10)
H(14A)	3220(50)	2920(30)	10520(40)	66(12)
H(14B)	3080(40)	2047(19)	10040(30)	30(8)
H(14C)	4760(50)	2420(30)	10500(30)	55(11)
H(16A)	-820(30)	4900(20)	5990(30)	33(7)
H(16B)	-1610(40)	4640(20)	4670(30)	41(8)
H(16C)	200(30)	4423(17)	5310(20)	17(6)
H(17A)	1220(40)	5145(18)	3630(20)	29(7)
H(17B)	-560(40)	5289(19)	3060(30)	32(8)
H(17C)	530(30)	6036(18)	3200(20)	22(6)
H(18A)	-1840(30)	6435(18)	5280(20)	23(7)
H(18B)	-1280(30)	6801(17)	4330(20)	16(6)
H(18C)	-2510(40)	6092(19)	3940(20)	28(7)
H(20A)	3390(40)	6416(19)	4020(30)	30(7)
H(20B)	4830(30)	7034(17)	4650(20)	18(6)
H(20C)	4750(40)	6100(20)	5090(20)	29(7)
H(21A)	1240(30)	7489(17)	4110(20)	20(6)
H(21B)	1100(40)	7781(19)	5400(30)	31(7)
H(21C)	2650(40)	8091(18)	4880(20)	26(7)
H(22A)	4830(40)	6730(20)	7040(30)	39(9)
H(22B)	4920(40)	7610(20)	6530(30)	49(10)
H(22C)	3620(30)	7410(19)	7190(20)	25(7)
H(25)	2400(30)	3187(17)	5330(20)	19(6)
H(26)	890(40)	2878(18)	3330(20)	24(7)
H(27)	1560(40)	3545(18)	1740(30)	26(7)
H(28)	3920(40)	4470(20)	2200(30)	35(8)
H(29)	5490(30)	4810(20)	4110(20)	25(6)

Table S12. Torsion angles [°] for **2**.

C(1)-C(2)-O(2)-P(2)	-0.3(2)
C(1)-C(6)-O(1)-P(1)	5.7(2)
Cr(1)-C(23)-C(24)-C(25)	-64.5(2)
Cr(1)-C(23)-C(24)-C(29)	114.97(17)

Table S13. Hydrogen bonds for **2** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(14)-H(14A)...O(1)	0.86(4)	2.59(4)	3.010(3)	111(3)

A purple, prism-like specimen of **3**, approximate dimensions 0.120 mm × 0.270 mm × 0.410 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured (λ = 0.71073 Å) on a *Bruker D8 Venture* X-ray diffractometer equipped with a CMOS IμS 3.0 Mo source and PHOTON detector. A total of 1654 frames were collected. The total exposure time was 3.69 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 201845 reflections to a maximum θ angle of 28.70° (0.74 Å resolution), of which 13866 were independent (average redundancy 14.557, completeness = 99.9%, R_{int} = 7.76%, R_{sig} = 4.10%) and 11893 (85.77%) were greater than $2\sigma(F^2)$. The final cell constants of a = 15.7583(16) Å, b = 14.4111(13) Å, c = 24.856(2) Å, β = 107.974(4)°, volume = 5369.2(9) Å^3, are based upon the refinement of the XYZ-centroids of 9310 reflections above 20 σ(*I*) with 4.456° < 2θ < 57.29°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.898. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8020 and 0.9350. The structure was solved and refined using the Bruker SHELXTL Software Package[5, 8], using the space group $P2_1/n$, with Z = 4 containing two **3** molecules and a half diethyl ether solvent molecule. The asymmetric unit contains a reasonably well ordered complex molecule and a highly disordered solvent molecule being located on a 2-fold symmetry axis. Attempts to model the disordered diethyl ether solvent molecule did not succeed, and the electron density due to the solvent molecule was removed using the SQUEEZE/PLATON program.[9] The program calculated 81 electrons in a void-space volume of 433 Å^3, and the values are interpreted as diffused electron density resulting from two diethyl ether molecules in the unit cell. Views of the **3** and its packing are shown in **Figures S32** and **S33**. The final refinement parameters are R_1 = 6.54% and wR_2 = 16.68% for data with $F > 4\sigma(F)$ giving the data to parameter ratio of 26. The final anisotropic full-matrix least-squares refinement on F^2 with 530 variables converged at $R1$ = 6.54%, for the observed data and $wR2$ = 17.31% for all data. The goodness-of-fit was 1.053. The largest peak in the final difference electron density synthesis was 2.066 e$^-$/Å^3 and the largest hole was -1.046 e$^-$/Å^3 with an RMS deviation of 0.095 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.193 g/cm^3 and F(000), 2068 e$^-$.

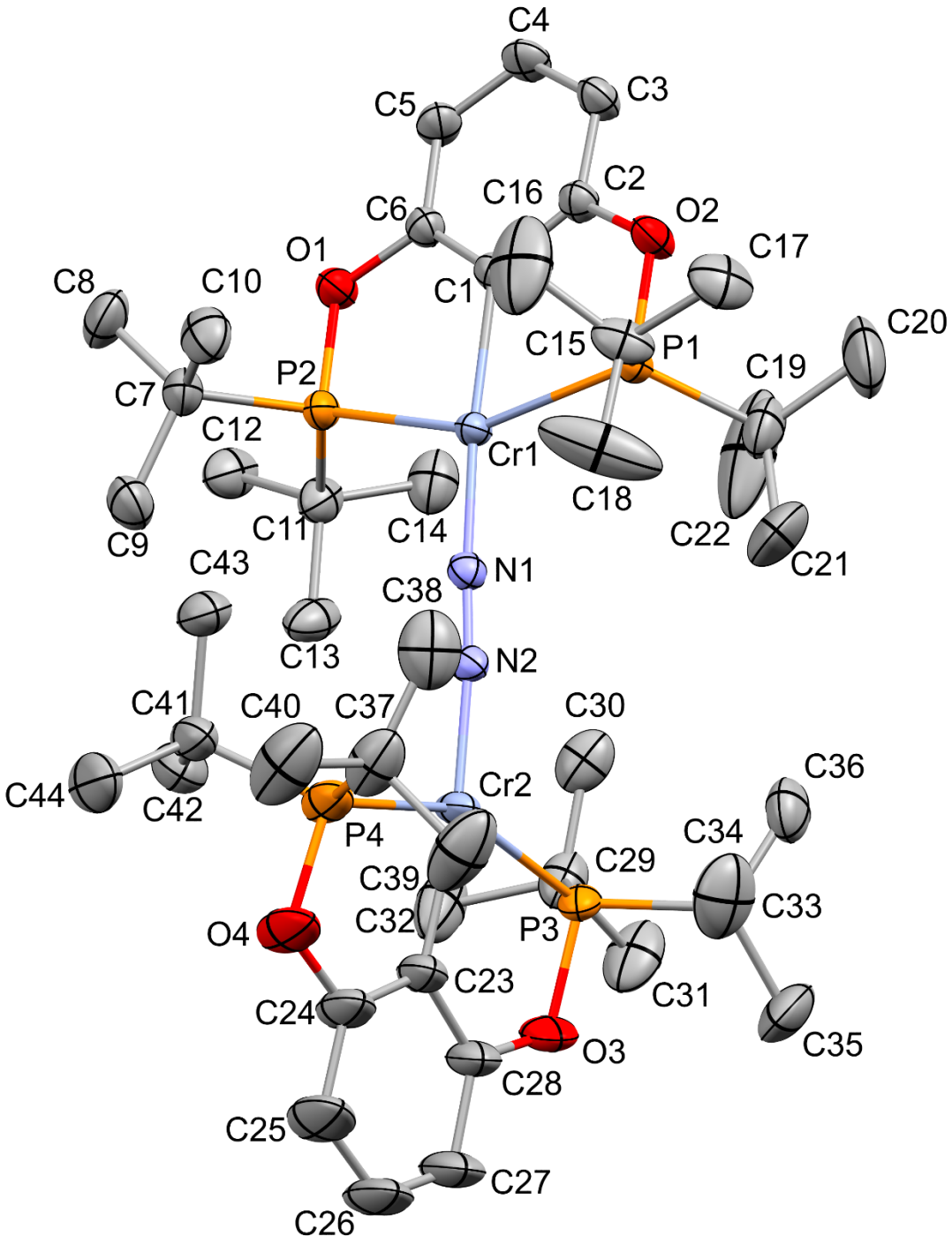

Figure S32. X-Ray crystal structure of [(POCOP^{tBu})Cr]$_2$(μ-N$_2$) (**3**) with atom labelling. Thermal parameters are drawn at 50% probability. All H atoms are omitted for clarity.

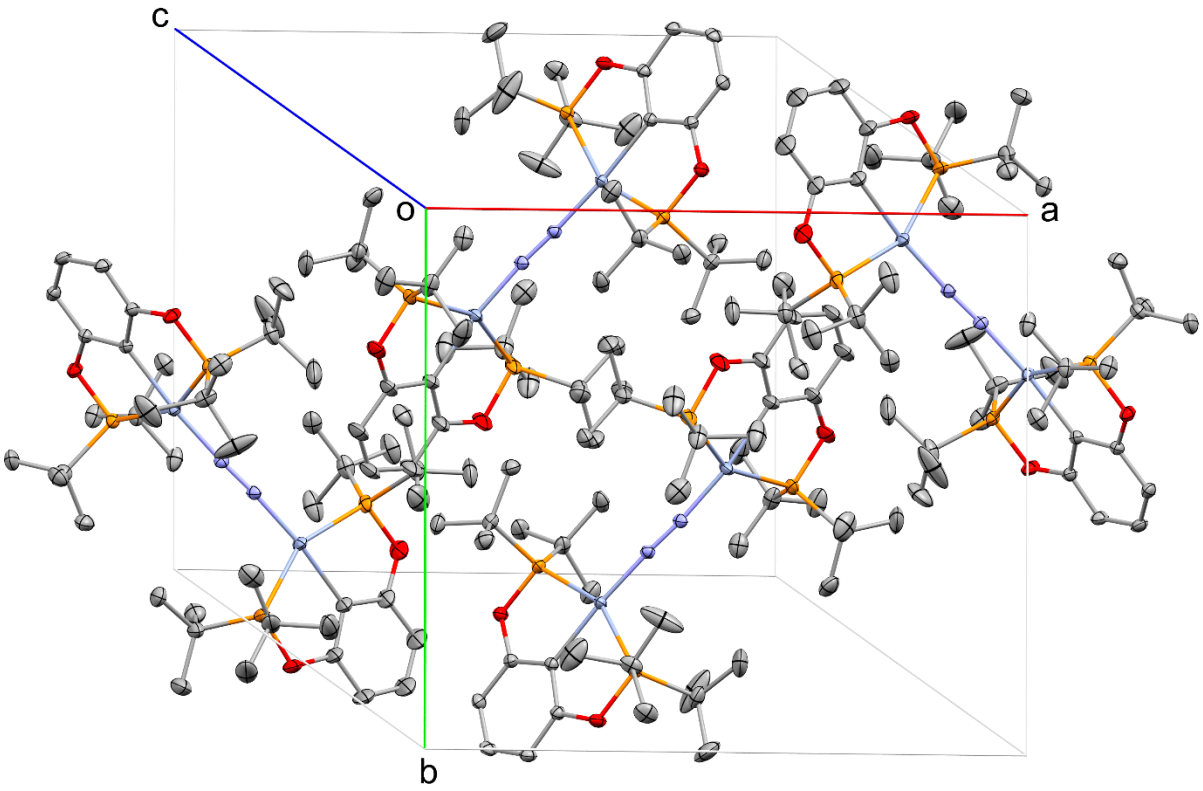

Figure S33. Packing of [(POCOP$^{t\text{Bu}}$)Cr]$_2$(μ-N$_2$)·½Et$_2$O (**3**) crystals. All atoms are unlabeled, and the thermal ellipsoids are drawn at 30% probability. H atoms are omitted for clarity.

Table S14. Crystal data and structure refinement for **3**.

Chemical formula	$C_{46}H_{83}Cr_2N_2O_{4.50}P_4$	
Formula weight	964.02 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.120 × 0.270 × 0.410 mm	
Crystal habit	purple prism	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 15.7583(16) Å	α = 90°
	b = 14.4111(13) Å	β = 107.974(4)°

	c = 24.856(2) Å γ = 90°
Volume	5369.2(9) Å^3
Z	4
Density (calculated)	1.193 g/cm^3
Absorption coefficient	0.564 mm^{-1}
F(000)	2068
Theta range for data collection	2.23 to 28.70°
Index ranges	$-21 \leq h \leq 21$, $-19 \leq k \leq 19$, $-33 \leq l \leq 33$
Reflections collected	201845
Independent reflections	13866 [R(int) = 0.0776]
Coverage of independent reflections	99.9%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9350 and 0.8020
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2018/2
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	13866 / 0 / 530
Goodness-of-fit on F^2	1.053
Δ/σ_{max}	0.001
Final R indices	11893 data; $I > 2\sigma(I)$ $R1$ = 0.0654, $wR2$ = 0.1668
	all data $R1$ = 0.0746, $wR2$ = 0.1731
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0657P)^2 + 12.2581P]$ where $P = (F_o^2+2F_c^2)/3$
Largest diff. peak and hole	2.066 and -1.046 eÅ^{-3}
R.M.S. deviation from mean	0.095 eÅ^{-3}

Table S15. Atomic coordinates and equivalent isotropic atomic displacement parameters ($Å^2$) for **3**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	**y/b**	**z/c**	**U(eq)**
Cr1	0.56110(3)	0.15720(3)	0.64607(2)	0.02246(11)
C1	0.64135(17)	0.04185(18)	0.64433(11)	0.0240(5)
P1	0.63582(5)	0.20153(5)	0.57915(3)	0.02629(15)
P2	0.53081(5)	0.05330(5)	0.71233(3)	0.02405(14)
N1	0.48272(15)	0.25215(15)	0.64597(9)	0.0244(4)
N2	0.42834(15)	0.31007(15)	0.64524(10)	0.0255(4)
Cr2	0.34893(3)	0.40597(3)	0.63829(2)	0.03171(12)
C23	0.2679(2)	0.5244(2)	0.6206(2)	0.0507(10)
P3	0.43732(6)	0.51939(6)	0.69966(5)	0.0431(2)
P4	0.21281(5)	0.35181(6)	0.57325(3)	0.03225(17)
C2	0.64428(18)	0.96248(18)	0.67742(12)	0.0269(5)
O2	0.59430(15)	0.96115(14)	0.71509(10)	0.0357(5)
C3	0.6930(2)	0.88299(19)	0.67529(13)	0.0323(6)
C4	0.7438(2)	0.8826(2)	0.63835(13)	0.0334(6)
C5	0.7449(2)	0.9582(2)	0.60439(13)	0.0321(6)
C6	0.69373(18)	0.03516(18)	0.60812(12)	0.0264(5)
O1	0.69657(14)	0.11029(14)	0.57314(9)	0.0317(4)
C7	0.7261(2)	0.2904(2)	0.60233(14)	0.0350(6)
C8	0.8030(2)	0.2770(3)	0.57740(19)	0.0517(9)
C9	0.6866(3)	0.3878(2)	0.58960(17)	0.0450(8)
C10	0.7625(2)	0.2776(3)	0.66694(16)	0.0479(8)
C11	0.5655(2)	0.2165(2)	0.50453(13)	0.0355(6)
C12	0.6183(2)	0.2316(3)	0.46252(15)	0.0450(8)
C13	0.5000(2)	0.2967(3)	0.50129(16)	0.0462(8)

	x/a	y/b	z/c	U(eq)
C14	0.5125(3)	0.1254(3)	0.49037(15)	0.0493(9)
C15	0.5689(3)	0.0894(2)	0.78787(13)	0.0408(7)
C16	0.6685(4)	0.1118(5)	0.7989(2)	0.098(2)
C17	0.5620(3)	0.0146(3)	0.82971(15)	0.0516(9)
C18	0.5202(6)	0.1764(4)	0.79446(19)	0.115(3)
C19	0.4188(2)	0.9994(3)	0.69079(16)	0.0460(8)
C20	0.4142(4)	0.9071(4)	0.7191(3)	0.0808(16)
C21	0.3545(3)	0.0669(5)	0.7076(3)	0.100(2)
C22	0.3948(4)	0.9909(6)	0.6272(2)	0.121(3)
C24	0.2945(3)	0.6095(3)	0.6459(3)	0.0666(14)
O3	0.38028(18)	0.61804(18)	0.68481(17)	0.0690(10)
C25	0.2417(3)	0.6893(3)	0.6358(3)	0.098(2)
C26	0.1566(3)	0.6822(3)	0.5981(4)	0.107(3)
C27	0.1259(3)	0.6017(3)	0.5707(3)	0.091(2)
C28	0.1818(2)	0.5245(3)	0.5822(2)	0.0609(12)
O4	0.14850(17)	0.44352(18)	0.55310(14)	0.0574(8)
C29	0.2169(2)	0.3072(3)	0.50332(13)	0.0439(8)
C30	0.2762(2)	0.2227(3)	0.51275(15)	0.0489(9)
C31	0.1246(3)	0.2862(4)	0.46079(16)	0.0649(13)
C32	0.2612(3)	0.3873(4)	0.48083(19)	0.0687(14)
C33	0.1396(2)	0.2799(3)	0.60292(15)	0.0419(7)
C34	0.1642(4)	0.3109(4)	0.6649(2)	0.0754(15)
C35	0.0394(3)	0.2928(4)	0.5730(3)	0.0777(16)
C36	0.1629(3)	0.1779(3)	0.60195(18)	0.0528(9)
C37	0.4539(3)	0.5087(3)	0.7765(2)	0.0579(11)
C38	0.4949(3)	0.4153(3)	0.79704(18)	0.0646(12)

	x/a	y/b	z/c	U(eq)
C39	0.3584(3)	0.5122(4)	0.7806(3)	0.0790(16)
C40	0.5099(3)	0.5867(4)	0.8127(2)	0.0785(17)
C41	0.5404(2)	0.5534(2)	0.68353(18)	0.0455(8)
C42	0.5146(3)	0.5440(3)	0.61872(18)	0.0548(10)
C43	0.6142(2)	0.4832(3)	0.71146(17)	0.0453(8)
C44	0.5718(3)	0.6531(3)	0.6994(3)	0.0681(13)

Table S16. Bond lengths (Å) and bond angles (°) for **3**.

Cr1-N1	1.843(2)	Cr1-C1	2.097(3)
Cr1-P2	2.3807(8)	Cr1-P1	2.4020(8)
C1-C6	1.400(4)	C1-C2	1.401(4)
P1-O1	1.660(2)	P1-C11	1.856(3)
P1-C7	1.869(3)	P2-O2	1.651(2)
P2-C19	1.850(3)	P2-C15	1.860(3)
N1-N2	1.192(3)	N2-Cr2	1.836(2)
Cr2-C23	2.095(3)	Cr2-P3	2.3722(10)
Cr2-P4	2.3840(9)	C23-C24	1.384(5)
C23-C28	1.398(5)	P3-O3	1.661(3)
P3-C37	1.853(5)	P3-C41	1.855(4)
P4-O4	1.647(2)	P4-C33	1.864(3)
P4-C29	1.873(4)	C2-C3	1.389(4)
C2-O2	1.397(3)	C3-C4	1.392(4)
C3-H3	0.950000	C4-C5	1.382(4)
C4-H4	0.950000	C5-C6	1.391(4)
C5-H5	0.950000	C6-O1	1.398(3)
C7-C9	1.528(5)	C7-C8	1.534(5)
C7-C10	1.541(5)	C8-H8A	0.980000
C8-H8B	0.980000	C8-H8C	0.980000
C9-H9A	0.980000	C9-H9B	0.980000
C9-H9C	0.980000	C10-H10A	0.980000
C10-H10B	0.980000	C10-H10C	0.980000
C11-C13	1.535(5)	C11-C14	1.537(5)
C11-C12	1.539(4)	C12-H12A	0.980000

C12-H12B	0.980000	C12-H12C	0.980000
C13-H13A	0.980000	C13-H13B	0.980000
C13-H13C	0.980000	C14-H14A	0.980000
C14-H14B	0.980000	C14-H14C	0.980000
C15-C18	1.506(5)	C15-C17	1.524(5)
C15-C16	1.543(7)	C16-H16A	0.980000
C16-H16B	0.980000	C16-H16C	0.980000
C17-H17A	0.980000	C17-H17B	0.980000
C17-H17C	0.980000	C18-H18A	0.980000
C18-H18B	0.980000	C18-H18C	0.980000
C19-C22	1.512(6)	C19-C20	1.517(6)
C19-C21	1.551(7)	C20-H20A	0.980000
C20-H20B	0.980000	C20-H20C	0.980000
C21-H21A	0.980000	C21-H21B	0.980000
C21-H21C	0.980000	C22-H22A	0.980000
C22-H22B	0.980000	C22-H22C	0.980000
C24-C25	1.396(5)	C24-O3	1.403(5)
C25-C26	1.382(8)	C25-H25	0.950000
C26-C27	1.357(8)	C26-H26	0.950000
C27-C28	1.393(5)	C27-H27	0.950000
C28-O4	1.388(5)	C29-C30	1.509(6)
C29-C31	1.540(5)	C29-C32	1.541(5)
C30-H30A	0.980000	C30-H30B	0.980000
C30-H30C	0.980000	C31-H31A	0.980000
C31-H31B	0.980000	C31-H31C	0.980000
C32-H32A	0.980000	C32-H32B	0.980000
C32-H32C	0.980000	C33-C36	1.516(6)

C33-C34	1.535(6)	C39-H39C	0.980000
C34-H34A	0.980000	C40-H40B	0.980000
C34-H34C	0.980000	C41-C44	1.531(5)
C35-H35B	0.980000	C41-C42	1.541(6)
C36-H36A	0.980000	C42-H42B	0.980000
C36-H36C	0.980000	C43-H43A	0.980000
C37-C40	1.537(5)	C43-H43C	0.980000
C38-H38A	0.980000	C44-H44B	0.980000
C38-H38C	0.980000		
C39-H39B	0.980000	N1-Cr1-C1	175.34(10)
C40-H40A	0.980000	C1-Cr1-P2	76.50(7)
C40-H40C	0.980000	C1-Cr1-P1	76.64(7)
C41-C43	1.537(5)	C6-C1-C2	113.7(2)
C42-H42A	0.980000	C2-C1-Cr1	123.08(19)
C42-H42C	0.980000	O1-P1-C7	99.51(13)
C43-H43B	0.980000	O1-P1-Cr1	105.73(8)
C44-H44A	0.980000	C7-P1-Cr1	117.28(11)
C44-H44C	0.980000	O2-P2-C15	100.37(14)
C33-C35	1.535(5)	O2-P2-Cr1	106.64(8)
C34-H34B	0.980000	C15-P2-Cr1	116.84(12)
C35-H35A	0.980000	N1-N2-Cr2	173.7(2)
C35-H35C	0.980000	N2-Cr2-P3	102.13(7)
C36-H36B	0.980000	N2-Cr2-P4	105.18(7)
C37-C38	1.512(7)	P3-Cr2-P4	152.69(3)
C37-C39	1.541(6)	C24-C23-Cr2	123.2(3)
C38-H38B	0.980000	O3-P3-C37	101.2(2)
C39-H39A	0.980000	C37-P3-C41	112.97(18)

C37-P3-Cr2	118.28(14)	O4-P4-Cr2	106.50(11)
O4-P4-C33	99.73(16)	C29-P4-Cr2	117.42(11)
C33-P4-C29	112.25(17)	C3-C2-C1	124.7(3)
C33-P4-Cr2	116.82(12)	C2-O2-P2	114.87(17)
C3-C2-O2	116.5(2)	C2-C3-H3	121.100000
O2-C2-C1	118.8(2)	C4-C3-H3	121.100000
C2-C3-C4	117.8(3)	C5-C4-H4	119.400000
N1-Cr1-P2	100.98(7)	C4-C5-C6	118.1(3)
N1-Cr1-P1	105.85(7)	C6-C5-H5	120.900000
P2-Cr1-P1	153.14(3)	C5-C6-C1	124.5(3)
C6-C1-Cr1	123.16(19)	C6-O1-P1	115.31(17)
O1-P1-C11	100.66(13)	C9-C7-C10	108.8(3)
C11-P1-C7	113.06(15)	C9-C7-P1	110.0(2)
C11-P1-Cr1	116.97(10)	C10-C7-P1	104.0(2)
O2-P2-C19	100.73(16)	C7-C8-H8B	109.500000
C19-P2-C15	113.03(17)	C7-C8-H8C	109.500000
C19-P2-Cr1	116.17(12)	H8B-C8-H8C	109.500000
N2-N1-Cr1	176.4(2)	C7-C9-H9B	109.500000
N2-Cr2-C23	170.48(15)	C7-C9-H9C	109.500000
C23-Cr2-P3	76.86(11)	H9B-C9-H9C	109.500000
C23-Cr2-P4	76.21(11)	C7-C10-H10B	109.500000
C24-C23-C28	113.8(3)	C7-C10-H10C	109.500000
C28-C23-Cr2	123.0(3)	H10B-C10-H10C	109.500000
O3-P3-C41	100.12(16)	C13-C11-C12	110.7(3)
O3-P3-Cr2	106.06(11)	C13-C11-P1	108.9(2)
C41-P3-Cr2	115.00(13)	C12-C11-P1	114.4(2)
O4-P4-C29	100.80(17)	C11-C12-H12B	109.500000

C11-C12-H12C	109.500000
H12B-C12-H12C	109.500000
C11-C13-H13B	109.500000
C11-C13-H13C	109.500000
H13B-C13-H13C	109.500000
C5-C4-C3	121.2(3)
C3-C4-H4	119.400000
C4-C5-H5	120.900000
C5-C6-O1	116.5(2)
O1-C6-C1	119.0(2)
C9-C7-C8	110.8(3)
C8-C7-C10	108.7(3)
C8-C7-P1	114.2(2)
C7-C8-H8A	109.500000
H8A-C8-H8B	109.500000
H8A-C8-H8C	109.500000
C7-C9-H9A	109.500000
H9A-C9-H9B	109.500000
H9A-C9-H9C	109.500000
C7-C10-H10A	109.500000
H10A-C10-H10B	109.500000
H10A-C10-H10C	109.500000
C13-C11-C14	108.8(3)
C14-C11-C12	109.6(3)
C14-C11-P1	104.2(2)
C11-C12-H12A	109.500000
H12A-C12-H12B	109.500000
H12A-C12-H12C	109.500000
C11-C13-H13A	109.500000
H13A-C13-H13B	109.500000
H13A-C13-H13C	109.500000
C11-C14-H14A	109.500000
C11-C14-H14B	109.500000
C11-C14-H14C	109.500000
H14B-C14-H14C	109.500000
C18-C15-C16	109.3(5)
C18-C15-P2	109.0(3)
C16-C15-P2	103.4(3)
C15-C16-H16B	109.500000
C15-C16-H16C	109.500000
H16B-C16-H16C	109.500000
C15-C17-H17B	109.500000
C15-C17-H17C	109.500000
H17B-C17-H17C	109.500000
C15-C18-H18B	109.500000
C15-C18-H18C	109.500000
H18B-C18-H18C	109.500000
C22-C19-C21	111.0(5)
C22-C19-P2	104.2(3)
C21-C19-P2	107.6(3)
C19-C20-H20B	109.500000
C19-C20-H20C	109.500000
H20B-C20-H20C	109.500000
C19-C21-H21B	109.500000

C19-C21-H21C	109.500000
H21B-C21-H21C	109.500000
C19-C22-H22B	109.500000
C19-C22-H22C	109.500000
H22B-C22-H22C	109.500000
H14A-C14-H14B	109.500000
H14A-C14-H14C	109.500000
C18-C15-C17	111.6(4)
C17-C15-C16	108.1(4)
C17-C15-P2	115.0(3)
C15-C16-H16A	109.500000
H16A-C16-H16B	109.500000
H16A-C16-H16C	109.500000
C15-C17-H17A	109.500000
H17A-C17-H17B	109.500000
H17A-C17-H17C	109.500000
C15-C18-H18A	109.500000
H18A-C18-H18B	109.500000
H18A-C18-H18C	109.500000
C22-C19-C20	112.5(5)
C20-C19-C21	107.3(4)
C20-C19-P2	114.3(3)
C19-C20-H20A	109.500000
H20A-C20-H20B	109.500000
H20A-C20-H20C	109.500000
C19-C21-H21A	109.500000
H21A-C21-H21B	109.500000
H21A-C21-H21C	109.500000
C23-C24-O3	118.9(3)
C24-O3-P3	114.7(2)
C26-C25-H25	121.300000
C27-C26-C25	121.7(4)
C25-C26-H26	119.200000
C26-C27-H27	120.800000
O4-C28-C27	116.8(4)
C27-C28-C23	124.1(4)
C30-C29-C31	110.9(4)
C31-C29-C32	109.6(3)
C31-C29-P4	114.2(3)
C29-C30-H30A	109.500000
H30A-C30-H30B	109.500000
H30A-C30-H30C	109.500000
C29-C31-H31A	109.500000
H31A-C31-H31B	109.500000
H31A-C31-H31C	109.500000
C29-C32-H32A	109.500000
C19-C22-H22A	109.500000
H22A-C22-H22B	109.500000
H22A-C22-H22C	109.500000
C23-C24-C25	124.6(4)
C25-C24-O3	116.5(4)
C26-C25-C24	117.4(5)
C24-C25-H25	121.300000
C27-C26-H26	119.200000

C26-C27-C28	118.3(5)	H36A-C36-H36C	109.500000
C28-C27-H27	120.800000	C38-C37-C40	110.2(4)
O4-C28-C23	119.1(3)	C40-C37-C39	109.5(3)
C28-O4-P4	114.7(2)	C40-C37-P3	114.5(4)
C30-C29-C32	109.4(3)	C37-C38-H38A	109.500000
C30-C29-P4	109.3(2)	H38A-C38-H38B	109.500000
C32-C29-P4	103.2(3)	H38A-C38-H38C	109.500000
C29-C30-H30B	109.500000	C37-C39-H39A	109.500000
C29-C30-H30C	109.500000	H39A-C39-H39B	109.500000
H30B-C30-H30C	109.500000	H39A-C39-H39C	109.500000
C29-C31-H31B	109.500000	C37-C40-H40A	109.500000
C29-C31-H31C	109.500000	H40A-C40-H40B	109.500000
H31B-C31-H31C	109.500000	H40A-C40-H40C	109.500000
C29-C32-H32B	109.500000	C29-C32-H32C	109.500000
H32A-C32-H32B	109.500000	H32B-C32-H32C	109.500000
H32A-C32-H32C	109.500000	C36-C33-C35	109.2(4)
C36-C33-C34	108.1(4)	C36-C33-P4	110.5(2)
C34-C33-C35	110.7(4)	C35-C33-P4	114.2(3)
C34-C33-P4	103.9(3)	C33-C34-H34B	109.500000
C33-C34-H34A	109.500000	C33-C34-H34C	109.500000
H34A-C34-H34B	109.500000	H34B-C34-H34C	109.500000
H34A-C34-H34C	109.500000	C33-C35-H35B	109.500000
C33-C35-H35A	109.500000	C33-C35-H35C	109.500000
H35A-C35-H35B	109.500000	H35B-C35-H35C	109.500000
H35A-C35-H35C	109.500000	C33-C36-H36B	109.500000
C33-C36-H36A	109.500000	C33-C36-H36C	109.500000
H36A-C36-H36B	109.500000	H36B-C36-H36C	109.500000

C38-C37-C39	109.4(4)
C38-C37-P3	109.4(3)
C39-C37-P3	103.6(3)
C37-C38-H38B	109.500000
C37-C38-H38C	109.500000
H38B-C38-H38C	109.500000
C37-C39-H39B	109.500000
C37-C39-H39C	109.500000
H39B-C39-H39C	109.500000
C37-C40-H40B	109.500000
C37-C40-H40C	109.500000
H40B-C40-H40C	109.500000
C44-C41-C43	111.2(3)
C43-C41-C42	109.4(3)
C43-C41-P3	108.7(3)
C41-C42-H42A	109.500000
H42A-C42-H42B	109.500000
H42A-C42-H42C	109.500000
C41-C43-H43A	109.500000
H43A-C43-H43B	109.500000
H43A-C43-H43C	109.500000
C41-C44-H44A	109.500000
H44A-C44-H44B	109.500000
H44A-C44-H44C	109.500000
C44-C41-C42	108.2(4)
C44-C41-P3	115.3(3)
C42-C41-P3	103.7(2)
C41-C42-H42B	109.500000
C41-C42-H42C	109.500000
H42B-C42-H42C	109.500000
C41-C43-H43B	109.500000
C41-C43-H43C	109.500000
H43B-C43-H43C	109.500000
C41-C44-H44B	109.500000
C41-C44-H44C	109.500000
H44B-C44-H44C	109.500000

Table S17. Anisotropic atomic displacement parameters (Å^2) for **3**. The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr1	0.0231(2)	0.02063(19)	0.0251(2)	0.00332(15)	0.00968(16)	0.00367(15)
C1	0.0249(12)	0.0212(11)	0.0262(12)	-0.0006(9)	0.0083(10)	0.0004(9)
P1	0.0263(3)	0.0254(3)	0.0298(3)	0.0055(3)	0.0126(3)	0.0023(3)
P2	0.0274(3)	0.0234(3)	0.0228(3)	0.0020(2)	0.0098(3)	0.0034(2)
N1	0.0261(10)	0.0234(10)	0.0235(10)	0.0032(8)	0.0074(8)	0.0005(8)
N2	0.0235(10)	0.0218(10)	0.0266(11)	0.0000(8)	0.0011(8)	0.0000(8)
Cr2	0.0234(2)	0.0215(2)	0.0446(3)	-0.00099(18)	0.00216(19)	0.00571(16)
C23	0.0321(16)	0.0257(15)	0.089(3)	0.0047(16)	0.0114(17)	0.0072(12)
P3	0.0306(4)	0.0269(4)	0.0692(6)	-0.0167(4)	0.0118(4)	0.0020(3)
P4	0.0213(3)	0.0351(4)	0.0360(4)	0.0104(3)	0.0024(3)	0.0031(3)
C2	0.0304(13)	0.0225(12)	0.0303(13)	-0.0015(10)	0.0131(11)	0.0003(10)
O2	0.0491(13)	0.0239(9)	0.0454(12)	0.0099(9)	0.0310(10)	0.0102(9)
C3	0.0417(16)	0.0196(12)	0.0389(16)	0.0011(11)	0.0170(13)	0.0027(11)
C4	0.0394(15)	0.0230(12)	0.0406(16)	-0.0054(11)	0.0165(13)	0.0066(11)
C5	0.0333(14)	0.0292(14)	0.0388(15)	-0.0044(12)	0.0183(12)	0.0026(11)
C6	0.0266(12)	0.0227(12)	0.0311(13)	0.0001(10)	0.0105(10)	-0.0011(10)
O1	0.0355(10)	0.0281(10)	0.0384(11)	0.0051(8)	0.0214(9)	0.0050(8)
C7	0.0322(14)	0.0318(15)	0.0425(17)	0.0021(12)	0.0140(13)	-0.0051(12)
C8	0.0369(17)	0.052(2)	0.074(3)	-0.0081(19)	0.0283(18)	-0.0095(15)
C9	0.052(2)	0.0295(15)	0.057(2)	0.0015(14)	0.0219(17)	-0.0044(14)
C10	0.0429(18)	0.049(2)	0.0452(19)	0.0001(16)	0.0037(15)	-0.0100(15)
C11	0.0328(14)	0.0457(17)	0.0289(14)	0.0095(13)	0.0109(12)	0.0030(13)
C12	0.0454(18)	0.060(2)	0.0346(16)	0.0152(15)	0.0191(14)	0.0091(16)
C13	0.0354(16)	0.063(2)	0.0423(18)	0.0203(16)	0.0150(14)	0.0137(15)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C14	0.048(2)	0.063(2)	0.0347(17)	0.0004(16)	0.0098(15)	-0.0139(17)
C15	0.058(2)	0.0392(17)	0.0214(13)	0.0006(12)	0.0063(13)	0.0119(15)
C16	0.093(4)	0.139(6)	0.046(3)	-0.005(3)	-0.004(3)	-0.061(4)
C17	0.068(2)	0.058(2)	0.0290(16)	0.0105(15)	0.0146(16)	0.0098(19)
C18	0.218(8)	0.084(4)	0.030(2)	-0.003(2)	0.017(3)	0.092(5)
C19	0.0350(16)	0.059(2)	0.0448(19)	0.0072(16)	0.0139(14)	-0.0139(15)
C20	0.080(3)	0.063(3)	0.094(4)	0.015(3)	0.019(3)	-0.040(3)
C21	0.036(2)	0.113(5)	0.158(6)	0.027(4)	0.039(3)	0.002(3)
C22	0.099(4)	0.211(8)	0.043(3)	-0.020(4)	0.008(3)	-0.103(5)
C24	0.0356(18)	0.0301(17)	0.127(4)	-0.007(2)	0.015(2)	0.0096(14)
O3	0.0398(14)	0.0278(12)	0.131(3)	-0.0232(15)	0.0136(16)	0.0053(10)
C25	0.053(3)	0.0279(19)	0.201(7)	-0.008(3)	0.024(3)	0.0120(18)
C26	0.047(2)	0.036(2)	0.221(8)	0.011(3)	0.014(4)	0.0229(19)
C27	0.042(2)	0.042(2)	0.174(6)	0.028(3)	0.010(3)	0.0193(18)
C28	0.0344(17)	0.0368(18)	0.102(3)	0.020(2)	0.007(2)	0.0137(15)
O4	0.0332(12)	0.0421(14)	0.082(2)	0.0184(13)	-0.0037(12)	0.0123(10)
C29	0.0351(16)	0.069(2)	0.0243(14)	0.0094(15)	0.0043(12)	-0.0089(15)
C30	0.0426(18)	0.072(3)	0.0322(16)	-0.0145(16)	0.0114(14)	-0.0096(17)
C31	0.045(2)	0.106(4)	0.0323(18)	0.013(2)	-0.0051(15)	-0.015(2)
C32	0.050(2)	0.103(4)	0.049(2)	0.032(2)	0.0096(18)	-0.016(2)
C33	0.0307(15)	0.0515(19)	0.0472(19)	0.0033(15)	0.0173(14)	-0.0034(14)
C34	0.083(3)	0.097(4)	0.064(3)	-0.020(3)	0.049(3)	-0.020(3)
C35	0.0281(18)	0.098(4)	0.108(4)	0.026(3)	0.023(2)	0.001(2)
C36	0.055(2)	0.053(2)	0.052(2)	0.0127(17)	0.0186(18)	-0.0149(18)
C37	0.050(2)	0.061(2)	0.070(3)	-0.038(2)	0.029(2)	-0.0124(18)
C38	0.079(3)	0.073(3)	0.046(2)	-0.012(2)	0.025(2)	-0.018(2)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C39	0.061(3)	0.096(4)	0.092(4)	-0.046(3)	0.042(3)	-0.020(3)
C40	0.061(3)	0.084(3)	0.096(4)	-0.064(3)	0.032(3)	-0.019(2)
C41	0.0322(15)	0.0303(15)	0.069(2)	-0.0024(15)	0.0082(15)	-0.0003(12)
C42	0.051(2)	0.047(2)	0.063(2)	0.0163(18)	0.0129(18)	0.0038(17)
C43	0.0327(16)	0.0477(19)	0.054(2)	0.0017(16)	0.0103(14)	0.0060(14)
C44	0.052(2)	0.0362(19)	0.109(4)	-0.008(2)	0.015(2)	-0.0094(17)

Table S18. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for **3**.

	x/a	y/b	z/c	U(eq)
H3	0.6917	-0.1693	0.6983	0.039000
H4	0.7783	-0.1707	0.6364	0.040000
H5	0.7796	-0.0424	0.5792	0.039000
H8A	0.8482	0.3251	0.5921	0.078000
H8B	0.7801	0.2816	0.5361	0.078000
H8C	0.8299	0.2157	0.5881	0.078000
H9A	0.7310	0.4337	0.6096	0.068000
H9B	0.6337	0.3927	0.6022	0.068000
H9C	0.6698	0.3994	0.5488	0.068000
H10A	0.8119	0.3208	0.6827	0.072000
H10B	0.7837	0.2137	0.6756	0.072000
H10C	0.7148	0.2900	0.6837	0.072000
H12A	0.5774	0.2298	0.4238	0.068000
H12B	0.6632	0.1825	0.4674	0.068000
H12C	0.6481	0.2921	0.4696	0.068000

	x/a	y/b	z/c	U(eq)
H13A	0.4519	0.2937	0.4652	0.069000
H13B	0.5316	0.3559	0.5040	0.069000
H13C	0.4747	0.2916	0.5326	0.069000
H14A	0.4724	0.1279	0.4514	0.074000
H14B	0.4773	0.1169	0.5164	0.074000
H14C	0.5539	0.0733	0.4943	0.074000
H16A	0.6959	0.1274	0.8389	0.148000
H16B	0.6743	0.1646	0.7754	0.148000
H16C	0.6987	0.0576	0.7894	0.148000
H17A	0.5904	0.0367	0.8684	0.077000
H17B	0.5921	-0.0418	0.8232	0.077000
H17C	0.4990	0.0010	0.8244	0.077000
H18A	0.5512	0.2057	0.8308	0.173000
H18B	0.4591	0.1607	0.7933	0.173000
H18C	0.5186	0.2194	0.7636	0.173000
H20A	0.3535	-0.1176	0.7049	0.121000
H20B	0.4304	-0.0839	0.7601	0.121000
H20C	0.4559	-0.1367	0.7106	0.121000
H21A	0.2927	0.0500	0.6873	0.150000
H21B	0.3659	0.1305	0.6976	0.150000
H21C	0.3644	0.0630	0.7484	0.150000
H22A	0.3328	-0.0296	0.6117	0.181000
H22B	0.4343	-0.0545	0.6177	0.181000
H22C	0.4020	0.0513	0.6111	0.181000
H25	0.2634	0.7463	0.6541	0.117000
H26	0.1187	0.7350	0.5912	0.129000

	x/a	y/b	z/c	U(eq)
H27	0.0677	0.5981	0.5442	0.110000
H30A	0.2929	0.2102	0.4786	0.073000
H30B	0.2442	0.1691	0.5212	0.073000
H30C	0.3302	0.2340	0.5446	0.073000
H31A	0.1313	0.2723	0.4237	0.097000
H31B	0.0858	0.3404	0.4576	0.097000
H31C	0.0982	0.2327	0.4740	0.097000
H32A	0.2716	0.3681	0.4456	0.103000
H32B	0.3182	0.4030	0.5090	0.103000
H32C	0.2219	0.4417	0.4737	0.103000
H34A	0.1278	0.2767	0.6839	0.113000
H34B	0.1530	0.3775	0.6665	0.113000
H34C	0.2275	0.2981	0.6839	0.113000
H35A	0.0054	0.2560	0.5924	0.117000
H35B	0.0250	0.2722	0.5336	0.117000
H35C	0.0239	0.3585	0.5739	0.117000
H36A	0.1351	0.1429	0.6259	0.079000
H36B	0.2278	0.1703	0.6163	0.079000
H36C	0.1408	0.1547	0.5631	0.079000
H38A	0.4955	0.4057	0.8362	0.097000
H38B	0.5561	0.4134	0.7952	0.097000
H38C	0.4596	0.3663	0.7730	0.097000
H39A	0.3591	0.4931	0.8185	0.119000
H39B	0.3200	0.4702	0.7525	0.119000
H39C	0.3353	0.5757	0.7733	0.119000
H40A	0.5055	0.5834	0.8511	0.118000

	x/a	y/b	z/c	U(eq)
H40B	0.4876	0.6470	0.7960	0.118000
H40C	0.5724	0.5797	0.8141	0.118000
H42A	0.5657	0.5609	0.6062	0.082000
H42B	0.4644	0.5853	0.6009	0.082000
H42C	0.4973	0.4797	0.6078	0.082000
H43A	0.6632	0.4897	0.6952	0.068000
H43B	0.5901	0.4201	0.7048	0.068000
H43C	0.6366	0.4950	0.7522	0.068000
H44A	0.6208	0.6676	0.6843	0.102000
H44B	0.5925	0.6594	0.7406	0.102000
H44C	0.5222	0.6960	0.6833	0.102000

XIV. Computational Methodology

Electronic structure calculations reported in this work were carried out with the ORCA quantum chemistry software, version 4.2.1.[10] We used density functional theory (DFT), and the BP86 and B3LYP exchange-correlation functionals. The geometry optimizations and thermochemical calculations are based on the BP86 functional,[11, 12] and TDDFT (time-dependent DFT) simulations on the B3LYP functional. Geometry optimizations relied on the def2-TZVP[13] basis set, used for all atoms, except hydrogen atoms which were treated at the def2-SVP level. For BP86 simulations the auxiliary basis def2/J was employed, and the RIJCOSX method was applied in B3LYP calculations. The thermochemical and geometry-optimization computations were performed under the ORCA TightSCF and TightOPT convergence thresholds, and sixth-level grid, which led to all-positive vibrational frequencies. A broken-symmetry DFT simulation was used to compare the high-spin state of the chromium dimer and the antiferromagnetic state, in which the two spin-up electrons of dinitrogen are inverted; for the antiferromagnetic state we found broken-symmetry DFT and unrestricted DFT with $S = 3$ to be equivalent. TDDFT simulations were based on the def2-TZVPD basis set, an energy threshold of 10^{-5} eV, and 35 roots computed for the chromium monomer. The continuous polarizable solvation model was used to mimic the presence of toluene.

A ground-state optimization of ($POCOP^{tBu}$)Cr(N_2)(Bn) indicated that dinitrogen does not bind to the chromium site.

Based on the orbital level alignment of the quintet state of **2**, we note that the spin-up highest-occupied orbital represents the benzyl-Cr bond, and the spin-up lowest occupied orbital corresponds to a Cr *d* level. This indicates that an optical transition between these two levels must give homolytic bond cleavage due to its ligand-to-metal electron-transfer character. The septet ground-state DFT optimization, for example, illustrates this cleavage by failing to bind the alkyl ligand to the metal center; the septet simulation transfers electron from ligand to metal. TDDFT/B3LYP (toluene solvent) simulations of the quintet state show that this ligand-to-metal electron transfer transition is optically active at around 380 nm wavelength, confirming the experimental findings. The optical transitions at higher wavelengths are due to a local optical transition at the metal site.

The Raman spectrum indicates the vibrational mode for the bridging $[N_2]^{2-}$ ligand is 1639 cm^{-1}. The vibrational frequency for the bridging $[N_2]^{2-}$ ligand of **3** was determined to be 1694 cm^{-1} by DFT calculations (see table of vibrational frequencies below).

J-coupling calculation

We estimated the antiferromagnetic coupling constant following steps reported in Ref. 18 of main document. First, we performed a BP86 simulation in high-spin state ($S = 5$) for **3**, followed by a broken-symmetry calculation where the two nitrogen-site spins are flipped; in our case this is equivalent to simply using unrestricted DFT with $S = 3$. The J coupling is obtained as:

$$J_{\mathrm{AF}} = \frac{1}{8}[E_{\mathrm{HS}} - E_{\mathrm{BS}}]$$

where E_{HS} and E_{BS} are the high-spin and broken-symmetry electronic energies, respectively.

Optimized Geometries of Cr Complexes

Optimized structures are obtained with the following ORCA settings below:

```
!UKS BP86 def2-TZVP def2/J TightSCF Freq Grid6  CPCM(TOLUENE)
%basis
newGTO H "def2-SVP" end
end
```

Geometries :

Complex **3** ($S = 3$):

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Cr	4.206797	12.157529	8.405377
C	3.040022	13.906496	8.560076
P	2.515738	11.548836	10.002664
P	5.073998	13.561481	6.673110
N	5.439876	10.782467	8.437927
N	6.295790	9.948970	8.502466
Cr	7.518849	8.577144	8.683958
C	8.666044	6.861132	9.110521
P	6.691963	6.958745	7.130431
P	9.162360	9.388045	10.241471
C	1.970492	14.036789	9.467699
O	1.600779	12.943849	10.247473
C	1.139821	10.379446	9.403525
C	-0.219053	10.632462	10.076263

H	-0.975035	9.990631	9.592810
H	-0.209840	10.386633	11.145632
H	-0.537452	11.677134	9.963450
C	1.562780	8.914828	9.590326
H	0.862923	8.265420	9.038653
H	2.573355	8.725693	9.199326
H	1.534568	8.609203	10.645447
C	1.009541	10.678291	7.895116
H	0.220446	10.038539	7.465151
H	0.735823	11.727120	7.707907
H	1.949825	10.465135	7.361271
C	3.026953	11.221262	11.796854
C	1.859678	11.102259	12.787419
H	2.262832	11.075671	13.814118
H	1.176716	11.960566	12.717071
H	1.283137	10.178527	12.638887
C	3.909587	9.962437	11.845237
H	4.393096	9.900997	12.833846
H	3.329928	9.040990	11.703353
H	4.699375	9.993106	11.079931
C	3.884068	12.448891	12.173403
H	4.309860	12.292700	13.178207
H	4.720119	12.592965	11.470603
H	3.287485	13.371473	12.193398
C	4.541068	13.134116	4.899888
C	2.998474	13.147320	4.929101
H	2.623138	12.804841	3.950595
H	2.597579	12.475289	5.703313
H	2.601922	14.155103	5.114359
C	5.026229	14.120165	3.827754
H	4.540983	13.870348	2.868762
H	6.112010	14.060728	3.670290
C	5.018175	11.709051	4.575273
H	4.584444	11.393158	3.611820
H	6.110716	11.645188	4.485567
H	4.697758	10.993462	5.347274

C	7.798145	13.006550	6.299720
H	8.841213	13.259916	6.550719
H	7.559660	12.043383	6.777489
H	7.745307	12.879680	5.208993
H	6.895057	13.428149	8.877111
C	8.424052	5.609029	8.510679
O	7.435617	5.501269	7.532596
C	9.117245	4.434381	8.826361
H	8.874511	3.497792	8.321440
C	10.122769	4.497464	9.796071
H	10.675995	3.594071	10.061320
C	10.428944	5.707313	10.426477
H	11.216707	5.770657	11.179133
C	9.701099	6.848147	10.066141
O	10.050482	8.033101	10.709400
C	8.589695	9.963521	11.952755
C	7.722160	11.223669	11.792066
H	7.206784	11.428029	12.744728
H	8.319816	12.110476	11.542953
H	6.958140	11.092518	11.011460
C	9.720654	10.214467	12.960702
H	9.280298	10.384949	13.957928
H	10.400441	9.354071	13.036548
H	10.308280	11.107390	12.705669
C	7.704989	8.805520	12.461815
H	7.256204	9.095781	13.425943
H	6.884904	8.583480	11.760664
H	8.286400	7.886008	12.616605
C	10.574968	10.451863	9.538882
C	10.784181	9.916285	8.106680
H	11.599300	10.481647	7.624285
H	11.060946	8.851734	8.103731
H	9.876460	10.039186	7.494161
C	11.896075	10.314429	10.312518
H	12.682550	10.860198	9.764098
H	11.837884	10.742186	11.321172

H	12.207794	9.264970	10.397393
C	10.149633	11.925896	9.465673
H	10.878486	12.479997	8.851059
H	9.160315	12.045176	8.999837
H	10.127295	12.398620	10.457386
C	7.270807	7.150133	5.331427
C	6.757019	8.491699	4.783774
H	7.230811	8.688354	3.807613
H	5.669535	8.491637	4.631998
H	7.006745	9.322992	5.459995
C	8.810592	7.206908	5.412680
H	9.211360	7.395874	4.403068
H	9.153924	8.018250	6.072890
H	9.238104	6.263683	5.779862
C	6.860956	5.997090	4.404307
H	7.377978	6.115892	3.436909
H	7.145158	5.018753	4.817324
H	5.781449	5.994520	4.200573
C	4.888288	6.400624	7.280626
C	4.637940	6.373617	8.804218
H	3.587753	6.095219	8.992437
H	5.278448	5.633864	9.306819
H	4.820776	7.358983	9.261423
C	3.974059	7.451694	6.631091
H	2.927325	7.233928	6.899633
H	4.207941	8.469923	6.979457
H	4.041277	7.432667	5.533987
C	4.596759	5.002081	6.713055
H	3.571143	4.712998	6.998932
H	4.654985	4.971607	5.618052
H	5.285489	4.249959	7.121074
C	3.301783	15.071915	7.812142
O	4.326432	15.058656	6.865732
C	6.875572	14.132496	6.792774
C	1.227247	15.209726	9.649396
H	4.760918	15.157851	4.075385

C	2.595359	16.273006	7.946943
C	7.184472	15.448385	6.060514
C	7.093664	14.348822	8.305889
C	1.554292	16.329541	8.878774
H	0.412461	15.239440	10.374873
H	2.855140	17.137729	7.333891
H	7.147117	15.341657	4.969462
H	6.492055	16.247409	6.358066
H	8.205887	15.767963	6.328300
H	6.446631	15.147442	8.697875
H	8.141112	14.645328	8.481311
H	0.989832	17.256005	9.003828

(POCOP^{tBu})Cr(I)-N_2 complex:

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Cr	8.068101	9.064044	8.722697
C	8.967537	7.225529	9.078804
P	6.887578	7.646206	7.253384
P	9.631551	9.598995	10.405558
C	8.591581	6.050845	8.394547
O	7.577636	6.108329	7.444488
C	9.185155	4.800721	8.609670
H	8.851143	3.925127	8.050621
C	10.210282	4.708701	9.556449
H	10.686881	3.743233	9.739811
C	10.635871	5.832475	10.271843
H	11.435295	5.762961	11.011319
C	10.007457	7.057836	10.016895
O	10.456184	8.155712	10.743108
C	8.946595	9.986251	12.132221
C	8.096230	11.267639	12.066775
H	7.584008	11.404320	13.033701
H	8.701092	12.165305	11.882415
H	7.326874	11.205186	11.283098
C	10.019595	10.109243	13.223765

H	9.524242	10.167968	14.207777
H	10.690804	9.238863	13.236823
H	10.623526	11.019555	13.105817
C	8.020537	8.796403	12.462454
H	7.524343	8.989354	13.427886
H	7.235211	8.668038	11.700333
H	8.577241	7.852819	12.545707
C	11.113583	10.677999	9.914167
C	11.420855	10.253782	8.461528
H	12.270818	10.846697	8.084366
H	11.693302	9.190348	8.394060
H	10.561717	10.435975	7.795908
C	12.370823	10.453119	10.769312
H	13.207511	11.013854	10.319288
H	12.247569	10.812120	11.798697
H	12.652393	9.392055	10.801052
C	10.707932	12.160964	9.929568
H	11.497404	12.753557	9.438270
H	9.768828	12.338538	9.383908
H	10.594822	12.546759	10.952500
C	7.186784	7.875270	5.392987
C	6.312946	9.022702	4.860164
H	6.651341	9.289408	3.845215
H	5.254404	8.735222	4.789896
H	6.388484	9.925403	5.485293
C	8.672403	8.286444	5.300371
H	8.934757	8.456864	4.242849
H	8.869678	9.220637	5.850798
H	9.339138	7.504797	5.693075
C	6.974855	6.602942	4.556974
H	7.311777	6.799375	3.525053
H	7.559473	5.760170	4.949557
H	5.920269	6.303808	4.509229
C	5.085998	7.242557	7.690806
C	5.136946	6.754621	9.154235
H	4.107548	6.572066	9.504252

H	5.704602	5.819402	9.255888
H	5.589527	7.507681	9.819260
C	4.247509	8.531926	7.630960
H	3.238198	8.318272	8.020543
H	4.685442	9.330211	8.248299
H	4.134409	8.913361	6.607509
C	4.454125	6.149484	6.816583
H	3.476826	5.869065	7.244933
H	4.274722	6.495788	5.789343
H	5.076802	5.244384	6.780443
N	6.849176	11.785328	8.100967
N	7.297445	10.763807	8.342084

Complex **2**:

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Cr	7.939892	9.153151	8.683932
C	8.936175	7.306383	9.018031
P	6.750821	7.572289	7.215857
P	9.601761	9.716045	10.418806
C	8.594136	6.115848	8.353877
O	7.551624	6.117086	7.421062
C	9.232831	4.886762	8.554292
H	8.913057	4.001733	8.001811
C	10.281249	4.828406	9.477011
H	10.796413	3.881628	9.651657
C	10.674929	5.971081	10.178704
H	11.489829	5.938518	10.903765
C	9.995345	7.170288	9.932031
O	10.430865	8.278034	10.660285
C	8.928266	10.010270	12.164878
C	8.031061	11.259673	12.152986
H	7.537426	11.353068	13.134468
H	8.595872	12.183611	11.972851
H	7.246370	11.183389	11.385711
C	10.013125	10.133080	13.244559

H	9.529592	10.155183	14.235833
H	10.704140	9.278372	13.227816
H	10.594091	11.059995	13.141558
C	8.051003	8.776105	12.463521
H	7.553147	8.922837	13.436023
H	7.266589	8.638917	11.701876
H	8.643879	7.852737	12.517469
C	11.071318	10.829830	9.975498
C	11.313619	10.549979	8.476354
H	12.179240	11.142052	8.135739
H	11.536523	9.488893	8.287995
H	10.444944	10.842925	7.866279
C	12.352637	10.492862	10.756411
H	13.175414	11.105808	10.351515
H	12.265246	10.721301	11.826048
H	12.630546	9.436373	10.646730
C	10.704692	12.309628	10.163859
H	11.497644	12.930323	9.715450
H	9.758354	12.574965	9.669491
H	10.635372	12.581880	11.226818
C	6.968277	7.779852	5.341656
C	5.971076	8.810560	4.788050
H	6.250989	9.054156	3.749970
H	4.943479	8.421263	4.769889
H	5.978234	9.750203	5.360614
C	8.404871	8.325729	5.190550
H	8.623452	8.476017	4.120387
H	8.527923	9.294810	5.699807
H	9.152603	7.626439	5.592942
C	6.857869	6.460294	4.559387
H	7.135257	6.652965	3.509402
H	7.540375	5.696832	4.955588
H	5.838753	6.053819	4.563738
C	4.994763	7.072033	7.721182
C	5.128610	6.615911	9.189819
H	4.124932	6.380248	9.579807

H	5.753212	5.717169	9.286408
H	5.559253	7.406435	9.825012
C	4.073732	8.304434	7.670824
H	3.095361	8.031994	8.099807
H	4.477330	9.140357	8.260684
H	3.898277	8.659052	6.646558
C	4.405941	5.925338	6.886600
H	3.460558	5.595697	7.349618
H	4.176203	6.239502	5.859034
H	5.080983	5.058619	6.848864
C	6.748048	10.928152	8.228353
C	7.375139	12.262009	8.083953
H	5.956815	10.952574	9.000308
H	6.260995	10.655126	7.276518
C	7.205222	13.287030	9.044031
C	8.165892	12.587691	6.955101
C	8.746898	13.846131	6.797321
C	8.568223	14.840557	7.767287
C	7.788670	14.547084	8.891416
H	6.581264	13.091017	9.920175
H	7.623554	15.311761	9.655182
H	8.314639	11.830714	6.178948
H	9.344113	14.055192	5.905804
H	9.019820	15.826767	7.643795

(POCOP^{tBu})Cr(I) complex:
66

Cr	8.085908	9.013931	8.741536
C	8.973084	7.221496	9.078541
P	6.893784	7.674624	7.264440
P	9.613123	9.607179	10.388621
C	8.590978	6.047719	8.391073
O	7.577894	6.108017	7.445715
C	9.187042	4.798024	8.609397
H	8.852761	3.921115	8.051781

C	10.212994	4.705828	9.556011
H	10.688980	3.739834	9.739412
C	10.639922	5.829545	10.271692
H	11.439516	5.757694	11.011363
C	10.014248	7.058207	10.019630
O	10.459572	8.154348	10.743876
C	8.944127	9.980887	12.130471
C	8.075113	11.249763	12.066684
H	7.570447	11.392729	13.037327
H	8.664724	12.153666	11.861553
H	7.296875	11.165665	11.291607
C	10.020541	10.124831	13.215263
H	9.532924	10.185233	14.203434
H	10.700857	9.261648	13.228690
H	10.615212	11.040072	13.086506
C	8.037098	8.781287	12.475062
H	7.538544	8.972810	13.440124
H	7.254357	8.631889	11.713670
H	8.610269	7.848193	12.563179
C	11.120890	10.672067	9.918537
C	11.426097	10.262847	8.461636
H	12.274836	10.858550	8.084948
H	11.695933	9.199425	8.384496
H	10.563025	10.447769	7.800632
C	12.376261	10.425882	10.770203
H	13.221974	10.978153	10.325658
H	12.257779	10.778194	11.802592
H	12.641488	9.360617	10.794558
C	10.736525	12.160179	9.949011
H	11.537550	12.752504	9.475460
H	9.804389	12.352973	9.394429
H	10.611799	12.534006	10.975446
C	7.191653	7.867240	5.392554
C	6.310423	8.997757	4.837133
H	6.638065	9.244431	3.813141
H	5.251264	8.707552	4.784269

H	6.388898	9.913798	5.443974
C	8.672775	8.290993	5.293205
H	8.934485	8.459266	4.234753
H	8.862628	9.228511	5.841961
H	9.346150	7.517982	5.691474
C	6.992760	6.583042	4.572101
H	7.330155	6.765915	3.537424
H	7.582323	5.751254	4.979795
H	5.940783	6.274138	4.526694
C	5.090595	7.248569	7.697658
C	5.139461	6.745603	9.155361
H	4.110365	6.563074	9.507837
H	5.705185	5.808074	9.244784
H	5.599960	7.489005	9.826278
C	4.251738	8.538249	7.651701
H	3.239931	8.326970	8.037545
H	4.693649	9.328146	8.279621
H	4.143953	8.933336	6.632388
C	4.455399	6.165926	6.814014
H	3.476162	5.882396	7.236654
H	4.279457	6.520796	5.788803
H	5.077343	5.260690	6.771263

Complex **1**:

80

Cr	8.053916	9.146635	8.661123
C	8.946647	7.267315	9.071062
P	6.881111	7.632292	7.147333
P	9.690240	9.675815	10.392721
C	8.572412	6.086282	8.407439
O	7.571286	6.127664	7.431171
C	9.142263	4.831652	8.654762
H	8.805241	3.952042	8.103756
C	10.148261	4.740695	9.621808
H	10.608181	3.773081	9.832983

C	10.572137	5.874957	10.321299
H	11.356766	5.813677	11.077265
C	9.962692	7.100669	10.027657
O	10.420406	8.206554	10.751737
C	9.016038	10.129784	12.102887
C	8.429180	11.551691	12.074737
H	7.832778	11.708163	12.988761
H	9.211623	12.322172	12.055792
H	7.767963	11.707416	11.208384
C	10.039976	9.987147	13.239165
H	9.516642	10.092443	14.204374
H	10.528822	9.003036	13.226098
H	10.813910	10.764698	13.198460
C	7.869894	9.119467	12.329492
H	7.398123	9.328771	13.303605
H	7.091913	9.206109	11.554013
H	8.231700	8.081414	12.341973
C	11.211635	10.672735	9.863698
C	11.586538	10.072959	8.490677
H	12.460165	10.614057	8.091401
H	11.849704	9.007900	8.563172
H	10.764623	10.178437	7.764597
C	12.412159	10.536771	10.812787
H	13.295626	10.992902	10.335277
H	12.247790	11.056885	11.765424
H	12.648131	9.484441	11.022884
C	10.831045	12.151148	9.675483
H	11.647237	12.663698	9.140124
H	9.911840	12.267873	9.080869
H	10.691470	12.666393	10.635256
C	7.248355	7.812035	5.298153
C	6.508101	9.036728	4.733879
H	6.913107	9.268236	3.735014
H	5.431898	8.850387	4.618370
H	6.642165	9.927396	5.366869
C	8.769130	8.075947	5.246353

H	9.070884	8.221575	4.196048
H	9.042239	8.985960	5.804382
H	9.347431	7.233444	5.652297
C	6.932482	6.556928	4.470131
H	7.336442	6.692902	3.452851
H	7.396549	5.658596	4.900331
H	5.852855	6.383170	4.375670
C	5.071676	7.242886	7.549000
C	5.071592	7.011792	9.076095
H	4.038786	6.811234	9.405510
H	5.694018	6.152422	9.363546
H	5.432375	7.898706	9.621416
C	4.190142	8.462743	7.229739
H	3.195382	8.309890	7.679935
H	4.608834	9.393516	7.641964
H	4.046689	8.597262	6.149450
C	4.529112	5.986158	6.851241
H	3.547736	5.733420	7.286864
H	4.379528	6.145471	5.775098
H	5.192661	5.121274	6.991039
C	5.310345	14.912981	7.396937
C	5.945785	13.577028	7.692928
C	7.078138	13.137054	6.986666
C	5.434578	12.722211	8.680246
C	6.032292	11.482654	8.945467
C	7.172530	11.009151	8.252586
C	7.664301	11.897077	7.262333
H	7.506061	13.778004	6.207988
H	8.545972	11.618226	6.672134
H	4.552941	13.033068	9.251175
H	5.578411	10.866338	9.731320
H	4.444989	15.094595	8.050214
H	4.963764	14.970484	6.352124
H	6.025048	15.739252	7.543359

Complex **2** TD-DFT Spectrum data, generated with the ORCA input line below:

!UKS B3LYP RIJCOSX def2-TZVPD NormalSCF Grid6 SlowConv PrintBasis
CPCM(TOLUENE)

ABSORPTION SPECTRUM VIA TRANSITION ELECTRIC DIPOLE MOMENTS

State	Energy (cm-1)	Wavelength (nm)	fosc (au**2)	T2 (au)	TX (au)	TY (au)	TZ
1	20726.2	482.5	0.001073339	0.01705	-0.07055	-0.10630	-0.02778
2	21098.9	474.0	0.008405236	0.13115	0.22720	0.08507	0.26887
3	21795.0	458.8	0.001112300	0.01680	0.00663	-0.12938	-0.00412
4	23719.5	421.6	0.000317512	0.00441	-0.01305	0.06433	-0.00993
5	24734.5	404.3	0.003189519	0.04245	0.14998	0.10224	0.09749
6	26319.0	380.0	0.017871031	0.22354	0.01674	0.42654	-0.20328
7	27274.1	366.6	0.021488105	0.25937	0.12872	-0.49031	0.04897
8	24680.1	405.2	0.007796295	0.10400	-0.03300	0.31567	-0.05711
9	28053.4	356.5	0.038576886	0.45271	0.28430	-0.60692	0.05935
10	26450.6	378.1	0.015147554	0.18853	-0.11044	0.41170	-0.08266
11	28980.2	345.1	0.002503932	0.02844	0.15425	-0.04190	-0.05380
12	29544.6	338.5	0.016008536	0.17838	0.16815	0.23309	-0.30948
13	29606.7	337.8	0.029924760	0.33275	-0.16657	0.55224	0.00584
14	30475.0	328.1	0.000241140	0.00260	0.01858	0.01362	0.04554
15	30462.1	328.3	0.032377171	0.34991	-0.07583	0.57217	-0.12956
16	31688.2	315.6	0.001698708	0.01765	0.07626	0.07084	0.08255
17	32247.8	310.1	0.025787213	0.26326	0.35735	0.04427	0.36551
18	32440.2	308.3	0.018172332	0.18442	0.01061	-0.42890	-0.01866
19	33501.7	298.5	0.010372896	0.10193	0.06821	-0.20112	0.23839
20	33954.2	294.5	0.002950701	0.02861	-0.02476	-0.01616	0.16654
21	34298.2	291.6	0.007884275	0.07568	0.18513	0.04160	-0.19918
22	35350.9	282.9	0.005343619	0.04976	0.09077	-0.20325	0.01465
23	35543.2	281.3	0.000800185	0.00741	-0.06138	0.02494	-0.05497
24	35834.1	279.1	0.010031153	0.09216	0.17053	0.14252	0.20679
25	36033.7	277.5	0.000808231	0.00738	0.05256	0.03119	0.06041
26	35971.4	278.0	0.003111522	0.02848	0.10208	0.12376	0.05235
27	36056.2	277.3	0.006923016	0.06321	-0.00469	-0.23440	-0.09080

28	36285.4	275.6	0.026135628	0.23712	0.15785	-0.41657	0.19666
29	36374.8	274.9	0.047498611	0.42989	0.00064	-0.63038	0.18030
30	35314.6	283.2	0.012741153	0.11878	0.04078	0.33177	-0.08392
31	35172.9	284.3	0.004406841	0.04125	-0.12486	-0.07589	-0.14106
32	35361.5	282.8	0.014318532	0.13330	0.04456	0.36164	-0.02312
33	35409.4	282.4	0.011589018	0.10775	-0.07659	-0.31804	-0.02700
34	36321.7	275.3	0.004474525	0.04056	-0.12425	-0.03378	-0.15484
35	35451.1	282.1	0.001538882	0.01429	0.07136	0.02513	0.09255

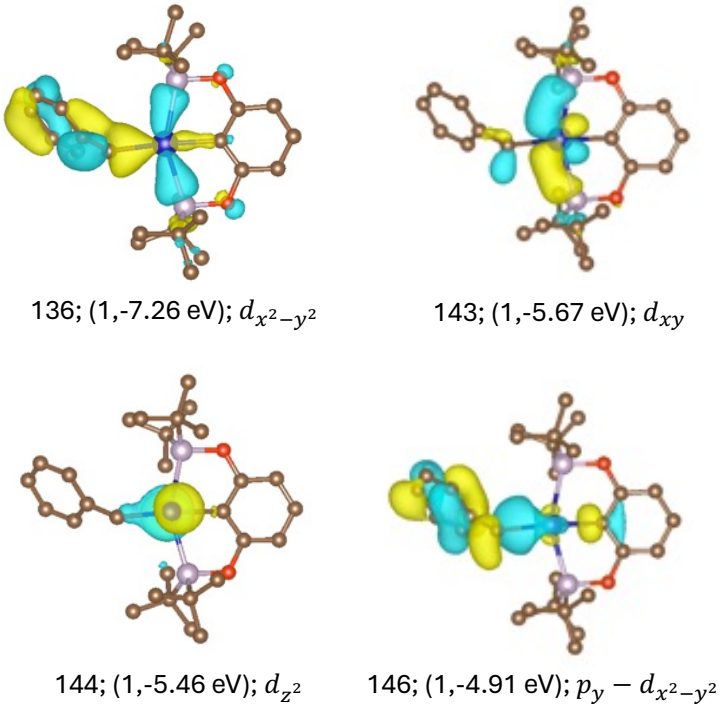

Figure S34. Computationally derived representation of the frontier molecular orbitals of (POCOP^{tBu})**Cr-Bn**. [orbital #; (electron occupancy #, orbital energy); character] Isosurface value is 0.035.

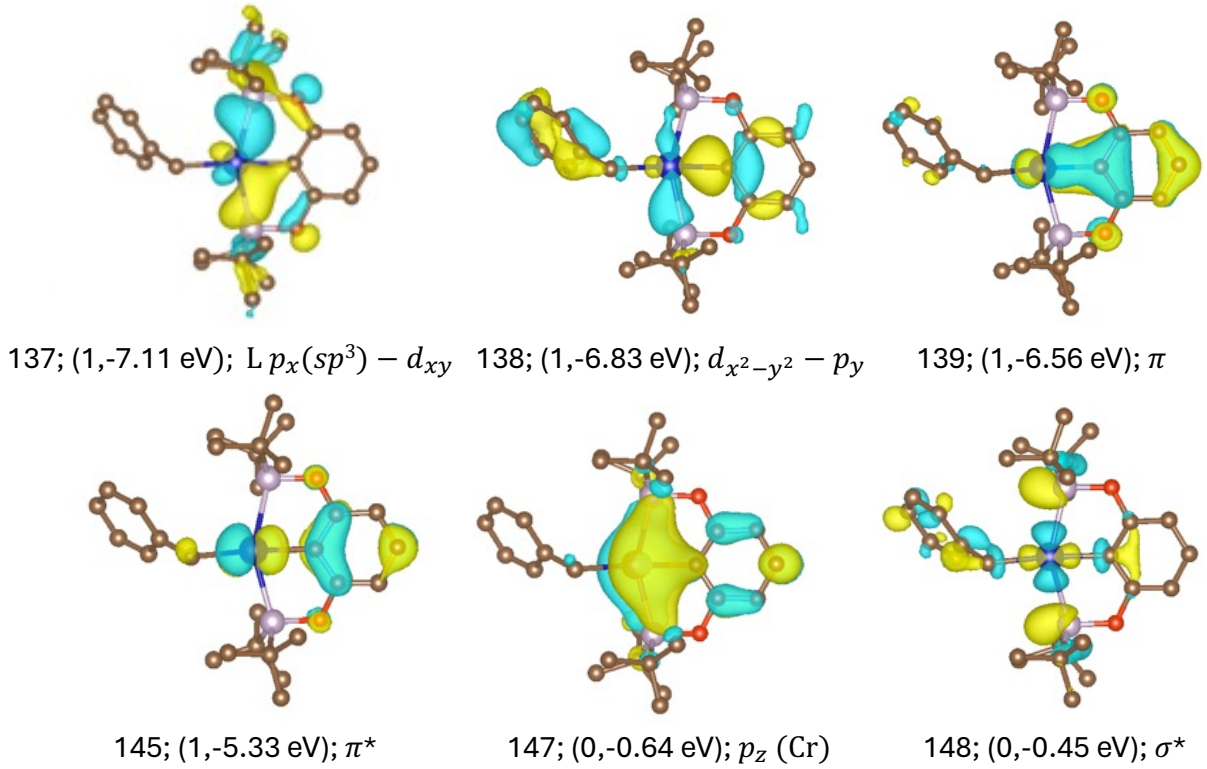

Figure S35. Computationally derived representation of the frontier molecular orbitals of **(POCOP^{tBu})Cr**-Bn. [orbital #; (electron occupancy #, orbital energy); character] Isosurface value is 0.035.

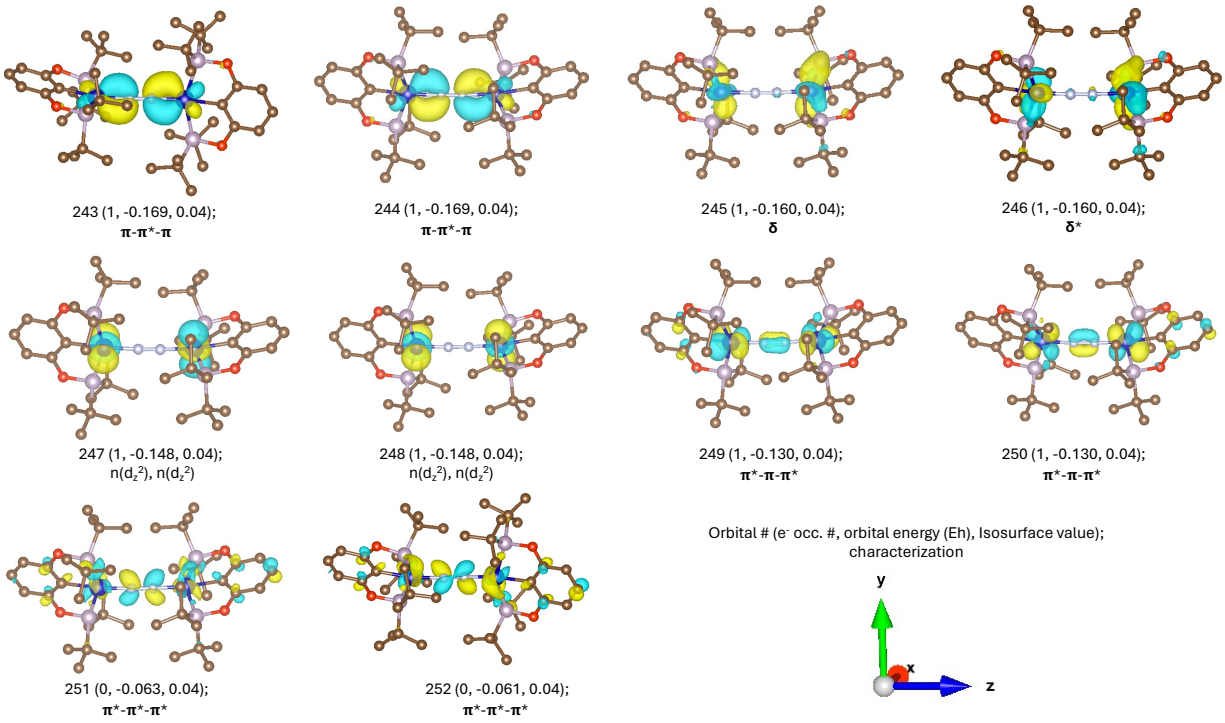

Figure S36. Computationally derived representation of the frontier molecular orbitals of complex **3**. [orbital #; (electron occupancy #, orbital energy); character] Isosurface value is 0.035.

Calculated IR vibrational frequencies for **3**

Mode	freq (cm**-1)	T**2	TX	TY	TZ
8:	3.46	0.000000	(0.000000	0.000000	0.000000)
9:	9.17	0.071314	(-0.045637	-0.045736	-0.259113)
10:	14.50	0.660038	(0.588184	0.508968	0.234583)
11:	19.42	0.117757	(0.062033	0.028368	-0.336310)
12:	28.44	0.024994	(-0.105894	-0.075952	0.089505)
13:	32.34	0.442788	(-0.505493	-0.400210	0.164613)
14:	33.12	0.462326	(-0.002564	-0.055786	-0.677649)
15:	79.39	0.661179	(-0.514816	-0.421095	0.467784)
16:	82.71	0.349366	(-0.279472	-0.222493	0.470913)
17:	84.30	1.209642	(0.561398	0.527799	0.784795)
18:	93.20	0.055979	(0.117212	0.074868	-0.191402)
19:	97.44	0.001292	(0.024322	0.024425	0.010213)
20:	136.36	0.618365	(-0.663868	0.113390	-0.405939)
21:	136.92	0.581627	(0.221245	0.319898	-0.656005)
22:	139.59	2.144904	(0.682427	-1.292345	-0.095086)
23:	145.83	0.390430	(0.541419	-0.310626	-0.028391)
24:	158.37	0.254833	(0.398933	-0.203620	-0.232860)
25:	166.57	0.012193	(-0.006388	0.005783	0.110085)
26:	166.84	0.018083	(-0.116855	-0.062170	0.023724)
27:	167.67	0.013964	(0.023489	0.067379	-0.094193)
28:	174.62	0.488559	(-0.448749	-0.130716	0.519708)
29:	176.50	0.513990	(-0.449760	-0.373989	-0.414534)
30:	189.23	1.341593	(-0.963556	0.639256	-0.067120)

31:	190.81	0.625314	(-0.076583	0.665056	-0.420890)
32:	192.23	0.369137	(0.138914	0.318134	0.498629)
33:	194.97	1.947847	(0.769877	-1.162705	0.057048)
34:	196.05	1.268444	(0.680735	-0.896408	0.038687)
35:	197.75	0.026524	(-0.129279	0.098441	-0.010968)
36:	198.20	0.018523	(0.095112	-0.097224	-0.004888)
37:	211.71	0.315191	(0.171202	-0.040340	-0.533154)
38:	212.16	0.470747	(-0.531155	-0.433127	-0.031978)
39:	215.88	1.149746	(-0.349385	-0.223742	-0.988744)
40:	216.12	4.840541	(1.253875	0.916699	-1.558205)
41:	216.71	4.178326	(1.174518	1.023930	1.323026)
42:	236.03	6.147133	(-1.574860	-1.211501	1.482974)
43:	237.08	6.041057	(1.060052	1.024200	1.966815)
44:	277.61	2.478541	(-1.059943	1.163653	-0.031197)
45:	285.45	0.740667	(0.479652	0.493465	0.516811)
46:	285.95	18.106515	(2.597299	1.822728	-2.835175)
47:	286.36	17.538959	(-2.064924	-1.870473	-3.126720)
48:	287.26	0.050639	(0.021553	0.017462	-0.223314)
49:	302.67	0.030168	(-0.119299	-0.095847	0.082155)
50:	304.36	0.086916	(-0.234343	0.032429	-0.175920)
51:	313.77	0.496116	(0.457445	-0.535063	0.023823)
52:	314.76	132.831287	(-7.133192	9.026964	-0.680278)
53:	347.80	20.121935	(2.792790	1.900300	-2.951461)
54:	348.09	20.207774	(-2.196425	-1.978752	-3.386448)
55:	367.02	0.006283	(0.030198	-0.059203	-0.043194)
56:	398.53	21.901693	(-1.579544	-1.767890	-4.035009)
57:	398.72	21.749878	(-3.338672	-2.275678	2.329042)
58:	407.64	141.182947	(7.399188	-9.264173	0.781059)
59:	410.84	0.295390	(-0.265087	0.460007	-0.116245)
60:	480.51	0.767839	(-0.491700	-0.317095	0.652319)
61:	481.55	0.783658	(0.485696	0.430595	0.601951)
62:	509.76	6.946404	(1.346011	0.805586	-2.117945)
63:	511.32	6.891855	(-1.606253	-1.371605	-1.559008)
64:	558.17	0.504668	(-0.436978	0.557655	-0.052333)
65:	561.03	0.000881	(-0.026976	0.002800	0.012049)
66:	594.54	5.313742	(1.209169	1.060975	1.651056)
67:	594.57	5.240800	(1.334991	0.949142	-1.599290)
68:	607.28	23.705299	(-3.023637	3.805786	-0.280920)
69:	611.40	0.000421	(-0.016030	0.012103	-0.004134)
70:	611.76	0.000067	(-0.003337	-0.005736	-0.004759)
71:	667.84	133.148118	(7.071741	-9.101728	0.545107)
72:	671.35	108.984064	(-0.842812	-1.317389	-10.321735)
73:	671.45	112.429198	(-8.352074	-6.335907	1.590078)
74:	672.08	4.527130	(-0.615332	-0.639615	-1.933750)
75:	687.37	0.588385	(-0.455624	0.615630	0.042315)
76:	688.42	232.482061	(-9.569080	11.831882	-0.959859)
77:	691.85	32.292263	(3.136082	2.390681	-4.091686)
78:	692.13	31.484770	(-2.945515	-2.808301	-3.862921)
79:	697.32	4.501260	(1.296767	0.762726	-1.495963)
80:	698.21	4.803331	(-1.658644	-1.225668	0.741599)
81:	698.42	11.853033	(-1.801357	-1.164547	2.692950)
82:	698.65	19.557935	(-2.218539	-2.048899	-3.230794)
83:	748.40	11.591049	(1.816489	1.636861	2.368987)
84:	748.60	11.604076	(1.888937	1.392356	-2.469279)

85:	755.32	83.905670	(4.890763	3.611889	-6.851304)
86:	755.34	84.150633	(-5.154285	-4.597825	-6.036885)
87:	796.01	0.011033	(-0.059182	0.045344	-0.073991)
88:	796.51	0.064002	(-0.058162	-0.069345	0.236242)
89:	799.47	20.737022	(-2.035920	-1.578838	-3.754906)
90:	799.72	20.851137	(3.070597	2.140163	-2.615773)
91:	803.62	10.619743	(2.130370	-2.464829	-0.076711)
92:	804.38	755.434559	(17.098894	-21.451370	1.703266)
93:	825.09	8.468843	(1.919083	1.691157	-1.387785)
94:	826.80	9.971568	(1.964198	1.535592	-1.937899)
95:	827.10	12.487359	(2.529673	1.963559	-1.494173)
96:	827.31	30.400659	(-2.047011	-2.017717	-4.705233)
97:	838.27	0.222128	(-0.315146	-0.023221	0.349674)
98:	838.95	0.029842	(0.058478	0.157333	-0.040843)
99:	841.99	0.003509	(-0.055454	0.020795	0.001009)
100:	842.40	0.000113	(0.002761	0.004220	-0.009353)
101:	866.31	486.834141	(-13.780853	17.183518	-1.284120)
102:	869.30	5.975911	(-1.354135	2.006109	-0.343158)
103:	886.81	0.025930	(-0.087201	-0.060624	0.121042)
104:	887.01	0.032688	(-0.086878	-0.093405	-0.128123)
105:	919.72	253.091301	(-12.065112	-10.166756	2.039962)
106:	919.91	255.777477	(-0.563930	-2.312565	-15.814914)
107:	921.17	40.287166	(5.117434	-3.592859	1.091055)
108:	926.92	0.013922	(-0.088449	0.014859	-0.076667)
109:	977.00	340.064633	(-8.333652	-7.790419	-14.488763)
110:	977.13	337.976584	(11.853102	8.295116	-11.343351)
111:	986.37	0.032813	(0.157142	-0.077586	-0.045826)
112:	989.89	22.140746	(-2.927808	3.669918	-0.316832)
113:	1060.17	0.366610	(-0.411872	0.443325	0.020841)
114:	1060.64	36.203109	(3.750735	-4.689571	0.378170)
115:	1130.70	0.324386	(0.303173	0.280646	0.392058)
116:	1130.71	0.318337	(0.324184	0.210969	-0.410773)
117:	1179.10	123.066702	(6.010273	5.366816	7.624998)
118:	1179.13	123.151759	(6.335407	4.273011	-8.047096)
119:	1187.85	137.258958	(7.335721	-9.108982	0.687465)
120:	1188.34	0.071779	(-0.009494	-0.147396	0.223525)
121:	1243.50	9.658141	(-2.318018	-1.476286	1.451038)
122:	1244.76	12.710745	(-2.093759	-1.490818	2.470705)
123:	1244.97	22.372903	(2.518601	2.312691	3.268181)
124:	1245.03	5.773774	(0.202408	0.048017	-2.393846)
125:	1254.87	8.936067	(-1.879242	1.212875	-1.983293)
126:	1255.71	12.435185	(-3.058084	1.267436	1.215282)
127:	1255.80	28.349871	(-2.124644	4.881084	-0.103830)
128:	1256.26	3.174704	(-1.176169	0.978986	-0.912643)
129:	1314.04	11.675935	(-1.953142	-1.297454	2.485515)
130:	1314.23	11.607472	(-1.845109	-1.660387	-2.333701)
131:	1375.92	6.689023	(1.644485	1.495363	1.322339)
132:	1377.49	5.744857	(1.195912	1.130639	1.742501)
133:	1377.76	16.249551	(2.304561	1.614800	-2.886343)
134:	1378.09	3.988255	(0.941122	0.813792	1.562142)
135:	1379.25	0.015563	(-0.106874	-0.046522	-0.044459)
136:	1379.60	20.168616	(2.856322	-3.439230	0.426304)
137:	1382.14	0.418397	(0.102110	-0.425446	-0.476409)
138:	1382.43	0.114164	(-0.065114	0.249635	0.218188)

139:	1382.63	0.011095	(	0.004280	-0.021748	-0.102974)
140:	1382.70	0.004284	(	0.030208	0.052799	-0.024158)
141:	1385.39	5.709636	(	1.603248	-1.236285	-1.269185)
142:	1386.16	4.406788	(	-1.686667	0.047217	-1.248884)
143:	1386.29	11.652025	(	1.259762	-3.118173	0.584827)
144:	1386.78	0.575840	(	-0.541797	0.060567	0.527852)
145:	1396.15	7.131516	(	-1.255240	-2.325614	-0.383938)
146:	1396.32	7.675824	(	-0.628920	0.015198	2.698157)
147:	1397.00	18.663765	(	3.218018	-2.832447	0.534202)
148:	1397.28	0.087261	(	-0.177146	-0.220927	0.084088)
149:	1402.60	174.949536	(	-9.103633	-7.677584	-5.755702)
150:	1402.62	174.868638	(	-5.042027	-2.904252	11.874844)
151:	1537.53	83.114579	(	5.211368	3.506136	-6.607815)
152:	1537.61	83.164038	(	4.917589	4.420934	6.279865)
153:	1552.24	5.281146	(	-1.359244	1.834208	-0.263218)
154:	1552.34	58.149151	(	-4.801909	5.908017	-0.431458)
155:	1692.68	0.038992	(	-0.129339	-0.066820	0.133411)
156:	2957.44	6.045272	(	1.426803	1.594951	1.210635)
157:	2957.69	7.423283	(	-0.840050	-0.262930	-2.578462)
158:	2957.84	8.453047	(	-0.623033	-1.574611	-2.363361)
159:	2957.87	11.211178	(	-2.598801	-1.865209	0.989143)
160:	2957.90	1.393478	(	0.859872	0.535703	0.605905)
161:	2958.02	16.022398	(	1.576195	1.402072	-3.401794)
162:	2958.08	3.815579	(	-1.882343	-0.094759	0.513208)
163:	2958.12	4.706591	(	1.353766	1.146214	1.249041)
164:	3047.66	0.483608	(	0.287193	0.632032	-0.040780)
165:	3048.08	0.399509	(	-0.157454	-0.612136	-0.002492)
166:	3048.10	0.729182	(	-0.383671	0.081909	-0.758465)
167:	3048.12	0.196638	(	-0.432155	-0.054218	-0.083312)
168:	3049.75	15.679972	(	0.397334	-3.015435	-2.535596)
169:	3050.02	17.006014	(	1.525451	3.084895	-2.272100)
170:	3050.08	35.564316	(	-4.782955	3.497610	-0.674078)
171:	3050.14	4.637843	(	0.829937	0.444297	1.936917)
172:	3059.58	3.258435	(	0.720134	0.174321	1.646042)
173:	3059.66	2.837125	(	-0.661143	-1.474037	-0.476686)
174:	3059.75	3.927208	(	-1.845721	-0.403894	0.597823)
175:	3059.79	1.194355	(	1.043315	-0.036117	-0.323333)
176:	3059.90	3.727980	(	0.253295	1.375318	-1.331286)
177:	3059.94	0.308107	(	-0.526997	-0.161574	-0.065382)
178:	3059.95	3.018662	(	0.192292	-0.615175	-1.613458)
179:	3060.04	1.019627	(	0.534177	0.573246	0.636922)
180:	3100.51	0.316416	(	-0.357254	0.434443	-0.006673)
181:	3100.63	0.213187	(	-0.264330	0.373703	-0.060523)
182:	3114.29	13.864278	(	-2.179508	-1.360596	2.694959)
183:	3114.31	13.810339	(	-2.039056	-1.769363	-2.553810)
184:	3122.61	62.483643	(	4.923742	-6.167799	0.445715)
185:	3122.67	8.379502	(	1.756378	-2.285806	0.264059)

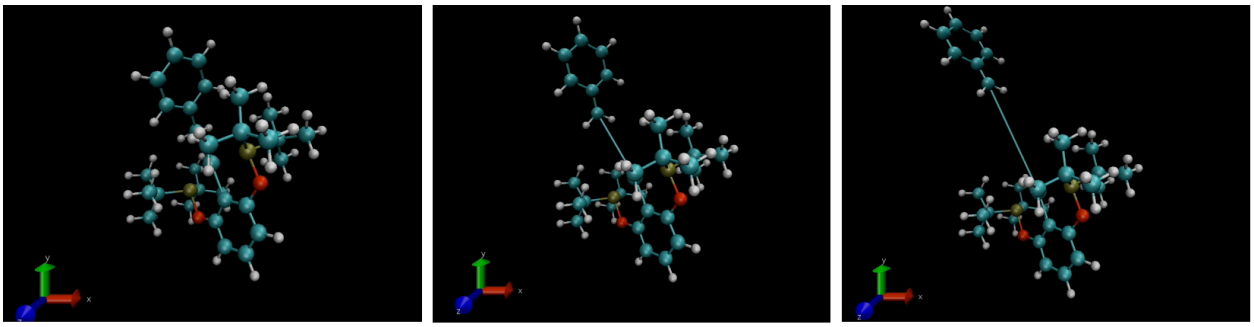

Figure S37. Computationally derived representation showing the dissociation of the benzyl radical of **2**. Initially **2** is an $S = 2$ ground state. Geometry optimization of a spin-flip from the Cr-benzyl bond to the Cr centre results in an $S = 5/2$ (Cr^{I}) excited state and dissociation of the benzyl ($S = ½$) radical from the Cr centre.

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