Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Electrosynthesis of Iminophosphoranes and Applications in Nickel Catalysis

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1. Additional Applications of P(V) Structures as Ligands, Catalysts, Pharmaceuticals, and Materials

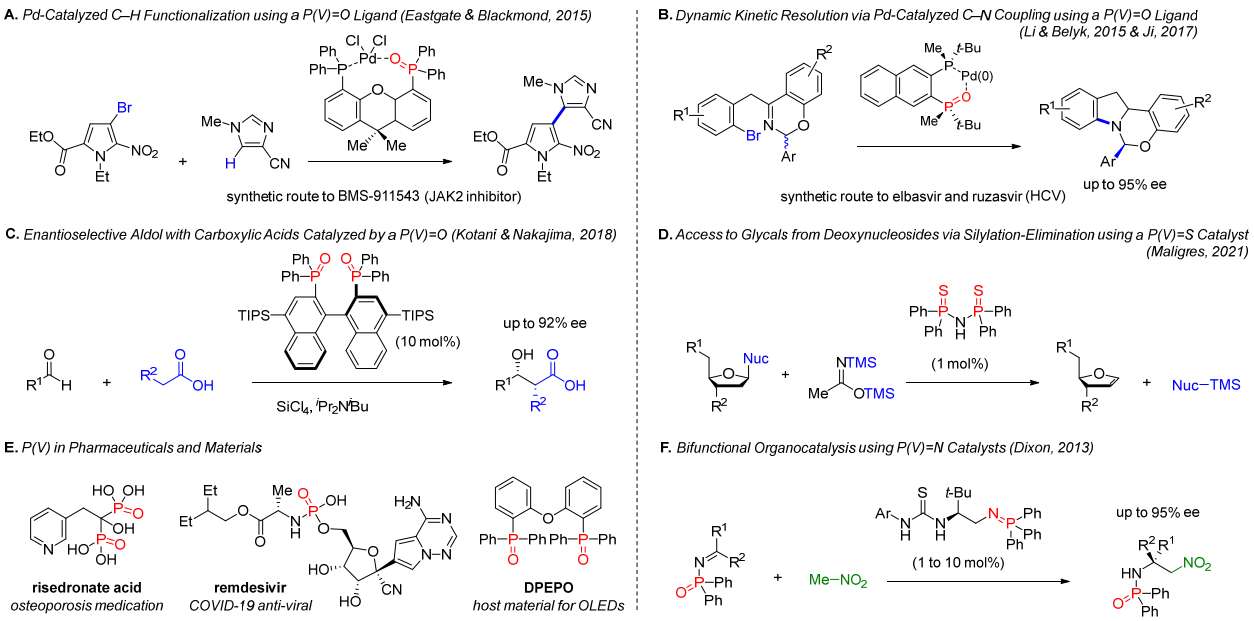


Figure S1. Applications of P(V) structures as ligands, catalysts, pharmaceuticals, and materials. (A) Pd-catalyzed C–H functionalization using a P(V)=O Ligand (see Ref. 1). (B) Dynamic kinetic resolution via Pd-catalyzed C–N coupling using P(V)=O (see Ref. 2). (C) Enantioselective aldol with carboxylic acids catalyzed by a P(V)=O (see Ref. 3). (D). Access to glycals from deoxynucleosides via silylation-elimination using a P(V)=S catalyst (see Ref. 4). (E). P(V) in pharmaceuticals and materials (see Ref. 5 & 6). (F) bifunctional organocatalysis using P(V)=N catalysts (see Ref. 7).

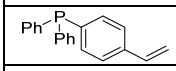
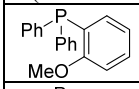
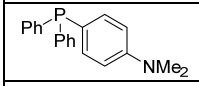
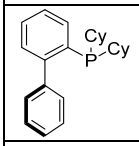
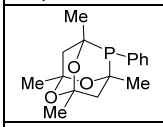
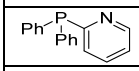
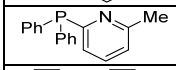
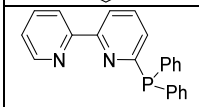
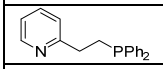
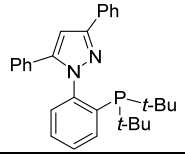
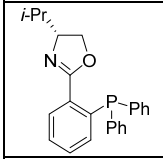
2. General Experimental Details

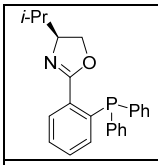
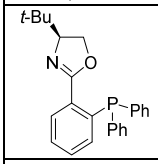
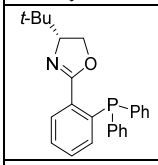
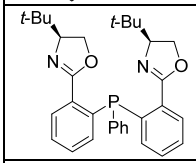
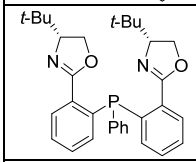
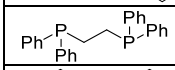
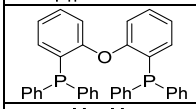
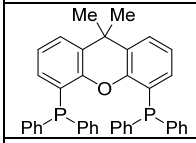
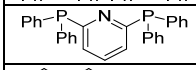
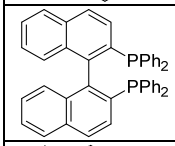
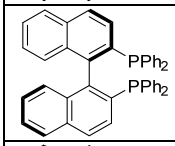
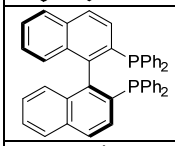
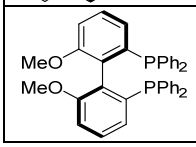
Unless otherwise noted, all reactions were performed under an N_2-atmosphere. Heating of reaction mixtures was performed using a temperature-controlled hotplate equipped with stirring and an active thermocouple. Stirring of reaction mixtures was performed using magnetic stirring, unless noted otherwise. Evaporation of solvent (concentration) was done *in vacuo* using variable vacuum using a rotary evaporator attached to a vacuum controller (ca. 400–40 mmHg).

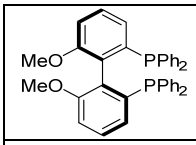
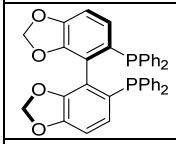
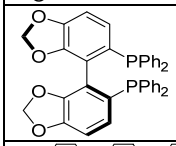
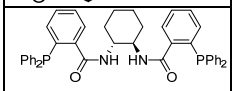
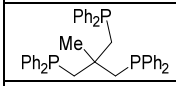
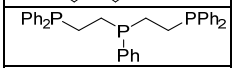
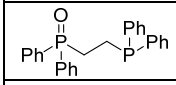
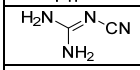
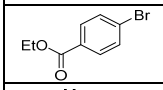
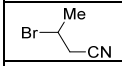
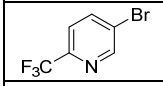
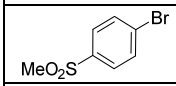
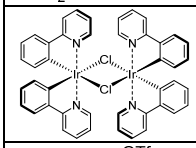
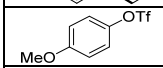
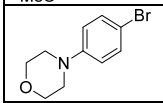
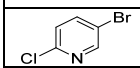
2.1. Materials

Reagents were purchased in reagent grade from commercial suppliers and used without further purification, unless otherwise described. Specific details regarding the commercial source of the aryl halide and sodium sulfinate reagents are provided in Table S1. Tetrabutylammonium hexafluorophosphate (CAS 3109-63-5, Bu_4NPF_6, 95%) was purchased from Sigma-Aldrich (436143-25G) in electrochemical grade (≥99.0%). The following anhydrous solvents were deoxygenated prior to being used for electrochemical reactions (no additional drying/purification): acetonitrile (anhydrous, 99.8%, Sigma Aldrich catalog 271004-100ML), N-methylpyrrolidine (anhydrous, 99.5%, Sigma Aldrich catalog 328634-100ML), and methanol (anhydrous, 99.8%, Sigma Aldrich catalog 322415-100ML). Water (0.03 micron filtered, Thermo Scientific™ catalog number W81, UHPLC-MS, 1 L, Clear Borosilicate Glass Bottle) was deoxygenated prior to being used for photochemical reactions. NMR solvents, specifically, CD_3CN (99.8% *d*-content, catalog DLM-21-10X0.75), CD_3OD (99.8% *d*-content, DLM-24-10X0.75), CD_2Cl_2 (99.8% *d*-content, catalog DLM-23-10X0.75), and d_9-NMP (99% *d*-content, catalog DLM-1988-5) were purchased from Cambridge Isotope Laboratories in sealed ampules and used as received. The acetonitrile and water used to prepare the UPLC mobile phases were purchased from Thermo Scientific™: acetonitrile (0.1 micron filtered, catalog number A9561, UHPLC-MS, 1 L, Clear Borosilicate Glass Bottle) and water (0.03 micron filtered, catalog number W81, UHPLC-MS, 1 L, Clear Borosilicate Glass Bottle).

Table S1. Source of Phosphine Substrates

Structure	Name	CAS	Vendor	Catalog	Purity
$NC–NH_2$	Cyanamide	420-04-2	Sigma-Aldrich	187364-25G	99%
TMS-N=C=N-TMS	Bis(trimethylsilyl)carbodimide	1000-70-0	Gelest	SIB1856.0	97%
Me_4NOAc	Tetramethylammonium acetate	10581-12-1	TCI	T1048	>98%
PPh_3	Triphenylphosphine	603-35-0	Sigma-Aldrich	T84409-1KG	99%
$P(p\text{-}MeO\text{-}C_6H_4)_3$	Tris(4-methoxyphenyl)phosphine	855-38-9	Acros	422240100	95%
$P(p\text{-}F\text{-}C_6H_4)_3$	Tris(4-fluorophenyl)phosphine	18437-78-0	Sigma-Aldrich	395099-5G	98%
$P(p\text{-}Cl\text{-}C_6H_4)_3$	Tris(4-chlorophenyl)phosphine	1159-54-2	Sigma-Aldrich	249491-1G	95%
$P(p\text{-}CF_3\text{-}C_6H_4)_3$	Tris(4-trifluoromethylphenyl) phosphine	13406-29-6	Sigma-Aldrich	666629-5G	98%
	4-(Diphenylphosphino)styrene	40538-11-2	Sigma-Aldrich	708127-5G	97%
$P(o\text{-}Me\text{-}C_6H_4)_3$	Tri(*o*-tolyl)phosphine	6163-58-2	Strem	15-8050	99%
	Diphenyl(2-methoxyphenyl)phosphine	53111-20-9	Aldrich	28,786-5	98%
	4-(Dimethylamino) phenyldiphenylphosphine	739-58-2	Sigma-Aldrich	395021	95%
$CyPPh_2$	Diphenylcyclohexylphosphine	6372-42-5	Strem	15-0900	98%
$PhPCy_2$	Dicyclohexylphenylphosphine	6476-37-5	Sigma-Aldrich	288284	95%
	CyJohnPhos = 2-(Dicyclohexyl phosphino)biphenyl	247940-06-3	Strem	15-1140	98%
	^{me}CgPPh = 1,3,5,7-Tetramethyl-6-phenyl-2,4,8-trioxa-6-phosphaadamantane	97739-46-3	Sigma-Aldrich	695459	97%
PBn_3	Tribenzylphosphine	7650-89-7	Sigma-Aldrich	336947-2G	98%
	Diphenyl-2-pyridylphosphine	37943-90-1	Combi-Blocks	OR-0960	98%
	2-Diphenylphosphino-6-methylpyridine	132682-77-0	Ambeed	A673598	NA
	6-(Diphenylphosphino)-2,2'-bipyridine	152194-39-3	ChemScene, LLC	CS-0203236-1G	≥98.0%
	2-(2-(Diphenylphosphino) ethyl)pyridine	10150-27-3	Ambeed	A617728	NA
	1-(2-Di-*t*-butylphosphinophenyl)-3,5-diphenyl-*1H*-pyrazole	628333-86-8	Strem	15-1720	98%
	*(R)*-2-(2-(Diphenylphosphino) phenyl)-4-isopropyl-4,5-dihydrooxazole	164858-78-0	Ambeed	A965930	98%, 99% ee

	*(S)*-2-(2-(Diphenylphosphino) phenyl)-4-isopropyl-4,5-dihydrooxazole	148461-14-7	Ambeed	A597105	98%, 99% ee
	(*S*)-4-(*tert*-Butyl)-2-(2-(diphenylphosphino)phenyl)-4,5-dihydrooxazole	148461-16-9	Ambeed	A934451	98%, 99% ee
	(*R*)-4-(*tert*-Butyl)-2-(2-(diphenylphosphino)phenyl)-4,5-dihydrooxazole	164858-79-1	Ambeed	A935663	NA
	(4*S*,4'*S*)-2,2'-((Phenylphosphanediyl)bis(2,1-phenylene))bis(4-(*tert*-butyl)-4,5-dihydrooxazole)	642491-11-0	Ambeed	A1371331	97%
	(4*R*,4'*R*)-2,2'-((Phenylphosphanediyl)bis(2,1-phenylene))bis(4-(*tert*-butyl)-4,5-dihydrooxazole)	NA	Ambeed	A1371642	98%
	DPPE = 1,2-Bis(diphenylphosphino)ethane	1663-45-2	TCI	B1137	>97%
	DPEPhos = Bis[(2-diphenylphosphino)phenyl] ether	166330-10-5	Strem	15-0380	97%
	4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene = Xantphos	161265-03-8	Oakwood	036098-25g	97%
	bis(DPP-Py) = 2,6-Bis(diphenylphosphino)pyridine	64741-27-1	abcr	AB494874	95%
	(*rac*)-BINAP	98327-87-8	Sigma-Aldrich	481084	97%
	(*R*)-BINAP = (*R*)-(+)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene	76189-55-4	Sigma-Aldrich	295817	97%
	(*S*)-BINAP = (*S*)-(–)-2,2′-Bis(diphenylphosphino)-1,1′-binaphthalene	76189-56-5	Sigma-Aldrich	295825	97%
	(*R*)-(+)-2,2'-Bis(diphenylphosphino)-6,6'-dimethoxy-1,1'-biphenyl = (*R*)-BIPHEP®	133545-16-1	Ambeed	A284492	NA

	(*S*)-(–)-2,2'-Bis(diphenylphosphino)-6,6'-dimethoxy-1,1'-biphenyl = (*S*)-BIPHEP®	133545-17-2	Strem	15-0179	≥97%
	(*R*)-SEGPHOS® = (*R*)-(+)-5,5'-Bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole	244261-66-3	Strem	15-0136	98%
	(*S*)-SEGPHOS® = (*S*)-(–)-5,5'-Bis(diphenylphosphino)-4,4'-bi-1,3-benzodioxole	210169-54-3	Ambeed	A313682	98%, 99% ee
	(*1R,2R*)-(+)-1,2-Diaminocyclohexane-*N,N'*-bis(2'-diphenylphosphinobenzoyl); (*R,R*)-DACH-Phenyl Trost Ligand	138517-61-0	Strem	15-0960	98%
	1,1,1-Tris(diphenylphosphinomethyl) ethane = triphos	22031-12-5	Aldrich	380741-5G	NA
	Bis(2-diphenylphosphinoethyl) phenylphosphine	23582-02-7	Sigma-Aldrich	259101-5G	97%
	1,3-Bis(diphenylphosphino)propane monooxide	984-43-0	Strem	15-0205	97%
	1-Cyanoguanidine	461-58-5	Sigma-Aldrich	D76609-25G	99%
$NiBr_2•3H_2O$	Nickel(II) bromide trihydrate	7789-49-3	Ambeed	A565841	97%
Bu_4NPF_6	Tetrabutylammonium hexafluorophosphate	3109-63-5	Sigma-Aldrich	86879-100G	>99.0%
Ni(COD)(DQ)	Bis(1,5-cyclooctadiene)(duroquinone) nickel(0) = Ni(COD)(DQ)	40759-64-6	Sigma-Aldrich	912794-1G	>95%
	Ethyl 4-bromobenzoate	5798-75-4	Sigma-Aldrich	363774-100G	98%
	3-Bromobutyronitrile	20965-20-2	TCI	B1452	>98.0%
	5-Bromo-2-(trifluoromethyl)pyridine	436799-32-5	Sigma-Aldrich	661104-5G	97%
Bu_4NOAc	Tetrabutylammonium acetate	10534-59-5	Sigma-Aldrich	86835-25G	>99.0%
	4-Bromophenyl methyl sulfone	3466-32-8	Sigma-Aldrich	556327-5G	≥99%
	Di-μ-chlorotetrakis[2-(2-pyridinyl-kN)phenyl-kC]diiridium(III)	603109-48-4	Strem	7704-55	≥99%
	4-Methoxyphenyl triflourosulfonate	66107-29-7	Ambeed	A235732	97%
	4-(5-Bromo-2-pyridyl)morpholine	200064-11-5	Ambeed	A567997	96%
Zn	Zinc dust, <10 μm	7440-66-6	Sigma-Aldrich	209988	≥98%
	2-chloro-5-bromopyridine	53939-30-3	Sigma-Aldrich	551902-5G	95%

	pyrrolidine	123-75-1	Sigma-Aldrich	394238-100ML	≥99.5%
$PdCl_2$(dppp)	(1,3-Bis(diphenylphosphino)propane)palladium(II) chloride	59831-02-6	Sigma-Aldrich	696676-2G	
KF	Potassium fluoride	7789-23-3	Sigma-Aldrich	229814-10G	≥99.97%

2.2. Instrumentation

Proton nuclear magnetic resonance (^{1}H NMR) spectra, proton decoupled carbon nuclear magnetic resonance (^{13}C{^{1}H} NMR) spectra, proton decoupled phosphorus nuclear magnetic resonance (^{31}P{^{1}H} NMR), proton coupled fluorine nuclear magnetic resonance (^{19}F NMR), proton decoupled fluorine nuclear magnetic resonance (^{19}F{^{1}H} NMR) were recorded at 25 °C (unless stated otherwise) on a Bruker DRX-500 spectrometer. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual proton of the NMR solvent according to values reported in the literature.[8] Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the NMR solvent. For samples in $CDCl_3$ the residual solvent signal was referenced to 7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C{^{1}H}, for samples in CD_3CN the residual solvent signal was referenced to 1.94 ppm for ^{1}H and 118.26 ppm for ^{13}C{^{1}H}, for samples in d_6-DMSO the residual solvent signal was referenced to 2.50 ppm for ^{1}H and 39.52 ppm for ^{13}C{^{1}H}, for samples in CD_3OD the residual solvent signal was referenced to 3.31 ppm for ^{1}H and 49.0 ppm for ^{13}C{^{1}H}, and for samples in CD_2Cl_2 the residual solvent signal was referenced to 5.32 ppm for ^{1}H and 53.84 ppm for ^{13}C{^{1}H}. Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, dt = doublet of triplets), coupling constants (*J*) in Hertz (Hz). Quantitative ^{1}H NMR analysis (^{1}H qNMR) refers to standard ^{1}H NMR using the following parameters: d1 = 60 seconds, number of scans = 4. Quantitative ^{31}P{^{1}H} NMR spectroscopy (^{31}P{^{1}H} qNMR) refers to standard ^{31}P{^{1}H} NMR using the following parameters: d1 = 40 seconds, number of scans = 8, P1 (pulse width) = 11.25 μs with the transmitter offset being centered at 10 ppm to approximately center it with regards to the ^{31}P signals of interest. HRMS data was obtained using a Waters Acquity UPLC interfaced with a Waters Xevo G2 QTof ESI with the source temperature set to 120 °C. UV-vis absorption spectra were collected using a Horiba Duetta Simultaneous EEM Fluorescence and UV-Vis-NIR Spectrophotometer using a 1 cm × 1 cm quartz cuvette. Single Crystal X-ray diffraction (SCXRD) data was obtained using a Rigaku XtaLAB Synergy instrument equipped with graphite monochromated Cu Kα radiation (λ = 1.5406 Å) to a resolution of 0.79 Å unless otherwise stated. Data was processed using CrysAlisPro Version 1.171.42.54a, and an absorption correction using spherical harmonics was implemented using SCALE3 ABSPACK scaling algorithm. Structures were solve using the intrinsic phasing method with SHEL-XT.[9] Structures were refined using the least squares method with SHEL-XL.[10] All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were modelled isotropically with constraints on bond lengths and angles. Graphical representation of crystallographic data was done using Mercury version 4.3.1.[11]

2.3. Electrochemistry Equipment

Batch electrosynthesis experiments were conducted using either an HT*e*⁻Chem (Analytical Sales) or an IKA Electrasyn 2.0. HT*e*⁻Chem reactor (constant current model, including electrode starter kit, catalog number 700150) was purchased from Analytical Sales and Services, Inc., as were the following electrodes: graphite (catalog number 700500), 316 stainless steel (catalog number 700700), nickel (catalog number 700750), and platinum (catalog number 700656).[12] Reactions performed using the HT*e*⁻Chem were performed in 1 mL clear glass shell vials (8 mm × 30 mm, purchased from Analytical Sales (catalog number 884001). HT*e*⁻Chem was connected to a calibrated DC power supply, 4 output multi range, 420 W combined output (catalog number 700050; made by Aim & Thurlby Thandar Instruments (ATTi), model MX100QP) using the set of breakout cables (catalog number 700060), both purchased from Analytical Sales.

Electrodes used with the IKA Electrasyn 2.0 were purchased from IKA, specifically: Pt foil (catalog number 0040005015), graphite SK-50 (catalog number 0040002858), stainless steel (catalog number 0040002851), nickel (catalog number 0040002859), and nickel foam (catalog number 0040002861). Electrolysis in the IKA Electrasyn 2.0 used either 5 mL vials (catalog number 0040003327) or 20 mL vials (catalog number 0040003324).

Details of the setup used for the flow electrolysis are provided in Section 5.1.

Cyclic voltammetry experiments were done using a Bioanalytical Systems, Inc. (BASi) Epsilon EClipse™ Potentiostat/Galvanostat/Bipotentiostat interfaced with the BASi C-3 cell stand. Epsilon EClipse™ software was used to control the equipment as well as perform the data analysis. All electrodes used for cyclic voltammetry were purchased from BASi, specifically: the working electrode was a 3.0 mm diameter disk glassy carbon electrode (catalog number MF-2012), the counter electrode was a 0.5 mm diameter × 7.5 cm long platinum wire (catalog number MW-1032), and the reference electrode was prepared as described below using the BASi Non-Aqueous Reference Electrode Kit (catalog number MF-2062). To a 25 mL volumetric flask was added $AgNO_3$ (0.0425 g, 0.25 mmol), followed by Bu_4NPF_6 (0.387 g, 1.00 mmol) and MeCN was added to fill the volumetric up to the 25 mL mark and mixed until homogenous, achieving a 0.010 M $AgNO_3$ and 0.10 M Bu_4NPF_6 in MeCN. This solution was added to the above BASi non-aqueous reference electrode glass tube (~7.5 cm tall) stoppered at one end with a 1/8 inch thick chunk of CoralPor® acting as a frit held in place by a piece of heat shrink Teflon tubing until was the solution filled about ~80% of the glass tube's capacity, and the silver wire was immersed into this solution to provide the $Ag/AgNO_3$ reference electrode used for all cyclic voltammetry experiments. Cyclic voltammetry was conducted under an atmosphere of nitrogen in the absence of stirring, after having deoxygenated the analyte solutions (10 mL, 0.010 M of analyte in 0.10 M Bu_4NPF_6, unless noted otherwise) via sparging with nitrogen for approximately 1 min with the aid of magnetic rotary stirring. Unless noted otherwise, cyclic voltammograms were collected using a scan rate of 500 mV/s.

2.4. UPLC MS Methods for Monitoring the Iminophosphorane Syntheses

Samples were dissolved in MeCN (ca. 1 mM) and 1 µL injection volumes were used. A Waters UPLC was equipped with an ACQUITY UPLC™ BEH C18 VanGuard Pre-column (130 Å pore size, 1.7 µm particle size, 2.1 mm × 5 mm length; part number for 3/pkg: 186003975) flowing into an ACQUITY UPLC™ BEH C18 Column (130 Å pore size, 1.7 µm particle size, 2.1 mm internal diameter × 50 mm length; part number 186002350) operating at 50 °C with a 0.8 mL/min flow rate of a binary eluent mixture (eluent A and B, prepared as described below). The 4 min method used the following eluent gradient: gradient from 95.0%A, 5.0%B at t = 0 min to 0.1%A, 99.0%B at t = 3.50 min, followed by holding this eluent mixture constant until t = 3.90 min, and a subsequent change to 95.0%A, 5.0%B at t = 3.91 min and holding this new elutent mixture constant until t = 4.00 min. Two different eluent systems were used: eluent A = aqueous mobile phase (3960 mL H_2O, 40 mL pH 3.5 buffer, details below), eluent B = organic mobile phase (3600 mL MeCN, 360 mL H_2O, 40 mL pH 3.5 buffer, details below. The pH 3.5 buffer is prepared by dissolving ammonium formate (12.6 g, 0.200 mol) and formic acid (7.9 mL, 9.6 g, 0.21 mol) in 1000 mL H_2O.

2.5. UPLC MS Methods for Monitoring the XEC Reactions

Samples were dissolved in MeCN (ca. 1 mM) and 1 µL injection volumes were used. A Waters UPLC was equipped with an ACQUITY UPLC™ BEH C18 VanGuard Pre-column (130 Å pore size, 1.7 µm particle size, 2.1 mm × 5 mm length; part number for 3/pkg: 186003975) flowing into an ACQUITY UPLC™ BEH C18 Column (130 Å pore size, 1.7 µm particle size, 2.1 mm internal diameter × 50 mm length; part number 186002350) operating at 50 °C with a 0.8 mL/min flow rate of a binary eluent mixture (eluent A and B, prepared as described below).

The 10 min method used the following eluent gradient: gradient from 95.0%A, 5.0%B at t = 0 min to 0.1%A, 99.9%B at t = 9.50 min, followed by holding this eluent mixture constant until t = 9.90 min, and a subsequent change to 95.0%A, 5.0%B at t = 9.91 min and holding this new elutent mixture constant until t = 10.00 min. Two different eluent systems were used: eluent A = aqueous mobile phase (3960 mL H_2O, 40 mL pH 3.5 buffer, details below), eluent B = organic mobile phase (3600 mL MeCN, 360 mL H_2O, 40 mL pH 3.5 buffer, details below. The pH 3.5 buffer is prepared by dissolving ammonium formate (12.6 g, 0.200 mol) and formic acid (7.9 mL, 9.6 g, 0.21 mol) in 1000 mL H_2O.

2.6. UPLC MS Methods for Monitoring the Electrochemical C–N Coupling Reactions

Samples were dissolved in MeCN (ca. 1 mM) and 1 µL injection volumes were used. A Waters UPLC was equipped with an ACQUITY UPLC™ BEH C18 VanGuard Pre-column (130 Å pore size, 1.7 µm particle size, 2.1 mm × 5 mm length; part number for 3/pkg: 186003975) flowing into an ACQUITY UPLC™ BEH C18 Column (130 Å pore size, 1.7 µm particle size, 2.1 mm internal diameter × 50 mm length; part number 186002350) operating at 50 °C with a 0.8 mL/min flow rate of a binary eluent mixture (eluent A and B, prepared as described below).

The 8 min method used the following eluent gradient: gradient from 95.0%A, 5.0%B at t = 0 min to 0.1%A, 99.9%B at t = 7.50 min, followed by holding this eluent mixture constant until t = 7.90 min, and a subsequent change to 95.0%A, 5.0%B at t = 7.91 min and holding this new elutent mixture constant until t = 8.00 min. Two different eluent systems were used: eluent A = aqueous mobile phase (3960 mL H_2O, 40 mL pH 3.5 buffer, details below), eluent B = organic mobile phase (3600 mL MeCN, 360 mL H_2O, 40 mL pH 3.5 buffer, details below. The pH 3.5 buffer is prepared by dissolving ammonium formate (12.6 g, 0.200 mol) and formic acid (7.9 mL, 9.6 g, 0.21 mol) in 1000 mL H_2O.

2.7. UPLC MS Methods for High Resolution (HR) ESI MS Determination

Samples were dissolved in DMSO (ca. 1 mM) and 1 µL injection volumes were used. A Waters Xevo XS Tof (Time of Flight ESI) UPLC-MS was equipped with an ACQUITY UPLC™ BEH C18 VanGuard Pre-column (130 Å pore size, 1.7 µm particle size, 2.1 mm × 5 mm length; part number for 3/pkg: 186003975) flowing into an ACQUITY UPLC™ BEH C18 Column (130 Å pore size, 1.7 µm particle size, 2.1 mm internal diameter × 50 mm length; part number 186002350) operating at 40 °C with a 0.8 mL/min flow rate of a binary eluent mixture (eluent A and B, prepared as described below). Eluent A = aqueous mobile phase containing 0.1% (v/v) formic acid, eluent B = organic mobile phase containing MeCN with containing 0.1% (v/v) formic acid. The method used a gradient from 95%A, 5%B at t = 0 min to 0%A, 100%B at t = 1.40 min, followed by holding the gradient at 0%A, 100%B until at t = 1.80 min, and a subsequent change to 95%A, 5%B at t = 1.82 min until t = 2.00 min.

2.8. Method for Assay Yield via $^{31}P\{^1H\}$ NMR Spectroscopy

Assay yields were determined using triethylphosphate as the internal standard added at the end of the reaction. Quantitative $^{31}P\{^1H\}$ NMR spectroscopy was used to determine the ratio between the various ^{31}P signals via integration of their respective signals (Note: triphenylphosphate is observed as a singlet in the $^{31}P\{^1H\}$ NMR at –17.45 ppm in CD_3OD). Quantitative $^{31}P\{^1H\}$ NMR spectroscopy ($^{31}P\{^1H\}$ qNMR) refers to standard $^{31}P\{^1H\}$ NMR using the following parameters: d1 = 40 seconds, number of scans = 8, P1 (pulse width) = 11.25 µs with the transmitter offset being centered at 10 ppm to approximately center it with regards to the ^{31}P signals of interest.

2.9. Abbreviations

bpy, 2,2'-bipyridine; dppe, (diphenylphosphino)ethane; dppp, (diphenylphosphino)propane; EA = electron affinity, ESI = electrospray ionization (ESI^+ and ESI^- denote positive or negative mode, respectively), Fc = ferrocene, Fc^+ = ferrocenium, GC = gas chromatography, HPLC = high performance liquid chromatography, HR = high resolution, ID = internal diameter, LC = liquid chromatography, LED = light emitting diode, MeCN = acetonitrile, MeOH = methanol, MS = mass spectrometry, NA = not available,

ND = not detected, NF = not found, PTFE = polytetrafluoroethylene, qNMR = quantitative NMR, QToF = quadrupole time of flight, RBF = round bottom flask, rpm = rounds per minute, RT = room temperature (ca. 25 °C), SCE = Saturated Calomel Electrode, SCXRD = single crystal X-ray diffraction, UPLC = ultra-performance liquid chromatography, v/v = volume per volume percent, w/v = weight per volume percent, XEC = cross-electrophile coupling.

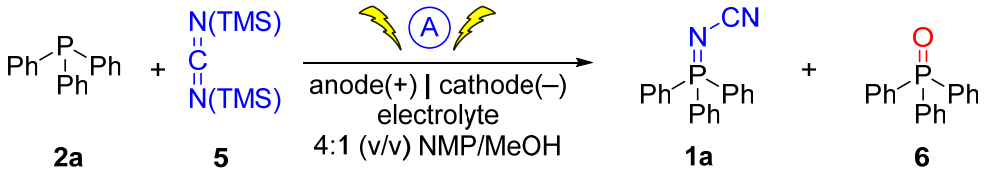
2.10. Symbols

δ = parts per million (ppm), $[compound]_o$ = initial concentration of specific *compound*, A_e = electrode surface area exposed to electrolyte, $E^{\circ,calc}$ = standard potential calculated from DFT data, E_{ox} = oxidation potential, F = Faraday's constant, i = current, j = current density, Q = total charged passed through the electrochemical reaction (given in F/mol), t_r = retention time.

3. Reaction Optimization

To HT*e*⁻Chem reactor[12] (24 well plate) was added 8 × 30 mm vials (Analytical Sales, Inc., catalog number 84001-CASE) containing pre-dosed supporting electrolyte (35 μmol per well), see below for identity and arrangement in the plate design. PTFE coated stir bars (5 mm length × 2 mm diameter; Aldrich catalog Z328839-10EA, alternatively, analogous stir bars can be obtained from ChemGlass, catalog CG-2003-120) were added to each vial, 300 μL of a 0.11 M solution of triphenylphosphine in 4:1 v/v NMP to MeOH (0.283 g, 1.07 mmol of PPh_3 in 9.9 mL of 4:1 (v/v) NMP/MeOH) was added to each well. The lower gasket (0.5 mm holes, part # 701005) and electrode alignment plate were inserted on the four corner alignment bolts and the screwed into place with the center screw (25.2 mm length screw). The approximate torque applied was 5 lbf-in (0.6 Nm); this can be achieve using a Milwaukee M4 volt lithium-ion cordless 1/4 in. hex screwdriver with the speed setting set to 1 and the torque setting set to 3). Ensure not to overtighten the screws is critical to optimal operation of the HT*e*⁻Chem reactor; overtightening can lead to poor electrical connectivity while under tightening can lead to leaking.

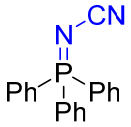
Electrodes (31.3 mm length × 1.6 mm diameter, 48 electrodes in total) were inserted into the alignment plate to serve as both the anode and cathode. The upper gasket (1.5 mm holes, part # 701015) and the sealing plate was placed on the reactor and screwed into place using the four corner screws (36.1 mm length screws) with an approximate applied torque of 5 lbf-in (0.6 Nm); this can be achieve using a Milwaukee M4 Volt Lithium-Ion Cordless 1/4 in. Hex Screwdriver with the speed setting set to 1 and the torque setting set to 3. The HT*e*⁻Chem was equipped with the constant current printed circuit board, followed by the rectangular framing lid, and finally the four nuts were screwed onto the alignment bolts to secure the framing lid and printed circuit board. The reactor was placed onto of an IKA RET basic stir plate and the reactions were stirred (rotary stirring) at 800 RPM at room temperature. The HT*e*⁻Chem reactor was connected to a power supply and a constant current of 1.5 mA was applied until a total charge of 2 F/mol (64.3 min) had passed through each reaction. The current was turned off and the HT*e*⁻Chem reactor was opened. A 25 uL aliquot of each reaction mixture (theoretical max. of 2.5 μmol of product) was added to a 0.25 mM solution of biphenyl in MeCN (700 μL, 1 μmol) followed by mixing. This mixture was characterized using HPLC analysis. A product to internal standard ratio was obtained (internal standard = biphenyl). A solution of triphenyl phosphate (0.359 g, 1.10 mmol) in 4:1 (v/v) NMP/MeOH (10 mL) was used as an internal standard for ^{31}P NMR characterization by taking a 100 uL aliquot from the reaction mixture and a 100 uL aliquot of the phosphate solution, adding 500 uL of CD_2Cl_2. The ratio obtained from the ^{31}P NMR was used to calculate all the assay yields from the HTE plate HPLC analysis, to determine the optimal electrode and supporting electrolyte system.



2a **5** **1a** **6**

HTe-Chem	LiCl	LiBr	Bu_4NCl	Me_4NOAc	Et_4NBr	Bu_4NPF_6
Ni(–) | C(+)	32	31	58	59	40	55
Pt(–) | C(+)	56	11	60	62	54	57
SS(–) | C(+)	22	14	57	59	46	54
Cu(–) | C(+)	33	31	50	11	27	53

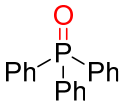
assay yield for:



1a

Ni(–) | C(+)	51	54	35	37	48	18
Pt(–) | C(+)	35	57	32	27	39	20
SS(–) | C(+)	49	55	30	27	45	22
Cu(–) | C(+)	45	49	37	48	49	19

assay yield for:



6

Figure S2. Heat map of assay yields obtained using HT*e*-Chem to screen electrolytes and electrode for the synthesis of iminophosphorane **1a** using bis(trimethylsilyl)carbodiimide); heat map for the side-product triphenylphosphine oxide **6** is shown immediately below. Conditions: 30 µmol scale (0.1 M) using constant current (1.5 mA) using 2 F/mol charge at room temperature. Note: C = graphite, SS = stainless steel.

4. Substrate Scope

4.1. General Procedure A (Electrochemical Synthesis of *N*-Cyano Iminophosphoranes)

In an N_2 filled glovebox, a 20 mL Electrasyn vial was charged with a PTFE coated magnetic stir bar, phosphine substrate (2.00 mmol), bis(trimethylsilyl)carbodiimide (3.00 mmol per phosphorus atom in the phosphine substrate) and tetramethylammonium acetate (0.200 g, 1.50 mmol) followed by NMP (12.0 mL) and MeOH (3.0 mL). Electrodes (graphite anode, platinum foil connected to the Electrasyn vial cap) were immersed into the solution. The Electrasyn vial cap was connected to the Electrasyn 2.0 and the reaction mixture was electrolyzed under a constant current of 10 mA (current density of 4.2 mA/cm^2 for anode surface based on 31.4 mm × 7.49 mm of graphite area exposed to solvent) for a total of 2.5 F/mol of charge per phosphorus accompanied by magnetic stirring (900 rpm). Upon completing the electrolysis, a $^{31}P\{^1H\}$ NMR assay yield was measured (with triphenyl phosphate as internal standard). Workup and purification was carried out as described by one of the following methods, as specified in the individual procedure associate with the compound of interest.

Workup and Purification Methods

Method 1: The reaction mixture was transferred to an Erlenmeyer flask using MeCN (20 mL), and subsequently H_2O (200 mL) was added to this mixture which was stirred during the water addition process. The mixture was stirred for a total of 2 hours at room temperature. The resulting precipitate was collected via filtration and purified using liquid column chromatography (silica gel stationary phase, gradient 10% to 80% (v/v) of mobile phase B in hexanes, in which mobile phase B was a mixture of ethyl acetate containing 4% (v/v) isopropylamine, using a Teledyne ISCO CombiFlash® Rf+ chromatography system using prepacked single-use silica packed cartridges (RediSep® Rf Gold Normal-Phase Silica, 20–40 micron average particle size, 60 Å average pore size, with cartridge sizes 80 g (part number 69-2203-348) 80 mL/min.

Method 2: The reaction mixture was transferred to an Erlenmeyer flask using MeCN (20 mL), and subsequently H_2O (200 mL) was added to this mixture which was stirred during the water addition process. The mixture was stirred for a total of 2 hours at room temperature. The resulting precipitate was collected via filtration. Crystal growth was achieved by dissolving 100 – 200 mg of the product in 5 mL MeCN and 1 mL MeOH, then 1 mL H_2O added as anti-solvent and samples left to recrystallize through slow evaporation.

Method 3: The reaction mixture was transferred to an Erlenmeyer flask using MeCN (20 mL), and subsequently H_2O (200 mL) was added to this mixture which was stirred during the water addition process. The mixture was stirred for a total of 2 hours at room temperature. The resulting precipitate was collected via filtration. Preparative supercritical fluid chromatography (prep-SFC) provided the product.

Method 4: The reaction mixture was transferred to an Erlenmeyer flask using MeCN (20 mL), and subsequently H_2O (200 mL) was added to this mixture which was stirred during the water addition process. The reaction mixture was diluted with dichloromethane (100 mL) and transferred into a separatory funnel for a liquid-liquid extraction. The organic phase was washed with water H_2O (3 × 100 mL). The organic phases were combined and dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was redissolved in minimal amount of dichloromethane (ca. 3.0 mL) and loaded onto a silica gel column for purification via liquid column chromatography (silica gel stationary phase, gradient 10% to 80% (v/v) of mobile phase B in hexanes, in which mobile phase B was a mixture of dichloromethane containing 4% (v/v) isopropylamine, using a Teledyne ISCO CombiFlash® Rf+ chromatography system using prepacked single-use silica packed cartridges (RediSep® Rf Gold Normal-Phase Silica, 20–40 micron average particle size, 60 Å average pore size, with cartridge sizes 80 g (part number 69-2203-348) 80 mL/min.

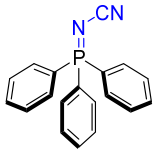
4.2. General Procedure B (Electrochemical Synthesis of *N*-Cyano Iminophosphoranes)

In an N_2 filled glovebox, a 20 mL Electrasyn vial was charged with a PTFE coated magnetic stir bar, phosphine substrate (1.00 mmol), bis(trimethylsilyl)carbodiimide (3.00 mmol per phosphorus atom in the phosphine substrate) and tetramethylammonium acetate (0.200 g, 1.50 mmol) followed by NMP (14.0 mL) and MeOH (1.0 mL). Electrodes (graphite anode, platinum foil connected to the Electrasyn vial cap) were immersed into the solution. The Electrasyn vial cap was connected to the Electrasyn 2.0 and the reaction mixture was electrolyzed under a constant current of 10 mA (current density of 4.2 mA/cm^2 for anode surface based on 31.4 mm × 7.49 mm of graphite area exposed to solvent) for a total of 2.5 F/mol of charge per phosphorus accompanied by magnetic stirring (900 rpm). Upon completing the electrolysis, an $^{31}P\{^1H\}$ NMR assay yield was measured (with triphenyl phosphate as internal standard). Workup and purification were carried out as described by one of the following methods, as specified in the individual procedure associate with the compound of interest.

4.3. General Procedure C (Electrochemical Synthesis of *N*-Cyanoguanidine Iminophosphoranes)

In an N_2 filled glovebox, a 20 mL Electrasyn vial was charged with a PTFE coated magnetic stir bar, phosphine substrate (2.00 mmol), 1-cyanoguanidine (3.00 mmol per phosphorus atom in the phosphine substrate) and tetramethylammonium acetate (0.200 g, 1.50 mmol) followed by NMP (12.0 mL) and MeOH (3.0 mL). Electrodes (graphite anode, platinum foil connected to the Electrasyn vial cap) were immersed into the solution. The Electrasyn vial cap was connected to the Electrasyn 2.0 and the reaction mixture was electrolyzed under a constant current of 5 mA (current density of 21.3 mA/cm^2 for anode surface based on 31.4 mm × 7.49 mm of graphite area exposed to solvent) for a total of 2.5 F/mol of charge per phosphorus accompanied by magnetic stirring (900 rpm). Upon completing the electrolysis, an $^{31}P\{^1H\}$ NMR assay yield was measured (with triphenyl phosphate as internal standard). Workup and purification were carried out as described by one of the methods described in general procedure A, as specified in the individual procedure associate with the compound of interest.

4.4. Specific Examples of Substrate Scope



Synthesis of **1a** was prepared following General Procedure **A** in 83% assay yield (average of two runs) from triphenylphosphine (0.525 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3.0 equiv). Purification was achieved using method 1 to afford a white solid. ^1H NMR (500 MHz, DMF-d_7) δ 7.82 (dd, J = 13.0, 7.7 Hz, 9H), 7.73 (td, J = 7.6, 3.2 Hz, 6H). $^{13}C\{^1H\}$ NMR (126 MHz, DMF-d_7) δ 133.96 (d, J = 2.9 Hz), 132.64 (d, J = 10.3 Hz), 129.80 (d, J = 12.7 Hz), 127.24 (d, J = 102.7 Hz), 118.04. $^{31}P\{^1H\}$ NMR (203 MHz, CD_3OD) δ 26.0 (s, 1P). ESI$^+$ HRMS *m/z* calcd. for $C_{19}H_{16}N_2P$ ($[M + H]^+$) 303.1051, found 303.1045.

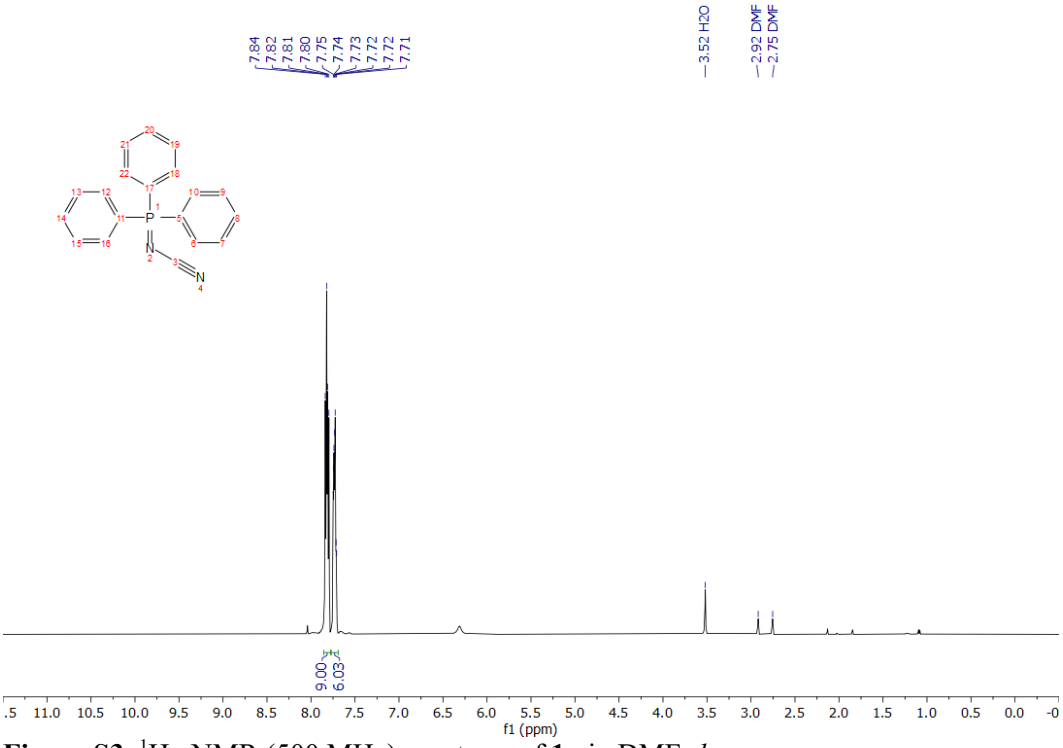


Figure S3. ^{1}H qNMR (500 MHz) spectrum of **1a** in DMF-d_7.

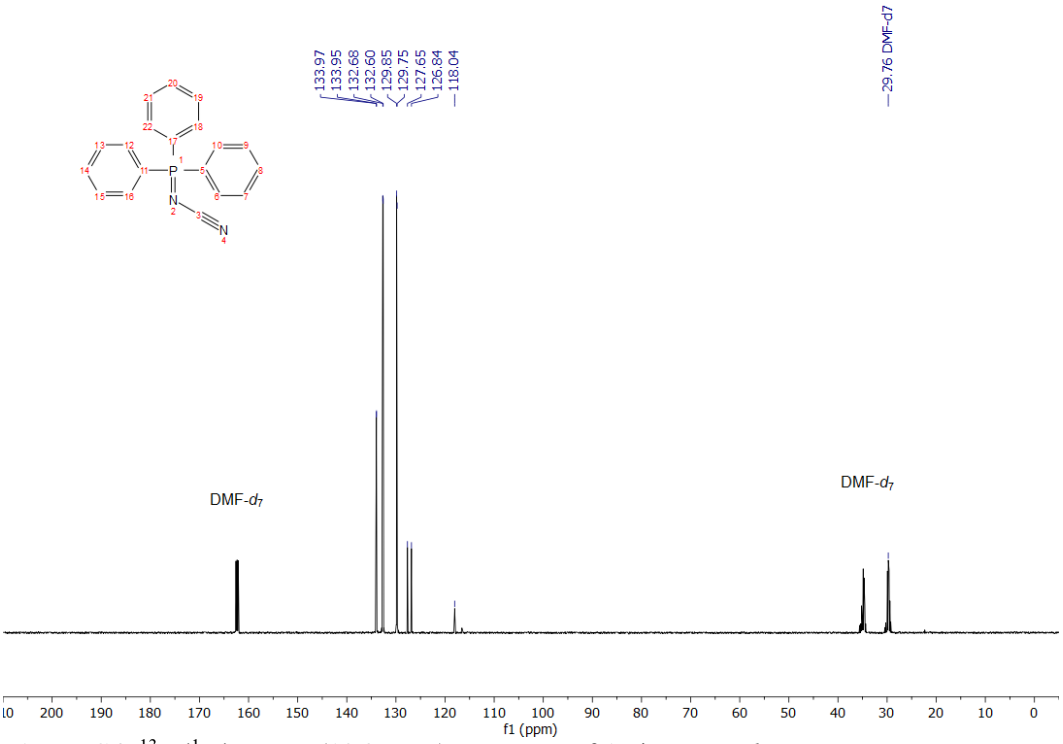


Figure S4. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **1a** in DMF-d_7.

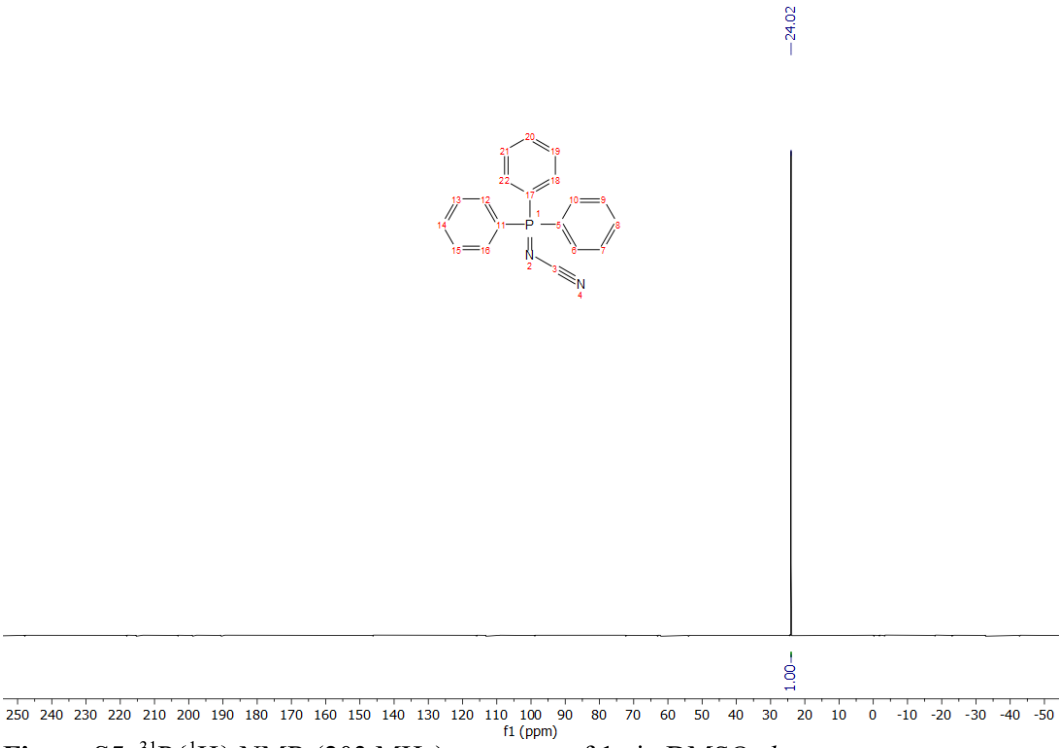
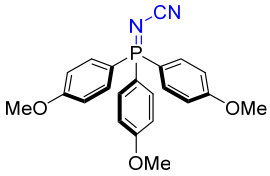


Figure S5. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **1a** in DMSO-d_6.



Synthesis of **7** was prepared following General Procedure **A** in 74% assay yield from tris(4-methoxyphenyl)phosphine (0.705 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3.0 equiv). Purification was achieved using method 4 to afford a white solid. ^{1}H NMR (500 MHz, CD2Cl2) δ 7.58 (dd, J = 12.2, 8.8 Hz, 6H), 7.04 (dd, J = 8.8, 2.3 Hz, 6H), 3.86 (s, 9H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ 163.90 (d, J = 2.9 Hz), 134.67 (d, J = 11.8 Hz), 119.22, 118.72 (d, J = 110.9 Hz), 115.04 (d, J = 13.8 Hz), 55.94. $^{31}P\{^{1}H\}$ NMR (203 MHz, CD_2Cl_2) δ 24.37. ESI^{+} HRMS *m/z* calcd. for $C_{22}H_{22}N_2O_3P$ ([M + H]$^{+}$) 393.1368, found 393.1362.

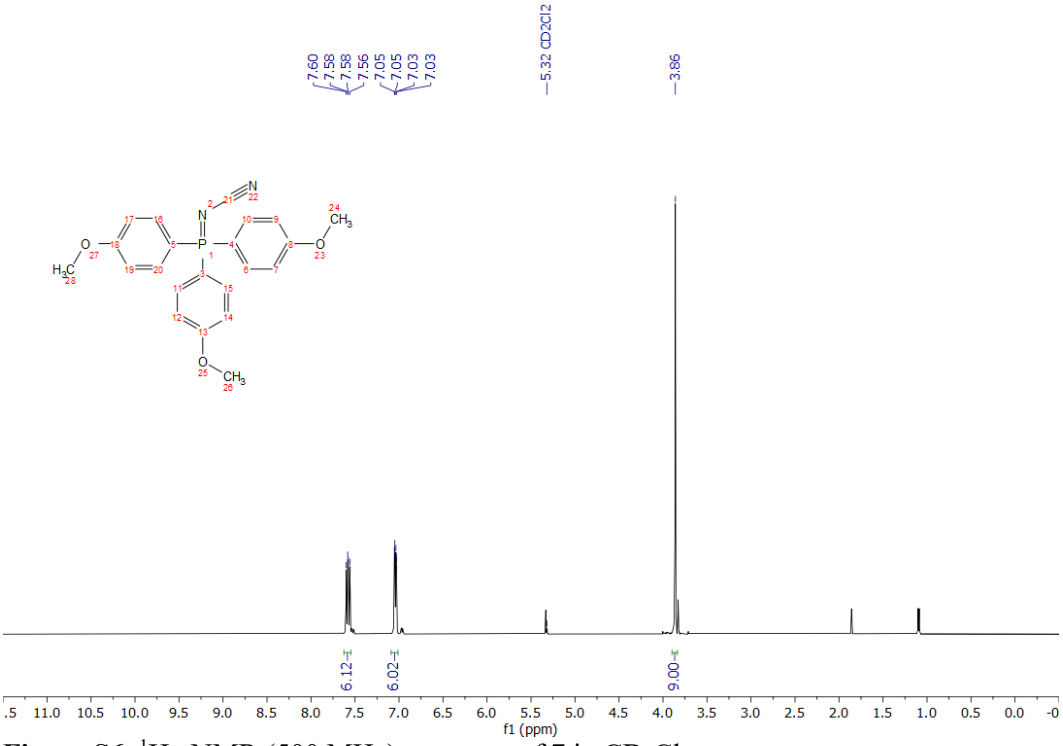


Figure S6. ^{1}H qNMR (500 MHz) spectrum of **7** in CD_2Cl_2.

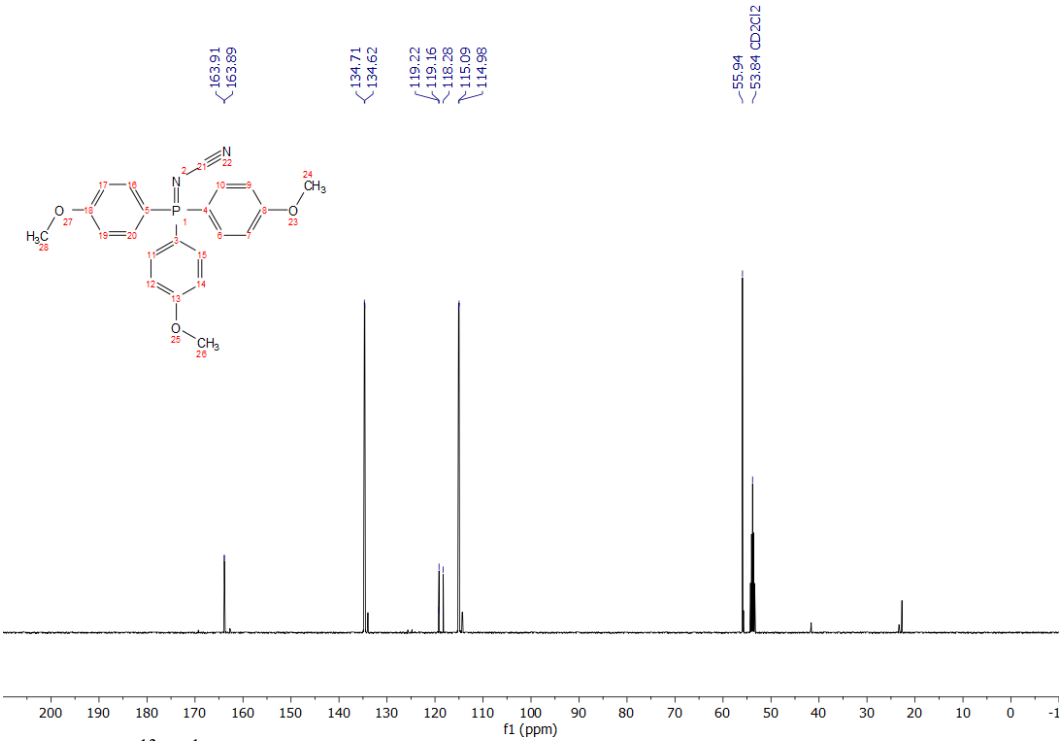


Figure S7. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **7** in CD_2Cl_2.

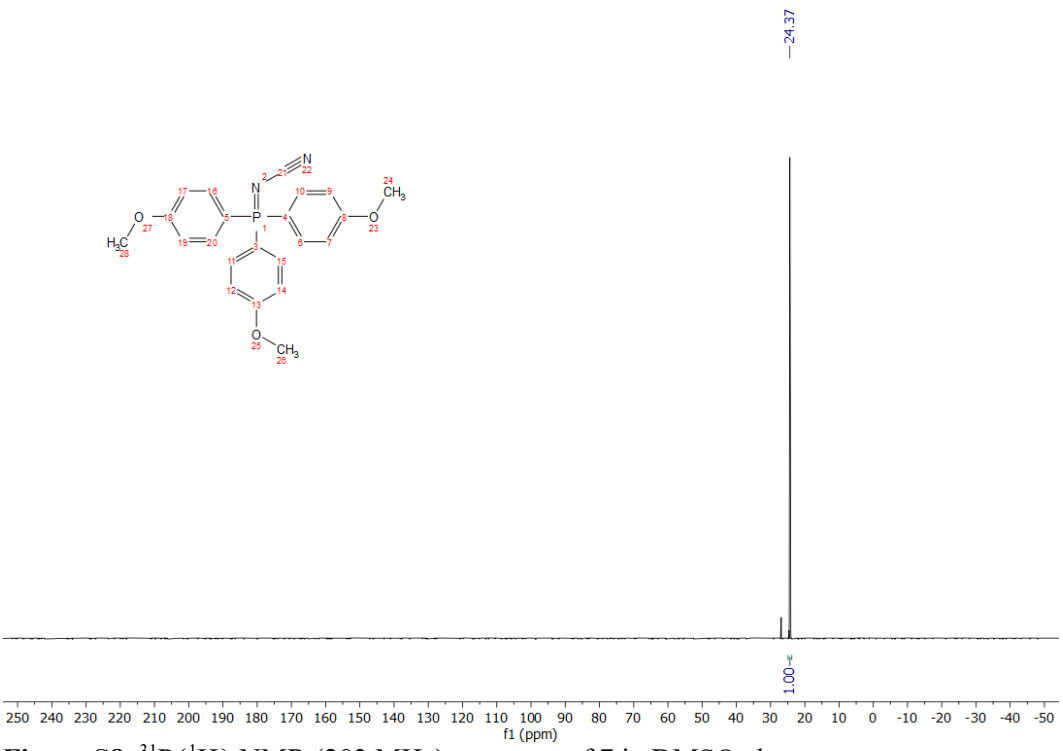
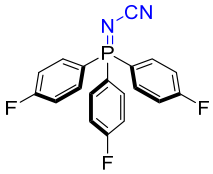


Figure S8. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **7** in DMSO-d_6.



Synthesis of **8** was prepared following General Procedure **A** in 92% assay yield from tris(4-fluorophenyl)phosphine (0.633 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3.0 equiv). Purification was achieved using method 4 to afford a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.79 (ddd, J = 13.3, 8.3, 5.7 Hz, 6H), 7.58 – 7.48 (m, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 165.34 (dd, J = 253.8, 3.4 Hz), 135.26 (dd, J = 12.3, 9.6 Hz), 122.25 (dd, J = 107.3, 3.2 Hz), 117.25, 117.08 (dd, J = 22.0, 14.1 Hz). $^{31}P\{^{1}H\}$ NMR (203 MHz, DMSO-d_6) δ 23.08 – 23.04 (m, 1P). $^{19}F\{^{1}H\}$ NMR (471 MHz, CD_2Cl_2) δ –104.24 (s, 1F). ESI^+ HRMS *m/z* calcd. for $C_{19}H_{13}F_3N_2P$ ($[M + H]^+$) 357.0768, found 357.0768.

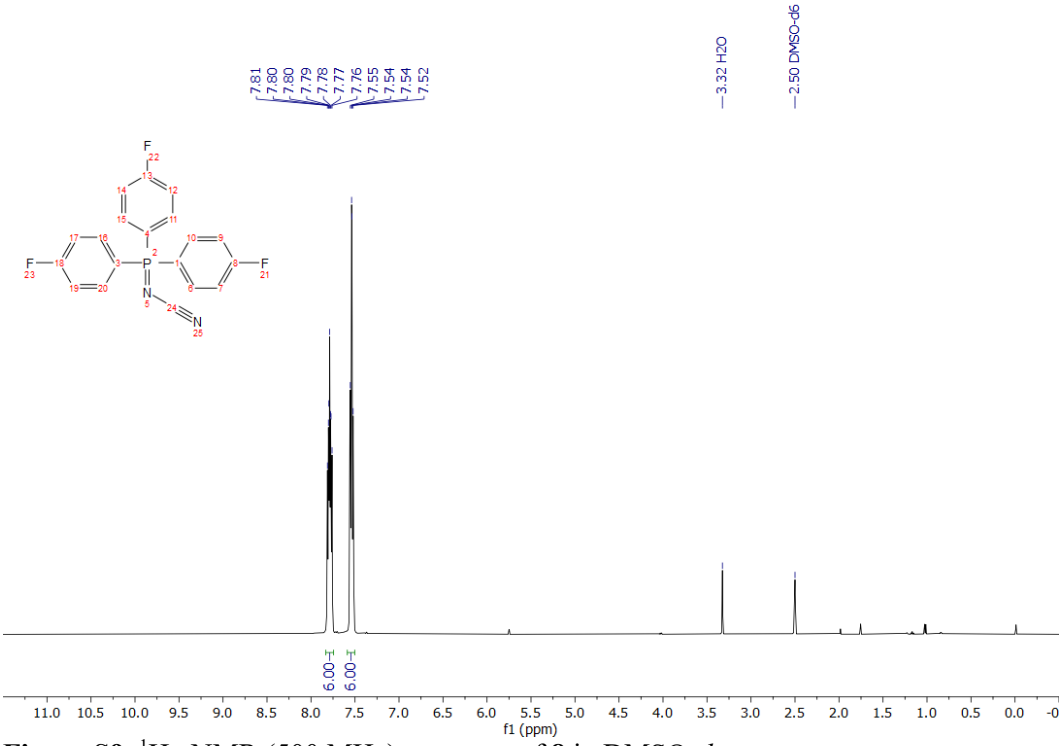


Figure S9. ^{1}H qNMR (500 MHz) spectrum of **8** in DMSO-d_6.

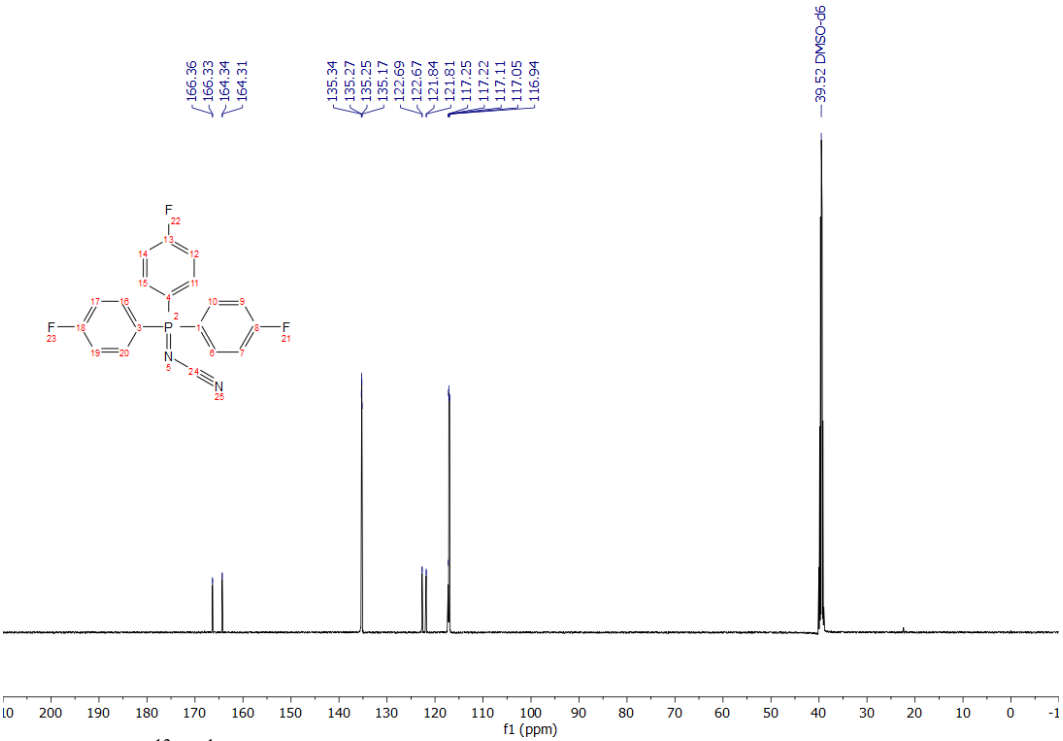


Figure S10. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **8** in DMSO-d_6.

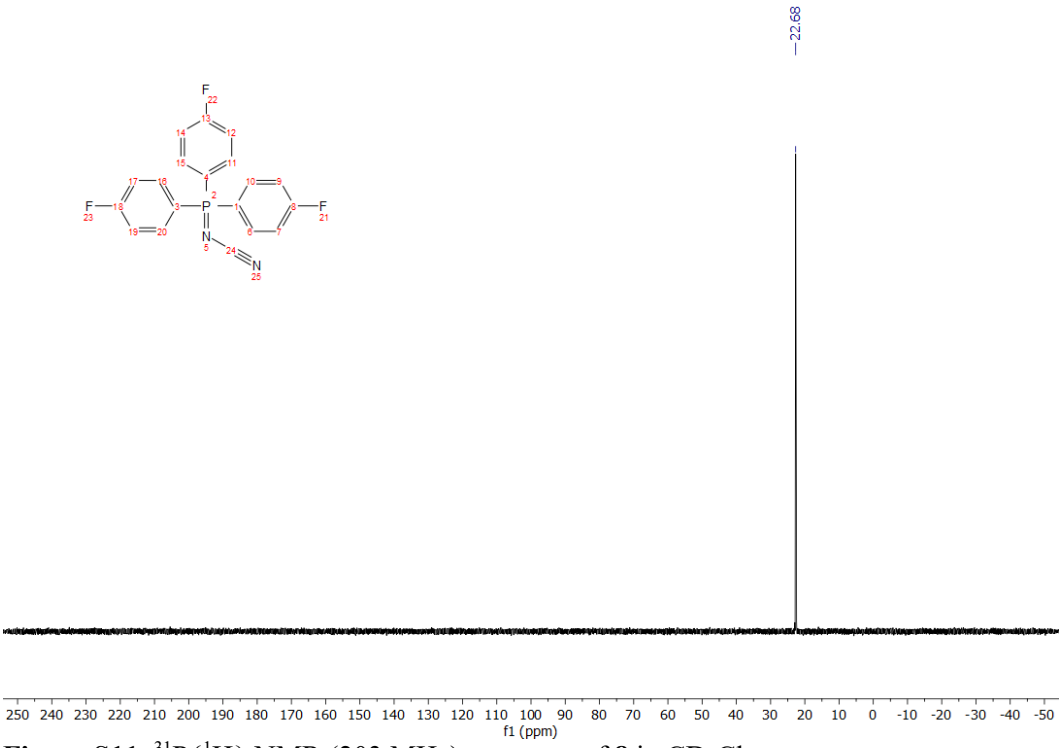


Figure S11. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **8** in CD_2Cl_2.

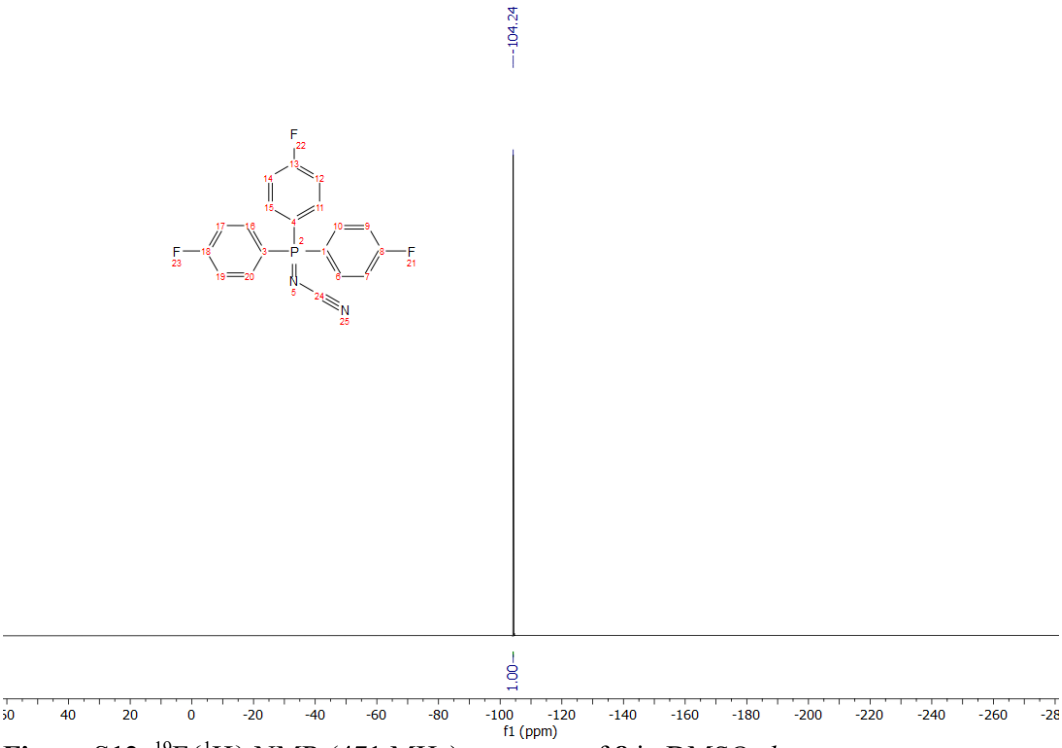
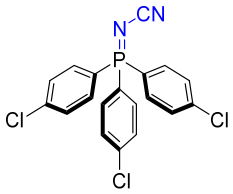


Figure S12. $^{19}F\{^{1}H\}$ NMR (471 MHz) spectrum of **8** in DMSO-d_6.



Synthesis of **9** was prepared following General Procedure **A** in 73% assay yield from tris(4-chlorophenyl)phosphine (0.731 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3.0 equiv). Purification was achieved using method 3 to afford a white solid. Preparative purification of **9** was performed using preparative SFC. Temperature: 35 °C. Flow rate: 40 mL/min. BPR: 100 bar. UV detection: Max Absorbance and 210 nm. Column: 2-Ethylpyrridine, 250 (L) × 21.2 (ID) mm. Mobile phase: 80%CO_2 and 20% MeOH. The collected peak fractions were dried *in vacuo*. ^{1}H NMR (500 MHz, CD_3OD) δ 7.77 – 7.64 (m, 12H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3OD) δ 142.06 (d, J = 3.6 Hz), 135.18 (d, J = 11.8 Hz), 131.10 (d, J = 13.8 Hz), 125.48 (d, J = 106.8 Hz), 119.76. $^{31}P\{^{1}H\}$ NMR (203 MHz, CD_3OD) δ 24.93 (s, 1P). ESI^{+} HRMS *m/z* calcd. for $C_{19}H_{13}Cl_3N_2P$ ($[M + H]^{+}$) 404.9882, found 404.9879.

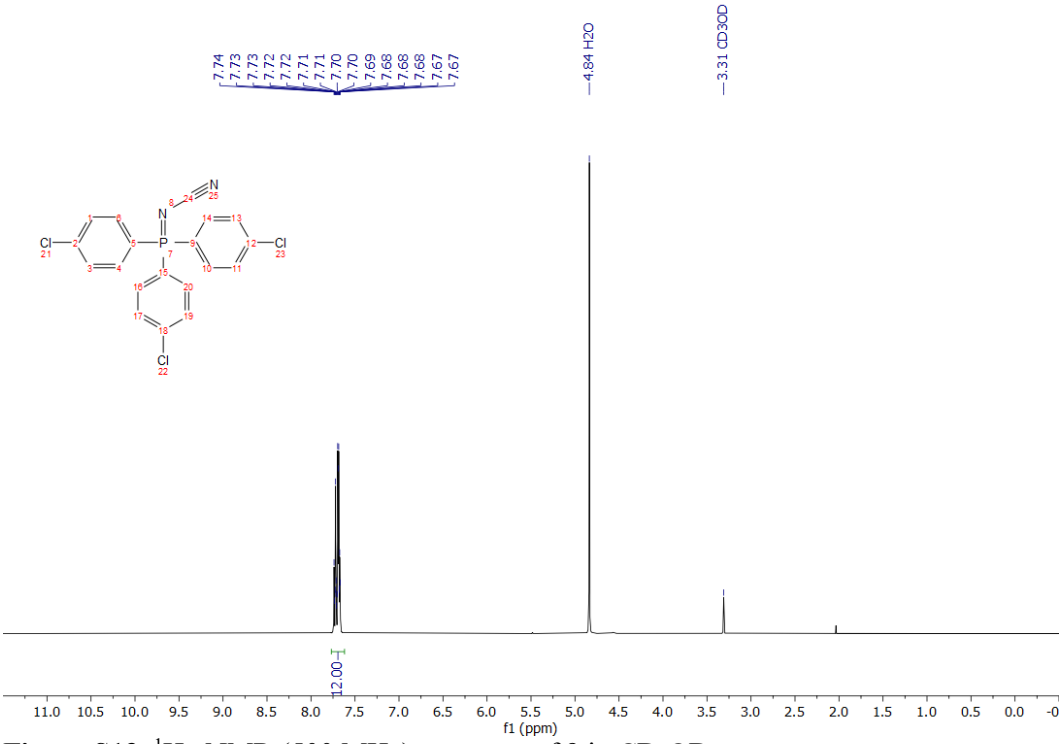


Figure S13. ^{1}H qNMR (500 MHz) spectrum of **9** in CD_3OD.

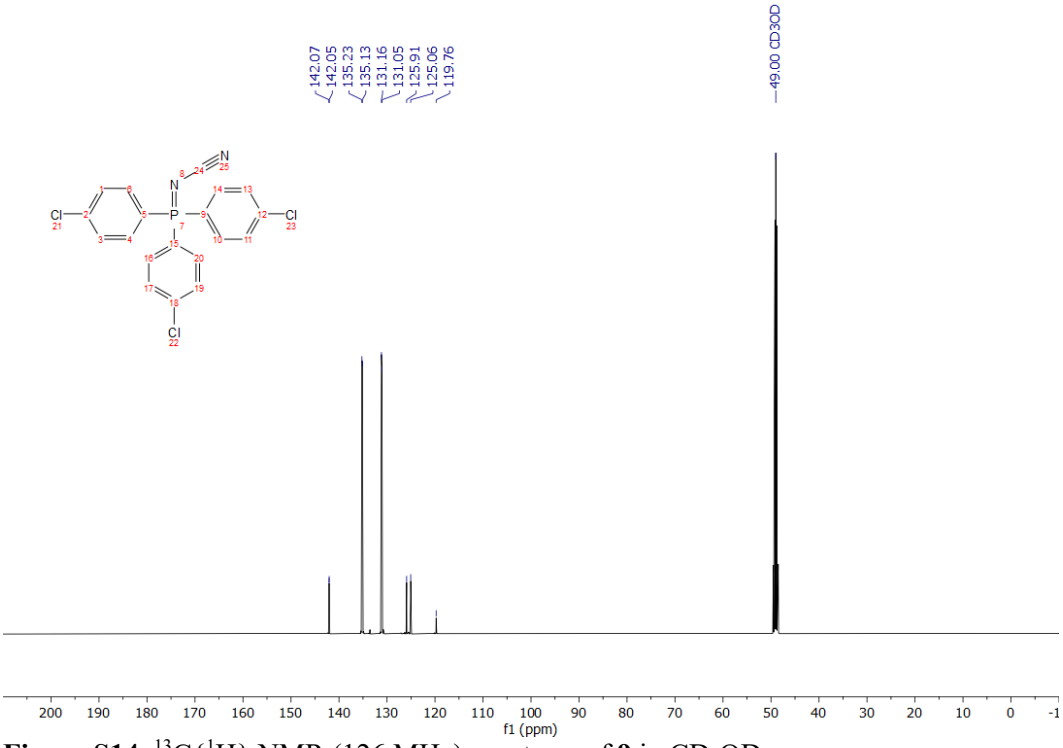


Figure S14. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **9** in CD_3OD.

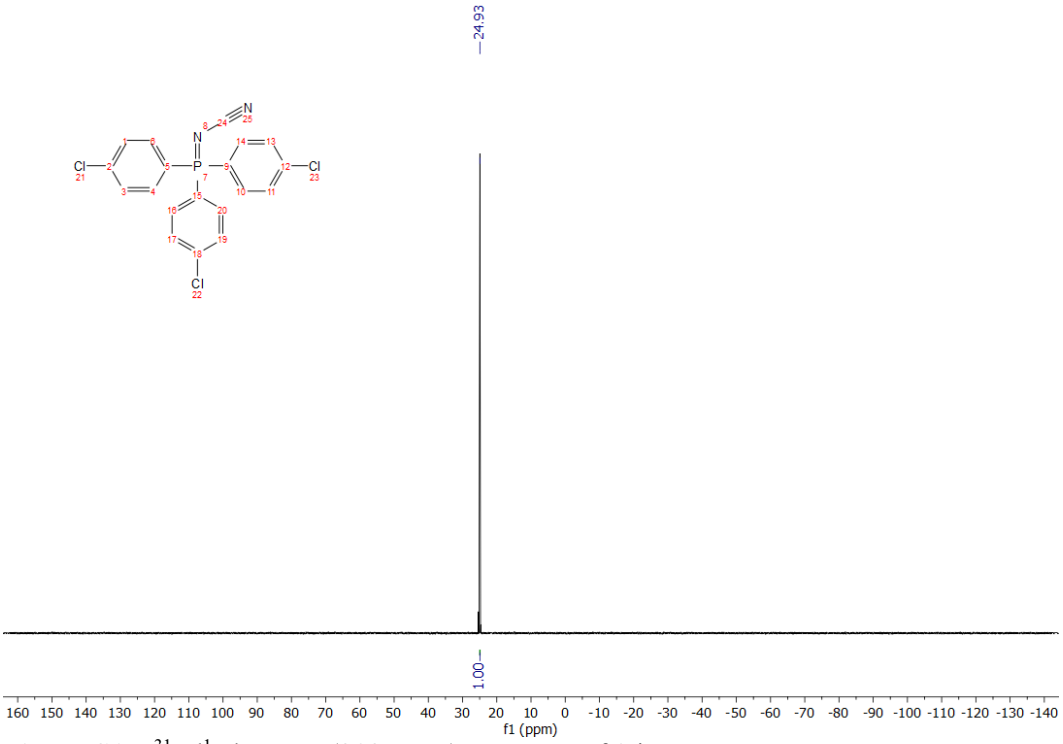
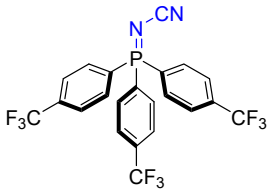


Figure S15. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **9** in CD_3OD.



Synthesis of **10** was prepared following General Procedure **A** in 83% assay yield from tris(4-trifluoromethylphenyl)phosphine (0.933 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3.0 equiv). Purification was achieved using method 1 to afford a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.92 – 7.84 (m, 12H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 135.95 (qd, J = 33.2, 3.1 Hz), 133.56 (d, J = 11.0 Hz), 130.26 (br dq, J = 102.9, 0.7 Hz), 126.91 (dq, J = 13.3, 3.7 Hz), 123.67 (qd, J = 273.1, 1.0 Hz), 116.89. ^{19}F{^{1}H} NMR (471 MHz, CD_2Cl_2) δ -63.86. ^{31}P{^{1}H} NMR (203 MHz, CD_2Cl_2) δ 21.56. ESI^{+} HRMS *m/z* calcd. for $C_{22}H_{13}F_9N_2P$ ([M + H]$^{+}$) 507.0672, found 507.0672.

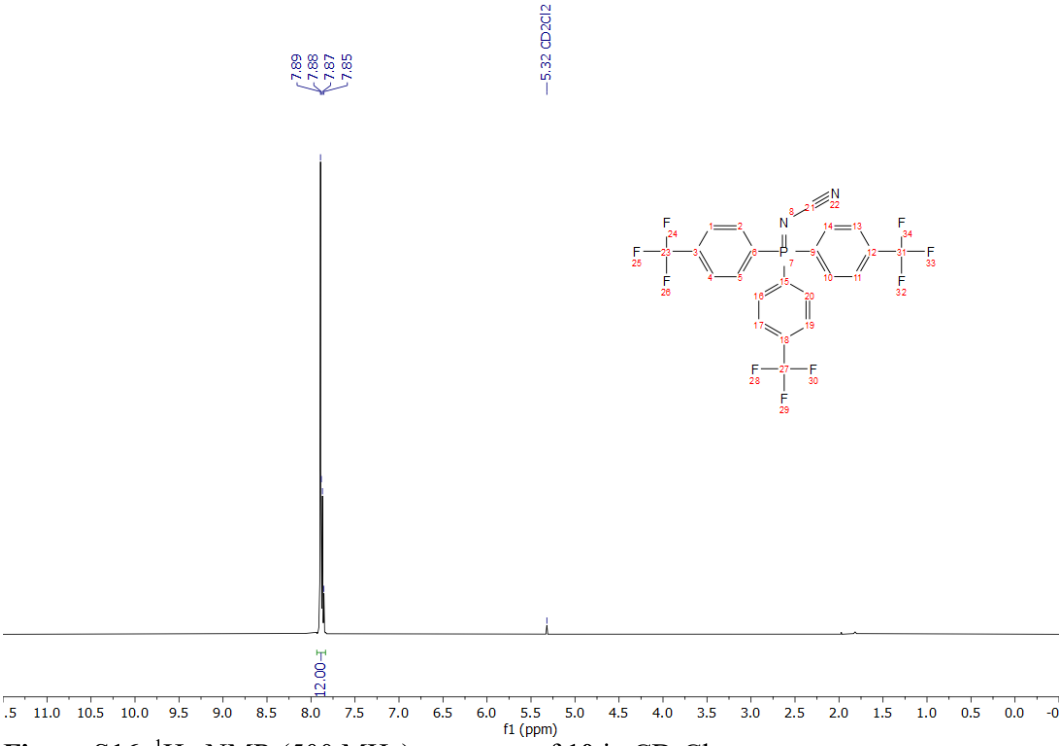


Figure S16. ^{1}H qNMR (500 MHz) spectrum of **10** in CD_2Cl_2.

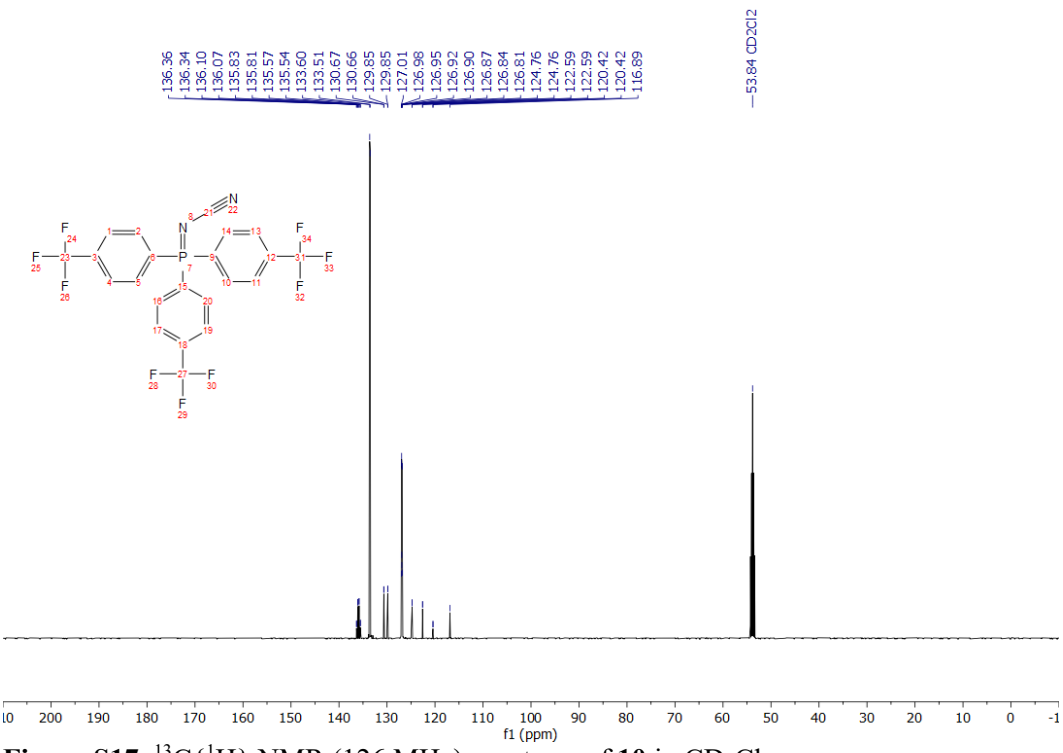


Figure S17. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **10** in CD_2Cl_2.

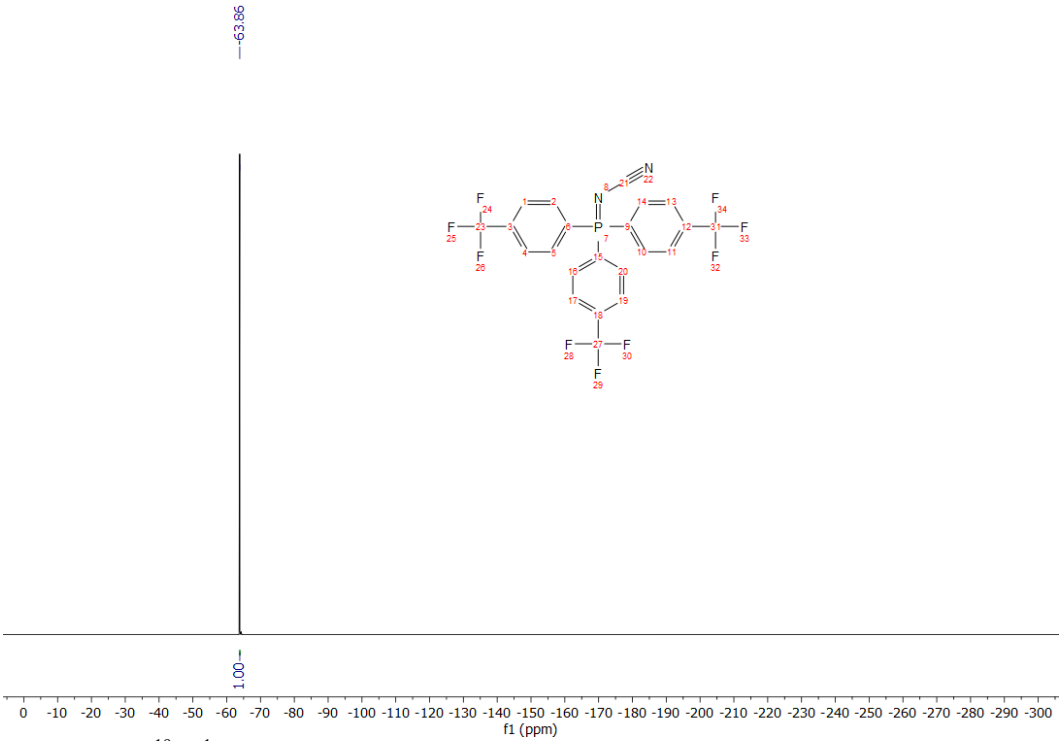


Figure S18. $^{19}F\{^{1}H\}$ NMR (471 MHz) spectrum of **10** in CD_2Cl_2.

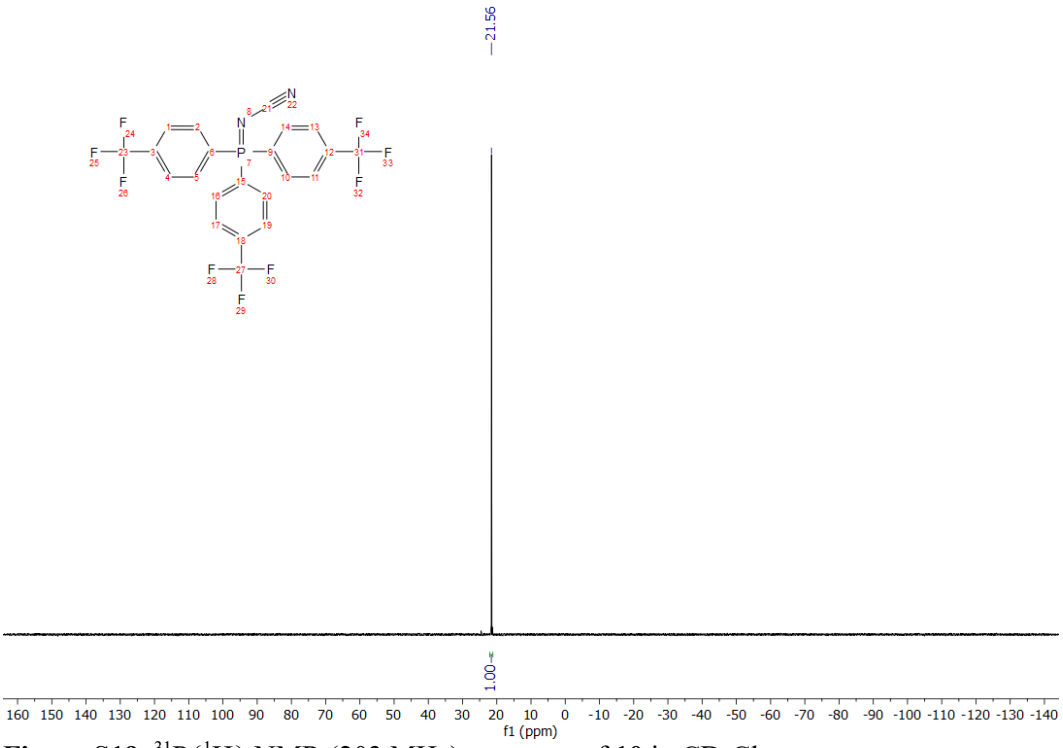
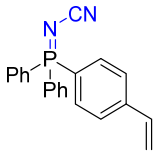


Figure S19. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **10** in CD_2Cl_2.



Synthesis of **11** was prepared following General Procedure **A** in 79% assay yield from 4-(diphenylphosphino)styrene (0.577 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3.0 equiv). Purification was achieved using method 2 to afford a light tan crystal solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.72 – 7.54 (m, 10H), 6.79 (dd, J = 17.6, 10.9 Hz, 1H), 5.93 (d, J = 17.6 Hz, 1H), 5.46 (d, J = 10.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ 142.96, 135.90, 133.79 (d, J = 2.9 Hz), 133.22 (d, J = 10.6 Hz), 132.86 (d, J = 10.4 Hz), 129.59 (d, J = 12.8 Hz), 127.30 (d, J = 103.6 Hz), 127.20 (d, J = 13.3 Hz), 126.01 (d, J = 105.2 Hz), 118.53, 117.99. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2) δ 24.30 (S, 1P). ESI^{+} HRMS *m/z* calcd. for $C_{21}H_{17}N_2P$ ($[M + H]^{+}$) 329.1207, found 329.1205.

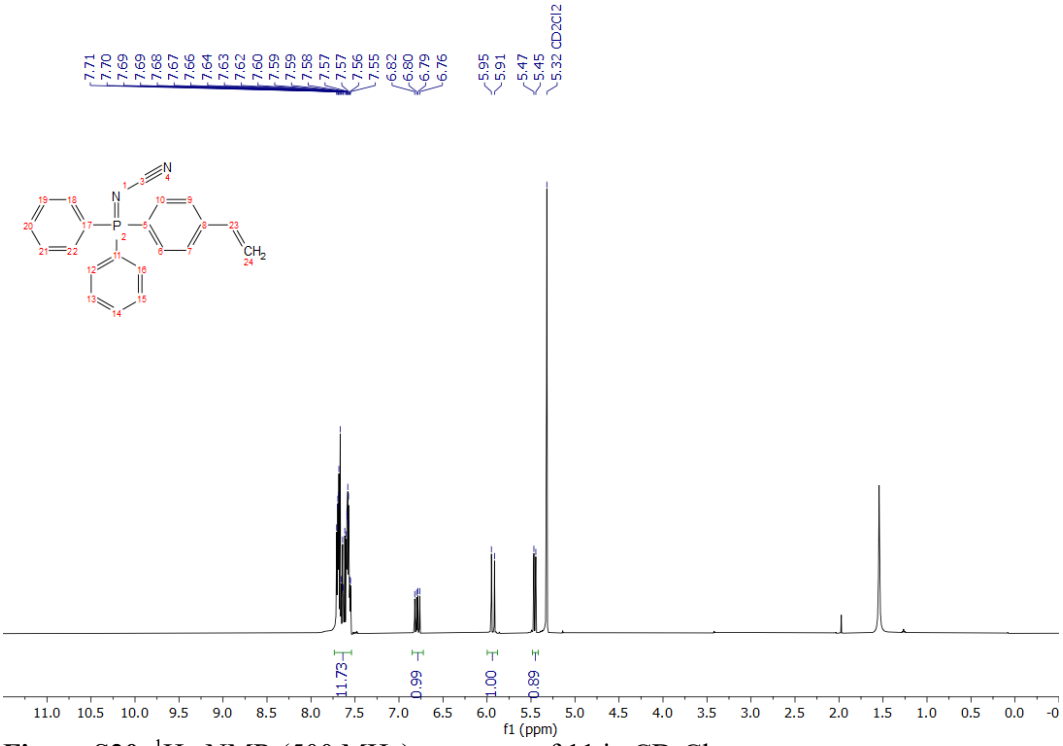


Figure S20. ^{1}H qNMR (500 MHz) spectrum of **11** in CD_2Cl_2.

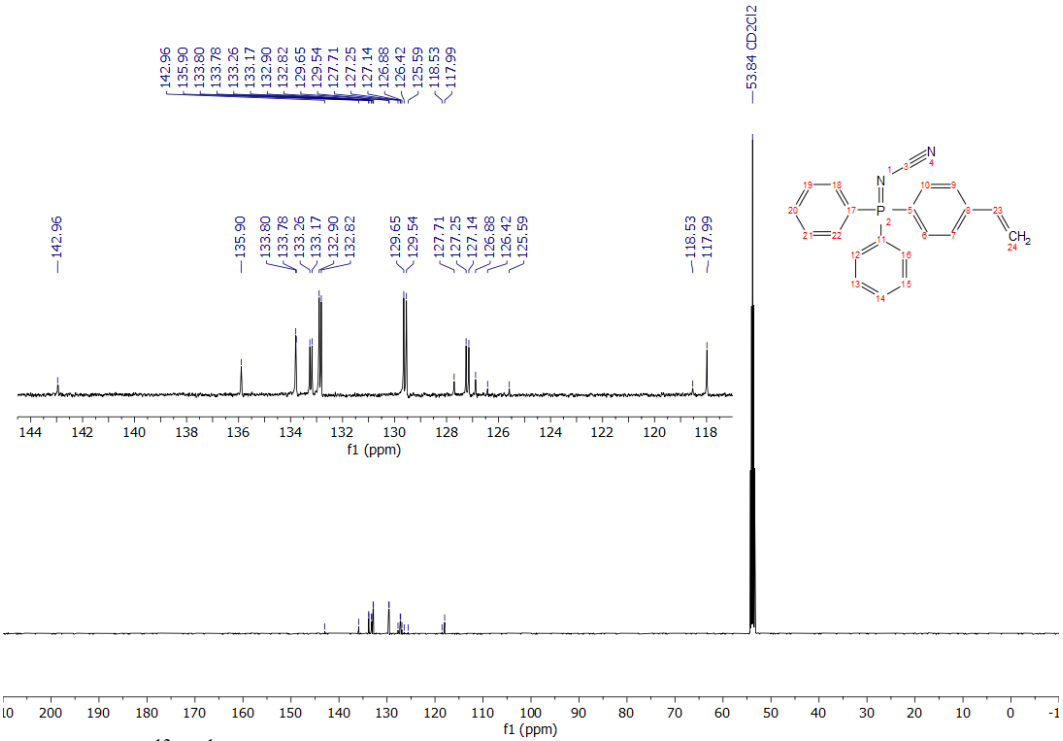


Figure S21. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **11** in CD_2Cl_2.

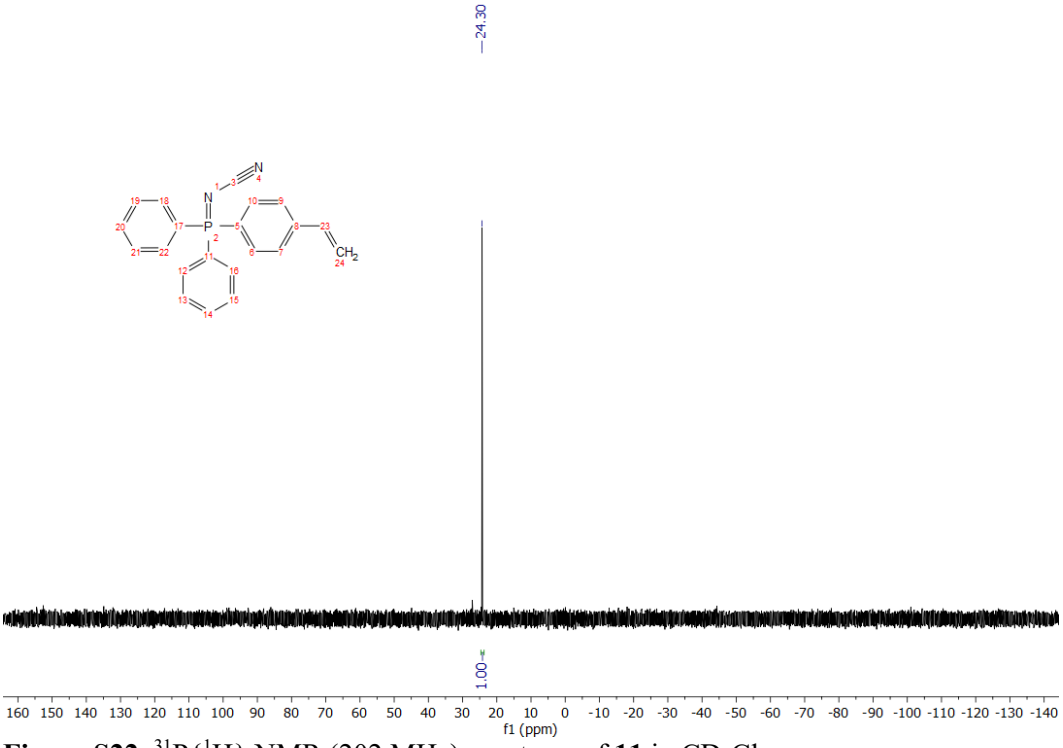
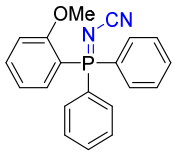


Figure S22. $^{31}P\{^{1}H\}$ NMR (202 MHz) spectrum of **11** in CD_2Cl_2.



Synthesis of **12** was prepared following General Procedure **A** in 86% assay yield from diphenyl(2-pyridinyl)phosphine (0.527 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 1 to afford a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.76 (t, J = 7.8 Hz, 1H), 7.71 (t, J = 7.0 Hz, 2H), 7.68 – 7.57 (m, 9H), 7.25 (dt, J = 15.0, 6.9 Hz, 2H), 3.59 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 161.07 (d, J = 3.8 Hz), 136.33 (d, J = 1.8 Hz), 133.83 (d, J = 7.0 Hz), 133.07 (d, J = 2.9 Hz), 131.63 (d, J = 10.7 Hz), 129.07 (d, J = 12.9 Hz), 126.82 (d, J = 105.3 Hz), 121.46 (d, J = 11.9 Hz), 117.76, 113.33 (d, J = 105.0 Hz), 112.86 (d, J = 6.8 Hz), 55.81. $^{31}P\{^{1}H\}$ NMR (203 MHz, DMSO-d_6) δ 23.53 (s, 1P). ESI^{+} HRMS *m/z* calcd. for $C_{27}H_{25}N_2OP_2$ ($[M + H]^{+}$) 333.1156, found 333.1155.

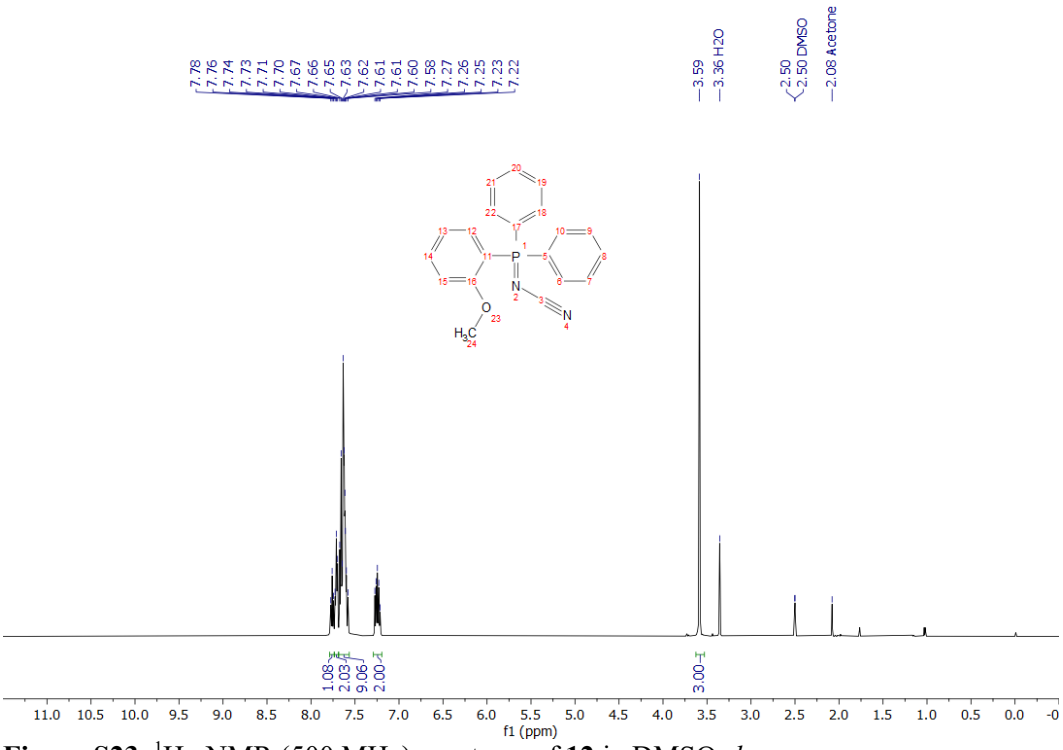


Figure S23. ^{1}H qNMR (500 MHz) spectrum of **12** in DMSO-d_6.

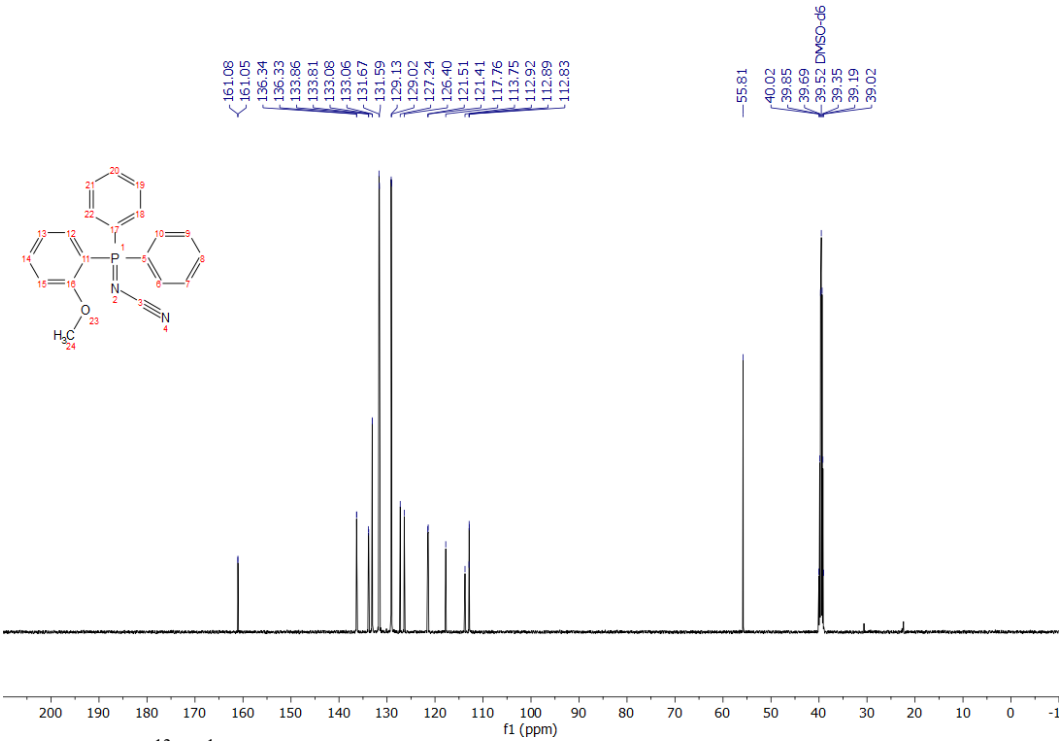


Figure S24. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **12** in DMSO-d_6.

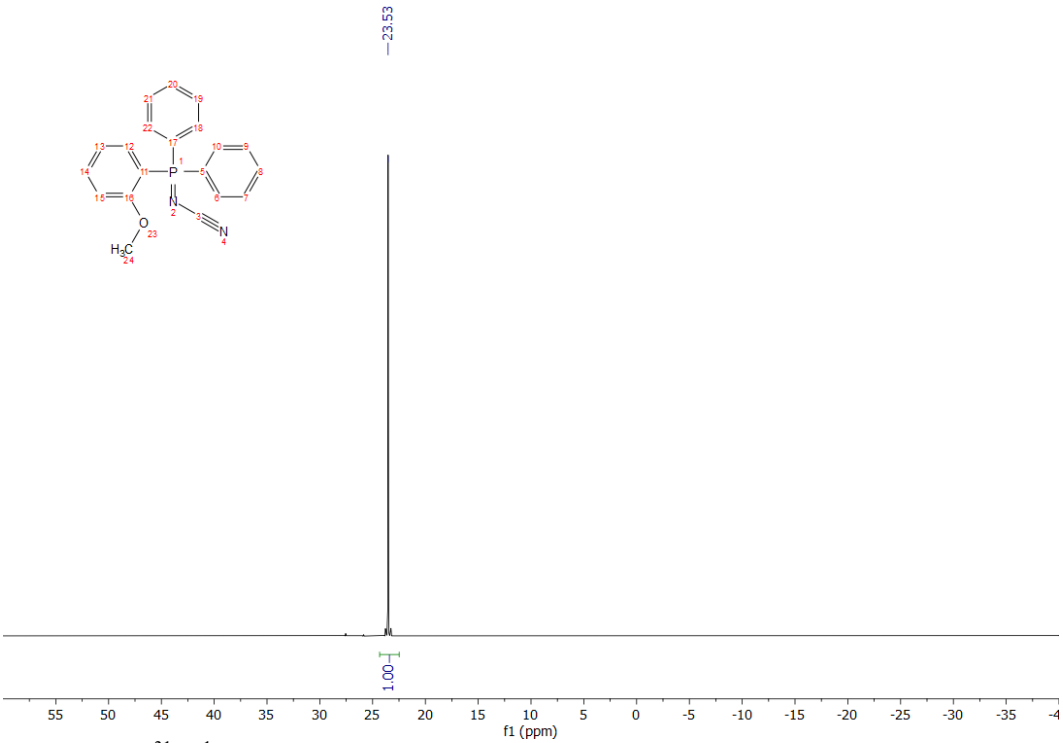
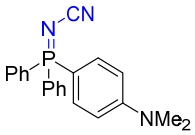


Figure S25. $^{31}P\{^{1}H\}$ NMR (203 MHz, DMSO-d_6) spectrum of **12** in DMSO-d_6.



Synthesis of **13** was prepared following General Procedure **A** in 39% assay yield from 4-(dimethylamino)phenyldiphenylphosphine (0.611 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using SFC (ethanol as modifier, see details below) to afford a white solid (the product was characterized by NMR spectroscopy as the hemi-solvate with ethanol). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.69 (dd, J = 12.8, 8.0 Hz, 4H), 7.64 (t, J = 7.5 Hz, 2H), 7.54 (td, J = 7.7, 3.0 Hz, 4H), 7.44 (dd, J = 12.0, 8.8 Hz, 2H), 6.77 (dd, J = 8.9, 2.4 Hz, 2H), 3.04 (s, 5H).$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ 153.80 (d, J = 2.4 Hz), 134.23 (d, J = 11.8 Hz), 133.27 (d, J = 2.9 Hz), 132.73 (d, J = 10.3 Hz), 129.32 (d, J = 12.7 Hz), 128.56 (d, J = 104.3 Hz), 119.29, 111.96 (d, J = 13.6 Hz), 109.45 (d, J = 114.2 Hz), 40.09. $^{31}P\{^{1}H\}$ NMR (203 MHz, CD_2Cl_2) δ 25.14 (s, 1P). ESI^+ HRMS *m/z* calcd. for $C_{21}H_{21}N_3P$ ($[M + H]^+$) 346.1473, found 346.1470. Preparative purification of **13** was performed using preparative SFC. Temperature: 35 °C. Flow rate: 85 mL/min. BPR: 100 bar. UV detection: 220 nm. Column: ColumnTek Enantiocel® C2-5, 250 (L) × 30 (ID) mm. Mobile phase: 60% CO_2 and 40% EtOH. The collected peak fractions were dried *in vacuo* at approximately 30°C without a co-solvent.

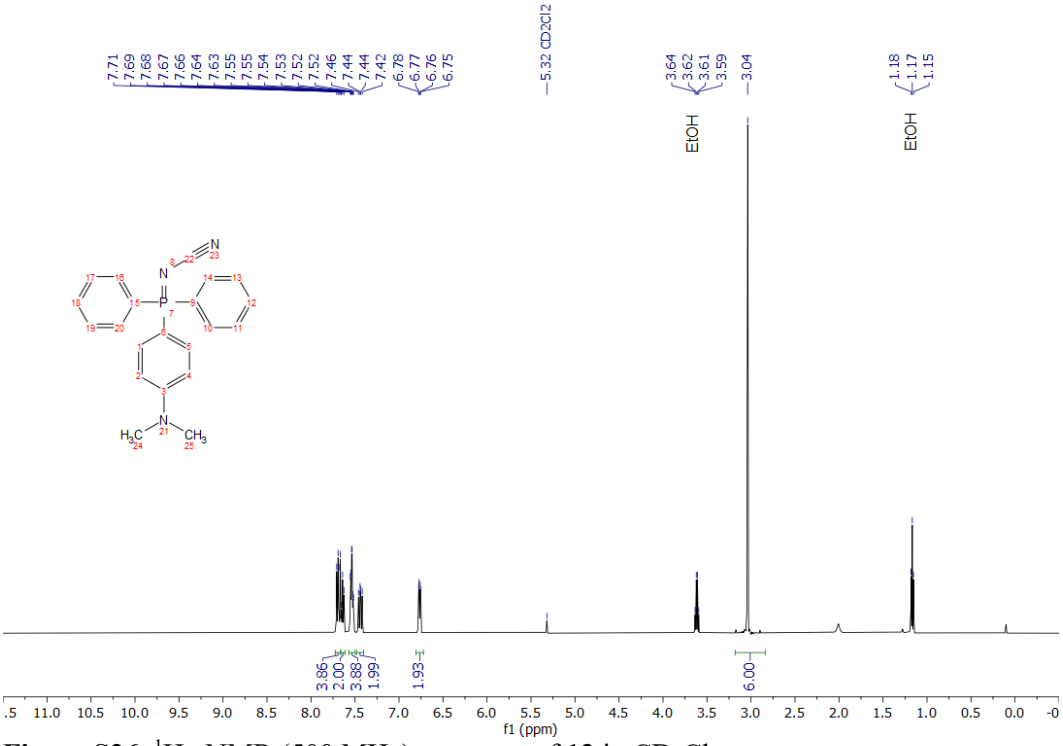


Figure S26. ^{1}H qNMR (500 MHz) spectrum of **13** in CD_2Cl_2.

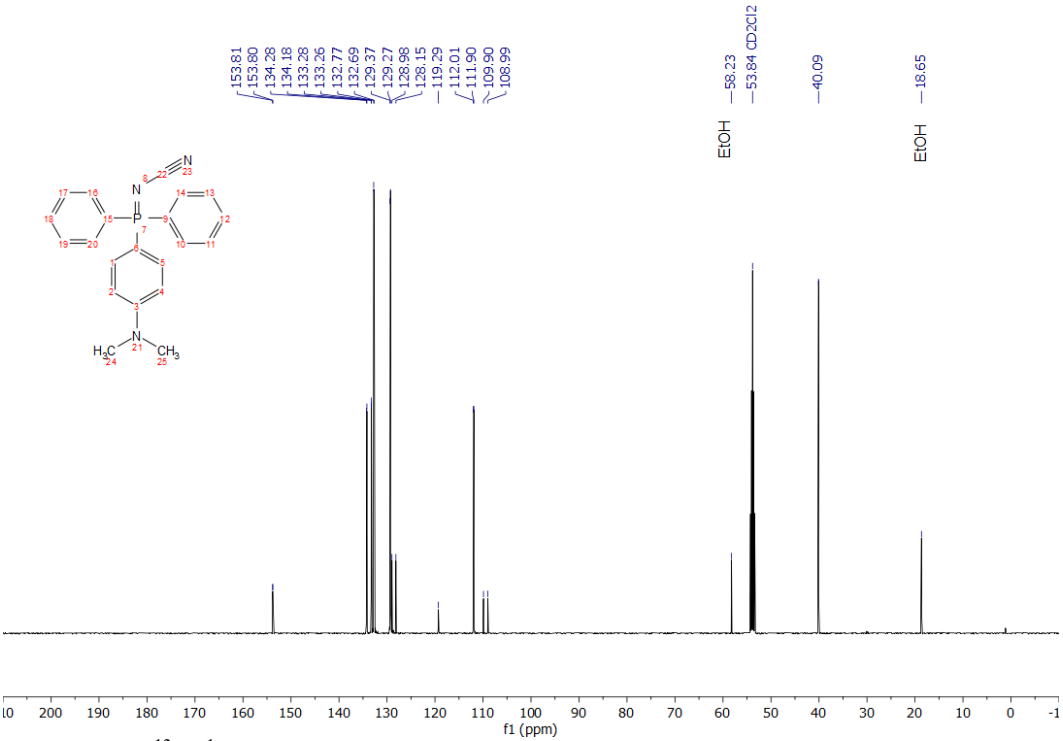


Figure S27. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **13** in CD_2Cl_2.

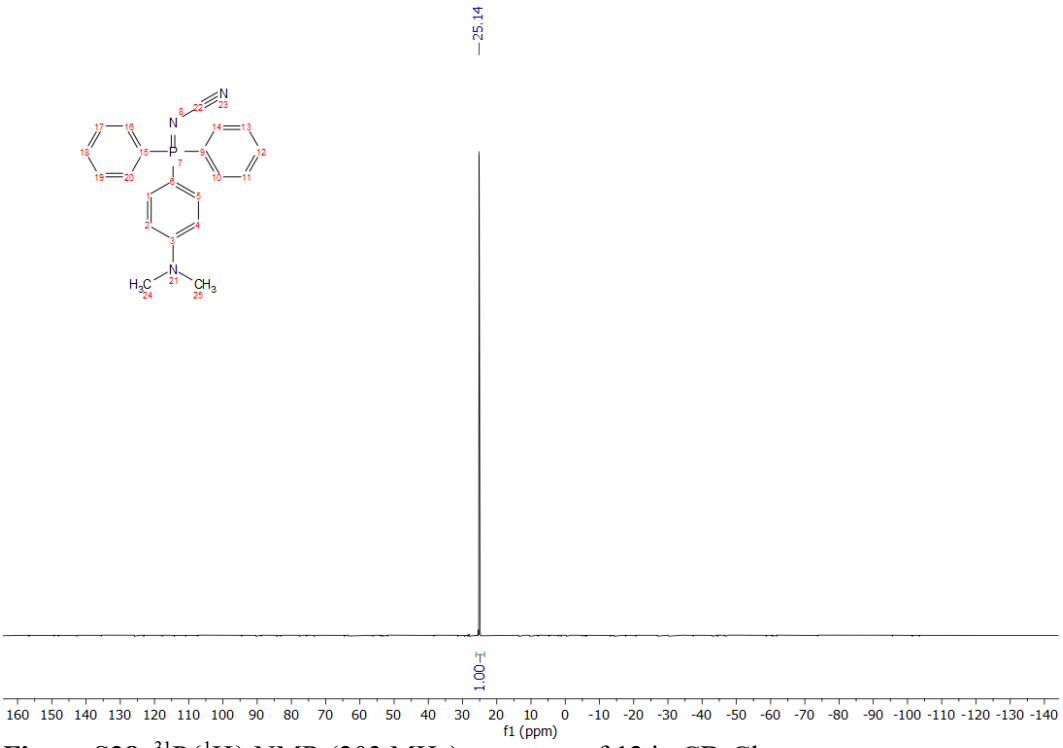


Figure S28. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **13** in CD_2Cl_2.

Synthesis of **14** was prepared following General Procedure **A** in 56% assay yield from cyclohexyldiphenylphosphine (0.537 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 1 to afford a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.89 (dd, J = 11.7, 7.9 Hz, 4H), 7.71 – 7.60 (m, 6H), 3.16 – 3.05 (m, 1H), 1.77 – 1.70 (m, 2H), 1.69 – 1.58 (m, 3H), 1.52 – 1.39 (m, 2H), 1.32 (q, J = 12.8 Hz, 2H), 1.13 (q, J = 12.9 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 132.99 (d, J = 2.8 Hz), 131.20 (d, J = 9.5 Hz), 129.33 (d, J = 11.9 Hz), 125.98 (d, J = 94.4 Hz), 118.29 (s), 34.56 (d, J = 65.5 Hz), 25.24 (d, J = 11.5 Hz, note: right hand side signal of this doublet appears as a shoulder on the signal as 25.17 ppm), 25.17 (s), 24.49 (d, J = 3.2 Hz). $^{31}P\{^{1}H\}$ NMR (203 MHz, DMSO-d_6) δ 30.14 (s, 1P). ESI$^+$ HRMS *m/z* calcd. for $C_{19}H_{22}N_2P$ ($[M + H]^+$) 309.1520, found 309.1516.

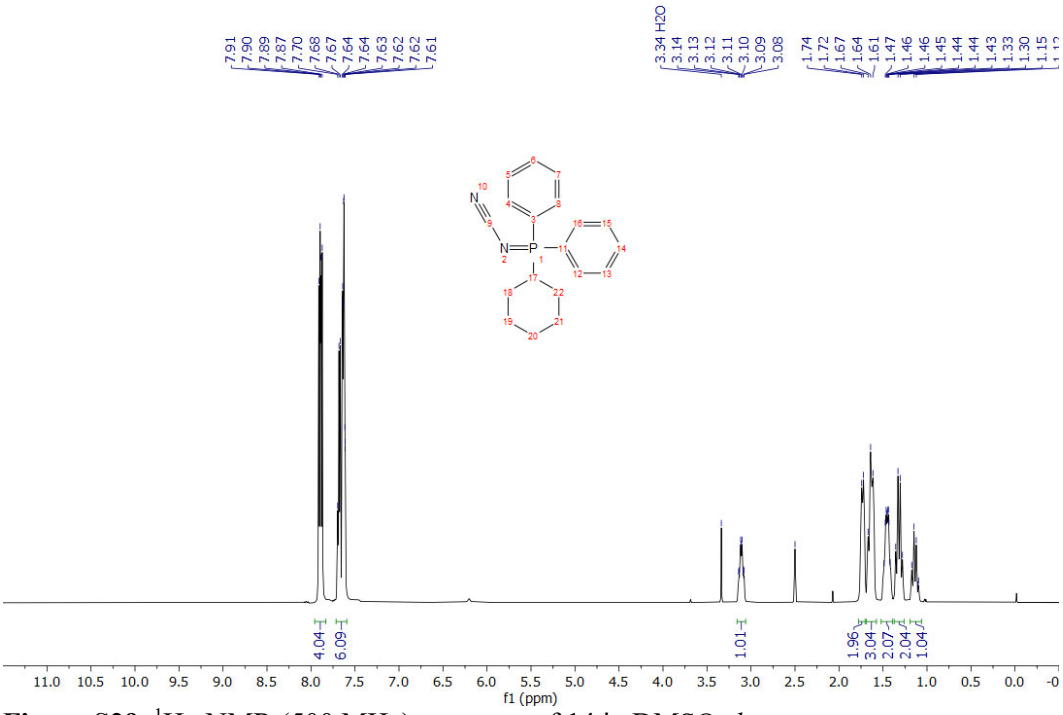


Figure S29. ^{1}H qNMR (500 MHz) spectrum of **14** in DMSO-d_6.

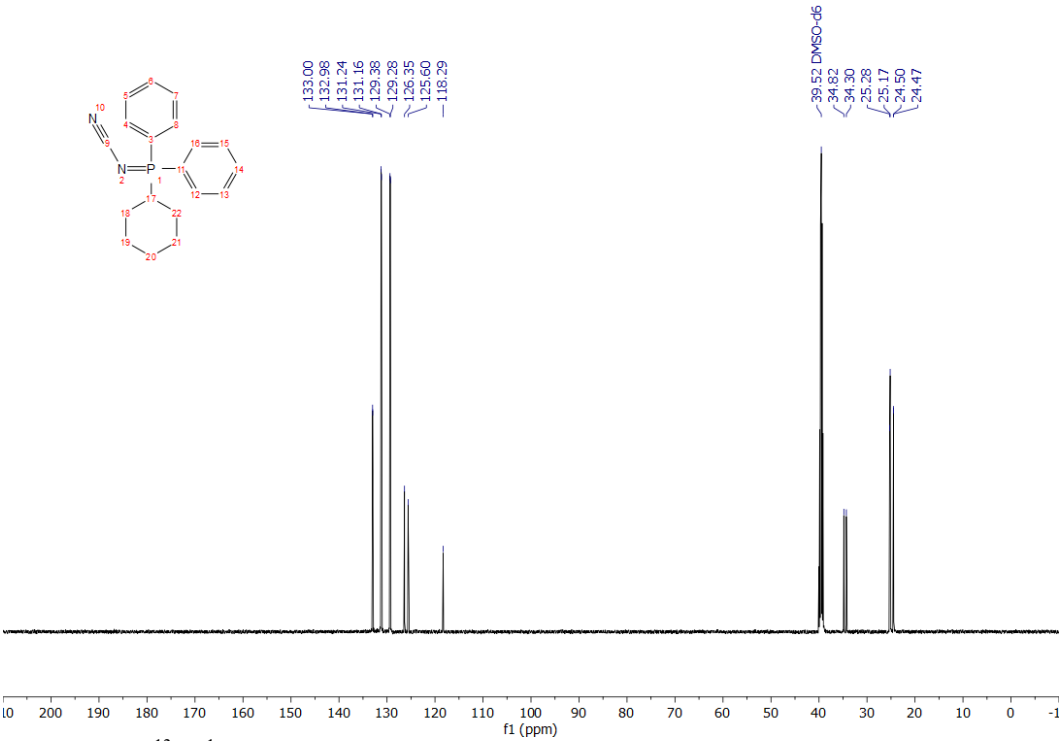


Figure S30. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **14** in DMSO-d_6.

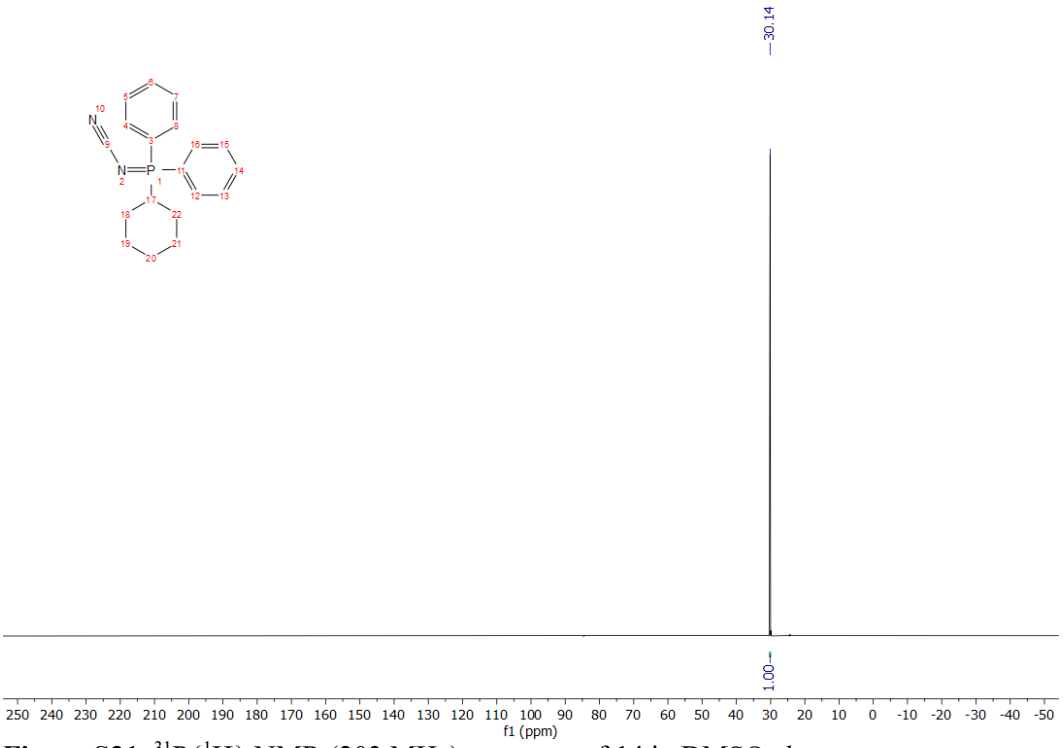


Figure S31. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **14** in DMSO-d_6.

Synthesis of **15** was prepared following General Procedure **A** in 82% assay yield from dicyclohexylphenylphosphine (0.549 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 1 to afford a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.74 – 7.67 (m, 2H), 7.64 (td, J = 7.3, 1.4 Hz, 1H), 7.60 – 7.53 (m, 2H), 2.39 – 2.27 (m, 2H), 2.13 – 2.02 (m, 2H), 1.84 (d, J = 9.0 Hz, 2H), 1.81 – 1.73 (m, 2H), 1.73 – 1.60 (m, 4H), 1.43 – 1.22 (m, 8H), 1.14 (qt, J = 12.7, 3.4 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ 133.10 (d, J = 2.8 Hz), 132.29 (d, J = 8.3 Hz), 129.34 (d, J = 11.4 Hz), 123.60 (d, J = 89.6 Hz), 119.45, 34.43 (d, J = 60.8 Hz), 26.40 (dd, J = 13.0, 12.1 Hz), 25.87 (d, J = 1.5 Hz), 25.48 (d, J = 2.7 Hz), 24.97 (d, J = 3.8 Hz). $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2) δ 39.50 (s, 1P). ESI$^+$ HRMS *m/z* calcd. for $C_{19}H_{28}N_2P$ ($[M + H]^+$) 315.1990, found 315.1985.

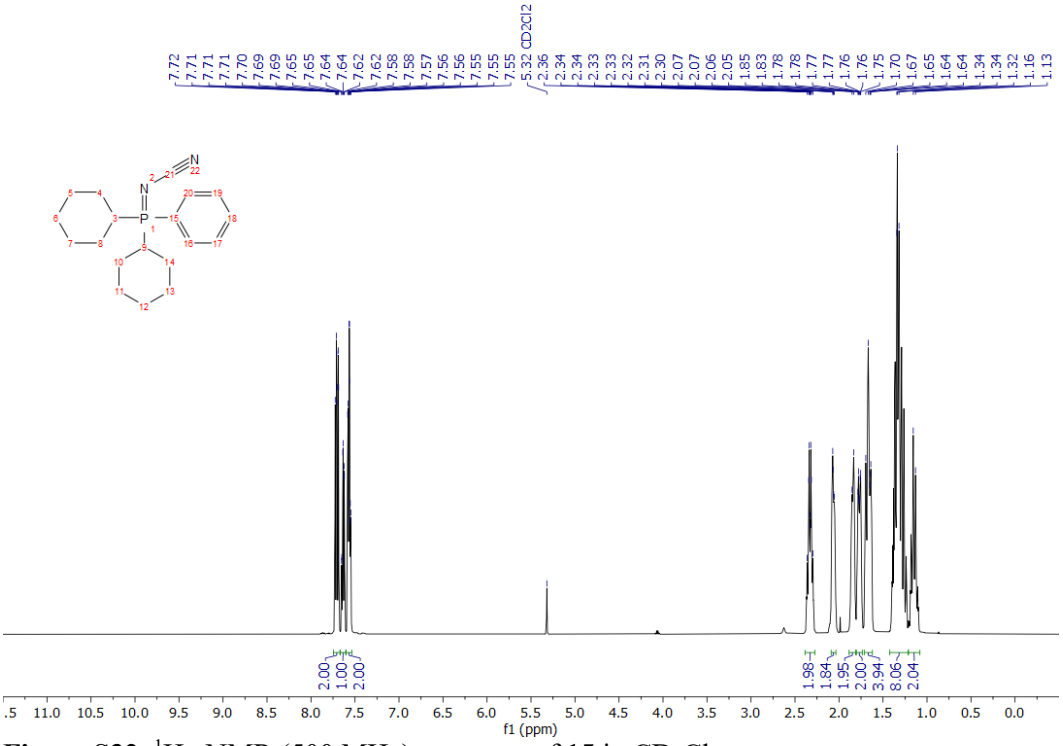


Figure S32. ^{1}H qNMR (500 MHz) spectrum of **15** in CD_2Cl_2.

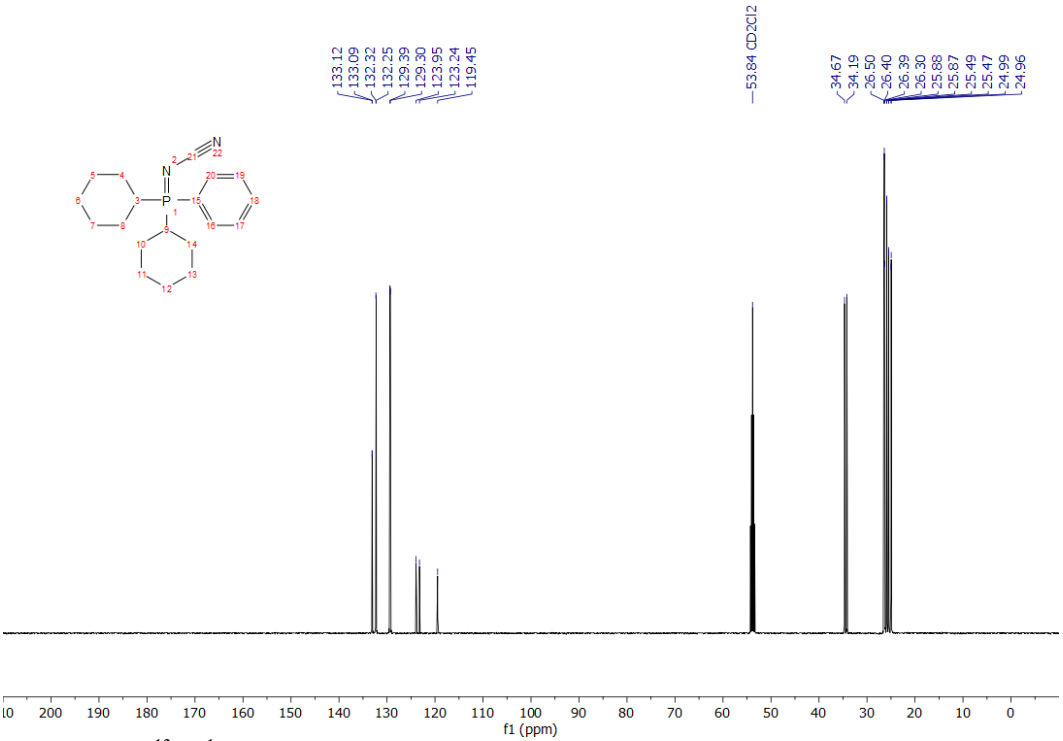


Figure S33. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **15** in CD_2Cl_2.

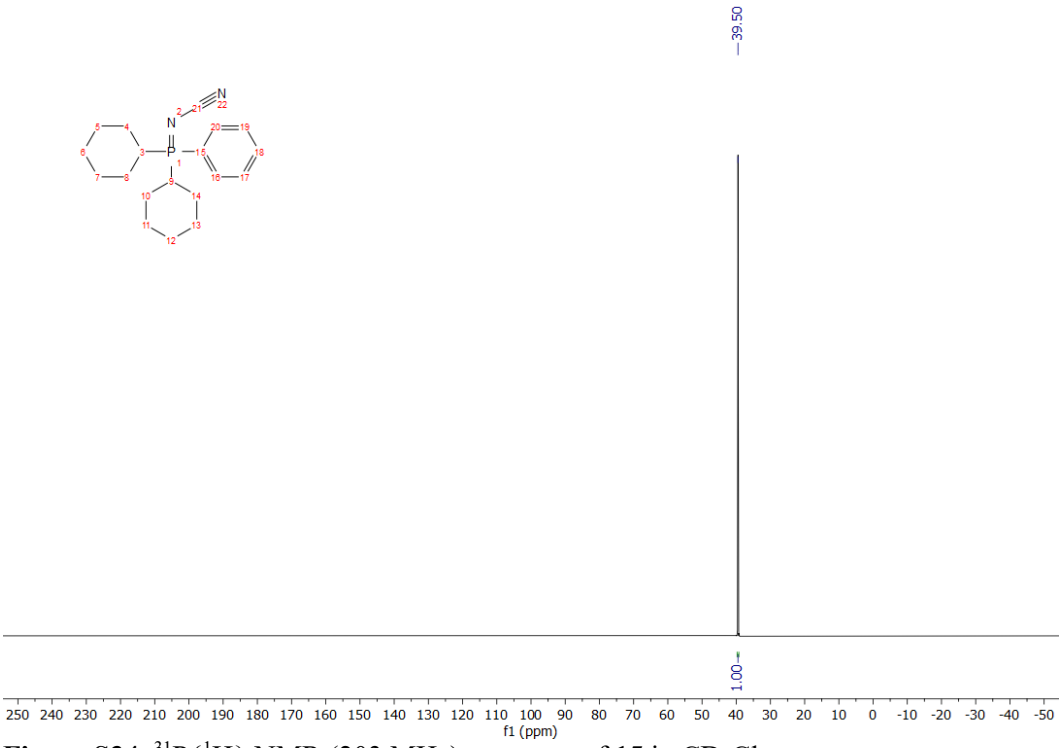
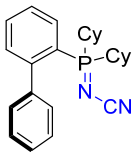


Figure S34. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **15** in CD_2Cl_2.



Synthesis of **16** was prepared following General Procedure **A** in 75% assay yield from 2-(dicyclohexylphosphino)biphenyl (0.701 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 4 to afford a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.13 (dddd, J = 13.2, 7.6, 6.0, 3.8 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.53 – 7.44 (m, 3H), 7.31 (ddt, J = 6.5, 4.6, 2.1 Hz, 1H), 7.25 – 7.19 (m, 2H), 1.92 – 1.82 (m, 2H), 1.82 – 1.49 (m, 10H), 1.41 (qd, J = 7.9, 2.7 Hz, 4H), 1.20 (qt, J = 12.8, 3.4 Hz, 2H), 1.08 (dtdd, J = 16.4, 12.8, 8.6, 3.5 Hz, 4H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ 144.62 (d, J = 10.5 Hz), 141.36 (d, J = 2.4 Hz), 134.68 (d, J = 6.7 Hz), 132.35, 132.30 (d, J = 7.3 Hz), 129.14, 128.98, 128.75, 128.40 (d, J = 10.4 Hz), 124.73 (d, J = 80.6 Hz), 119.70, 38.45 (d, J = 60.4 Hz), 27.06 (d, J = 4.5 Hz), 26.98 (d, J = 4.0 Hz), 26.70 (d, J = 5.2 Hz), 26.59 (d, J = 4.6 Hz), 25.74 (d, J = 1.5 Hz). $^{31}P\{^{1}H\}$ NMR (203 MHz, CD_2Cl_2) δ 43.06 (s, 1P). ESI^{+} HRMS *m/z* calcd. for $C_{25}H_{32}N_2P$ ($[M + H]^{+}$) 391.2303, found 391.2301.

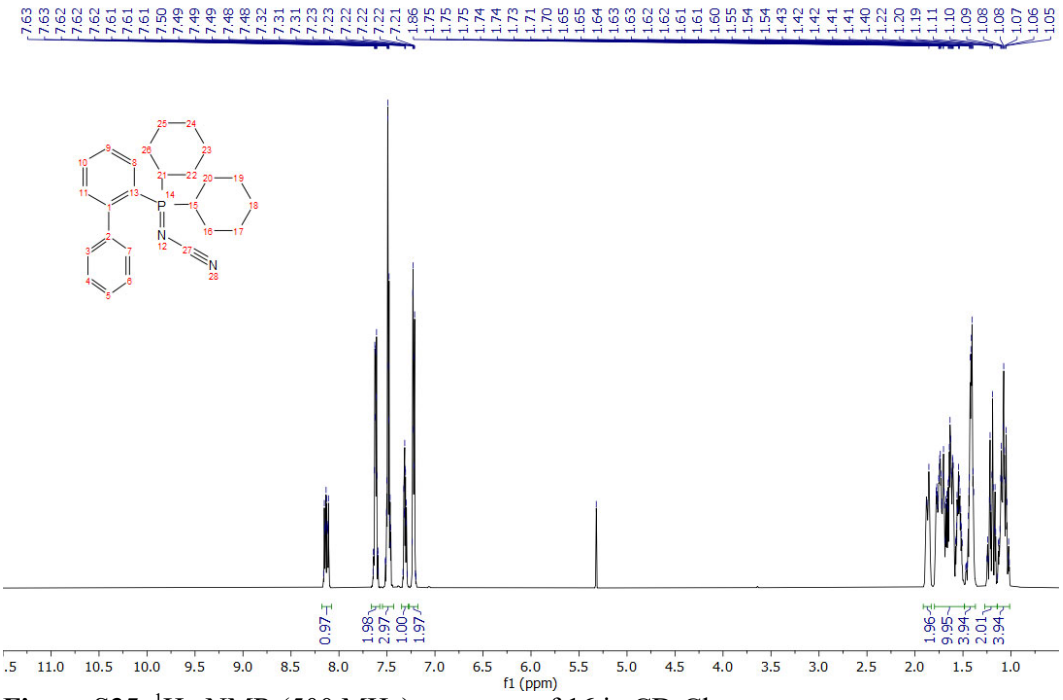


Figure S35. ^{1}H qNMR (500 MHz) spectrum of **16** in CD_2Cl_2.

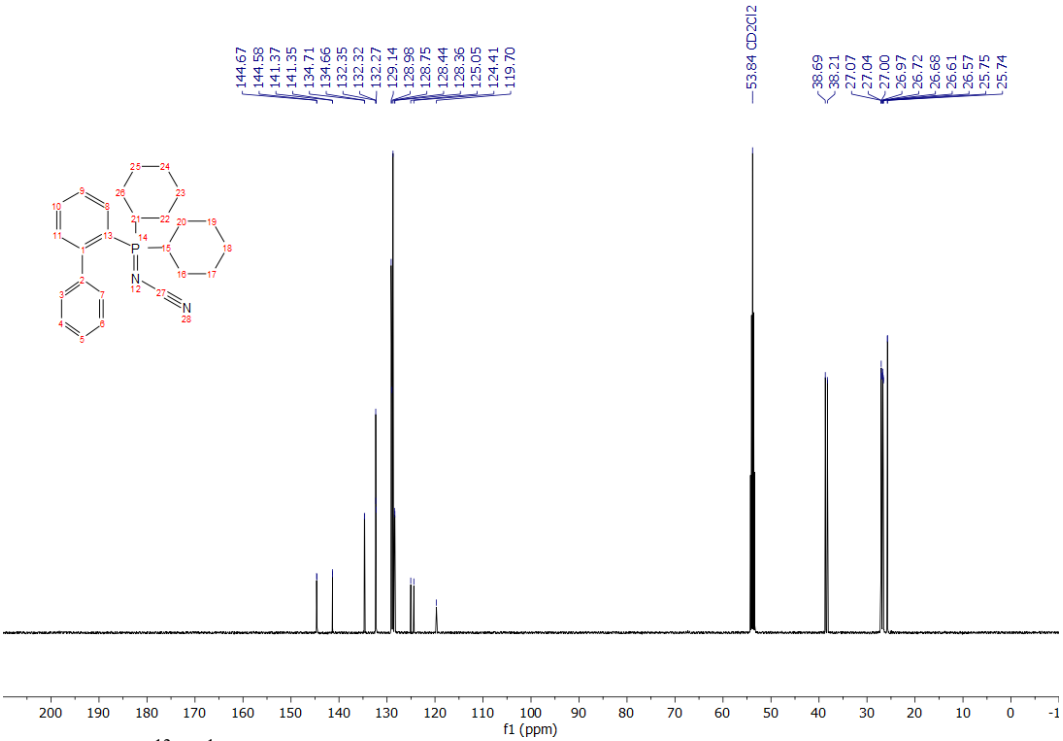


Figure S36. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **16** in CD_2Cl_2.

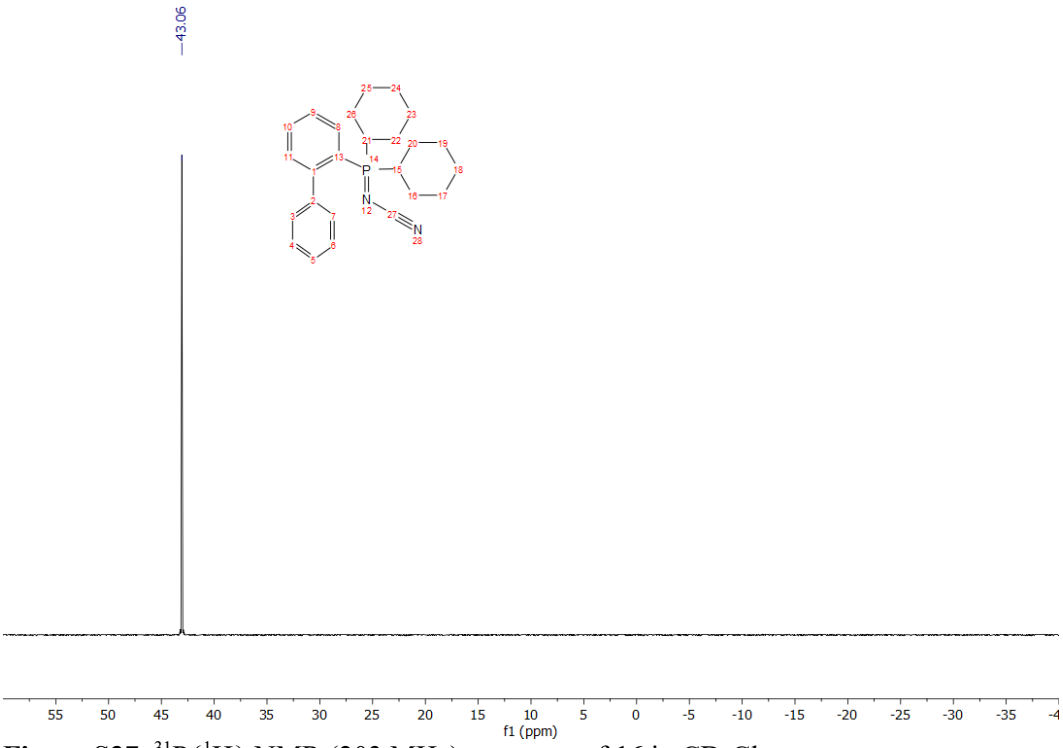
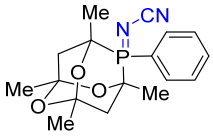


Figure S37. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **16** in CD_2Cl_2.



Synthesis of **17** was prepared following General Procedure **A** in 70% assay yield from 1,3,5,7-tetramethyl-6-phenyl-2,4,8-trioxa-6-phosphaadamantane (0.729 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 4 to afford a white solid. ^{1}H NMR (500 MHz, DMF-d_7) δ 8.23 – 8.15 (m, 2H), 7.86 (t, J = 7.4 Hz, 1H), 7.77 (td, J = 7.7, 3.4 Hz, 2H), 2.74 (dd, J = 14.0, 2.3 Hz, 1H), 2.28 – 2.08 (m, 3H), 1.52 (s, 3H), 1.50 – 1.43 (m, 6H), 1.31 (d, J = 13.6 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMF-d_7) δ 134.49 (d, J = 3.0 Hz), 133.90 (d, J = 8.4 Hz), 130.00 (d, J = 11.7 Hz), 120.52 (d, J = 90.5 Hz), 117.25, 97.18 (d, J = 2.6 Hz), 74.51 (d, J = 81.4 Hz), 74.04 (d, J = 84.3 Hz), 41.65 (d, J = 5.0 Hz), 40.30 (d, J = 2.1 Hz), 26.85 (d, J = 16.7 Hz), 20.74 (d, J = 137.4 Hz). $^{31}P\{^{1}H\}$ NMR (203 MHz, DMF-d_7) δ 8.18 (s, 1P). ESI$^+$ HRMS *m/z* calcd. for $C_{17}H_{22}N_2O_3P$ ($[M + H]^+$) 333.1368, found 333.1363.

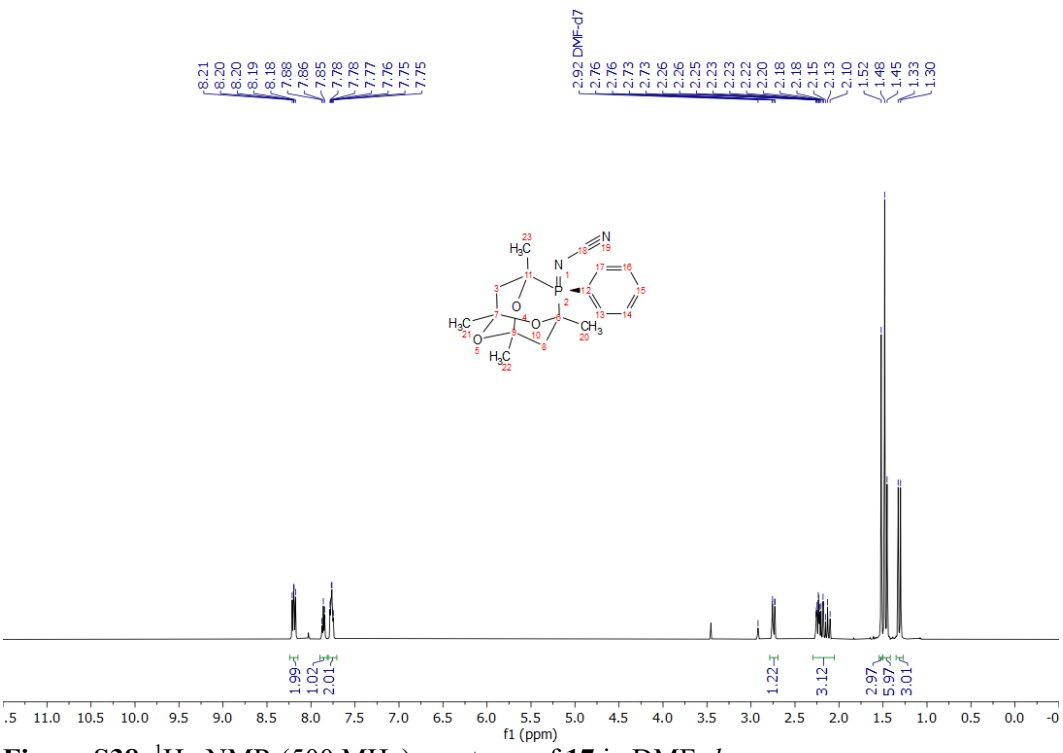


Figure S38. ^{1}H qNMR (500 MHz) spectrum of **17** in DMF-d_7.

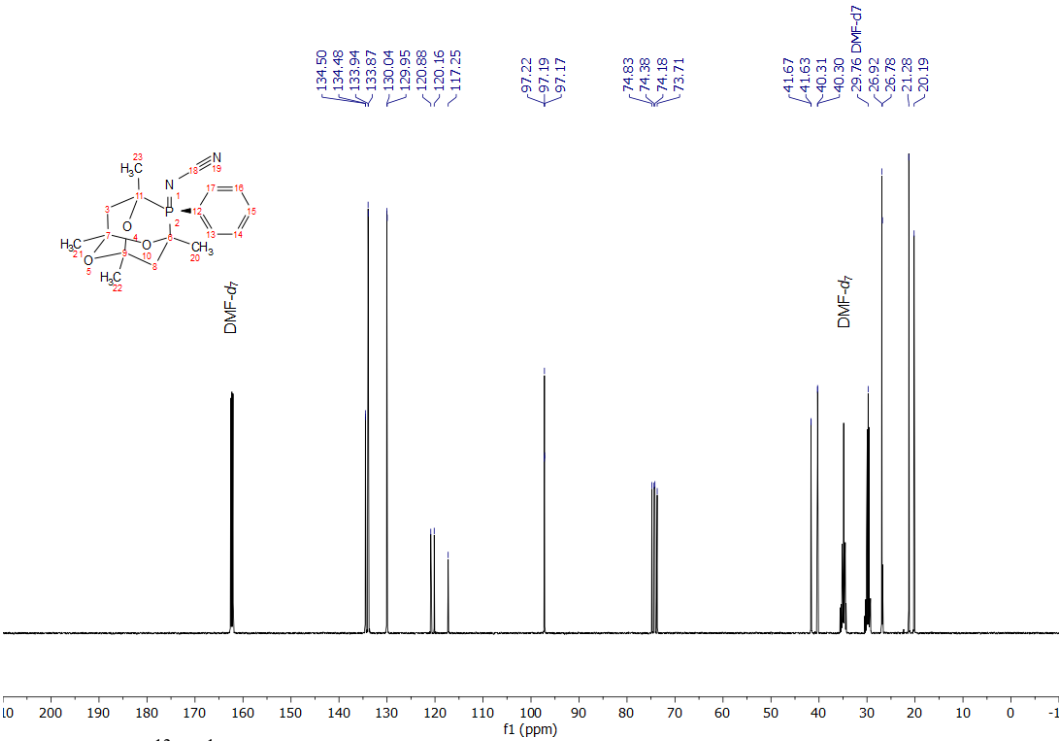


Figure S39. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **17** in DMF-d_7.

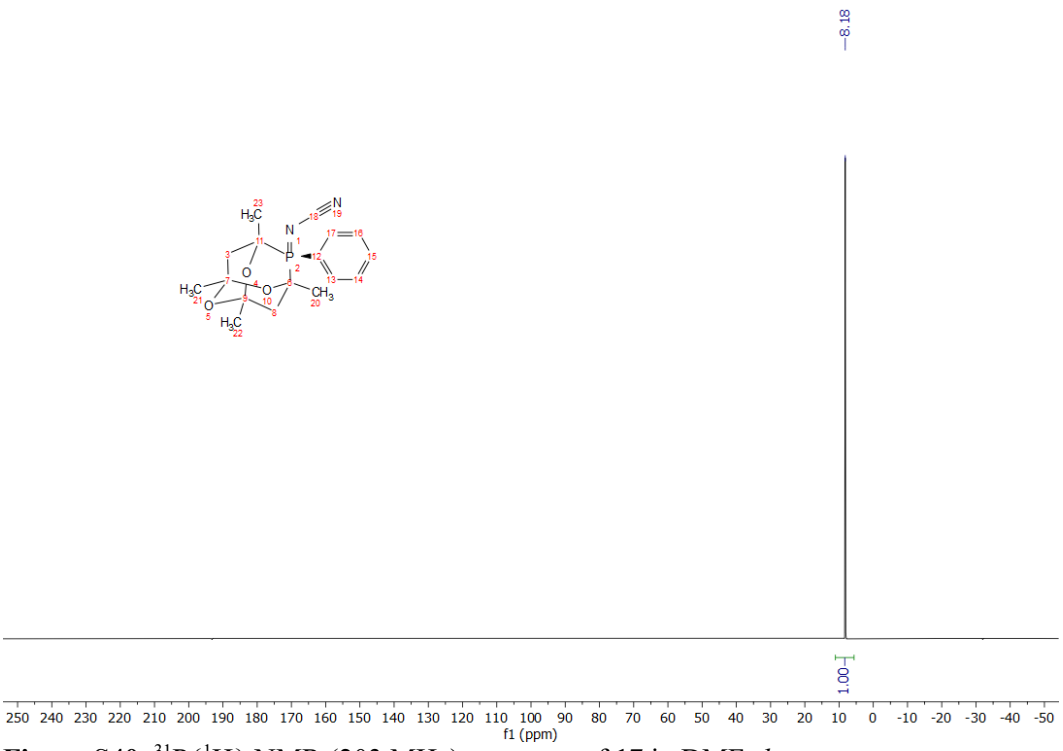


Figure S40. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **17** in DMF-d_7.

Synthesis of **18** was prepared following General Procedure **A** in 43% assay yield from tris(benzyl)phosphine (0.609 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 4 to afford a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.35 – 7.25 (m, 9H), 7.25 – 7.19 (m, 6H), 3.39 (d, J = 13.7 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 130.19 (d, J = 5.2 Hz), 129.95 (d, J = 8.5 Hz), 128.58 (d, J = 2.7 Hz), 127.18 (d, J = 3.2 Hz), 117.62 (d, J = 2.2 Hz), 32.38 (d, J = 57.7 Hz). $^{31}P\{^{1}H\}$ NMR (202 MHz, DMSO-d_6) δ 35.60 (s, 1H). ESI^{+} MS *m/z* calcd. for $C_{22}H_{22}N_2P$ ($[M + H]^{+}$) 345.2, found 345.3.

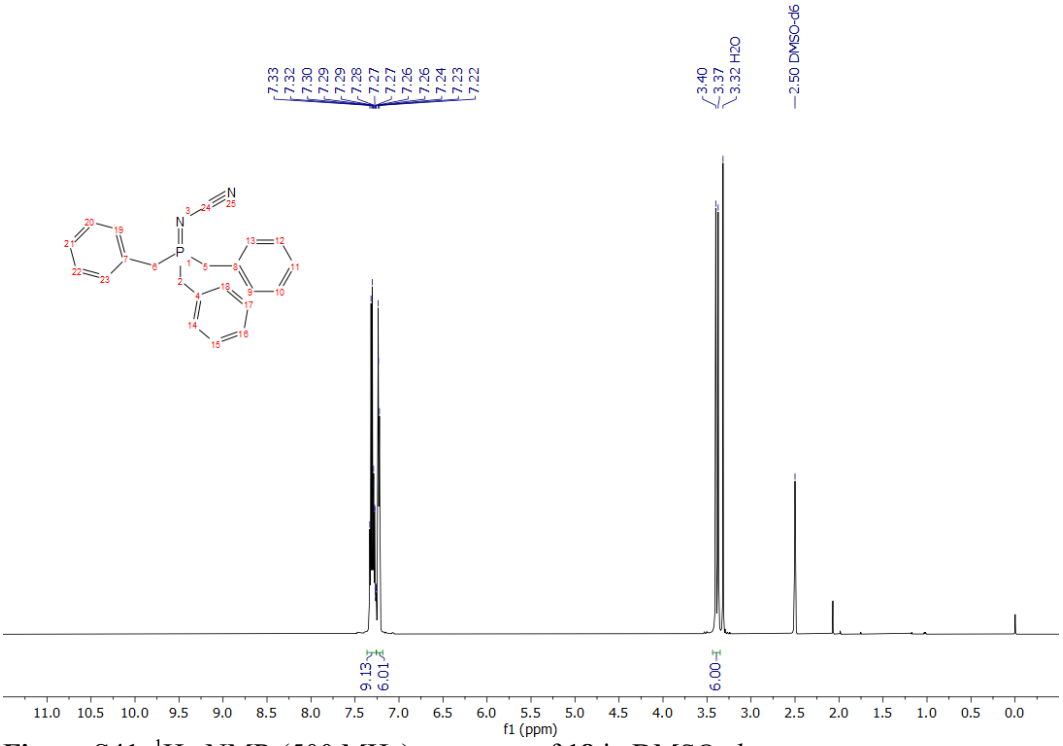


Figure S41. ^{1}H qNMR (500 MHz) spectrum of **18** in DMSO-d_6.

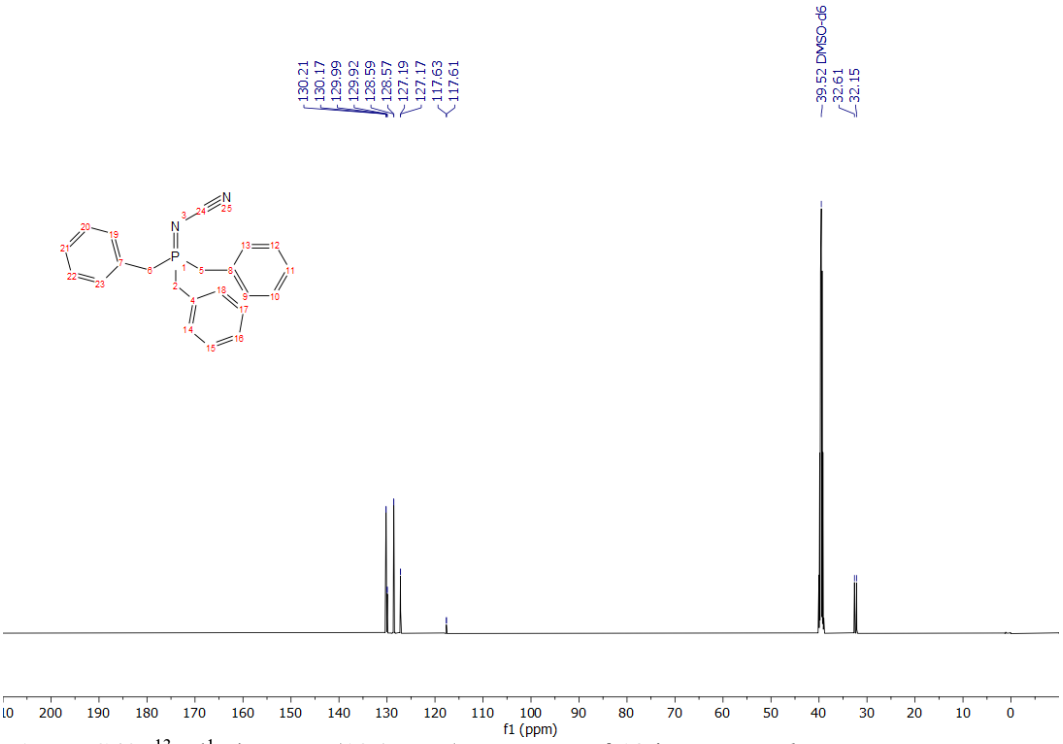


Figure S42. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **18** in DMSO-d_6.

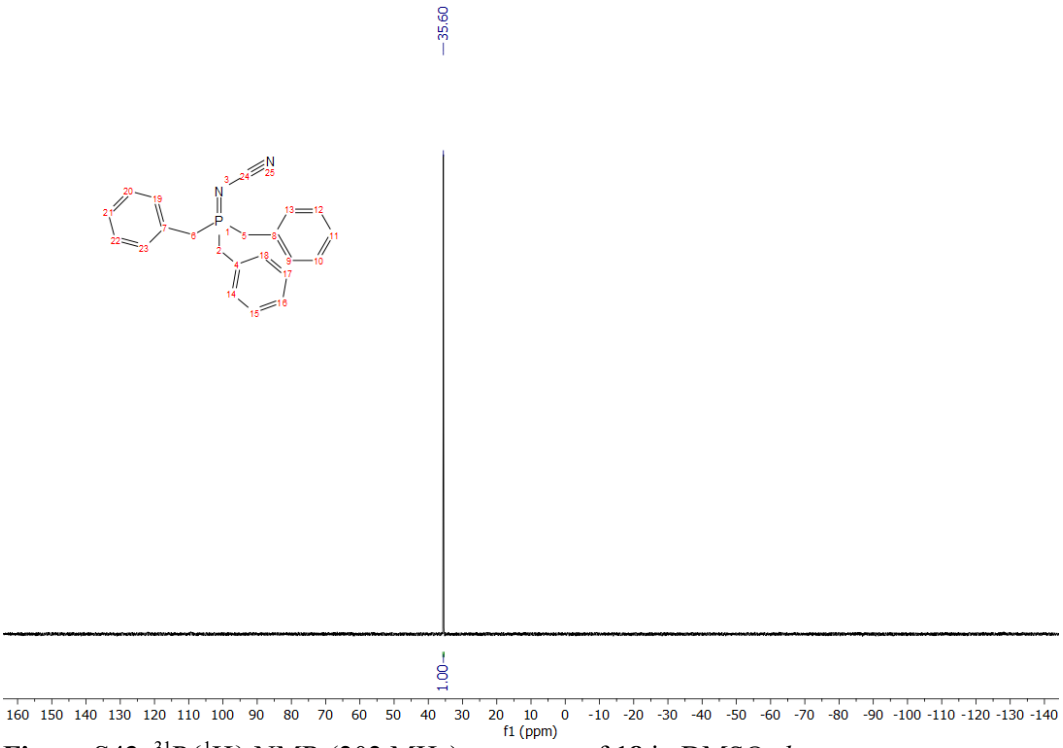
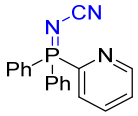


Figure S43. $^{31}P\{^{1}H\}$ NMR (202 MHz) spectrum of **18** in DMSO-d_6.



Synthesis of **19** was prepared following General Procedure **A** in 86% assay yield from diphenyl(2-pyridinyl)phosphine (0.527 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 4 to afford a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.88 (d, J = 4.6 Hz, 1H), 8.20 (t, J = 6.7 Hz, 1H), 8.17 – 8.11 (m, 1H), 7.75 (ddd, J = 19.6, 13.1, 7.0 Hz, 7H), 7.64 (td, J = 7.5, 3.0 Hz, 4H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 151.22 (d, J = 20.7 Hz), 150.17 (d, J = 137.4 Hz), 137.70 (d, J = 9.6 Hz), 133.60 (d, J = 2.9 Hz), 132.16 (d, J = 10.1 Hz), 129.31 (d, J = 12.6 Hz), 128.75 (d, J = 21.5 Hz), 127.19 (d, J = 3.4 Hz), 125.88 (d, J = 101.2 Hz), 117.44. $^{31}P\{^{1}H\}$ NMR (203 MHz, , DMSO-d_6) δ 17.29 (s, 1P). ESI^{+} HRMS *m/z* calcd. for $C_{18}H_{15}N_3P$ ([M + H]$^{+}$) 304.1003, found 304.0998.

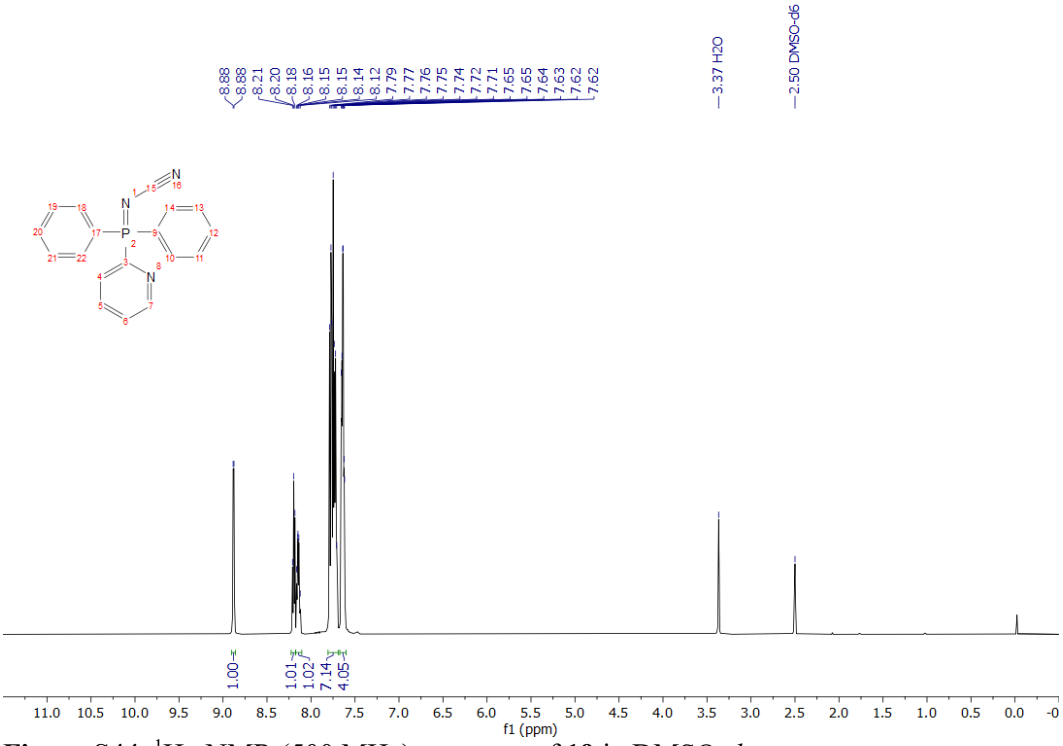


Figure S44. ^{1}H qNMR (500 MHz) spectrum of **19** in DMSO-d_6.

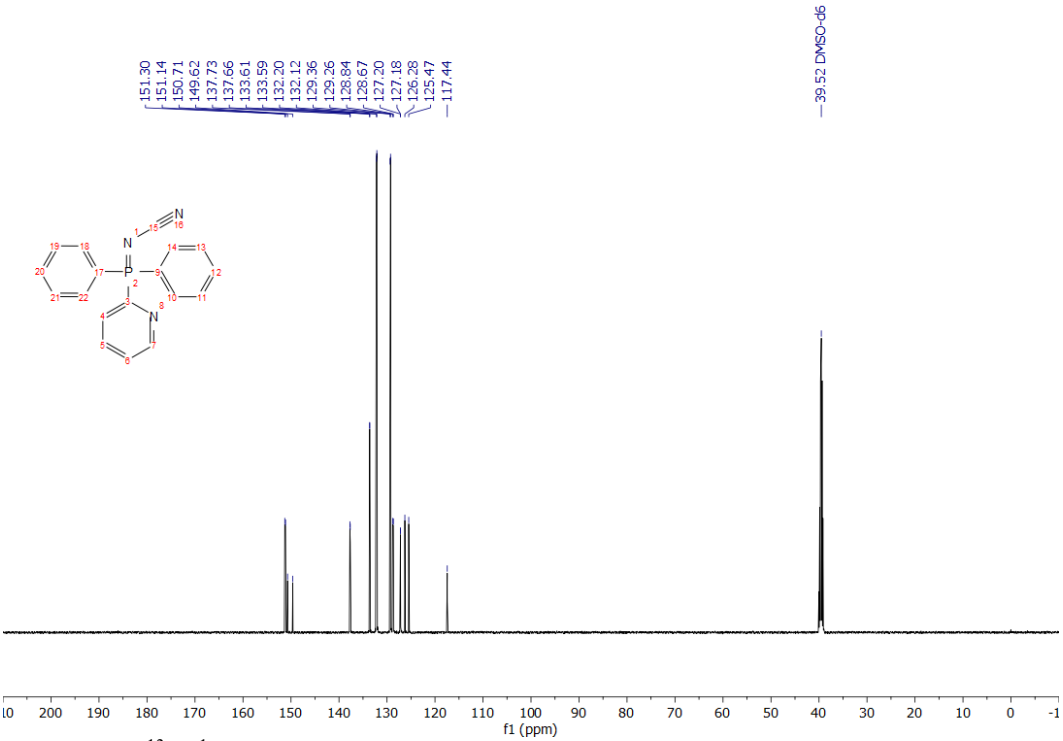


Figure S45. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **19** in DMSO-d_6.

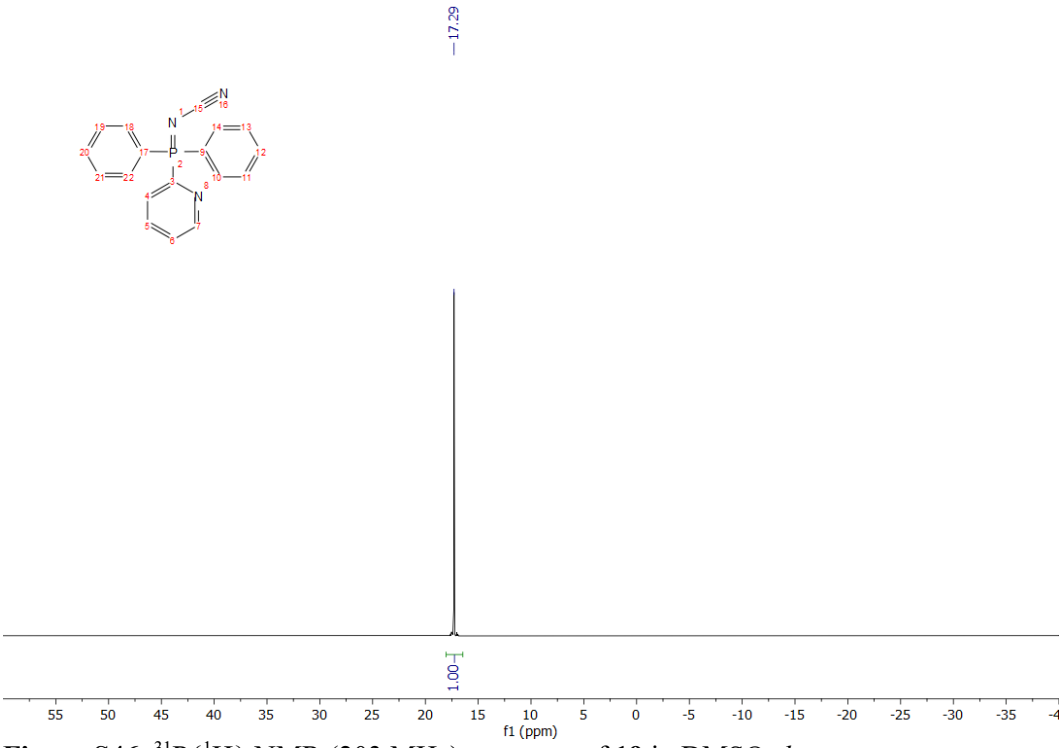
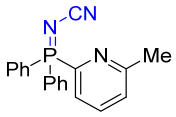


Figure S46. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **19** in DMSO-d_6.



Synthesis of **20** was prepared following General Procedure **A** in 87% assay yield from 2-diphenylphosphino-6-methylpyridine (0.555 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 4 to afford a white. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.14 (t, J = 6.9 Hz, 1H), 7.91 – 7.80 (m, 5H), 7.65 (t, J = 7.5 Hz, 2H), 7.54 (td, J = 7.7, 3.3 Hz, 4H), 7.38 (dd, J = 7.9, 2.0 Hz, 1H), 2.58 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ 160.72 (d, J = 20.8 Hz), 150.57 (d, J = 138.8 Hz), 137.29 (d, J = 10.3 Hz), 133.54 (d, J = 2.9 Hz), 132.94 (d, J = 9.9 Hz), 129.25 (d, J = 12.7 Hz), 127.57, 126.76 (d, J = 3.3 Hz), 126.65 (d, J = 21.3 Hz), 118.44, 24.62. $^{31}P\{^{1}H\}$ NMR (203 MHz, CD_2Cl_2) δ 15.29. ESI^{+} HRMS *m/z* calcd. for $C_{19}H_{17}N_3P$ ($[M + H]^{+}$) 318.1160, found 318.1154.

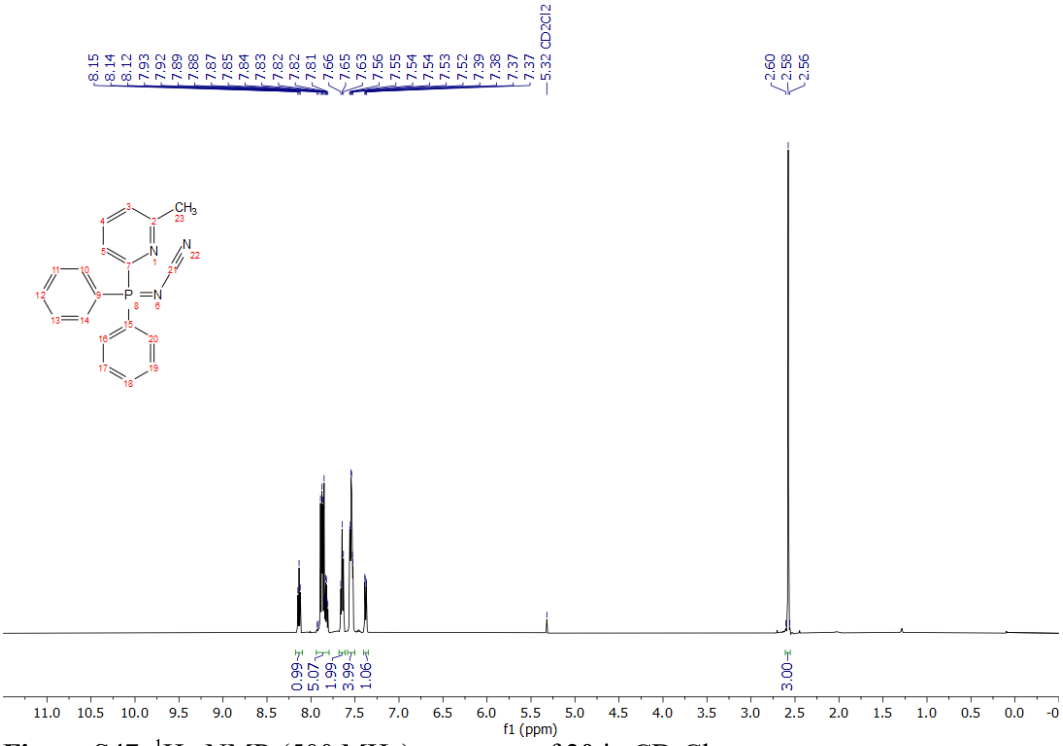


Figure S47. ^{1}H qNMR (500 MHz) spectrum of **20** in CD_2Cl_2.

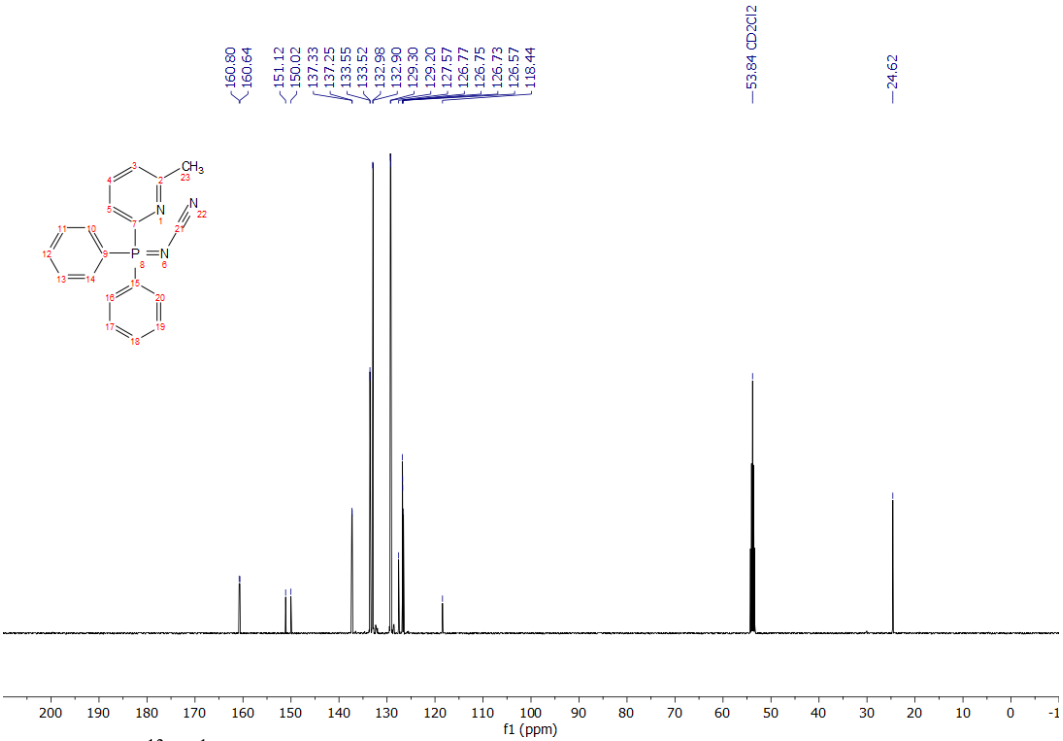


Figure S48. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **20** in CD_2Cl_2.

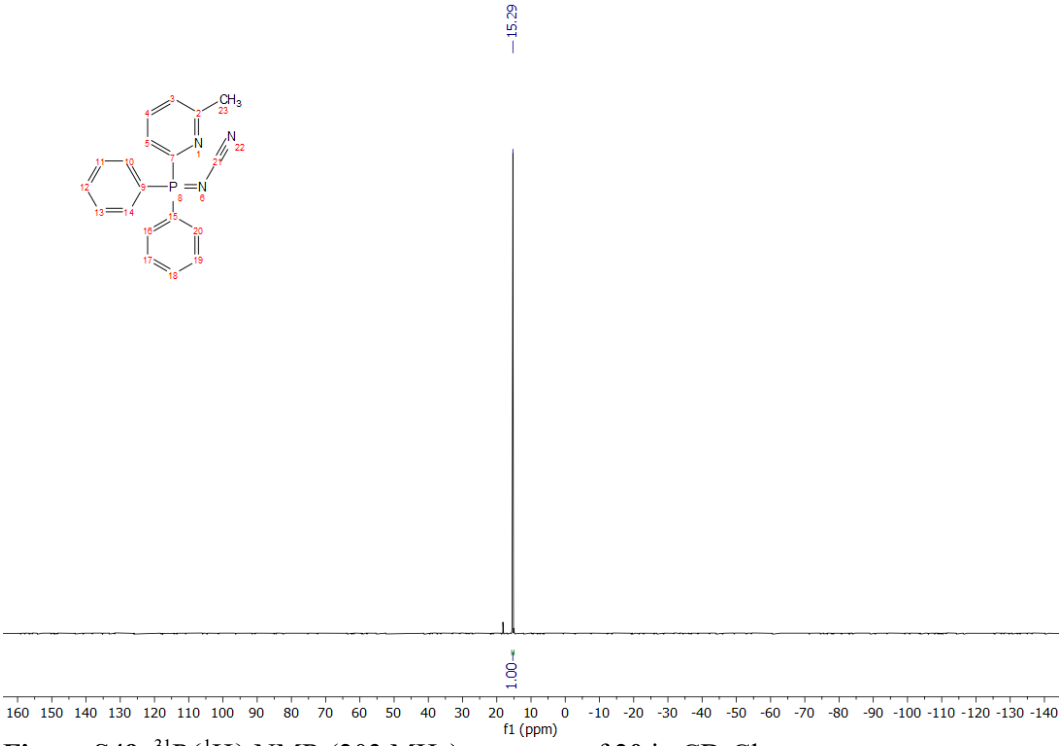
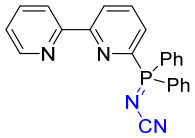


Figure S49. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **20** in CD_2Cl_2.



Synthesis of **21** was prepared following General Procedure **A** in 83% assay yield from 6-(Diphenylphosphino)-2,2'-bipyridine (681 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 1 to afford a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.72 – 8.64 (m, 2H), 8.30 (ddd, J = 7.5, 5.7, 1.0 Hz, 1H), 8.18 (d, J = 8.0 Hz, 1H), 8.08 (td, J = 7.9, 4.7 Hz, 1H), 7.94 – 7.85 (m, 4H), 7.79 (td, J = 7.8, 1.8 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.60 – 7.52 (m, 4H), 7.35 (ddd, J = 7.5, 4.8, 1.1 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ 157.63 (d, J = 20.2 Hz), 154.89, 151.32, 150.22, 149.72, 138.40 (d, J = 9.8 Hz), 137.53, 133.73 (d, J = 2.9 Hz), 133.02 (d, J = 10.0 Hz), 129.38 (d, J = 12.8 Hz), 129.19 (d, J = 21.3 Hz), 127.01 (d, J = 101.9 Hz), 124.95, 124.13 (d, J = 3.3 Hz), 121.46, 118.33. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2) δ 16.57 (s, 1P). ESI^{+} HRMS *m/z* calcd. for $C_{23}H_{18}N_4P$ ($[M + H]^{+}$) 381.1269, found 381.1265.

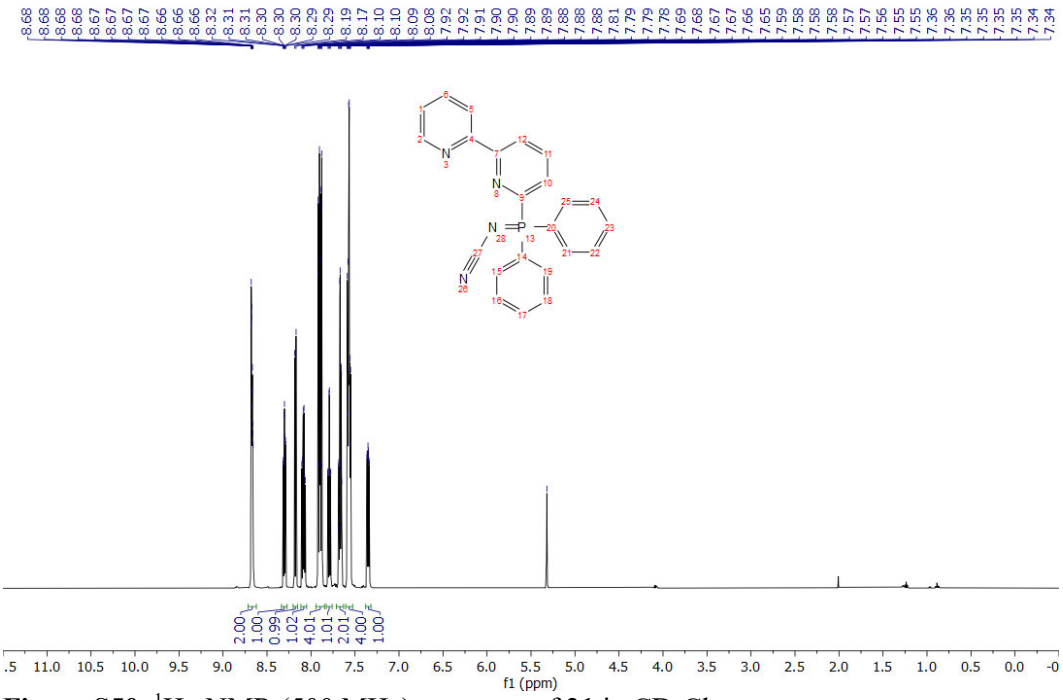


Figure S50. ^{1}H qNMR (500 MHz) spectrum of **21** in CD_2Cl_2.

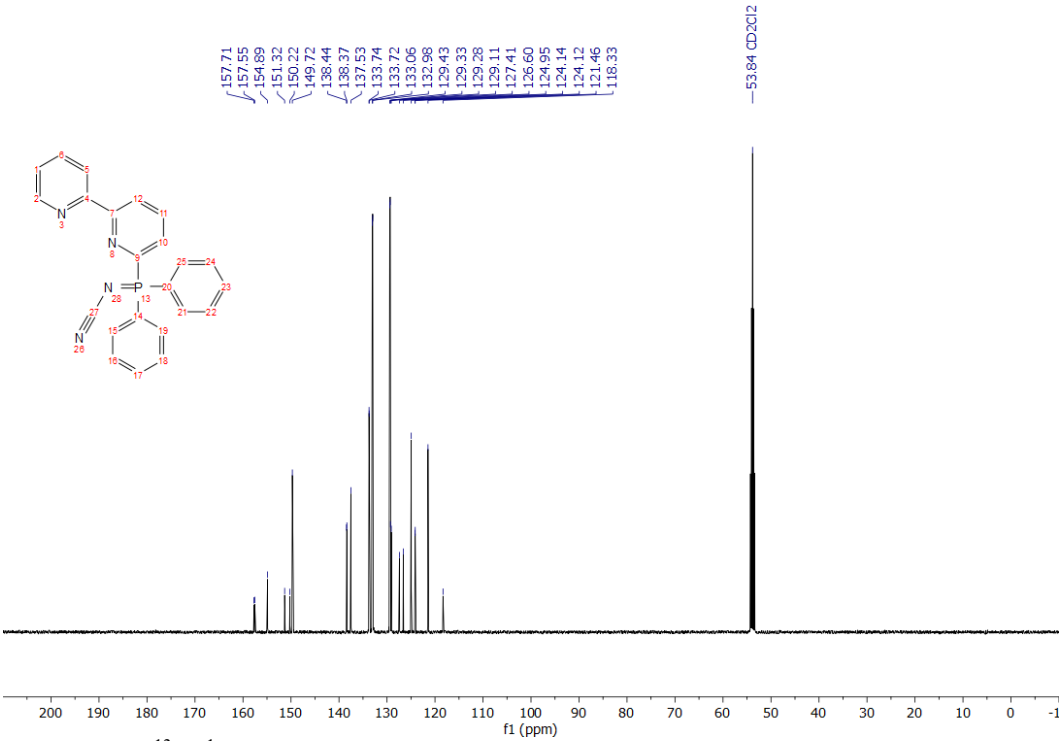


Figure S51. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **21** in CD_2Cl_2.

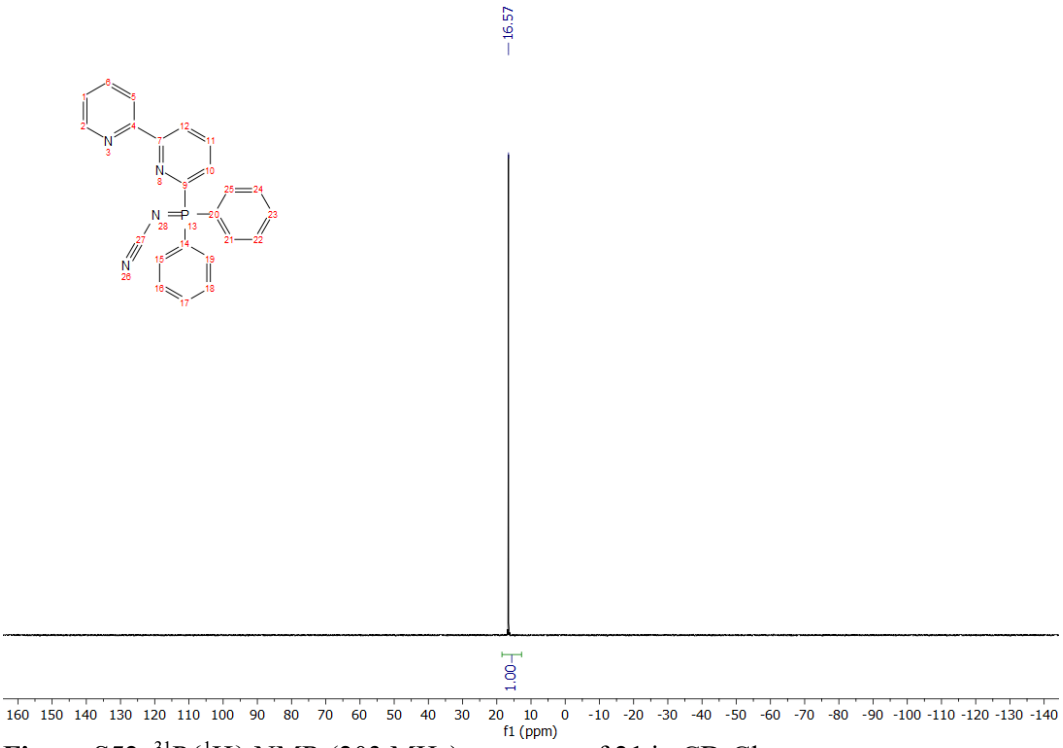
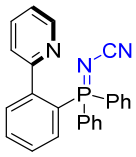


Figure S52. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **21** in CD_2Cl_2.



Synthesis of **22** was prepared following General Procedure **A** in 65% assay yield from 2-(2-(diphenylphosphanyl)phenyl)pyridine[13] (0.679 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 4 to afford a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.04 (q, J = 4.6 Hz, 2H), 7.88 (ddt, J = 7.7, 4.5, 2.4 Hz, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.68 (td, J = 9.4, 4.0 Hz, 3H), 7.61 (dd, J = 12.9, 7.3 Hz, 4H), 7.55 – 7.48 (m, 2H), 7.43 (td, J = 7.6, 3.4 Hz, 4H), 7.05 (dd, J = 7.2, 5.0 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 154.30 (d, J = 1.9 Hz), 147.88, 143.95 (d, J = 5.9 Hz), 137.07, 136.11 (d, J = 12.0 Hz), 133.70 (d, J = 2.5 Hz), 131.83 (d, J = 2.8 Hz), 130.72 (d, J = 9.9 Hz), 130.11 (d, J = 9.3 Hz), 130.08 (d, J = 110.8 Hz), 129.14 (d, J = 13.0 Hz), 128.67 (d, J = 12.8 Hz), 124.69 (d, J = 97.6 Hz), 122.41 (d, J = 99.2 Hz), 117.85. $^{31}P\{^{1}H\}$ NMR (203 MHz, DMSO-d_6) δ 24.23 (s, 1P). ESI^{+} LRMS *m/z* calcd. for $C_{24}H_{19}N_3P$ ($[M + H]^{+}$) 380.1, found 380.3.

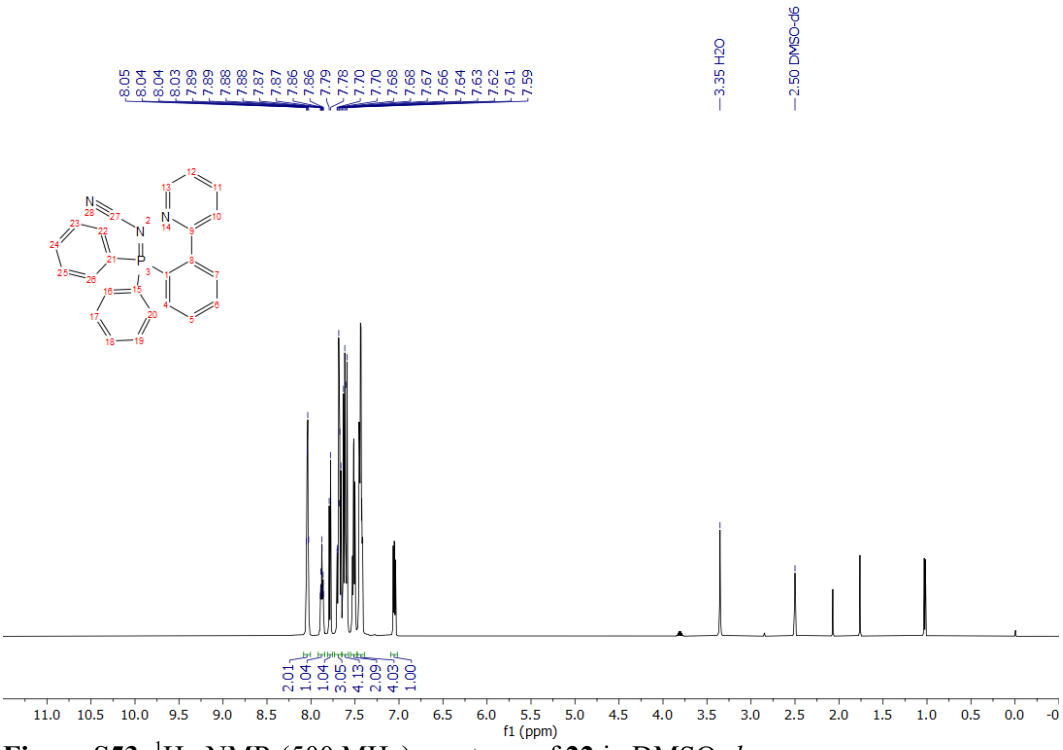


Figure S53. ^{1}H qNMR (500 MHz) spectrum of **22** in DMSO-d_6.

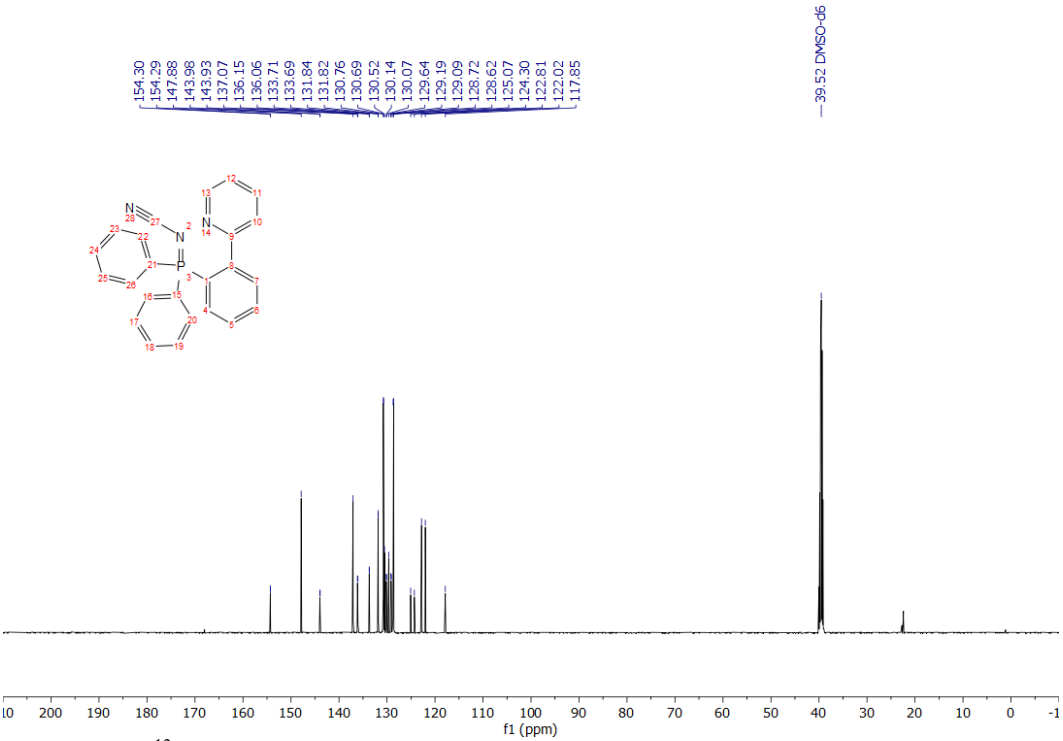


Figure S54. ^{13}C NMR (500 MHz) spectrum of **22** in DMSO-d_6.

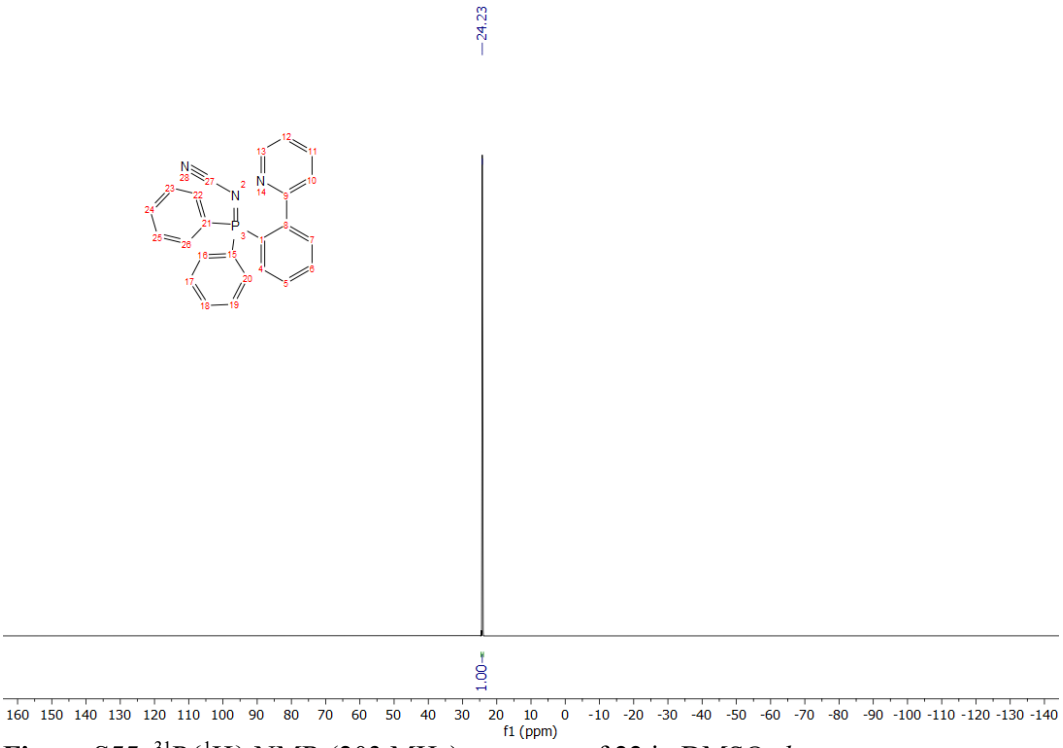
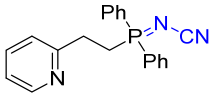


Figure S55. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **22** in DMSO-d_6.



Synthesis of **23** was prepared following General Procedure **A** in 85% assay yield from diphenyl-2-pyridylphosphine (0.583 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 4 to afford a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.46 (d, J = 4.7 Hz, 1H), 7.88 (dd, J = 12.4, 7.8 Hz, 4H), 7.74 – 7.60 (m, 7H), 7.31 (d, J = 7.8 Hz, 1H), 7.20 (dd, J = 7.2, 5.1 Hz, 1H), 3.23 (td, J = 11.2, 6.4 Hz, 2H), 3.03 – 2.93 (m, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 158.56 (d, J = 15.4 Hz), 148.93, 136.60, 133.23 (d, J = 2.8 Hz), 131.15 (d, J = 10.1 Hz), 129.33 (d, J = 12.2 Hz), 126.85 (d, J = 96.9 Hz), 122.88, 121.81, 117.97, 28.96 (d, J = 3.3 Hz), 25.20 (d, J = 68.0 Hz). $^{31}P\{^{1}H\}$ NMR (203 MHz, DMSO-d_6) δ 29.80 (s, 1P). ESI^{+} HRMS *m/z* calcd. for $C_{20}H_{19}N_3P$ ($[M + H]^{+}$) 332.1316, found 332.1313.

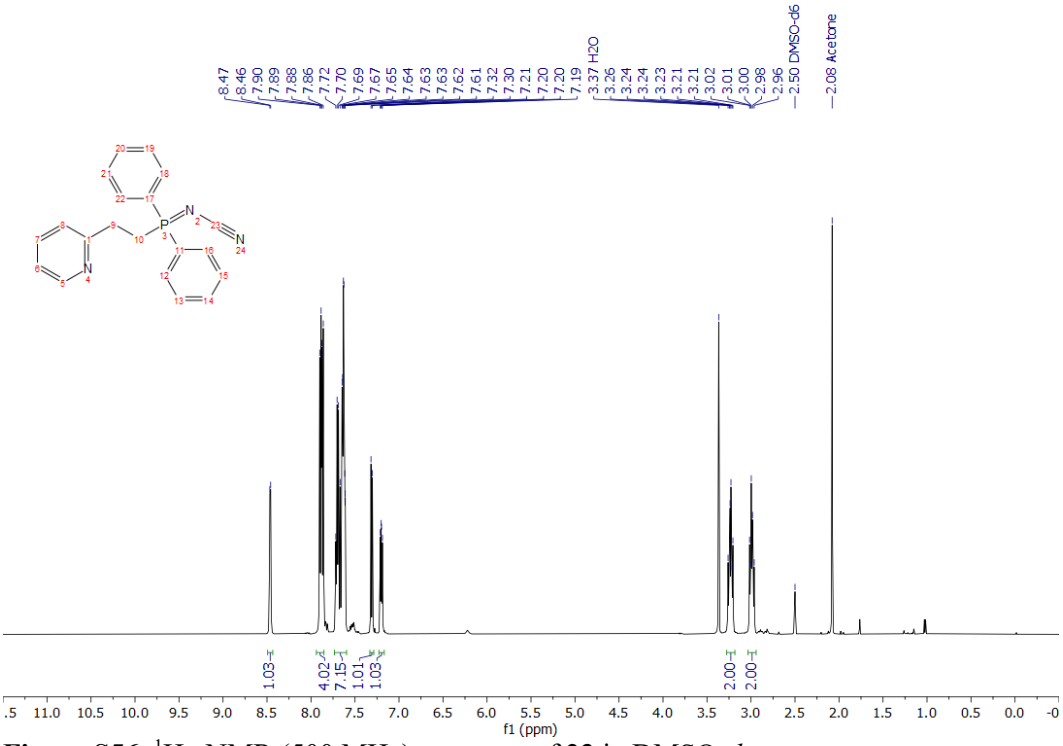


Figure S56. ^{1}H qNMR (500 MHz) spectrum of **23** in DMSO-d_6.

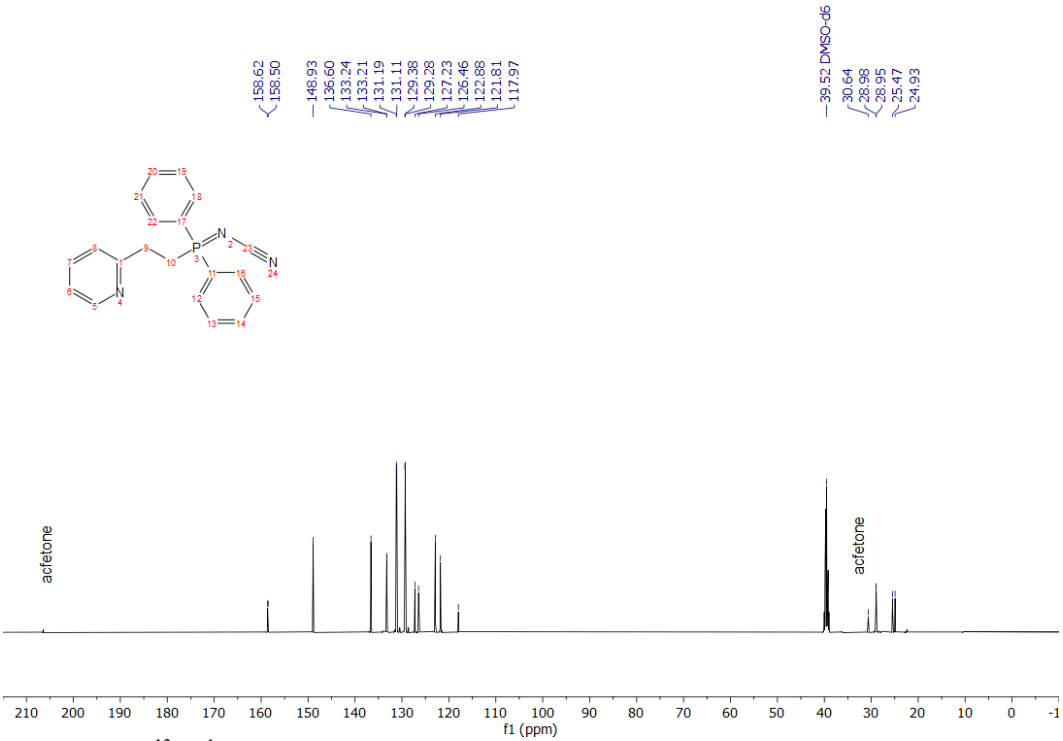


Figure S57. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **23** in DMSO-d_6.

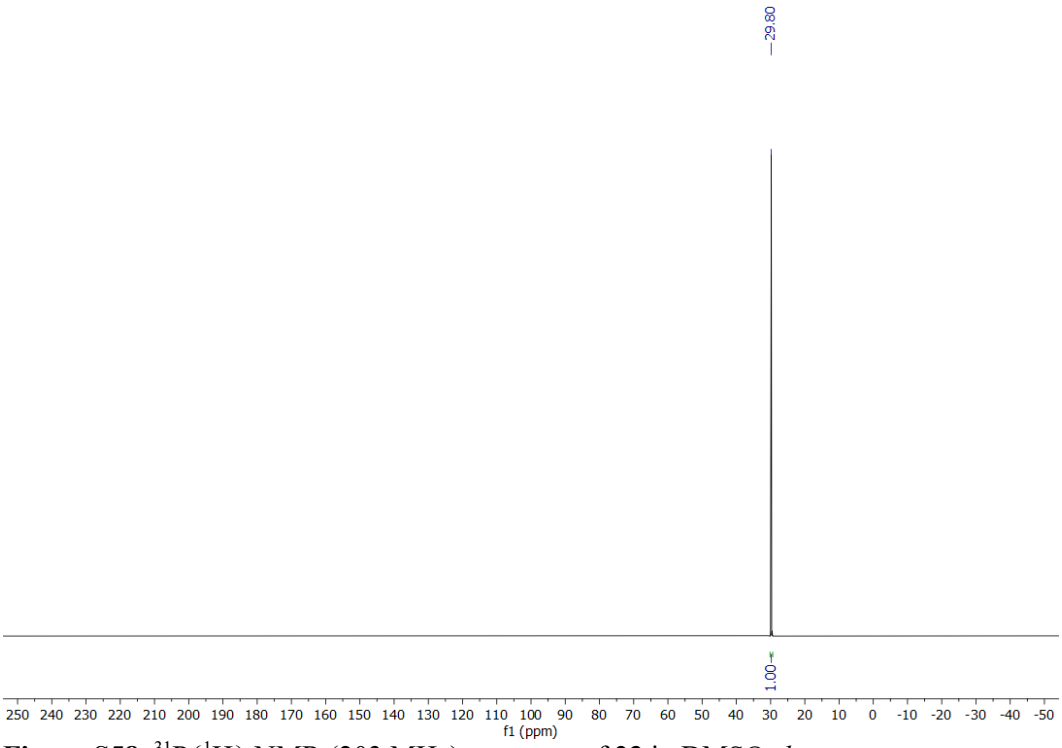
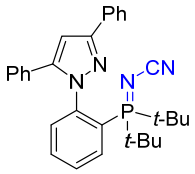


Figure S58. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **23** in DMSO-d_6.



Synthesis of **24** was prepared following General Procedure **A** in 81% assay yield from 1-(2-(di-*tert*-butylphosphanyl)phenyl)-3,5-diphenyl-*1H*-pyrazole (0.881 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 1 to afford a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.89 (d, J = 7.6 Hz, 2H), 7.78 – 7.64 (m, 3H), 7.60 (t, J = 6.9 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.34 (t, J = 7.2 Hz, 1H), 7.25 (d, J = 7.1 Hz, 3H), 6.92 (s, 1H), 1.42 (d, J = 15.3 Hz, 9H), 1.14 (d, J = 15.1 Hz, 9H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ 151.21, 147.74, 145.76 (d, J = 1.3 Hz), 134.07 (d, J = 6.5 Hz), 134.02, 133.30 (d, J = 2.5 Hz), 133.05 (d, J = 12.9 Hz), 131.21, 129.32, 128.88, 128.51 (d, J = 12.7 Hz), 128.50, 128.21, 127.90, 126.04, 123.39 (d, J = 93.3 Hz), 117.34 (d, J = 4.4 Hz), 103.67, 41.04 (d, J = 110.1 Hz), 40.67 (d, J = 105.1 Hz), 27.74 (d, J = 55.4 Hz). $^{31}P\{^{1}H\}$ NMR (203 MHz, CD_2Cl_2) δ 44.20 (s, 1P). ESI^+ HRMS *m/z* calcd. for $C_{30}H_{33}N_4P$ ($[M + H]^+$) 481.2521, found 481.2519.

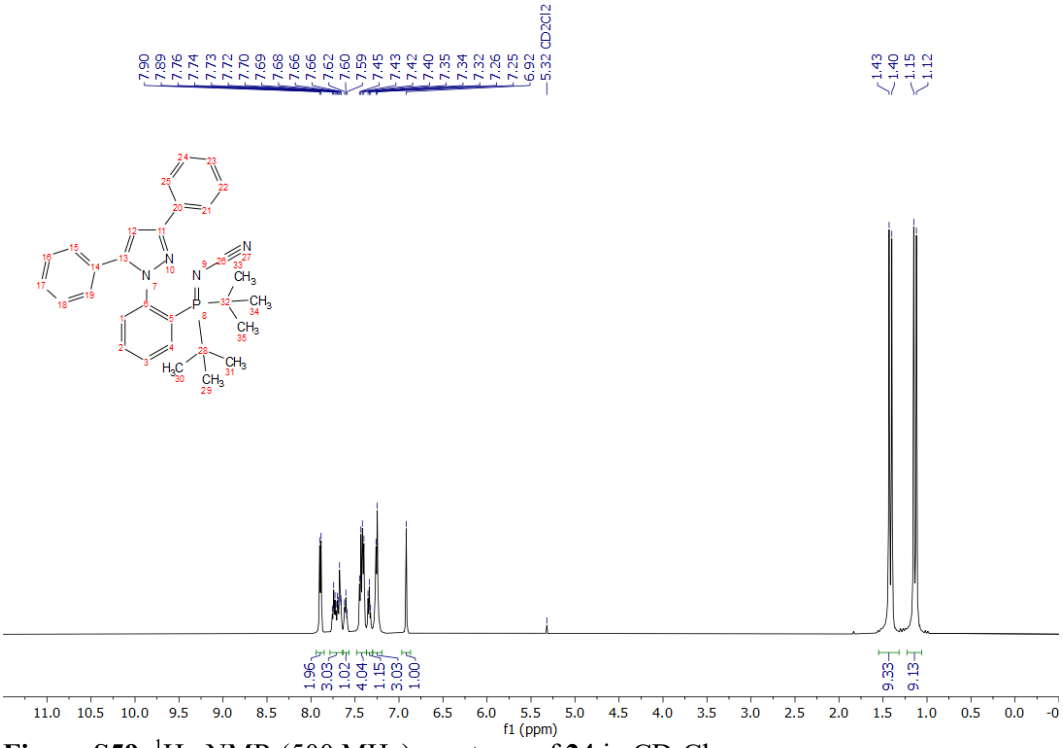


Figure S59. ^{1}H qNMR (500 MHz) spectrum of **24** in CD_2Cl_2.

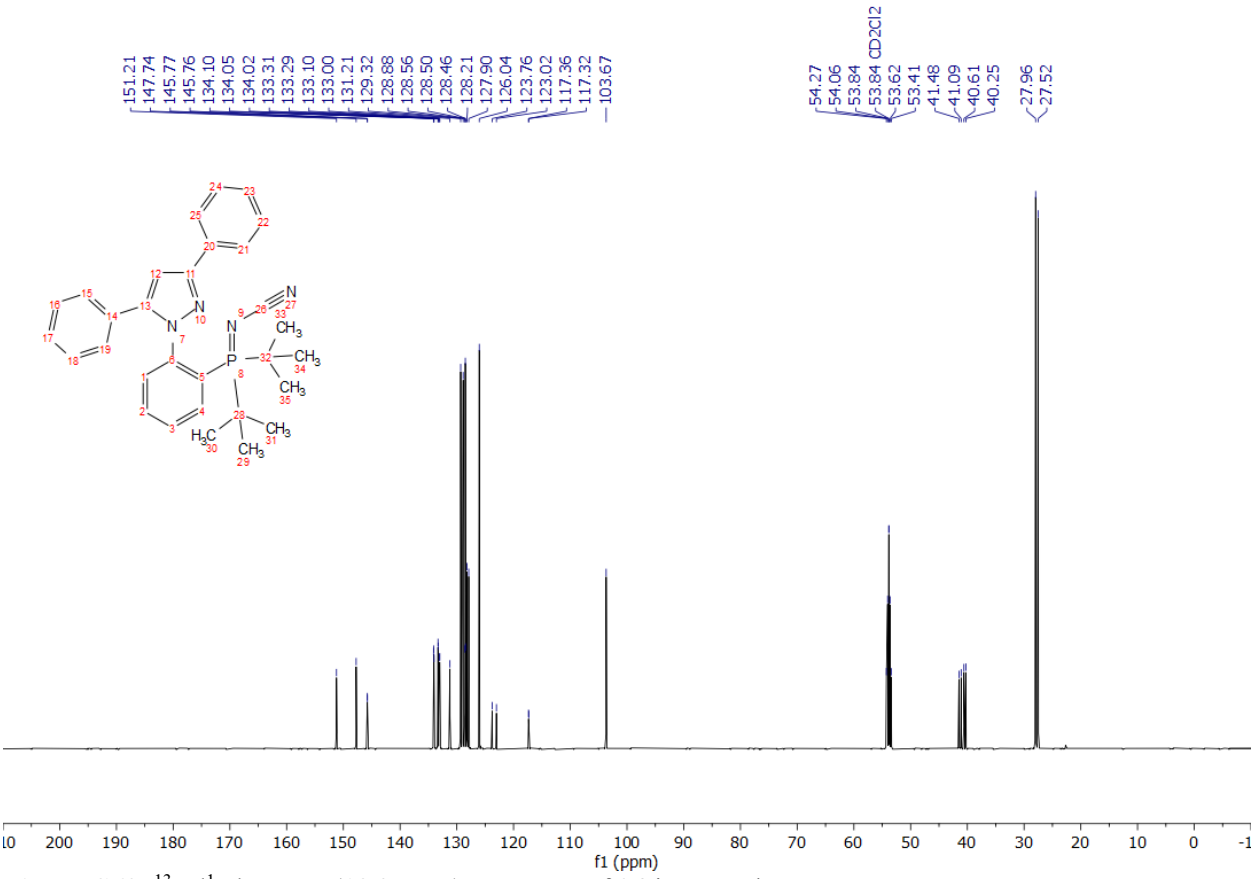


Figure S60. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **24** in CD_2Cl_2.

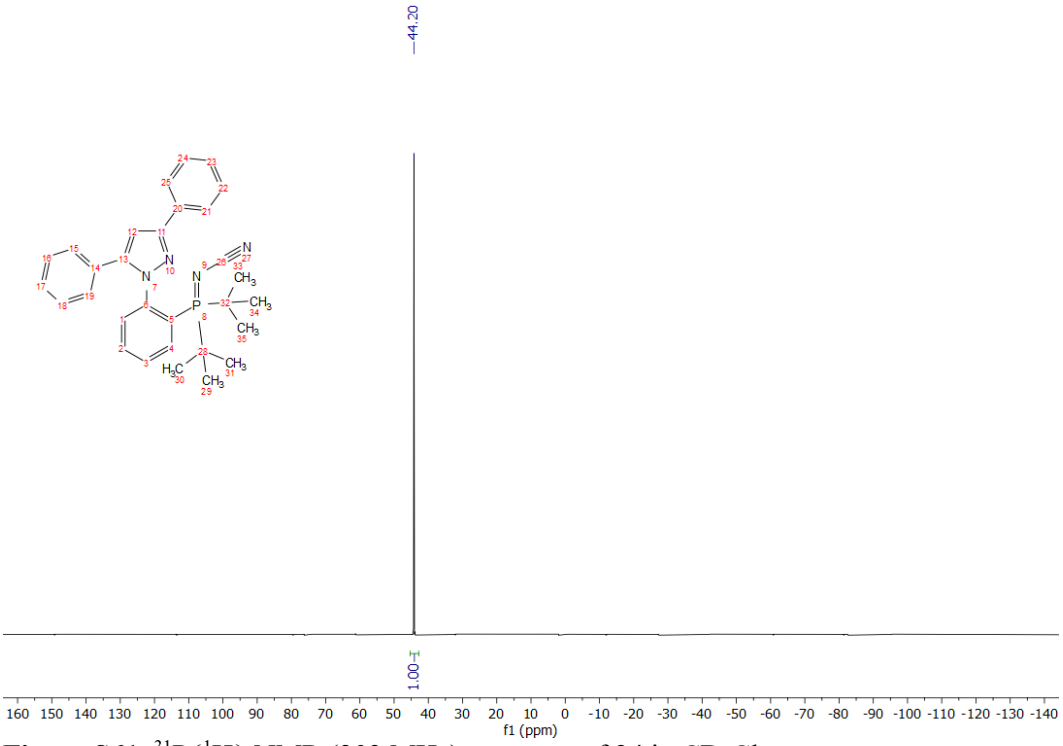
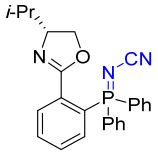


Figure S61. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **24** in CD_2Cl_2.



Synthesis of (*R*)-**25** was prepared following General Procedure **A** in 70% assay yield from (*R*)-(+)-2-(2-(diphenylphosphino)phenyl)-4-isopropyl-4,5-dihydrooxazole (0.747 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 4 to afford a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.03 – 7.97 (m, 1H), 7.89 (t, J = 7.5 Hz, 1H), 7.85 – 7.54 (m, 12H), 3.92 (t, J = 9.1 Hz, 1H), 3.65 (t, J = 8.9 Hz, 1H), 3.35–3.28 (m, 1H, note H_2O is overlapping with this multiplet), 1.33 (m, 1H), 0.63 (d, J = 6.6 Hz, 3H), 0.59 (d, J = 6.7 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 160.29 (d, J = 2.0 Hz), 135.47 (d, J = 10.4 Hz), 133.81 (d, J = 2.5 Hz), 132.74 (d, J = 2.8 Hz), 132.44 (d, J = 2.8 Hz), 131.81 (d, J = 10.2 Hz), 131.72 (d, J = 6.6 Hz), 131.53 (d, J = 12.2 Hz), 130.80 (d, J = 10.2 Hz), 130.76 (d, J = 8.9 Hz), 129.05, 128.99 (d, J = 6.3 Hz), 128.88 (d, J = 6.3 Hz), 128.20 (d, J = 2.8 Hz), 127.32, 125.50 (d, J = 96.8 Hz), 117.37, 72.44, 70.45, 31.82, 18.53, 18.49. $^{31}P\{^{1}H\}$ NMR (203 MHz, DMSO-d_6) δ 25.93 (s, 1P). ESI$^+$ HRMS *m/z* calcd. for $C_{25}H_{25}N_3OP$ ($[M + H]^+$) 414.1735, found 414.1735. Chiral SFC method used to determine ee: A Waters SFC-MS equipped with an Chirapak IA-3 column (3 µm particle size, 4.6 mm ID × 150 mm length; part number 80524) operating at 40 °C with a 2.5 mL/min flow rate of a binary eluent mixture (eluent A and B, prepared as described below). Eluent A = CO_2, eluent B = 25 mM isobutylamine in methanol. The method used a gradient from 99.0%A, 1.0%B at t = 0 min to 60.0%A, 40.0%B at t = 8.00 min, followed by holding the gradient at 60.0%A, 40.0%B until at t = 8.80 min, and a subsequent change to 99.0%A, 1.0%B at t = 8.90 min until t = 9.00 min. Retention times for (*R*)-**25** is t_r = 5.18 min and for (*S*)-**25** is t_r = 5.09 min.

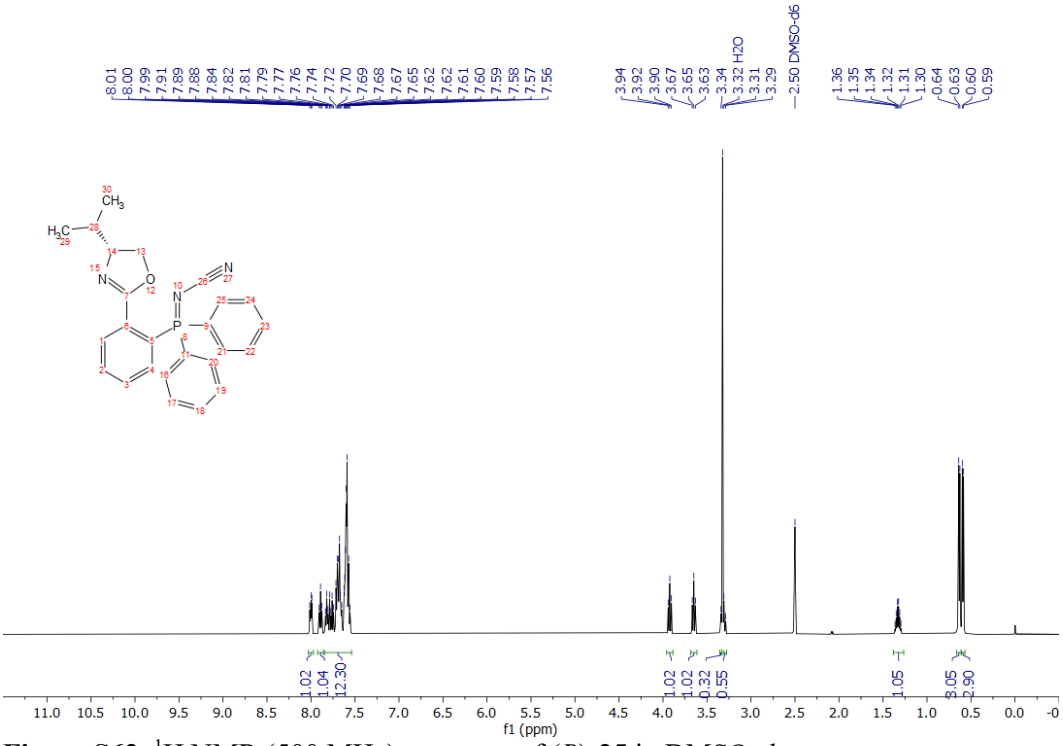


Figure S62. ^{1}H NMR (500 MHz) spectrum of (*R*)-**25** in DMSO-d_6.

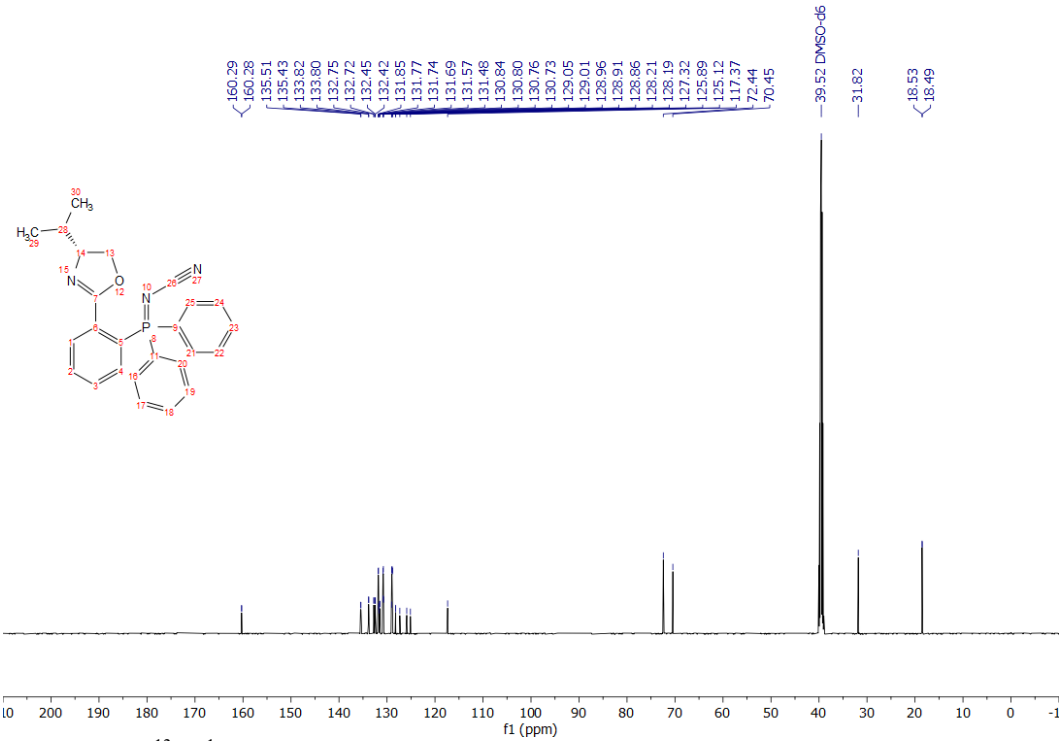


Figure S63. ^{13}C{^{1}H} NMR (126 MHz) spectrum of (*R*)-**25** in DMSO-d_6.

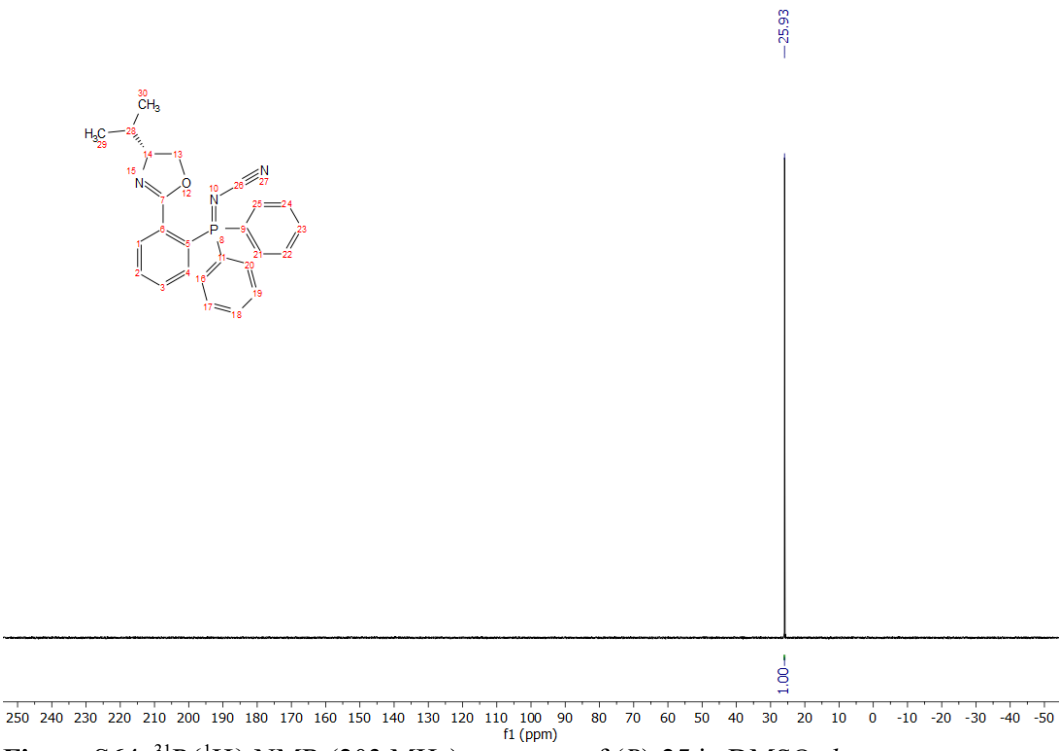


Figure S64. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of (*R*)-**25** in DMSO-d_6.

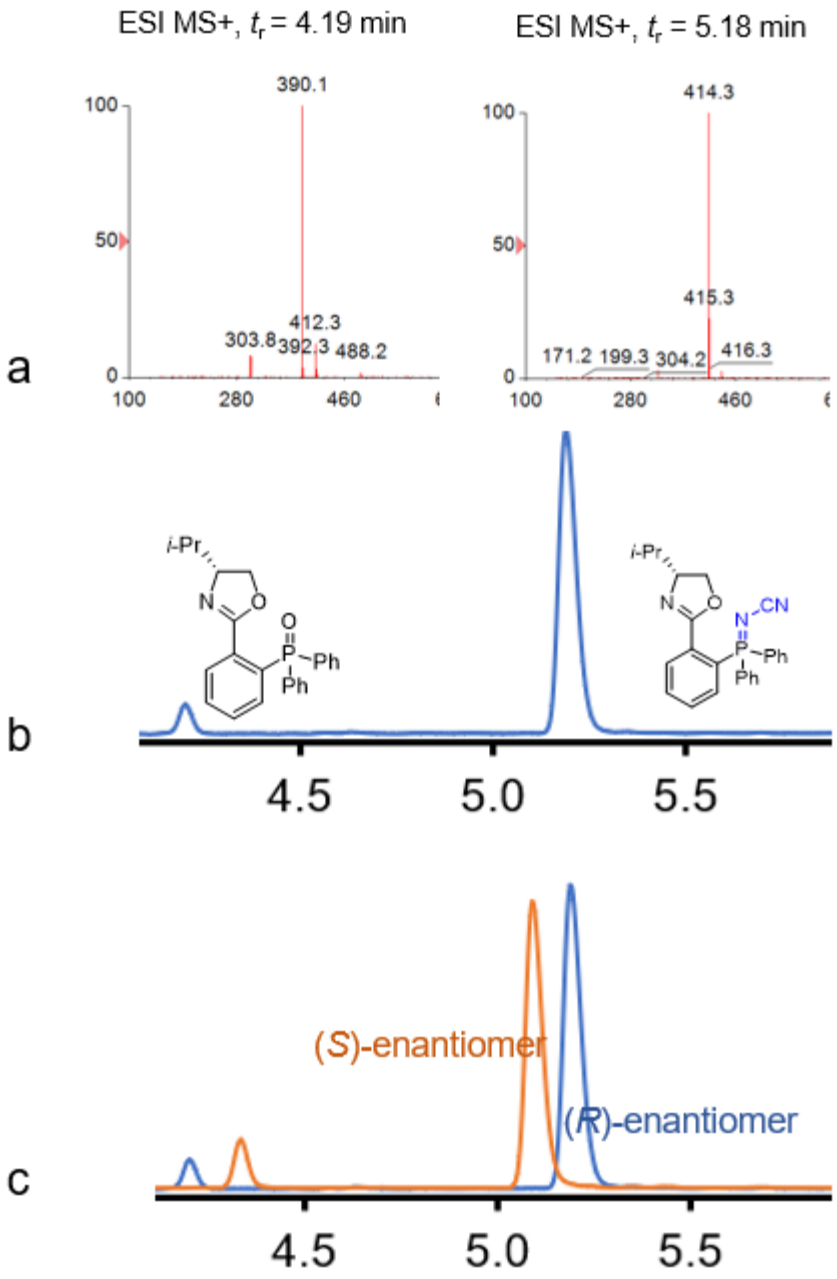
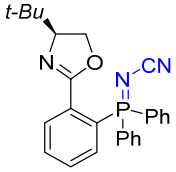


Figure S65. Chiral SFC-MS analysis associated with products **25** derived from the electrolysis reaction using the *R*- and *S*-enantiomers of phosphine(III) starting material: (a) ESI MS^+ showing PO peak at t_r = 4.19 min and the desired PN peak at t_r = 5.18 min, (b) UV chromatogram (λ = 210 nm) of the product mixture derived from the *R*-enantiomer of the staring material, (c) overlay of the UV chromatograms (λ = 210 nm) associated with the products derived from the electrolysis reaction using the *R*- and *S*-enantiomers of starting material. Retention times for (*R*)-**25** is t_r = 5.18 min and for (*S*)-**25** is t_r = 5.09 min.



Synthesis of (*S*)-**26** was prepared following General Procedure **A** in 69% assay yield from (*S*)-4-*tert*-Butyl-2-[2-(diphenylphosphino)phenyl]-2-oxazoline (0.775 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Chromatographic purification by method 4 produced a white wax-like solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.04 (ddd, J = 7.7, 4.6, 1.0 Hz, 1H), 7.93 – 7.85 (m, 1H), 7.83 – 7.72 (m, 3H), 7.68 – 7.48 (m, 9H), 3.91 – 3.78 (m, 2H), 3.36 (t, J = 9.7 Hz, 1H), 0.66 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 161.20 (d, J = 1.9 Hz), 136.26 (d, J = 10.4 Hz), 133.60 (d, J = 2.6 Hz), 132.96 (d, J = 10.3 Hz), 132.95 (d, J = 3.0 Hz), 132.71 (d, J = 6.5 Hz), 132.52 (d, J = 3.0 Hz), 131.42 (d, J = 2.2 Hz), 131.33, 131.21 (d, J = 9.0 Hz), 129.67 (d, J = 107.0 Hz), 129.08 (d, J = 11.0 Hz), 128.98 (d, J = 11.1 Hz), 128.41 (d, J = 113.6 Hz), 126.53 (d, J = 97.8 Hz), 118.28, 76.73, 69.32, 33.58, 25.89. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2) δ 26.27 (s, 1P). ESI^{+} HRMS *m/z* calcd. for $C_{26}H_{27}N_3OP$ ([M + H]$^{+}$) 428.1891, found 428.1891. Chiral SFC method used to determine ee: A Waters SFC-MS equipped with an Chirapak ID-3 column (3 µm particle size, 4.6 mm ID × 150 mm length; part number 80524) operating at 40 °C with a 2.5 mL/min flow rate of a binary eluent mixture (eluent A and B, prepared as described below). Eluent A = CO_2, eluent B = 25 mM isobutylamine in methanol. The method used a gradient from 99.0%A, 1.0%B at t = 0 min to 60.0%A, 40.0%B at t = 5.00 min, followed by holding the gradient at 60.0%A, 40.0%B until at t = 5.80 min, and a subsequent change to 99.0%A, 1.0%B at t = 5.90 min until t = 6.00 min. Retention times for (*R*)-**26** is t_r = 5.19 min and for (*S*)-**26** is t_r = 5.05 min.

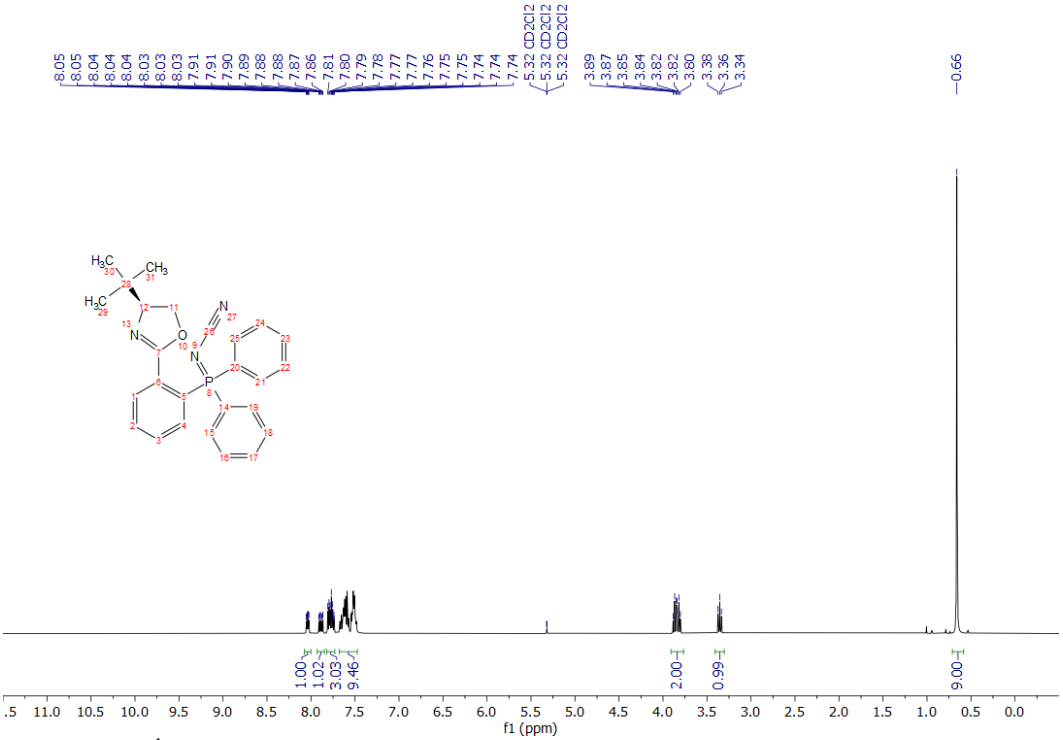


Figure S66. ^{1}H qNMR (500 MHz) spectrum of (*S*)-**26** in CD_2Cl_2.

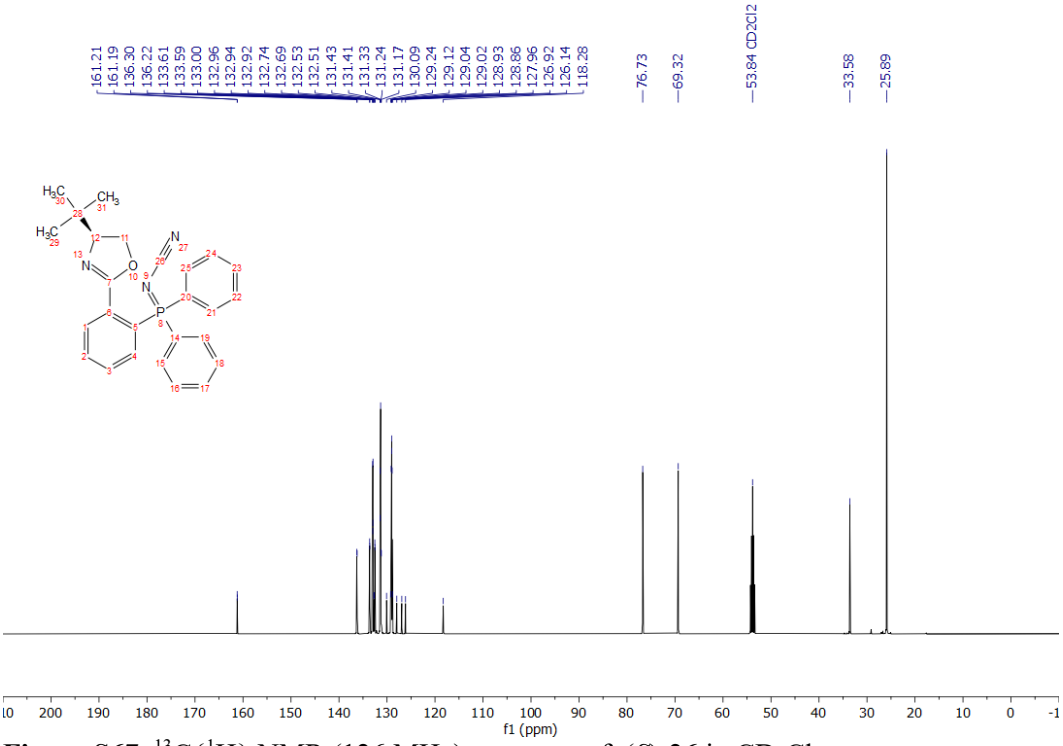


Figure S67. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of (*S*)-**26** in CD_2Cl_2.

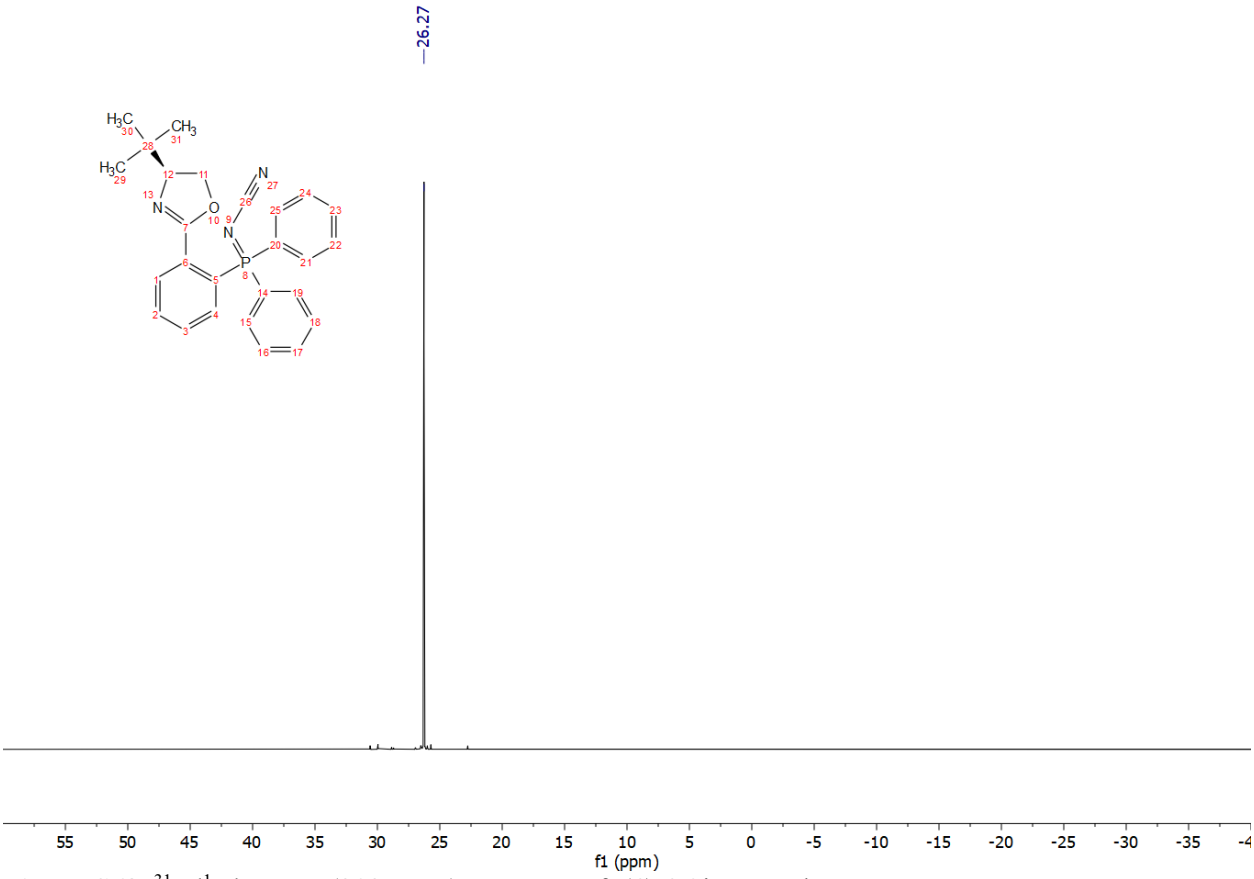


Figure S68. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of (*S*)-**26** in CD_2Cl_2.

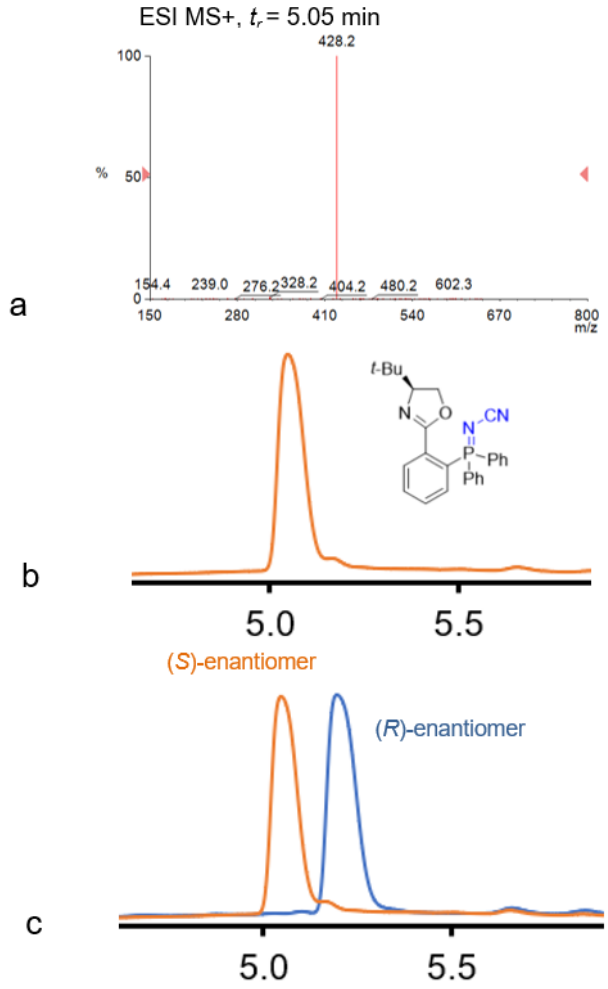
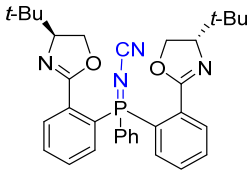


Figure S69. Chiral SFC-MS analysis associated with products **26** derived from the electrolysis reaction using the *R*- and *S*-enantiomers of the corresponding phosphine(III) starting material: (a) ESI MS^+ showing the desired PN peak at t_r = 5.05 min, (b) UV chromatogram (λ = 210 nm) of the product mixture derived from the *S*-enantiomer of the staring material, (c) overlay of the UV chromatograms (λ = 210 nm) associated with the products derived from the electrolysis reaction using the *R*- and *S*-enantiomers of starting material. Retention times for (*R*)-**26** is t_r = 5.19 min and for (*S*)-**26** is t_r = 5.05 min.



Synthesis of (*S,S*)-**27** was prepared following General Procedure **A** in 55% assay yield from (*4S,4'S*)-2,2'-((Phenylphosphanediyl)bis(2,1-phenylene))bis(4-(*tert*-butyl)-4,5-dihydrooxazole) (1.03 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 4 to afford a white, waxy solid. ^{1}H NMR (500 MHz, MeOD) δ 8.07 – 8.01 (m, 1H), 7.98 – 7.93 (m, 1H), 7.93 – 7.87 (m, 2H), 7.80 – 7.70 (m, 3H), 7.68 – 7.64 (m, 2H), 7.61 (tdd, *J* = 7.7, 2.6, 1.3 Hz, 1H), 7.55 (td, *J* = 7.8, 3.6 Hz, 2H), 7.43 (dd, *J* = 15.9, 7.4 Hz, 1H), 4.13 – 3.97 (m, 3H), 3.93 (t, *J* = 8.7 Hz, 1H), 3.52 (dd, *J* = 10.1, 9.0 Hz, 1H), 3.24 (t, *J* = 9.7 Hz, 1H), 0.77 (s, 9H), 0.72 (s, 9H). ^{13}C{^{1}H} NMR (126 MHz, CD_3OD) δ 163.53 (d, *J* = 2.5 Hz), 163.38 (d, *J* = 2.2 Hz), 135.73 (d, *J* = 12.4 Hz), 135.17 (d, *J* = 10.6 Hz), 134.39

(d, J = 10.3 Hz), 134.00 (d, J = 2.9 Hz), 133.60 (d, J = 2.8 Hz), 133.35 (d, J = 2.7 Hz), 132.33 (d, J = 9.0 Hz), 132.22 (d, J = 9.5 Hz), 132.14 (d, J = 5.6 Hz), 131.90 (d, J = 9.3 Hz), 131.85 (d, J = 98.0 Hz), 131.53 (d, J = 9.5 Hz), 130.67 (d, J = 21.0 Hz), 129.79 (d, J = 13.4 Hz), 129.66 (d, J = 101.8 Hz), 120.26, 77.56, 70.51, 70.45, 34.50, 34.31, 26.35, 26.30. $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_3OD) δ 29.81 (s, 1P). ESI^+ HRMS *m/z* calcd. for $C_{33}H_{38}N_4O_2P$ ($[M + H]^+$) 553.2732, found 553.2729. Chiral SFC method used to determine ee: A Waters SFC-MS equipped with an Chirapak ID-3 column (3 µm particle size, 4.6 mm ID × 150 mm length; part number 84524) operating at 40 °C with a 2.5 mL/min flow rate of a binary eluent mixture (eluent A and B, prepared as described below). Eluent A = CO_2, eluent B = 25 mM isobutylamine in methanol. The method used a gradient from 99.0%A, 1.0%B at t = 0 min to 60.0%A, 40.0%B at t = 5.00 min, followed by holding the gradient at 60.0%A, 40.0%B until at t = 5.80 min, and a subsequent change to 99.0%A, 1.0%B at t = 5.90 min until t = 6.00 min. Retention times for (*R*)-**27** is t_r = 5.35 min and for (*S*)-**27** is t_r = 4.83 min.

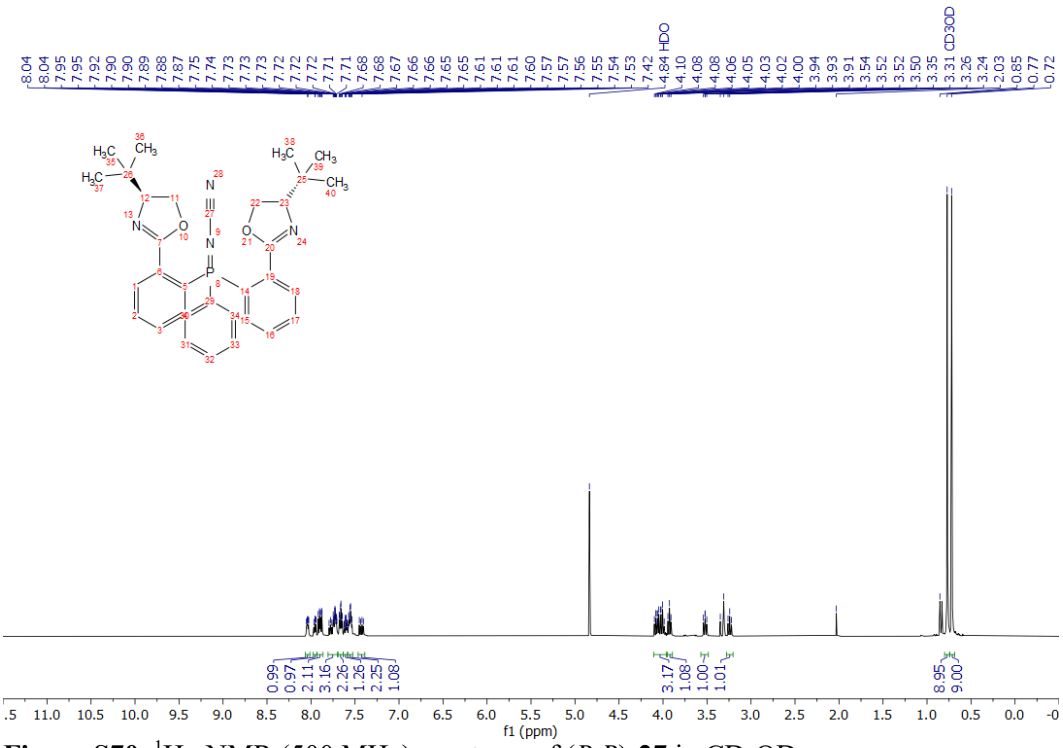


Figure S70. ^{1}H qNMR (500 MHz) spectrum of (*R,R*)-**27** in CD_3OD.

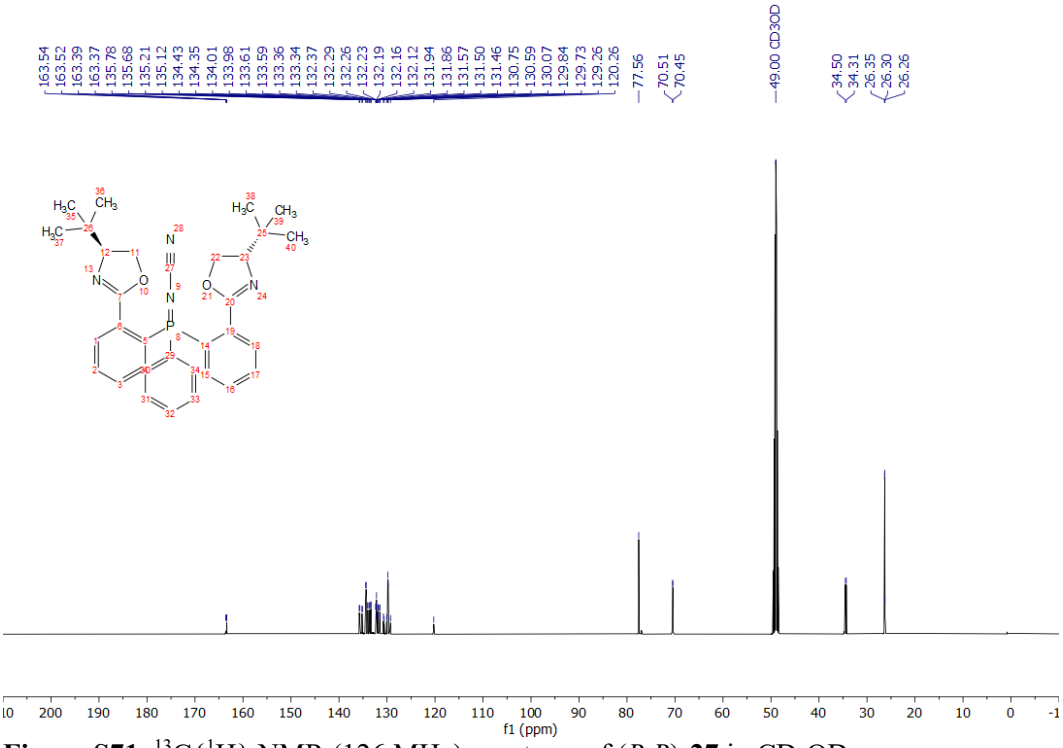


Figure S71. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of (*R,R*)-**27** in CD_3OD.

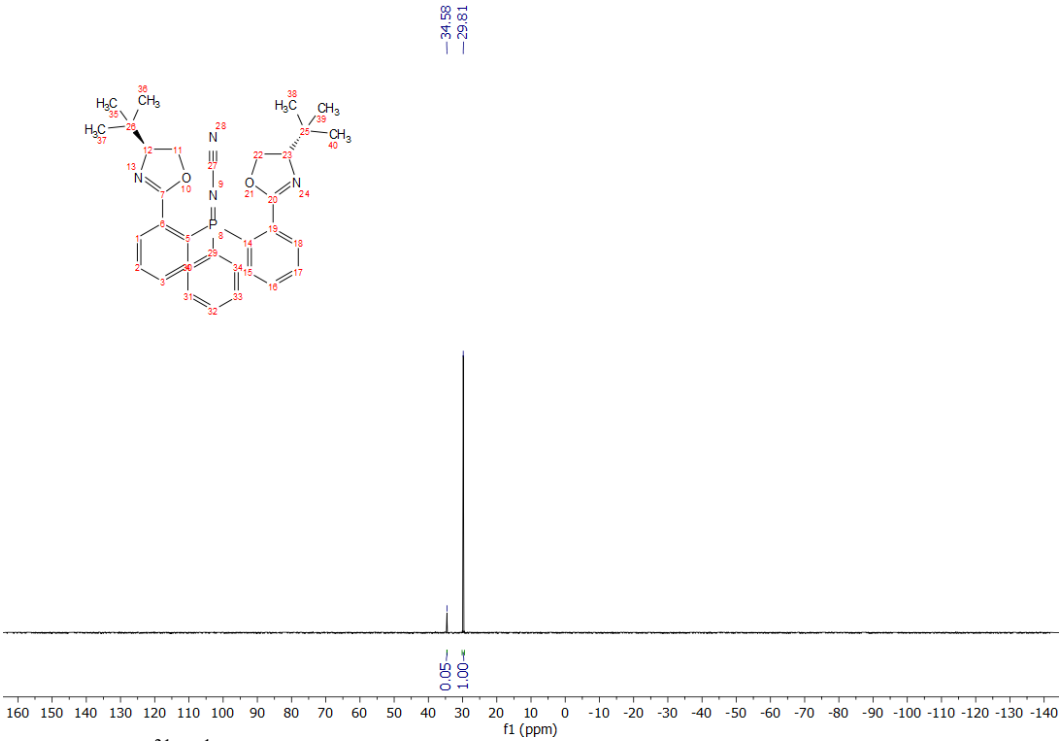


Figure S72. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of (*R,R*)-**27** in CD_3OD.

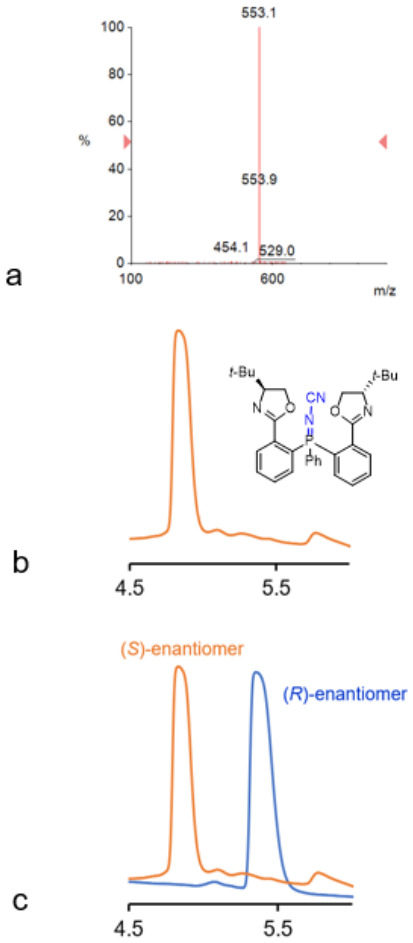
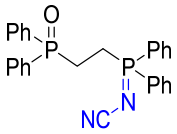


Figure S73. Chiral SFC-MS analysis associated with products **27** derived from the electrolysis reaction using the (*R,R*)- and (*S,S*)-enantiomers of the corresponding phosphine(III) starting material: (a) ESI MS^+ showing the desired PN peak at t_r = 4.83 min, (b) UV chromatogram (λ = 210 nm) of the product mixture derived from the *S*-enantiomer of the staring material, (c) overlay of the UV chromatograms (λ = 210 nm) associated with the products derived from the electrolysis reaction using the (*R,R*)- and (*S,S*)-enantiomers of starting material. Retention times for (*R*)-**27** is t_r = 5.35 min and for (*S*)-**27** is t_r = 4.83 min.



Synthesis of **28** was prepared following General Procedure **A** in 87% assay yield from 1,2-bis(diphenylphosphino)ethane (0.797 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (2.24 g, 12.00 mmol, 6 equiv). Purification was achieved using method 1 to afford a white solid. Virtual coupling[14] is observed in the $^{13}C\{^1H\}$ NMR spectrum which complicates the interpretation. Therefore, we have collected $^{13}C\{^1H,^{31}P\}$ NMR data to support our proposed structure which is consistent with our X-ray crystallographic data and HRMS data. Virtual coupling in the $^{13}C\{^1H\}$ NMR data for the structurally related compound 1,2-bis(diphenylphosphino)ethane is also known.[15] ^1H NMR (500 MHz, CD_2Cl_2) δ 7.81–7.43 (m, 8H), 7.70–7.65 (m, 4H), 7.61–7.54 (m, 8H), 2.79–2.82 (m, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ 134.15 (s), 131.71–131.63 (m), 130.05–129.95 (m), 126.38–125.24 (m), 118.03 (s), 21.51–20.50 (m). $^{13}C\{^1H, ^{31}P\}$ NMR (151 MHz, CD_2Cl_2) 134.11 (s), 131.62 (s), 129.95 (s), 125.70 (s), 118.03 (s), 20.92 (s).

$^{31}P\{^{1}H\}$ NMR (203 MHz, CD_2Cl_2) δ 28.44 (s, 2P). ESI$^+$ HRMS *m/z* calcd. for $C_{28}H_{25}N_4P_2$ ($[M + H]^+$) 479.1554, found 479.1548.

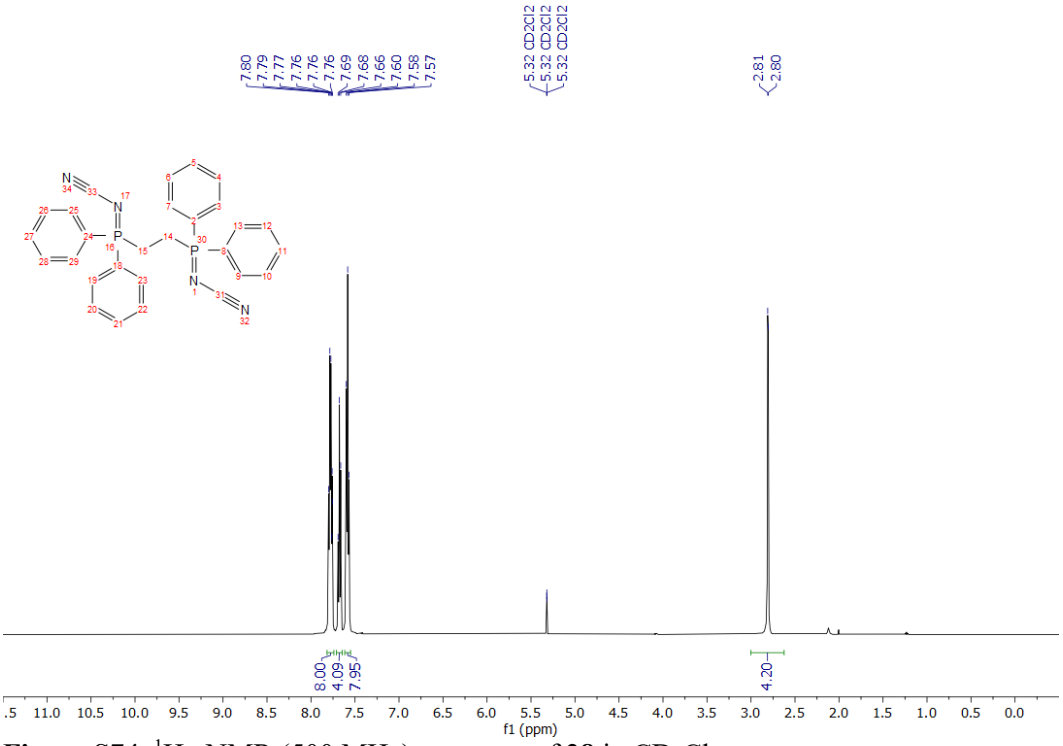


Figure S74. ^{1}H qNMR (500 MHz) spectrum of **28** in CD_2Cl_2.

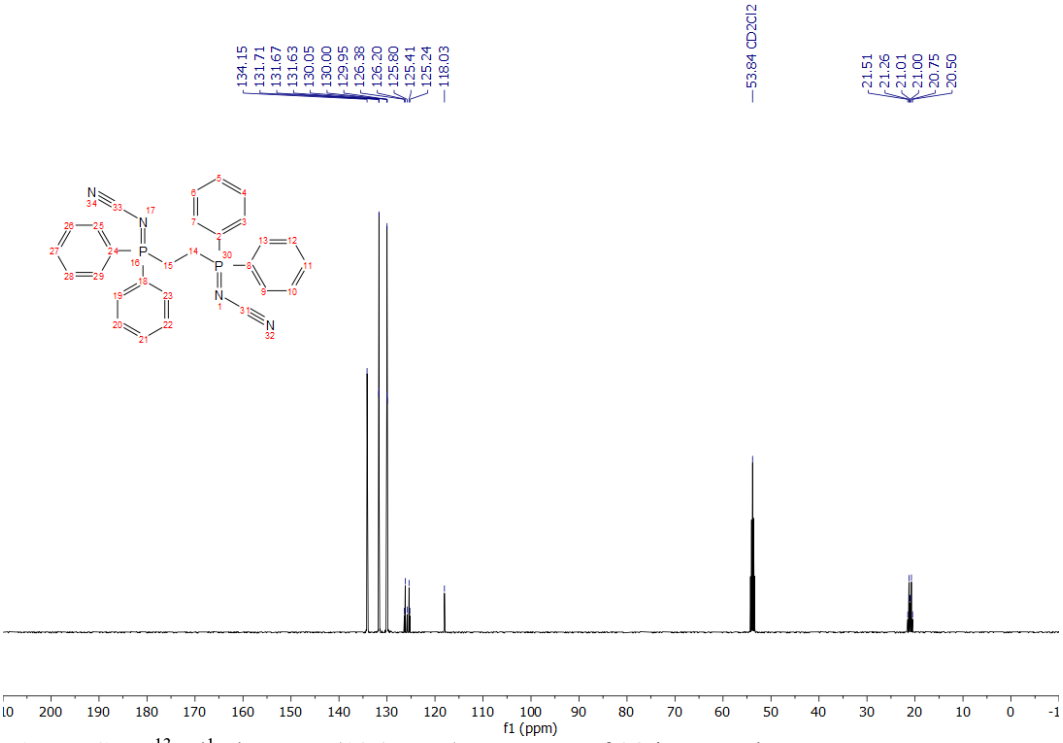


Figure S75. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **28** in CD_2Cl_2.

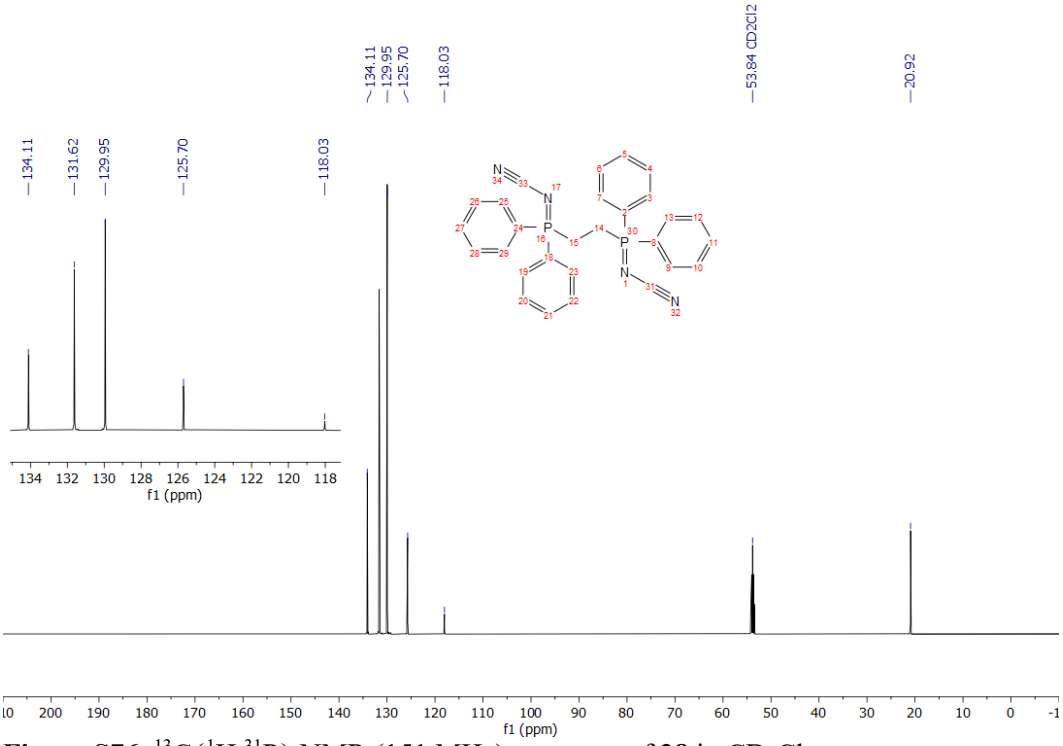


Figure S76. $^{13}C\{^{1}H,^{31}P\}$ NMR (151 MHz) spectrum of **28** in CD_2Cl_2.

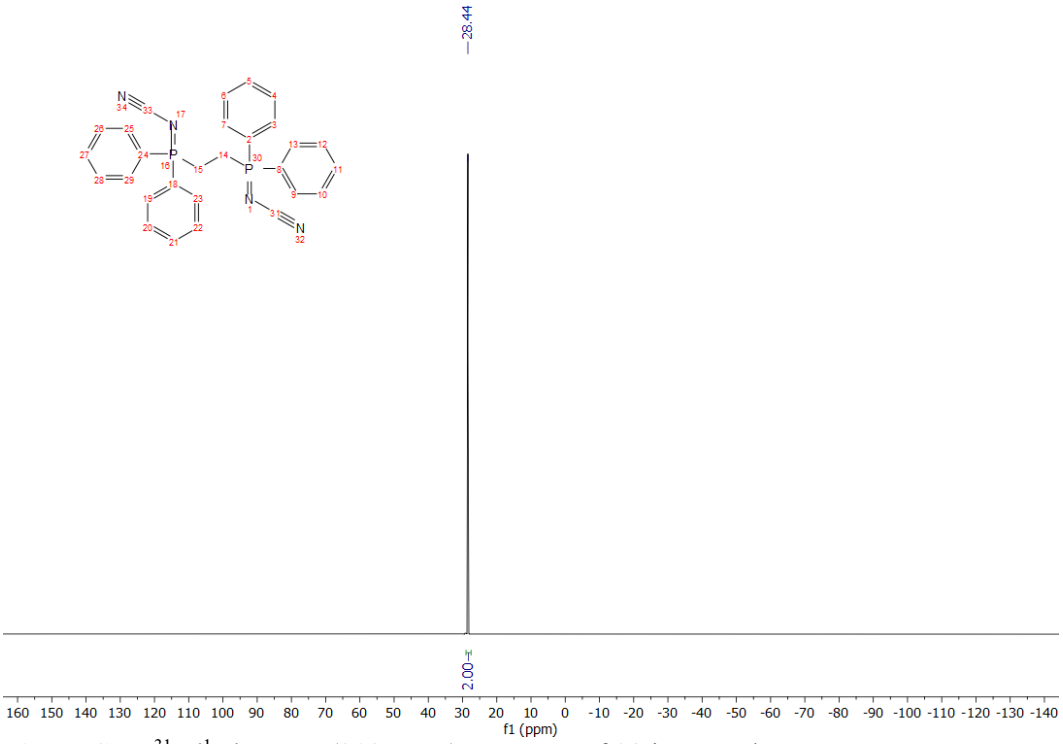
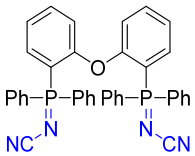


Figure S77. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **28** in CD_2Cl_2.



Synthesis of **29** was prepared following General Procedure **A** in 63% assay yield from bis[(2-diphenylphosphino)phenyl] ether (1.08 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (2.24 g, 12.0 mmol, 6 equiv). Purification was achieved using method 4 to afford a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.71 (t, J = 6.7 Hz, 2H), 7.63 – 7.44 (m, 22H), 7.34 (t, J = 7.5 Hz, 2H), 6.37 – 6.31 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ 158.48 (d, J = 2.9 Hz), 136.01 (d, J = 1.1 Hz), 134.08 (d, J = 7.5 Hz), 133.57 (d, J = 2.5 Hz), 133.12 (d, J = 2.5 Hz), 131.87 (d, J = 10.7 Hz), 131.73 (d, J = 10.7 Hz), 129.31 (d, J = 13.0 Hz), 129.08 (d, J = 12.8 Hz), 126.24 (d, J = 100.8 Hz), 125.37 (d, J = 100.7 Hz), 124.99 (d, J = 18.5 Hz), 120.60 (d, J = 6.6 Hz), 117.53, 117.12 (d, J = 105.2 Hz). ^{31}P{^{1}H} NMR (203 MHz, DMSO-d_6) δ 22.6 (s, 2P). ESI^{+} HRMS *m/z* calcd. for $C_{38}H_{29}N_4OP_2$ ([M + H]$^{+}$) 619.1816, found 619.1821.

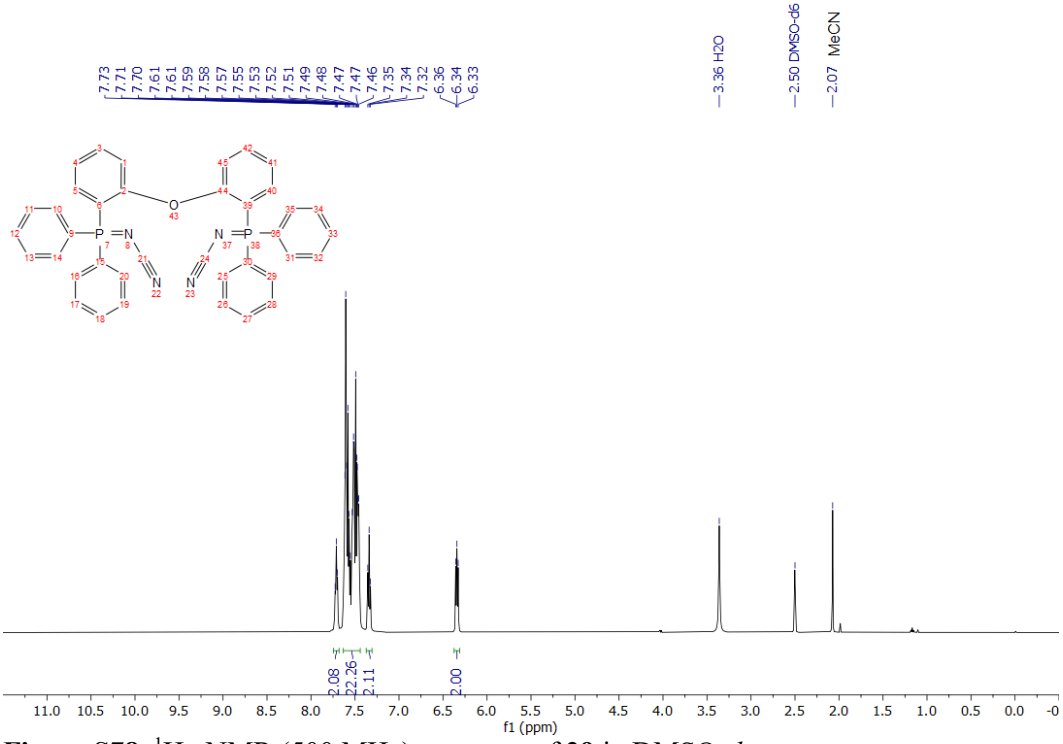


Figure S78. ^{1}H qNMR (500 MHz) spectrum of **29** in DMSO-d_6.

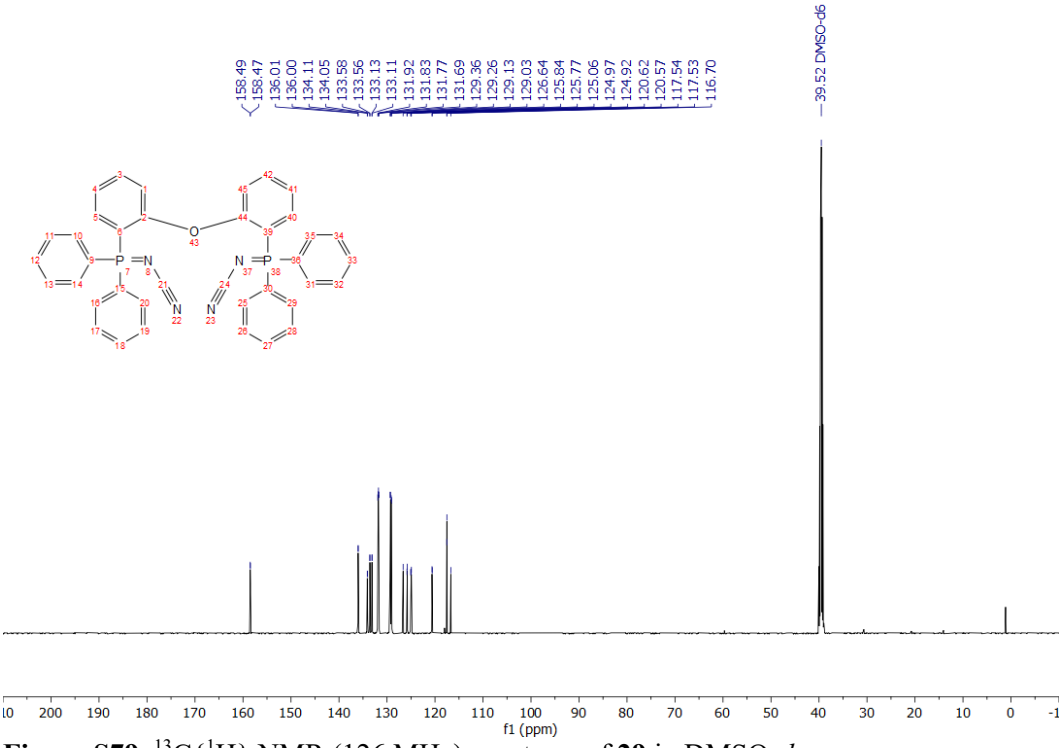


Figure S79. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **29** in DMSO-d_6.

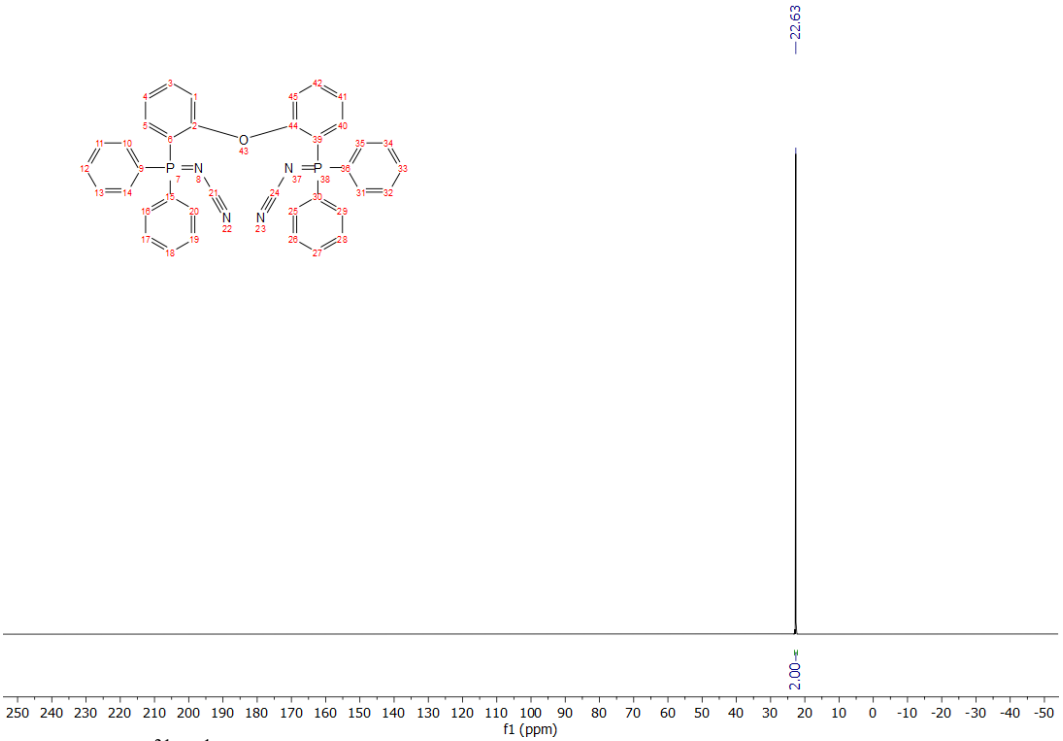
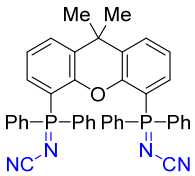


Figure S80. $^{31}P\{^{1}H\}$ NMR (203 MHz, DMSO-d_6) spectrum of **29**.



Synthesis of **30** was prepared following General Procedure **A** in 79% assay yield from xantphos (1.16 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (2.24 g, 12.0 mmol, 6 equiv). Purification was achieved using method 4 to afford a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.80 (d, J = 7.7 Hz, 2H), 7.64 (t, J = 7.4 Hz, 4H), 7.52 (td, J = 7.7, 3.4 Hz, 8H), 7.44 (dd, J = 13.4, 7.9 Hz, 8H), 7.13 (td, J = 7.7, 2.0 Hz, 2H), 6.76 (dd, J = 15.3, 7.6 Hz, 2H), 1.77 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 153.16 (d, J = 1.0 Hz), 135.64 (d, J = 10.1 Hz), 133.34 (d, J = 2.9 Hz), 133.09 (d, J = 2.3 Hz), 132.79 (d, J = 10.4 Hz), 131.71 (d, J = 6.1 Hz), 129.31 (d, J = 13.3 Hz), 128.53 (d, J = 110.5 Hz), 124.20 (d, J = 13.1 Hz), 118.92, 34.77, 33.35. ^{31}P{^{1}H} NMR (203 MHz, CD_2Cl_2) δ 27.97 (s, 2P). ESI^{+} HRMS *m/z* calcd. for $C_{41}H_{33}N_4OP_2$ ([M + H]$^{+}$) 659.2129, found 659.2118.

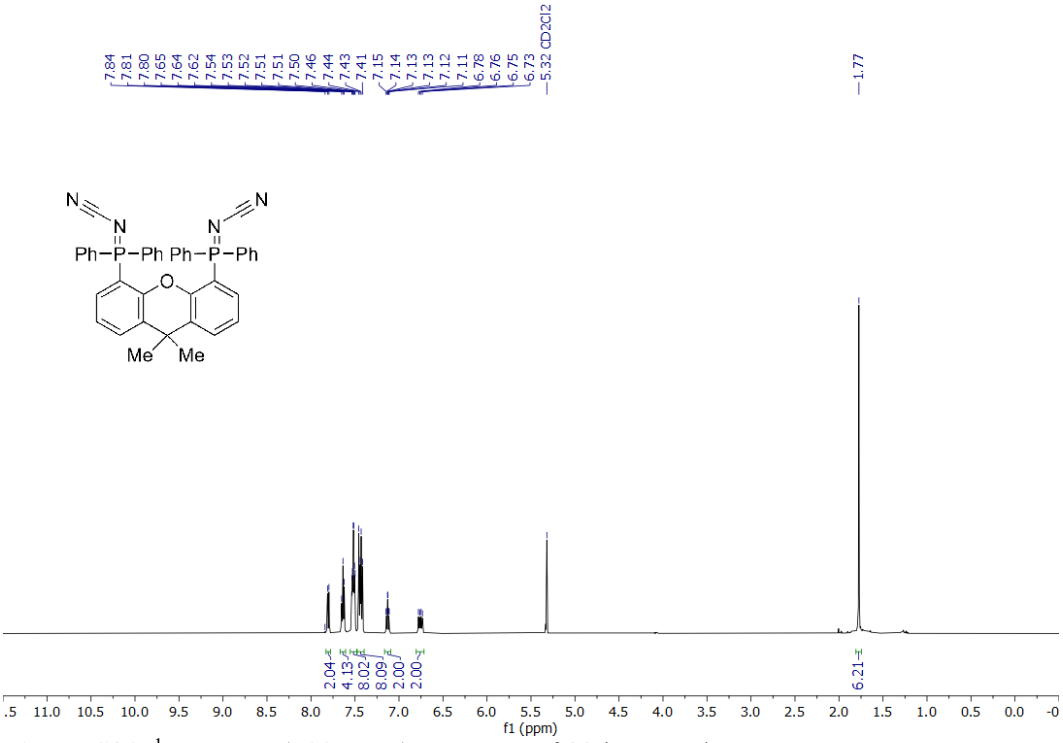


Figure S81. ^{1}H qNMR (500 MHz) spectrum of **30** in CD_2Cl_2.

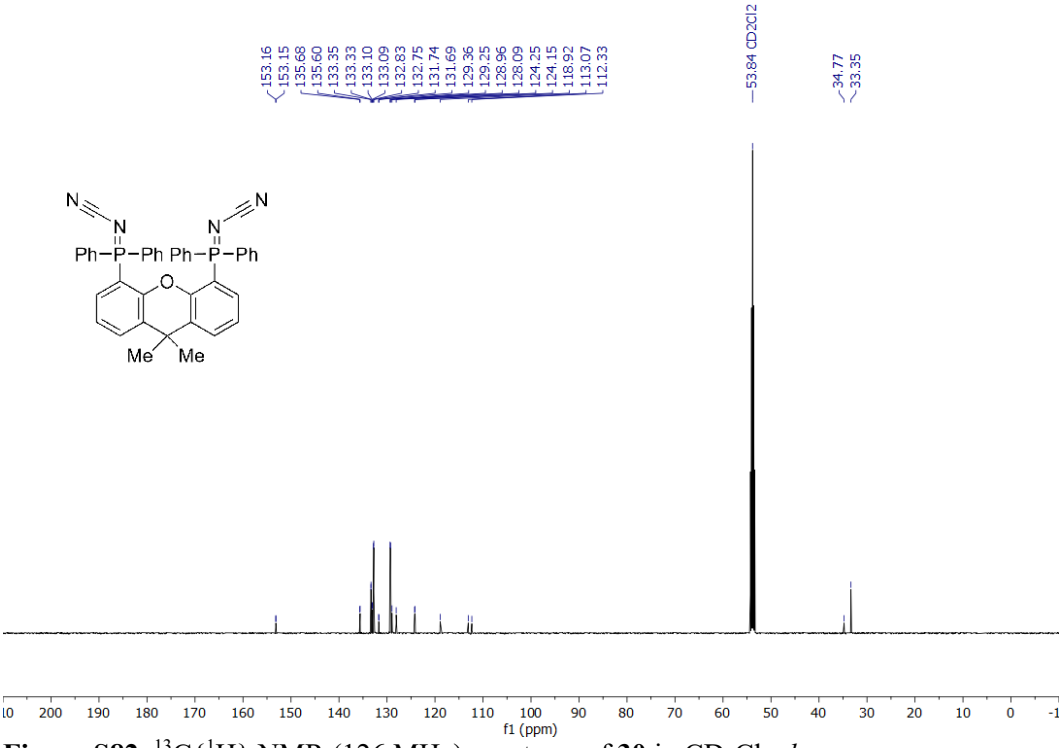


Figure S82. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **30** in CD_2Cl_2-d_6.

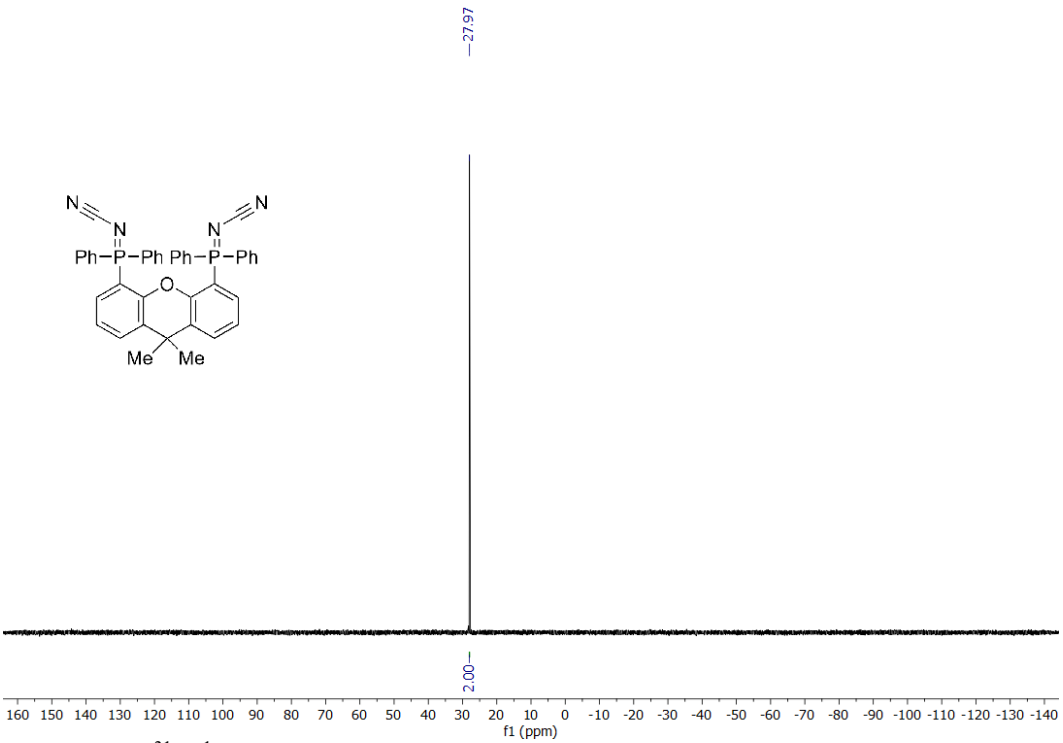


Figure S83. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **30** in CD_2Cl_2.

Synthesis of **31** was prepared following General Procedure **A** in 68% assay yield from 2,6-bis(diphenylphosphino)pyridine (0.895 mg, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (2.24 g, 12.0 mmol, 6 equiv). Purification was achieved using method 1 followed by method 2 to afford a white solid (isolated and characterized as the mono-solvate with MeOH). ^{1}H NMR (500 MHz, DMSO-d_6) δ ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.48 (dd, J = 4.4, 2.6 Hz, 3H), 7.79 – 7.68 (m, 4H), 7.61 – 7.40 (m, 16H), 4.08 (q, J = 5.2 Hz, 1H; signal from $CH_3O\mathit{H}$), 3.17 (d, J = 5.2 Hz, 3H; signals from $\mathit{CH_3}OH$). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ 152.42 (dd, J = 135.0, 19.6 Hz), 139.81 (t, J = 8.4 Hz), 133.84 (br s), 132.06 (d, J = 10.6 Hz), 131.05 (dd, J = 20.5, 3.2 Hz), 129.33 (d, J = 13.1 Hz), 124.95 (d, J = 101.6 Hz), 116.95, 48.57 (signal from $\mathit{C}H_3OH$). ^{31}P{^{1}H} NMR (203 MHz, DMSO-d_6) δ 17.46 (s, 2P). ESI^{+} HRMS *m/z* calcd. for $C_{31}H_{24}N_5P_2$ ([M + H]$^{+}$) 528.1507, found 528.1506.

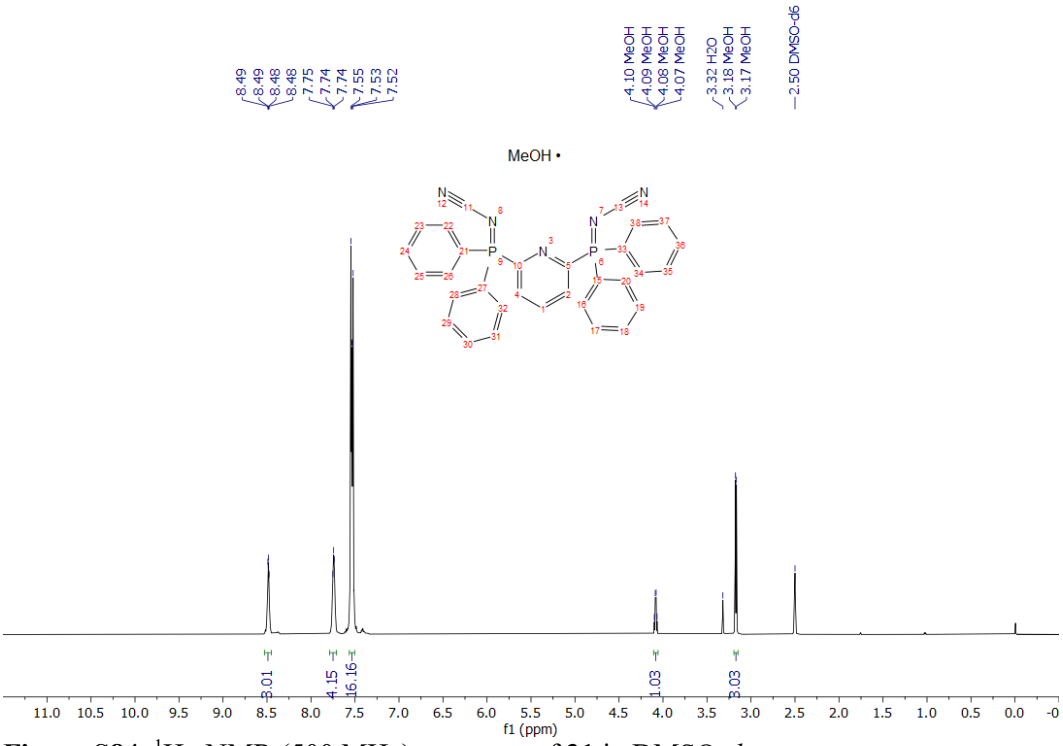


Figure S84. ^{1}H qNMR (500 MHz) spectrum of **31** in DMSO-d_6.

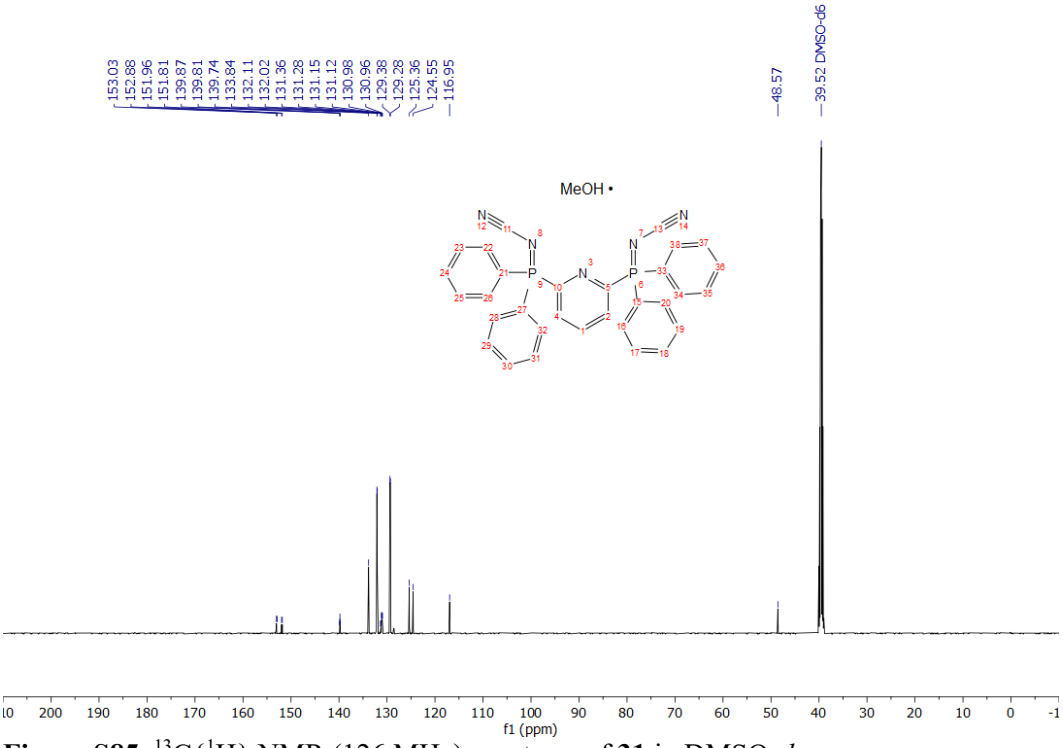


Figure S85. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **31** in DMSO-d_6.

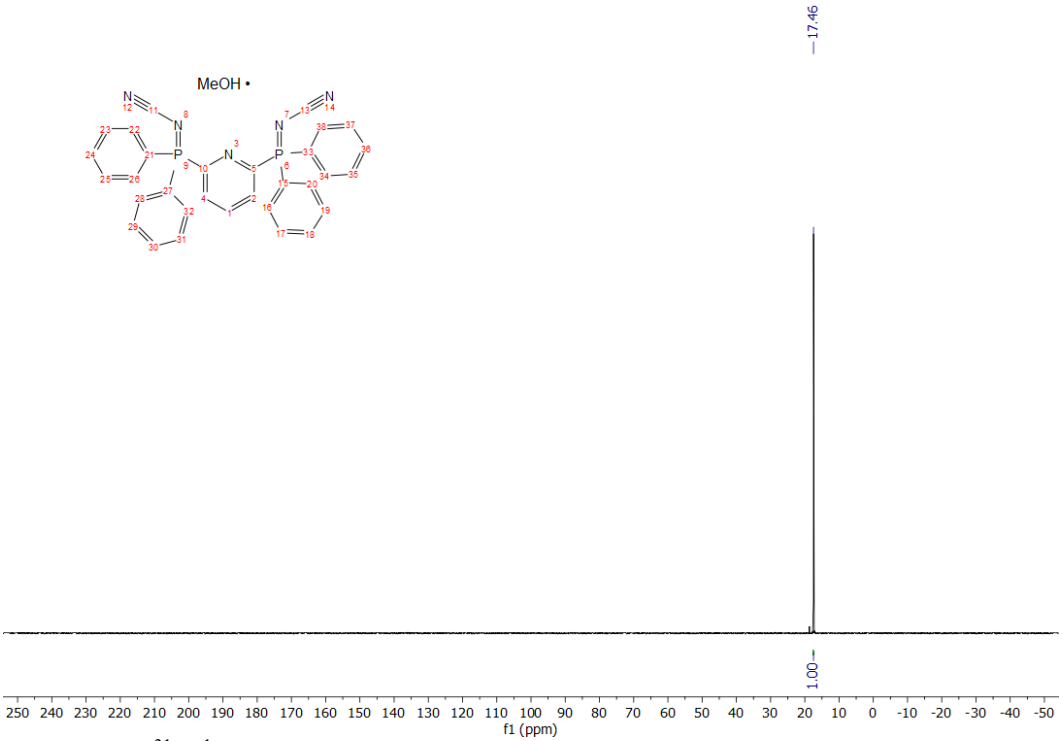
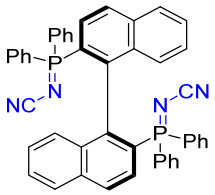


Figure S86. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **31** in DMSO-d_6.



Synthesis of (*S*)-**32** was prepared following General Procedure **B** in 62% assay yield from (*S*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthalene (0.622 g, 1.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 1 to afford a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.11 (dd, J = 8.7, 2.1 Hz, 2H), 7.98 (d, J = 8.3 Hz, 2H), 7.63 (t, J = 7.4 Hz, 2H), 7.59 – 7.45 (m, 14H), 7.41 – 7.30 (m, 8H), 6.91 (t, J = 7.7 Hz, 2H), 6.59 (d, J = 8.6 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ 140.80 (d, J = 4.7 Hz), 140.75 (d, J = 4.3 Hz), 134.15 (d, J = 2.3 Hz), 133.12 (d, J = 2.7 Hz), 132.82 (d, J = 2.8 Hz), 132.49 (d, J = 10.4 Hz), 132.41 (d, J = 12.0 Hz; left signal of this doublet appears as a shoulder under the signal at 132.45 ppm), 131.62 (d, J = 10.1 Hz), 128.95 (d, J = 12.8 Hz), 128.81 (d, J = 12.6 Hz), 128.62, 127.97, 127.81 (d, J = 14.6 Hz), 127.09 (d, J = 96.1 Hz), 126.95, 126.65 (d, J = 100.7 Hz), 126.32, 122.74 (d, J = 112.1 Hz), 116.88. ^{31}P{^{1}H} NMR (203 MHz, DMSO-d_6) δ 25.83 (s, 2P). ESI^{+} HRMS *m/z* calcd. for $C_{46}H_{33}N_4P_2$ ([M + H]$^{+}$) 703.2180, found 703.2179.

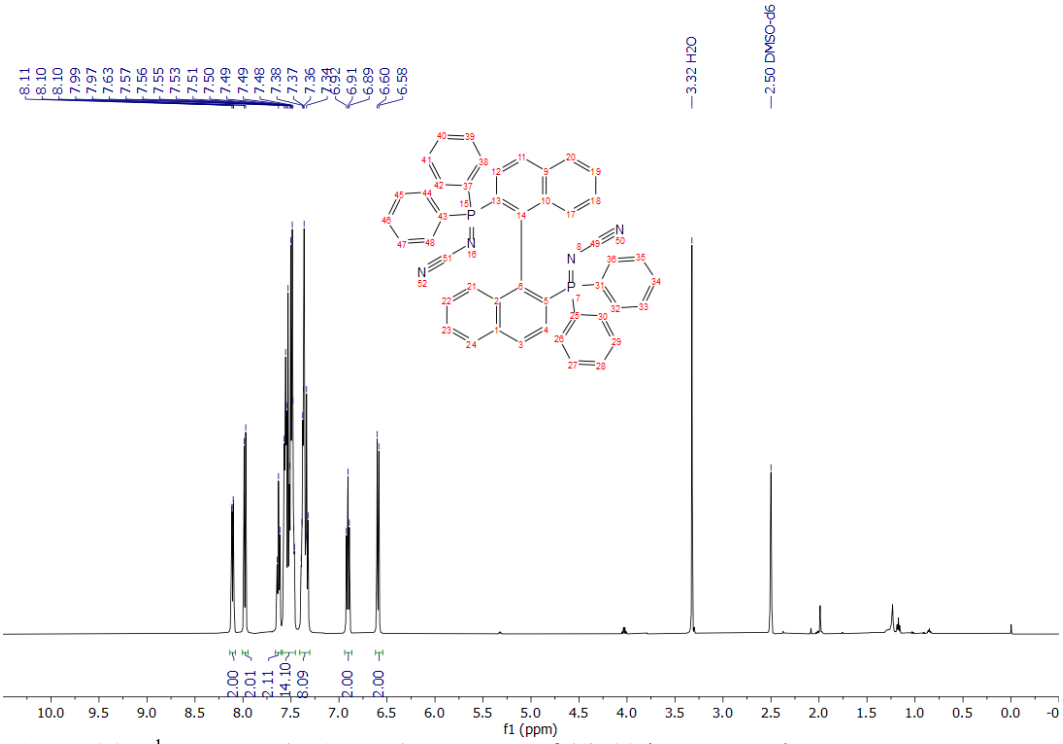


Figure S87. ^{1}H qNMR (500 MHz) spectrum of (*S*)-**32** in DMSO-d_6.

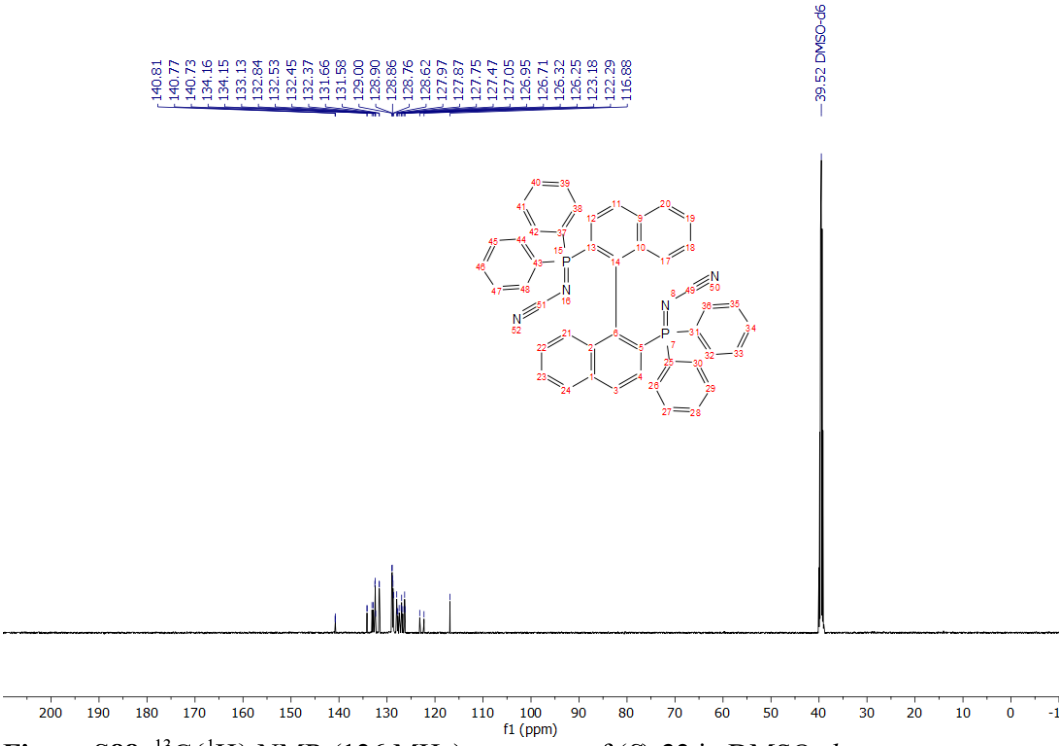


Figure S88. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of (*S*)-**32** in DMSO-d_6.

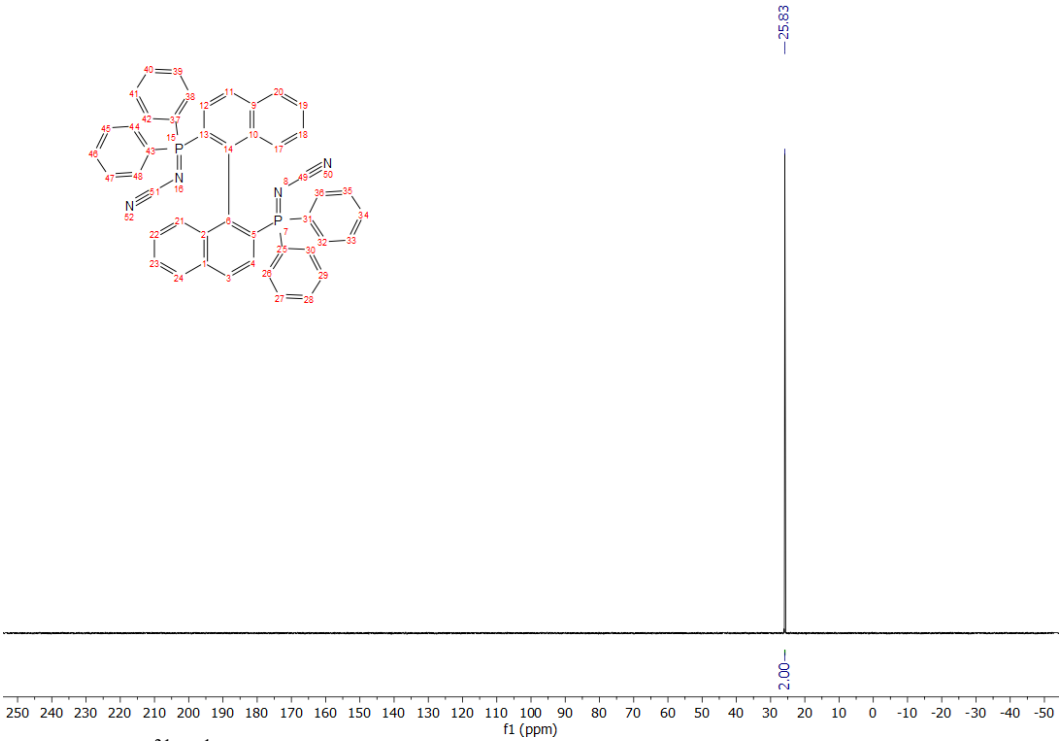
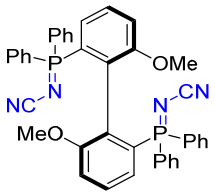


Figure S89. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of (*S*)-**32** in DMSO-d_6.



Synthesis of (*S*)-**33** was prepared following General Procedure **A** in 68% assay yield from (*S*)-BIPHEP (1.17 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide 2.24 g, 12.00 mmol, 6 equiv). Purification was achieved using method 4 to afford a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.69 – 7.52 (m, 16H), 7.46 (td, *J* = 7.7, 3.1 Hz, 4H), 7.37 (td, *J* = 8.1, 4.0 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 6.93 (dd, *J* = 14.8, 7.8 Hz, 2H), 3.18 (s, 6H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 157.93 (d, *J* = 15.1 Hz), 133.35 (d, *J* = 10.4 Hz), 133.16 (d, *J* = 2.9 Hz), 133.05 (d, *J* = 2.9 Hz), 132.80 (d, *J* = 10.0 Hz), 129.57 (d, *J* = 4.1 Hz), 129.51 (d, *J* = 4.1 Hz), 129.22 (d, *J* = 6.3 Hz), 129.27 – 129.27 (m, overlapping signals prevent the interpretation of the multiplicity and coupling constant of additional signals in this region), 129.12 (d, *J* = 6.1 Hz), 129.09 (d, *J* = 7.3 Hz), 128.32Me2 (d, *J* = 14.9 Hz), 126.51 (d, *J* = 14.2 Hz), 126.17 (d, *J* = 113.2 Hz), 117.88, 115.01 (d, *J* = 2.8 Hz), 55.17. ^{31}P{^{1}H} NMR (203 MHz, CD_2Cl_2) δ 25.38 (s, 2P). ESI^{+} HRMS *m/z* calcd. for $C_{40}H_{33}N_4O_2P_2$ ([M + H]$^{+}$) 663.2078, found 663.2090.

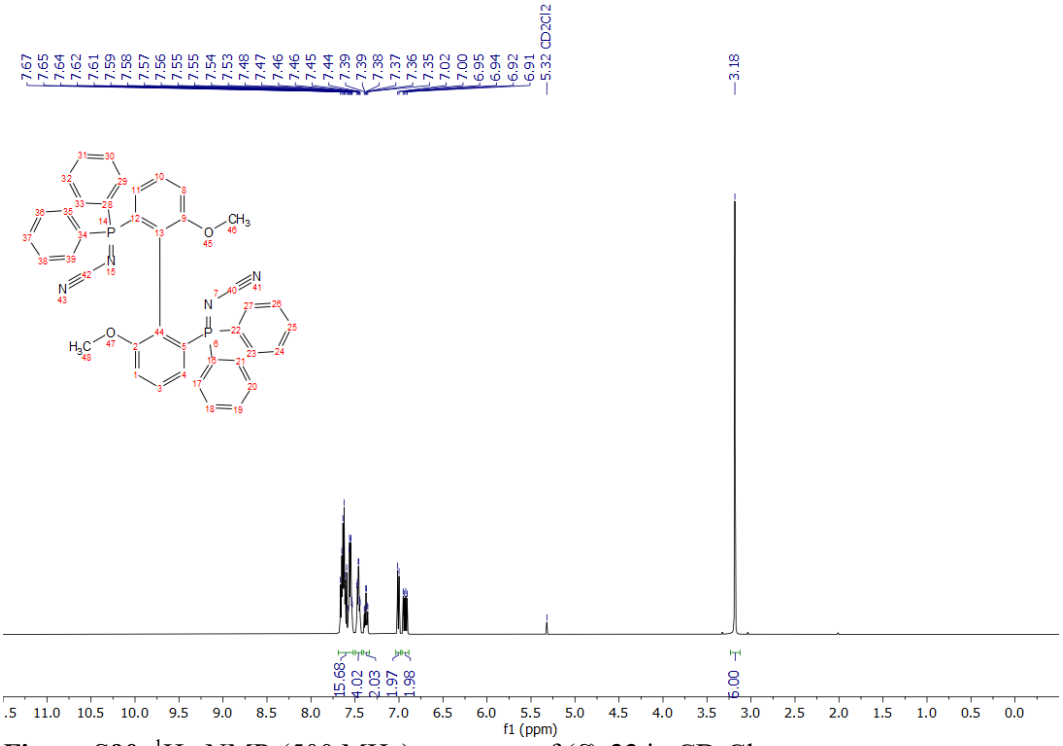


Figure S90. ^{1}H qNMR (500 MHz) spectrum of (*S*)-**33** in CD_2Cl_2.

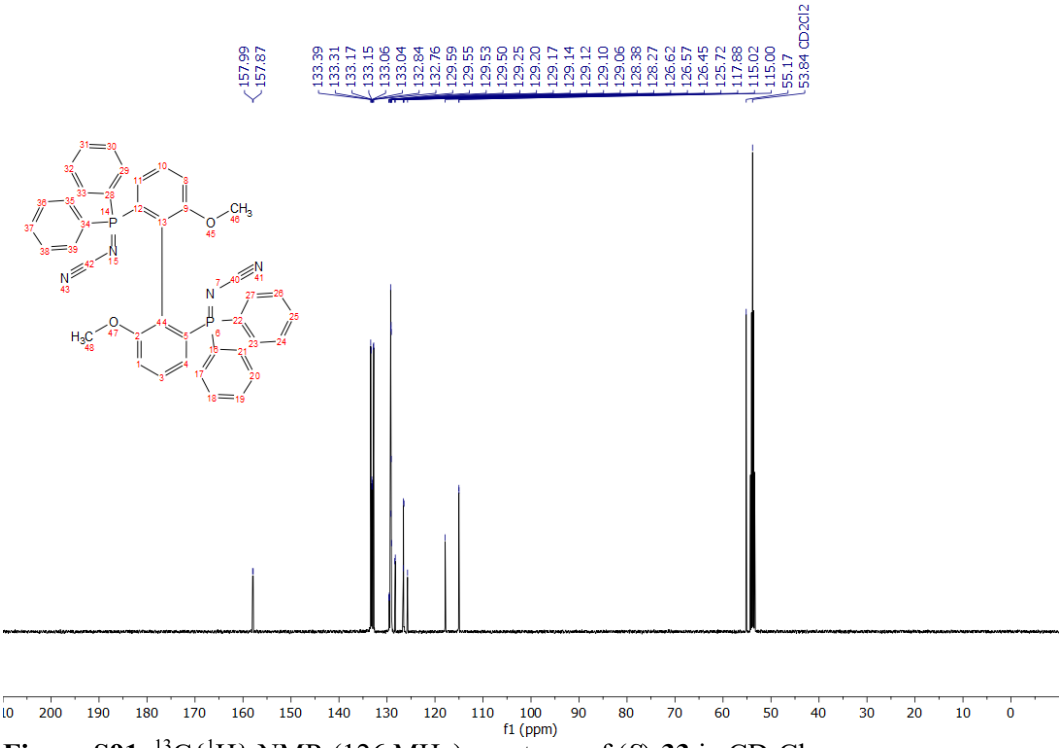


Figure S91. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of (*S*)-**33** in CD_2Cl_2.

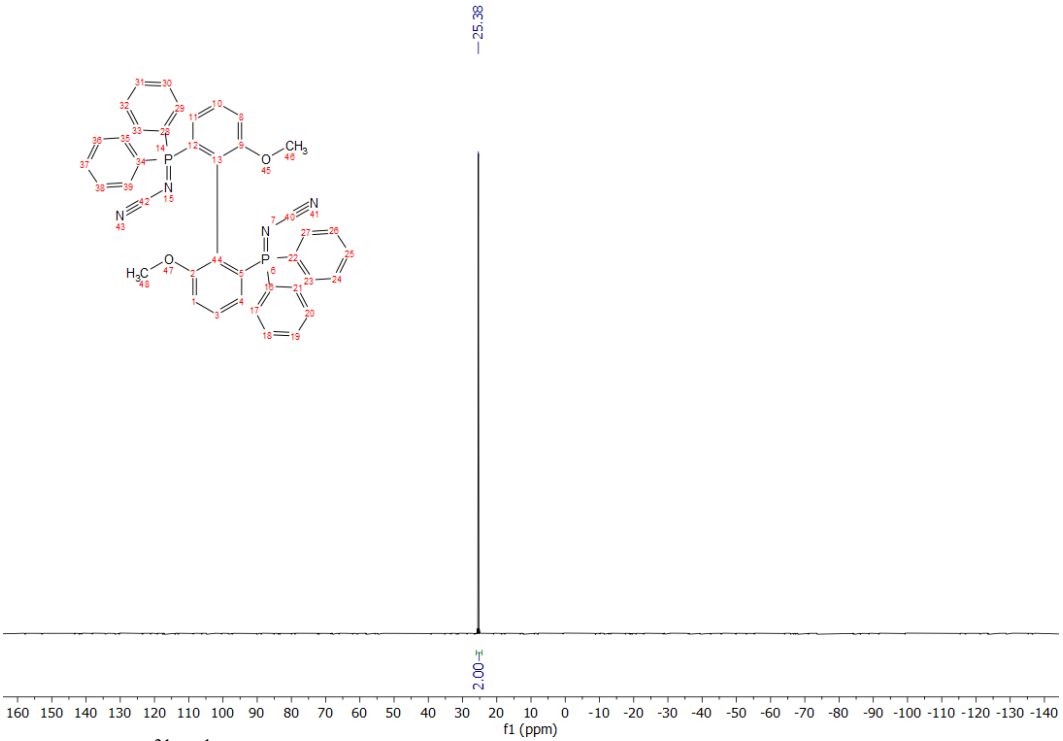
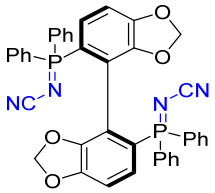


Figure S92. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of (*S*)-**33** in CD_2Cl_2.



Synthesis of (*R*)-**34** was prepared following General Procedure **A** in 43% assay yield from (*R*)-SEGPHOS (1.22 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (2.24 g, 12.00 mmol, 6 equiv). Purification was achieved using method 4 to afford a white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74 – 7.58 (m, 16H), 7.53 (td, J = 7.5, 3.5 Hz, 4H), 6.98 (dd, J = 8.2, 2.5 Hz, 2H), 6.89 (dd, J = 15.4, 8.2 Hz, 2H), 5.97 – 5.86 (m, 2H), 5.39 – 5.30 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6) δ 168.00, 150.61 (d, J = 3.0 Hz), 146.85 (d, J = 17.0 Hz), 133.17 (d, J = 2.8 Hz), 133.08 (d, J = 3.0 Hz), 132.47 (d, J = 10.5 Hz), 132.06 (d, J = 10.3 Hz), 130.47 (d, J = 14.7 Hz), 128.90 (d, J = 12.5 Hz), 127.89 (d, J = 101.0 Hz), 127.34 (d, J = 101.3 Hz), 117.30 (dd, J = 3.1, 10.1 Hz), 117.34 (d, J = 114.7 Hz), 117.24, 108.39 (d, J = 17.3 Hz), 102.12. ^{31}P{^{1}H} NMR (203 MHz, DMSO-d_6) δ 25.16 (s, 2P). ESI^{+} HRMS *m/z* calcd. for $C_{40}H_{29}N_4O_4P_2$ ([M + H]$^{+}$) 691.1664, found 691.1665. Chiral SFC method used to determine ee: A Waters SFC-MS equipped with an Chirapak OJ-3 column (3 µm particle size, 4.6 mm ID × 150 mm length; part number 17524) operating at 40 °C with a 2.5 mL/min flow rate of a binary eluent mixture (eluent A and B, prepared as described below). Eluent A = CO_2, eluent B = 25 mM isobutylamine in methanol. The method used a gradient from 99.0%A, 1.0%B at t = 0 min to 75.0%A, 25.0%B at t = 11.00 min, followed by holding the gradient at 75.0%A, 25.0%B until at t = 11.80 min, and a subsequent gradient reaching 99.0%A, 1.0%B at t = 11.90 min and holding that mixture until t = 6.00 min.

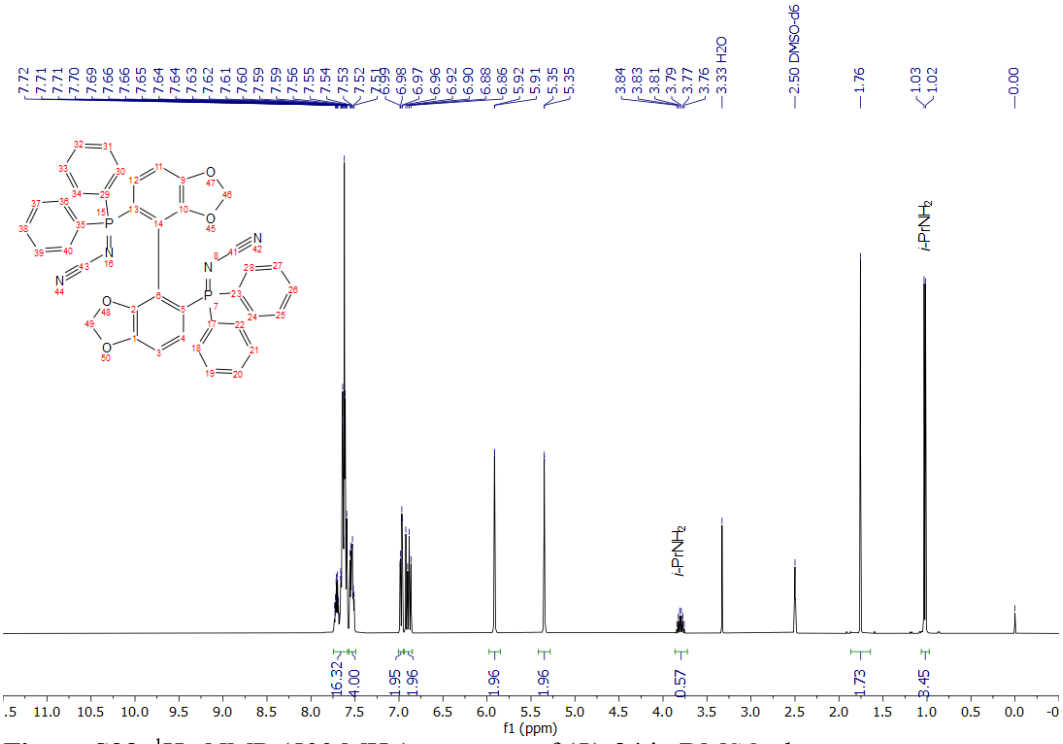


Figure S93. ^{1}H qNMR (500 MHz) spectrum of (*R*)-**34** in DMSO-d_6.

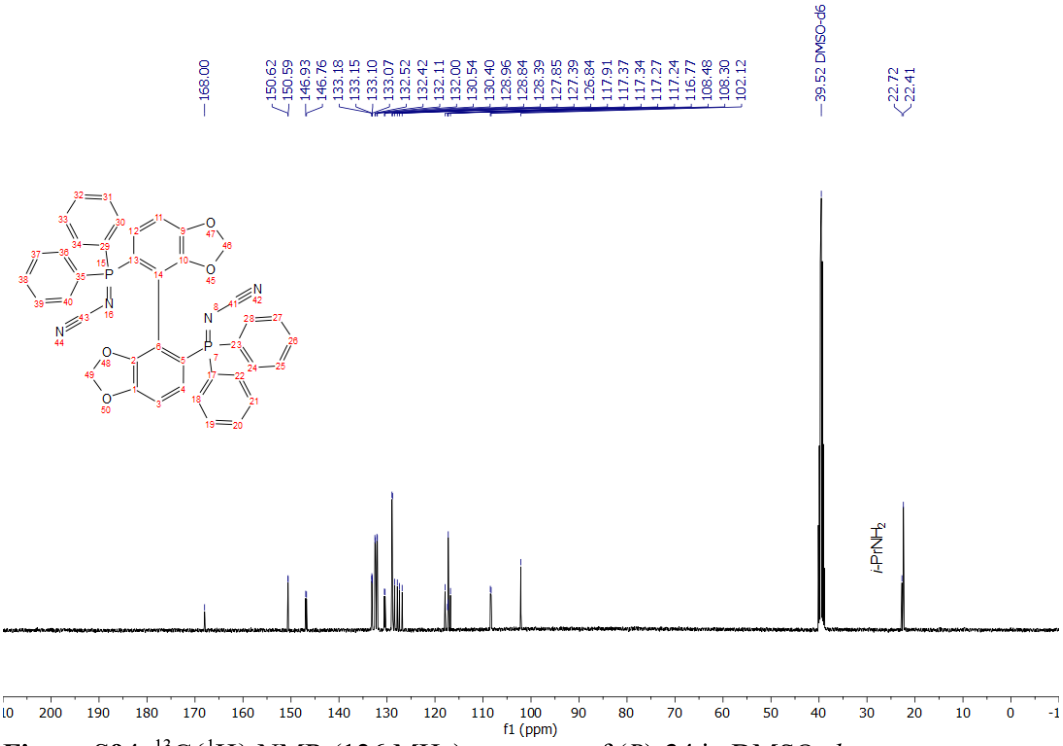


Figure S94. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of (*R*)-**34** in DMSO-d_6.

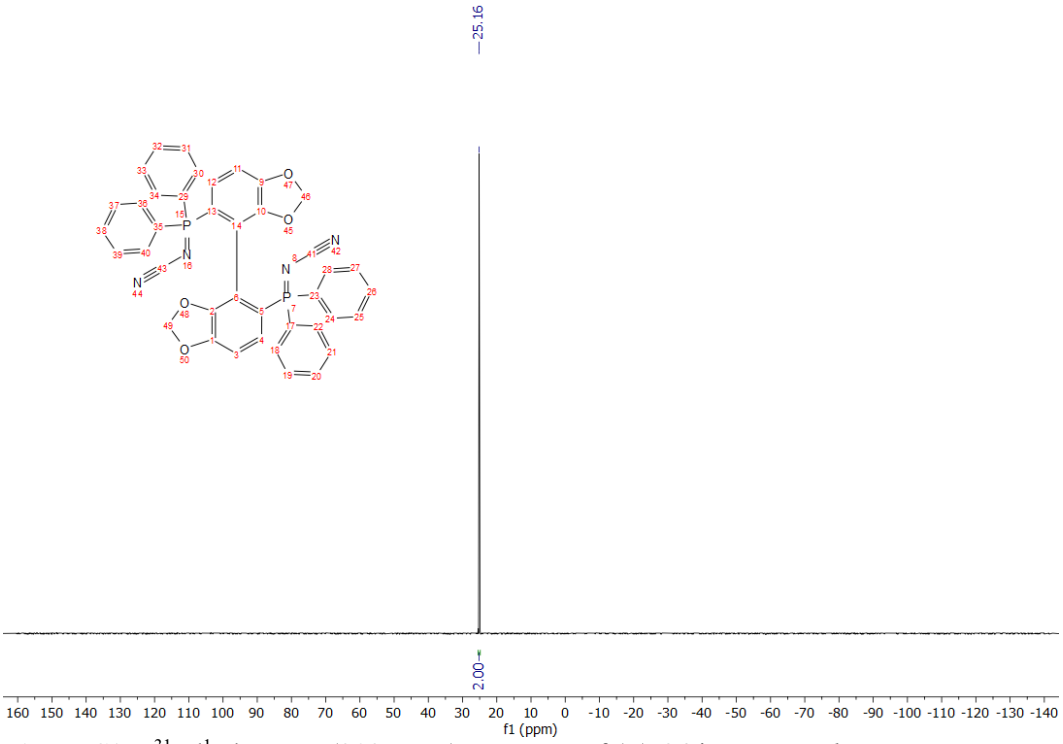


Figure S95. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of (*R*)-**34** in DMSO-d_6.

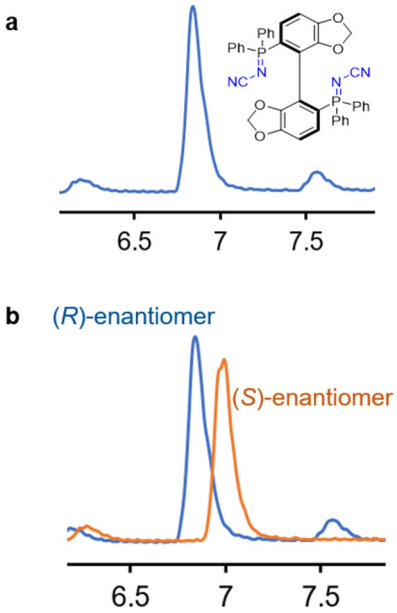
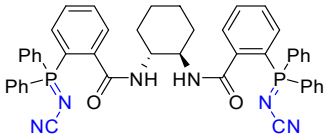


Figure S96. Chiral SFC-MS analysis associated with products **34** derived from the electrolysis reaction using the *R*- and *S*-enantiomers corresponding phosphine(III) starting material: (a) UV chromatogram (λ = 210 nm) of the product mixture derived from the *R*-enantiomer of the staring material, (b) overlay of the UV chromatograms (λ = 210 nm) associated with the products derived from the electrolysis reaction using the *R*- and *S*-enantiomers of starting material. Retention times for (*R*)-**34** is t_r = 6.85 min and for (*S*)-**34** is t_r = 6.99 min.



Synthesis of **35** was prepared following General Procedure **A** in 76% assay yield from (*S,S*)-DACH (1.58 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (2.24 g, 12.0 mmol, 6 equiv). Purification was achieved using method 1 to afford a white solid ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.24 (d, J = 7.7 Hz, 2H), 8.03 (ddd, J = 14.1, 5.4, 3.4 Hz, 2H), 7.80–7.70 (m, 10H), 7.69–7.59 (m, 6H), 7.50 (dt, J = 13.0, 6.3 Hz, 10H), 3.08 (s, 2H), 1.50 (d, J = 6.5 Hz, 2H), 1.02 (br s, 4H), 0.94–0.83 (m, 2H). ^{13}C{^{1}H} NMR (DMSO-d_6) δ 165.82, 140.39 (d, J = 7.8 Hz), 134.53 (d, J = 8.5 Hz), 133.30, 132.72, 132.36 (d, J = 10.3 Hz), 132.16, 131.60 (d, J = 10.0 Hz), 130.63 (d, J = 12.0 Hz), 128.92–128.09 (m), 127.54 (d, J = 35.2 Hz), 124.66 (d, J = 102.7 Hz), 118.04, 52.88, 29.88, 24.31. ^{31}P{^{1}H} NMR (203 MHz, DMSO-d_6) δ 27.96 (s, 2P). ESI^{+} LRMS *m/z* calcd. for $C_{46}H_{41}N_6O_2P_2$ ([M + H]$^{+}$) 771.8, found 772.0.

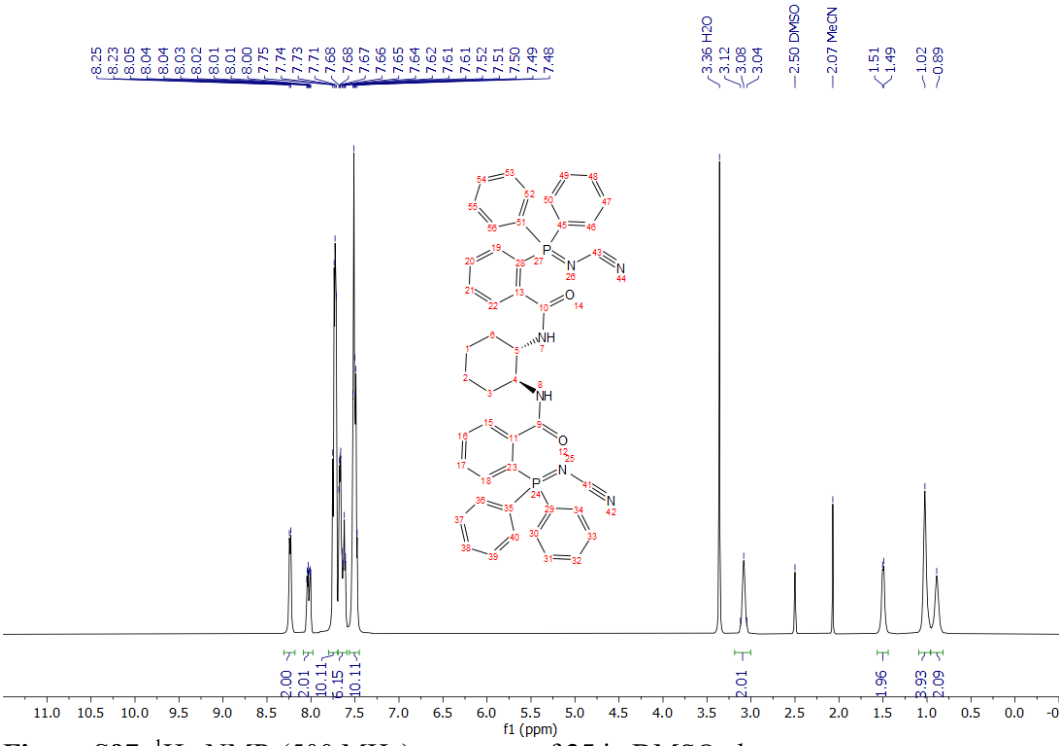


Figure S97. ^{1}H qNMR (500 MHz) spectrum of **35** in DMSO-d_6.

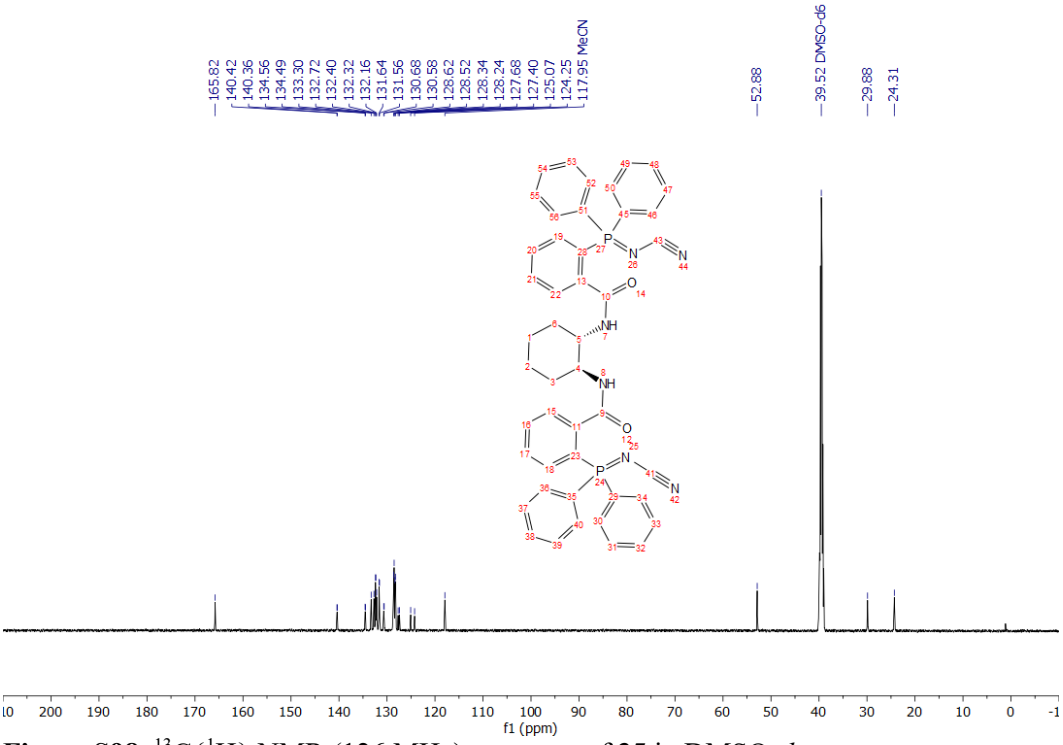


Figure S98. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **35** in DMSO-d_6.

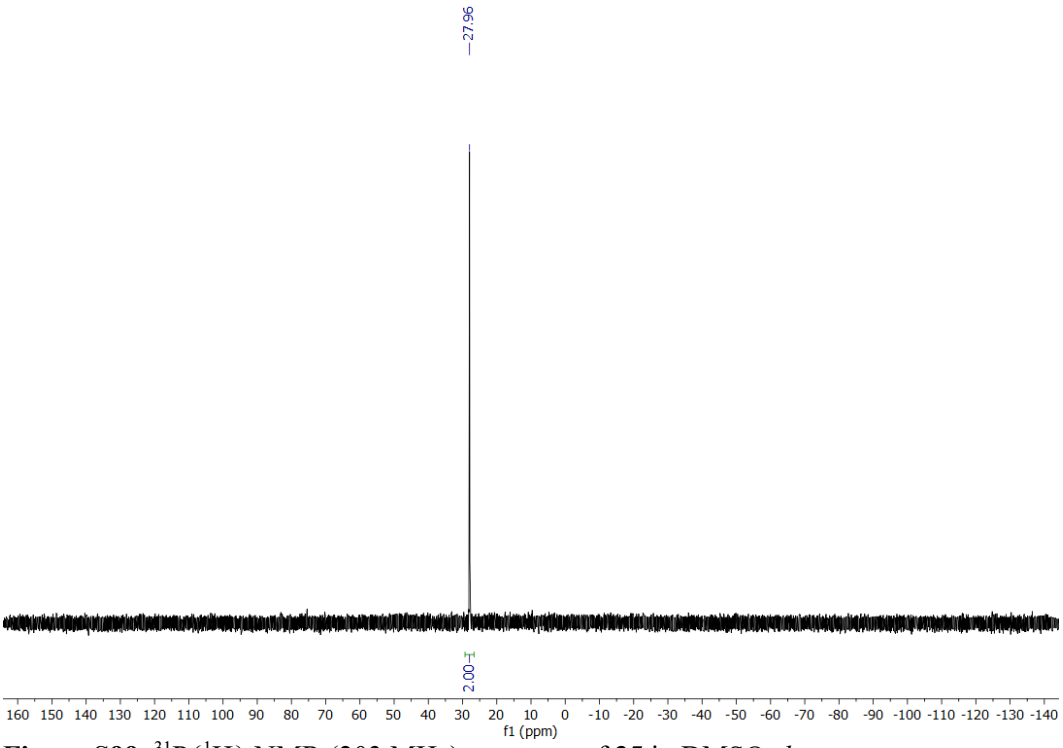
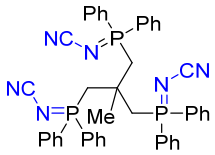


Figure S99. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **35** in DMSO-d_6.



Synthesis of **36** was prepared following General Procedure **A** in 44% assay yield from 1,1,1-tris(diphenylphosphinomethyl)ethane (1.25 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (3.36 g, 18.00 mmol, 9 equiv). Purification was achieved using method 1 to afford a white solid. ^{1}H NMR (500 MHz, CD_3OD) δ 7.78 (dd, J = 12.6, 7.7 Hz, 12H), 7.71 (t, J = 7.3 Hz, 6H), 7.63 (td, J = 7.6, 3.2 Hz, 12H), 3.43 (d, J = 12.1 Hz, 6H), 0.80 (s, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3OD) δ 134.98 (d, J = 2.7 Hz), 132.48 (d, J = 10.3 Hz), 130.82 (d, J = 12.7 Hz), 128.42 (d, J = 96.0 Hz), 119.75, 40.76 (q, J = 5.5 Hz), 38.65 (dt, J = 70.5, 7.0 Hz), 27.65 (d, J = 5.6 Hz). $^{31}P\{^{1}H\}$ NMR (203 MHz, CD_3OD) δ 26.47 (s, 3P). ESI^{+} HRMS *m/z* calcd. for $C_{44}H_{40}N_6P_3$ ($[M + H]^{+}$) 745.2527, found 745.2524.

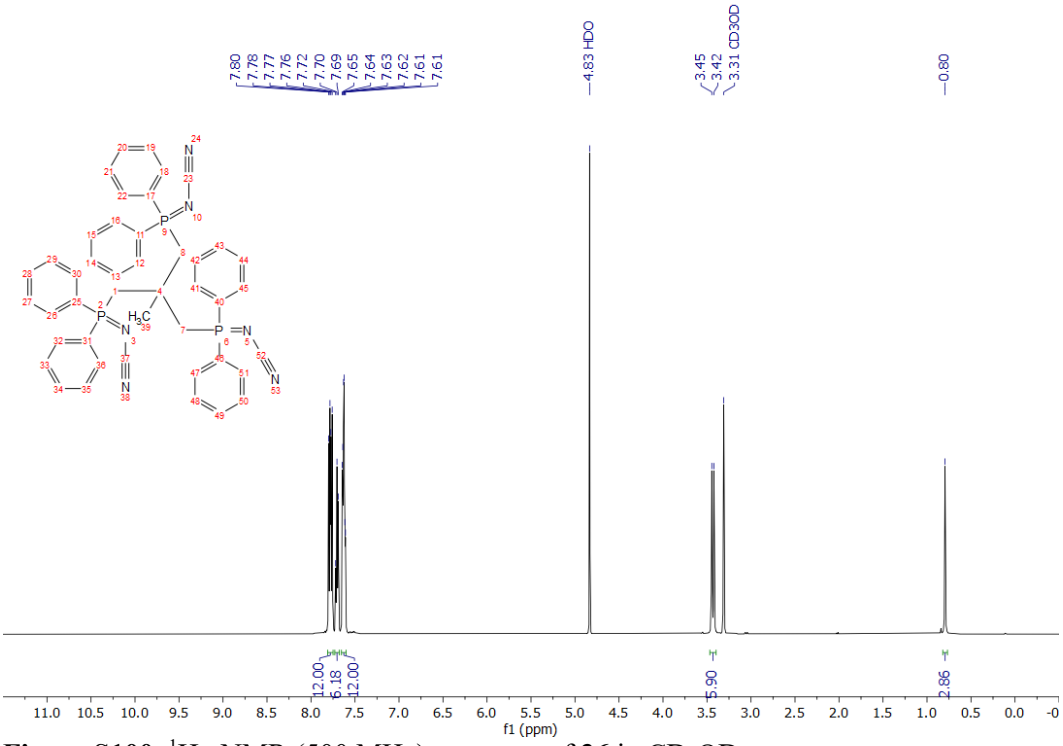


Figure S100. ^{1}H qNMR (500 MHz) spectrum of **36** in CD_3OD.

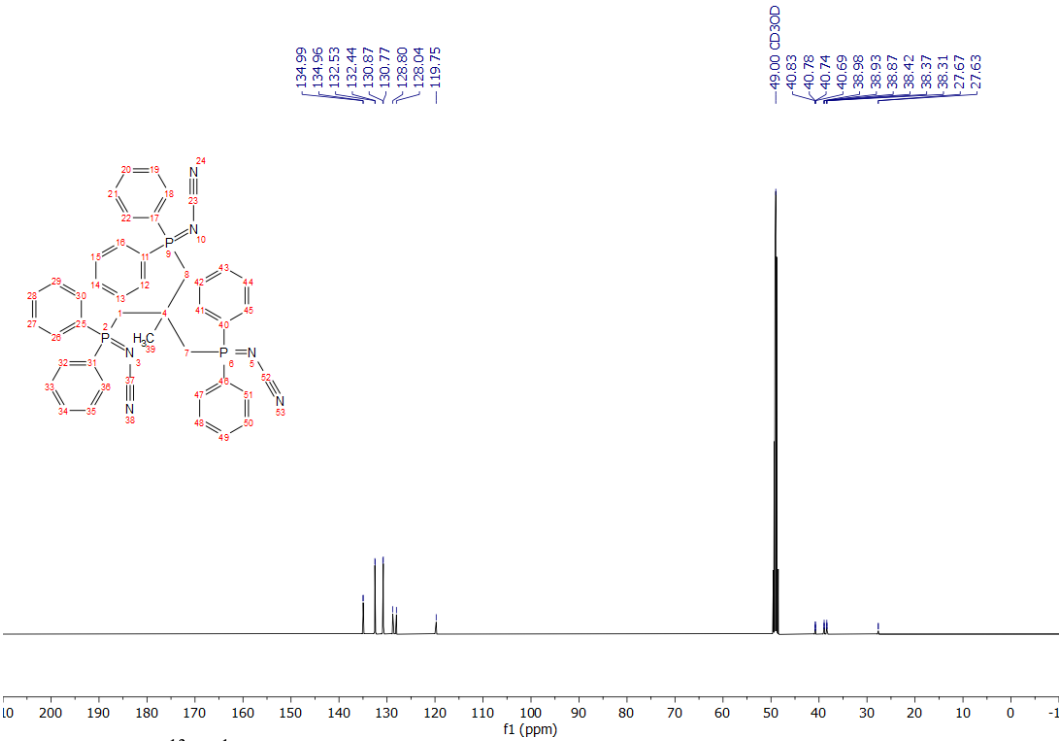


Figure S101. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **36** in CD_3OD.

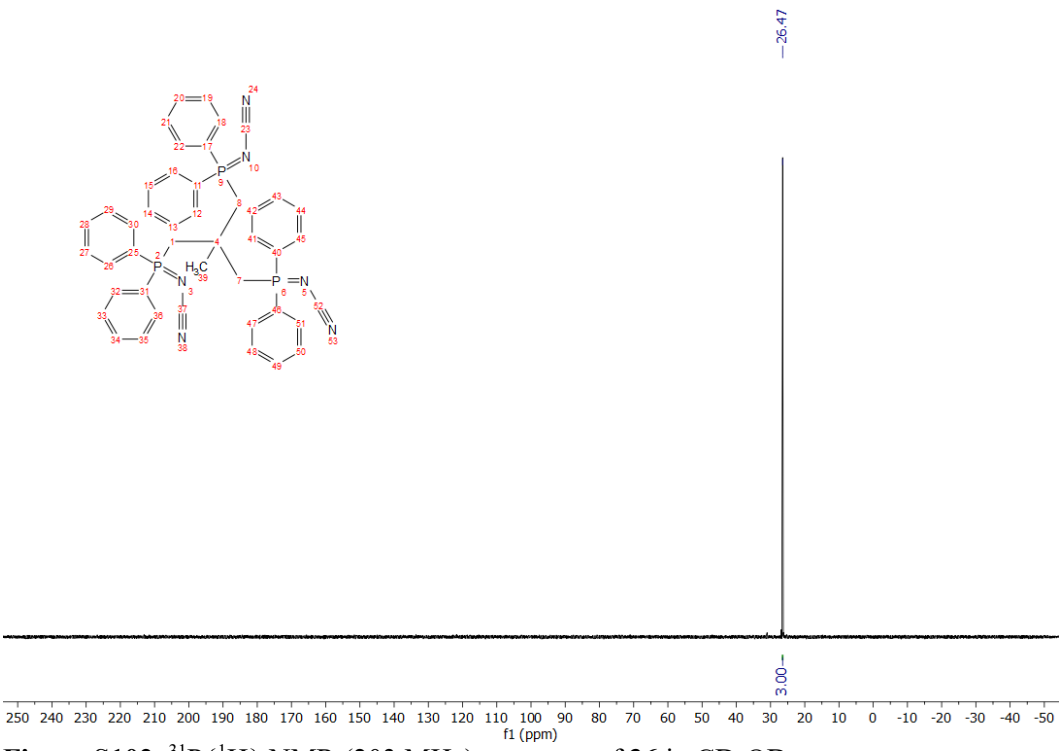
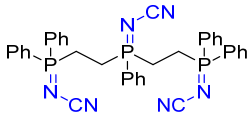


Figure S102. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **36** in CD_3OD.



Synthesis of **37** was prepared following General Procedure **A** in 74% assay yield (average of 2 reactions) from bis(2-diphenylphosphinoethyl)phenylphosphine (1.25 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (3.36 g, 18.00 mmol, 9 equiv). Purification was achieved using method 1 to afford a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.82 – 7.42 (m, 25H), 2.97 – 2.14 (m, 8H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ 134.74 (d, J = 2.9 Hz), 134.22 (dd, J = 9.7, 2.9 Hz), 131.86 (d, J = 10.3 Hz), 131.67 (d, J = 10.2 Hz), 131.59 (d, J = 10.1 Hz), 131.59 (dd, 10.1, 13.0 Hz), 131.10 (dd, J = 13.3, 9.5 Hz), 130.49 (d, J = 12.5 Hz), 130.03 (d, J = 24.9 Hz), 130.03, 129.32 (dd, J = 11.8, 8.5 Hz), 125.78 (d, J = 98.8 Hz), 125.44 (d, J = 99.3 Hz), 123.06 (d, J = 96.2 Hz), 21.10 (dd, J = 41.5, 4.0 Hz), 20.57 (dd, J = 46.7, 4.1 Hz). $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2) δ 36.72 (d, J = 52.0 Hz, 1P), 28.25 (d, J = 51.9 Hz, 2P). ESI^{+} HRMS *m/z* calcd. for $C_{37}H_{34}N_6P_3$ ($[M + H]^{+}$) 655.2058, found 655.2052.

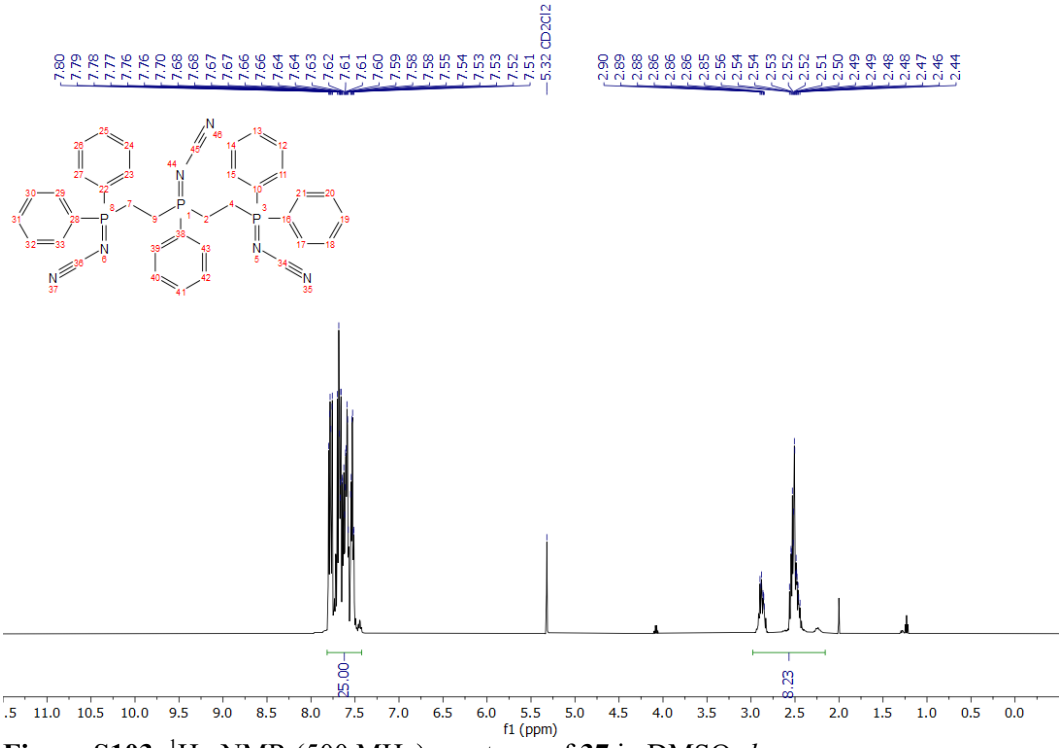


Figure S103. ^{1}H qNMR (500 MHz) spectrum of **37** in DMSO-d_6.

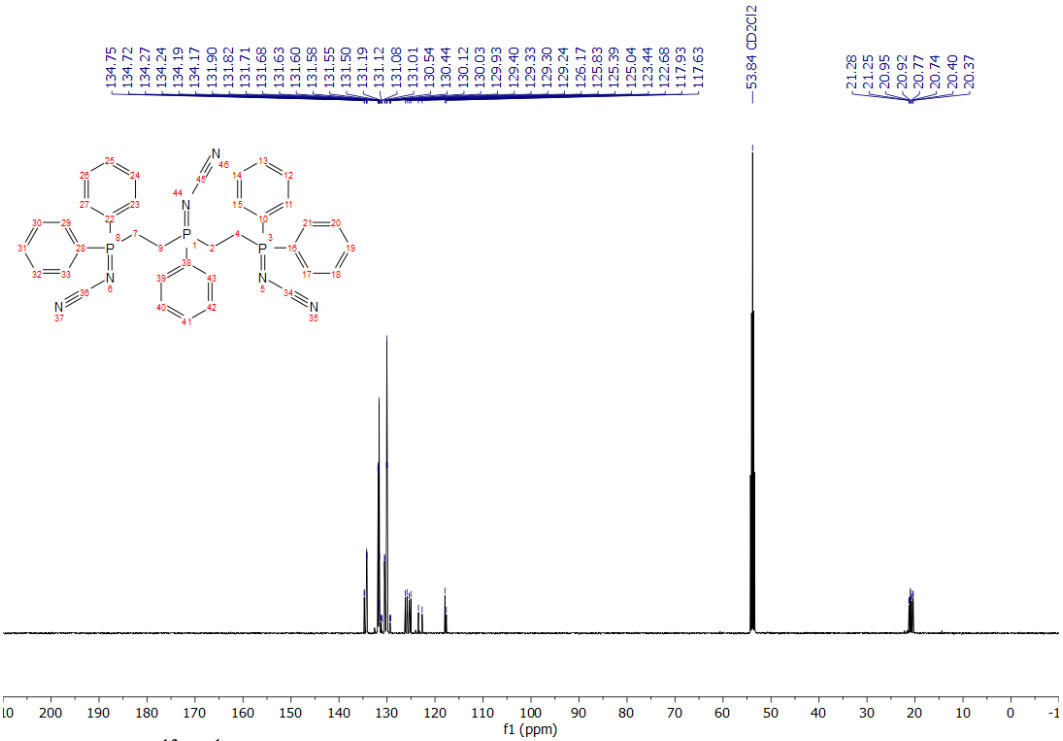


Figure S104. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **37** in DMSO-d_6.

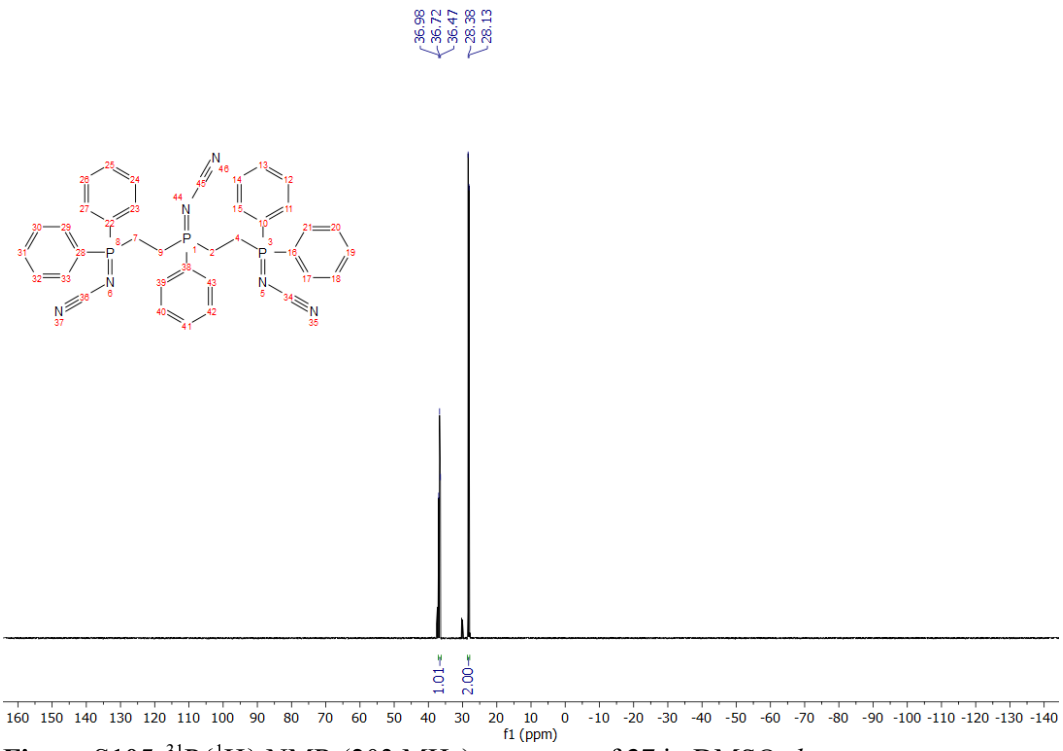
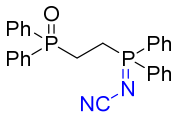


Figure S105. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **37** in DMSO-d_6.



Synthesis of **38** was prepared following General Procedure **A**, except only 2.5 F/mol of charge was used, in 76% assay yield from 1,2-bis(diphenylphosphino)ethane monooxide (1.21 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 1 to afford a white solid. Preparative purification of **35** was performed using preparative SFC. Temperature: 35 °C. Flow rate: 50 mL/min. BPR: 100 bar. UV detection: Max Absorbance Spectrum and 210 nm. Column: Epic Diol, 250 (L) × 21.2 (ID) mm. Mobile phase: 80%CO_2 and 20% MeOH. The collected peak fractions were dried *in vacuo*. ^{1}H NMR (500 MHz, CD_3OD) δ 7.82 – 7.67 (m, 10H), 7.61 (dd, J = 7.6, 3.9 Hz, 6H), 7.54 (td, J = 7.6, 2.9 Hz, 4H), 2.86 – 2.78 (m, 2H), 2.66 – 2.57 (m, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_3OD) δ 135.07 (d, J = 2.9 Hz), 133.92 (d, J = 2.8 Hz), 132.56 (d, J = 10.3 Hz), 131.88 (d, J = 9.8 Hz), 131.84 (d, J = 101.8 Hz), 130.77 (d, J = 12.7 Hz), 130.31 (d, J = 12.1 Hz), 126.63 (d, J = 98.9 Hz), 120.33, 22.46 (dd, J = 69.4, 4.7 Hz), 21.11 (dd, J = 69.0, 3.1 Hz). $^{31}P\{^{1}H\}$ NMR (203 MHz, CD_3OD) δ 35.43 (d, J = 53.0 Hz, 1P), 31.63 (d, J = 53.0 Hz, 1P). ESI^+ HRMS *m/z* calcd. for $C_{27}H_{25}N_2OP_2$ ($[M + H]^+$) 455.1442, found 455.1442.

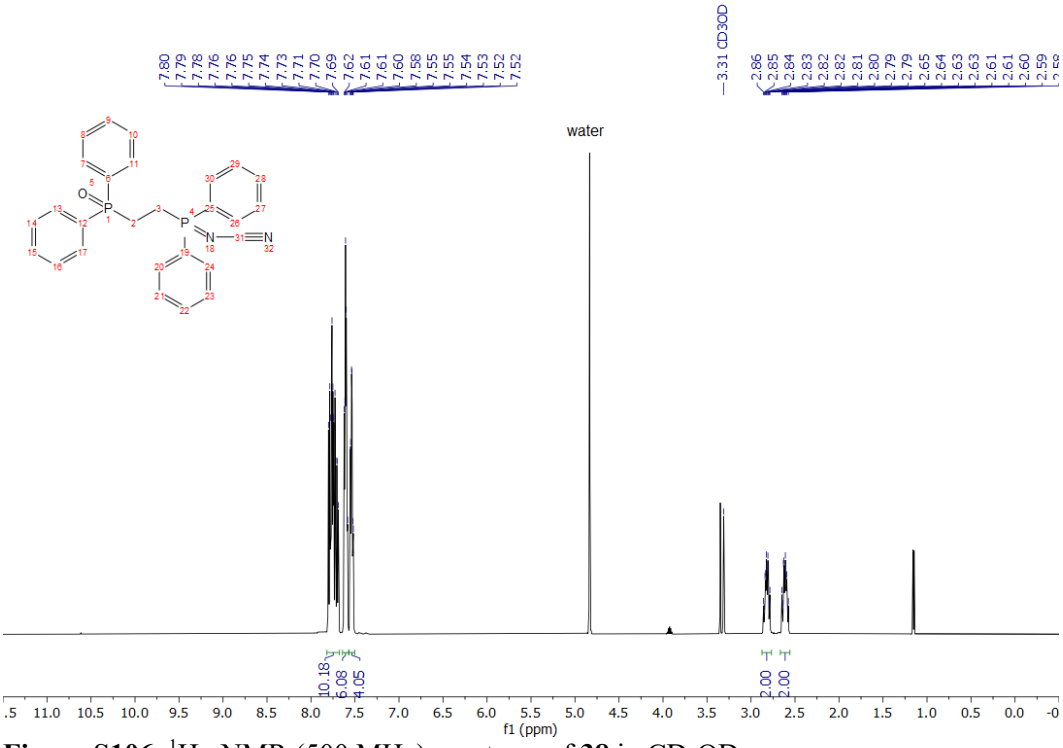


Figure S106. ^{1}H qNMR (500 MHz) spectrum of **38** in CD_3OD.

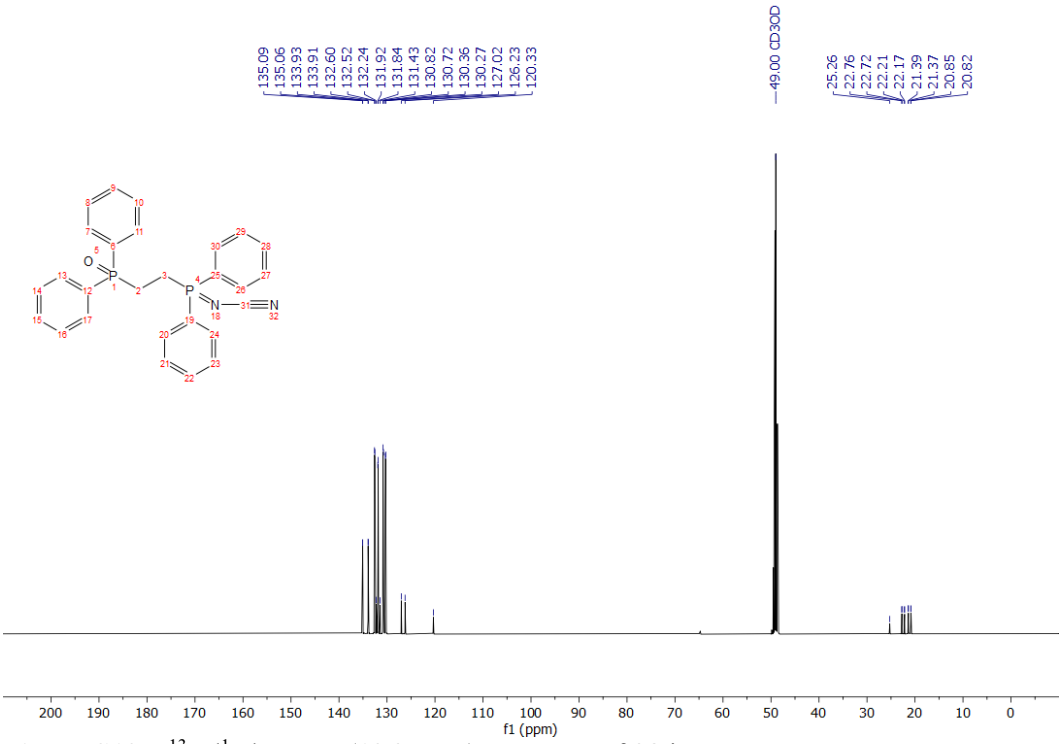


Figure S107. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **38** in CD_3OD.

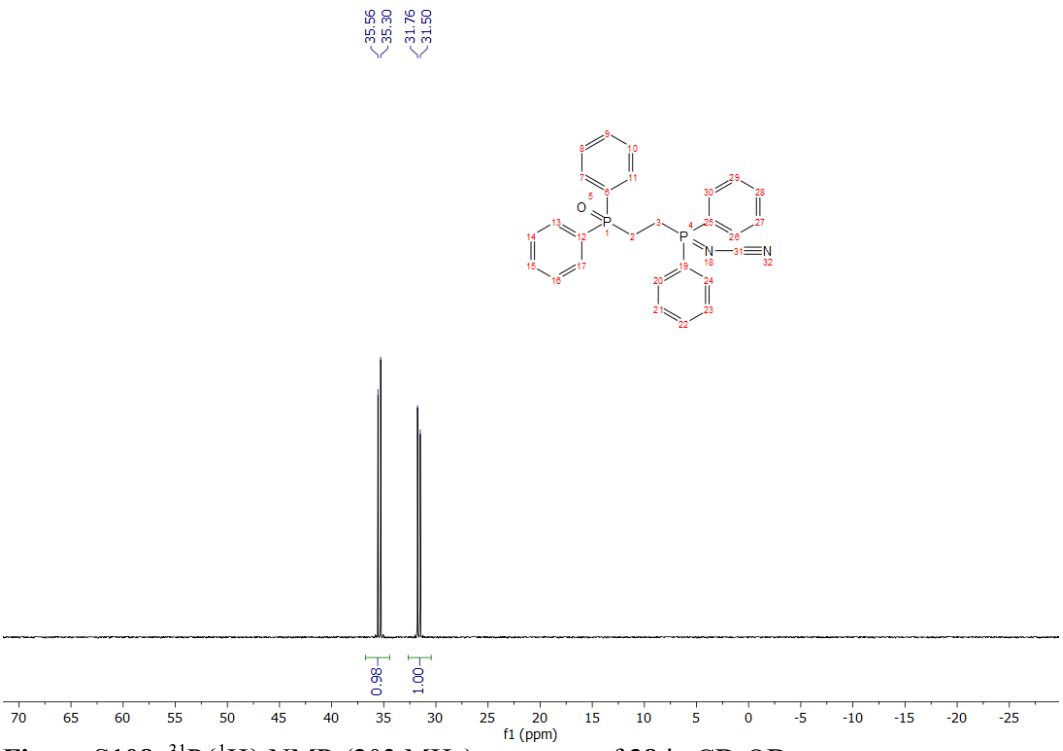
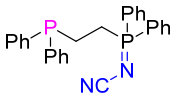


Figure S108. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **38** in CD_3OD.



Synthesis of **39** was prepared following General Procedure **A**, except only 2.5 F/mol of charge was used, in 32% assay yield from 1,2-bis(diphenylphosphino)ethlylene (0.797 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (1.12 g, 6.00 mmol, 3 equiv). Purification was achieved using method 1 to afford a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.68 – 7.62 (m, 6H), 7.57 – 7.51 (m, 4H), 7.36 (dtp, *J* = 6.4, 4.4, 2.2 Hz, 10H), 2.55 – 2.44 (m, 2H), 2.34 – 2.25 (m, 2H).$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ 137.31 (d, *J* = 13.7 Hz), 133.71 (d, *J* = 2.9 Hz), 133.06 (d, *J* = 19.0 Hz), 131.67 (d, *J* = 9.8 Hz), 129.73 (d, *J* = 12.3 Hz), 129.54, 129.11 (d, *J* = 6.8 Hz), 126.87 (d, *J* = 97.4 Hz), 118.39, 24.65 (dd, *J* = 67.4, 19.2 Hz), 19.43 (dd, *J* = 16.9, 5.2 Hz). $^{31}P\{^{1}H\}$ NMR (202 MHz, CD_2Cl_2) δ 29.11 (d, *J* = 48.1 Hz, 1P), –12.77 (d, *J* = 48.1 Hz, 1P). ESI^{+} HRMS *m/z* calcd. for $C_{27}H_{25}N_2P_2$ ($[M + H]^{+}$) 439.1493, found 439.1492.

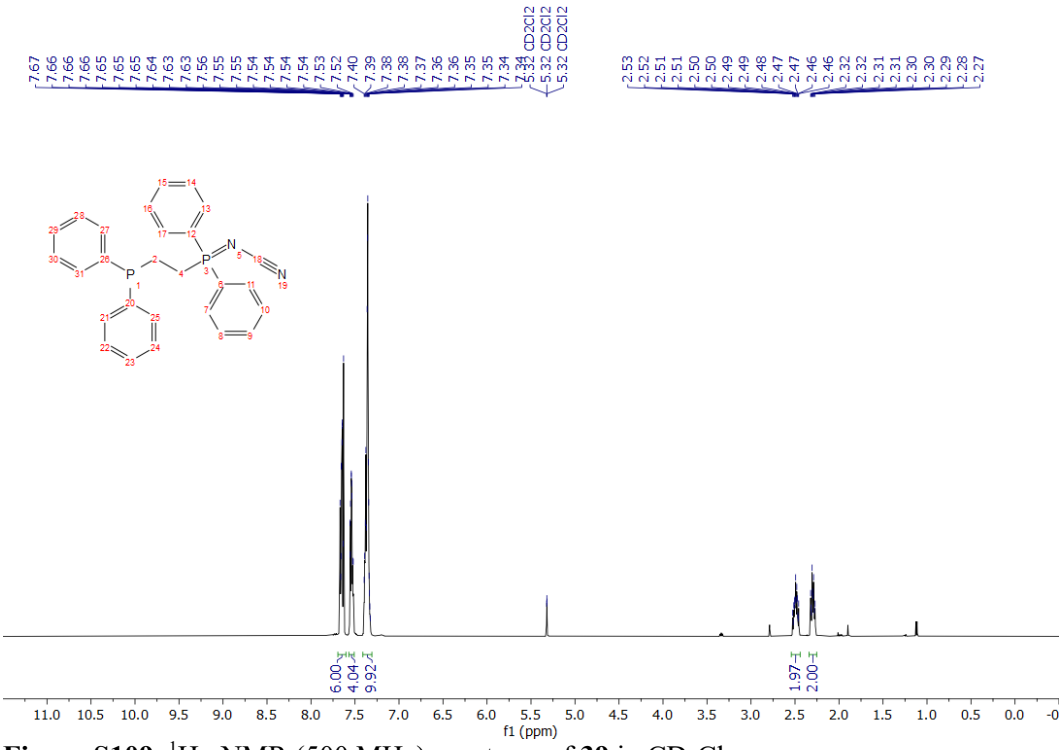


Figure S109. ^{1}H qNMR (500 MHz) spectrum of **39** in CD_2Cl_2.

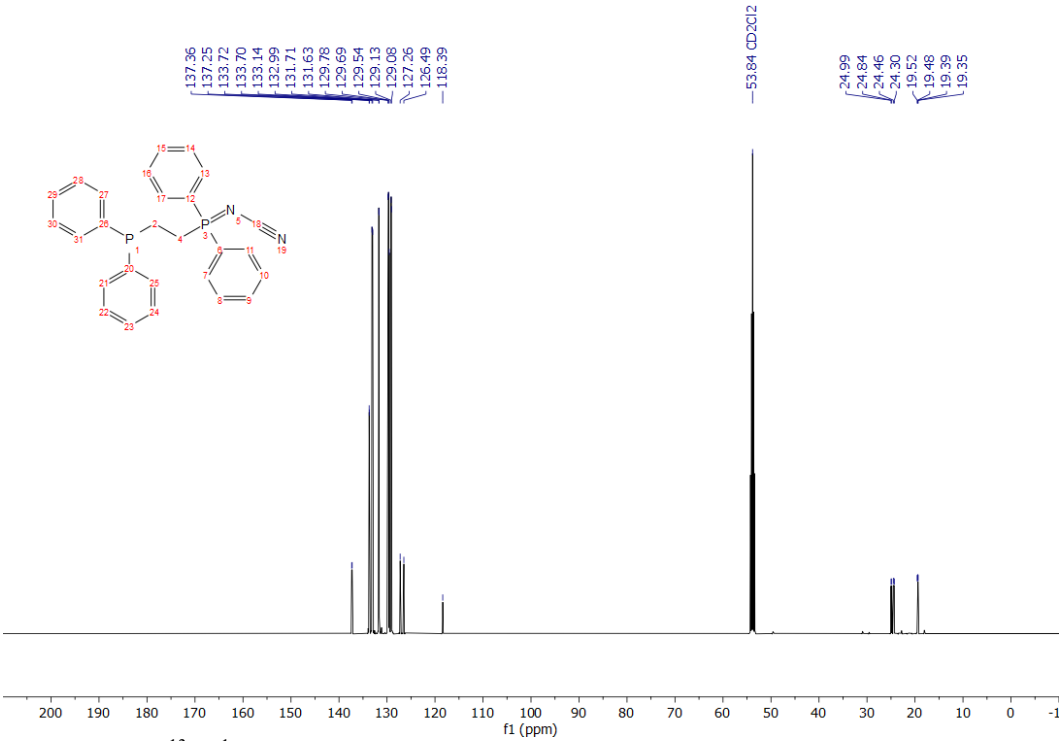


Figure S110. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **39** in CD_2Cl_2.

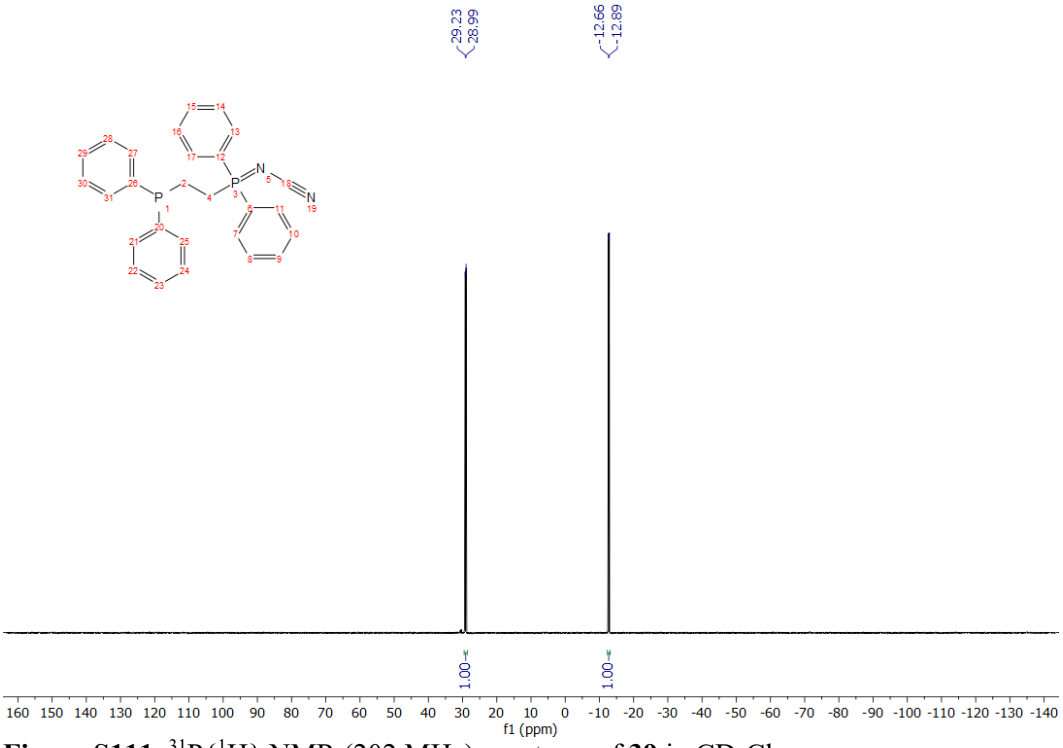
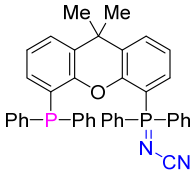


Figure S111. $^{31}P\{^{1}H\}$ NMR (202 MHz) spectrum of **39** in CD_2Cl_2.



Synthesis of **40** was prepared following General Procedure **A**, except only 2.5 F/mol of charge was used, in 34% assay yield from xantphos (1.16 g, 2.00 mmol) and bis(trimethylsilyl)carbodiimide (2.24 g, 12.0 mmol, 6 equiv). Purification was achieved using method 4 to afford a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.85 (d, J = 7.8 Hz, 1H), 7.79 (dd, J = 13.5, 7.7 Hz, 4H), 7.70 (dd, J = 14.5, 7.5 Hz, 1H), 7.47 (dt, J = 9.1, 5.0 Hz, 3H), 7.36 – 7.22 (m, 11H), 7.01 (t, J = 7.6 Hz, 1H), 6.92 (t, J = 7.1 Hz, 4H), 6.66 – 6.59 (m, 1H), 1.70 (s, 6H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ 152.51 (d, J = 20.8 Hz), 138.23 (d, J = 16.1 Hz), 134.66 (d, J = 1.7 Hz), 134.41 (d, J = 7.5 Hz), 133.67 (d, J = 19.9 Hz), 133.28 (d, J = 2.9 Hz), 133.03 (d, J = 2.2 Hz), 132.72 (d, J = 2.8 Hz), 132.63 (d, J = 2.8 Hz), 132.25 (d, J = 6.3 Hz), 130.08 (d, J = 2.5 Hz), 129.16 (d, J = 13.3 Hz), 128.62 (d, J = 6.0 Hz), 128.54, 127.99 (d, J = 1.3 Hz), 127.87, 125.33 (d, J = 22.4 Hz), 124.73, 124.39 (d, J = 12.6 Hz), 118.76, 113.19 (d, J = 100.9 Hz), 34.81, 32.73. $^{31}P\{^{1}H\}$ NMR (203 MHz, CD_2Cl_2) δ 25.21 (s, 1P), -22.21 (s, 1P). ESI^{+} HRMS *m/z* calcd. for $C_{40}H_{33}N_2OP_2$ ($[M + H]^{+}$) 619.2068, found 619.2062.

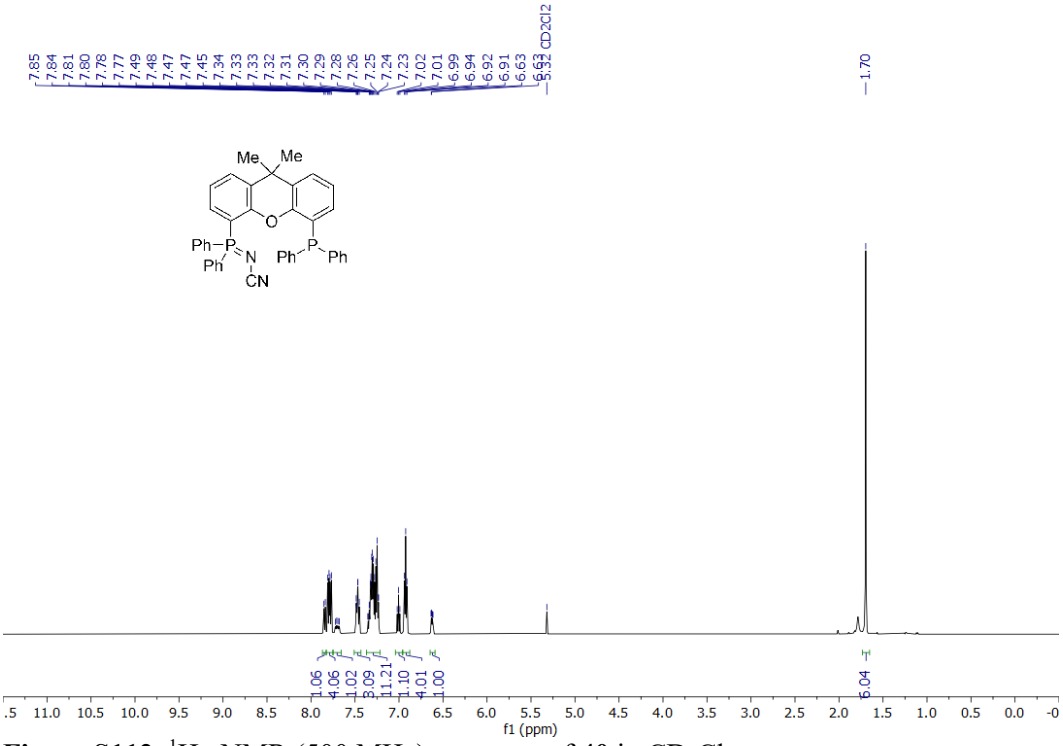


Figure S112. ^{1}H qNMR (500 MHz) spectrum of **40** in CD_2Cl_2.

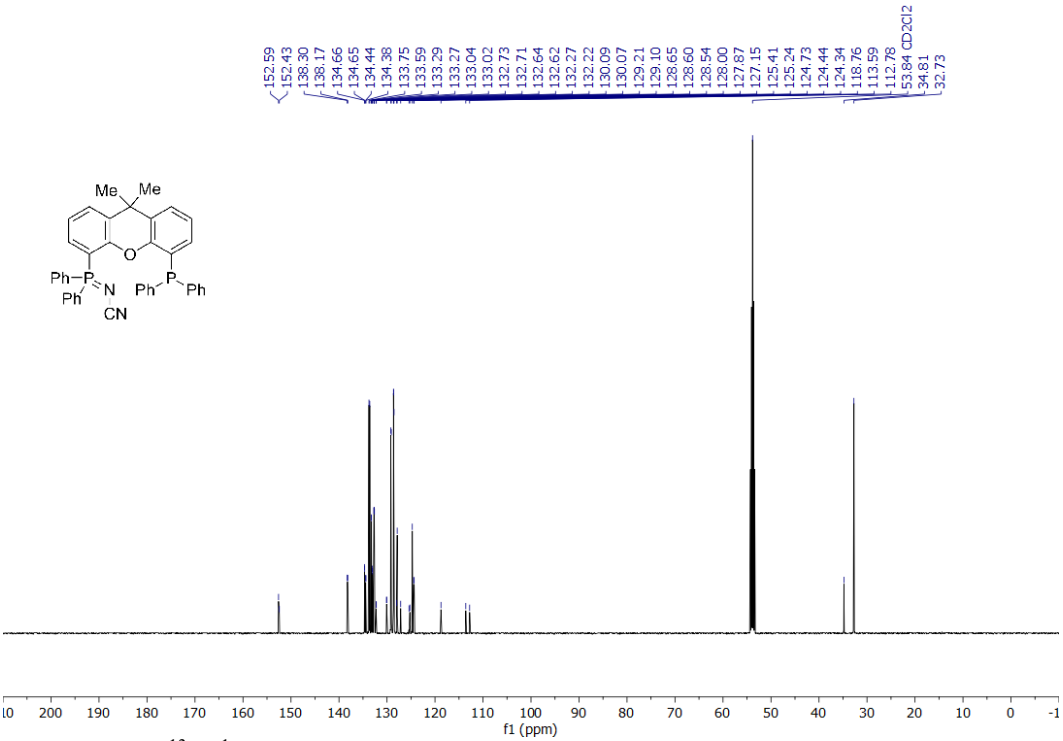


Figure S113. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **40** in CD_2Cl_2.

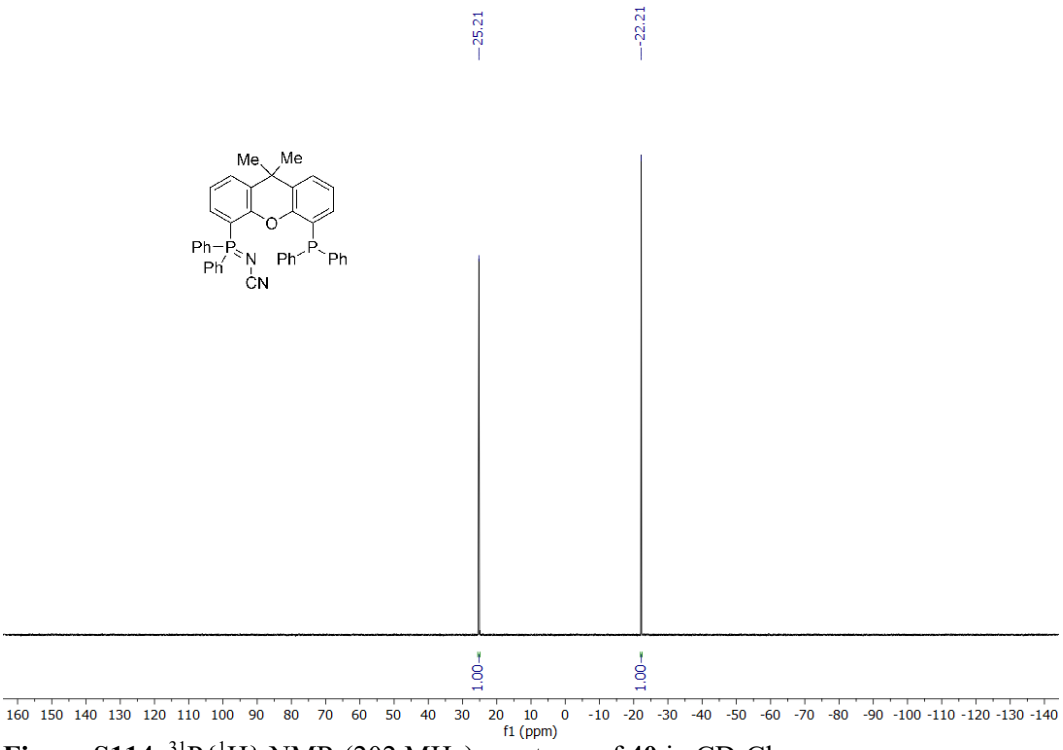
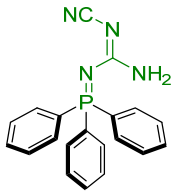


Figure S114. $^{31}P\{^{1}H\}$ NMR (202 MHz) spectrum of **40** in CD_2Cl_2.



Synthesis of **4** was prepared following General Procedure **C** in 49% assay yield from triphenylphosphine (0.525 g, 2.00 mmol) and 1-cyanoguanidine (0.504 g, 6.00 mmol, 3 equiv). Purification was achieved using method 1 to afford a white solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.76 – 7.68 (m, 6H), 7.68 – 7.62 (m, 3H), 7.61 – 7.54 (m, 6H), 6.92 (br s, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, DMSO-d_6) δ 166.51, 132.63 (d, J = 9.9 Hz), 132.49 (d, J = 2.7 Hz), 128.78 (d, J = 12.2 Hz), 127.81 (d, J = 101.6 Hz), 118.18. $^{31}P\{^{1}H\}$ NMR (203 MHz, DMSO-d_6) δ 16.57 (s, 1P). ESI^{+} HRMS *m/z* calcd. for $C_{20}H_{18}N_4P$ ($[M + H]^{+}$) 345.1269, found 345.1264.

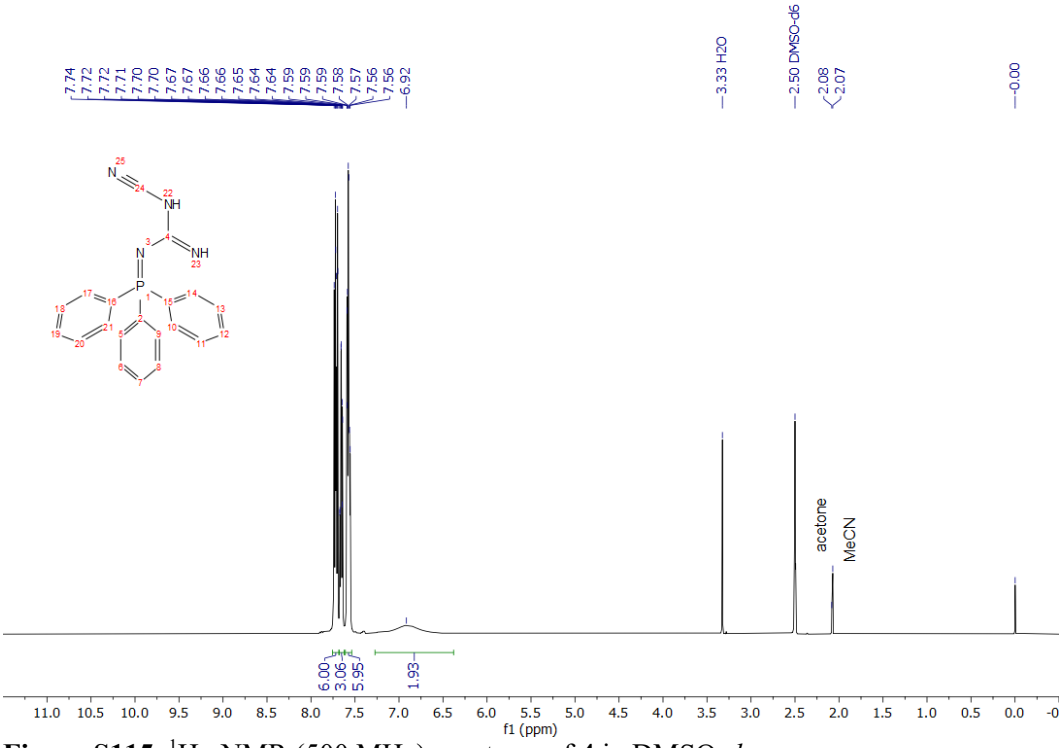


Figure S115. ^{1}H qNMR (500 MHz) spectrum of **4** in DMSO-d_6.

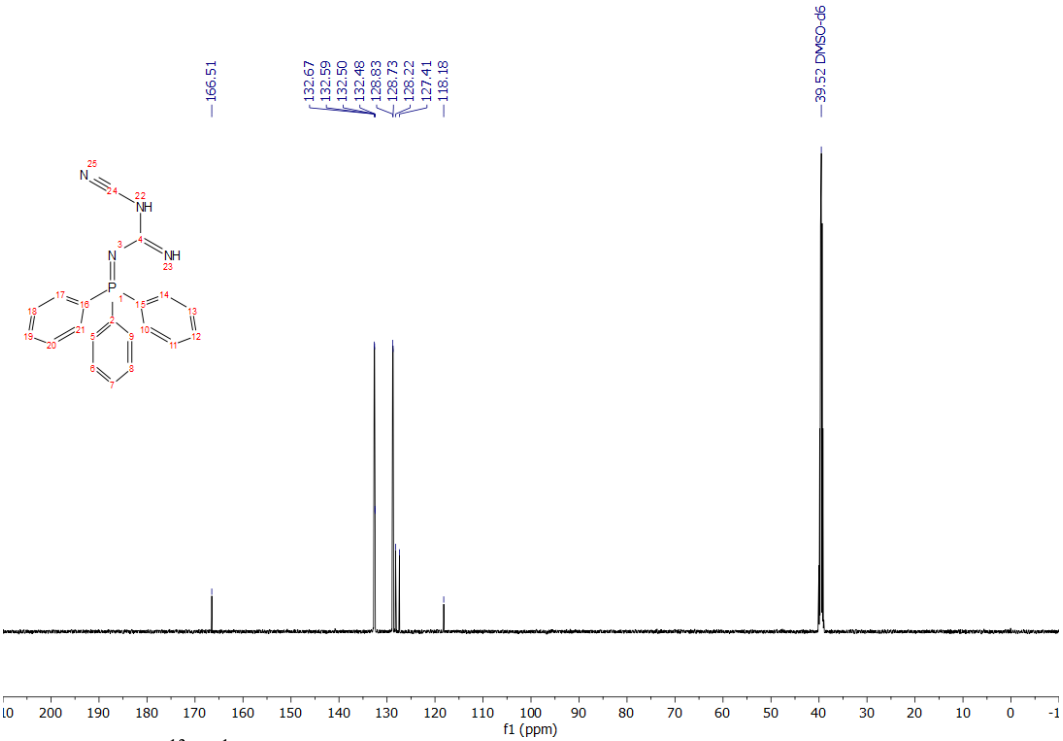


Figure S116. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **4** in DMSO-d_6.

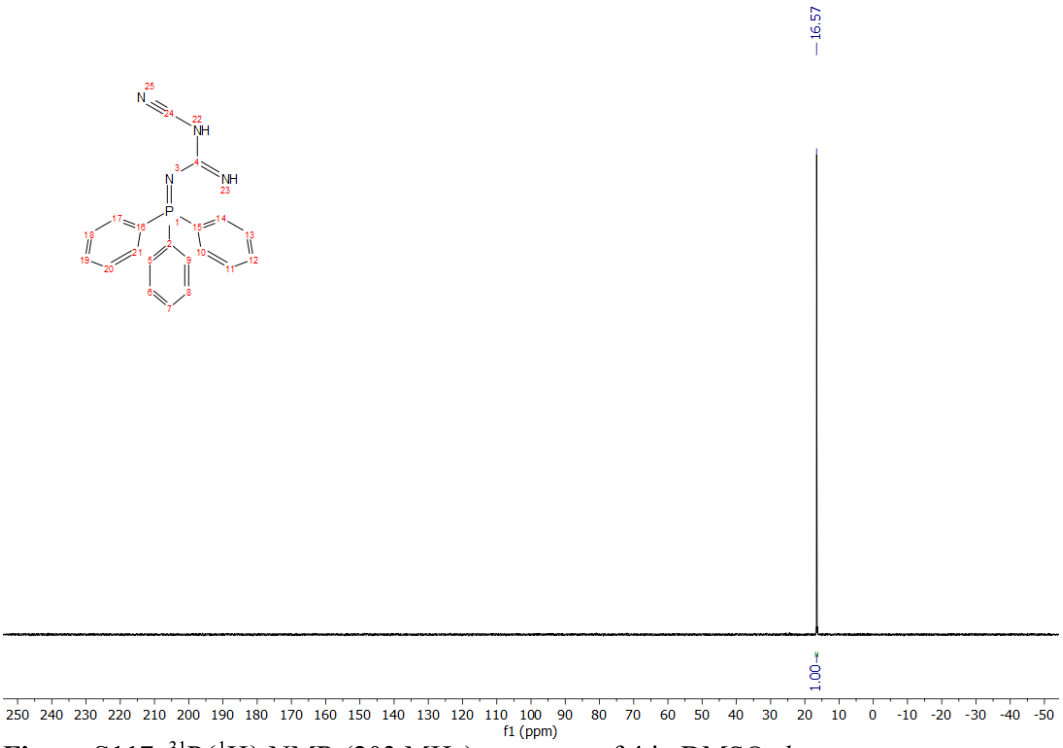


Figure S117. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **4** in DMSO-d_6.

4.5. Substrate Scope Limitations

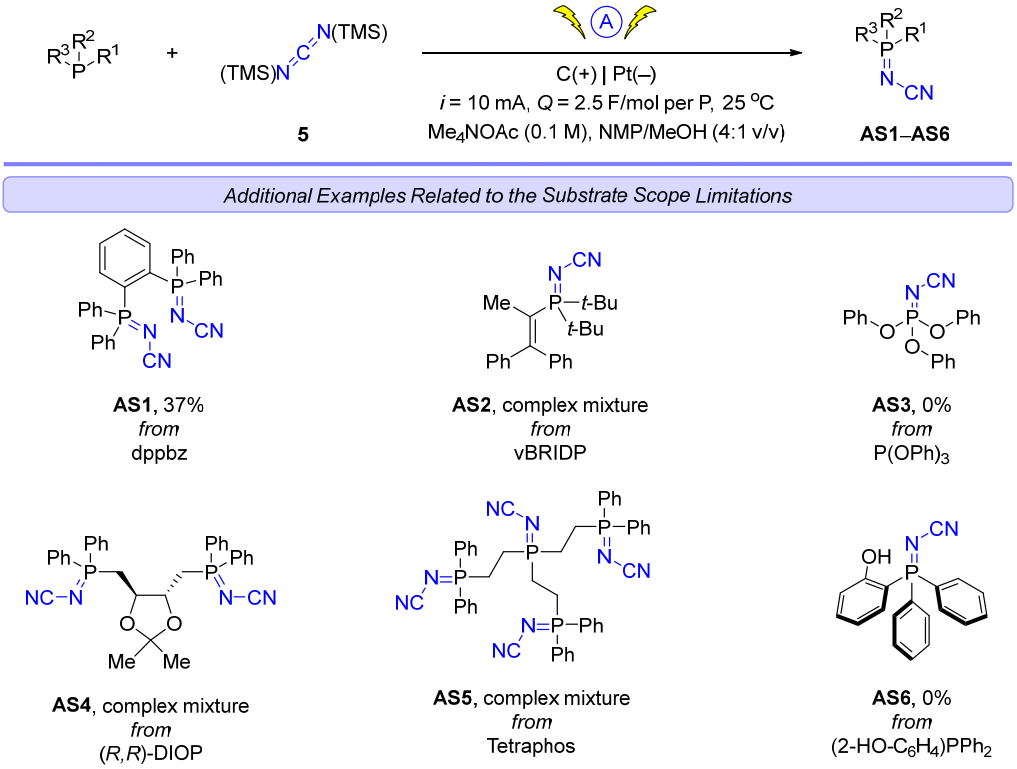


Figure S118. Additional substrates (**AS1–AS6**) explored which provided low assay yield or no product.

The above figure provides insight into additional examples of substrates that were explored towards synthesizing *N*-cyanoiminophosphorane derivatives but provided sub-optimal results when using General Procedure A.

5. Flow Electrolysis Experiments

5.1. General Setup Details

Flow electrolysis experiments were conducted with a parallel plate flow cell purchased from ElectroCell A/S (Denmark)[16] , specifically a Micro Flow Cell® (MFC) reactor operated in an undivided configuration and in a recirculating mode. Assembly of the Micro Flow Cell was performed analogous to previously described.[17] The Micro Flow Cell parallel plate reactor was configured with graphite felt (ElectroCell catalog ESC-GFS3) on polymer-filled graphite (Material Name: "FC-GR347B graphite, Graphtek LLC", Vendor: The Graphite Store; material characteristics: 25.4 µm particle size, 0% volume porosity, electrical resistivity 511 µohm•inch, flex strength 9425 lbs/in^2, Shore Hardness 76, apparent density 1.99 g/cm^3) as the anode (A_e =10 cm^2), a polypropylene turbulence mesh to promote mixing, "Shiny" platinum clad niobium electrode (ElectroCell catalog 4-40001-05) as the cathode (A_e =10 cm^2), and EPDM gaskets (ElectroCell). A Masterflex Digital Gear Pump (model 75211-70) equipped with the following pump head: Micropump A-Mount Suction Shoe Pump Head (model GJ-N25.PF1S.A, 0.091 mL/rev, P/N 81808); FEP tubing with 1/16 inch internal diameter, 1/8 inch outer diameter and 0.030 inch wall thickness (Altaflow LLC, P/N 200-0125-030-0C) was used and the reaction mixture was pumped at 445 mL/min (experimentally determined). Tubing was connected to the electrochemical reactors or pumps via stainless steel Swagelok® fittings of appropriate size. A BK Precision Power Supply (model 9206) was used for lab scale electrolysis (i <10 A).

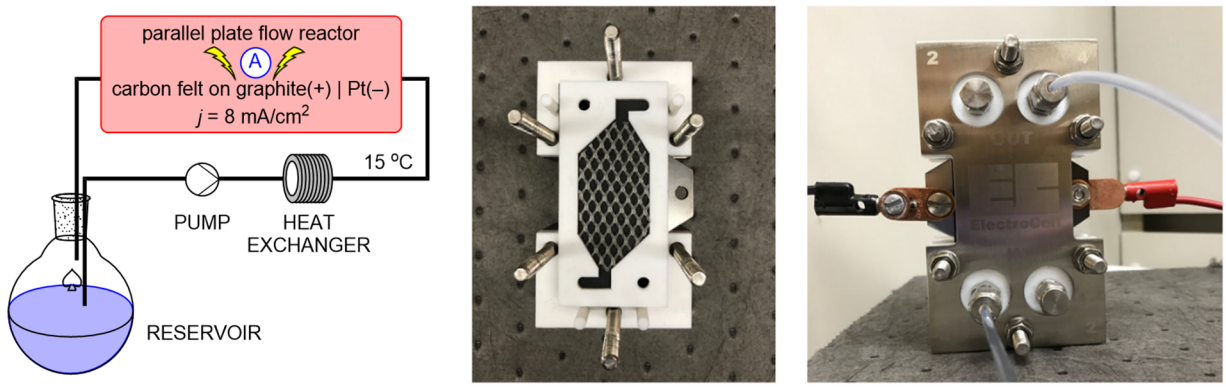
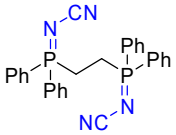


Figure S119. (Left) Schematic representation of recirculating flow electrolysis setup. (Middle) Illustration of flow path inside the Micro Flow Cell® equipped with a turbulent mesh over the graphite felt on graphite anode. (Right) Fully assembled Micro Flow Cell® equipped a graphite felt on graphite anode and a Pt cathode connected to a power supply.

5.2. Multi-Gram Scale Flow Electrolysis of Iminophosphorane 28



In a glovebox, a 250 mL 3-neck round bottom flask containing a PTFE stir bar was charged with DPPE (7.96 g, 20 mmol), bis(trimethylsilyl)carbodiimide (44.8 g, 120 mmol, 6 equiv), tetrabutylammonium acetate (6.03 g, 20.0 mmol) followed by adding of NMP (120 mL) and MeOH (60 mL). The flask capped using rubber septa and the mixture was rendered homogenous via rotary stirring for 15 min at room temperature. The reaction mixture was then brought out of the glovebox and connected to a nitrogen manifold to place under positive pressure of N_2. Exit and return lines were connected to a recirculating loop consisting of FEP tubing, a MasterFlex pump, a Micro Flow Cell parallel plate reactor from ElectroCell configured with carbon felt on graphite as the anode (A_e =10 cm^2), a polypropylene turbulence mesh to

promote mixing, a platinum on niobium electrode (A_e = 10 cm^2) as the cathode (see detailed equipment description in Section 4.1). The mixture was electrolyzed with a current of 80 mA (j = 8.0 mA/cm^2) for 5.20 F/mol of charge while recirculating the reaction mixture through the reactor at a flow rate of 450 mL/min (linear velocity of approximately 298 cm/min) maintaining the inlet reaction temperature around 15 ºC using an inlet heat exchanger. Reaction monitoring was performed using UPLC MS analysis (using the method described in Section 1.4) to determine the extent of conversion by taking 15 μL aliquots of the reaction mixture and adding them to 1 mL in MeCN.

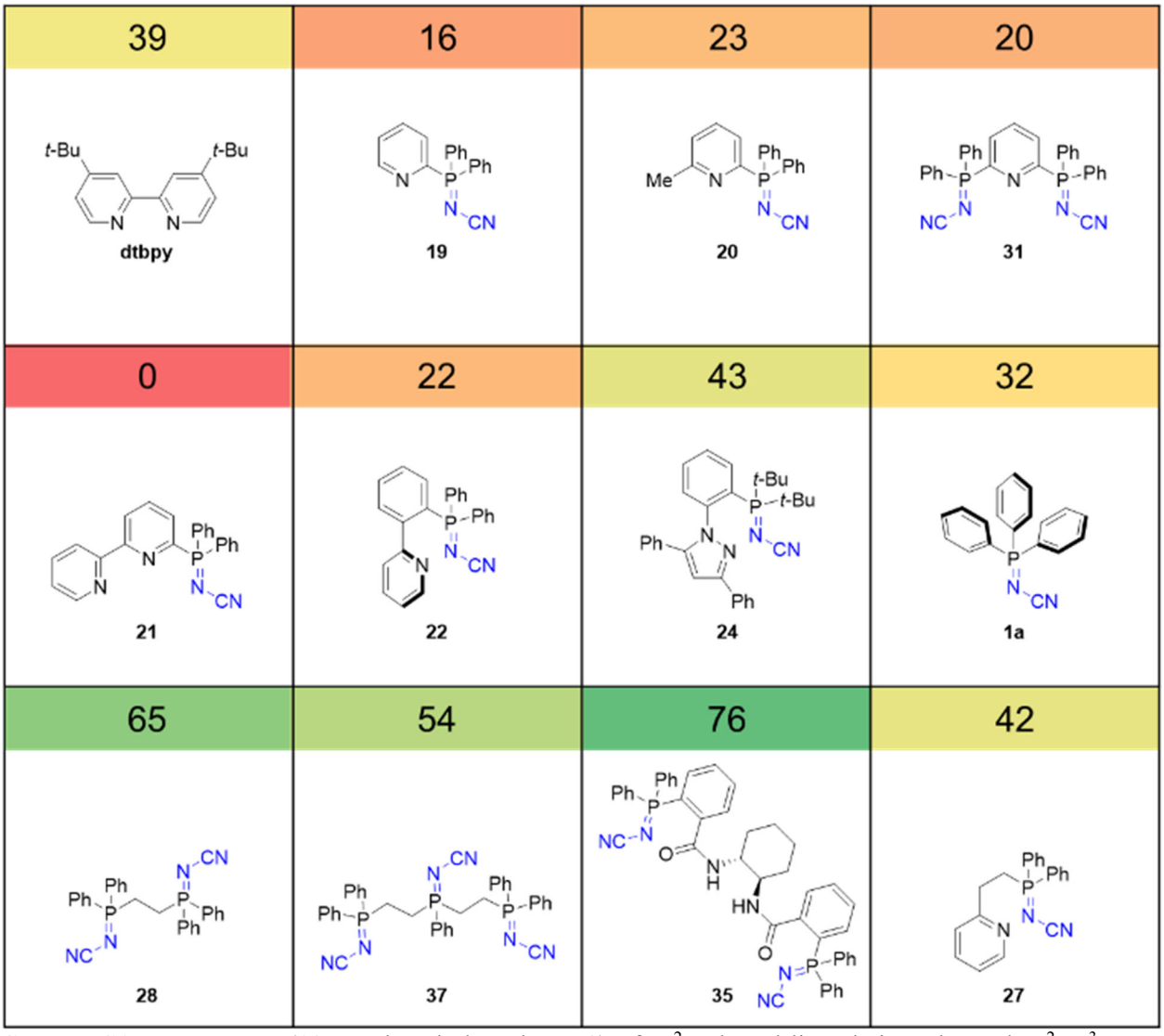
The final reaction mixture was transferred into a 2 L flask containing a PTFE stir bar using NMP (20 mL) to rinse out the flow reactor and recirculating loop. To the mixture was added H_2O (350 mL) over a period of 30 minutes while stirring the mixture using rotary stirring (850 rpm) at room temperature. Upon observing that crystallization of an off-white solid occurred via self-seeding, the mixture was aged for 15 minutes prior to adding additional H_2O (1.15 L) over 15 min and the mixture was allowed to age overnight with slow agitation (250 rpm rotary stirring). The suspension was filtered and the solid was washed using slurry washes of H_2O (3 × 100 mL) and dried via under dynamic vacuum for 15 min. The solid product which was further dried under vacuum for 24 h to afford **28** as a white solid (7.75 g of 94.7% purity based on ^{31}P NMR, with the mass balance being intermediate **38**; corrected yield for purity is 7.34 g corresponding to a yield of 77%.

6. Application of Iminophosphoranes to Ni-Catalyzed Cross-Couplings

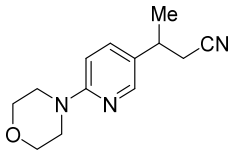
6.1. Thermal sp^2-sp^3 Cross-Electrophile Couplings

HTE Screen

In a nitrogen filled glovebox, a stock solution was prepared containing aryl halide **50** (243 mg, 1.0 mmol), alkyl bromide **51** (444 mg, 3.0 mmol), $NiBr_2 \bullet 3H_2O$ (27.3 mg, 0.1 mmol), biphenyl (38.6 mg, 0.25 mmol) in DMA (5.0 mL). To a 96 well plate (Analytical Sales, Inc.; SKU 96960) was loaded 12-pre-plated ligands (1 μmol of ligands per vial; see figure below for structures of each ligand) each in standard 1 mL glass shell vial (8 × 30 mm, Analytical Sales, Inc.; SKU 884001) containing a parylene encapsulated stainless steel cylinder tumble stir (Analytical Sales, Inc.; SKU 13258). To the above vials was added 50 μL of the above stock solution using an Eppendorf pipettor. The plate was placed in a temperature-controlled tumble stirring bay and cooled to 0 °C. Subsequently, to each vial was added a slurry of 10-micron zinc dust (0.654 mg, 10.00 μmol) in DMA (50 μL) to each vial using an Eppendorf pipettor to initiate the reactions. [Note: the sock solution used for dosing the Zn dust was prepared as follows: to a 2 dram vial (ChemGlass catalog CG-4912-02, with pressure relief septa caps) containing a PTFE coated stir bar was added 10-micron zinc dust (262 mg, 4.0 mmol) followed by DMA (5.0 mL); this mixture was stirred using rotary stirring while taking 50 μL doses for the above dispensing operation]. The 96-well plate was sealed, and the reactions were mixed using tumble stirring for 22 hours while maintain the reaction block at 0 °C using cooling fluid from a recirculating chiller connected to a low temperature, 3-plate well (SLAS) thermal unit from mécour (part number 80-03 FRSL) placed above a 5-postion tumble stirring unit (V&P Scientific, Inc.; Model: VP 710E5X, Vertical Tumble Stirrer, Double Stack Servo Motor, 5 SLAS Positions, Manual Control).



Scheme S1. HTE screen (10 μmol scale based on **50**) of sp^2-*N*-based ligands in a thermal sp^2-sp^3 XEC coupling. The numbers in the colored box above each ligand is the assay yield for **52**.



In an N_2 filled glovebox, a 2 dram vial (ChemGlass catalog CG-4912-02, with pressure relief septa caps) equipped with a stir bar, the following were added to the vial: 4-(4-bromophenyl)morpholine (0.242 g, 1.00 mmol), 3-bromobutanenitrile (0.444 g, 3.00 mmol), $NiBr_2$•$3H_2O$ (0.027 g, 0.100 mmol), ligand **35** (0.077 g, 0.100 mmol), 10 µm particle size zinc dust (0.262 g, 4.00 mmol). The reaction mixture was stirred at 0 °C for 18 h. The crude reaction mixture was diluted with CH_2Cl_2 (50 mL) and the organic phase was washed with H_2O (3 × 50 mL), and dried over anhydr. Na_2SO_4, filtered, and concentrated *in vacuo*. Purification using liquid column chromatography (silica gel stationary phase, gradient 0% to 50% (v/v) of ethyl acetate in hexanes using a Teledyne ISCO CombiFlash® Rf+ chromatography system using prepacked single-use silica packed cartridges (RediSep® Rf Gold Normal-Phase Silica, 20-40 micron average particle size, 60 Å average pore size, with cartridge sizes 40 g (part number 69-2203-347) 40 mL/min. ^{1}H NMR (400 MHz, CD_3CN) δ 8.07 (d, J = 2.5 Hz, 1H), 7.53 – 7.45 (m, 1H), 6.72 (d, J = 8.8 Hz, 1H), 3.77 – 3.68 (m, 4H), 3.42 (dd, J = 5.5, 4.3 Hz, 4H), 3.07 (h, J = 7.0 Hz, 1H), 2.62 (dd, J = 7.0, 2.1 Hz, 2H), 1.33 (d, J = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN) δ 159.96, 147.34, 136.80, 129.43, 120.02, 107.72, 67.27, 46.39, 34.08, 26.38, 20.85. ESI$^+$ LRMS *m/z* calcd. for $C_{13}H_{18}N_3O$ ([M + H]$^+$) 232.1, found 232.2.

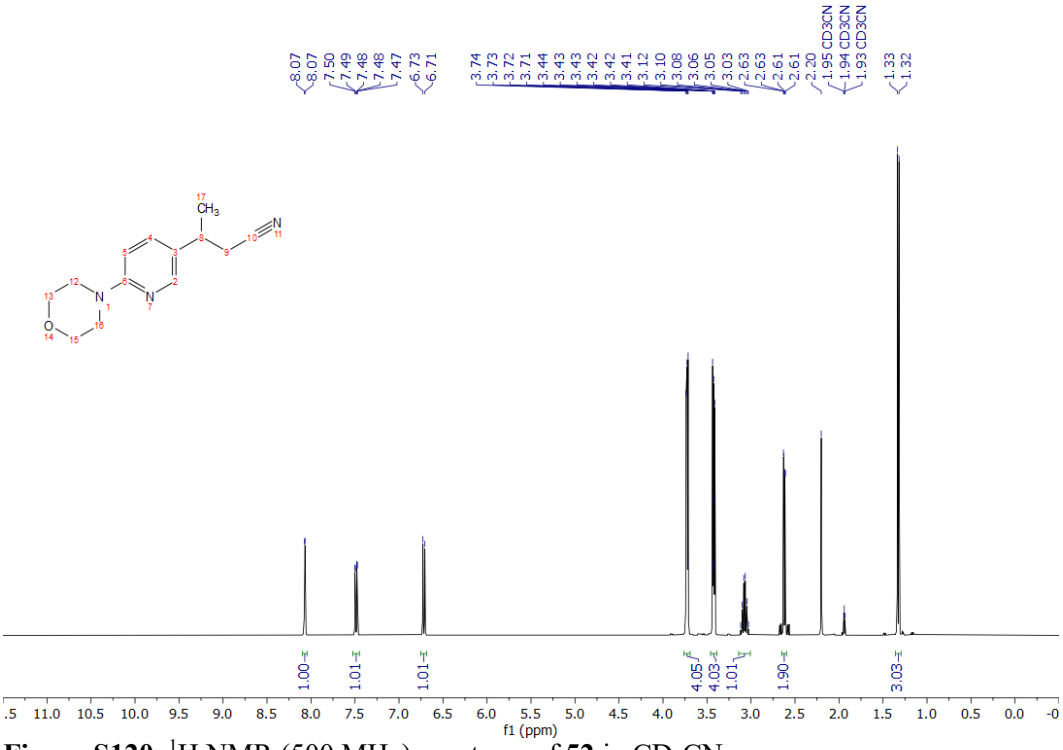


Figure S120. ^{1}H NMR (500 MHz) spectrum of **52** in CD_3CN.

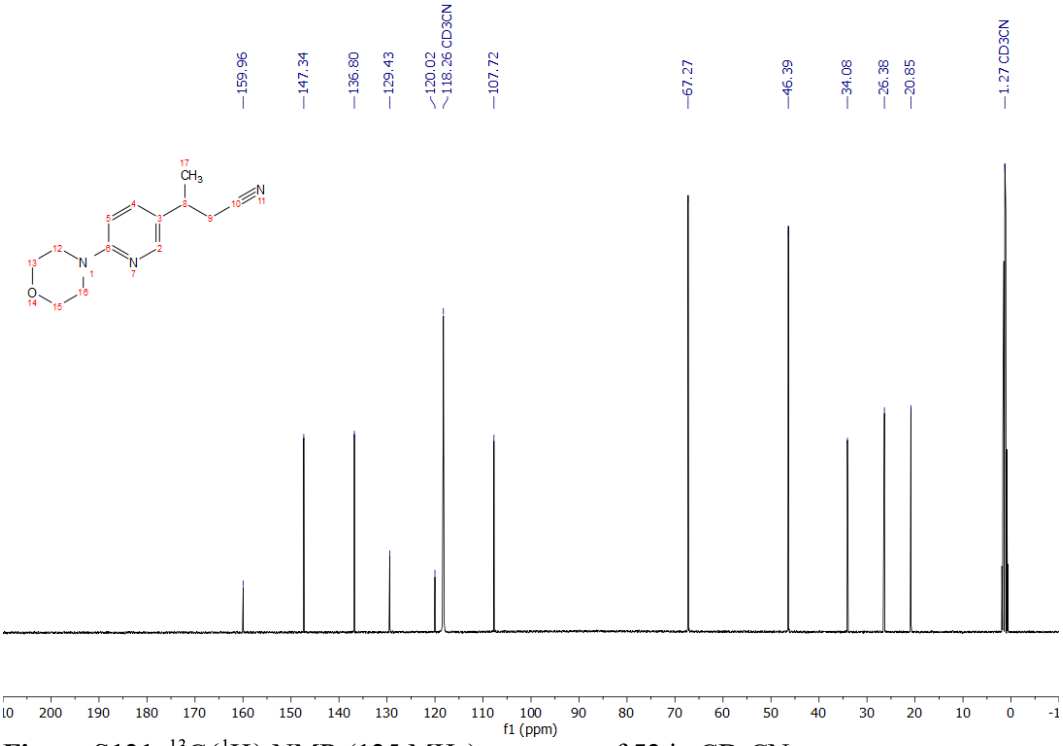


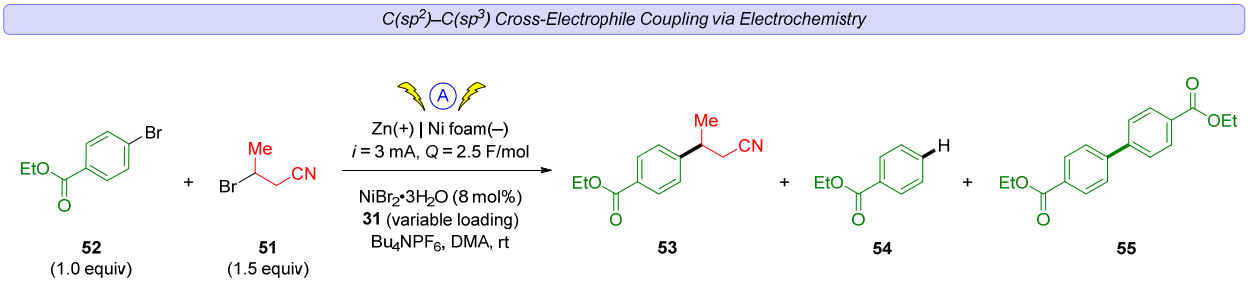
Figure S121. $^{13}C\{^{1}H\}$ NMR (125 MHz) spectrum of **52** in CD_3CN.

6.2. Electrochemical sp^2-sp^2 Cross-Electrophile Couplings

6.2.1. General Procedure D (Evaluating Iminophosphorane Ligands for Electrochemical XEC)

In an N_2 filled glovebox, a 5 mL Electrasyn vial was charged with a PTFE coated magnetic stir bar, $NiBr_2 \bullet 3H_2O$ (0.0070 g, 0.026 mmol), an iminophosphorane ligand (0.033 mmol), and DMA (5 mL). The mixture was heated to 75 °C for 15 min and cooled back to RT prior to adding tetrabutylammonium hexafluorophosphate (0.19 g, 0.50 mmol), ethyl 4-bromobenzoate (0.076 g, 0.33 mmol) and 3-bromobutanenitrile (0.074 g, 0.50 mmol). Electrodes (zinc anode, nickel foam cathode) were connected to the Electrasyn vial cap and the electrodes were immersed into the above solution. The Electrasyn vial cap was connected to the Electrasyn 2.0 and the reaction mixture was electrolyzed under a constant current of 3 mA for a total of 2.5 F/mol of charge accompanied by rotary magnetic stirring (900 rpm). Zinc electrode dimensions exposed to solution: 8.04 mm (width) × 1.98 mm (thickness) × 26.2 mm height; Nickel foam dimensions exposed to solution: 8.04 mm (width) × 2.10 mm (thickness) × 26.2 mm height. Upon completing the electrolysis, internal standard (biphenyl) was added to the reaction mixture, the mixture was rendered homogenous and the assay yield was measured via UPLC based on a calibration curve.

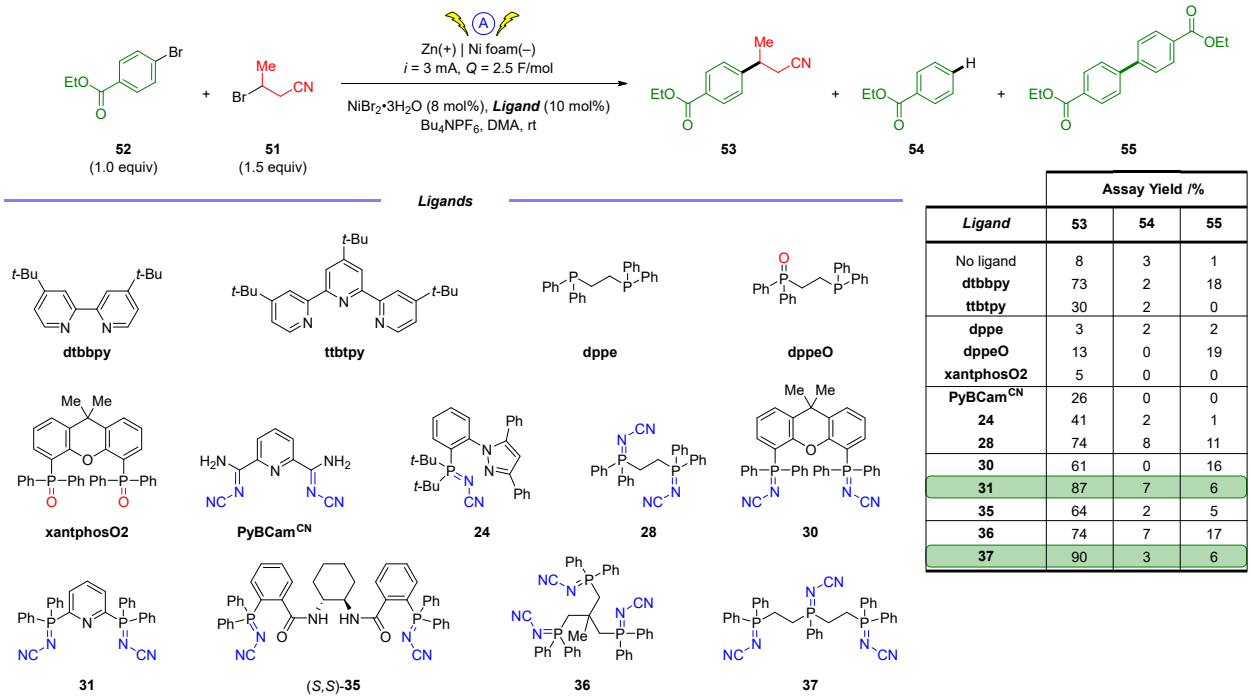
A metal to ligand ratio screen was carried out using the procedure shown above with the exception that the ligand loading was varied (4, 8, 10, 20 mol%) and all screens were performed using ligand **31**.



	Assay Yield /%		
31 /mol%	**53**	**54**	**55**
4	59	9	10
8	76	8	7
10	87	8	6
16	94	3	5

Figure S122. Metal to ligand ratio screen summary using ligand **31** in the electrochemical sp^2-sp^3 cross-electrophile coupling for C– C bond formation.

Below is an overview of the ligands screened in the electrochemical sp^2-sp^3 cross-electrophile coupling for C– C bond formation.



Ligand	Assay Yield /%		
	53	54	55
No ligand	8	3	1
dtbbpy	73	2	18
ttbtpy	30	2	0
dppe	3	2	2
dppeO	13	0	19
xantphosO2	5	0	0
PyBCam^{CN}	26	0	0
24	41	2	1
28	74	8	11
30	61	0	16
31	87	7	6
35	64	2	5
36	74	7	17
37	90	3	6

Figure S123. Overview of ligands evaluated for the electrochemical cross-electrophile coupling for C–C bond formation.

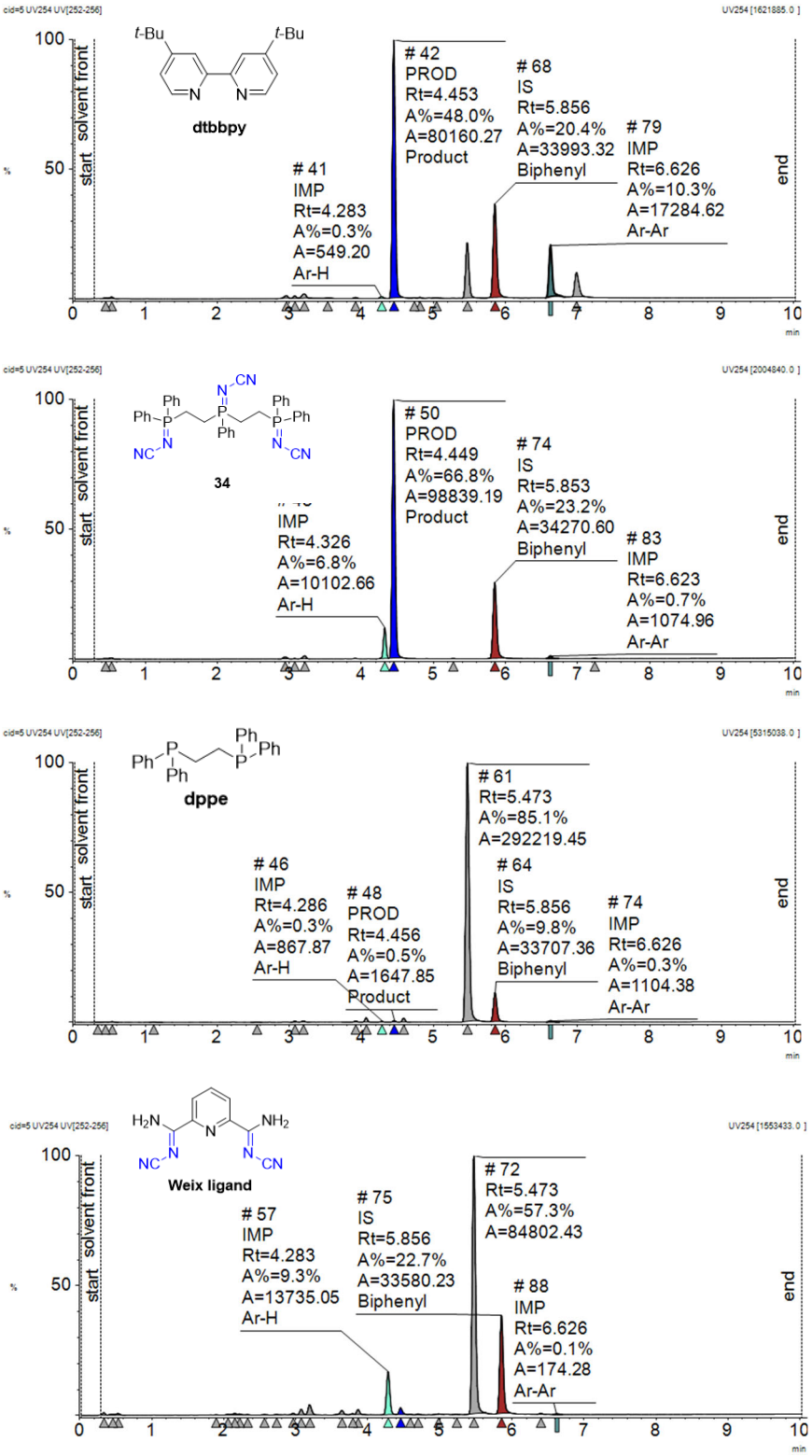
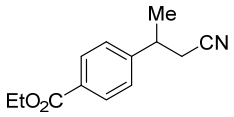


Figure S124. UPLC-MS traces from select ligands evaluated in the XEC showing the desbromo (**Ar-H**), desired product (**Product**), internal standard (**Biphenyl**) and the homocoupling product (**Ar-Ar**).

6.2.2. Cross-Electrophile Coupling to 53 using Iminophosphorane Ligand 37



The cross-electrophile coupling product was synthesize using General Procedure E described in Section 5.1.2. The isolation was achieved via the following procedure. The crude reaction mixture was diluted with dichloromethane (50 mL) and the organic phase was washed with H_2O (3 × 50 mL), and dried over anhydr. Na_2SO_4, filtered, and concentrated *in vacuo*. Purification using liquid column chromatography (silica gel stationary phase, gradient 0% to 40% (v/v) of ethyl acetate in hexanes using a Teledyne ISCO CombiFlash® Rf+ chromatography system using prepacked single-use silica packed cartridges (RediSep® Rf Gold Normal-Phase Silica, 20–40 micron average particle size, 60 Å average pore size, with cartridge sizes 40 g (part number 69-2203-347) 40 mL/min. Product **53** was isolated as a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.01 (d, J = 8.1 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 4.35 (q, J = 7.1 Hz, 1H), 3.23 (h, J = 7.0 Hz, 1H), 2.62 (dd, J = 6.9, 3.5 Hz, 1H), 1.44 (d, J = 7.0 Hz, 1H), 1.38 (t, J = 7.1 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 166.43, 148.75, 130.30, 130.12, 127.14, 118.64, 61.32, 36.95, 26.25, 20.75, 14.50. ESI$^+$ LRMS *m/z* calcd. for $C_{13}H_{16}NO_2$ ([M + H]$^+$) 218.1, found 218.2.

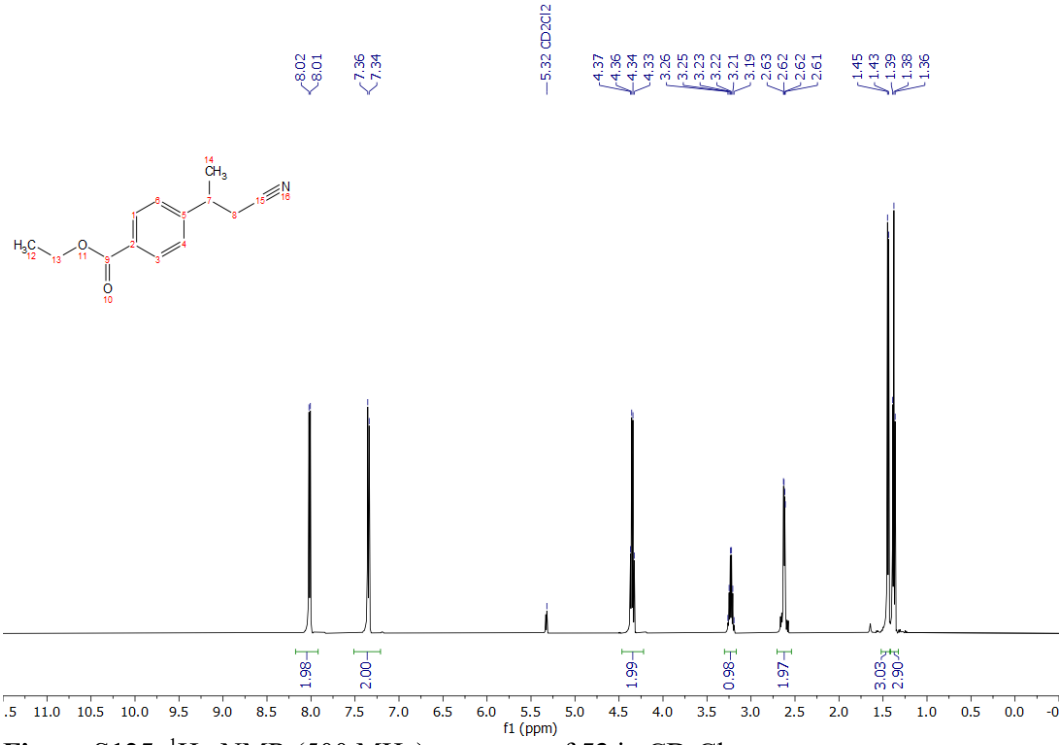


Figure S125. ^{1}H qNMR (500 MHz) spectrum of **53** in CD_2Cl_2.

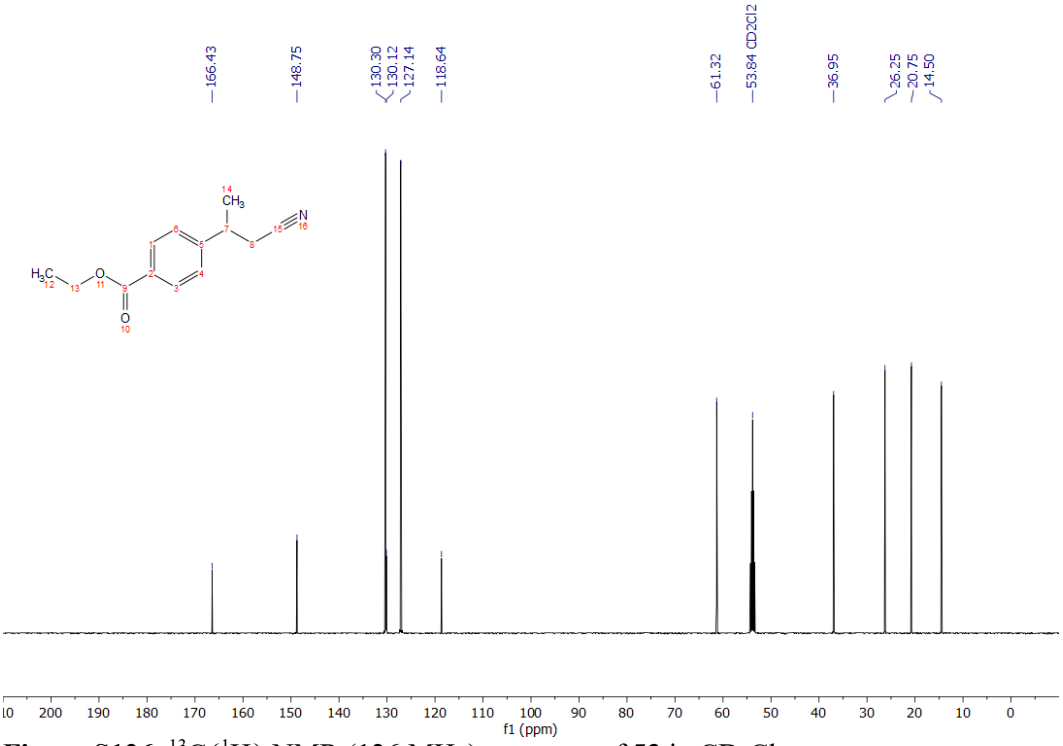
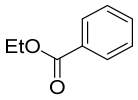


Figure S126. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **53** in CD_2Cl_2.

6.2.3. Characterization of Impurities Related to Electrochemical Cross-Electrophile Couplings



Ethyl benzoate (**54**), hydrodehalogenation impurity (des-bromo impurity). Clear colorless liquid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.08 (d, J = 7.9 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 1.41 (t, J = 7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ 166.74, 133.15, 131.15, 129.84, 128.75, 61.30, 14.55.

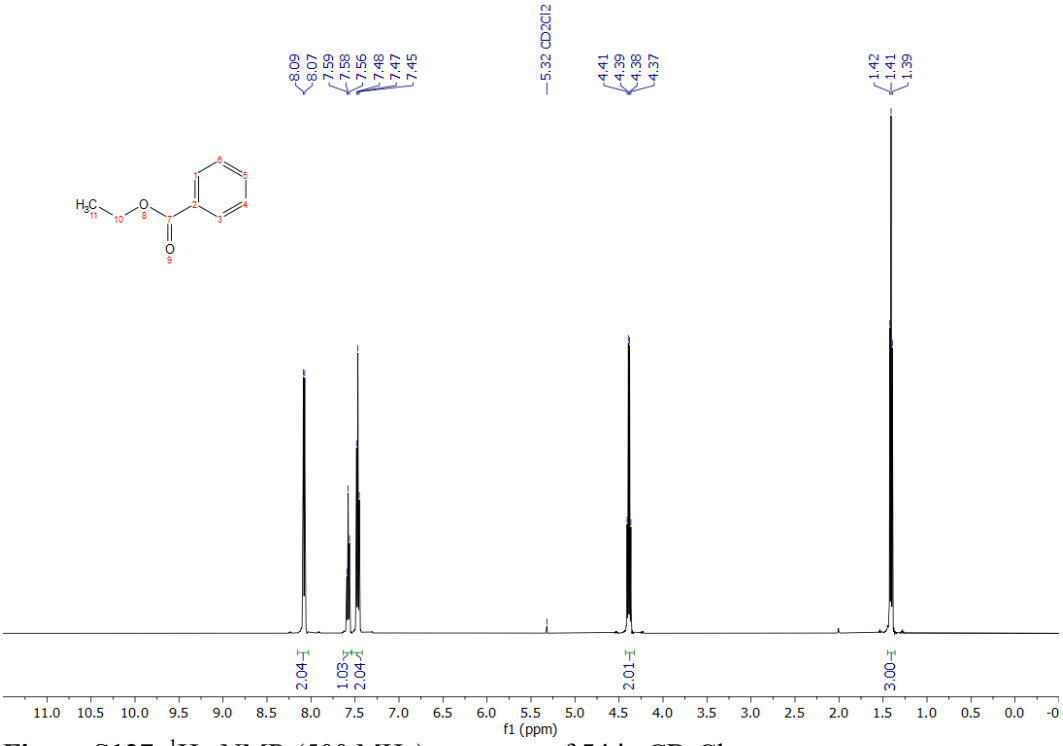


Figure S127. ^{1}H qNMR (500 MHz) spectrum of **54** in CD_2Cl_2.

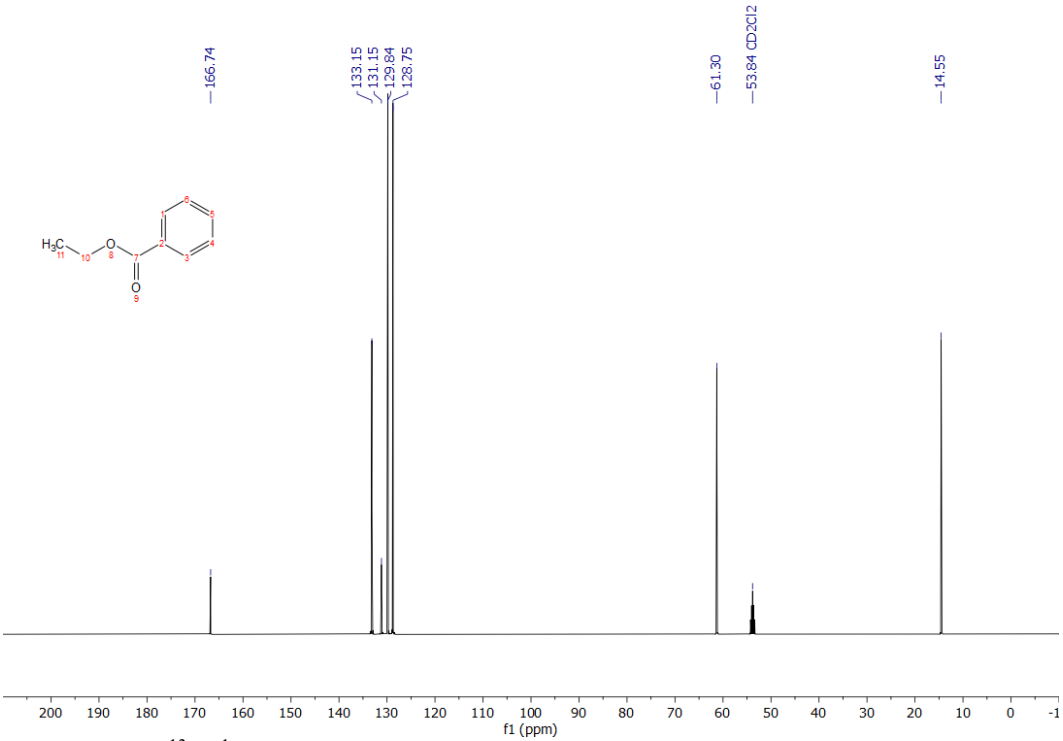
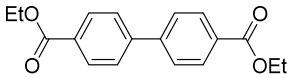


Figure S128. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **54** in CD_2Cl_2.



Biaryl homocoupling impurity **55**, white solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.12 (d, J = 8.2 Hz, 4H), 7.72 (d, J = 8.2 Hz, 4H), 4.38 (q, J = 7.1 Hz, 4H), 1.41 (t, J = 7.1 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 166.49, 144.57, 130.63, 130.42, 127.59, 61.47, 14.54. NMR data was consistent with previously reported data.[18]

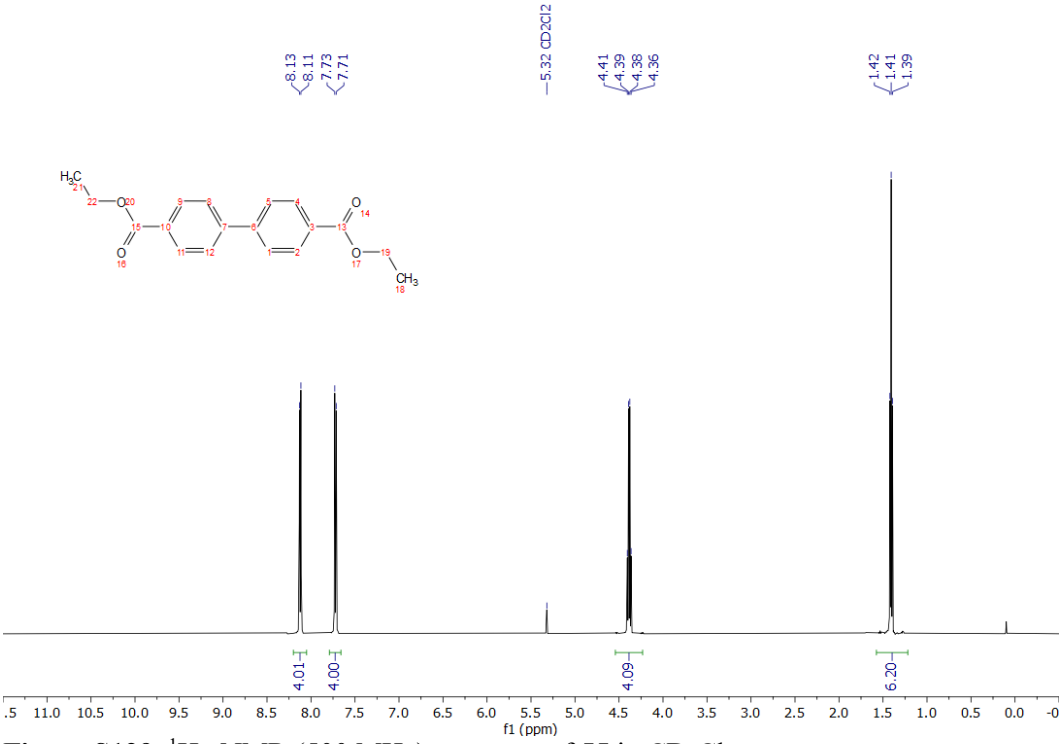


Figure S129. ^{1}H qNMR (500 MHz) spectrum of **55** in CD_2Cl_2.

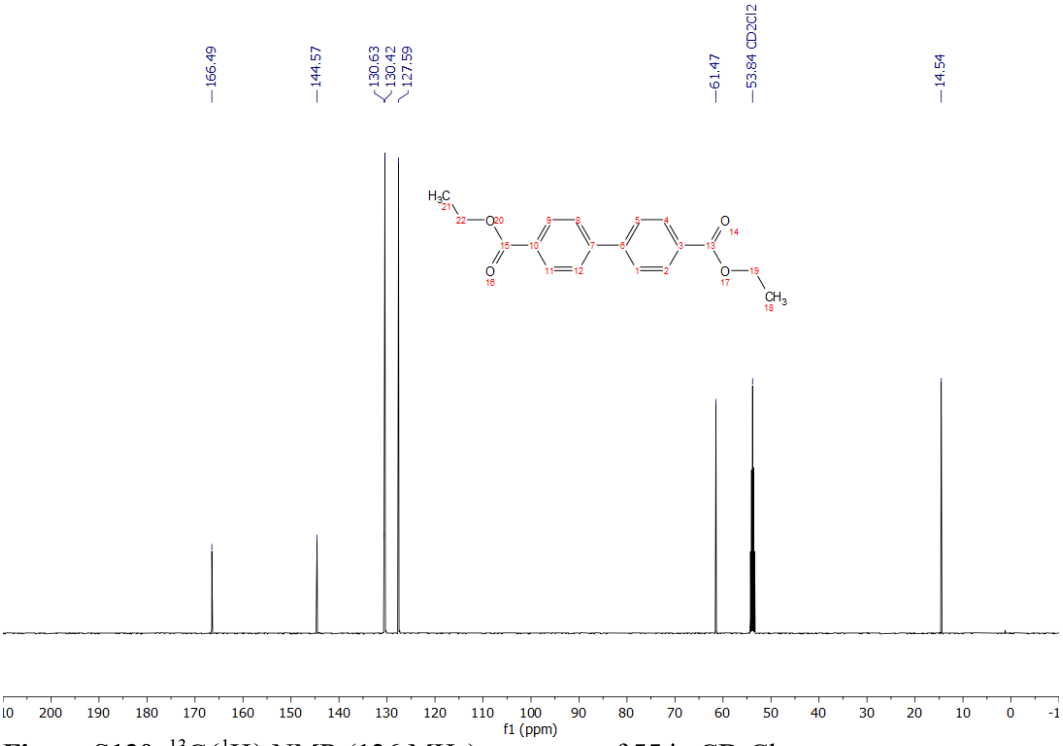
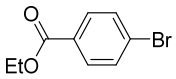


Figure S130. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **55** in CD_2Cl_2.



Ethyl 4-bromobenzoate (**52**, starting material aryl halide), pale yellow liquid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.90 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 4.35 (q, J = 7.1 Hz, 2H), 1.38 (t, J = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ 166.03, 132.05, 131.41, 130.07, 128.08, 61.62, 14.48.

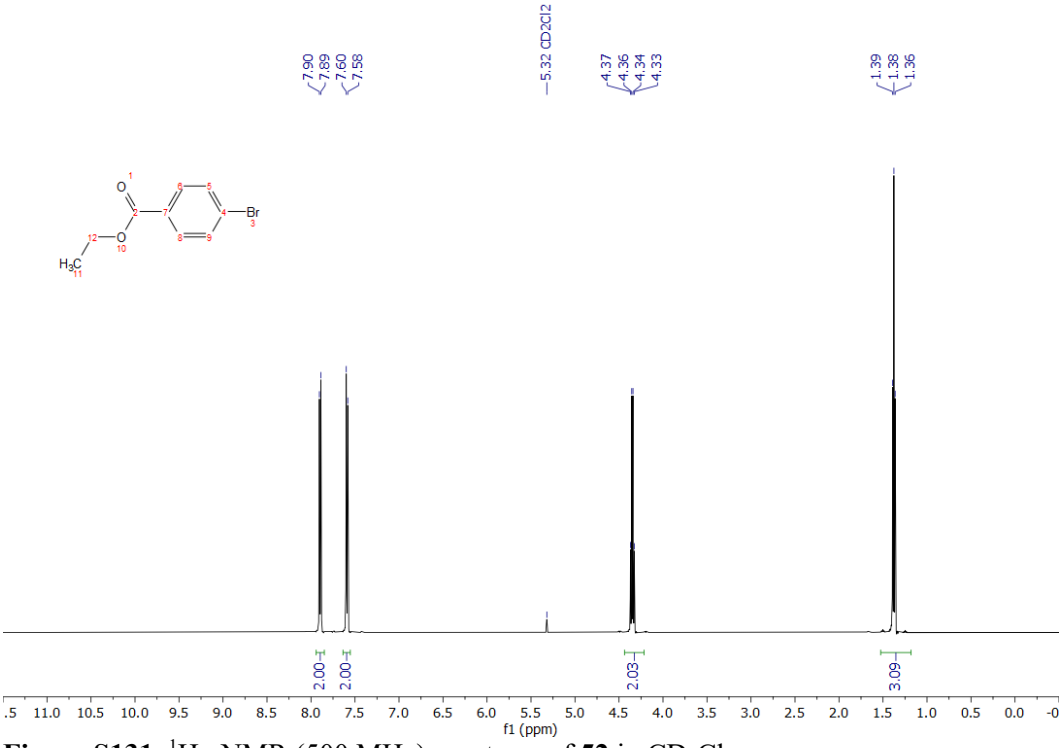


Figure S131. ^{1}H qNMR (500 MHz) spectrum of **52** in CD_2Cl_2.

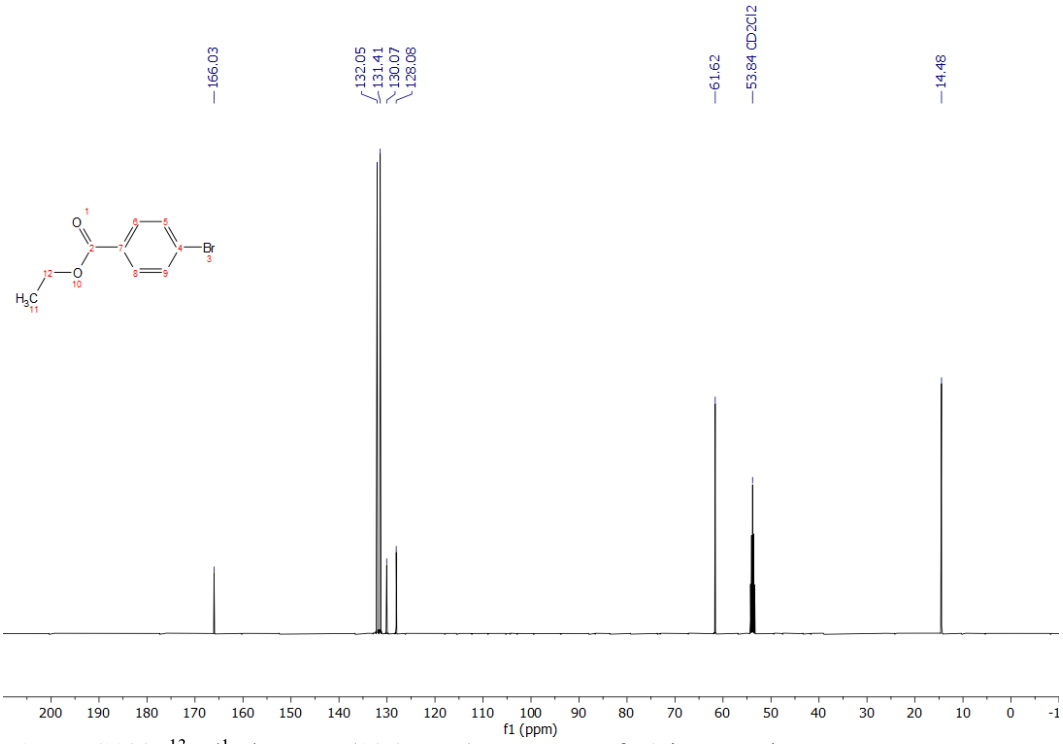
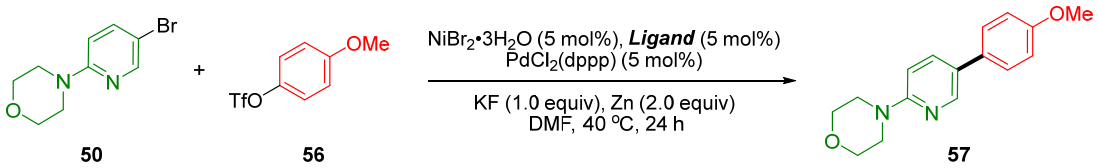


Figure S132. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **52** in CD_2Cl_2.

6.3. sp^2-sp^2 Cross-Electrophile Couplings



50
1 equiv
(1.0 mmol)

56
1 equiv
(1.0 mmol)

57

Ligand	Assay Yield /%
No ligand	2
bpy	74
20	0
21	64
31	15
37	3

6.3.1. Representative Procedure for the sp^2-sp^2 Cross-Electrophile Couplings

In an N_2 filled glovebox, a 40 mL vial (ChemGlass catalog CG-4912-06, with pressure relief septa caps) equipped with a stir bar, the following were added to the vial: 4-(5-bromopyridin-2-yl)morpholine (243 mg, 1.00 mmol), 4-methoxyphenyl trifluoromethanesulfonate (0.256 g, 1.00 mmol), $NiBr_2$•$3H_2O$ (13.6 mg, 0.05 mmol), iminophosphorane ligand **21** (19.0 mg, 0.05 mmol), $PdCl_2$(dppp) (29.5 mg, 0.05 mmol), KF (58.1, 1.0 mmol), Zn dust (<10 µm particle size, 130.8 mg, 2.0 mmol) an (0.033 mmol) and DMF (5 mL). The vial was capped with a pressure relief septa cap and the reaction mixture was heated, while stirring for 24 hours. Then, the crude reaction mixture was diluted with dichloromethane (50 mL) and the organic phase was washed with H_2O (3 × 50 mL), and dried over anhydr. Na_2SO_4, filtered, and concentrated in vacuo. Purification using liquid column chromatography (silica gel stationary phase, gradient 0% to 40% (v/v) of ethyl acetate in hexanes using a Teledyne ISCO CombiFlash® Rf+ chromatography system using prepacked single-use silica packed cartridges (RediSep® Rf Gold Normal-Phase Silica, 20–40 micron average particle size, 60 Å average pore size, with cartridge sizes 40 g (part number 69-2203-347) 40 mL/min. Product **57** was isolated as a white solid. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.40 (d, J = 2.5 Hz, 1H), 6.71 (dd, J = 8.8, 2.6 Hz, 1H), 6.50 – 6.43 (m, 2H), 6.00 – 5.93 (m, 2H), 5.70 (d, J = 8.8 Hz, 1H), 2.83 (s, 3H), 2.82 – 2.78 (m, 4H), 2.53 – 2.48 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 159.34, 159.00, 146.01, 135.98, 131.16, 127.57, 126.69, 114.72, 106.97, 67.10, 55.69, 46.15. ESI$^+$ LRMS *m/z* calcd. for $C_{16}H_{18}N_2O_2$ ($[M + H]^+$) 271.1446, found 271.1446.

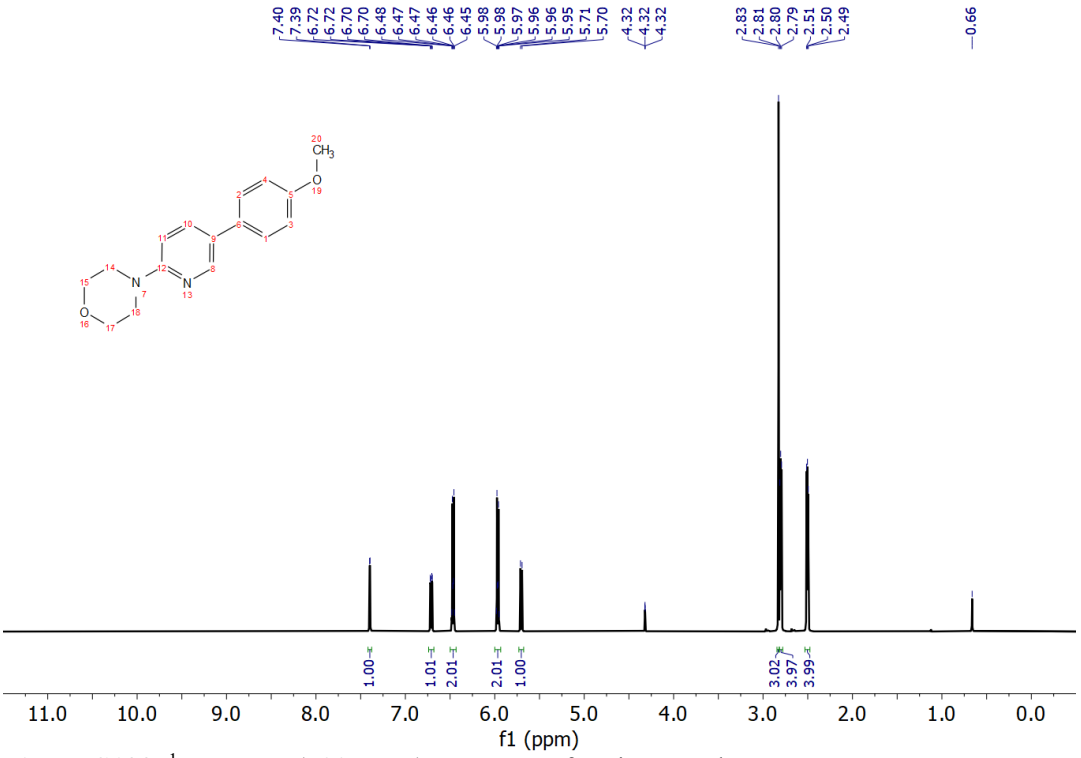


Figure S133. ^{1}H qNMR (500 MHz) spectrum of **57** in CD_2Cl_2.

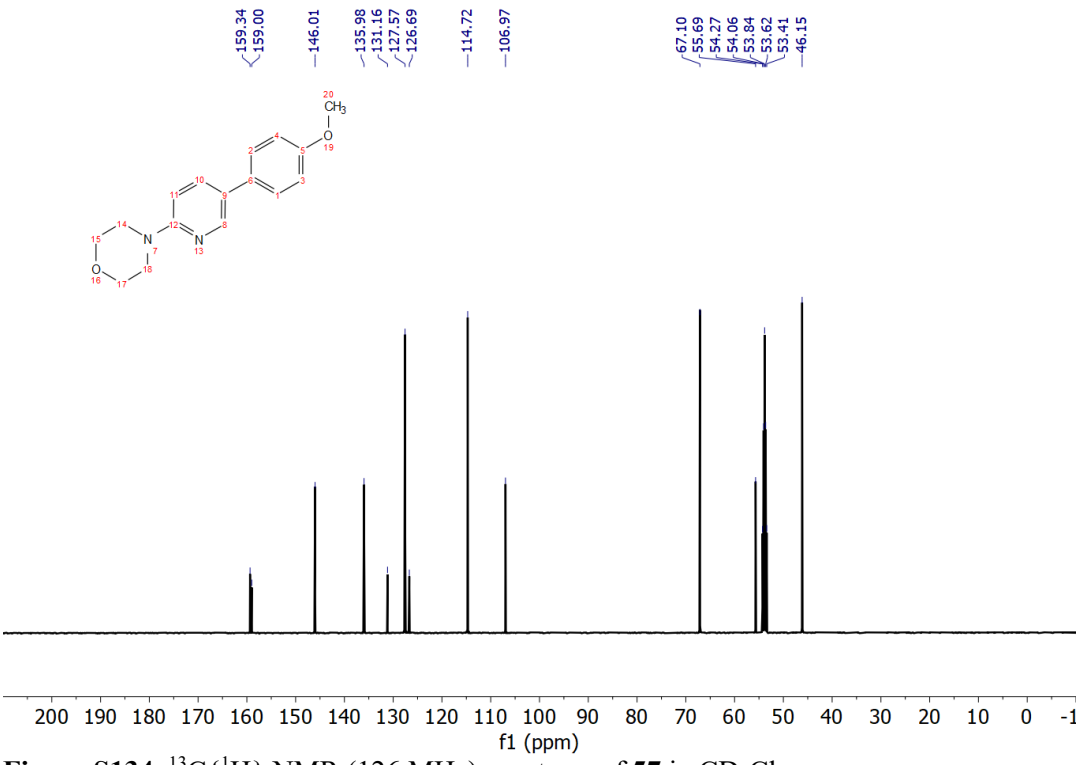
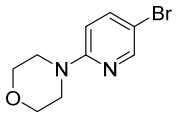


Figure S134. ^{13}C{^{1}H} NMR (126 MHz) spectrum of **57** in CD_2Cl_2.

6.3.2. Spectral Data of Starting Materials for the sp^2-sp^2 XEC



4-(5-bromopyridin-2-yl)morpholine (**50**, starting material) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.53 (d, *J* = 9.0 Hz, 1H), 6.51 (d, *J* = 9.0 Hz, 1H), 3.81 – 3.76 (m, 4H), 3.48 – 3.42 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.09, 148.54, 139.89, 108.33, 108.27, 66.66, 45.59.

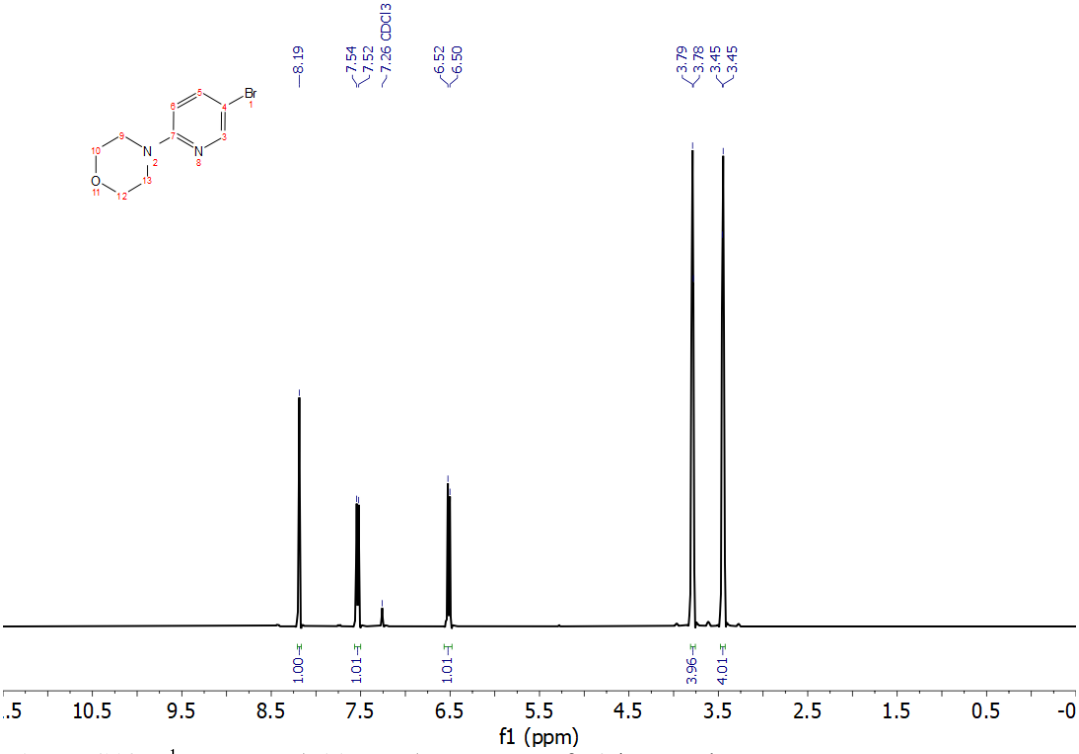


Figure S135. ^{1}H qNMR (500 MHz) spectrum of **50** in $CDCl_3$.

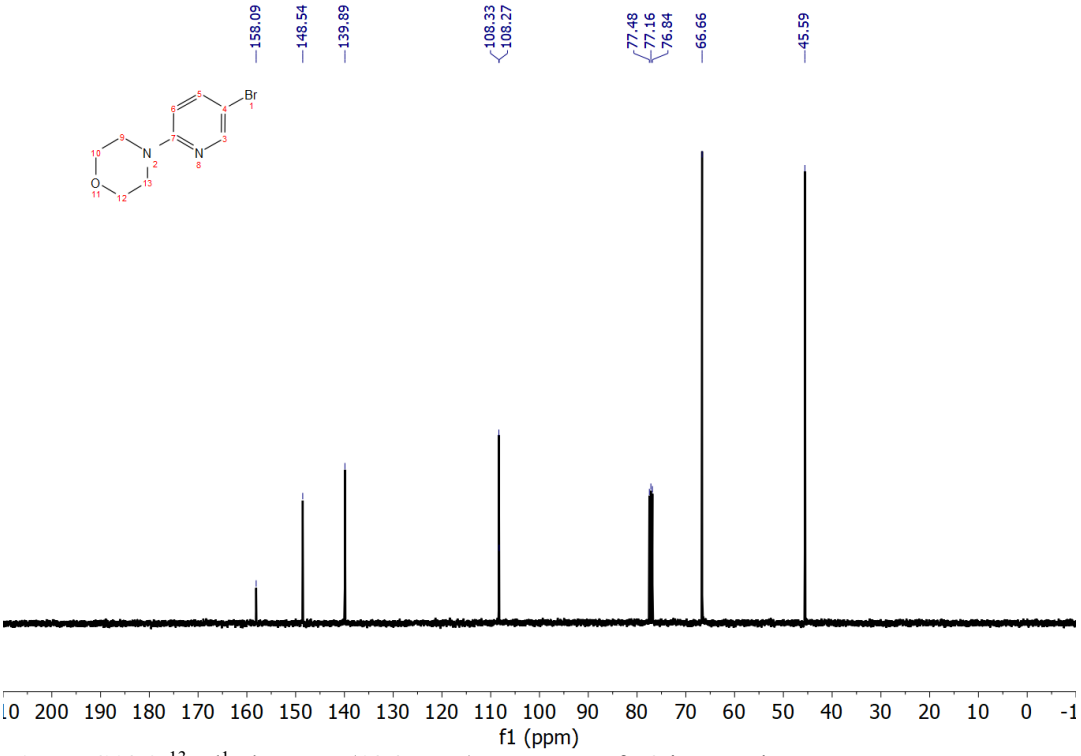
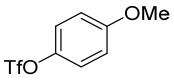


Figure S136. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **50** in $CDCl_3$.



4-methoxyphenyl trifluoromethanesulfonate (**56**, starting material) ^{1}H NMR (400 MHz, CD_3CN) δ 7.33 – 7.26 (m, 2H), 7.04 – 6.97 (m, 2H), 3.80 (s, 3H). ^{19}F NMR (471 MHz, CD_3CN) δ -73.92. ^{13}C NMR (126 MHz, CD_3CN) δ 160.44, 144.03, 123.48, 119.77 (q, J = 319.7 Hz), 116.20, 56.53.

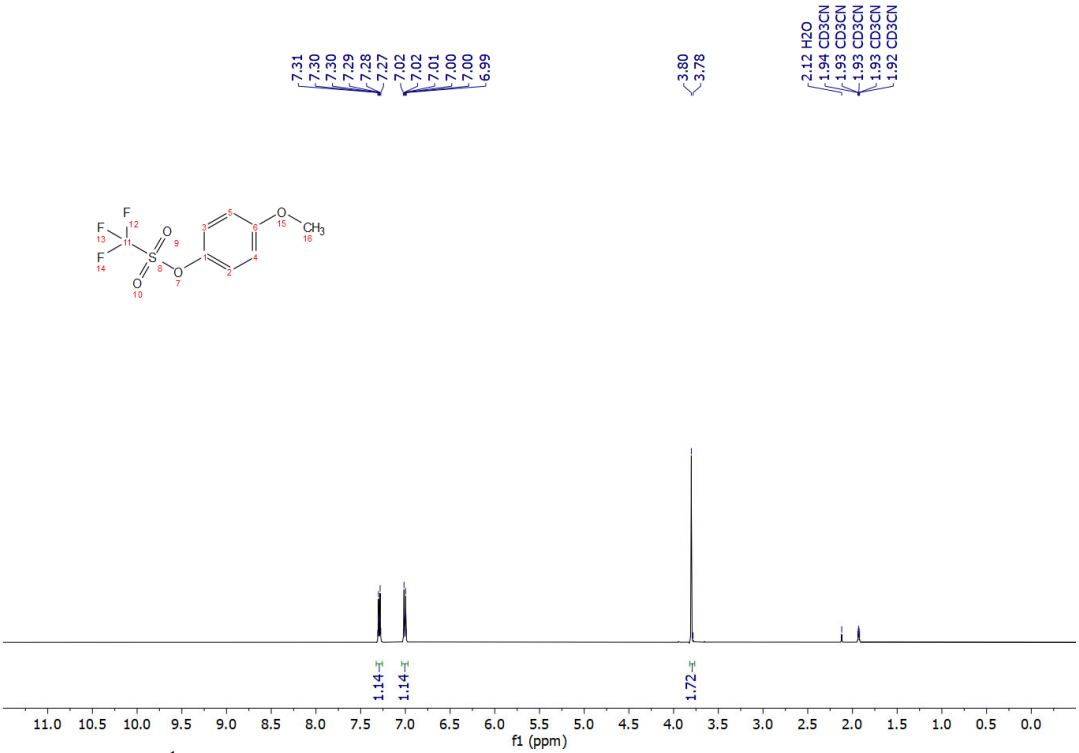


Figure S137. ^{1}H qNMR (500 MHz) spectrum of **56** in CD_3CN

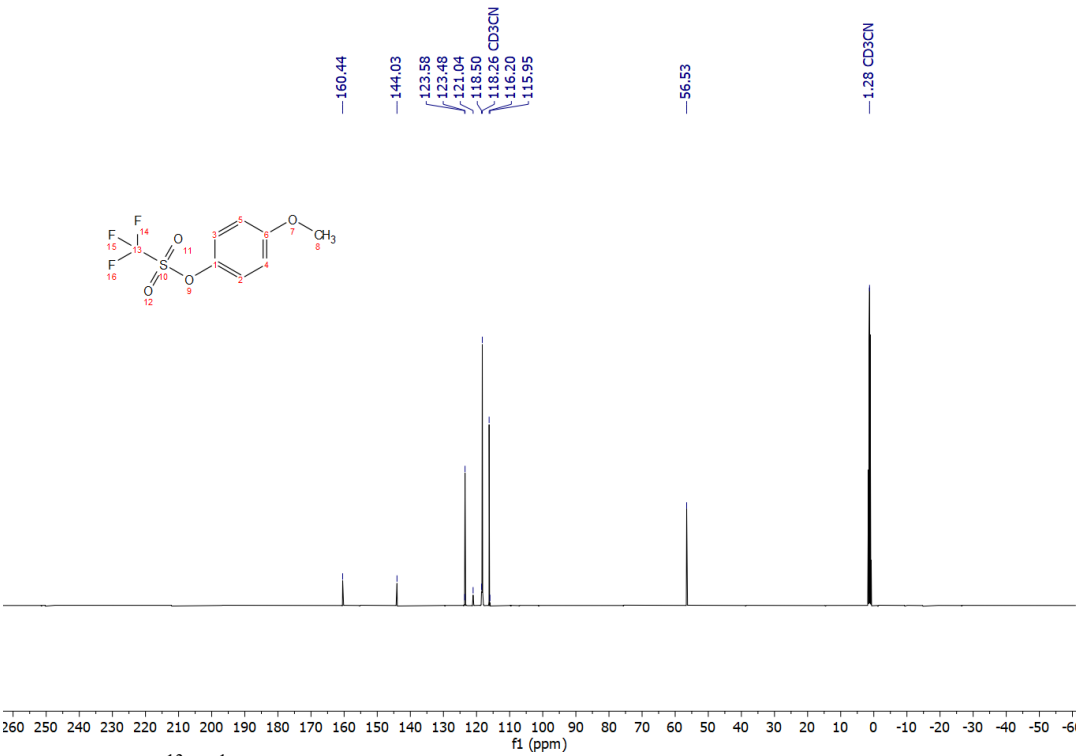


Figure S138. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **56** in CD_3CN.

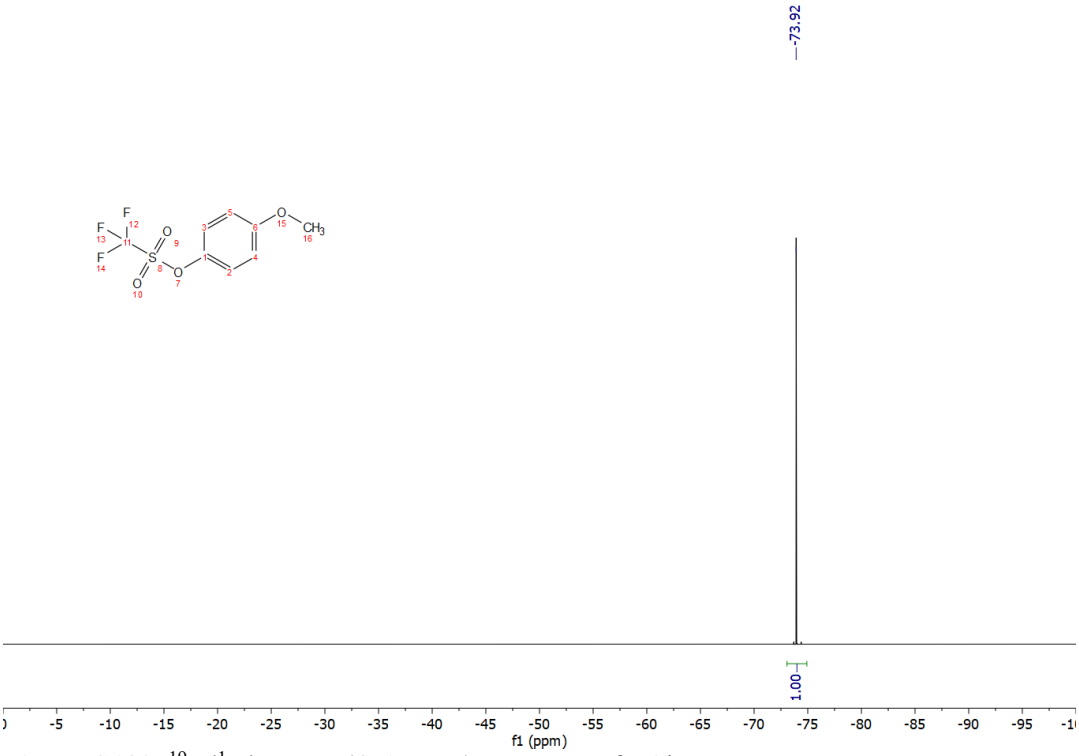
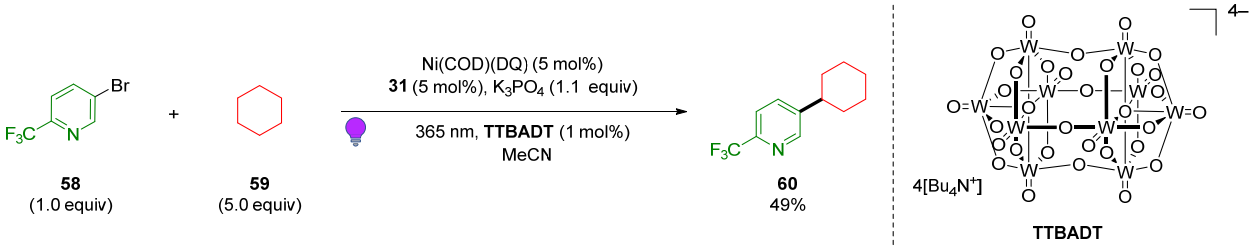


Figure S139. $^{19}F\{^{1}H\}$ NMR (471 MHz) spectrum of **56** in CD_3CN.

6.4. C–H Functionalization via HAT Photocatalysis using Iminophosphorane Ligand 31



58 (1.0 equiv) **59** (5.0 equiv) **60** 49%

In an N_2 filled glovebox, a 10 mL Restek vial (23 × 46 mm, flat bottom , clear, crimp; catalog 24683) equipped with a PTFE stir bar and the following were added to the vial: Ni(COD)(DQ) (0.0083 mg, 0.025 mmol, 5.0 mol%), iminophosphorane ligand **31** (0.013 g, 0.025 mmol, 5.0 mol%), tetrabutylammonium decatungstate (0.017 g, 0.0050 mmol, 1.0 mol%), 5-bromo-2-(trifluoromethyl)pyridine (0.113 g, 0.500 mmol, 1.0 equiv), cyclohexane (210 mg, 270 µL, 2.5 mmol, 5.0 equiv.), and K_3PO_4 (0.117 g, 0.550 mmol, 1.1 equiv), and MeCN (5.0 mL). The vial was sealed with an aluminum seal with septa (PTFE silicone, catalog 21767) with the assistance of a vial cap crimper (catalog 23398). The vial was brought out of the N_2 filled glovebox and placed in an air-cooled TAK120 photoreactor and irradiated at 365 nm for 24 h (1.55 W/vial intensity) while applying rotary stirring (650 rpm). Assay yield determination using ^{1}H NMR spectroscopy and mesitylene as an internal standard provided 49% assay yield. Purification by column chromatography (silica gel, gradient 1% to 10% EtOAc in hexanes) yielded compound **60** as a pale, yellow oil. ^{1}H NMR (500 MHz, CD_3CN) δ 8.60 (s, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.69 (d, J = 8.1 Hz, 1H), 2.68 (t, J = 11.4 Hz, 1H), 1.85 (s, 4H), 1.75 (d, J = 12.8 Hz, 1H), 1.46 (tt, J = 25.8, 12.2 Hz, 4H), 1.36 – 1.22 (m, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 150.35, 147.88, 146.09 (q, J = 34.1 Hz), 136.70, 123.11 (q, J = 272.7 Hz), 121.29 (q, J = 2.8 Hz), 42.59, 34.50, 27.30, 26.55. HRMS *m/z* calcd. for $C_{12}H_{15}F_3N$ ($[M + H]^+$) 230.1156, found 230.1154. NMR spectroscopic data was consistent with that reported in the literature.[19]

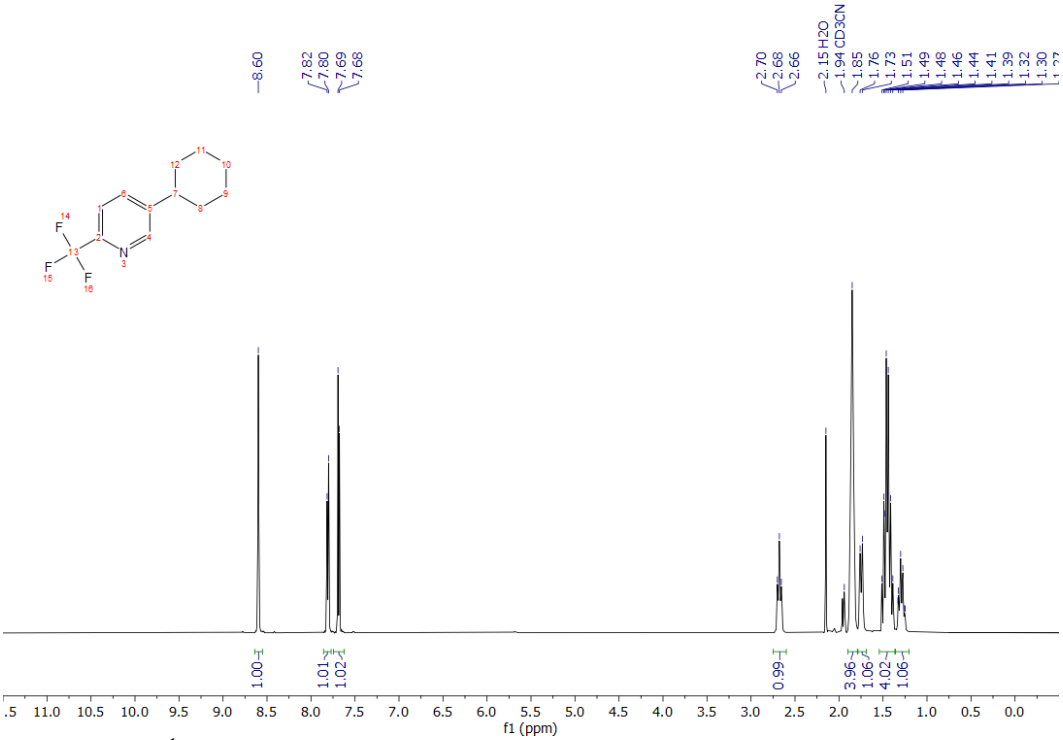


Figure S140. ^{1}H qNMR (500 MHz) spectrum of **60** in CD_3CN.

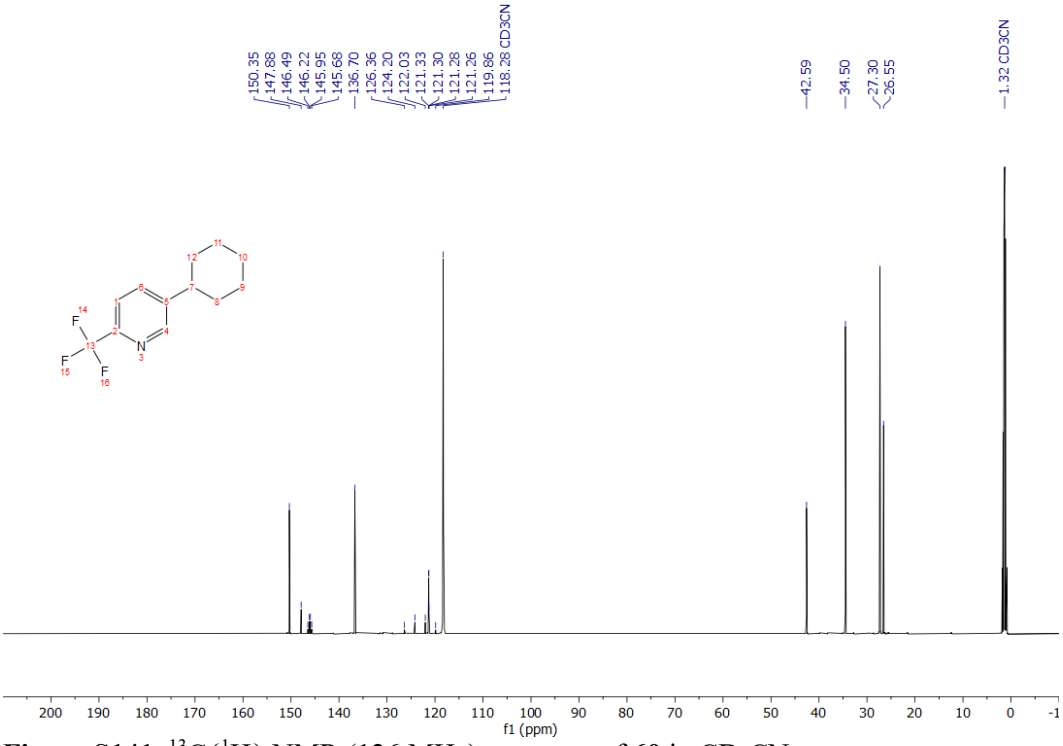
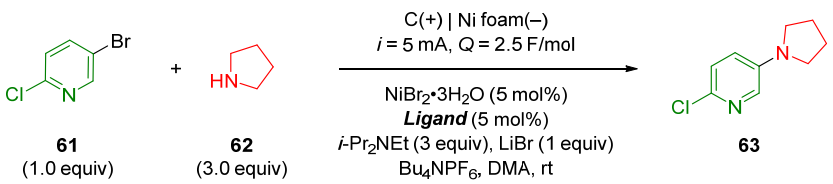


Figure S141. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **60** in CD_3CN.

6.5. C–N Bond Formation via Electrochemistry



61 (1.0 equiv) **62** (3.0 equiv) **63**

Ligand	Assay Yield of 63 /%
No ligand	26
dtbbpy	22
21	62
35	24
31	28
19	21

6.5.1. Ligand Screen on 0.33 mmol Scale

In an N_2 filled glovebox, six 5 mL Electrasyn vial were charged with a PTFE coated magnetic stir bar, $NiBr_2$•$3H_2O$ (0.0045 g, 0.0165 mmol), a ligand (0.0165 mmol), tetrabutylammonium hexafluorophosphate (0.194 g, 0.5 mmol), 5-bromo-2-chloropyridine (0.0635 g, 0.33 mmol), pyrrolidine (0.0711 g, 1.00 mmol), *N,N*-diisopropylethylamine (0.129 g, 1.00 mmol) and DMA (5.0 mL). Electrodes (graphite anode, nickel foam cathode) were connected to the Electrasyn vial cap and the electrodes were immersed into the above solution. The Electrasyn vial cap was connected to the Electrasyn 2.0 and the reaction mixture was electrolyzed under a constant current of 5.0 mA for a total of 2.5 F/mol of charge accompanied by rotary magnetic stirring (900 rpm). Graphite electrode dimensions exposed to solution: 5.1 mm (width) × 0.04 mm (thickness) × 26.1 mm height; Nickel foam dimensions exposed to solution: 8.0 mm (width) × 2.1 mm (thickness) × 24.7 mm height. Upon completing the electrolysis, internal standard (1,3,5-trimethoxybenzene) was added to the reaction mixture, the mixture was rendered homogenous and the assay yield was measured via ^{1}H NMR spectroscopy. The crude reaction mixture was diluted with dichloromethane (50 mL) and the organic phase was washed with H_2O (3 × 50 mL), and dried over anhydr. Na_2SO_4, filtered, and concentrated in vacuo. Purification using liquid column chromatography (silica gel stationary phase, gradient 0% to 50% (v/v) of ethyl acetate in hexanes using a Teledyne ISCO CombiFlash®

Rf+ chromatography system using prepacked single-use silica packed cartridges (RediSep® Rf Gold Normal-Phase Silica, 20–40 micron average particle size, 60 Å average pore size, with cartridge sizes 40 g (part number 69-2203-347) 40 mL/min. Product **63** was isolated as a white solid. ^{1}H NMR (400 MHz, CD_3CN) δ 7.66 (d, J = 3.2 Hz, 1H), 7.16 – 7.09 (m, 1H), 6.89 (dd, J = 8.7, 3.2 Hz, 1H), 3.30 – 3.17 (m, 4H), 2.02 – 1.96 (m, 4H). ^{13}C NMR (101 MHz, CD_3CN) δ 144.25, 137.18, 133.76, 124.52, 122.22, 48.23, 25.99.

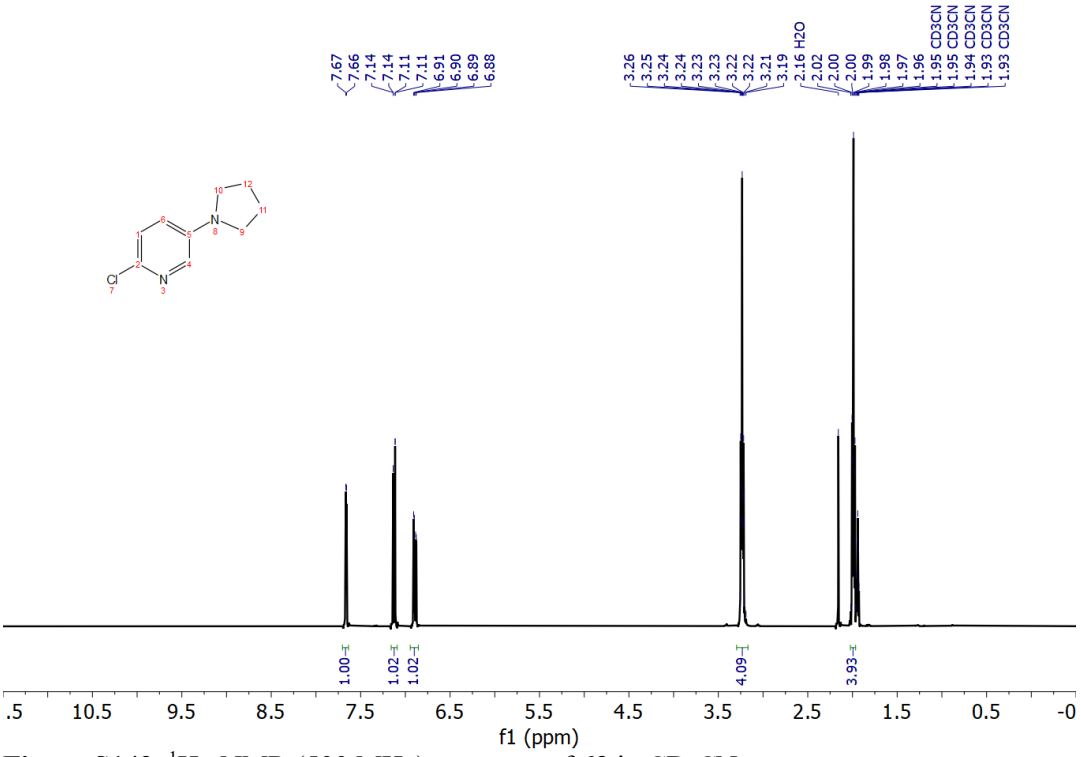


Figure S142. ^{1}H qNMR (500 MHz) spectrum of **63** in CD_3CN.

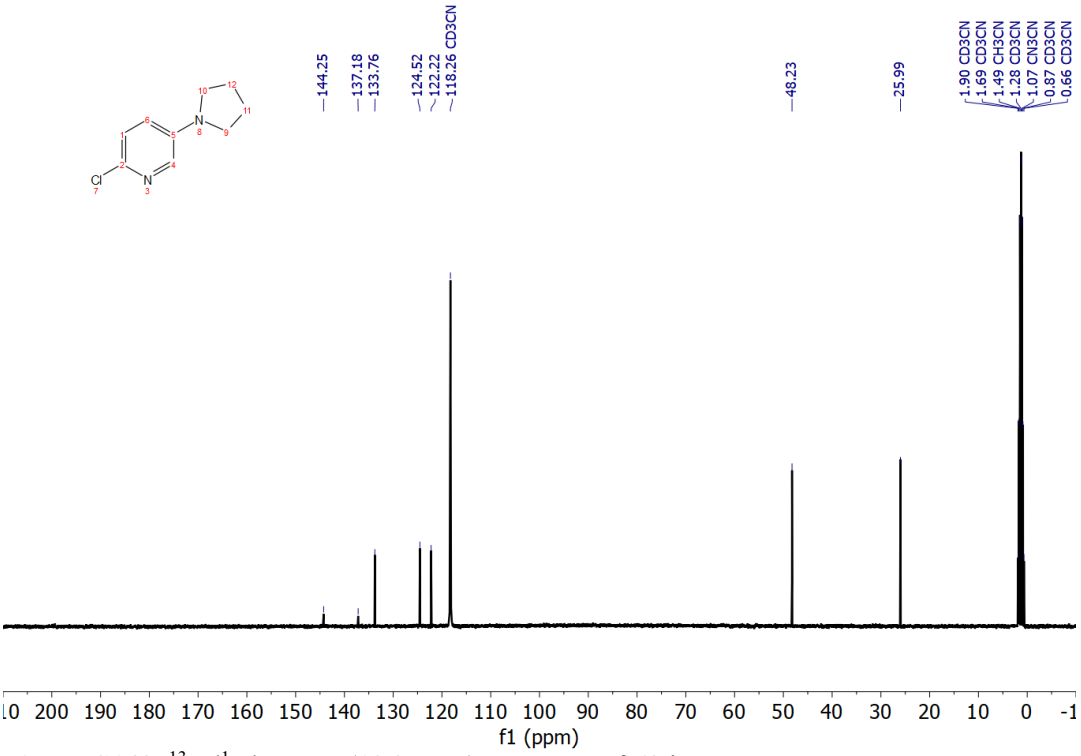
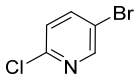


Figure S143. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **63** in CD_3CN.

6.5.2. Spectral Data for Starting Material



5-bromo-2-chloropyridine (**61**, starting material) ^{1}H NMR (400 MHz, CD_3CN) δ 8.47 (d, J = 2.5 Hz, 1H), 7.91 (dd, J = 8.5, 2.6 Hz, 1H), 7.35 (d, J = 8.5 Hz, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 151.59, 150.67, 142.77, 126.86, 120.05.

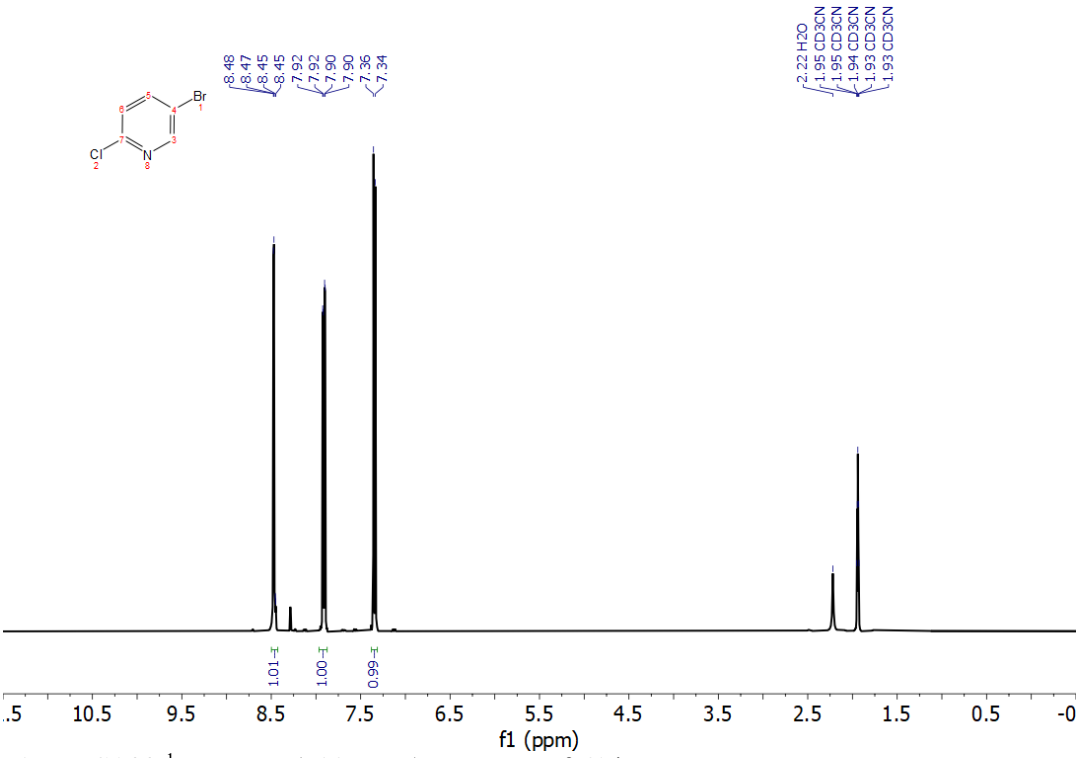


Figure S144. ^{1}H qNMR (500 MHz) spectrum of **61** in CD_3CN.

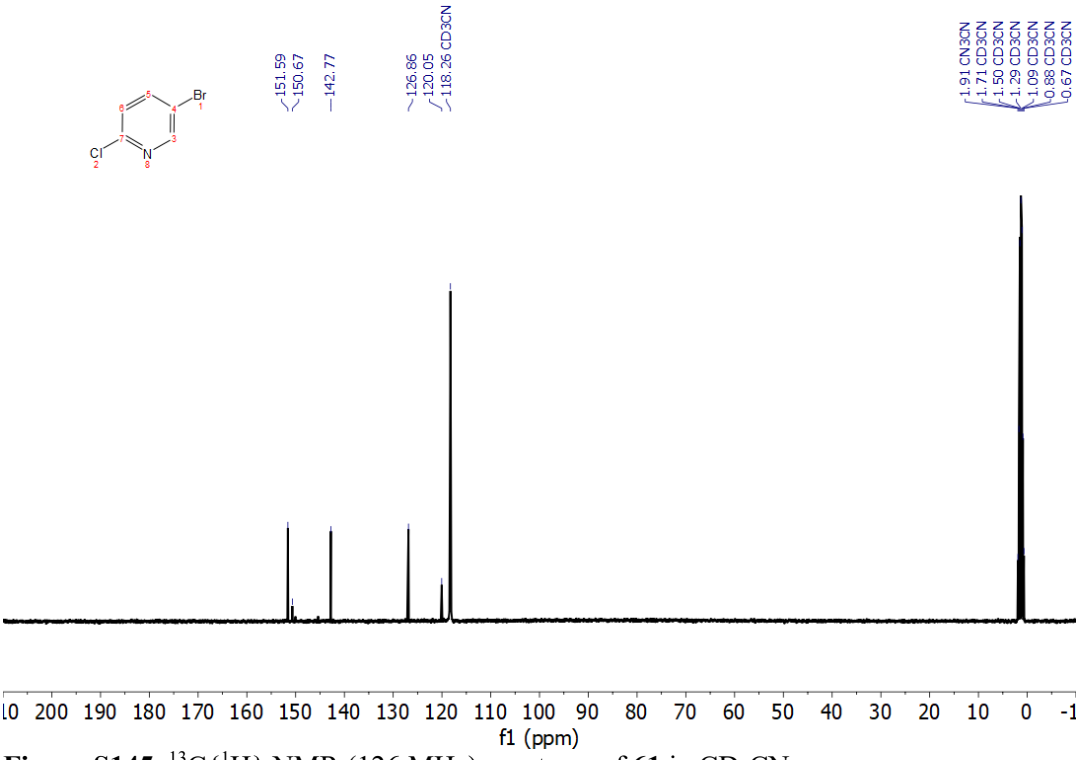
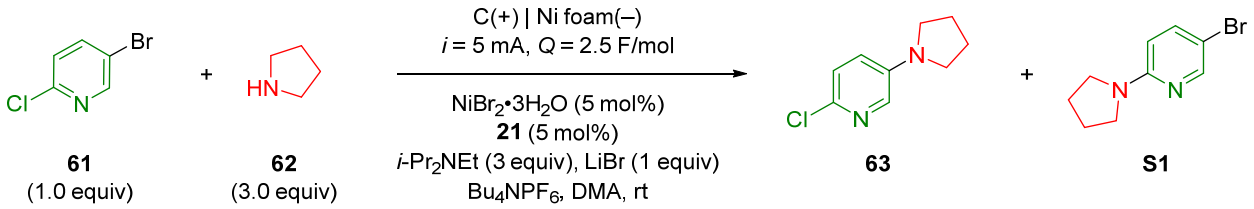


Figure S145. $^{13}C\{^{1}H\}$ NMR (126 MHz) spectrum of **61** in CD_3CN.

6.5.3. Evaluation of Regioselectivity in the C–N Bond Formation

Below is the evaluation of the regioselectivity in the C–N bond formation via electrochemistry using the top performing ligand (ligand **21**).



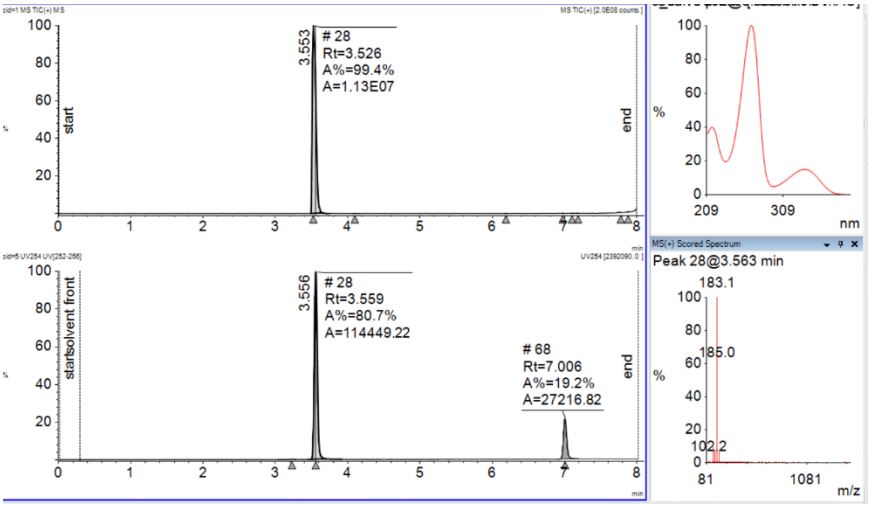


Figure S146. UPLC-MS traces of product **63** at t_r = 3.526 min (top: ESI$^+$, bottom: UV254 nm). Sample contains 4,4'-diisopropylbiphenyl internal standard (at t_r = 7.006 min)

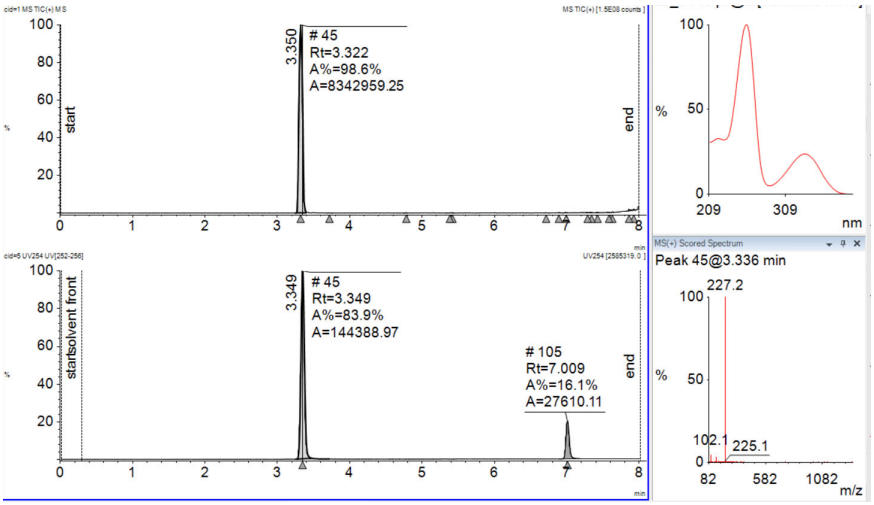


Figure S147. UPLC-MS traces of product **S1** at t_r = 3.349 min (top: ESI$^+$, bottom: UV254 nm). Sample contains 4,4'-diisopropylbiphenyl internal standard (at t_r = 7.009 min).

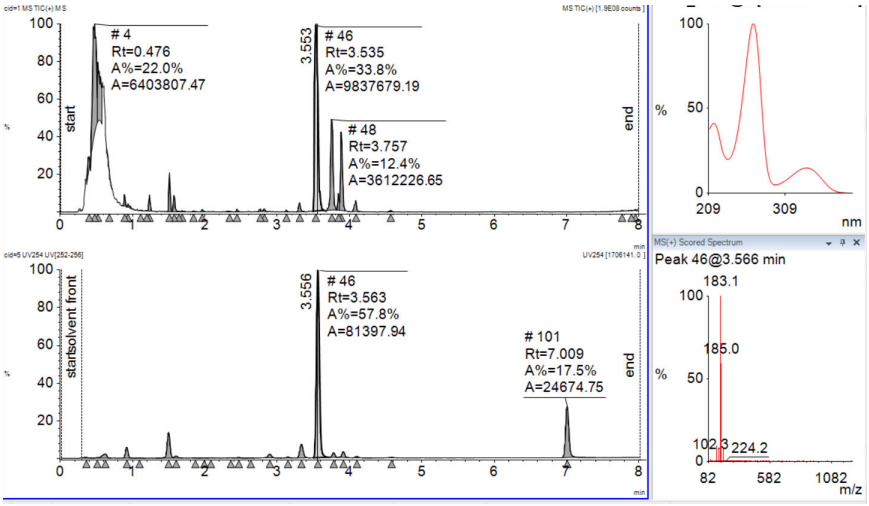


Figure S148. UPLC-MS traces of crude reaction mixture for the C-N electrochemical coupling using ligand **20** showing 67:1 LC area ratio for the major product **63** compared to product **S1**. Sample contains 4,4'-diisopropylbiphenyl internal standard (at t_r = 7.009 min).

7. Mechanistic Studies

7.1. Discussion of Mechanistic Studies

In order to gain mechanistic insight into the reaction, we conducted DFT calculations and followed up with a series of experiments based on NMR spectroscopy (^{1}H, ^{13}C, ^{31}P) and cyclic voltammetry. Five potential mechanisms were initially considered (Scheme S2). In mechanism 1 (Scheme S2A), a pre-equilibrium chemical step precedes the initial oxidation. Specifically, nucleophilic attack of carbodiimide **5** by phosphine **2a** would lead to zwitterionic intermediate **S2a** followed by an oxidation to afford distonic radical cation[20] **S3a**, which upon fragmentation affords *N*-centered radical **43** (stepwise formal 1,2-shift of the phosphine). Radical **43** could react with phosphine **2a–b** to generate **42a** followed by oxidation to get to **45a**. Alternatively, radical **S2** could directly generate **45a** via coupling with the radical cation of the phosphine (**S4a**) generated via anodic oxidation from the corresponding phosphine (radical-radical reactions are statistically less likely, especially when neither is a persistent radical). Finally, loss of the silyl group from **45a** would then afford iminophosphorane product **46a**.

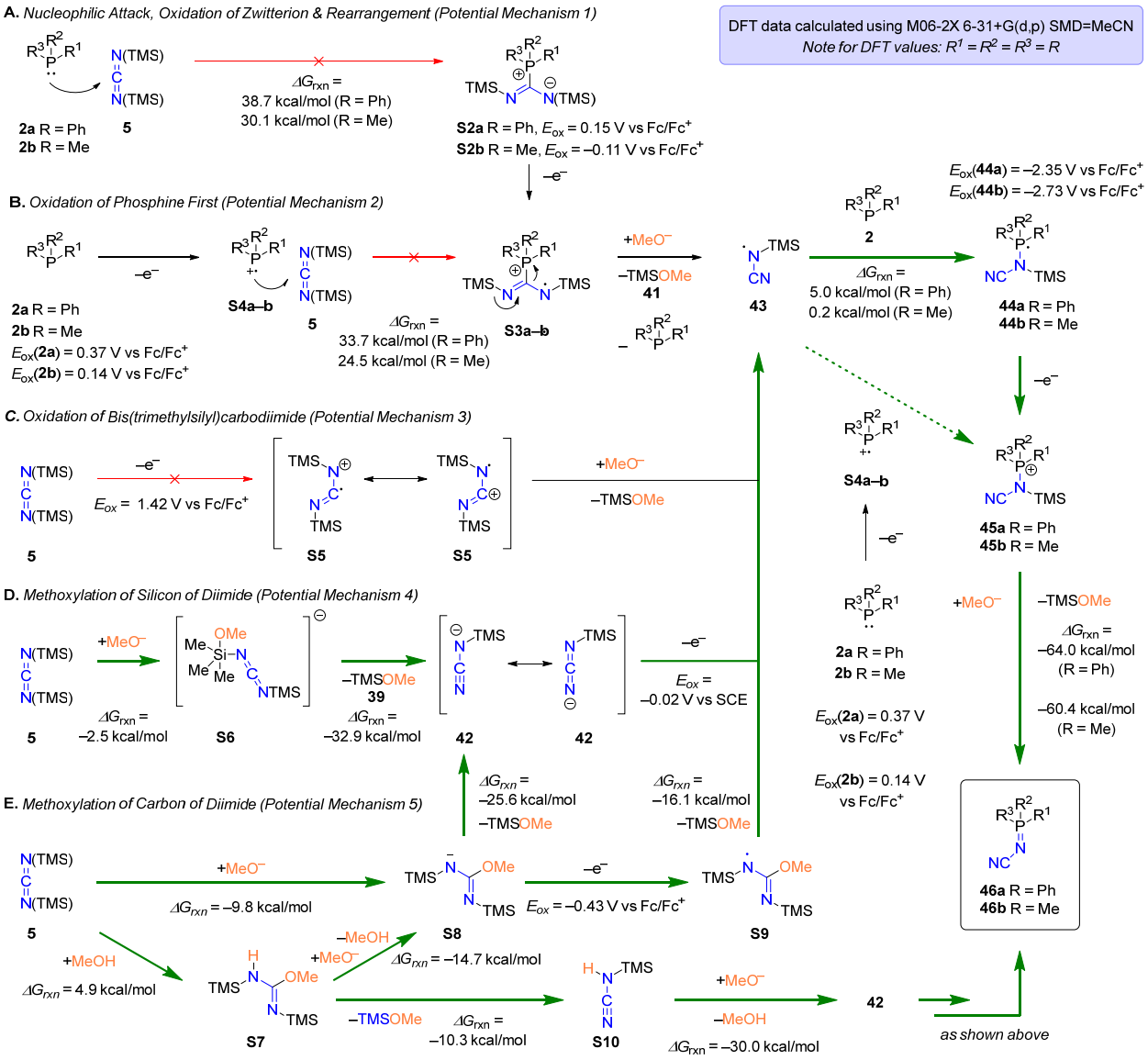
In mechanism 2 (Scheme S2B), oxidation of the phosphine (**2a** → **S4a**) followed by attack of the carbodiimide **5**, would afford intermediate **S3a**, with subsequent steps being identical to mechanism 1.

In mechanism 3 (Scheme S2C), oxidation of bis(trimethylsilyl)carbodiimide **5** would afford distonic radical cation **S5**/**S5'**, which upon loss of TMS–OMe would afford **43**, thereby once again ultimately leading to product via the identical final steps of mechanism 1.

In mechanism 4 (Scheme S2D), hydrogen evolution at the cathode via reduction of protons from methanol would generate methoxide that could attack a silicon in bis(trimethylsilyl)carbodiimide **5** to generate pentacoordinate silicate anion **S6** followed by loss of TMS–OMe to afford anion **42**. Oxidation of anion **42** would generate the key *N*-centered radical **43**, en route to product **46a–b** via the identical final pathway as shown in mechanism 1.

In mechanism 5 (Scheme S2E), methoxylation of bis(trimethylsilyl)carbodiimide at the carbon of the diimide results in either intermediate **S7** or **S8**, depending on whether MeOH or methoxide is the nucleophile. These two pathways can converge at intermediate **S8** which could subsequently generate key anion **42** via loss of TMS–OMe which intercepts mechanism 4 to ultimately lead to the iminophosphorane product **446**–**b** via radical **43**. Alternatively, oxidation of **S8** to **S9** and subsequent loss of TMS–OMe leads to radical **43**. Finally, intermediate **S7** can also lead to key intermediate **43** via trimethysilylcyanamide **S10**. Ultimately, more than one pathway may exist but all of them funnel through intermediate **43** en route to iminophosphorane product **46a**–**b**.

To summarize, the key question related to identifying the operating mechanism is focused on what is the initial step: an oxidation (e.g. oxidation of carbodiimide **5**) or a chemical step (e.g. pre-equilibrium formation of **S2**).



Scheme S2. Various reaction mechanisms initially considered (data is consistent with mechanisms D & E).

To probe mechanism 1, specifically the feasibility of a pre-equilibrium step to form zwitterion **S2** via nucleophilic attack of the carbodiimide **5** by the phosphine, we conducted DFT calculations using M06-2X/6-31+G(d,p) SMD=MeCN.[21] DFT results suggest that phosphine addition to carbodiimide **5** is endothermic and energetically inaccessible at room temperature: 38.7 kcal/mol for PPh_3, 30.1 kcal/mol for PMe_3 (a more electron rich & more nucleophilic trialkylphosphine compared to PPh_3). Experimentally, ^{31}P NMR spectroscopic experiments are consistent with the lack of forming zwitterion **S2** (or any new species containing phosphorus). Specifically, no new ^{31}P signals were observed when comparing the ^{31}P NMR spectra for the following three mixtures (all in 4:1 (v/v) NMP/CD_3OD with $(PhO)_3PO$ internal standard): (mixture 1) triphenylphosphine; (mixture 2) triphenylphosphine and 0.1 M Me_4NOAc electrolyte; and (mixture 3) a 3:1 molar ratio of bis(trimethylsilyl)carbodiimide **5** and triphenylphosphine in 0.1 M Me_4NOAc 4:1 (v/v) NMP/CD_3OD (see Figure S140).

Finally, cyclic voltammetry (CV) experiments (*vide infra*) of these mixtures of triphenylphosphine and bis(trimethylsilyl)carbodiimide **5** did not reveal the emergence of a redox event at a lower potential than that for PPh_3 (see Figure S141). Based on the data from DFT, NMR spectroscopy, and CV experiments we

ruled out mechanism 1 formation of zwitterion **S2** prior to electrolysis. However, a new oxidation wave was observed around 0.17 V vs Fc/Fc^+ when KOEt was added to solutions of the carbodiimide **5**, which is not present in the cyclic voltammogram of either of the individual components. The alkoxide was added as a surrogate for the electrogenerated base at the cathode upon reducing H^+ (from MeOH) to hydrogen. The above CV data supports the alkoxide mediated formation of anion **42** which can be oxidized to the *N*-centered radical **43** (DFT predicted oxidation at –0.02 V vs Fc/Fc^+, *vide infra*).

DFT calculations can predict oxidation potential as to which compound is easier to oxidize. Calculations[22,23] using M06-2X/6-31+G(d,p) SMD=MeCN predict the following oxidation potentials (all vs Fc/Fc^+): 0.37 V for Ph_3P, 1.42 V for bis(trimethylsilyl)carbodiimide **5**, 1.24 V for Ph_3P=N-CN (**1**) ,and 1.74 for Ph_3P=O (**6**). Cyclic voltammetry[24] provides experimental insight into which compound is easier to oxidize: the phosphine, the bis(trimethylsilyl)carbodiimide (**5**), or the mixture of the above two reagents (which would be consistent with oxidation of zwitterion **S2**). Cyclic voltammetry reveals that the oxidation of PPh_3 occurs at 0.76 V vs Fc/Fc^+, >1.5 V vs Fc/Fc^+ for bis(trimethylsilyl)carbodiimide **5**, and 0.79 V vs Fc/Fc^+ for the 1:1 mixture of PPh_3 and **5** (essentially within experimental error of that observed for PPh_3 alone). These data suggest that mechanisms 2, 4 or 5 could be operational (Schemes S1B & S1D), as these do not involve direct oxidation of bis(trimethylsilyl)carbodiimide **5**, unlike mechanism 3 (Scheme S1C).

DFT calculations of the ΔG_{rxn} for 1st step of mechanism 1 or the 2nd step of mechanism 2 have large endothermic values and thus are prohibitive for a room temperature reaction. This suggests that neither of these mechanisms are operational, leaving only mechanism 4 and 5 as feasible mechanisms.

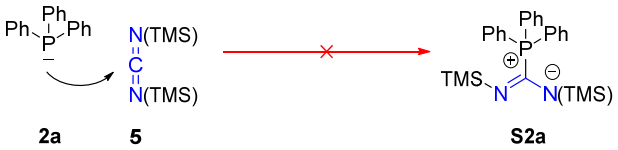
In support of mechanisms 4 and 5 (Scheme S1D & S1E), the omission of methanol results in significantly decreased reaction performance (12% of product **1a**). On the other hand, the identity of the alcohol is less critical other aliphatic alcohols provide iminophosphorane **1a**: EtOH (87%), *t*-amyl alcohol (82%) all give comparable yield to using MeOH (83%) when used in 4:1 v/v MeCN/ROH ratios under conditions otherwise identical to the optimal conditions. Even the use of electron-deficient alcohols (weakly nucleophilic alkoxides) such as trifluoroethanol (TFE) and hexafluoropropanol (HFIP) result in comparable product yields of **1** (91% and 82% respectively). We note that adventitious water may be reduced at the cathode to generate hydroxide which could play a role similar to the alkoxides generated from the alcohols above and may be associated with the 12% yield of **1** when an alcohol is omitted.

While both the DFT and experimental (CV, NMR spectroscopy, and control electrosynthetic experiments) are consistent with mechanisms 4 and 5, there could be two potential pathways from key intermediate **43** to the iminophosphorane product **46**. Either the *N*-centered radical **43** adds to the neutral phosphine **2a** or to the singly oxidized phosphine (i.e. radical cation **S4a**). Addition of **41** to neutral phosphines is thermally accessible (ΔG_{rxn} = 5.0 kcal/mol for triphenylphosphine and ΔG_{rxn} = 0.2 kcal/mol for trimethylphosphine), while oxidation of PPh_3 (**2a**) is more challenging (0.37 V Fc/Fc^+) than oxidation of **41** (–0.11 V vs Fc/Fc^+), suggesting that addition of **43** occurs to the neutral phosphine. Subsequent oxidation of the resulting radial intermediate **44a** is facile (–2.35 V vs Fc/Fc^+) thus access to **44a** is facile. Finally, loss of TMS from **S4a** provides desired product **46a** with an associated ΔG_{rxn} = –64.0 kcal/mol when R = Ph.

Based on the combination of experimental and computational data gathered in this mechanistic study is that the data is consistent with mechanisms D & E illustrated in Scheme S1.

7.2. ^{31}P NMR Spectroscopy of Reaction Mixture Prior to Electrolysis

Three mixtures were compared by $^{31}P\{^{1}H\}$ NMR spectroscopy to determine if any reaction intermediates precede the electrochemical step, particularly if intermediate **S2a** is formed chemically prior to electrochemical oxidation Scheme S2.



2a **5** **S2a**

Scheme S3. Probing viability of nucleophilic attack of **5** by triphenylphosphine to form zwitterion **S2a.**

Solution 1 (triphenylphosphine in NMP/CD_3OD). A 4 mL vial containing a PTFE coated stir bar was charged with triphenylphosphine (52 mg, 0.20 mmol) and 1.5 mL of 4/1 (v/v) NMP/CD_3OD). The mixture was stirred for 30 minutes.

Solution 2 (triphenylphosphine + Me_4NOAc in NMP/CD_3OD). A 4 mL vial containing a PTFE coated stir bar was charged with tetramethylammonium acetate (20 mg, 0.075 mmol), bis(trimethylsilyl)carbodiimide (112 mg, 0.60 mmol) and 1.5 mL of 4/1 (v/v) NMP/CD_3OD). The mixture was stirred for 30 minutes.

Solution 3 (triphenylphosphine + Me_4NOAc + bis(trimethylsilyl)carbodiimide NMP/CD_3OD). A 4 mL vial containing a PTFE coated stir bar was charged with triphenylphosphine (52 mg, 0.20 mmol), tetramethylammonium acetate (20 mg, 0.075 mmol), bis(trimethylsilyl)carbodiimide (112 mg, 0.60 mmol) and 1.5 mL of 4/1 (v/v) NMP/CD_3OD). The mixture was stirred for 30 minutes.

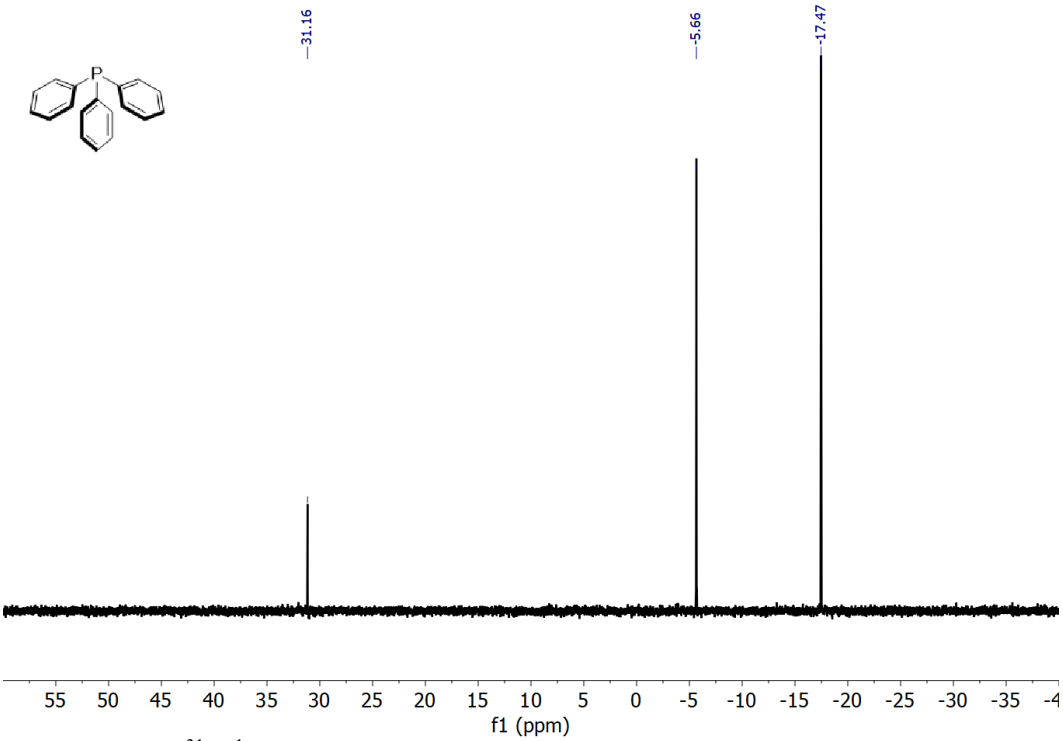


Figure S149. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **Solution 1** (triphenylphosphine in 4:1 (v/v) NMP/CD_3OD).

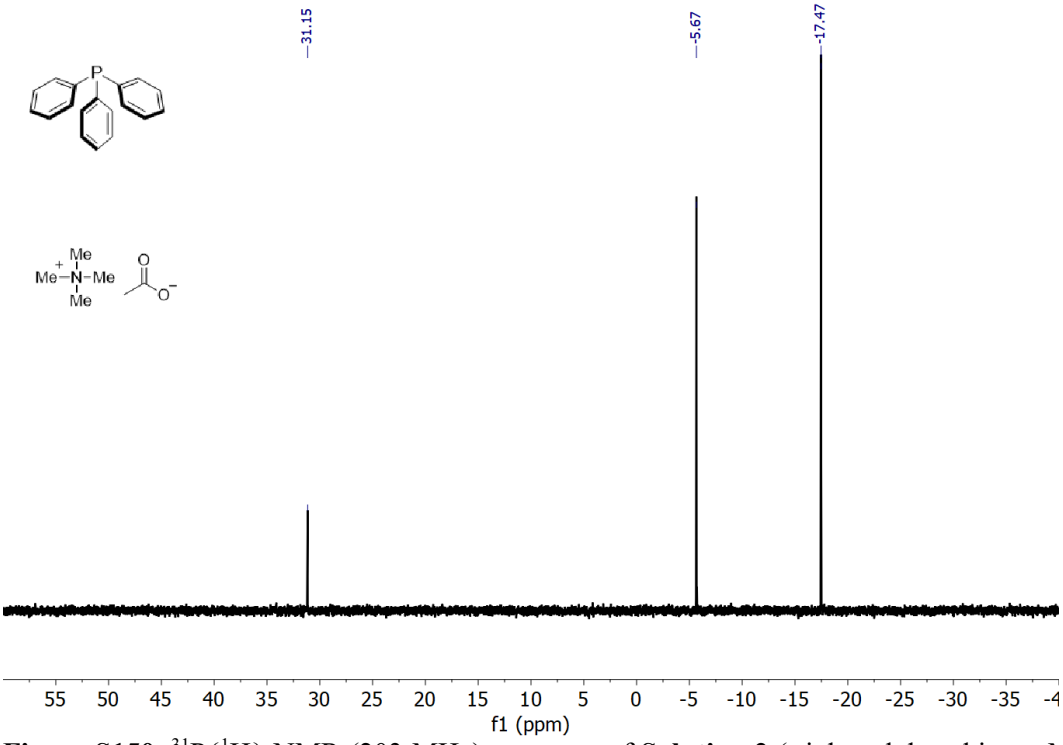


Figure S150. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **Solution 2** (triphenylphosphine + Me_4NOAc in 4:1 (v/v) NMP/CD_3OD).

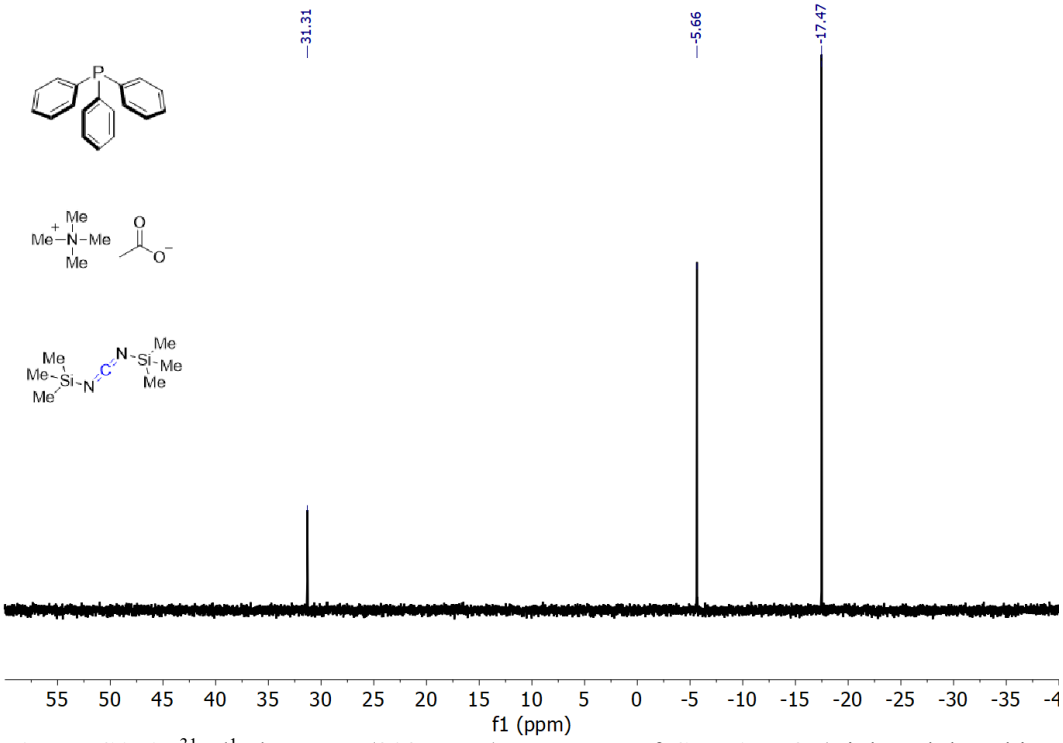


Figure S151. $^{31}P\{^{1}H\}$ NMR (203 MHz) spectrum of **Solution 3** (triphenylphosphine + Me_4NOAc + bis(trimethylsilyl)carbodiimide in 4:1 (v/v) NMP/CD_3OD).

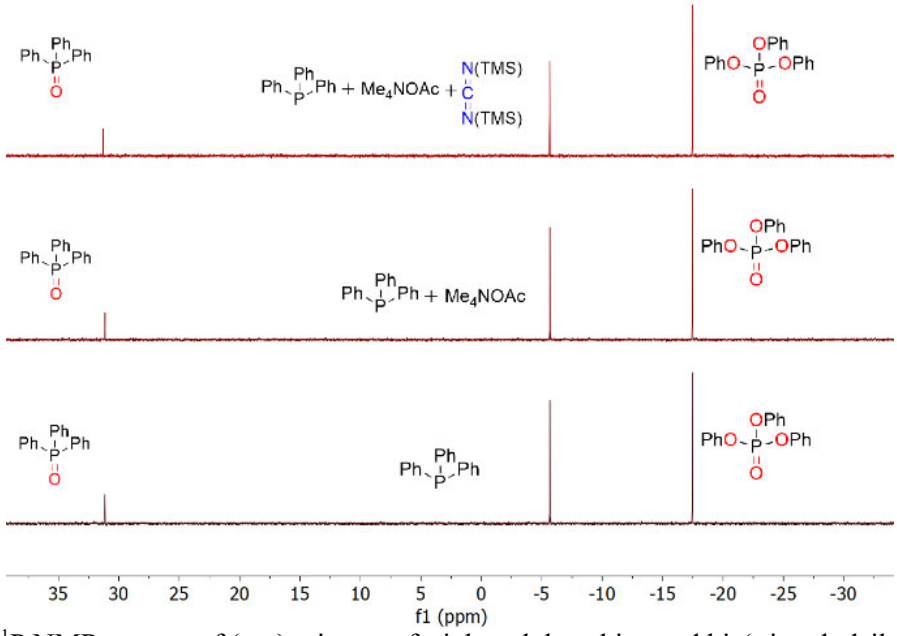


Figure S152. ^{31}P NMR spectra of (top) mixture of triphenylphosphine and bis(trimethylsilyl)carbodiimide (1:3 molar ratio) in 0.1 M Me_4NOAc electrolyte, (middle) triphenylphosphine and 0.1 M Me_4NOAc electrolyte (bottom) triphenylphosphine. All samples are in 4:1 (v/v) NMP/CD_3OD containing $(PhO)_3P{=}O$ internal standard. Note: samples were prepared in air and contain triphenylphosphine oxide.

7.3. Cyclic Voltammetry of Reaction Components

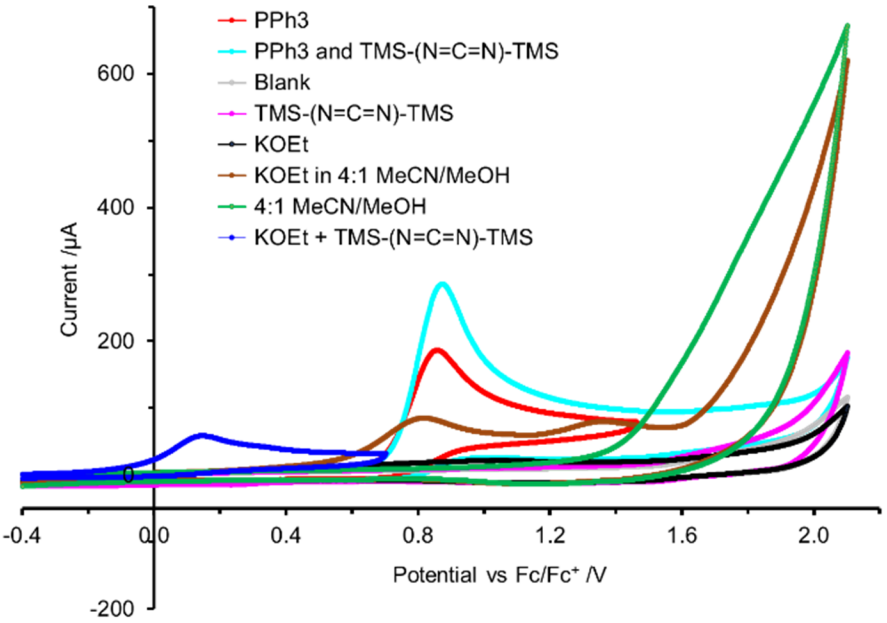


Figure S153. Overlayed cyclic voltammograms of various components containing 0.1 M Bu_4NPF_6 in MeCN measured vs Fc/Fc^+ (ν = 500 mV/s, glassy carbon working electrode, Pt wire counter electrode). See Section 2.3 for experimental setup details.

7.4. Cyclic Voltammetry of Selected P(V) Compounds

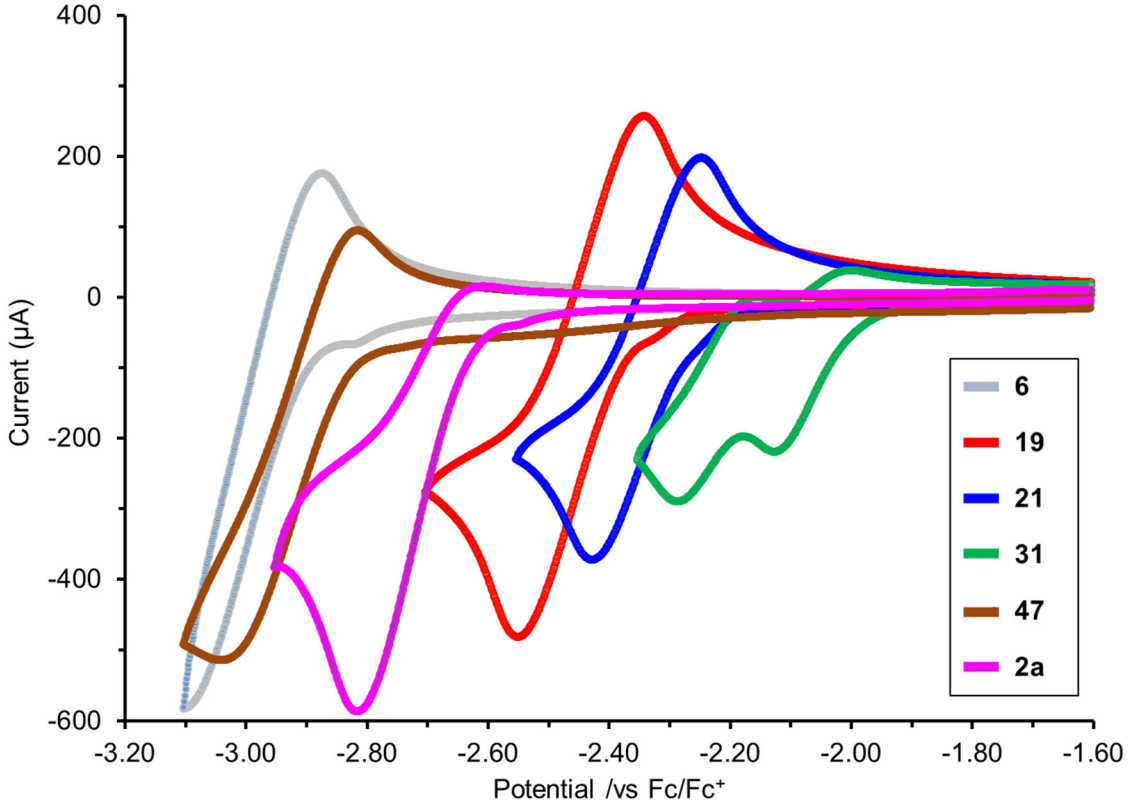


Figure S154. Overlayed cyclic voltammograms of various P(V) compounds (10 mM) in 0.1 M Bu_4NPF_6 in MeCN measured vs Fc/Fc^+ (ν = 500 mV/s, glassy carbon working electrode, Pt wire counter electrode). See Section 2.3 for experimental setup details.

8. X-Ray Crystallography

8.1. Crystal Data and Structure Refinement for Compound 4 (CCDC 2259467)

A single crystal, grown from acetonitrile, acetone, and hexane solution by solvent evaporation, was selected for single crystal X-ray data analysis. The crystal was a cut plate with dimensions of 0.247 mm × 0.184 mm × 0.104 mm. Data collection was performed on a Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer at 297K using CuKα radiation. The unit cell was determined to be monoclinic in space group $P2_1/c$. The structure contained two molecules in the crystallographic asymmetric unit. Some minor positional disorder was observed and modeled.

Crystallographic data is summarized in Table S2. Figure S155 shows a thermal ellipsoid representation of Compound **4** with thermal ellipsoids set at the 50% probability level. Coordinates, refinement details and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2259467).

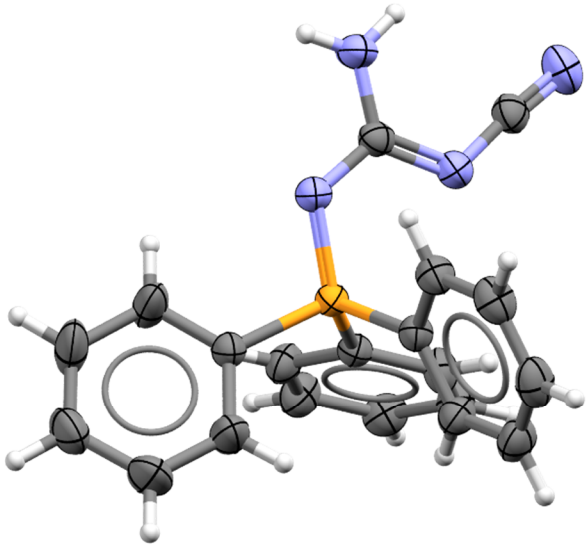


Figure S155. Thermal ellipsoid representation of one molecule of compound **4** from the ASU with thermal ellipsoids set at the 50% probability level is shown. The minor positional disorder is removed for image clarity.

Table S2. Crystal Data and Structure Refinement for Compound **4** [CCDC 2259467]

Empirical formula	$C_{20}H_{17}N_4P$
Formula weight	344.35
Temperature/K	297(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	17.8140(3)
b/Å	14.2764(2)
c/Å	14.7633(2)
α/°	90
β/°	107.840(2)
γ/°	90
Volume/Å^3	3574.06(10)
Z	8
ρ_{calc}g/cm^3	1.280
μ/mm^{-1}	1.428
F(000)	1440.0
Crystal size/mm^3	0.247 × 0.184 × 0.104
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.212 to 154.87
Index ranges	$-22 \leq h \leq 21$, $-17 \leq k \leq 16$, $-18 \leq l \leq 14$
Reflections collected	33748
Independent reflections	7085 [R_{int} = 0.0299, R_{sigma} = 0.0218]
Data/restraints/parameters	7085/35/590
Goodness-of-fit on F^2	1.061
Final R indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 = 0.1047
Final R indexes [all data]	R_1 = 0.0428, wR_2 = 0.1099
Largest diff. peak/hole / e Å^{-3}	0.25/-0.32

8.2. Crystal Data and Structure Refinement for Compound 13 (CCDC 2258974)

A single crystal grown from acetonitrile/methanol/water by solvent evaporation was selected for single crystal X-ray data analysis. The crystal was a cut prism with dimensions of 0.18 mm × 0.15 mm × 0.08 mm. Data collection was performed on a Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer at 100 K using CuKα radiation. The unit cell was determined to be monoclinic in space group $P2_1/n$. The structure contained one molecule in the crystallographic asymmetric unit.

Crystallographic data is summarized in Table S3. Figure S156 shows a thermal ellipsoid representation of Compound **13** with thermal ellipsoids set at the 50% probability level. Coordinates, refinement details and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2258974).

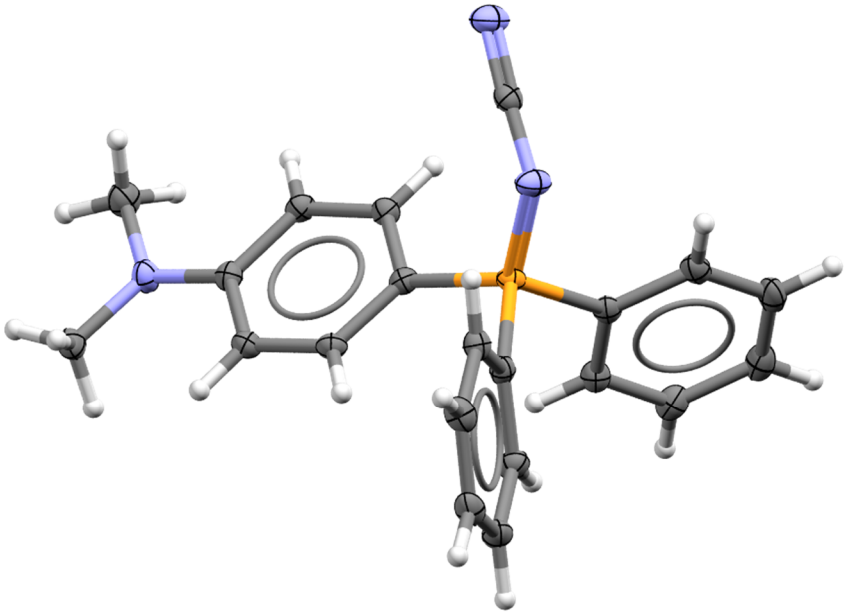


Figure S156. Thermal ellipsoid representation of compound **13** with thermal ellipsoids set at the 50% probability level.

Table S3. Crystal Data and Structure Refinement for Compound **13** [CCDC **2258974**]

Empirical formula	$C_{21}H_{20}N_3P$
Formula weight	345.37
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.7059(3)
b/Å	10.7086(2)
c/Å	12.8648(2)
α/°	90
β/°	92.7679(18)
γ/°	90
Volume/Å^3	1748.38(6)
Z	4
ρ_{calc}g/cm^3	1.312
μ/mm^{-1}	1.441
F(000)	728.0
Crystal size/mm^3	0.184 × 0.149 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.556 to 154.43
Index ranges	$-16 \leq h \leq 15$, $-13 \leq k \leq 12$, $-16 \leq l \leq 16$
Reflections collected	31285
Independent reflections	3506 [R_{int} = 0.0457, R_{sigma} = 0.0224]
Data/restraints/parameters	3506/0/228
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0401, wR_2 = 0.1046
Final R indexes [all data]	R_1 = 0.0435, wR_2 = 0.1070
Largest diff. peak/hole / e Å^{-3}	0.54/-0.33

8.3. Crystal Data and Structure Refinement for Compound 24 (CCDC 2258975)

A single crystal grown from acetonitrile/methanol/water by solvent evaporation was selected for single crystal X-ray data analysis. The crystal was a cut prism with dimensions of 0.22 mm × 0.19 mm × 0.09 mm. Data collection was performed on a Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer at 100K using CuKα radiation. The unit cell was determined to be monoclinic in space group $P2_1/n$. The structure contained one molecule in the crystallographic asymmetric unit.

Crystallographic data is summarized in Table S4. Figure S157 shows a thermal ellipsoid representation of Compound **24** with thermal ellipsoids set at the 50% probability level. Coordinates, refinement details and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2258975).

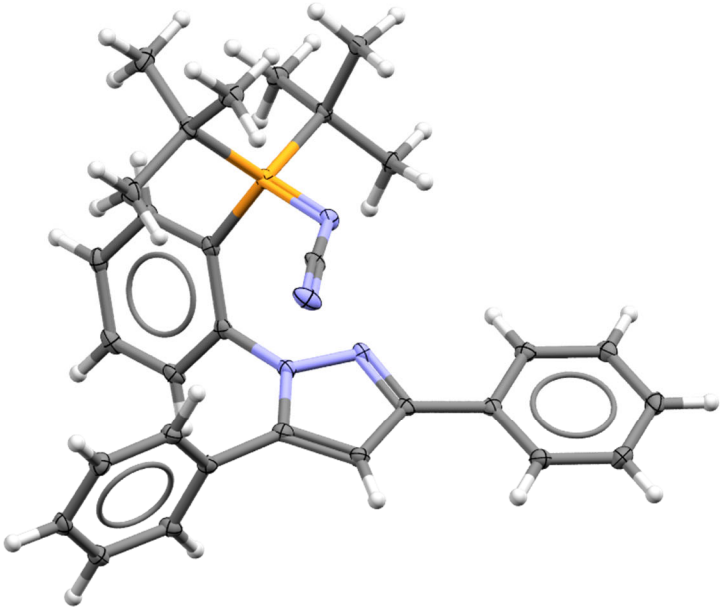


Figure S157. Thermal ellipsoid representation of compound **24** with thermal ellipsoids set at the 50% probability level.

Table S4. Crystal Data and Structure Refinement for Compound **24** [CCDC 2258975]

Empirical formula	$C_{30}H_{33}N_4P$
Formula weight	480.57
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	15.3525(2)
b/Å	9.81549(15)
c/Å	17.3460(2)
α/°	90
β/°	98.1105(13)
γ/°	90
Volume/Å^3	2587.77(6)
Z	4
ρ_{calc}g/cm^3	1.234
μ/mm^{-1}	1.127
F(000)	1024.0
Crystal size/mm^3	0.22 × 0.186 × 0.094
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.202 to 154.898
Index ranges	$-19 \leq h \leq 19$, $-11 \leq k \leq 11$, $-21 \leq l \leq 21$
Reflections collected	25482
Independent reflections	5086 [R_{int} = 0.0352, R_{sigma} = 0.0256]
Data/restraints/parameters	5086/0/322
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0334, wR_2 = 0.0847
Final R indexes [all data]	R_1 = 0.0370, wR_2 = 0.0877
Largest diff. peak/hole / e Å^{-3}	0.29/-0.35

8.4. Crystal Data and Structure Refinement for Compound (*R*)-25 (CCDC 2259466)

A single crystal, grown from a saturated solution of acetonitrile and acetone, was selected for single crystal X-ray data analysis. The crystal was a cut block with dimensions of 0.325 mm × 0.212 mm × 0.188mm. Data collection was performed on a Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer at 100K using CuKα radiation. The unit cell was determined to be orthorhombic in space group $P2_12_12_1$. The structure contained one molecule in the crystallographic asymmetric unit.

Absolute configuration was established by anomalous-dispersion effects in diffraction measurements on the crystal and confirmed that the stereochemistry was as shown.

Crystallographic data is summarized in Table S5. Figure S158 shows a thermal ellipsoid representation of Compound (*R*)-**25** with thermal ellipsoids set at the 50% probability level. Coordinates, refinement details and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2259466).

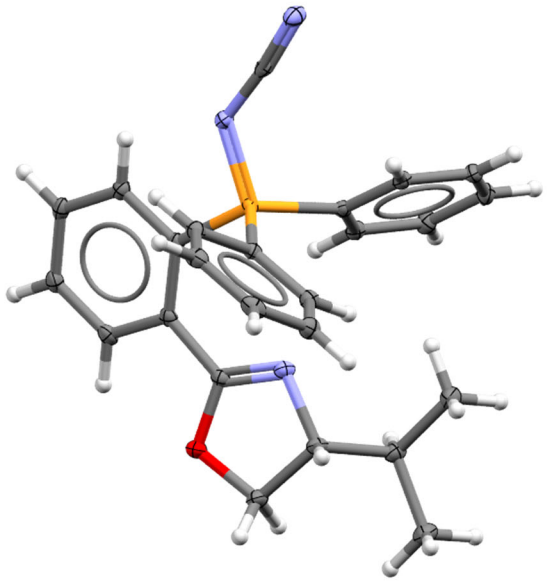


Figure S158. Thermal ellipsoid representation of compound (*R*)-**25** with thermal ellipsoids set at the 50% probability level.

Table S5. Crystal Data and Structure Refinement for compound (*R*)-**25** [CCDC 2259466]

Empirical formula	$C_{25}H_{24}N_3OP$
Formula weight	413.44
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.39428(9)
b/Å	11.00098(13)
c/Å	20.6966(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2138.91(4)
Z	4
ρ_{calc}g/cm^3	1.284
μ/mm^{-1}	1.303
F(000)	872.0
Crystal size/mm^3	0.325 × 0.212 × 0.188
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.544 to 155.12
Index ranges	$-8 \le h \le 11$, $-13 \le k \le 13$, $-26 \le l \le 25$
Reflections collected	20050
Independent reflections	4197 [R_{int} = 0.0321, R_{sigma} = 0.0227]
Data/restraints/parameters	4197/0/274
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0257, wR_2 = 0.0644
Final R indexes [all data]	R_1 = 0.0263, wR_2 = 0.0649
Largest diff. peak/hole / e Å^{-3}	0.23/-0.28
Flack parameter	-0.014(7)

8.5. Crystal Data and Structure Refinement for Compound 28 (CCDC 2258976)

A single crystal grown from acetonitrile/methanol/water by solvent evaporation was selected for single crystal X-ray data analysis. The crystal was a cut block with dimensions of 0.34 mm × 0.10 mm × 0.07mm. Data collection was performed on a Rigaku XtaLAB Synergy , Dualflex, HyPix diffractometer at 100 K using CuKα radiation. The unit cell was determined to be monoclinic in space group R-3. The structure contained two molecules in the crystallographic asymmetric unit, the analyte **28** and a water molecule.

Crystallographic data is summarized in Table S6. Figure S159 shows a thermal ellipsoid representation of Compound **28** with thermal ellipsoids set at the 50% probability level. Coordinates, refinement details and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2258976).

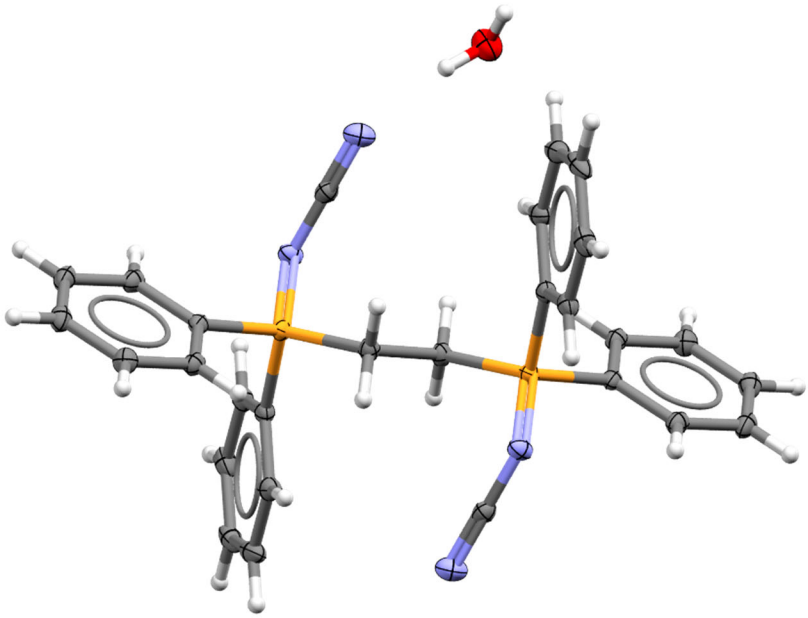


Figure S159. Thermal ellipsoid representation of compound **28** with thermal ellipsoids set at the 50% probability level.

Table S6. Crystal Data and Structure Refinement for Compound **28** [CCDC 2258976]

Empirical formula	$C_{14}H_{14}N_2OP$
Formula weight	257.24
Temperature/K	100.00(10)
Crystal system	trigonal
Space group	R-3
a/Å	24.4855(4)
b/Å	24.4855(4)
c/Å	11.1476(2)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	5788.0(2)
Z	18
ρ_{calc}g/cm^3	1.328
μ/mm^{-1}	1.803
F(000)	2430.0
Crystal size/mm^3	0.154 × 0.133 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.22 to 151.328
Index ranges	$-25 \leq h \leq 28$, $-29 \leq k \leq 29$, $-13 \leq l \leq 14$
Reflections collected	11893
Independent reflections	2504 [R_{int} = 0.0569, R_{sigma} = 0.0345]
Data/restraints/parameters	2504/0/166
Goodness-of-fit on F^2	1.102
Final R indexes [I>=2σ (I)]	R_1 = 0.0421, wR_2 = 0.1208
Final R indexes [all data]	R_1 = 0.0445, wR_2 = 0.1229
Largest diff. peak/hole / e Å^{-3}	0.82/-0.48

8.6. Crystal Data and Structure Refinement for Compound 29 (CCDC 2258980)

A single crystal, grown from a mixture of isopropylamine and ethyl acetate (4 v/v%) and hexanes via slow evaporation, was selected for single crystal X-ray data analysis. The crystal was a cut prism with dimensions of 0.18 mm × 0.14 mm × 0.12 mm. Data collection was performed on a Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer at 100K using CuKα radiation. The unit cell was determined to be triclinic in space group P-1. The structure contained one molecule in the crystallographic asymmetric unit.

Crystallographic data is summarized in Table S7. Figure S160 shows a thermal ellipsoid representation of compound **29** with thermal ellipsoids set at the 50% probability level. Coordinates, refinement details and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2258980).

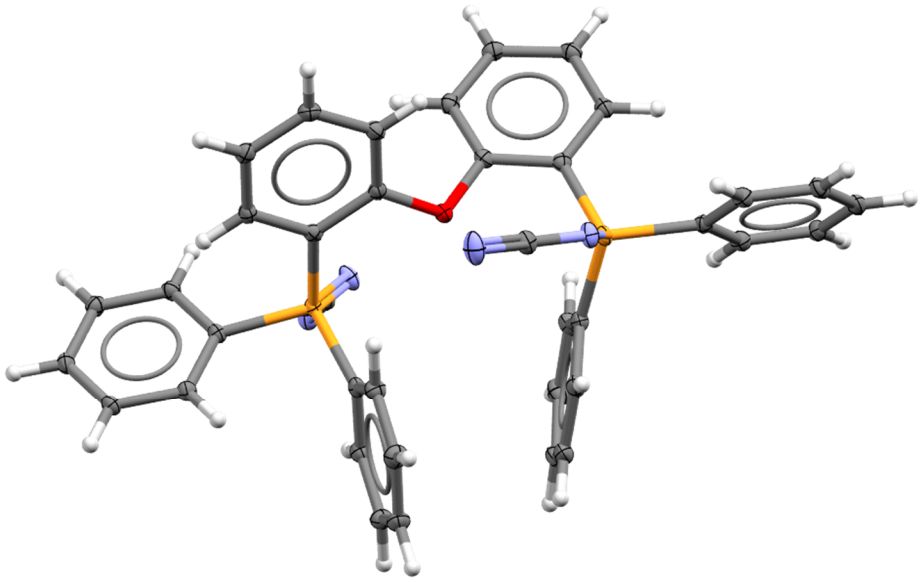


Figure S160. Thermal ellipsoid representation of Compound **29** with thermal ellipsoids set at the 50% probability level.

Table S7. Crystal Data and Structure Refinement for Compound **29** [CCDC 2258980]

Empirical formula	$C_{38}H_{28}N_4OP_2$
Formula weight	618.58
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	9.8545(2)
b/Å	12.6257(3)
c/Å	13.2615(3)
α/°	83.686(2)
β/°	72.463(2)
γ/°	75.875(2)
Volume/Å^3	1524.55(6)
Z	2
ρ_{calc}g/cm^3	1.348
μ/mm^{-1}	1.599
F(000)	644.0
Crystal size/mm^3	0.175 × 0.142 × 0.115
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.996 to 155.234
Index ranges	$-11 \leq h \leq 12$, $-15 \leq k \leq 15$, $-16 \leq l \leq 16$
Reflections collected	28447
Independent reflections	6145 [R_{int} = 0.0340, R_{sigma} = 0.0259]
Data/restraints/parameters	6145/0/406
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0327, wR_2 = 0.0850
Final R indexes [all data]	R_1 = 0.0364, wR_2 = 0.0878
Largest diff. peak/hole / e Å^{-3}	0.42/-0.34

8.7. Crystal Data and Structure Refinement for Compound (*S*)-33 (CCDC 2258977)

A single crystal grown from acetonitrile/water by solvent evaporation was selected for single crystal X-ray data analysis. The crystal was a cut prism with dimensions of 0.30 mm × 0.24 mm × 0.17 mm. Data collection was performed on a Rigaku XtaLAB Synergy , Dualflex, HyPix diffractometer at 100K using CuKα radiation. The unit cell was determined to be monoclinic in space group $P2_1$. The structure contained two analyte molecules and five solvent molecules (four acetonitrile and one water) in the crystallographic asymmetric unit.

Absolute configuration was established by anomalous-dispersion effects in diffraction measurements on the crystal and confirmed that the stereochemistry was as shown.

Crystallographic data is summarized in Table S8. Figure S161 shows a thermal ellipsoid representation of Compound (*S*)-**33** with thermal ellipsoids set at the 50% probability level. Coordinates, refinement details and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2258977).

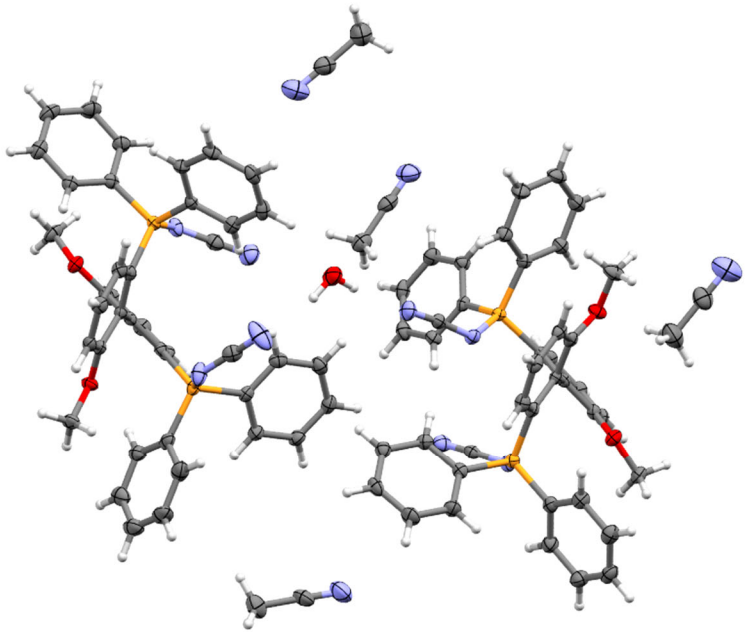


Figure S161. Thermal ellipsoid representation of compound (*S*)-**33** with thermal ellipsoids set at the 50% probability level.

Table S8. Crystal Data and Structure Refinement for Compound (*S*)-**33** [CCDC 2258977]

Empirical formula	$C_{35.2}H_{31.2}N_{4.8}O_2P_{1.6}$
Formula weight	603.00
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	12.02580(10)
b/Å	17.46940(10)
c/Å	19.01960(10)
α/°	90
β/°	102.9480(10)
γ/°	90
Volume/Å^3	3894.11(5)
Z	5
ρ_{calc}g/cm^3	1.286
μ/mm^{-1}	1.391
F(000)	1580.0
Crystal size/mm^3	0.3 × 0.24 × 0.17
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.768 to 155.2
Index ranges	$-15 \le h \le 15$, $-21 \le k \le 16$, $-23 \le l \le 24$
Reflections collected	137025
Independent reflections	14585 [R_{int} = 0.0379, R_{sigma} = 0.0181]
Data/restraints/parameters	14585/1/993
Goodness-of-fit on F^2	1.030
Final R indexes [I>=2σ (I)]	R_1 = 0.0302, wR_2 = 0.0820
Final R indexes [all data]	R_1 = 0.0307, wR_2 = 0.0824
Largest diff. peak/hole / e Å^{-3}	0.63/-0.23
Flack parameter	-0.005(4)

8.8. Crystal Data and Structure Refinement for Compound 38 (CCDC 2258978)

A single crystal grown from a solution of **38** in acetonitrile by cooling was selected for single crystal X-ray data analysis. The crystal was a cut block with dimensions of 0.20 mm × 0.12 mm × 0.08 mm. Data collection was performed on a Rigaku XtaLAB Synergy , Dualflex, HyPix diffractometer at 100 K using CuKα radiation. The unit cell was determined to be triclinic in space group P-1. The structure contained one molecule in the crystallographic asymmetric unit.

Crystallographic data is summarized in Table S9. Figure S162 shows a thermal ellipsoid representation of Compound **38** with thermal ellipsoids set at the 50% probability level. Coordinates, refinement details and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2258978).

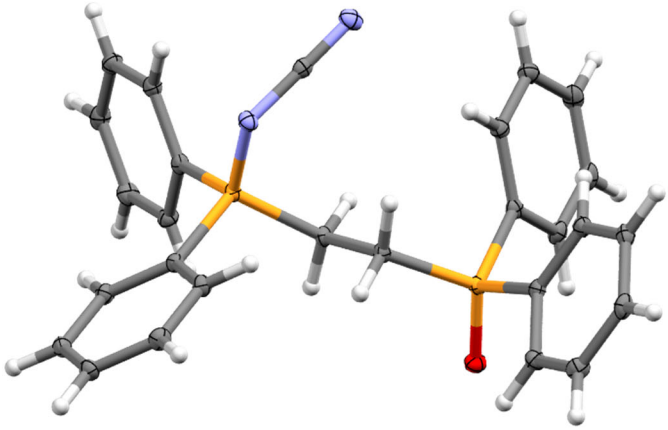


Figure S162. Thermal ellipsoid representation of compound **38** with thermal ellipsoids set at the 50% probability level.

Table S9. Crystal Data and Structure Refinement for Compound **38** [CCDC 2258978]

Empirical formula	$C_{27}H_{24}N_2OP_2$
Formula weight	454.42
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.0468(2)
b/Å	10.5532(2)
c/Å	11.2334(2)
α/°	81.121(2)
β/°	72.014(2)
γ/°	84.044(2)
Volume/Å^3	1117.26(4)
Z	2
ρ_{calc}g/cm^3	1.351
μ/mm^{-1}	1.943
F(000)	476.0
Crystal size/mm^3	0.202 × 0.123 × 0.082
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.346 to 155
Index ranges	$-12 \leq h \leq 12$, $-13 \leq k \leq 11$, $-13 \leq l \leq 14$
Reflections collected	37877
Independent reflections	4462 [R_{int} = 0.0345, R_{sigma} = 0.0193]
Data/restraints/parameters	4462/0/289
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0340, wR_2 = 0.0866
Final R indexes [all data]	R_1 = 0.0360, wR_2 = 0.0879
Largest diff. peak/hole / e Å^{-3}	0.49/-0.36

8.9. Crystal Data and Structure Refinement for Compound 39 (CCDC 2258979)

A single crystal grown from acetonitrile/methanol/water by solvent evaporation was selected for single crystal X-ray data analysis. The crystal was a cut irregular with dimensions of 0.326 mm × 0.204 mm × 0.174 mm. Data collection was performed on a Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer at 100K using CuKα radiation. The unit cell was determined to be monoclinic in space group $P2_1$. The structure contained two molecules in the crystallographic asymmetric unit.

Crystallographic data is summarized in Table S10. Figure S163 shows a thermal ellipsoid representation of Compound **39** with thermal ellipsoids set at the 50% probability level. Coordinates, refinement details and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2258979).

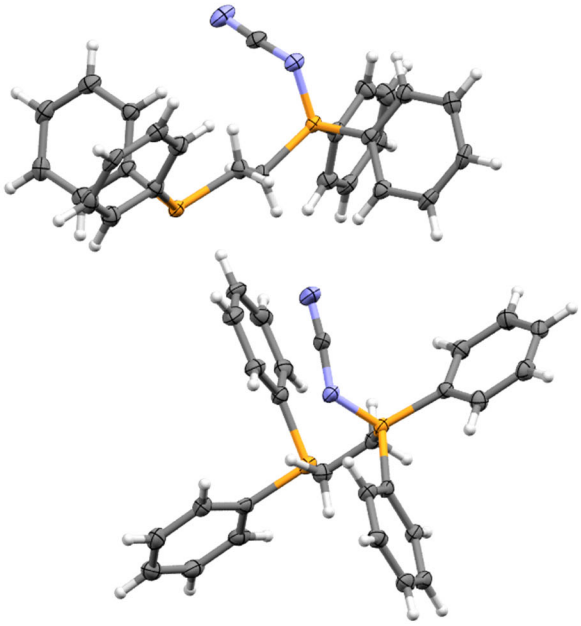


Figure S163. Thermal ellipsoid representation of compound **39** with thermal ellipsoids set at the 50% probability level.

Table S10. Crystal Data and Structure Refinement for Compound **39** [CCDC 2258979]

Empirical formula	$C_{54}H_{48}N_4P_4$
Formula weight	876.84
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.10450(10)
b/Å	26.3845(3)
c/Å	9.35170(10)
α/°	90
β/°	93.6980(10)
γ/°	90
Volume/Å^3	2241.77(4)
Z	2
ρ_{calc}g/cm^3	1.299
μ/mm^{-1}	1.882
F(000)	920.0
Crystal size/mm^3	0.326 × 0.204 × 0.174
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.7 to 155.924
Index ranges	$-11 \leq h \leq 11$, $-33 \leq k \leq 30$, $-11 \leq l \leq 11$
Reflections collected	42537
Independent reflections	8774 [R_{int} = 0.0573, R_{sigma} = 0.0407]
Data/restraints/parameters	8774/1/559
Goodness-of-fit on F^2	1.104
Final R indexes [I>=2σ (I)]	R_1 = 0.0512, wR_2 = 0.1588
Final R indexes [all data]	R_1 = 0.0526, wR_2 = 0.1603
Largest diff. peak/hole / e Å^{-3}	0.99/-0.60
Flack parameter	-0.013(11)

8.10. Summary of Key Metrics from X-ray Crystallographic Data of Iminophosphoranes

Table S11. Summary of key metrics (interatomic distances and bond angles) from the X-ray crystallographic data of **4**, **13**, **24**, (*R*)-**25**, **28**, **29**, (*S*)-**33**, **38**, and **39**.

Cmpd	Atom 1	Atom 2	P=O	P=N (Å)	P-C (Å)	N-CN (Å)	Atom1	Atom2	Atom3	Angle (°)
Compound **4** CCDC 2259467	P1A	N1A		1.607(1)			P1A	N1A	C19A	119.8(1)
	P1B	N1B		1.593(2)			P1B	N1B	C19B	120.3(5)
	P1A	C1A			1.802(2)					
	P1A	C7A			1.799(2)					
	P1A	C13A			1.802(2)					
	P1B	C1B			1.800(2)					
	P1B	C7B			1.802(2)					
	P1B	C13B			1.77(1)					
	N1B	C19B			1.39(1)					
	N1A	C19A				1.343(2)				
	N2B	C19B				1.408(9)				
	N3B	C19B				1.35(2)				
	N3B	C20B				1.33(1)				
	N4B	C20B				1.17(1)				
Compound (*R*)-**25** CCDC 2259466	P1	N1		1.607(2)			P1	N1	C1	124.9(1)
	P1	C2			1.823(2)					
	P1	C14			1.807(2)					
	P1	C20			1.799(2)					
	N1	C1				1.304(2)				
	N2	C1				1.168(2)				
Compound **38** CCDC 2258978	P2	O1	1.488(1)				P1	N1	C13	122.0(1)
	P1	N1		1.601(1)			O1	P2	C15	113.75(7)
	P2	C15			1.813(2)		O1	P2	C22	111.62(7)
	P2	C22			1.803(2)		O1	P2	C16	111.32(7)
	P2	C16			1.810(1)					
	P1	C7			1.803(2)					
	P1	C1			1.798(1)					
	P1	C14			1.812(2)					
	N1	C13				1.312(2)				
	N2	C13				1.163(2)				
Compound **28** CCDC 2258976	P1	N1		1.599(1)			P1	N1	C13	120.3(1)
	P1	N1		1.599(1)**			P1	N1	C13	120.3(1)*
	P1	C7			1.796(2)					
	P1	C1			1.785(2)					
	P1	C14			1.811(2)					
	P1	C7			1.796(2)**					

	P1	C1		1.785(2)**					
	P1	C14		1.811(2)**					
	N1	C13			1.304(3)				
	N2	C13			1.161(4)				
	N1	C13			1.304(3)**				
	N2	C13			1.161(4)**				
Compound **13** CCDC 2258974	P1	N1	1.595(2)			P1	N1	C21	126.2(1)
	P1	C1		1.807(2)					
	P1	C7		1.799(2)					
	P1	C13		1.781(2)					
	N1	C21			1.301(2)				
	N2	C21			1.163(2)				
Compound **24** CCDC 2258975	P1	N1	1.595(1)			P1	N1	C15	126.39(9)
	P1	C1		1.834(1)					
	P1	C11		1.852(1)					
	P1	C7		1.882(1)					
	N1	C15			1.305(2)				
	N2	C15			1.164(2)				
Compound **29** CCDC 2258980	P1	N1	1.597(1)			P1	N1	C19	122.8(1)
	P2	N3	1.587(1)			P2	N3	C38	128.7(1)
	P1	C1		1.800(2)					
	P1	C7		1.800(1)					
	P1	C12		1.796(2)					
	P2	C26		1.801(1)					
	P2	C21		1.805(2)					
	P2	C32		1.798(2)					
	N1	C19			1.309(2)				
	N2	C19			1.161(2)				
	N3	C38			1.306(2)				
	N4	C38			1.159(2)				
Compound **39** CCC 2258979	P1	N1	1.602(4)			P1	N1	C27	122.6(4)
	P3	N3	1.607(4)			P3	N3	C54	120.0(4)
	P1	C13		1.812(5)					
	P1	C7		1.781(5)					
	P1	C1		1.799(5)					
	P2	C15		1.838(5)*					
	P2	C21		1.834(5)*					
	P2	C14		1.859(5)*					
	P3	C40		1.804(5)					
	P3	C34		1.801(5)					
	P3	C28		1.782(5)					
	P4	C42		1.843(5)*					

	P4	C48		1.845(5)*					
	P4	C41		1.847(5)*					
	N1	C27			1.320(7)				
	N2	C27			1.161(7)				
	N3	C54			1.310(6)				
	N4	C54			1.172(7)				
Compound (*S*)-**33** CCDC 2258977	P1	N1	1.593(2)			P1	N1	C28	128.2(2)
	P2	N3	1.597(2)			P2	N3	C13	124.7(2)
	P3	N5	1.591(3)			P3	N5	C53	127.0(2)
	P4	N7	1.592(2)			P4	N7	C68	128.4(2)
	P1	C29		1.803(2)					
	P1	C35		1.804(2)					
	P1	C26		1.807(2)					
	P2	C7		1.800(3)					
	P2	C14		1.817(3)					
	P2	C1		1.804(2)					
	P3	C54		1.814(2)					
	P3	C41		1.811(3)					
	P3	C47		1.805(3)					
	P4	C75		1.802(3)					
	P4	C66		1.817(2)					
	P4	C69		1.804(2)					
	N1	C28			1.297(3)				
	N2	C28			1.161(3)				
	N3	C13			1.316(3)				
	N4	C13			1.161(3)				
	N5	C53			1.294(4)				
	N6	C53			1.155(5)				
	N7	C68			1.291(4)				
	N8	C68			1.172(4)				

[*] denotes P(III) atom. [**] denotes related by symmetry.

8.11. Comparison of X-ray Crystallographic P=N Bond Metrics with Data in the Cambridge Structural Database

Iminophosphoranes are a relatively well studied class of molecule, and as such the Cambridge Structural Database (CSD)[25] has a fair number of these structures. We chose to utilize ConQuest[26] to mine the database (CSD v5.41) for iminophosphoranes, where the phosphorus atom has three arene derivatives, and the nitrogen atom has a singular substitution, being restricted to carbon. We chose to only include organic, non-disordered structures, where the structures were determined through single crystal structures (not powder diffraction data). We also chose to omit any structures where the nitrogen atom was coordinating to a heteroatom (e.g., boron) or the nitrogen atom was charged, as this would strongly affect the P=N bond length.

A list of all iminophosphorane structures we chose to use (total of 114), along with refcodes are given below in Table S12. In many cases the crystal structure in question had more than one P=N bond (Frag.), and this was also reflected in the histogram shown below. In total 148 P=N bonds were found and used to create a histogram, Figure S164.

We found several notable crystal structures during our search, many of which are shown on the histogram with their accompanying refcodes. For example, TAYTUI, BAKWUF, ECISOZ, GEHRIU, and NTPABF. On TAYTUI the triphenylphosphine imino group is bound to a proton, resulting in a very short P=N bond (ca. 1.525 Å). Structure BAKWUF, where the nitrogen of the iminophosphorane has an alkyl (sp^3-carbon) substituent on the nitrogen atom also has a short P=N bond (ca. 1.564 Å). Adding more electron withdrawing groups to the substituent on the nitrogen of the iminophosphorane, such as an *sp*-carbon as part of a cyano group (i.e., *N*-cyano iminophosphoranes) further increases P=N bond lengths, as seen for ECISOC (ca. 1.577 Å). A phenyl substituent (sp^2-carbon) on the iminophosphorane nitrogen, as seen for GEHRUI, results in a P=N bond length of ca. 1.603 Å. In contrast, the longest bond P=N bound length is seen for NTYPABF (ca. 1.627 Å) as a result of significant electron withdrawing ability of the heterocyclic motif.

The iminophosphorane in this work all have comparable bond lengths to GEHRIU. For example, compounds **4**, ***R*-25**, **28**, **29**, **38** and **39** all have P=N bond lengths within 0.004 Å of GEHRIU (1.603 Å). While compounds **13**, **24** and ***S*-33** have P=N bond lengths between 1.592 and 1.595 Å, which are slightly shorter than GEHRIU.

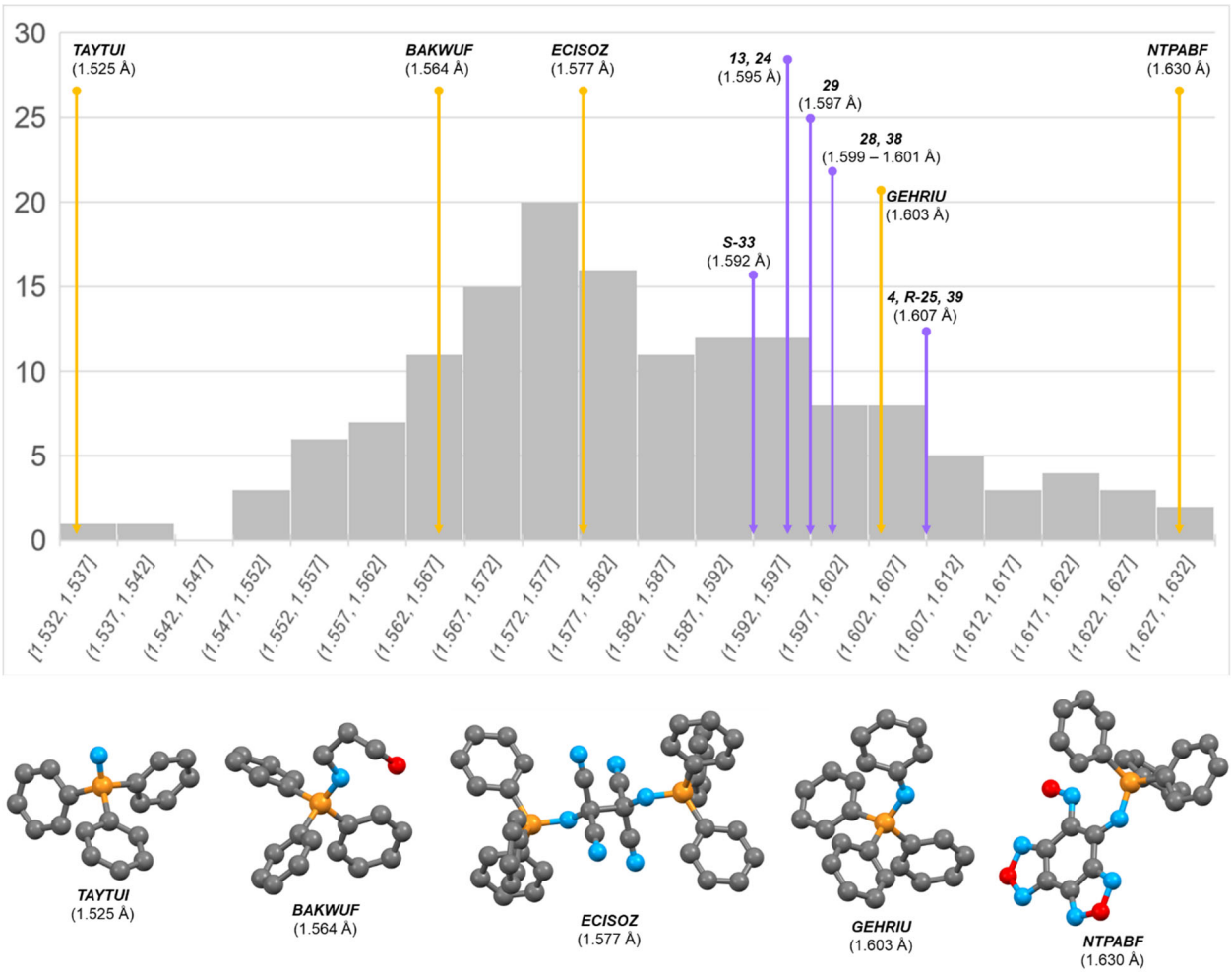


Figure S164. (Top) Histogram of P=N bond lengths found in the CSD through a ConQuest search. Select structures of note are indicated by yellow lines along with accompanying CSD refcodes and approximate bond lengths. Structures in this work are indicated by purple lines with accompanying bond lengths. (Bottom) Structures of relevant crystal structures found in the CSD, with hydrogen atoms and solvent molecules omitted for clarity. Color code: phosphorus (orange), carbon (grey), oxygen (red), nitrogen (blue).

Table S12. Data for relevant iminophosphoranes found through a ConQuest search of the CSD.

#	REFCODE	Frag.	P=N	#	REFCODE	Frag.	P=N	#	REFCODE	Frag.	P=N	#	REFCODE	Frag.	P=N	#	REFCODE	Frag.	P=N	#	REFCODE	Frag.	P=N
1	ABAKAR	1	1.578	26	ELIROI	1	1.568	51	LALQUK	1	1.604	76	PAMXAF	1	1.577	101	RABZIG	2	1.55	126	VEPVAO	1	1.576
2	AFURIE	1	1.57	27	EXOROY	1	1.563	52	LALTUN	1	1.566	77	PAMXEJ	1	1.572	102	RAZREP	1	1.573	127	VETQES	1	1.591
3	AKABEU	1	1.549	28	FETTAA	1	1.571	53	LALTUN	2	1.586	78	PAMXEJ	2	1.583	103	RIHSUW	1	1.597	128	VETQIW	1	1.593
4	AKABEU	2	1.565	29	FIFKUA	1	1.588	54	LANLIW	1	1.575	79	PAMXIN	1	1.585	104	RISSIY	1	1.604	129	VETQIW	2	1.591
5	BAKWUF	1	1.564	30	FOHJAQ	1	1.575	55	LEXKEG	1	1.581	80	PAMXIN	2	1.577	105	SADQAP	1	1.573	130	VETQIW	3	1.592
6	BAKWUF	2	1.574	31	GEHRIU	1	1.603	56	LEXKEG	2	1.568	81	PAMXOT	1	1.587	106	SADQAP	2	1.56	131	WEXBAC	1	1.589
7	BEMZAU	1	1.58	32	GEHRUG	1	1.554	57	LEXKOQ	1	1.56	82	PAMXOT	2	1.568	107	SANJOG	1	1.568	132	WIZMEY	1	1.597
8	BPITPP	1	1.566	33	GEHRUG	2	1.571	58	LEXKOQ	2	1.542	83	PAXKUV	1	1.562	108	SAPFEV	1	1.58	133	WIZMIC	1	1.594
9	CIDNAH	1	1.593	34	HATXOP	1	1.564	59	LIXGAA	1	1.609	84	PEHJUK	1	1.573	109	SAPFEV01	1	1.578	134	XESVOG	1	1.624
10	CIDNAH	2	1.595	35	HCYIPP	1	1.615	60	MANGOX	1	1.605	85	PEKHAR	1	1.58	110	SIYZEH	1	1.571	135	XESVOG	2	1.628
11	CIJGAF	1	1.548	36	HCYIPP01	1	1.618	61	MAPDAJ	1	1.571	86	PEPQUW	1	1.592	111	TEMVUC	1	1.566	136	YETPIX	1	1.532
12	CIJGEJ	1	1.561	37	IQOROV	1	1.557	62	NEFVUQ	1	1.573	87	PEPSUY	1	1.588	112	TEMVUC	2	1.578	137	YETPIX	2	1.557
13	COXCAU	1	1.559	38	IQOSIQ	1	1.596	63	NODHEW	1	1.598	88	PHCLCE	1	1.608	113	TIZFOX	1	1.599	138	YEZDUE	1	1.587
14	CPTPPN	1	1.58	39	ITEQED	1	1.553	64	NOSMUD	1	1.601	89	PHSRBZ	1	1.626	114	TOPKIS	1	1.579	139	YEZFAM	1	1.596
15	DAMVAP	1	1.604	40	JISVOW	1	1.575	65	NTPABF	1	1.63	90	PIXGEJ	1	1.558	115	TOPKUE	1	1.566	140	YEZFEQ	1	1.599
16	DEHMUY	1	1.594	41	JOZYIG	1	1.57	66	NUCHAU	1	1.592	91	POWBUY	1	1.607	116	UHEBIT	1	1.569	141	YUGBOS	1	1.58
17	DIXLUS	1	1.575	42	JOZYIG	2	1.573	67	OBEWAT	1	1.585	92	PUCQIO	1	1.61	117	UKAJUN	1	1.605	142	YUGBOS	2	1.569
18	DIXLUS	2	1.593	43	KANHUD	1	1.619	68	OBEWAT	2	1.588	93	QAPZIR	1	1.587	118	ULOXAU	1	1.601	143	ZAQNIO	1	1.601
19	DIZNAB	1	1.597	44	KIRYIU	1	1.572	69	OBEWAT	3	1.586	94	QAPZIR	2	1.589	119	UQEYAS	1	1.577	144	ZUBCEE	1	1.584
20	DIZNEF	1	1.599	45	LAGCUR	1	1.56	70	OBEWAT	4	1.598	95	QAQBEQ	1	1.59	120	UQEYAS	2	1.571	145	ZUBCEE	2	1.603
21	DULLIG	1	1.573	46	LAGCUR	2	1.579	71	OBEWAT	5	1.581	96	QUQMUL	1	1.58	121	UXATAP	1	1.566	146	ZUJYOS	1	1.579
22	DULLOM	1	1.575	47	LAGDAY	1	1.567	72	OBEWAT	6	1.592	97	QUQNAS	1	1.557	122	UZEREY	1	1.585	147	ZUNROR	1	1.574
23	DUVZID	1	1.594	48	LAGDAY	2	1.573	73	OBEWEX	1	1.611	98	QUWKEZ	1	1.621	123	VAPSUC	1	1.575	148	ZUNROR	2	1.578
24	ECISOZ	1	1.577	49	LALQOE	1	1.582	74	OBEWEX	2	1.625	99	QUWPUU	1	1.615	124	VEFTOP	1	1.614				
25	ECUDOV	1	1.62	50	LALQOE	2	1.587	75	PAMWUY	1	1.566	100	RABZIG	1	1.556	125	VEFTOP	2	1.608				

8.12. Crystal Data and Structure Refinement for Compound Ni-1 (CCDC 2329725)

A single crystal grown from acetonitrile/methanol by solvent evaporation was selected for single crystal X-ray data analysis. The crystal was a cut irregular with dimensions of 0.143 mm × 0.134 mm × 0.041 mm. Data collection was performed on a Rigaku XtaLAB Synergy, Dualflex, HyPix diffractometer at 100K using MoKα radiation. The unit cell was determined to be monoclinic in space group $P2_1/c$.

Ni-1 exists as a tetranuclear complex in the solid-state. The crystal has some substitutional disorder on one nickel atom on the asymmetric unit, where either a bromine atom or methanol molecule can coordinate. The occupancy of these two donor groups was freely refined and gave a 25/75 ratio of bromine to methanol for one nickel center, and vice-verse for another nitrogen atom. This resulted in a total occupancy (in the symmetric unit) of two bromine and two methanol. Additionally, a bromine on a nickel atom is not disorder, while another bromine exists as a bromide counter ion, resulting in four bromine atoms in the asymmetric unit. There is a molecule of acetonitrile in the asymmetric unit as well.

Crystallographic data is summarized in Table S13. Figure S163 shows a thermal ellipsoid representation of Compound **Ni-1** with thermal ellipsoids set at the 50% probability level. Coordinates, refinement details and structure factors have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2329725).

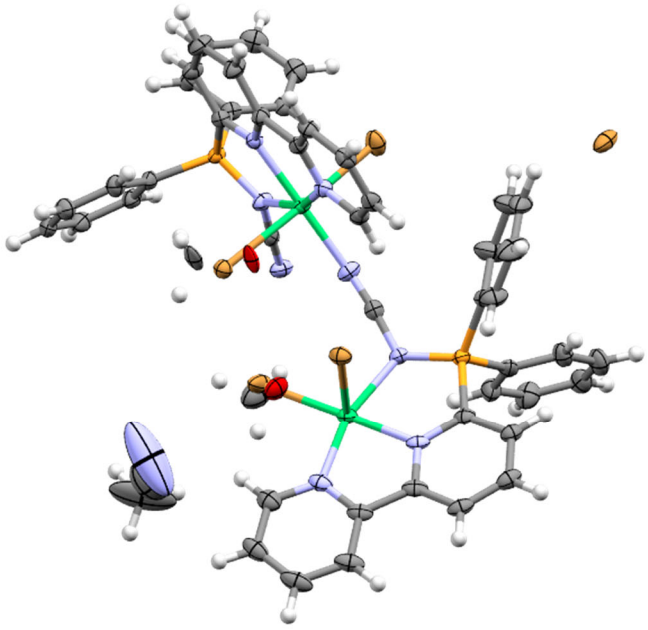


Figure S165. Thermal ellipsoid representation of compound **Ni-1** (asymmetric unit) with thermal ellipsoids set at the 50% probability level.

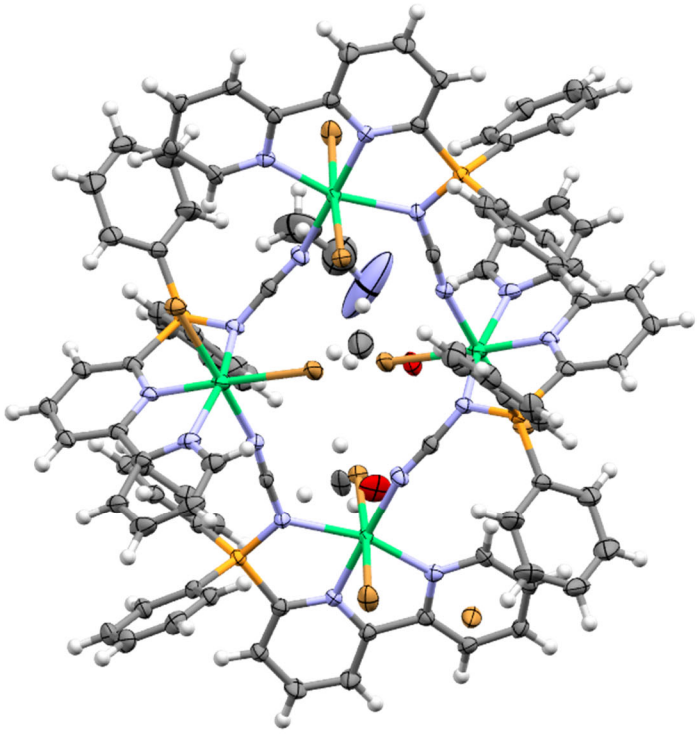


Figure S166. Thermal ellipsoid representation of compound **Ni-1** (full grown structure)with thermal ellipsoids set at the 50% probability level.

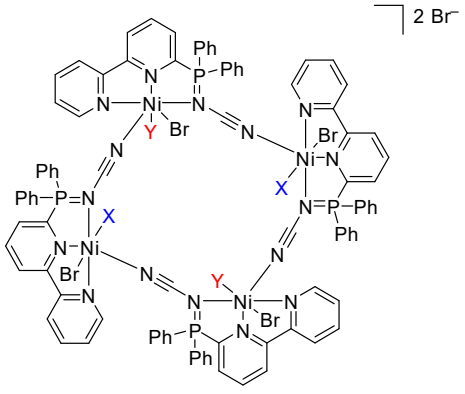


Figure S167. Structure of compound **Ni-1** showing occupancies at positions X and Y.

Table S13. Crystal Data and Structure Refinement for Compound **Ni-1** [CCDC 2329725]

Empirical formula	$C_{49}H_{40}Br_4N_9Ni_2OP_2$
Formula weight	1269.90
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.0937(3)
b/Å	27.1340(6)
c/Å	15.1168(3)
α/°	90
β/°	104.658(2)
γ/°	90
Volume/Å^3	4799.11(19)
Z	4
ρ_{calc}g/cm^3	1.758
μ/mm^{-1}	4.231
F(000)	2524.0
Crystal size/mm^3	0.143 × 0.134 × 0.041
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.598 to 54.206
Index ranges	$-15 \le h \le 15$, $-34 \le k \le 33$, $-19 \le l \le 19$
Reflections collected	59035
Independent reflections	10590 [R_{int} = 0.0453, R_{sigma} = 0.0351]
Data/restraints/parameters	10590/17/635
Goodness-of-fit on F^2	1.056
Final R indexes [I>=2σ (I)]	R_1 = 0.0497, wR_2 = 0.1131
Final R indexes [all data]	R_1 = 0.0663, wR_2 = 0.1196
Largest diff. peak/hole / e Å^{-3}	2.20/-0.78
Empirical formula	$C_{49}H_{40}Br_4N_9Ni_2OP_2$

9. Computational Studies

9.1. Computational Methods

The quantum chemical calculations were performed using the Gaussian 16 program.[27]

For the calculations of reaction energies, redox potentials, and orbital energies, geometry optimizations and frequency calculations were performed at the M06-2X/6-31+G(d) level of theory[28,29] with SMD[30] solvation in acetonitrile. in acetonitrile. The stationary points were confirmed to be minima by vibrational analysis. The Gibbs energies were calculated for a temperature of 298.15 K and a pressure of 1 atm using the quasiharmonic approximation proposed by Ribeiro et al.,[31] in which the real vibrational frequencies lower than 100 cm^{-1} were set to 100 cm^{-1} before the thermal corrections were computed with the usual harmonic oscillator model. The DFT-calculated redox potentials against Fc/Fc^+ were obtained using equation S24:

$$E^{\circ,\mathrm{calc}} = -[(\text{energy of reduced species} - \text{energy of oxidized species})/(n_e \bullet F)] - 3.96\ \mathrm{V} - 0.244\ \mathrm{V} - 0.380\ \mathrm{V} \qquad \text{(S24)}$$

where $n_e = 1$, and $n_e \bullet F = 23.061\ \mathrm{kcal \bullet mol^{-1} \bullet V^{-1}}$. Here, "reduced species" refer to the closed-shell neutral molecules 1, 2 or 3, while "oxidized species" refer to the corresponding radical cations. The value of SHE in MeCN of 4.59 V was adopted from the review of Marenich et al.,[32] while the conversion factors from SHE to SCE (–0.244 V) and from SCE to Fc/Fc^+ (–0.380 V) were taken from Pavlishchuk et al.[33]

For the prediction of Tolman electronic parameters, the procedure reported by Gusev[34] was followed. Geometry optimizations and frequency calculations were performed using the mPW1PW91 density functional[35] with the following basis sets: H, C, N, O, P: 6-311+G(d,p); Ni: 6-311+G(2d). The A_1 stretching frequencies reported here were scaled by a factor of 0.9540.

The orbital diagrams were rendered by PyMOL[36] from cube files generated from the corresponding Gaussian 16 formatted checkpoint files.

9.2. Summary of NBO Spin Density Analysis of 44a and 44b

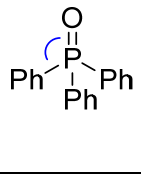
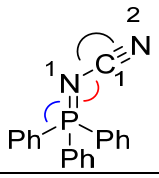
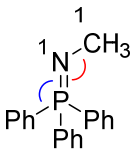
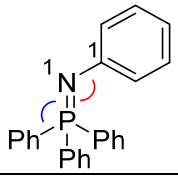
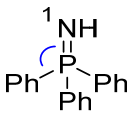
The NBO spin density analyses showed that for both **44a** and **44b** (M06-2X/6-31+G**, SMD(acetonitrile)), the phosphorus atom remains the most important radical center. The phenyl ring of **44a** is a better acceptor in spin density than the methyl group of **44b**, but the difference in the extent of spin delocalization is only minor.

Table S14. Summary of NBO spin density analysis for radicals **44a** and **44b**.

Location	**44a**	**44b**
P	0.56	0.62
NCN	0.27	0.27
TMS	0.00	0.00
Ph^1	0.16	-
Ph^2	0.01	-
Ph^3	0.00	-
Me^1	-	0.10
Me^2	-	0.00
Me^3	-	0.00

9.3. DFT-Computed Metrics (Bond Distances and Angles) for Selected P(V) Structures

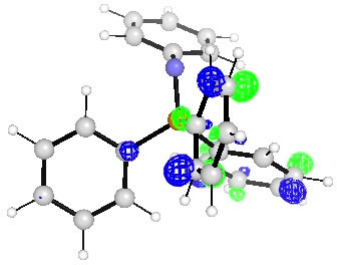
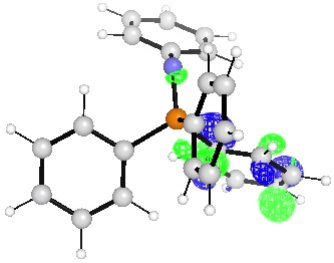
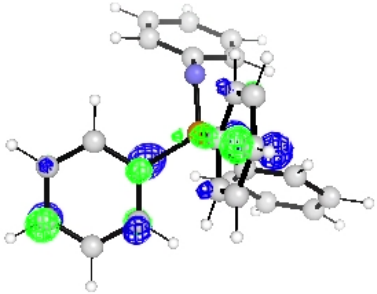
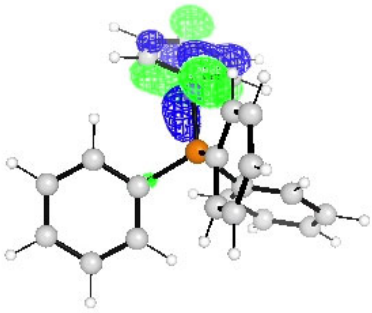
Table S15. DFT[a] predicted metrics (selected bond lengths, bond angles and Mulliken charges).[b]

					
P=X [X = O or N1] /Å	1.508	1.622	1.588	1.590	1.592
N1–C1 /Å	NA	1.306	1.460	1.402	NA
C1≡N2 /Å	NA	1.174	NA	NA	NA
P–N1–C1 /°	NA	122.2	117.9	122.9	NA
$C_{(Ph)}$–P–X [X = O or N1] /°	112.6 112.6 112.6 **Avg: 112.6**	114.0 112.2 105.6 **Avg: 110.6**	108.1 114.8 115.6 **Avg: 112.8**	115.77444 107.33824 114.33460 **Avg: 112.5**	107.4 115.5 116.3 **Avg: 113.1**
N1–C–N2 /°	NA	176.06	NA	NA	NA
Mulliken charges	P: +0.369 O: –0.621	P: +0.518 N1: –0.527 C1: +0.009 N2: –0.533	P: +0.133 N1: –0.527 C1: +0.009	P: +0.398 N1: –0.598 C1: –0.593	P: +0.482 N1: –1.03 (N1)H: +0.431
Mulliken charge ratio for X/P [X = O or N1]	1.7	1.0	4.9	1.5	2.1

[a]M06-2X/6-31+G(d) SMD=MeCN. [b]Atom numbers correspond to the numbers in the structural drawing of the column headers.

9.4. DFT-Computed Frontier Molecular Orbitals of Selected P(V) Structures

Table S16. Summary of Frontier Molecular Orbitals for $Ph_3P{=}N{-}Ph$ (**47**).

Orbital	Energy /eV	Image of Orbital
LUMO+2	0.0139	
LUMO+1	–0.213	
LUMO	–0.339	
HOMO	–7.055	

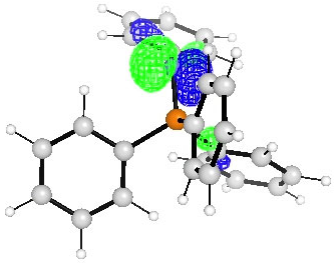
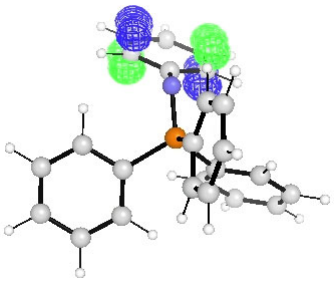
HOMO–1	–7.762	
HOMO–2	–8.188	

Table S17. Summary of Frontier Molecular Orbitals for Ph_3P (**2a**).

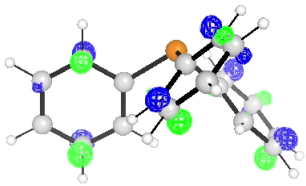
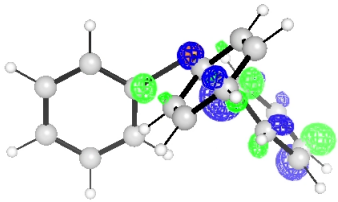
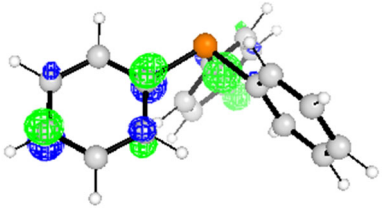
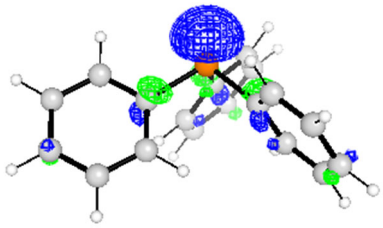
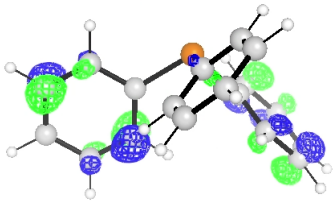
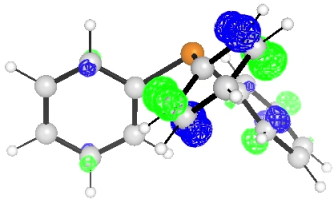
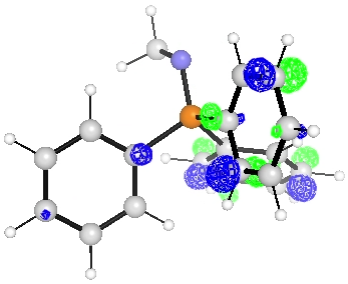
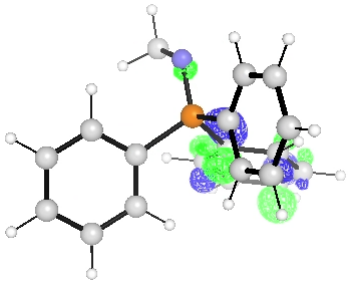
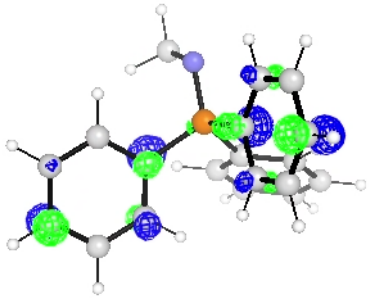
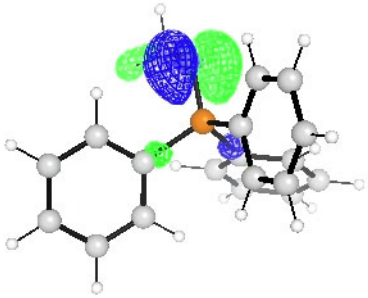
Orbital	Energy /eV	Image of Orbital
LUMO+2	0.053	
LUMO+1	–0.002	
LUMO	–0.005	
HOMO	–7.313	
HOMO–1	–8.357	
HOMO–2	–8.358	

Table S18. Summary of Frontier Molecular Orbitals for Ph_3P=N-Me (**48**).

Orbital	Energy /eV	Image of Orbital
LUMO+2	+0.099	
LUMO+1	–0.120	
LUMO	–0.308	
HOMO	–7.240	

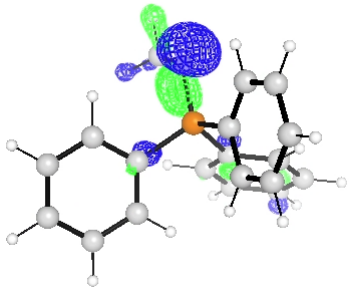
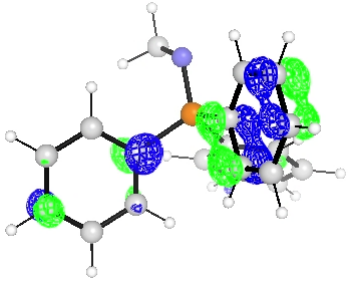
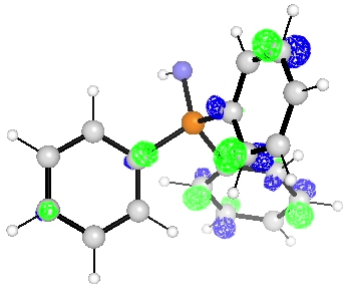
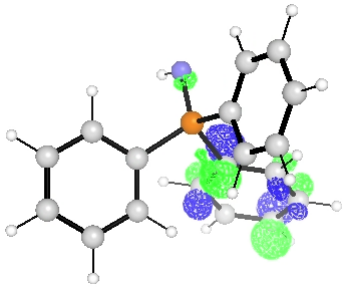
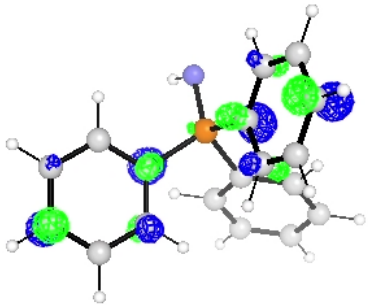
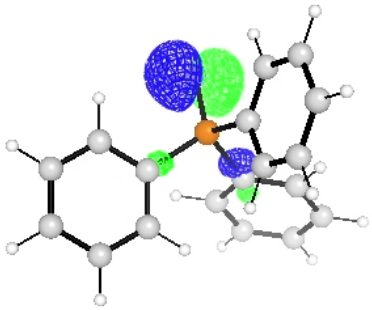
HOMO–1	–8.163	
HOMO–2	–8.363	

Table S19. Summary of Frontier Molecular Orbitals for $Ph_3P{=}NH$ (**49**).

Orbital	Energy /eV	Image of Orbital
LUMO+2	+0.0876	
LUMO+1	–0.107	
LUMO	–0.313	
HOMO	–7.733	

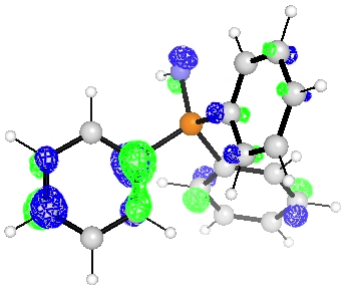
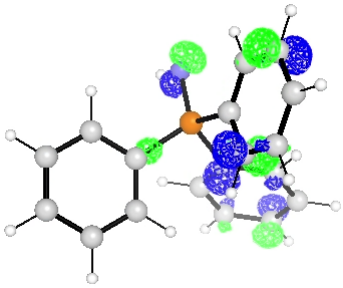
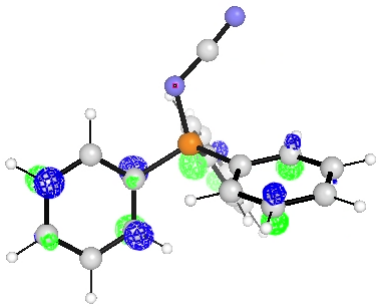
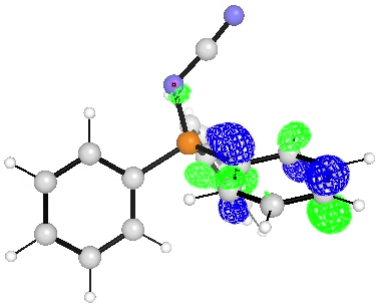
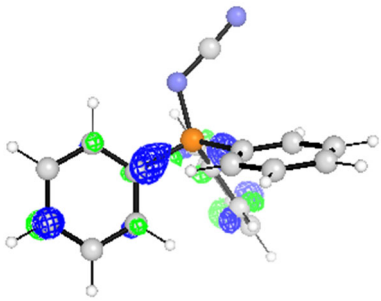
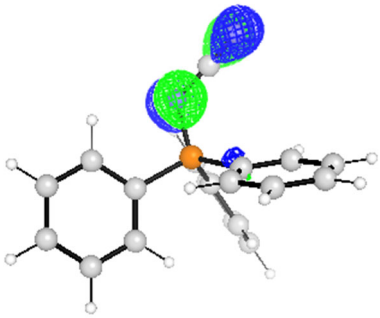
HOMO–1	–8.332	
HOMO–2	–8.454	

Table S20. Summary of Frontier Molecular Orbitals for Ph_3P=N-CN (**1a**).

Orbital	Energy /eV	Image of Orbital
LUMO+2	–0.114	
LUMO+1	–0.413	
LUMO	–0.580	
HOMO	–8.129	

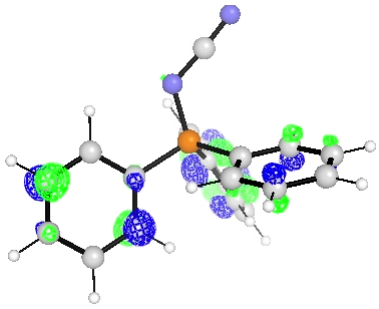
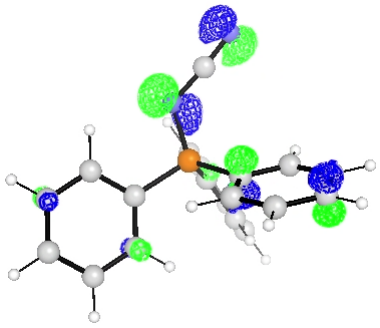
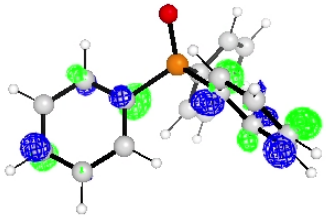
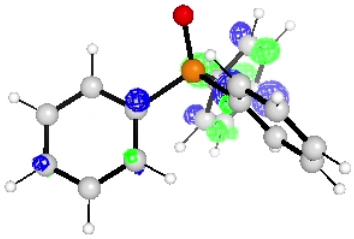
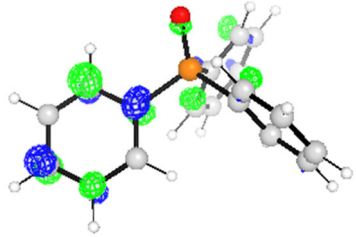
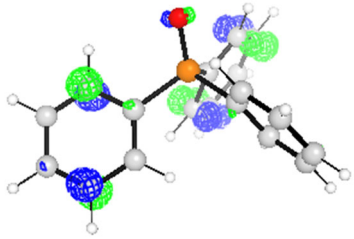
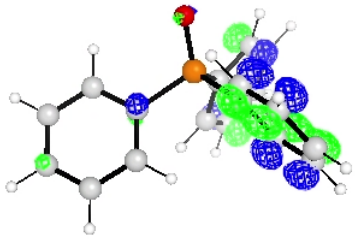
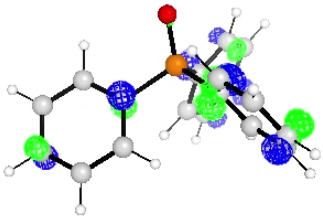
HOMO–1	–8.546	
HOMO–2	–8.613	

Table S21. Summary of Frontier Molecular Orbitals for $Ph_3P{=}O$ (**6**).

Orbital	Energy /eV	Image of Orbital
LUMO+2	–0.103	
LUMO+1	–0.112	
LUMO	–0.144	
HOMO	–8.487	
HOMO–1	–8.490	

HOMO–2	–8.516	

9.5. Cartesian Coordinates of DFT-Optimized Structures

```
Structure: 2a
Charge =  0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy:         -1036.021686 hartree
SCF Energy + ZPVE:  -1035.746324 hartree
Enthalpy:           -1035.729514 hartree
Free Energy:        -1035.792683 hartree
Free Energy with quasiharmonic correction:  -1035.787565 hartree
P 0.003490 -0.003295 -1.263473
C -0.555485 1.550191 -0.440578
C -0.106232 2.757116 -0.995223
C -1.385299 1.589708 0.686341
C -0.462324 3.978159 -0.424514
H 0.529864 2.742171 -1.877792
C -1.752506 2.812990 1.250205
H -1.745736 0.666731 1.132977
C -1.290036 4.008146 0.699142
H -0.102701 4.904124 -0.863337
H -2.398905 2.829921 2.122810
H -1.577234 4.958374 1.139417
C -1.067931 -1.260710 -0.444007
C -0.689217 -2.004473 0.679794
C -2.340349 -1.465189 -0.996366
C -1.570159 -2.928217 1.244967
H 0.293857 -1.865884 1.121273
C -3.225471 -2.376800 -0.423058
H -2.643333 -0.904410 -1.878386
C -2.840637 -3.111994 0.699563
H -1.262382 -3.499967 2.115604
H -4.210924 -2.518531 -0.856562
H -3.526009 -3.827773 1.143488
C 1.627082 -0.297917 -0.438635
C 2.456998 -1.278488 -1.001104
C 2.067903 0.392226 0.697134
C 3.692981 -1.577403 -0.429268
H 2.133061 -1.812973 -1.891992
C 3.310990 0.102040 1.262056
H 1.442894 1.158319 1.147903
C 4.123359 -0.885080 0.703919
H 4.322483 -2.342708 -0.873501
H 3.641684 0.646807 2.141577
H 5.089022 -1.110607 1.146417

Structure: 2b
Charge =  0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy:         -460.998472 hartree
SCF Energy + ZPVE:  -460.885258 hartree
Enthalpy:           -460.877683 hartree
```

Free Energy: -460.914473 hartree
Free Energy with quasiharmonic correction: -460.914473 hartree
P 0.000101 0.000087 0.599198
C -1.059389 1.237543 -0.276515
C 1.601823 0.298214 -0.276570
C -0.542536 -1.535865 -0.276417
H -0.498430 -1.412142 -1.364570
H 0.101732 -2.371432 0.014200
H -1.568984 -1.780983 0.013432
H -0.974421 1.137475 -1.364700
H -2.104991 1.096479 0.014201
H -0.759151 2.249147 0.013649
H 1.472585 0.275398 -1.364748
H 2.003466 1.273675 0.014628
H 2.327293 -0.468273 0.012945

Structure: 5
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -965.973956 hartree
SCF Energy + ZPVE: -965.735625 hartree
Enthalpy: -965.716874 hartree
Free Energy: -965.781924 hartree
Free Energy with quasiharmonic correction: -965.778380 hartree
C 0.000028 -0.005214 -0.001676
N 1.206029 -0.004641 -0.001657
N -1.205960 -0.005975 -0.002181
Si -2.937377 -0.000230 -0.000050
Si 2.937392 0.000275 0.000252
C -3.515105 0.372848 1.740475
H -4.610293 0.385137 1.783955
H -3.155419 -0.385379 2.444322
H -3.150745 1.350600 2.073539
C -3.515038 1.323302 -1.190284
H -3.155976 1.122744 -2.205504
H -4.610296 1.358103 -1.217455
H -3.150879 2.310690 -0.886412
C -3.524506 -1.690195 -0.548263
H -4.619935 -1.727060 -0.559353
H -3.166360 -1.922055 -1.557095
H -3.164695 -2.470211 0.131237
C 3.522231 -0.670304 -1.646171
H 3.160057 -0.051012 -2.473919
H 4.617657 -0.682294 -1.684440
H 3.165595 -1.694096 -1.802421
C 3.519998 -1.089319 1.405745
H 4.615304 -1.113825 1.439997
H 3.158083 -0.714380 2.369066
H 3.160914 -2.116488 1.280518
C 3.512358 1.764556 0.242193
H 3.148478 2.169504 1.192610

H 4.607480 1.810555 0.249535
H 3.150551 2.409108 -0.566252

Structure: S2a
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -2001.960064 hartree
SCF Energy + ZPVE: -2001.444847 hartree
Enthalpy: -2001.408860 hartree
Free Energy: -2001.512842 hartree
Free Energy with quasiharmonic correction: -2001.504238 hartree
C -1.121029 0.332838 -0.182443
N -1.755780 -0.781603 -0.099747
N -1.466475 1.579745 -0.313378
Si -3.163791 2.009818 -0.354574
Si -1.792817 -2.481379 0.105249
C -4.070434 1.460241 1.204561
H -5.081173 1.885486 1.230172
H -4.159919 0.369547 1.248329
H -3.541847 1.795455 2.104884
C -3.223890 3.886604 -0.455320
H -2.707590 4.245555 -1.353305
H -4.257975 4.248556 -0.491841
H -2.736844 4.340773 0.415628
C -4.040923 1.298569 -1.864158
H -5.075699 1.659206 -1.911886
H -3.536486 1.601505 -2.789059
H -4.063982 0.203868 -1.831769
C -1.358382 -3.403020 -1.480540
H -0.274767 -3.463822 -1.628342
H -1.747231 -4.427709 -1.428561
H -1.797384 -2.919260 -2.360753
C -3.567336 -2.921328 0.560351
H -3.685879 -4.004090 0.688464
H -3.861024 -2.437014 1.499110
H -4.264188 -2.593155 -0.220097
C -0.699882 -3.161004 1.487159
H -1.028472 -2.807702 2.471036
H -0.774991 -4.256423 1.483325
H 0.356164 -2.897242 1.366990
P 0.820450 0.209962 -0.024888
C 1.243246 -0.088717 1.712548
C 2.590157 -0.144412 2.098355
C 0.232252 -0.188633 2.673320
C 2.919137 -0.328142 3.438363
H 3.377631 -0.039659 1.355268
C 0.569663 -0.364461 4.015288
H -0.813210 -0.135381 2.380821
C 1.908421 -0.440103 4.396234
H 3.962099 -0.377332 3.735061
H -0.216234 -0.442607 4.760120

H 2.167131 -0.579151 5.441595
C 1.706991 1.725873 -0.484199
C 1.470166 2.874415 0.285500
C 2.601742 1.777188 -1.557391
C 2.118343 4.065400 -0.026898
H 0.781669 2.836952 1.125458
C 3.247514 2.975891 -1.865190
H 2.807367 0.892266 -2.151374
C 3.005223 4.118182 -1.105083
H 1.931209 4.951953 0.571037
H 3.943039 3.010232 -2.698028
H 3.510049 5.048632 -1.347020
C 1.424382 -1.132248 -1.079502
C 1.068152 -1.075215 -2.435314
C 2.212918 -2.185465 -0.607158
C 1.520614 -2.054111 -3.315041
H 0.442253 -0.265148 -2.804534
C 2.651845 -3.171036 -1.492168
H 2.484661 -2.246729 0.442391
C 2.313391 -3.102275 -2.843286
H 1.246803 -2.003192 -4.364188
H 3.260963 -3.990031 -1.122533
H 2.661700 -3.869099 -3.528604

Structure: S2b
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1426.948213 hartree
SCF Energy + ZPVE: -1426.594348 hartree
Enthalpy: -1426.567869 hartree
Free Energy: -1426.648046 hartree
Free Energy with quasiharmonic correction: -1426.644922 hartree
C -0.217375 0.510502 0.001142
N 0.353694 -0.653302 -0.028803
N -1.478328 0.867660 0.009758
Si -2.732169 -0.351881 -0.003084
Si 1.766322 -1.609249 0.005849
C -2.697505 -1.442212 1.537192
H -3.570143 -2.106800 1.553907
H -1.796927 -2.064713 1.570328
H -2.723670 -0.833210 2.448484
C -4.367802 0.581198 -0.016701
H -4.450790 1.213941 -0.908221
H -5.218178 -0.110734 -0.013646
H -4.456356 1.229180 0.863225
C -2.680170 -1.453901 -1.534586
H -3.583852 -2.073740 -1.586429
H -2.635032 -0.852376 -2.450172
H -1.811662 -2.120788 -1.522861
C 3.220758 -1.011018 -1.047888
H 3.656788 -0.061701 -0.719594

H 4.015076 -1.767814 -1.010262
H 2.921005 -0.903018 -2.097228
C 1.299789 -3.301209 -0.680151
H 2.146641 -3.996904 -0.639563
H 0.474032 -3.736686 -0.104836
H 0.977052 -3.223891 -1.725289
C 2.361111 -1.861570 1.778929
H 1.554919 -2.282875 2.391289
H 3.204337 -2.562642 1.804764
H 2.684780 -0.926477 2.248729
P 0.892608 2.044924 -0.000255
C -0.028477 3.549545 0.376334
C 1.643846 2.260095 -1.630445
C 2.209503 1.897451 1.229041
H 2.200355 1.361909 -1.905441
H 0.848448 2.435330 -2.359854
H 2.318721 3.120247 -1.605722
H 0.660957 4.398813 0.369038
H -0.805548 3.694436 -0.376558
H -0.488910 3.453053 1.362355
H 2.796271 2.820514 1.228465
H 1.760755 1.747437 2.214715
H 2.864034 1.057676 0.991616

Structure: S3a
Charge = 1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -2001.763529 hartree
SCF Energy + ZPVE: -2001.247143 hartree
Enthalpy: -2001.211528 hartree
Free Energy: -2001.313424 hartree
Free Energy with quasiharmonic correction: -2001.307080 hartree
C -0.095633 -0.907882 0.826062
N 0.903239 -1.655118 0.963670
N -1.328914 -1.092504 1.362638
Si -2.537558 -2.342256 0.850736
Si 2.624071 -1.879502 0.670733
C -3.608556 -2.620091 2.348716
H -4.385386 -3.360075 2.126662
H -3.017179 -2.988280 3.193263
H -4.099538 -1.688163 2.648778
C -3.486374 -1.581894 -0.569486
H -2.838206 -1.401128 -1.432846
H -4.274889 -2.280599 -0.873907
H -3.958641 -0.637471 -0.278791
C -1.588398 -3.863307 0.325696
H -2.299892 -4.645003 0.034400
H -0.945097 -3.650808 -0.534929
H -0.965976 -4.252212 1.137619
C 2.844049 -2.568685 -1.057369
H 2.838363 -1.773698 -1.810018

```
H 3.811965 -3.081126 -1.114436
H 2.062185 -3.293568 -1.308615
C 3.162340 -3.141336 1.944114
H 4.235687 -3.345047 1.856724
H 2.966422 -2.779630 2.959709
H 2.622450 -4.085171 1.808713
C 3.648111 -0.322808 0.890622
H 3.649813 0.016977 1.931448
H 4.683263 -0.563291 0.615835
H 3.316632 0.504986 0.255896
P -0.032540 0.750622 -0.116165
C 0.837083 1.949900 0.909244
C 0.997029 3.252974 0.416200
C 1.274389 1.612613 2.193285
C 1.626202 4.209394 1.206566
H 0.628957 3.518510 -0.572182
C 1.894949 2.582043 2.979349
H 1.137781 0.608356 2.584455
C 2.075711 3.872988 2.485543
H 1.758473 5.217359 0.826985
H 2.235428 2.324376 3.977048
H 2.561905 4.623618 3.101060
C -1.695288 1.382598 -0.430560
C -2.476822 1.737207 0.679198
C -2.193066 1.528325 -1.728543
C -3.767715 2.216521 0.482516
H -2.080892 1.639937 1.686969
C -3.488210 2.011867 -1.913287
H -1.586371 1.272185 -2.591545
C -4.274118 2.349630 -0.812793
H -4.376383 2.487513 1.339226
H -3.878087 2.125467 -2.919707
H -5.282375 2.723565 -0.962481
C 0.799155 0.374047 -1.666966
C 0.268808 -0.671123 -2.438933
C 1.914194 1.092155 -2.108092
C 0.846963 -0.978470 -3.666005
H -0.589436 -1.241122 -2.085879
C 2.492219 0.767719 -3.335017
H 2.335102 1.892551 -1.507277
C 1.956725 -0.258111 -4.113268
H 0.437858 -1.784660 -4.266284
H 3.360302 1.319967 -3.680003
H 2.409933 -0.503331 -5.068890

Structure: S3b
Charge =  1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy:         -1426.760570 hartree
SCF Energy + ZPVE:  -1426.406097 hartree
Enthalpy:           -1426.379639 hartree
```

Free Energy: -1426.460554 hartree
Free Energy with quasiharmonic correction: -1426.457248 hartree
C 0.126703 0.599803 -0.242664
N 0.491079 -0.571111 -0.817164
N -0.997629 1.076990 0.104764
Si -2.577072 0.269918 -0.021979
Si 1.029606 -2.082362 0.029779
C -2.793514 -0.789540 1.509671
H -3.764361 -1.298138 1.483641
H -2.014791 -1.553318 1.601332
H -2.762533 -0.165146 2.409633
C -3.840447 1.648856 -0.040103
H -3.695418 2.301591 -0.908030
H -4.856643 1.241724 -0.088152
H -3.761380 2.261092 0.864914
C -2.696315 -0.723571 -1.608841
H -3.709531 -1.130224 -1.712431
H -2.503350 -0.080489 -2.475263
H -1.993224 -1.561087 -1.643059
C 2.639147 -2.571762 -0.780163
H 3.467485 -1.913893 -0.503867
H 2.894836 -3.589444 -0.462260
H 2.537317 -2.572712 -1.870300
C -0.294543 -3.346259 -0.345521
H 0.010953 -4.298547 0.104596
H -1.272618 -3.075698 0.061423
H -0.389518 -3.495603 -1.425908
C 1.205652 -1.702366 1.850658
H 0.282676 -1.274417 2.257962
H 1.429859 -2.617791 2.409857
H 2.023144 -0.993626 2.026718
P 1.556574 1.798886 -0.031370
C 1.438492 2.441848 1.641610
C 1.304568 3.118129 -1.226460
C 3.154681 1.020488 -0.301066
H 3.917727 1.803831 -0.257960
H 3.348463 0.286754 0.485394
H 3.172098 0.546169 -1.285683
H 2.244905 3.166538 1.785981
H 0.469528 2.929874 1.765519
H 1.541636 1.619383 2.353975
H 1.363757 2.706425 -2.236791
H 0.323807 3.568333 -1.056465
H 2.090388 3.864449 -1.079360

Structure: S4a
Charge = 1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -1035.816394 hartree
SCF Energy + ZPVE: -1035.540220 hartree
Enthalpy: -1035.523398 hartree

Free Energy: -1035.586536 hartree
Free Energy with quasiharmonic correction: -1035.582426 hartree
P -0.001663 0.001308 -0.679895
C 0.360937 -1.687847 -0.239149
C -0.464103 -2.699880 -0.760252
C 1.455196 -2.006174 0.581187
C -0.202648 -4.026475 -0.438736
H -1.300470 -2.447143 -1.407035
C 1.703966 -3.339084 0.892295
H 2.090280 -1.224222 0.985777
C 0.879898 -4.345088 0.384596
H -0.838714 -4.811493 -0.834210
H 2.540881 -3.591565 1.535172
H 1.083081 -5.382976 0.629791
C 1.281800 1.157913 -0.239036
C 1.015096 2.266042 0.580937
C 2.569457 0.945714 -0.761678
C 2.048066 3.144937 0.890482
H 0.020954 2.429867 0.985866
C 3.591060 1.831726 -0.441164
H 2.766634 0.095395 -1.409452
C 3.330569 2.929689 0.382212
H 1.851003 3.996234 1.533706
H 4.587753 1.669312 -0.837947
H 4.130566 3.620949 0.627837
C -1.645544 0.531589 -0.238894
C -2.105969 1.755520 -0.754207
C -2.472253 -0.259535 0.574785
C -3.385254 2.193409 -0.434067
H -1.467590 2.354848 -1.398012
C -3.750964 0.192311 0.885219
H -2.116175 -1.203178 0.975835
C -4.206411 1.413036 0.383227
H -3.743743 3.139040 -0.826959
H -4.390315 -0.408518 1.523583
H -5.206607 1.757018 0.627932

Structure: S4b
Charge = 1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -460.800977 hartree
SCF Energy + ZPVE: -460.687499 hartree
Enthalpy: -460.679695 hartree
Free Energy: -460.717857 hartree
Free Energy with quasiharmonic correction: -460.717857 hartree
P 0.000178 -0.000306 0.355562
C 1.600295 -0.636672 -0.160440
C -1.352046 -1.066682 -0.160336
C -0.248499 1.703652 -0.160278
H 1.620986 -0.647212 -1.256872
H 2.389882 0.015333 0.219033

H 1.728991 -1.651225 0.222182
H -1.369586 -1.081270 -1.256781
H -1.185480 -2.076277 0.220854
H -2.294693 -0.667779 0.220103
H -0.248005 1.726827 -1.256659
H -1.208315 2.061758 0.217438
H 0.565051 2.322652 0.223589

Structure: Methoxide
Charge = -1, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -115.153481 hartree
SCF Energy + ZPVE: -115.116561 hartree
Enthalpy: -115.112712 hartree
Free Energy: -115.137777 hartree
Free Energy with quasiharmonic correction: -115.137777 hartree
C 0.000000 -0.000000 -0.556731
H -0.000000 1.019643 -1.026451
H -0.883037 -0.509822 -1.026451
H 0.883037 -0.509822 -1.026451
O -0.000000 0.000000 0.802467

Structure: TMS-OMe (41)
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -524.295243 hartree
SCF Energy + ZPVE: -524.141810 hartree
Enthalpy: -524.130241 hartree
Free Energy: -524.178038 hartree
Free Energy with quasiharmonic correction: -524.176277 hartree
C -2.295680 -0.027143 -0.260775
H -2.439671 -0.852508 0.448227
H -3.073418 -0.092512 -1.026393
H -2.419002 0.922593 0.275794
O -1.032008 -0.105161 -0.899840
Si 0.379746 0.001193 0.008183
C 0.401892 -1.360403 1.297377
H 1.365932 -1.368676 1.819618
H -0.380820 -1.216385 2.050526
H 0.258646 -2.344368 0.836847
C 0.461999 1.671427 0.858110
H 1.417979 1.779990 1.383853
H 0.380525 2.490322 0.134673
H -0.337634 1.787023 1.598225
C 1.765220 -0.205995 -1.226284
H 2.738897 -0.164540 -0.725720
H 1.689040 -1.170363 -1.740265
H 1.738560 0.586690 -1.981797

Structure: 43
Charge = 0, Multiplicity = 2

Number of imaginary frequencies: 0
SCF Energy: -556.692848 hartree
SCF Energy + ZPVE: -556.570036 hartree
Enthalpy: -556.558484 hartree
Free Energy: -556.607339 hartree
Free Energy with quasiharmonic correction: -556.605473 hartree
C 2.071646 0.002123 -0.362550
N 3.212935 0.000050 0.013761
N 0.905690 0.004670 -0.820375
Si -0.683657 -0.000141 0.043560
C -1.514488 1.556825 -0.558270
H -2.517495 1.627829 -0.122743
H -0.948923 2.446070 -0.262652
H -1.611768 1.549815 -1.648413
C -1.512910 -1.552202 -0.573119
H -0.946123 -2.443526 -0.286160
H -2.515631 -1.628641 -0.137839
H -1.610698 -1.535092 -1.663077
C -0.392106 -0.009148 1.885149
H -1.352013 -0.011280 2.413829
H 0.164919 -0.900080 2.193801
H 0.165705 0.878247 2.202454

Structure: 44a
Charge = 0, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -1592.732936 hartree
SCF Energy + ZPVE: -1592.331637 hartree
Enthalpy: -1592.302912 hartree
Free Energy: -1592.393874 hartree
Free Energy with quasiharmonic correction: -1592.385074 hartree
P -0.211881 -0.008112 0.047550
C -1.689125 -0.468373 1.043315
C -1.969816 -1.837142 1.197469
C -2.450766 0.471754 1.751100
C -3.016156 -2.252276 2.014707
H -1.375636 -2.578172 0.666701
C -3.494330 0.047590 2.575247
H -2.248689 1.533960 1.651872
C -3.780817 -1.310219 2.708668
H -3.232596 -3.311697 2.114393
H -4.086695 0.785183 3.108565
H -4.593875 -1.635340 3.350568
C -0.339426 1.792359 -0.162409
C -0.836985 2.372051 -1.332324
C 0.098385 2.607412 0.890502
C -0.904877 3.762162 -1.443279
H -1.165498 1.749623 -2.159749
C 0.022110 3.992898 0.777521
H 0.504175 2.156860 1.794312
C -0.478771 4.571007 -0.391161

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H -1.287819 4.209479 -2.355377
H 0.360710 4.620200 1.596360
H -0.530650 5.651766 -0.482309
C -0.504712 -0.807544 -1.564219
C 0.555451 -1.288125 -2.342492
C -1.821033 -0.942059 -2.035060
C 0.301326 -1.893661 -3.573544
H 1.574639 -1.195607 -1.984700
C -2.067372 -1.543077 -3.266799
H -2.654733 -0.573132 -1.443887
C -1.006483 -2.021722 -4.037799
H 1.130475 -2.267178 -4.166604
H -3.088770 -1.636686 -3.622791
H -1.200666 -2.494089 -4.996104
N 1.940189 0.010001 0.033122
C 2.521058 1.008727 -0.562572
N 2.982792 1.927475 -1.140288
C 4.527868 -0.961778 1.082686
H 4.871619 0.044140 1.346992
H 4.999194 -1.670043 1.774044
H 4.879001 -1.191885 0.070996
C 2.073703 -2.820611 0.755062
H 2.443705 -3.120557 -0.231370
H 2.433114 -3.550002 1.490410
H 0.978562 -2.875984 0.741056
C 2.068160 -0.645584 2.922857
H 2.490149 -1.326740 3.671299
H 2.371571 0.374694 3.183025
H 0.975297 -0.706441 2.991336
Si 2.666172 -1.102553 1.205929

Structure: 44b
Charge =  0, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy:         -1017.714219 hartree
SCF Energy + ZPVE:  -1017.475194 hartree
Enthalpy:           -1017.455646 hartree
Free Energy:        -1017.522513 hartree
Free Energy with quasiharmonic correction:  -1017.519579 hartree
P 1.626178 -0.270721 0.050492
C 2.615273 -1.827099 0.018921
C 1.990705 0.515233 -1.548241
C 2.438807 0.743335 1.320007
N -0.393290 0.698217 0.355549
C -0.394330 1.972713 0.131145
N -0.300314 3.136861 -0.053157
C -3.340055 0.443027 0.194183
H -3.443158 1.232009 -0.558934
H -4.164677 -0.265324 0.053078
H -3.449659 0.897891 1.184666
C -1.532624 -1.815167 1.297026
```

H -1.630127 -1.425755 2.316231
H -2.309940 -2.572827 1.144597
H -0.558639 -2.312031 1.212787
C -1.494719 -1.147911 -1.694769
H -2.329883 -1.814211 -1.941651
H -1.465445 -0.348315 -2.443821
H -0.568329 -1.729109 -1.778419
Si -1.696978 -0.442725 0.033862
H 3.667769 -1.589694 -0.177116
H 2.525062 -2.331516 0.984314
H 2.232483 -2.482017 -0.768024
H 3.075676 0.566136 -1.686504
H 1.551083 -0.078437 -2.354495
H 1.576051 1.525856 -1.575261
H 3.519450 0.743177 1.146193
H 2.064918 1.769023 1.276900
H 2.229272 0.323769 2.307653

Structure: 45a
Charge = 1, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1592.634658 hartree
SCF Energy + ZPVE: -1592.228586 hartree
Enthalpy: -1592.201440 hartree
Free Energy: -1592.284444 hartree
Free Energy with quasiharmonic correction: -1592.279980 hartree
P -0.344474 0.005281 -0.099350
C 0.711679 -0.471834 -1.472845
C 1.538535 0.484449 -2.078719
C 0.729729 -1.805228 -1.905453
C 2.399216 0.095637 -3.102029
H 1.517179 1.522111 -1.760497
C 1.591923 -2.180384 -2.930368
H 0.084977 -2.550507 -1.450966
C 2.428488 -1.233503 -3.523638
H 3.042140 0.833842 -3.569961
H 1.608070 -3.211997 -3.265992
H 3.099825 -1.531863 -4.322949
C -1.861331 -0.959932 -0.035518
C -3.077459 -0.380056 -0.412692
C -1.808983 -2.293845 0.396737
C -4.241165 -1.145318 -0.371028
H -3.128077 0.657175 -0.727412
C -2.977907 -3.046084 0.435139
H -0.868564 -2.741670 0.708561
C -4.191409 -2.473338 0.049255
H -5.186061 -0.697114 -0.660106
H -2.940652 -4.076816 0.771907
H -5.101760 -3.063728 0.084001
C -0.693887 1.765252 -0.188926
C -0.535550 2.575641 0.939937

C -1.152131 2.305011 -1.399835
C -0.837971 3.933356 0.853675
H -0.174264 2.165518 1.877886
C -1.454842 3.660792 -1.472004
H -1.267811 1.674627 -2.278167
C -1.296737 4.472922 -0.347114
H -0.711493 4.566247 1.725851
H -1.809013 4.082394 -2.406928
H -1.529618 5.531467 -0.409329
N 0.496038 -0.346352 1.341623
C -0.255138 -0.519435 2.439092
N -0.888032 -0.680457 3.401053
C 2.544327 -0.771600 3.388309
H 2.150816 -1.770427 3.602033
H 3.617652 -0.779657 3.612995
H 2.066493 -0.049878 4.057464
C 2.895228 1.433723 1.253028
H 2.476295 2.117994 1.998042
H 3.988468 1.484672 1.320165
H 2.605539 1.782940 0.257614
C 3.126709 -1.590555 0.481715
H 4.122373 -1.814262 0.884284
H 2.547902 -2.519985 0.482771
H 3.249930 -1.246917 -0.549325
Si 2.354484 -0.313554 1.594947

Structure: 45b
Charge = 1, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1017.631012 hartree
SCF Energy + ZPVE: -1017.387000 hartree
Enthalpy: -1017.369219 hartree
Free Energy: -1017.429479 hartree
Free Energy with quasiharmonic correction: -1017.428375 hartree
P 1.540917 -0.272527 -0.007733
C 1.371937 -1.806223 -0.910905
C 2.766527 0.770837 -0.789910
C 1.998857 -0.591960 1.693622
N 0.038233 0.536990 -0.062775
C 0.081625 1.872250 -0.028171
N 0.102868 3.035187 -0.006882
C -2.809173 1.151473 0.253987
H -2.794557 1.848070 -0.590178
H -3.823359 0.742588 0.333300
H -2.596029 1.703940 1.174227
C -1.596759 -1.438525 1.454918
H -1.376037 -0.900765 2.382676
H -2.585204 -1.902050 1.557163
H -0.865642 -2.243916 1.330945
C -1.910513 -1.128508 -1.628250
H -2.980711 -1.343370 -1.732441

H -1.613816 -0.485400 -2.463361
H -1.370532 -2.076341 -1.702162
Si -1.639811 -0.272345 0.003842
H 2.989969 -1.055741 1.695788
H 2.030594 0.354187 2.240079
H 1.272367 -1.268720 2.148926
H 3.700286 0.201076 -0.816062
H 2.449602 1.009892 -1.808037
H 2.915171 1.682580 -0.206608
H 2.359638 -2.278068 -0.906446
H 0.660469 -2.474423 -0.420783
H 1.068691 -1.594116 -1.938961

Structure: S5
Charge = 1, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -965.726246 hartree
SCF Energy + ZPVE: -965.489833 hartree
Enthalpy: -965.469754 hartree
Free Energy: -965.540931 hartree
Free Energy with quasiharmonic correction: -965.534466 hartree
C 0.035571 -0.263748 0.325609
N 1.239900 -0.423835 0.482206
N -1.151561 -0.154186 0.223927
Si -2.940296 0.018628 -0.008984
Si 2.926385 0.041206 -0.028265
C -3.683575 -0.438894 1.629089
H -4.775241 -0.373655 1.561208
H -3.415668 -1.462074 1.909120
H -3.348707 0.243779 2.415997
C -3.189573 1.790296 -0.504862
H -2.649107 2.017833 -1.428585
H -4.256778 1.971680 -0.674523
H -2.848982 2.469157 0.282857
C -3.245234 -1.217169 -1.369919
H -4.316213 -1.209589 -1.603341
H -2.689927 -0.952344 -2.274084
H -2.964799 -2.226511 -1.056040
C 3.499725 -1.529545 -0.851387
H 2.880134 -1.769218 -1.720299
H 4.531709 -1.382124 -1.190315
H 3.478095 -2.369057 -0.150824
C 3.758629 0.395520 1.596729
H 4.806945 0.651730 1.406715
H 3.285321 1.239394 2.107257
H 3.727689 -0.481020 2.250495
C 2.792294 1.501699 -1.166673
H 2.324153 2.352099 -0.661212
H 3.793830 1.806870 -1.489998
H 2.206901 1.252577 -2.057375

Structure: S6
Charge = -1, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1081.184314 hartree
SCF Energy + ZPVE: -1080.906087 hartree
Enthalpy: -1080.882181 hartree
Free Energy: -1080.961941 hartree
Free Energy with quasiharmonic correction: -1080.954280 hartree
N 0.873962 -2.650210 -0.021945
C 1.838981 -1.974785 0.158058
N 2.898318 -1.292271 0.381212
Si 3.091341 0.384004 0.012002
C 4.679757 0.961349 0.830856
H 5.536719 0.380324 0.470947
H 4.872860 2.018105 0.612938
H 4.625991 0.843748 1.919144
C 1.640299 1.407620 0.648442
H 0.709941 1.106666 0.151781
H 1.504531 1.280474 1.728676
H 1.794028 2.475141 0.448075
C 3.219518 0.679042 -1.847018
H 3.356282 1.744508 -2.068568
H 4.066662 0.131921 -2.276376
H 2.308739 0.344513 -2.358530
Si -2.684297 -0.236688 -0.003096
C -3.138888 -2.045535 -0.090557
H -2.238142 -2.668679 -0.062738
H -3.775434 -2.330196 0.754359
H -3.678476 -2.269606 -1.017203
C -1.630189 0.270131 -1.469629
H -0.721952 -0.342632 -1.511497
H -2.177819 0.122311 -2.407688
H -1.324790 1.320765 -1.413835
O -4.152030 0.585621 -0.063262
C -1.814183 0.168157 1.608291
H -1.511062 1.219668 1.659728
H -2.468645 -0.042158 2.462220
H -0.912747 -0.446419 1.716604
C -4.174000 2.001855 -0.002057
H -3.607653 2.450578 -0.828630
H -5.213016 2.333726 -0.077681
H -3.762116 2.370210 0.946499

Structure: 42
Charge = -1, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -556.885726 hartree
SCF Energy + ZPVE: -556.761760 hartree
Enthalpy: -556.750471 hartree
Free Energy: -556.797504 hartree
Free Energy with quasiharmonic correction: -556.796324 hartree

N -3.196347 -0.039218 -0.026277
C -2.078403 0.296714 0.212124
N -0.904595 0.711442 0.504834
Si 0.594884 0.016398 0.010905
C 1.965537 1.102279 0.696680
H 1.912600 1.154473 1.790279
H 2.951885 0.709108 0.424443
H 1.888738 2.123578 0.306307
C 0.752625 -0.060800 -1.867578
H -0.037437 -0.682988 -2.304768
H 0.677115 0.938898 -2.310665
H 1.717848 -0.489963 -2.162559
C 0.810549 -1.735568 0.677069
H 1.774591 -2.157588 0.368153
H 0.770756 -1.748351 1.772381
H 0.020267 -2.398047 0.304090

Structure: 46a
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1183.589929 hartree
SCF Energy + ZPVE: -1183.299089 hartree
Enthalpy: -1183.279368 hartree
Free Energy: -1183.349015 hartree
Free Energy with quasiharmonic correction: -1183.343426 hartree
P 0.038696 0.025353 0.573306
C 1.775005 0.276872 0.157058
C 2.735596 0.342917 1.169198
C 2.149015 0.395960 -1.187241
C 4.076225 0.531361 0.832172
H 2.434679 0.248500 2.207621
C 3.488989 0.580832 -1.514948
H 1.402187 0.339895 -1.976251
C 4.451770 0.649679 -0.505214
H 4.824655 0.584982 1.616564
H 3.781248 0.671918 -2.556239
H 5.496225 0.795627 -0.763636
C -0.511482 -1.540780 -0.147053
C -1.885445 -1.786460 -0.278111
C 0.416407 -2.536510 -0.474541
C -2.324756 -3.023247 -0.743954
H -2.610201 -1.017084 -0.023890
C -0.031749 -3.770075 -0.944124
H 1.482175 -2.354533 -0.367568
C -1.398803 -4.012202 -1.079781
H -3.388506 -3.212402 -0.847647
H 0.687683 -4.539947 -1.204342
H -1.744182 -4.973633 -1.447639
C -0.943608 1.344593 -0.189417
C -1.218426 2.487022 0.570259
C -1.382023 1.257415 -1.516784

C -1.932159 3.540622 0.001797
H -0.876456 2.551618 1.599626
C -2.091279 2.316358 -2.079211
H -1.176485 0.370027 -2.109645
C -2.367091 3.455378 -1.320773
H -2.149563 4.424642 0.592924
H -2.432139 2.248980 -3.107524
H -2.924074 4.276558 -1.761647
N -0.030707 0.068939 2.193696
C -1.124142 -0.206972 2.852077
N -2.066429 -0.442085 3.512194

Structure: 46b
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -608.581364 hartree
SCF Energy + ZPVE: -608.452635 hartree
Enthalpy: -608.442273 hartree
Free Energy: -608.486819 hartree
Free Energy with quasiharmonic correction: -608.486134 hartree
P -0.554953 -0.022415 -0.001688
C -1.906180 -1.200464 -0.053383
C -0.704781 0.956904 1.504877
C -0.729787 1.112397 -1.391990
N 0.817139 -0.905291 -0.060125
C 1.997635 -0.354758 -0.024436
N 3.098194 0.059746 0.002716
H -1.690434 1.629966 -1.318622
H 0.081367 1.845414 -1.366290
H -0.684144 0.545232 -2.325227
H -2.856705 -0.662406 -0.015052
H -1.843786 -1.775716 -0.980492
H -1.826005 -1.872803 0.804442
H -1.665283 1.479971 1.501777
H -0.647039 0.292945 2.371118
H 0.107667 1.687953 1.545119

Structure: S7
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1081.667031 hartree
SCF Energy + ZPVE: -1081.372565 hartree
Enthalpy: -1081.350124 hartree
Free Energy: -1081.423345 hartree
Free Energy with quasiharmonic correction: -1081.419328 hartree
C -0.007496 0.809988 0.000050
N -0.598268 -0.326772 0.000135
N 1.350480 0.930416 0.000066
Si 2.466678 -0.458305 0.000015
Si -2.329885 -0.541927 0.000008
C 2.242884 -1.492475 1.544036

H 3.039756 -2.243255 1.603828
H 2.297875 -0.869529 2.443579
H 1.281801 -2.014893 1.542596
C 2.242318 -1.492873 -1.543658
H 2.296297 -0.870057 -2.443356
H 3.039600 -2.243182 -1.603891
H 1.281540 -2.015839 -1.541433
C 4.151935 0.360585 -0.000427
H 4.941233 -0.399402 -0.000286
H 4.289538 0.987439 -0.888533
H 4.289756 0.987989 0.887257
C -2.613404 -2.399263 0.000591
H -2.163330 -2.861868 0.886802
H -3.683305 -2.637346 0.000504
H -2.163051 -2.862470 -0.885165
C -3.130441 0.196529 -1.536043
H -4.201328 -0.038161 -1.562933
H -3.019502 1.285831 -1.552114
H -2.675030 -0.206471 -2.448006
C -3.130959 0.197544 1.535296
H -3.020196 1.286873 1.550594
H -4.201816 -0.037301 1.562049
H -2.675748 -0.204715 2.447685
O -0.739173 1.958254 -0.000093
C -0.100600 3.235350 0.000072
H 0.508364 3.372573 -0.898805
H -0.907924 3.967319 -0.000039
H 0.508049 3.372474 0.899177
H 1.744801 1.863407 0.000008

Structure: S8
Charge = -1, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1081.166036 hartree
SCF Energy + ZPVE: -1080.885360 hartree
Enthalpy: -1080.863255 hartree
Free Energy: -1080.935803 hartree
Free Energy with quasiharmonic correction: -1080.931828 hartree
C 0.058423 0.743602 0.000010
N 1.354313 0.957712 -0.000026
N -0.602866 -0.399451 0.000019
Si -2.321482 -0.522056 -0.000001
Si 2.483573 -0.346044 -0.000000
C -3.157334 0.225367 1.525171
H -4.234928 0.018371 1.522907
H -2.737667 -0.194340 2.447495
H -3.017609 1.311290 1.553735
C -3.157282 0.225394 -1.525186
H -2.737682 -0.194409 -2.447496
H -4.234900 0.018519 -1.522889
H -3.017435 1.311300 -1.553805

C -2.726055 -2.366881 -0.000024
H -3.809094 -2.539381 -0.000071
H -2.306151 -2.859694 -0.885336
H -2.306230 -2.859701 0.885323
C 2.386206 -1.454604 -1.529860
H 2.453059 -0.859199 -2.448525
H 3.215599 -2.172916 -1.536419
H 1.448648 -2.019595 -1.560949
C 2.386166 -1.454540 1.529901
H 3.215539 -2.172878 1.536493
H 2.453026 -0.859101 2.448541
H 1.448592 -2.019505 1.560993
C 4.202782 0.434425 -0.000001
H 4.346664 1.065387 0.885412
H 4.988656 -0.330399 -0.000018
H 4.346643 1.065404 -0.885406
O -0.760616 1.876742 0.000043
C -0.148763 3.153511 -0.000030
H -0.966885 3.878056 0.000039
H 0.471492 3.303405 0.889218
H 0.471326 3.303386 -0.889397

Structure: S9
Charge = 0, Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -1080.990837 hartree
SCF Energy + ZPVE: -1080.709073 hartree
Enthalpy: -1080.687051 hartree
Free Energy: -1080.758758 hartree
Free Energy with quasiharmonic correction: -1080.756144 hartree
C 0.012087 1.145437 0.376196
N 0.790023 0.147720 0.913298
N -1.182635 0.992688 -0.034947
Si -2.167524 -0.461635 0.012204
Si 2.101529 -0.619502 -0.049234
C -3.944412 0.131199 -0.056578
H -4.637923 -0.717195 -0.072457
H -4.185404 0.749927 0.815237
H -4.120207 0.731121 -0.956529
C -1.792219 -1.510045 -1.500387
H -0.778005 -1.923022 -1.462683
H -2.493088 -2.351376 -1.559824
H -1.887967 -0.923190 -2.420761
C -1.900082 -1.477116 1.571195
H -2.683922 -2.239453 1.656665
H -0.930102 -1.985873 1.560466
H -1.943148 -0.847370 2.467149
C 1.927390 -2.458220 0.233575
H 0.991057 -2.844040 -0.182530
H 2.756500 -2.988506 -0.248755
H 1.951795 -2.686730 1.304379

C 3.676452 0.053183 0.704888
H 4.542296 -0.400060 0.208590
H 3.739235 1.138973 0.581610
H 3.730502 -0.180995 1.772772
C 1.933290 -0.151558 -1.853339
H 2.058479 0.927886 -1.992889
H 2.702646 -0.659555 -2.446080
H 0.955382 -0.440142 -2.254195
O 0.672401 2.319696 0.339233
C -0.050948 3.442006 -0.177128
H -0.949843 3.626678 0.415609
H 0.632772 4.286622 -0.099774
H -0.327421 3.272467 -1.220429

Structure: S10
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -557.360460 hartree
SCF Energy + ZPVE: -557.224373 hartree
Enthalpy: -557.212465 hartree
Free Energy: -557.261253 hartree
Free Energy with quasiharmonic correction: -557.259475 hartree
N -3.113374 -0.095564 0.015052
C -2.056862 0.394007 0.091703
N -0.838291 0.902090 0.157097
Si 0.681435 -0.051594 -0.015015
C 1.989340 1.251407 -0.270198
H 2.021876 1.945613 0.576621
H 2.975659 0.783382 -0.358843
H 1.800431 1.825553 -1.183089
C 0.438456 -1.173777 -1.485220
H -0.391874 -1.869426 -1.320904
H 0.232884 -0.597348 -2.393083
H 1.342347 -1.769656 -1.654175
C 0.949144 -1.037061 1.548695
H 1.860505 -1.640511 1.468848
H 1.050475 -0.377483 2.416948
H 0.109454 -1.717411 1.729227
H -0.800653 1.886468 0.413745

Structure: Methanol
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -115.677789 hartree
SCF Energy + ZPVE: -115.626003 hartree
Enthalpy: -115.621741 hartree
Free Energy: -115.648747 hartree
Free Energy with quasiharmonic correction: -115.648747 hartree
C 0.666562 -0.019995 0.000000
H 1.090996 0.985961 -0.000002
H 1.019218 -0.549695 -0.892565

H 1.019218 -0.549691 0.892567
O -0.748128 0.123770 0.000000
H -1.143780 -0.756762 0.000000

Structure: $OPPh_3$
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1111.237653 hartree
SCF Energy + ZPVE: -1110.956948 hartree
Enthalpy: -1110.939193 hartree
Free Energy: -1111.004866 hartree
Free Energy with quasiharmonic correction: -1110.999058 hartree
C -2.895639 1.697357 -1.437675
C -3.151515 2.893638 -0.766930
C -1.954212 0.800288 -0.932306
C -1.264760 1.101750 0.246919
C -1.526146 2.301892 0.919395
H -1.761408 -0.131687 -1.458656
C -2.467412 3.195873 0.412173
H -2.668754 4.125116 0.937599
H -3.886217 3.590108 -1.161337
H -3.431061 1.459253 -2.352376
H -0.995965 2.532941 1.840421
C -0.321792 -1.645959 0.251248
C 0.328552 -2.125010 -0.890291
C -1.282006 -2.440336 0.891078
C 0.017140 -3.390164 -1.390266
H 1.078520 -1.517664 -1.391579
C -1.590846 -3.702995 0.389502
H -1.784017 -2.070320 1.782298
C -0.941309 -4.177504 -0.752212
H 0.525886 -3.759846 -2.275974
H -2.335117 -4.316651 0.889037
H -1.180947 -5.162850 -1.142270
C 1.588913 0.544057 0.248873
C 2.756536 0.145891 0.912051
C 1.678696 1.315050 -0.914889
C 4.004237 0.513325 0.411636
H 2.687782 -0.447524 1.820816
C 2.929503 1.680872 -1.413647
H 0.778133 1.632395 -1.435131
C 4.090457 1.280531 -0.751862
H 4.907380 0.204000 0.930037
H 2.995071 2.281324 -2.316501
H 5.063309 1.568349 -1.140690
P 0.001107 0.002065 0.948202
O 0.000053 0.006342 2.456812

Structure: 49 (related to Figure 4)
Charge = 0 Multiplicity = 1
Number of imaginary frequencies: 0

SCF Energy: -1091.3273939 hartree
SCF Energy + ZPVE: -1091.036079 hartree
Enthalpy: -1091.018001 hartree
Free Energy: -1091.082736 hartree
Free Energy with quasiharmonic correction: -1091.078559 hartree
C -2.313285 -2.294087 -1.593081
C -2.461008 -3.474496 -0.861854
C -1.575468 -1.234227 -1.068011
C -0.976956 -1.351894 0.193142
C -1.129422 -2.536161 0.921955
H -1.473921 -0.314925 -1.640424
C -1.869797 -3.594991 0.395725
H -1.986368 -4.510514 0.968816
H -3.040333 -4.297380 -1.271410
H -2.777457 -2.195929 -2.570365
H -0.670558 -2.624816 1.903891
C 1.690678 -0.174327 0.202686
C 1.853192 -0.229333 -1.186827
C 2.808535 -0.239227 1.038168
C 3.128323 -0.347770 -1.734900
H 0.988833 -0.174703 -1.845365
C 4.084614 -0.360036 0.485851
H 2.671991 -0.196977 2.114767
C 4.244956 -0.413770 -0.898250
H 3.250720 -0.388664 -2.813407
H 4.951650 -0.411524 1.138328
H 5.238789 -0.507503 -1.327163
C -0.692833 1.517854 0.282292
C 0.097390 2.544179 -0.245708
C -2.072539 1.716425 0.432408
C -0.488224 3.751275 -0.631210
H 1.170212 2.409543 -0.359248
C -2.654317 2.922438 0.048795
H -2.696761 0.927183 0.847725
C -1.861993 3.940531 -0.486474
H 0.131233 4.542071 -1.044808
H -3.724552 3.067555 0.165767
H -2.316310 4.880142 -0.788302
P 0.039005 -0.022920 0.940111
N 0.214975 -0.102370 2.520628
H -0.678148 0.002521 3.006877

Structure: 48 (related to Figure 4)
Charge = 0 Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1130.6082712 hartree
SCF Energy + ZPVE: -1130.288073 hartree
Enthalpy: -1130.268428 hartree
Free Energy: -1130.336827 hartree
Free Energy with quasiharmonic correction: -1130.332452 hartree
C -2.002897 -2.471989 -1.873966

C -2.095015 -3.653611 -1.136017
C -1.383858 -1.350464 -1.323328
C -0.844710 -1.408684 -0.032125
C -0.940378 -2.595562 0.703317
H -1.323857 -0.432157 -1.902858
C -1.565345 -3.714819 0.153274
H -1.639488 -4.631605 0.731348
H -2.581692 -4.524831 -1.565715
H -2.416232 -2.421725 -2.877380
H -0.525377 -2.638423 1.708180
C 1.748825 -0.083199 0.143603
C 2.002960 -0.143862 -1.231775
C 2.811143 -0.079966 1.050759
C 3.315389 -0.199326 -1.695552
H 1.179949 -0.142210 -1.943861
C 4.124569 -0.139232 0.582545
H 2.603059 -0.032830 2.115560
C 4.376917 -0.198249 -0.787832
H 3.509364 -0.244348 -2.763344
H 4.949426 -0.138716 1.289512
H 5.400062 -0.243709 -1.150494
C -0.724384 1.480584 0.026299
C 0.053345 2.578681 -0.360411
C -2.122394 1.583539 0.000956
C -0.559373 3.757104 -0.786432
H 1.138916 2.518449 -0.333358
C -2.732444 2.764381 -0.419601
H -2.738890 0.739192 0.303735
C -1.951100 3.850246 -0.817764
H 0.051278 4.601216 -1.094197
H -3.816272 2.835305 -0.438137
H -2.426984 4.768542 -1.150440
P 0.042731 -0.010021 0.754159
N 0.084287 -0.055884 2.340981
C -1.180494 0.063908 3.060208
H -0.989390 -0.042365 4.133650
H -1.669015 1.041810 2.915986
H -1.920385 -0.706954 2.785612

Structure: 1a (related to Figure 4)
Charge = 0 Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1183.5705842 hartree
SCF Energy + ZPVE: -1183.279102 hartree
Enthalpy: -1183.259398 hartree
Free Energy: -1183.328987 hartree
Free Energy with quasiharmonic correction: -1183.323436 hartree
C -2.085397 -2.332281 -2.073657
C -2.363853 -3.466481 -1.308880
C -1.377253 -1.269983 -1.515824
C -0.943554 -1.347858 -0.186370

C -1.220794 -2.485835 0.579374
H -1.168738 -0.386853 -2.114656
C -1.932598 -3.543331 0.015542
H -2.151351 -4.424134 0.611959
H -2.920010 -4.290722 -1.746352
H -2.423439 -2.271219 -3.103884
H -0.882604 -2.544357 1.610844
C 1.773578 -0.277228 0.156645
C 2.149290 -0.391828 -1.187728
C 2.733256 -0.348458 1.169237
C 3.489478 -0.576914 -1.514872
H 1.403212 -0.331877 -1.977685
C 4.074229 -0.537317 0.833158
H 2.431963 -0.257586 2.208411
C 4.451247 -0.650678 -0.504317
H 3.782873 -0.664200 -2.556751
H 4.821959 -0.594978 1.618713
H 5.496367 -0.796544 -0.762366
C -0.512257 1.539568 -0.152543
C 0.415572 2.539914 -0.466091
C -1.885448 1.782198 -0.297063
C -0.031117 3.774096 -0.935599
H 1.481277 2.361139 -0.348245
C -2.323792 3.019523 -0.762769
H -2.611360 1.010041 -0.052706
C -1.397447 4.012801 -1.084861
H 0.689232 4.547461 -1.185036
H -3.387563 3.205909 -0.876497
H -1.742114 4.975150 -1.452523
P 0.036993 -0.024850 0.571567
N -0.033484 -0.062720 2.192050
C -1.125529 0.224321 2.847795
N -2.066555 0.469885 3.505980

Structure: 6
Charge = 0 Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1111.2376816 hartree
SCF Energy + ZPVE: -1110.956912 hartree
Enthalpy: -1110.939161 hartree
Free Energy: -1111.004999 hartree
Free Energy with quasiharmonic correction: -1110.999019 hartree
C 1.174003 -3.166668 -1.412716
C 0.580765 -4.243856 -0.754086
C 1.022010 -1.872322 -0.913834
C 0.272484 -1.655055 0.246911
C -0.319820 -2.739106 0.907047
H 1.488942 -1.037369 -1.430988
C -0.166072 -4.030414 0.406379
H -0.625317 -4.868986 0.922025
H 0.702406 -5.250980 -1.143117

H 1.758523 -3.332217 -2.313233
H -0.896808 -2.571597 1.813582
C 1.298439 1.064033 0.248056
C 1.114897 1.819867 -0.914471
C 2.531444 1.095180 0.911747
C 2.160556 2.599114 -1.411048
H 0.160063 1.805176 -1.434683
C 3.573730 1.874191 0.413263
H 2.672487 0.513266 1.819623
C 3.388061 2.625900 -0.748793
H 2.013810 3.186911 -2.312674
H 4.527963 1.897204 0.931854
H 4.199977 3.235206 -1.136040
C -1.570647 0.592221 0.245073
C -2.231567 1.624687 0.922064
C -2.115786 0.072059 -0.933489
C -3.427196 2.135582 0.420309
H -1.811983 2.023443 1.842706
C -3.312740 0.586016 -1.433523
H -1.612394 -0.733313 -1.463262
C -3.967178 1.616444 -0.758062
H -3.938221 2.935093 0.949130
H -3.734660 0.178326 -2.347727
H -4.900385 2.013509 -1.147850
P -0.000826 0.000822 0.945236
O -0.003040 0.000844 2.453395

Structure: 2a (related to Figure 4)
Charge = 0 Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1036.0024812 hartree
SCF Energy + ZPVE: -1035.726575 hartree
Enthalpy: -1035.709772 hartree
Free Energy: -1035.773396 hartree
Free Energy with quasiharmonic correction: -1035.76779 hartree
C 0.614004 3.268454 1.243901
C 1.768504 3.828050 0.696764
C 0.054176 2.119515 0.681601
C 0.640990 1.521358 -0.439740
C 1.792520 2.100159 -0.991920
H -0.840619 1.690407 1.125790
C 2.359444 3.239632 -0.423006
H 3.255790 3.672318 -0.858929
H 2.203789 4.720542 1.137696
H 0.147643 3.723261 2.113754
H 2.252818 1.653567 -1.871607
C 0.996620 -1.315171 -0.438294
C 1.792617 -1.106579 0.694338
C 0.939312 -2.598513 -1.000095
C 2.510818 -2.163426 1.257356
H 1.855562 -0.118780 1.144562

C 1.645122 -3.657136 -0.429903
H 0.334116 -2.772302 -1.888106
C 2.435274 -3.440114 0.700454
H 3.127058 -1.987215 2.134973
H 1.585390 -4.647354 -0.873291
H 2.993060 -4.261355 1.141945
C -1.639685 -0.206694 -0.439102
C -1.861210 -1.008628 0.686394
C -2.719624 0.494685 -0.995331
C -3.136285 -1.100957 1.248471
H -1.040029 -1.564036 1.132980
C -3.989733 0.413909 -0.425904
H -2.564946 1.112763 -1.878081
C -4.200753 -0.387586 0.697659
H -3.294279 -1.728453 2.121524
H -4.814726 0.968853 -0.864207
H -5.191354 -0.458856 1.138284
P -0.001463 -0.000607 -1.259943

Structure: 47 (related to Figure 4)
Charge = 0 Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1322.2960985 hartree
SCF Energy + ZPVE: -1321.922728 hartree
Enthalpy: -1321.900018 hartree
Free Energy: -1321.976921 hartree
Free Energy with quasiharmonic correction: -1321.969729 hartree
C 1.018835 2.983711 2.509313
C 0.729067 4.136048 1.776285
C 0.899971 1.728433 1.914752
C 0.493322 1.620884 0.578459
C 0.206668 2.779066 -0.152654
H 1.123007 0.836436 2.495371
C 0.323416 4.033646 0.445563
H 0.095885 4.928396 -0.126930
H 0.818410 5.112766 2.243651
H 1.333775 3.061058 3.546093
H -0.107534 2.695386 -1.190038
C 2.022786 -0.378288 -0.898915
C 3.128091 -0.280937 -0.045058
C 2.192982 -0.809536 -2.216739
C 4.397444 -0.615815 -0.510744
H 3.003774 0.049675 0.984091
C 3.467356 -1.137928 -2.681085
H 1.329246 -0.882128 -2.871137
C 4.567580 -1.043044 -1.829604
H 5.252796 -0.542210 0.154608
H 3.597917 -1.469520 -3.707232
H 5.558859 -1.301292 -2.191640
C -0.049658 -1.191894 1.003587
C 0.539806 -2.461252 1.007662

C -1.082469 -0.903491 1.905871
C 0.108270 -3.428723 1.915250
H 1.334852 -2.699891 0.305002
C -1.514412 -1.873691 2.807915
H -1.554510 0.076929 1.903948
C -0.917848 -3.135956 2.814010
H 0.573859 -4.410104 1.918917
H -2.316134 -1.644624 3.504063
H -1.253748 -3.891153 3.519113
P 0.360334 0.018965 -0.294366
N -0.609678 0.037647 -1.553473
C -2.007079 0.015262 -1.438931
C -2.705156 -1.160265 -1.093441
C -2.768596 1.157327 -1.751958
C -4.097806 -1.182265 -1.044093
H -2.136405 -2.060258 -0.868907
C -4.162262 1.129647 -1.707582
H -2.248249 2.068477 -2.036962
C -4.838530 -0.037900 -1.349126
H -4.607581 -2.103819 -0.773061
H -4.722024 2.028079 -1.956410
H -5.924124 -0.058446 -1.315159

Structure: 48_neutral
Charge = 0 Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1130.63057 hartree
SCF Energy + ZPVE: -1130.311003 hartree
Enthalpy: -1130.291403 hartree
Free Energy: -1130.359282 hartree
Free Energy with quasiharmonic correction: -1130.355426 hartree
P 0.039347 0.021449 0.753269
C -1.013337 1.298838 -0.035060
C -1.263711 2.460359 0.704281
C -1.534392 1.176314 -1.329116
C -2.025204 3.491825 0.155034
H -0.861784 2.551194 1.710709
C -2.289989 2.211181 -1.878634
H -1.354345 0.275164 -1.909889
C -2.536676 3.367922 -1.136879
H -2.219946 4.388555 0.735512
H -2.689021 2.112333 -2.883639
H -3.129712 4.170445 -1.565411
C 1.724695 0.297777 0.142341
C 2.779714 0.418079 1.049961
C 1.970296 0.386154 -1.232978
C 4.077610 0.628041 0.582009
H 2.576725 0.347073 2.113930
C 3.267798 0.592122 -1.696196
H 1.154146 0.288401 -1.945327
C 4.321911 0.714188 -0.788261

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H 4.896217 0.722968 1.288991
H 3.455713 0.657772 -2.763452
H 5.332799 0.875921 -1.150617
C -0.536615 -1.554459 0.028523
C -1.910836 -1.829277 -0.006557
C 0.374221 -2.548895 -0.348137
C -2.366767 -3.077748 -0.426921
H -2.628625 -1.067210 0.289014
C -0.084907 -3.795157 -0.773886
H 1.443104 -2.354059 -0.314157
C -1.454119 -4.059582 -0.815271
H -3.432804 -3.282117 -0.453081
H 0.627235 -4.557765 -1.074184
H -1.809896 -5.030108 -1.148080
N 0.076013 0.075850 2.340087
C -1.162634 -0.198811 3.062927
H -1.992236 0.475391 2.792259
H -1.528627 -1.228463 2.919156
H -0.983590 -0.071420 4.135539

Structure: 48_radical_cation
Charge =  1 Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy:         -1130.4361013 hartree
SCF Energy + ZPVE:  -1130.117358 hartree
Enthalpy:           -1130.097324 hartree
Free Energy:        -1130.167448 hartree
Free Energy with quasiharmonic correction: -1130.162926 hartree
P -0.015548 -0.005040 0.579200
C 1.542161 -0.651338 -0.041393
C 2.049696 -1.814957 0.554892
C 2.203612 -0.049997 -1.116768
C 3.231833 -2.368444 0.074659
H 1.526116 -2.282690 1.386004
C 3.385273 -0.617055 -1.592302
H 1.804381 0.844048 -1.586198
C 3.897535 -1.769250 -0.997466
H 3.632369 -3.265815 0.534866
H 3.902461 -0.156322 -2.427585
H 4.819250 -2.205174 -1.370440
C -1.368947 -1.090233 0.121840
C -2.534885 -1.097874 0.898162
C -1.269194 -1.871768 -1.034529
C -3.604649 -1.900118 0.510256
H -2.602333 -0.487164 1.793231
C -2.348185 -2.667353 -1.413659
H -0.362689 -1.863299 -1.633679
C -3.510947 -2.681535 -0.642750
H -4.509917 -1.914735 1.108511
H -2.277323 -3.277778 -2.308002
H -4.347759 -3.305984 -0.940486
```

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C -0.301744 1.671765 -0.012143
C 0.664150 2.655330 0.248528
C -1.479813 1.986434 -0.697302
C 0.444955 3.957547 -0.187420
H 1.581327 2.406491 0.776875
C -1.685781 3.295165 -1.131037
H -2.227688 1.224536 -0.895881
C -0.728285 4.275686 -0.875951
H 1.189466 4.722324 0.007969
H -2.595529 3.544869 -1.667275
H -0.894438 5.293646 -1.214811
N -0.073871 0.076505 2.269314
C 1.085770 0.476163 3.020151
H 2.046662 0.341531 2.513261
H 0.958037 1.545549 3.257980
H 1.072585 -0.052973 3.977857

Structure: 47_neutral
Charge =  0 Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy:         -1322.3256626 hartree
SCF Energy + ZPVE:  -1321.953143 hartree
Enthalpy:           -1321.930498 hartree
Free Energy:        -1322.006369 hartree
Free Energy with quasiharmonic correction: -1322.000191 hartree
P -0.301866 -0.000951 -0.261079
C -0.420848 -1.581287 0.645955
C 0.346324 -2.658319 0.192492
C -1.297849 -1.753166 1.724861
C 0.244238 -3.900551 0.819974
H 1.018457 -2.526124 -0.651631
C -1.398414 -2.995192 2.347142
H -1.900378 -0.921369 2.082510
C -0.625902 -4.068266 1.896240
H 0.843853 -4.733835 0.466709
H -2.078601 -3.125828 3.183173
H -0.705766 -5.035048 2.384222
C -0.111638 1.318164 0.984935
C -0.341977 2.635614 0.564659
C 0.340196 1.074775 2.285679
C -0.136406 3.695972 1.443453
H -0.684885 2.833234 -0.448589
C 0.545265 2.139822 3.163528
H 0.537875 0.059826 2.619402
C 0.305029 3.447736 2.744800
H -0.320806 4.713690 1.113640
H 0.894397 1.944856 4.172820
H 0.463641 4.274629 3.430522
C -1.926559 0.256068 -1.026801
C -2.098092 -0.018166 -2.386822
C -3.014615 0.677666 -0.253557
```

C -3.355692 0.131290 -2.970780
H -1.248141 -0.338300 -2.981199
C -4.269056 0.825028 -0.842395
H -2.885699 0.900805 0.802781
C -4.440110 0.551376 -2.200384
H -3.486160 -0.078901 -4.027956
H -5.109943 1.157819 -0.241800
H -5.417809 0.669229 -2.658013
N 0.769145 0.016960 -1.446416
C 2.147026 0.018864 -1.285266
C 2.936478 0.262357 -2.432589
C 2.834835 -0.213794 -0.072464
C 4.324997 0.279214 -2.369578
H 2.426669 0.441172 -3.375713
C 4.228697 -0.192573 -0.016678
H 2.278089 -0.425924 0.836910
C 4.989004 0.054124 -1.159204
H 4.895635 0.471961 -3.274385
H 4.720670 -0.375769 0.935143
H 6.073278 0.068881 -1.110657

Structure: 47_radical_cation
Charge = 1 Multiplicity = 2
Number of imaginary frequencies: 0
SCF Energy: -1322.1362898 hartree
SCF Energy + ZPVE: -1321.763554 hartree
Enthalpy: -1321.74079 hartree
Free Energy: -1321.81782 hartree
Free Energy with quasiharmonic correction: -1321.811278 hartree
P -0.349306 -0.013211 -0.172831
C -0.291145 -1.530565 0.808386
C 0.528664 -2.590262 0.408069
C -1.128460 -1.658373 1.924909
C 0.519357 -3.777571 1.138977
H 1.165580 -2.502492 -0.467214
C -1.127958 -2.847282 2.648404
H -1.772510 -0.837467 2.230648
C -0.303713 -3.904417 2.256893
H 1.155497 -4.601160 0.831099
H -1.770440 -2.947198 3.517282
H -0.306416 -4.829898 2.824420
C -0.201669 1.439143 0.891761
C -0.559140 2.680766 0.347645
C 0.306853 1.354092 2.192336
C -0.409808 3.834316 1.112138
H -0.952818 2.748400 -0.663458
C 0.447214 2.514365 2.951244
H 0.594701 0.395893 2.615645
C 0.089549 3.750298 2.412974
H -0.686535 4.796302 0.693015
H 0.835876 2.449584 3.962392

H 0.200023 4.651425 3.008386
C -1.939016 0.071919 -1.020138
C -2.038638 -0.320304 -2.358239
C -3.076353 0.468089 -0.305681
C -3.285027 -0.309904 -2.983070
H -1.151151 -0.622088 -2.904864
C -4.316356 0.473424 -0.938608
H -2.997512 0.777775 0.733307
C -4.420082 0.084998 -2.275708
H -3.366074 -0.608614 -4.023384
H -5.199175 0.784427 -0.389245
H -5.388249 0.093584 -2.767016
N 0.770159 -0.026831 -1.400649
C 2.096517 0.011617 -1.274518
C 2.842335 0.096024 -2.503366
C 2.832458 -0.036152 -0.038406
C 4.216747 0.142064 -2.491610
H 2.278382 0.127642 -3.430128
C 4.206879 0.007003 -0.049763
H 2.302948 -0.121369 0.905616
C 4.908763 0.099727 -1.268135
H 4.768768 0.210535 -3.422930
H 4.756571 -0.032973 0.884695
H 5.993179 0.135608 -1.260207

Structure: Ni(CO)3(Ph-N=PPh3)
Charge = 0 Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -3171.1496834 hartree
SCF Energy + ZPVE: -3170.75297 hartree
Enthalpy: -3170.720424 hartree
Free Energy: -3170.821439 hartree
Free Energy with quasiharmonic correction: -3170.809464 hartree
Ni -2.505213 0.268519 -0.044447
O -3.225463 -2.494463 0.611054
C -2.865991 -1.439217 0.357769
O -3.592696 2.040295 2.032135
C -3.105351 1.378449 1.239834
O -3.693820 0.970800 -2.641780
C -3.191631 0.712795 -1.649553
C 2.333715 0.061446 -0.703661
C 2.840450 -0.552321 -1.850138
C 4.045703 -0.126532 -2.395689
C 4.748611 0.915820 -1.805279
C 4.247564 1.533405 -0.664693
C 3.047214 1.109370 -0.112665
C 0.225961 -1.957409 -0.828986
C 0.533100 -3.205568 -0.289627
C 0.182463 -4.362057 -0.975590
C -0.472215 -4.275436 -2.197780
C -0.782394 -3.031260 -2.736909

C -0.436840 -1.872943 -2.055597
C 2.319097 -1.300895 2.148685
C 1.068914 -0.838297 1.731218
C 0.035783 -0.706996 2.660886
C 0.251128 -1.037379 3.992531
C 1.496184 -1.499984 4.403158
C 2.529071 -1.631363 3.481872
P 0.717316 -0.418073 -0.012350
N -0.427131 0.674999 -0.257527
H 2.298941 -1.367205 -2.314830
H 4.434406 -0.612407 -3.282845
H 5.687319 1.247905 -2.233237
H 4.790462 2.350117 -0.204136
H 2.663953 1.599258 0.774124
H 1.029879 -3.278127 0.670274
H 0.412610 -5.330846 -0.548651
H -0.750457 -5.179038 -2.727534
H -1.304382 -2.962715 -3.683856
H -0.694501 -0.899273 -2.453252
H 3.130760 -1.394261 1.436356
H -0.932112 -0.343858 2.332748
H -0.554377 -0.931812 4.709576
H 1.663299 -1.755171 5.443176
H 3.501878 -1.985862 3.801903
C -0.114534 2.057664 -0.224800
C 0.007251 2.767650 -1.422250
C 0.032111 2.755844 0.978924
C 0.275021 4.130328 -1.416627
H -0.114720 2.234159 -2.357491
C 0.303337 4.118229 0.981816
H -0.080474 2.221324 1.915331
C 0.426905 4.813907 -0.215605
H 0.364053 4.661076 -2.357953
H 0.410019 4.639853 1.926523
H 0.631662 5.877907 -0.212497

Structure: Ni(CO)3(Me-N=PPh3)
Charge = 0 Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -2979.405863 hartree
SCF Energy + ZPVE: -2979.061806 hartree
Enthalpy: -2979.032516 hartree
Free Energy: -2979.124698 hartree
Free Energy with quasiharmonic correction: -2979.11567 hartree
Ni -2.472973 0.117064 -0.676396
O -3.011779 0.229786 2.203127
C -2.729404 0.183940 1.096482
O -3.629375 2.504613 -1.936052
C -3.117285 1.595304 -1.469758
O -3.769402 -2.285473 -1.770315
C -3.229464 -1.363590 -1.366300

C 2.339719 -0.509299 -0.874378
C 2.786664 -1.829700 -0.804518
C 3.976072 -2.199679 -1.419996
C 4.724398 -1.257937 -2.115582
C 4.283605 0.058167 -2.194200
C 3.098379 0.432764 -1.575412
C 0.323531 -1.232088 1.122104
C 0.687394 -1.043672 2.454425
C 0.396638 -2.021645 3.397725
C -0.255895 -3.187002 3.015528
C -0.625766 -3.375381 1.688095
C -0.339950 -2.401218 0.741979
C 2.278214 1.817417 1.321293
C 1.074496 1.565298 0.656505
C 0.092667 2.554620 0.611570
C 0.308261 3.780430 1.230193
C 1.502530 4.023109 1.897123
C 2.487598 3.041637 1.942220
P 0.722955 -0.028170 -0.172566
N -0.455409 -0.037116 -1.248185
C -0.209655 0.374056 -2.625190
H 2.211252 -2.568784 -0.260128
H 4.319068 -3.225349 -1.352595
H 5.651793 -1.548494 -2.595153
H 4.863667 0.795373 -2.736643
H 2.767347 1.463551 -1.632404
H 1.178232 -0.129201 2.763697
H 0.671032 -1.866492 4.434327
H -0.486877 -3.945182 3.754732
H -1.148312 -4.276786 1.390703
H -0.646001 -2.521992 -0.289899
H 3.057681 1.063808 1.343648
H -0.837343 2.352345 0.091999
H -0.458464 4.545020 1.189772
H 1.669635 4.979150 2.379583
H 3.422577 3.232746 2.455920
H -0.290411 1.460257 -2.764566
H 0.773083 0.058938 -2.996284
H -0.963201 -0.088927 -3.265381

Structure: Ni(CO)3(H-N=PPh3)
Charge = 0 Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -2940.1087157 hartree
SCF Energy + ZPVE: -2939.7931 hartree
Enthalpy: -2939.765238 hartree
Free Energy: -2939.855424 hartree
Free Energy with quasiharmonic correction: -2939.845292 hartree
Ni -2.554784 0.126973 -0.772514
O -3.160207 0.203383 2.095763
C -2.856502 0.172384 0.994077

O -3.574117 2.548705 -2.084573
C -3.129733 1.620285 -1.587339
O -3.847630 -2.244076 -1.942112
C -3.307100 -1.338427 -1.503941
C 2.279751 -0.491046 -1.042597
C 2.841277 -1.757921 -0.884891
C 3.981011 -2.108808 -1.599021
C 4.562404 -1.201704 -2.475776
C 4.006329 0.062904 -2.637938
C 2.871882 0.419764 -1.922753
C 0.418270 -1.222736 1.108970
C 0.894501 -1.043600 2.407314
C 0.658760 -2.015121 3.371808
C -0.052799 -3.163325 3.044979
C -0.536243 -3.340638 1.753418
C -0.304322 -2.373273 0.785175
C 2.364393 1.852142 1.125009
C 1.106565 1.570231 0.585064
C 0.095542 2.528951 0.651025
C 0.337417 3.753855 1.261004
C 1.586825 4.027150 1.804376
C 2.600670 3.077230 1.734944
P 0.723864 -0.025803 -0.216105
N -0.524170 -0.046594 -1.206861
H 2.392024 -2.468654 -0.201560
H 4.414498 -3.093272 -1.468314
H 5.450330 -1.478078 -3.032159
H 4.459350 0.773627 -3.318953
H 2.451464 1.412404 -2.043673
H 1.431757 -0.141464 2.673357
H 1.022040 -1.869147 4.382075
H -0.241084 -3.916287 3.801443
H -1.104709 -4.227959 1.501526
H -0.696209 -2.484750 -0.218427
H 3.164009 1.122681 1.056204
H -0.873536 2.307476 0.217572
H -0.451148 4.495487 1.308101
H 1.774364 4.983917 2.277787
H 3.578406 3.293814 2.149224
H -0.284143 0.214295 -2.154276

Structure: Ni(CO)3(NC-N=PPh3)_binding_via_CN
Charge = 0 Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -3032.3582702 hartree
SCF Energy + ZPVE: -3032.043268 hartree
Enthalpy: -3032.013663 hartree
Free Energy: -3032.111413 hartree
Free Energy with quasiharmonic correction: -3032.097093 hartree
C -1.382082 -1.253201 1.000273
C -2.275638 -2.317682 1.123468

C -2.046678 -3.305226 2.073525
C -0.925053 -3.239266 2.890865
C -0.026575 -2.185078 2.763303
C -0.252415 -1.190086 1.823494
C -3.142078 -0.260249 -1.136329
C -4.346509 0.117344 -0.540843
C -5.545569 -0.128211 -1.195550
C -5.543521 -0.743552 -2.442801
C -4.343129 -1.110984 -3.039280
C -3.138773 -0.871615 -2.389954
C -2.086245 1.729607 1.870974
C -1.629757 1.604876 0.557512
C -1.220153 2.736048 -0.150964
C -1.273931 3.984680 0.452374
C -1.737825 4.108625 1.757231
C -2.143250 2.983476 2.465710
P -1.571644 0.002923 -0.290110
N -0.450754 -0.055784 -1.442548
C 0.821317 -0.051661 -1.175713
N 1.969105 -0.048315 -0.997151
H -3.145067 -2.377069 0.479702
H -2.743368 -4.129279 2.170320
H -0.745623 -4.014702 3.626227
H 0.855818 -2.138854 3.389809
H 0.456146 -0.375304 1.726216
H -4.350757 0.612626 0.423426
H -6.480687 0.168285 -0.735959
H -6.480785 -0.930505 -2.953670
H -4.341943 -1.581608 -4.015072
H -2.193224 -1.137777 -2.846251
H -2.379995 0.850581 2.433227
H -0.848039 2.630625 -1.163511
H -0.945942 4.860378 -0.094405
H -1.774624 5.084471 2.226947
H -2.492909 3.079859 3.486624
Ni 3.902378 -0.050199 -0.501529
O 4.105701 -1.080022 2.241214
C 4.000878 -0.684127 1.173094
O 5.372678 -1.782082 -2.372642
C 4.766021 -1.117702 -1.670796
O 4.919820 2.706229 -0.653073
C 4.488468 1.649930 -0.610469

Structure: $NCNPPh_3$
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -1183.570584 hartree
SCF Energy + ZPVE: -1183.279101 hartree
Enthalpy: -1183.259398 hartree
Free Energy: -1183.328987 hartree
Free Energy with quasiharmonic correction: -1183.323437 hartree

C 2.085397 2.332281 -2.073657
C 2.363853 3.466481 -1.308880
C 1.377253 1.269983 -1.515824
C 0.943554 1.347858 -0.186370
C 1.220794 2.485835 0.579374
H 1.168738 0.386853 -2.114656
C 1.932598 3.543331 0.015542
H 2.151352 4.424134 0.611959
H 2.920011 4.290722 -1.746352
H 2.423439 2.271219 -3.103884
H 0.882604 2.544357 1.610844
C -1.773578 0.277228 0.156645
C -2.149290 0.391828 -1.187728
C -2.733256 0.348458 1.169237
C -3.489478 0.576914 -1.514872
H -1.403212 0.331877 -1.977685
C -4.074229 0.537317 0.833158
H -2.431963 0.257586 2.208411
C -4.451247 0.650678 -0.504317
H -3.782873 0.664200 -2.556751
H -4.821959 0.594979 1.618713
H -5.496367 0.796545 -0.762366
C 0.512257 -1.539568 -0.152543
C -0.415572 -2.539914 -0.466091
C 1.885448 -1.782198 -0.297063
C 0.031117 -3.774096 -0.935599
H -1.481277 -2.361139 -0.348245
C 2.323792 -3.019523 -0.762769
H 2.611360 -1.010041 -0.052706
C 1.397447 -4.012801 -1.084861
H -0.689232 -4.547461 -1.185036
H 3.387563 -3.205909 -0.876497
H 1.742113 -4.975150 -1.452523
P -0.036993 0.024850 0.571567
N 0.033484 0.062720 2.192050
C 1.125529 -0.224321 2.847795
N 2.066555 -0.469885 3.505980

Structure: $Ni(CO)_3(NCNPPh_3)$
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -3032.344923 hartree
SCF Energy + ZPVE: -3032.030115 hartree
Enthalpy: -3032.000530 hartree
Free Energy: -3032.094736 hartree
Free Energy with quasiharmonic correction: -3032.084244 hartree
Ni 2.539024 -0.175220 -0.596936
O 3.099749 0.197456 2.251396
C 2.800448 0.052466 1.158136
O 3.678016 -2.724968 -1.519384
C 3.170206 -1.761864 -1.184542

O 3.713734 2.049606 -2.118989
C 3.210194 1.196084 -1.555092
C -2.353962 0.448477 -0.880723
C -2.941088 1.702819 -0.704479
C -4.122352 2.013054 -1.365994
C -4.714718 1.079697 -2.207450
C -4.129944 -0.168759 -2.388180
C -2.954512 -0.491120 -1.725811
C -0.322537 1.380411 1.013847
C -0.609138 1.353434 2.377820
C -0.268952 2.439526 3.174438
C 0.353233 3.547090 2.612305
C 0.642071 3.573393 1.251694
C 0.307308 2.492723 0.449187
C -2.387450 -1.643099 1.523421
C -1.135834 -1.448909 0.933349
C -0.121285 -2.388939 1.117925
C -0.358387 -3.514138 1.896461
C -1.600226 -3.701278 2.491635
C -2.614099 -2.767580 2.305260
P -0.791961 0.020700 -0.070037
N 0.436759 -0.199391 -1.117461
C 0.181437 -0.809611 -2.263818
N -0.010112 -1.340114 -3.280283
H -2.481292 2.433391 -0.050347
H -4.577505 2.985857 -1.223956
H -5.633596 1.325957 -2.726479
H -4.585504 -0.893969 -3.051203
H -2.501777 -1.462793 -1.880585
H -1.078996 0.483695 2.820924
H -0.480992 2.414259 4.236373
H 0.623288 4.389913 3.237613
H 1.138222 4.432181 0.816155
H 0.546493 2.497394 -0.607146
H -3.185297 -0.927285 1.361124
H 0.842698 -2.237750 0.645722
H 0.427759 -4.246727 2.033230
H -1.782297 -4.581655 3.096777
H -3.585424 -2.920293 2.760275

Structure: $Ni(CO)_3(PPh_3)$
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -2884.776951 hartree
SCF Energy + ZPVE: -2884.476474 hartree
Enthalpy: -2884.450188 hartree
Free Energy: -2884.536681 hartree
Free Energy with quasiharmonic correction: -2884.527361 hartree
Ni 2.156976 0.002039 0.003325
O 3.013901 -2.038292 1.938208
C 2.676382 -1.248499 1.188769

O 3.022148 -0.652045 -2.728869
C 2.681433 -0.398371 -1.671084
O 3.014493 2.696933 0.805364
C 2.676674 1.653386 0.495145
P -0.093651 0.000609 -0.000583
C -0.877540 1.570203 -0.544746
C -0.307097 2.246658 -1.625920
C -0.869456 3.425911 -2.094860
C -1.998911 3.952843 -1.477861
C -2.564196 3.293656 -0.393676
C -2.009752 2.105732 0.070426
C -0.878957 -0.315139 1.629721
C -2.008423 -1.119824 1.784179
C -2.564345 -1.313661 3.044085
C -2.003284 -0.701944 4.157860
C -0.876634 0.100146 4.011741
C -0.312779 0.285515 2.756950
C -0.301751 -2.530189 -1.133157
C -0.873357 -1.256075 -1.090022
C -2.003937 -0.992554 -1.864304
C -2.555609 -1.989405 -2.661749
C -1.989173 -3.257467 -2.688401
C -0.861324 -3.526882 -1.920711
H 0.585796 1.849793 -2.096004
H -0.418471 3.939736 -2.935714
H -2.431920 4.879098 -1.837137
H -3.439965 3.703744 0.095896
H -2.457102 1.598842 0.917019
H -2.452426 -1.601328 0.921171
H -3.437980 -1.945888 3.153045
H -2.437406 -0.855304 5.138954
H -0.428979 0.573412 4.877804
H 0.577877 0.894635 2.649812
H 0.589825 -2.737919 -0.552062
H -2.452196 -0.006333 -1.850247
H -3.430165 -1.771583 -3.263851
H -2.420106 -4.032496 -3.311420
H -0.409456 -4.511629 -1.943544

Structure: $Ni(CO)_3(OPPh_3)$
Charge = 0, Multiplicity = 1
Number of imaginary frequencies: 0
SCF Energy: -2960.008976 hartree
SCF Energy + ZPVE: -2959.705069 hartree
Enthalpy: -2959.677187 hartree
Free Energy: -2959.769777 hartree
Free Energy with quasiharmonic correction: -2959.757209 hartree
Ni 2.651800 0.042160 -0.682326
O 3.389931 0.046260 2.151233
C 3.017562 0.041706 1.070992
O 3.665245 -2.349090 -2.052694

C 3.210335 -1.440510 -1.533461
O 3.653602 2.480585 -1.979520
C 3.209038 1.549526 -1.492741
C -2.137752 0.615213 -1.111587
C -2.119779 0.437560 -2.496014
C -3.192757 0.871353 -3.262818
C -4.283036 1.483162 -2.653696
C -4.299075 1.670282 -1.276439
C -3.226785 1.240757 -0.503925
C -0.612165 1.016974 1.331269
C -1.069053 0.576405 2.572885
C -0.961002 1.403233 3.685293
C -0.392594 2.664646 3.561755
C 0.072837 3.103761 2.326320
C -0.034622 2.284083 1.212477
C -2.429181 -2.146318 0.477624
C -1.117014 -1.685671 0.362815
C -0.052676 -2.540117 0.659740
C -0.303363 -3.839092 1.080589
C -1.612376 -4.291439 1.204878
C -2.673738 -3.446967 0.901249
P -0.715534 0.002650 -0.168571
O 0.536342 0.061332 -1.008268
H -1.256680 -0.023154 -2.962126
H -3.175271 0.737118 -4.337879
H -5.118173 1.823174 -3.254987
H -5.142261 2.159777 -0.803545
H -3.231783 1.406192 0.567679
H -1.497945 -0.413679 2.674509
H -1.312265 1.056625 4.649929
H -0.303183 3.305031 4.431476
H 0.527311 4.082826 2.232831
H 0.341959 2.616663 0.252080
H -3.259322 -1.496914 0.224920
H 0.966566 -2.187973 0.546908
H 0.525002 -4.500125 1.306003
H -1.805394 -5.306781 1.531120
H -3.693721 -3.802989 0.985528

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