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Enantiomerically Pure Phosphaalkene–Oxazolines (PhAk-Ox): Synthesis, Scope and Copolymerization with Styrene

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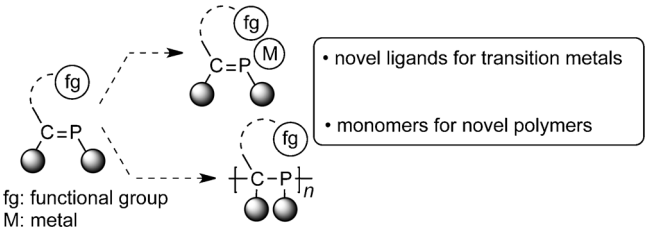
Abstract: The design of a synthetic route to a class of enantiomerically pure phosphaalkene–oxazolines (PhAk-Ox) is presented. The condensation of a lithium silylphosphide and a ketone (the phospha-Peterson reaction) was used as the P=C bond-forming step. Attempted condensation of PhC(=O)Ox (Ox = CNOCH(*i*Pr)CH$_2$) and MesP(SiMe$_3$)Li gave the unusual heterocycle (MesP)$_2$C(Ph)=CN-(*S*)-CH(*i*Pr)CH$_2$O (**3**). However, PhAk-Ox (*S*,*E*)-MesP=C(Ph)CMe$_2$Ox (**1a**) was successfully prepared by treating MesP(SiMe$_3$)Li with PhC(=O)CMe$_2$Ox (52%). To demonstrate the modularity and tunability of the phospha-Peterson synthesis several other phosphaalkene–oxazolines were prepared in an analogous manner to **1a**: TripP=C(Ph)-CMe$_2$Ox (**1b**; Trip = 2,4,6-triisopropylphenyl), 2-*i*PrC$_6$H$_4$P=C(Ph)CMe$_2$Ox (**1c**), 2-*t*BuC$_6$H$_4$P=C(Ph)CMe$_2$Ox (**1d**), MesP=C(4-MeOC$_6$H$_4$)CMe$_2$Ox (**1e**), MesP=C(Ph)C(CH$_2$)$_4$Ox (**1f**), and MesP=C(3,5-(CF$_3$)$_2$C$_6$H$_3$)C(CH$_2$)$_4$Ox (**1g**). To evaluate the PhAk-Ox compounds as prospective precursors to chiral phosphine polymers, monomer **1a** and styrene were subjected to radical-initiated copolymerization conditions to afford [{MesPC(Ph)(CMe$_2$-Ox)}$_x${CH$_2$CHPh}$_y$]$_n$ (**9a**: $x = 0.13n$, $y = 0.87n$; GPC: $M_w = 7400\ g\,mol^{-1}$, PDI = 1.15).

Keywords: asymmetric synthesis · inorganic polymers · main group elements · phosphaalkenes · phosphorus · polymers

Introduction

Phosphaalkenes are a fascinating class of molecules containing a low-coordinate phosphorus atom and a (3p–2p)π bond. Over the past decade, phosphaalkenes have evolved from simply being intellectual curiosities to compounds with potential applications ranging from polymer and materials science to catalysis.[1,2] One of the continuing challenges in the design of novel phosphaalkenes is the incorporation of increased structural complexity and chemical functionality in the face of a necessity to balance kinetic and thermodynamic stabilization. To permit isolation, phosphaalkenes require structural features that slow kinetic reactivity and/or increase π-bond stability through electronic delocalization. Phosphaalkenes can also be stabilized to permit isolation by protecting the P=C bond with sterically encumbering groups, such as 2,4,6-tri-*tert*-butylphenyl (Mes*). Incorporating such structural features can facilitate the isolation and characterization of what could otherwise be an intractable functional group.

We were intrigued by the challenge of developing a previously unexplored class of chiral P=C compounds that contain Lewis basic functional groups (Scheme 1). The key motivations were the potential applications of these compounds as 1) ligands in enantioselective metal catalysis, and 2) monomers for highly functionalized macromolecules. Previous studies have demonstrated that phosphaalkenes can be employed as precursors to poly(methylenephosphine)s through addition polymerization.[2,3] Therefore, the prospect of incorporating chiral moieties into phosphorus polymers is feasible and may permit the construction of materials with attractive properties.



Scheme 1.

There is considerable interest in incorporating the P=C bond motif into structurally complex molecules and polymers with potential relevance in materials science.[4] In addition, phosphaalkenes containing metal-chelating functional groups have been shown to be quite effective ligands for application in catalysis (Scheme 2).[1b,c,e,2,5] Ligand classes that have garnered the most attention include those based on the diphosphinidenecyclobutene **A** (DPCB),[6] 1,3-diphospha-

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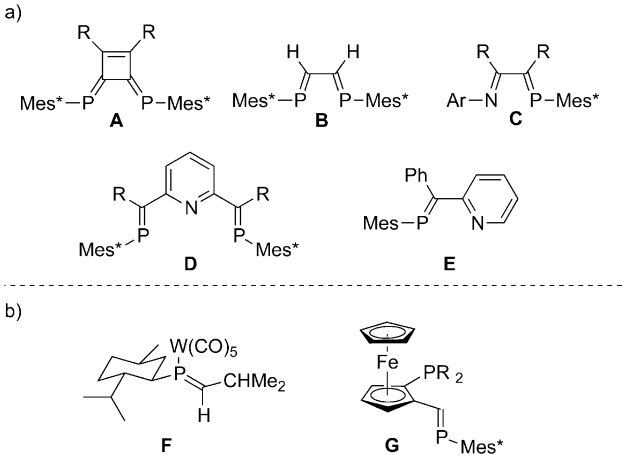
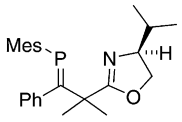


Scheme 2. Important classes of phosphaalkene ligands: a) **A**–**E** are chelate ligands that have been employed in catalytic transformations; b) **F** and **G** are known enantiomerically pure phosphaalkenes.

(1,3)-butadiene **B**,[7] phosphinidene-imine **C**,[8] and 2,6-bis-(phosphaethenyl)pyridine **D**.[9] These ligands incorporate the bulky Mes* substituent, and the effects of this large group on mechanistic processes relevant to catalysis (ligand exchange, substrate binding, turnover, etc.) are not well understood. We have previously shown that 2-pyridylphosphaalkene **E** can be prepared bearing the smaller 2,4,6-trimethylphenyl (Mes) substituent.[10] The Pd^{II} complex of this phosphaalkene was an effective catalyst for the Overman–Claisen rearrangement.[11]

Despite their successful use in catalysis, it is surprising that there is almost a complete absence of enantiomerically pure phosphaalkenes for application in asymmetric catalysis. We recently reported the isolation and characterization of an enantiomerically pure free phosphaalkene (**1a**).[12] Although chiral racemic phosphaalkenes were known in the literature,[13] to our knowledge, the menthol–phosphaalkene tungsten(0) complex **F** was the only example of an enantiomerically pure phosphaalkene derivative prior to our investigations.[14] Since our initial report, we have demonstrated that phosphaalkene–oxazoline (PhAk-Ox) ligands give high enantioselectivities in palladium(0)-catalyzed allylic alkylation reactions.[15] Concurrent to our work, Ozawa and co-workers reported a novel planar chiral phosphaalkene **G** for use in asymmetric catalysis.[16] Given the success of heterocyclic $P(\sigma^2,\lambda^3)$ ligands, such as phosphinines and phosphaferrocenes, in asymmetric catalysis,[17] the prospects for chiral acyclic phosphaalkene ligands are particularly exciting. Herein, we present the synthesis of several enantiomerically pure phosphaalkene–oxazolines, including the first copolymerization data for one of them.



1a

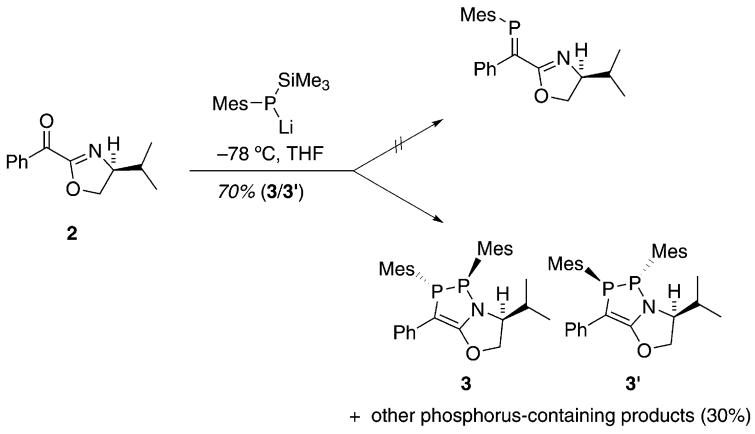
Results and Discussion

The underlying motivation behind these studies was the development of a new class of chiral phosphaalkene for application in asymmetric catalysis as monomers or polymers. Given that catalyst optimization often requires subtle tailoring of the ligands steric and electronic properties, our synthetic methodology incorporates features such as convergence and modularity. To achieve convergence, the final step involves a phospha-Peterson reaction to form the P=C bond from a ketone and a silylphosphine. This route was chosen because of its high conversion and tolerance of P substituents ranging from moderately sized (for example, Mes) to very bulky groups.[10,18,19] Moreover, this strategy also incorporates modularity since a small number of ketones and silylphosphines permits the construction of a large library of phosphaalkenes.

Another key feature of our ligand design involved the choice of oxazoline as the chirality inducing group. This choice was influenced by the successful phosphinooxazoline (PHOX)[20] and bisoxazoline (box)[21] ligand systems. Moreover, the oxazoline-containing ketone precursors can readily be constructed by using chiral pool amino acids as starting materials. It must also be taken into consideration that the ketone fragment requires a connection to the oxazoline moiety. This so-called linker is of critical importance. It must ensure that the ligating atoms of the oxazoline and the phosphaalkene are appropriately placed to permit chelation to a metal ion. At the same time, the linker must be adjacent to the P=C bond and therefore must assist in its kinetic and thermodynamic stabilization. The next section will clearly demonstrate the importance of the linker as it pertains to this latter point.

Evaluating the linker—novel heterocycles rather than phosphaalkenes: Benzoyl oxazoline **2** was an attractive ketone for phosphaalkene synthesis for the following reasons: a synthetic route to **2** was available in the literature,[22] and the resultant phosphaalkene would be expected to form a desirable five-membered chelate upon complexation. In the case of **2**, the linker is simply a covalent bond between the ketone and oxazoline.

Ketone **2** was treated with $MesP(SiMe_3)Li$ (1 equiv) and subsequent analysis of the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy did not reveal any resonances attributable to a phosphaalkene [that is, $\delta(^{31}P) \neq > 200$ ppm]. Instead, the major resonances (ca. 70% of the total) were consistent with the formation of two phosphine-containing compounds, each containing a P–P single bond [$\delta = 32$ (d, $^1J(P,P) = 202$ Hz), 4 ppm (d, $^1J(P,P) = 202$ Hz), and $\delta = 32$ (d, $^1J(P,P) = 196$ Hz), 0 ppm (d, $^1J(P,P) = 196$ Hz)]. Fortunately, crystals of the major products suitable for crystallographic analysis could be obtained from a saturated solution of the crude product in hexanes. Surprisingly, the solid-state molecular structure revealed that the product (**3** and **3′**) was composed of an unusual fused bicyclic system containing a C_2P_2N heterocycle (Figure 1). We speculate that the desired phos-



addition, the presence of additional methyl groups should function to provide steric protection to the P=C bond. The known oxazoline **4** was conveniently accessed in one step from L-valinol.[26,27] Subsequent treatment of **4** with *s*BuLi and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) for one hour at −78 °C formed the desired carbanion.[28] Claisen-type condensation of this anion with ethyl benzoate afforded ketone

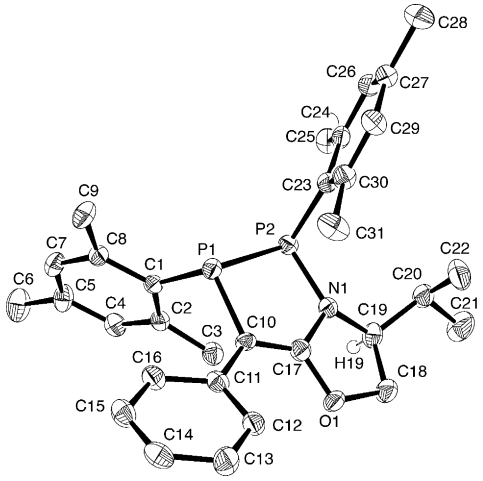
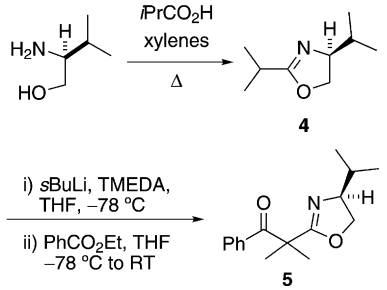


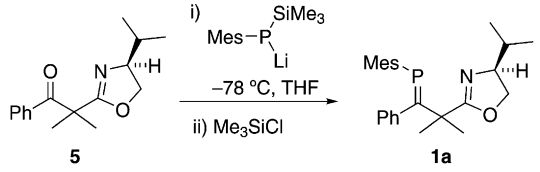
Figure 1. The molecular structure of **3** (one of two unique molecules, 50% probability ellipsoids). All hydrogen atoms (except H19) are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–P1 1.834(4), C10–C11 1.447(5), C10–C17 1.343(5), C10–P1 1.810(4), C17–O1 1.341(4), C17–N1 1.354(5), C23–P2 1.824(4), N1–P2 1.727(3), P1–P2 2.213(1); C17-C10-P1 113.0(3), C11-C10-P1 120.6(3), O1-C17-C10 126.3(4), O1-C17-N1 110.1(3), C10-C17-N1 123.6(4), C10-P1-C1 108.0(2), C10-P1-P2 93.2(1), N1-P2-C23 104.5(2), N1-P2-P1 92.0(1), C23-P2-P1 105.0(1).



phaalkene may be formed transiently and subsequently a second MesP fragment is added. Clearly, a redox process must take place to afford the cyclic products (**3**/**3′**), but the details of this type of process are unknown. Phosphorus-containing heterocycles similar to **3** are known, but are rare.[23]

A bulky linker—isolation of an enantiomerically pure phosphaalkene: We hypothesized that the addition of a methylene linker between the ketone and the oxazoline would permit phosphaalkene formation. Cognizant of the potential tautomerization of RP=C–CH_2(Ox) to form RPH–C=CH(Ox),[24] the known ketone PhC(O)CH_2(Ox) would not be a suitable precursor.[25] Moreover, the presence of a CH_2 moiety may not provide enough steric protection to the P=C bond in MesP=C(Ph)CH_2(Ox). Therefore, the *gem*-dimethyl ketone **5**, which has no enolizable protons, was prepared. In **5** in 49% isolated yield. Importantly, these synthetic steps were scalable to an approximately 20 g scale and purification did not require flash column chromatography.

Having secured a supply of ketone **5**, its phosphaolefination was attempted. A solution of MesP($SiMe_3$)Li in THF (−78 °C) was treated with a solution of **5** in THF and, subsequently, the reaction mixture was warmed slowly to room temperature (1 h). An aliquot was removed from the reaction mixture for analysis by $^{31}P\{^1H\}$ NMR spectroscopy. Importantly, the signal assigned to MesP($SiMe_3$)Li [$\delta(^{31}P) = -187$ ppm] was entirely consumed and was replaced by a new singlet resonance at $\delta(^{31}P) = 244$ ppm, which is consistent with that expected for phosphaalkene **1a** [compare with MesP=CPh_2: $\delta(^{31}P) = 233$ ppm]. The presence of only a single signal suggests that a single diastereomer of **1a** was obtained (that is, *E* or *Z*). The crude product was recrystallized from *n*-pentane to afford colorless crystals of **1a** (52%), which were characterized crystallographically. The optical activity of the product was confirmed by polarimetry and the Flack parameter [0.13(9)], determined crystallo-



graphically, suggested that the *S* configuration of **1a** was assigned correctly. Moreover, all of the compounds leading to phosphaalkene **1a** were similarly optically active. Together, these observations suggest that, as expected, the enantiomeric purity of L-valine was not lost during the synthetic sequence.

The molecular structure showing the *E* configuration of the P=C bond and metrical parameters for **1a** are given in Figure 2. The P=C bond length in **1a** [1.679(2) Å] is in the normal range found in C-substituted phosphaalkenes (1.61–1.71 Å).[29] The P–Mes bond in **1a** [P(1)–C(1) = 1.826(2) Å] is also similar to those found in other mesityl-substituted phosphaalkenes (ca. 1.83 Å).[10] Interestingly, the Mes-P=C bond angle in **1a** [C(1)-P(1)-C(10) = 105.3(1)°] is more acute than that found in related P-mesityl phosphaalkenes (ca. 108°).[10] Presumably, this smaller angle is a consequence of increased steric repulsion between the methyl groups of the *trans*-configured CMe_2 linker and the P–Mes substituent in **1a**. Of particular interest is the fact that the angle between the best plane of the C–Ph substituent and the plane of the P=C bond in **1a** (80.4°) is greater than in other Mes-substituted phosphaalkenes (ca. 49°).[10] Similarly, the dihedral angle between the best plane of the Mes substituent and the P=C bond (78.6°) is also greater than in other related P–Mes phosphaalkenes (ca. 71°).[10] In contrast to related phosphaalkenes, these large dihedral angles suggest that there is little to no π-conjugation between the P=C π-bond and the aromatic substituents in **1a**.

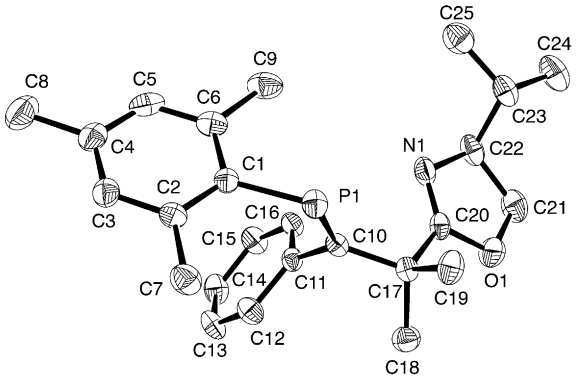
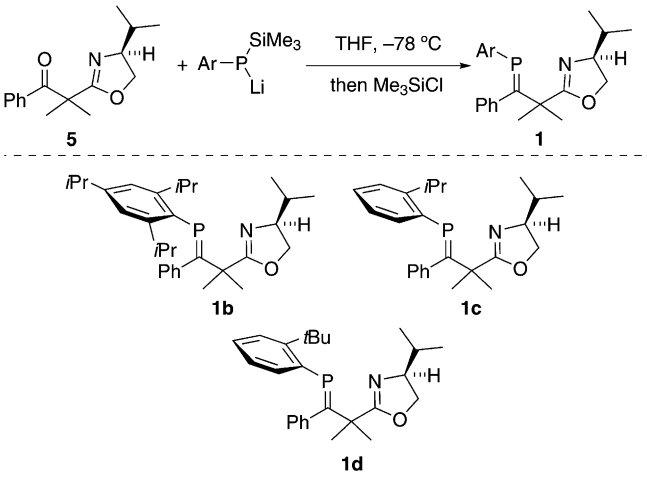


Figure 2. The molecular structure of **1a** (50% probability ellipsoids). All hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–P1 1.826(2), C10–P1 1.679(2), C10–C11 1.485(3), C10–C17 1.529(3), C17–C20 1.511(3), C20–O1 1.356(3), C20–N1 1.248(3); C10-P1-C1 105.3(1), C11-C10-P1 124.1(2), C17-C10-P1 119.2(2), C20-C17-C10 108.9(2), N1-C20-O1 118.6(2), N1-C20-C17 127.6(2), C25-C23-C24 110.5(2).

It is quite remarkable that phosphaalkene **1a**, bearing the moderately sized Mes substituent, is stable to air and moisture. Crystals of **1a** were stored open to the atmosphere in a well-lit laboratory for two months with no sign of decomposition, as evaluated by $^{31}P\{^1H\}$ NMR spectroscopy. Moreover, the $^{31}P\{^1H\}$ NMR spectrum of **1a** showed no change when a solution in toluene was heated at reflux (12 h) or when solutions in CH_2Cl_2 or THF were saturated with water or oxygen (about 1 h). These properties suggest that phosphaalkene **1a** can be manipulated without the need for special precautions, an advantageous property for its use in catalysis. However, it should be noted that phosphaalkene **1a**, dissolved in either THF or CH_2Cl_2, rapidly degrades upon treatment with aqueous acid (HCl) or in the presence of oxidizing agents, such as *meta*-chloroperoxybenzoic acid (MCPBA) or H_2O_2. Nevertheless, the surprising air and moisture stability of **1a** is highly unexpected.

Modularity and tunability of the PhAk-Ox design: With the isolation of enantiomerically pure phosphaalkene **1a**, the modularity of the synthetic route and the tunability of the ligand architecture could be investigated. Three distinct parts of the PhAk-Ox motif were modified: the *P*-aryl substituent, the *C*-aryl substituent, and the structure of the linker. This facilitates the building of a small library of PhAk-Ox compounds for future polymerization or catalyst optimization studies.

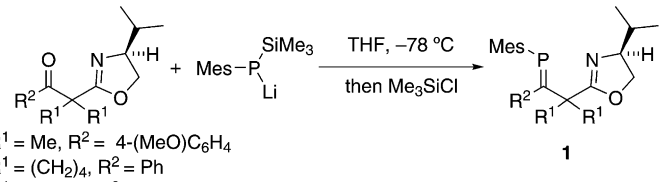
Variation of the steric bulk of the P substituent: Due to its close proximity to the metal-binding site, the steric properties of the P substituent are likely to significantly influence catalytic performance. The incorporation of a 2,4,6-triisopropylphenyl substituent within PhAk-Ox **1b** was quite straightforward. Treatment of a solution of in situ generated 2,4,6-(iPr)$_3$C$_6$H$_2$P(SiMe$_3$)Li ($\delta = -205$ ppm) in THF with ketone **5** afforded **1b** ($\delta = 248$ ppm) quantitatively by $^{31}P\{^1H\}$ NMR spectroscopy.



Isolable phosphaalkenes traditionally contain substituents in both the 2- and 6-positions of the *P*-aryl group to impart steric protection above and below the P=C bond plane. Substitution at only one *ortho*-aryl position would differentiate the face above from the face below the P=C bond plane and, consequently, might lead to useful applications in asymmetric catalysis. Isolable phosphaalkenes with mono-*ortho*-substituted *P*-aryl groups are rare, with examples being lim-

ited to 2-$RC_6H_4P{=}CR'(OSiMe_3)$ (R = $Me_3SiO(C{=}O)$ or $SiMe_3$ and R′ = *t*Bu, CMe_2Et, 1-Ad)[30] and the Ru^{II} complex of 3,3-diphenyl-3*H*-phosphindole, in which the P=C bond is contained within a ring.[31] A previous attempt at generating (2-MeC_6H_4)P=CPh_2 led to uncharacterized material presumed to be a polymer.[32]

Although the stability of a mono-*ortho*-aryl phosphaalkene was uncertain, we moved ahead and attempted to prepare new PhAk-Ox compounds from 2-*i*Pr$C_6H_4P(SiMe_3)_2$[33] and 2-*t*Bu$C_6H_4P(SiMe_3)_2$.[33] Remarkably, treatment of ketone **5** with in situ generated 2-*i*Pr$C_6H_4P(SiMe_3)$Li afforded phosphaalkene **1c** (85%) in analytical purity after distillation. The same procedure was repeated with in situ generated 2-*t*Bu$C_6H_4P(SiMe_3)$Li, yielding **1d** (83%). The spectroscopic data obtained for these novel phosphaalkenes include $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, mass spectrometry and optical rotations. These data fully support their formulation as **1c** and **1d**. Remarkably, both mono-*ortho*-aryl phosphaalkenes are stable at room temperature. These examples clearly demonstrate the power and generality of the phospha-Peterson route as a means to generate highly functionalized phosphaalkenes.



6: R^1 = Me, R^2 = 4-(MeO)C_6H_4
7: R^1 = $(CH_2)_4$, R^2 = Ph
8: R^1 = $(CH_2)_4$, R^2 = 3,5-$(CF_3)_2C_6H_3$

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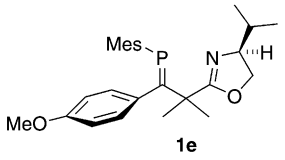

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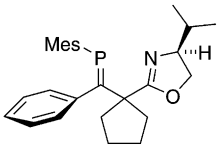

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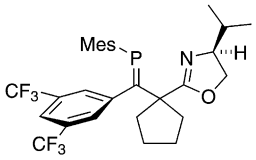
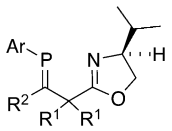


1g

Table 1. Selected $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectroscopic data for phosphaalkenes **1a**–**1g** in $CDCl_3$ solvent.



	R^1	R^2	Ar	$^{31}P\{^1H\}$ NMR δ [ppm]	$^{13}C\{^1H\}$ NMR $\delta_{P=C}$ [ppm] (^1J(P,C) [Hz])
1a	Me	Ph	Mes	244	203.3 (48)
1b	Me	Ph	2,4,6-(*i*Pr)$_3C_6H_2$	248	201.3 (56)
1c	Me	Ph	2-*i*PrC_6H_4	245	204.9 (49)
1d	Me	Ph	2-*t*BuC_6H_4	254	196.7 (50)
1e	Me	4-MeOC_6H_4	Mes	245	203.2 (48)
1f	$(CH_2)_4$	Ph	Mes	243	200.8 (47)
1g	$(CH_2)_4$	3,5-$(CF_3)_2C_6H_3$	Mes	254	196.9 (50)

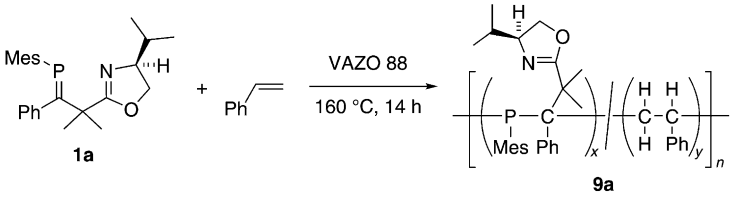
Variation of the C substituent and the linker: In addition to tuning the *P* substituent, the modification of the *C* substituent and the linker group are of considerable interest as a means to tune the donor–acceptor properties of the PhAk-Ox ligand architecture. Consequently, simple modifications to the electronic properties of the *C* substituent and the linker group were undertaken. Of particular interest was the potential to include electron-donating and electron-withdrawing *C* substituents. Following analogous procedures to those developed for the formation of **5**, three new ketones were synthesized (**6**, 72%; **7**, 70%; **8**, 90%). Importantly, treatment of the appropriate ketone with Mes$P(SiMe_3)$Li afforded phosphaalkenes **1e**, **1f**, and **1g** quantitatively, according to $^{31}P\{^1H\}$ NMR spectroscopy. The new phosphaalkenes were isolated as liquids and purified by bulb-to-bulb distillation in vacuo to afford analytically pure PhAk-Ox compounds (**1e**, 50%; **1f**, 50%, **1g**, 67%). In all cases, only a single isomer was observed, as determined by ^{31}P NMR spectroscopy.

NMR spectroscopic parameters for PhAk-Ox compounds: The synthesis of a small family of PhAk-Ox compounds facilitates a qualitative analysis of the effects of substitution on the P=C bond. Selected NMR spectroscopic data for new chiral phosphaalkenes **1a**–**1g** are presented in Table 1. The $^{31}P\{^1H\}$ NMR signal for phosphaalkene **1a** (δ = 244 ppm) is downfield relative to those of related *C*-substituted phosphaalkenes. Since the best compound for comparison, MesP=C(*t*Bu)Ph, is unknown, **1a** is compared to *C*-Ph-substituted MesP=CPh_2 and *C*-*t*Bu-substituted MesP=CH(*t*Bu) ($\delta(^{31}P)$ = 233 and 224 ppm, respectively).[18,32,34] Similarly, the $^{13}C\{^1H\}$ NMR resonance of the P=*C* carbon atom in **1a** [$\delta(^{13}C)$ = 203.3 ppm, ^1J(P,C) = 48 Hz] is downfield relative to that for MesP=CPh_2 [$\delta(^{13}C)$ = 193.4 ppm, ^1J(P,C) = 44 Hz], but is similar to the phosphaalkene carbon of MesP=CH(*t*Bu) [$\delta(^{13}C)$ = 203.3 ppm, ^1J(P,C) = 44 Hz].

Interestingly, there is no significant difference in the $^{31}P\{^1H\}$ NMR chemical shifts when π-donating *C*-aryl substituents are present [that is, **1e** vs. **1a**, $\Delta\delta(^{31}P)$ = 1 ppm]. There are also minimal changes in the $^{13}C\{^1H\}$ NMR chemical shifts of the P=*C* carbon atoms. Consistent with the structural data discussed earlier, this spectroscopic data suggests that there is poor π-conjugation between the *C*-aryl substituent and the P=C bond. This contrasts with previous observations on the influence of π-donating substituents by incorporating 4-$MeOC_6H_4$ as the *C* substituent on the P=C bond.[10,35] The presence of an inductively withdrawing *C* substituent results in a downfield shift in the $^{31}P\{^1H\}$ NMR resonances [that is, **1g** vs. **1a**, $\Delta\delta(^{31}P)$ = 10 ppm].

Copolymerization of PhAk-Ox (1a) with styrene: PhAk-Ox **1a** is an intriguing monomer for polymerization studies because of the fact that the resultant chiral polymer is expected to possess attractive properties. This type of chiral polymer is of considerable interest as ligands for polymer-supported asymmetric catalysis and for their potential properties, such as helicity. In our attempts to purify **1a** by vacuum distillation (ca. 200 °C), we occasionally noted the formation of a viscous residue that was soluble in THF and from which a small amount of polymer could be isolated after precipitation with hexanes. Analysis of the polymer was consistent with the formation of poly(methylenephosphine) ($^{31}P\{^1H\}$ NMR: $\delta = -13$ ppm; GPC: $M_w = 21\,000$ g mol^{-1}). Despite our efforts, we have thus far been unable to reproducibly obtain a homopolymer from **1a** either thermally or with radical initiators.

As a consequence of the difficulties in homopolymerizing **1a**, our attention shifted towards copolymerization of PhAk-Ox with styrene in the presence of radical initiators. When a mixture of monomers **1a** and styrene (ca. 1:2 ratio) was heated (160 °C) in the presence of a diazo initiator (VAZO 88; 1 mol %) the mixture exhibited an increase in viscocity suggestive of polymerization. Dissolution of the



sample in THF and successive precipitation from hexanes afforded a yellow solid free of monomer **1a**. Analysis of the yellow solid by multinuclear NMR spectroscopy and elemental microanalysis provided data that was consistent with its formulation as poly(methylenephosphine-*co*-styrene) **9a**. The $^{31}P\{^1H\}$ NMR spectrum is shown in Figure 3 and displays a broad resonance at −7 ppm that is consistent with polymerization through the P=C bond to afford a phosphine-containing polymer. The additional minor broad signals (about −25 and 5 ppm) are also consistent with phosphine moieties of the polymer. Similar patterns of signals have been observed in random copolymers of MesP=CPh$_2$ with styrene and have been attributed to the complex microstructure and regioirregularities within the copolymer.[3d] Particularly informative is the $^{13}C\{^1H\}$ NMR spectrum of **9a**, which is shown in Figure 4b. For comparison, the spectra of monomer **1a** and polystyrene (Figure 4a and c, respectively) are also given. Broad signals are detected that are consistent with the functional groups expected for a copolymer with the proposed formulation. Importantly, the doublet resonance assigned to the P=*C* bond of **1a** ($\delta = 203.3$ ppm) is absent in the copolymer. In addition, the characteristic signals assigned to the carbon atoms of the oxazoline ring are present in the polymer and, as expected, are considerably broader than those observed for **1a**.

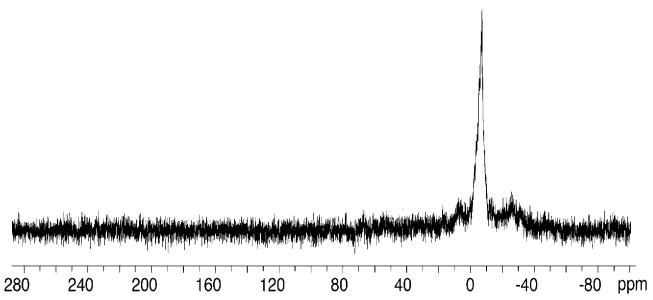


Figure 3. $^{31}P\{^1H\}$ NMR spectrum (162 MHz, 298 K) in $CDCl_3$ of poly(methylenephosphine-*co*-styrene) copolymer **9a**.

Analysis of a solution of copolymer **9a** in THF by using a gel permeation chromatograph (GPC) equipped with a laser-light scattering (LLS) detector revealed a modest weight-average molecular weight (M_w) of 7400 g mol^{-1} with a polydispersity index (PDI) of 1.15. The monomodal distribution is consistent with the formulation as copolymer **9a** rather than a blend of polystyrene and poly-**1a**. Elemental microanalysis of the polymer facilitated the estimation of the composition of the polymer. In particular, the phosphorus analysis (2.83 wt %) suggests that approximately 13 mol % phosphaalkene is incorporated into the copolymer (i.e. $x = 0.13n$, $y = 0.87n$). Although the tacticity and exact microstructure of the copolymer is not known at this time, an optical rotation was recorded on a 1.41 g per 100 mL solution of **9a** at 22 °C to give a specific rotation $[\alpha]_D^{22}$ of −14.0°. Therefore, it can be concluded that the polymer is chiral. The details of the complex microstructure of **9a** will be the subject of future investigations.

Conclusion

We have developed and demonstrated a synthetic sequence that enables a convergent and modular construction of chiral, enantiomerically enriched, isolable phosphaalkenes that feature oxazoline functional groups. Structural features within these PhAk-Ox compounds can be readily modified. In particular, this methodology permits the tuning of the carbon backbone and the aryl substituents on either the phosphorus or carbon atom of the phosphaalkene. We have demonstrated that chiral phosphaalkenes can act as monomers for radical-initiated copolymerization with styrene, generating phosphine-functionalized copolymers. Functionalized chiral copolymers such as these provide ample opportunities for the chemical exploration of coordination chemistry, asymmetric catalysis, and flow chemistry. In addition, further exploration of these and structurally related phosphaalkenes as P(σ^2,λ^3) ligands in asymmetric catalysis is an object of continuing investigation. Our results on these topics will be presented in due course.

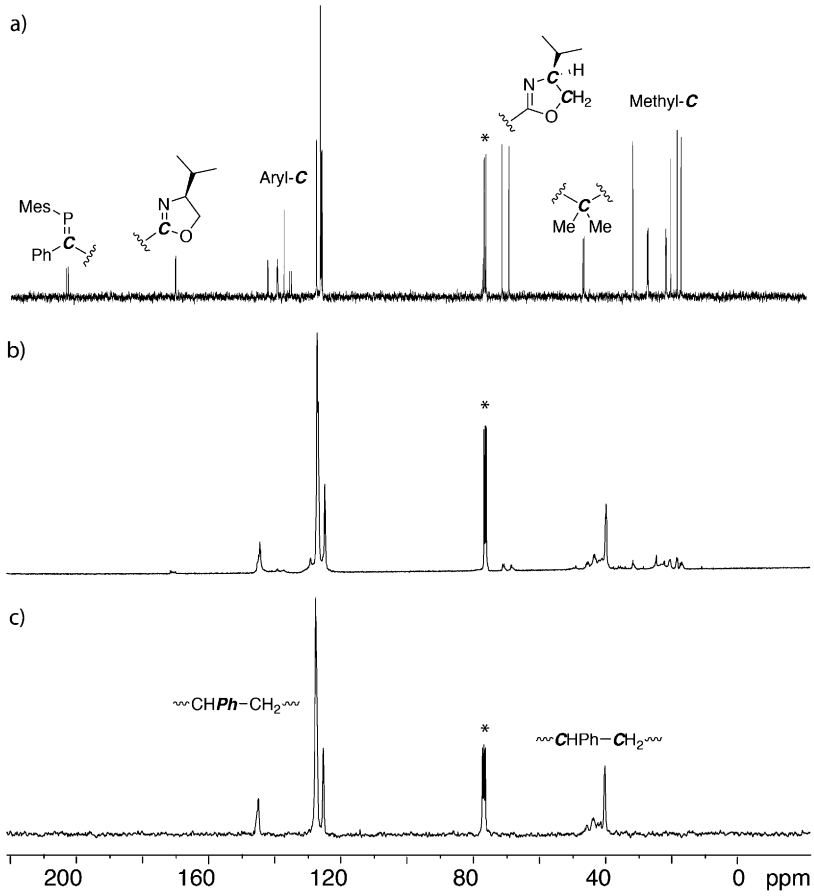


Figure 4. $^{13}C\{^1H\}$ NMR spectra (75.5 MHz, 298 K) in $CDCl_3$ of a) monomer **1a**, b) poly(methylenephosphine-*co*-styrene) **9a**, and c) polystyrene. Assignments for monomer **1a** were made with the aid of ^1H–^{13}C HMQC, ^1H–^{13}C HMBC and ^1H–^1H COSY experiments (* indicates $CDCl_3$).

Experimental Section

General procedures: All manipulations of air- and/or water-sensitive compounds were performed under a nitrogen atmosphere by using standard Schlenk or glovebox techniques. Hexanes and dichloromethane (CH_2Cl_2) were deoxygenated with nitrogen and dried by passing through a column containing activated alumina. Tetrahydrofuran (THF) was dried over sodium and benzophenone. Ethyl benzoate, methyl 4-methoxybenzoate, isobutyric acid, L-valine, cyclopentane carboxylic acid, chlorotrimethylsilane, and xylenes were purchased from Aldrich and used as received. *sec*-Butyllithium and methyllithium were purchased from Aldrich and titrated by using *N*-benzylbenzamide.[36] *N,N,N′,N′*-Tetramethylethylenediamine (TMEDA) was purchased from Aldrich and distilled over sodium prior to use. 1,1′-Azobis(cyclohexanecarbonitrile) (VAZO 88) was purchased from Aldrich and recrystallized from methanol prior to use. Styrene was purchased from Aldrich and distilled from CaH_2 prior to use. L-Valinol,[27] oxazoline **4**,[26] $MesP(SiMe_3)_2$,[19] 2,4,6-$(i\text{Pr})_3C_6H_2P(SiMe_3)_2$,[37] 2-$iPrC_6H_4$P(SiMe$_3$)$_2$,[33] and 2-$tBuC_6H_4$P(SiMe$_3$)$_2$[33] were prepared according to literature procedures. ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectra were recorded at 25 °C on Bruker Avance 300 or 400 MHz spectrometers. H_3PO_4 (85 %) was used as an external standard ($\delta = 0.0$ ppm for ^{31}P). ^1H NMR spectra were referenced to residual protonated solvent peaks and $^{13}C\{^1H\}$ NMR spectra were referenced to the deuterated solvent. Infrared spectra were recorded on a Thermo Nicolet 4700 FTIR spectrometer by using neat samples on NaCl plates. Elemental analyses were performed in the University of British Columbia Chemistry Microanalysis Facility. Mass spectra were recorded on a Kratos MS 50 instrument in EI mode (70 eV). The optical rotations were measured at a concentration in g per 100 mL and their values (average of 10 measurements) were obtained on a Jasco P-1010 polarimeter.

(*S,E*)-MesP=C(Ph)CMe$_2$Ox (1a): MeLi (1.6 M, 24 mL, 38 mmol) was added to a solution of $MesP(SiMe_3)_2$ (11.3 g, 38 mmol) in THF (25 mL). The reaction mixture was heated at 55 °C for 1–2 h. $^{31}P\{^1H\}$ NMR analysis of an aliquot removed from the reaction mixture suggested quantitative formation of $MesP(SiMe_3)Li$ ($\delta = -187$ ppm). The reaction mixture was cooled to −78 °C and treated with a solution of oxazoline **5** (9.9 g, 38 mmol) in THF (15 mL). After warming to room temperature, analysis of an aliquot removed from the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy revealed a singlet resonance, which is consistent with phosphaalkene **1a** ($\delta = 244$ ppm). The reaction mixture was quenched with Me_3SiCl (4.1 g, 38 mmol), the solvent evaporated in vacuo, and the product extracted into hexanes (1×20 mL, 2×10 mL). After filtration, the solvent was removed in vacuo. The product was recrystallized from *n*-pentane to give phosphaalkene **1b** as a colorless crystalline solid, which was washed with cold *n*-pentane (2×5 mL) and dried in vacuo (7.9 g, 52 %). $[\alpha]_D^{22} = -65.8$ ($c = 0.50$ in $CDCl_3$); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 244$ ppm; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.00$–6.50 (m, 7H), 4.23–4.18 (m, 1H), 3.99–3.95 (m, 1H), 3.88–3.82 (m, 1H), 2.26 (s, 3H), 2.21 (s, 3H), 2.09 (s, 3H), 1.75–1.66 (m, 1H), 1.67 (d, J(P,H) = 1 Hz, 3H), 1.64 (d, J(P,H) = 1 Hz, 3H), 0.90 (d, ^3J(H,H) = 7 Hz, 3H), 0.81 ppm (d, ^3J(H,H) = 7 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 203.3$ (d, ^1J(P,C) = 48 Hz), 170.6 (d, ^3J(P,C) = 6 Hz), 142.8 (d, J(P,C) = 15 Hz), 140.0 (d, J(P,C) = 7 Hz), 139.8 (d, J(P,C) = 6 Hz), 137.9, 135.9 (d, ^1J(P,C) = 41 Hz), 128.0 (d, J(P,C) = 4 Hz), 126.9, 126.7, 126.6, 126.3, 72.1, 70.0, 47.5 (d, ^2J(P,C) = 25 Hz), 32.6, 28.2 (d, J(P,C) = 9 Hz), 28.0 (d, J(P,C) = 7 Hz), 22.6 (d, J(P,C) = 7 Hz), 22.5 (d, J(P,C) = 7 Hz), 21.1, 19.2, 18.0 ppm; LRMS (EI): *m/z* (%): 394, 393 (4, 15) [M^+], 380, 379, 378 (12, 74, 100) [$M^+ - CH_3$], 275, 274 (5, 24) [M^+−Mes]; elemental analysis calcd (%) for $C_{25}H_{32}NOP$: C 76.31, H 8.20, N 3.56; found: C 76.56, H 8.17, N 3.56.

(*S,E*)-2,4,6-(iPr)$_3$C$_6$H$_2$P=C(Ph)CMe$_2$Ox (1b): MeLi (1.5 M, 1.75 mL, 2.6 mmol) was added to a solution of 2,4,6-$(i\text{Pr})_3C_6H_2P(SiMe_3)_2$ (1.0 g, 2.6 mmol) in THF (5 mL). The reaction mixture was heated at 55 °C for 1–2 h. $^{31}P\{^1H\}$ NMR analysis of an aliquot removed from the reaction mixture suggested quantitative formation of 2,4,6-$(i\text{Pr})_3C_6H_2P(Li)(SiMe_3)$ ($\delta = -205$ ppm). The reaction mixture was cooled to −78 °C and treated with a solution of oxazoline **5** (0.68 g, 2.6 mmol) in THF (5 mL). After warming to room temperature, analysis of an aliquot removed from the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy revealed a singlet resonance, which is consistent with phosphaalkene **1b** ($\delta = 248$ ppm). The reaction mixture was quenched with Me_3SiCl (0.29 g, 2.6 mmol), the solvent evaporated in vacuo, and the product extracted into hexanes (1×10 mL, 2×5 mL). After filtration, the solvent was removed in vacuo to give phosphaalkene **1b** as a yellow oil (1.2 g, 93 %). $[\alpha]_D^{18} = -32.9$ ($c = 2.4$ in CH_2Cl_2); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 248$ ppm; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.00$–6.62 (m, 7H), 4.25–4.16 (m, 1H), 4.01–3.94 (m, 1H), 3.92–3.83 (m, 1H), 3.40–3.25 (m, 2H), 2.68 (sept, ^3J(H,H) = 7 Hz 1H), 1.76–1.58 (m, 1H), 1.67 (s, 3H), 1.65 (s, 3H), 1.28–1.06 (m,

18H), 0.90 (d, ^3J(H,H) = 7 Hz, 3H), 0.82 ppm (d, ^3J(H,H) = 7 Hz, 3H); HRMS: *m/z* calcd for $C_{31}H_{44}NOP$: 477.3161; found: 477.3159; LRMS (EI): 479, 478, 477 (1, 3, 10) [M^+], 464, 463, 462 (6, 32, 100) [M^+-CH_3], 275, 274 (7, 23) [$M^+-(i\text{Pr})_3C_6H_2$].

(*S,E*)-2-*i*PrC$_6$H$_4$P=C(Ph)CMe$_2$Ox (1c): MeLi in Et_2O (1.5 M, 2.25 mL, 3.3 mmol) was added to a solution of 2-*i*PrC$_6$H$_4$P(SiMe$_3$)$_2$ (1.0 g, 3.3 mmol) in THF (10 mL). The reaction mixture was heated at 55 °C for 1–2 h. The solution was cooled to −78 °C and treated with a solution of oxazoline **5** (0.86 g, 3.3 mmol) in THF (5 mL). After warming to room temperature, analysis of an aliquot removed from the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy revealed a singlet resonance, which was assigned to be phosphaalkene **1c** (δ = 245 ppm). The reaction mixture was quenched with Me$_3$SiCl (0.36 g, 3.3 mmol), the solvent evaporated in vacuo and the product extracted into hexanes (3 × 10 mL). The solvent was removed in vacuo and the phosphaalkene was purified by bulb-to-bulb distillation (0.01 mmHg) to give phosphaalkene **1c** as a yellow oil (1.1 g, 85 %). $[\alpha]_D^{27} = -88.2$ (c = 1.9 in CH_2Cl_2); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 245 ppm; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.07–6.71 (m, 9H), 4.25–4.18 (m, 1H), 4.01–3.94 (m, 1H), 3.90–3.81 (m, 1H), 3.37–3.27 (m, 1H), 1.76–1.59 (m, 1H), 1.70 (s, 3H), 1.68 (s, 3H), 1.25–1.20 (m, 6H), 0.93 (d, ^3J(H,H) = 7 Hz, 3H), 0.84 ppm (d, ^3J(H,H) = 7 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 204.9 (d, ^1J(P,C) = 49 Hz), 170.4 (d, J(P,C) = 8 Hz), 151.4 (d, J(P,C) = 9 Hz), 141.9 (d, J(P,C) = 14 Hz), 139.0 (d, ^1J(P,C) = 41 Hz), 133.5 (d, J(P,C) = 5 Hz), 128.8, 128.5, 128.4, 127.0, 126.3, 125.0 (d, J(P,C) = 2 Hz), 124.5, 72.1, 70.0, 47.6 (d, ^2J(P,C) = 25 Hz), 32.8 (d, J(P,C) = 11 Hz), 32.6, 28.0, 27.8, 23.9, 23.8, 19.2, 18.1 ppm; HRMS: *m/z* calcd for $C_{23}H_{32}NOP$: 393.2222; found: 393.2220; LRMS (EI): *m/z* (%): 394, 393 (5, 12) [M^+], 380, 279, 378 (4, 27, 100) [M^+−Me]; elemental analysis calcd (%) for $C_{25}H_{32}NOP$: C 76.31, H 8.20, N 3.56; found: C 76.62, H 8.34, N 3.66.

(*S,E*)-2-*t*BuC$_6$H$_4$P=C(Ph)CMe$_2$Ox (1d): MeLi in Et_2O (1.5 M, 2.1 mL, 3.2 mmol) was added to a solution of 2-*t*BuC$_6$H$_4$P(SiMe$_3$)$_2$ (1.1 g, 3.2 mmol) in THF (10 mL). The reaction mixture was heated at 55 °C for 1–2 h. The solution was cooled to −78 °C and treated with a solution of oxazoline **5** (0.86 g, 3.3 mmol) in THF (5 mL). After warming to room temperature, analysis of an aliquot removed from the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy revealed a singlet resonance that was assigned to be a phosphaalkene (δ = 254 ppm). The reaction mixture was quenched with Me$_3$SiCl (0.35 g, 3.2 mmol), the solvent evaporated in vacuo and the product extracted into hexanes (3 × 10 mL). The solvent was removed in vacuo and the phosphaalkene was purified by bulb-to-bulb distillation (0.01 mmHg) to afford phosphaalkene **1d** as a yellow oil (1.2 g, 83 %). $[\alpha]_D^{27} = -64.5$ (c = 1.7 in CH_2Cl_2); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 254 ppm; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.15 (m. 1H), 7.05–6.88 (m, 5H), 6.83–6.77 (m, 2H), 6.73–6.67 (m, 1H), 4.25–4.17 (m, 1H), 4.02–3.95 (m, 1H), 3.87–3.83 (m, 1H), 1.79–1.65 (m, 1H), 1.66 (d, J(P,H) = 2 Hz, 3H), 1.63 (d, J(P,H) = 2 Hz, 3H), 1.51 (s, 9H), 0.90 (d, ^3J(H,H) = 7 Hz, 3H), 0.82 ppm (d, ^3J(H,H) = 7 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 196.7 (d, ^1J(P,C) = 50 Hz), 170.7 (d, ^3J(P,C) = 8 Hz), 153.1 (d, J(P,C) = 9 Hz), 142.0 (d, J(P,C) = 14 Hz), 139.6 (d, ^1J(P,C) = 52 Hz), 136.4, 128.6 (d, J(P,C) = 8 Hz), 128.2, 126.9, 126.1, 125.2, 124.7, 72.1, 69.9, 47.3 (d, ^2J(P,C) = 26 Hz), 37.0, 32.5 (d, J(P,C) = 10 Hz), 28.1 (d, J(P,C) = 6 Hz), 27.9 (d, J(P,C) = 3 Hz), 19.2, 18.0 ppm; HRMS: *m/z* calcd for $C_{26}H_{34}NOP$: 407.2378; found: 407.2380; LRMS (EI): *m/z* (%): 408, 407 (4, 7) [M^+], 394, 393, 392 (5, 37, 100) [M^+−*t*Bu], 275, 274 (7, 23) [$M^+-t\text{Bu}(C_6H_4)$]; elemental analysis calcd (%) for $C_{26}H_{34}NOP$: C 76.63, H 8.41, N 3.44; found: C 76.34, H 8.78, N 3.61.

(*S,E*)-MesP=C(4-(MeO)C$_6$H$_4$)CMe$_2$Ox (1e): MeLi (1.6 M, 11.3 mL, 18 mmol) was added to a solution of MesP(SiMe$_3$)$_2$ (5.4 g, 18 mmol) in THF (25 mL). The reaction mixture was heated at 55 °C for 1–2 h. $^{31}P\{^1H\}$ NMR analysis of an aliquot removed from the reaction mixture suggested quantitative formation of MesP(SiMe$_3$)Li (δ = −187 ppm). The reaction mixture was cooled to −78 °C and treated with a solution of oxazoline **6** (5.0 g, 18 mmol) in THF (15 mL). After warming to room temperature, analysis of an aliquot removed from the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy revealed a singlet resonance, which is consistent with phosphaalkene **1e** (δ = 245 ppm). The reaction mixture was quenched with Me$_3$SiCl (2.0 g, 18 mmol), the solvent evaporated in vacuo, and the product extracted into hexanes (1 × 20 mL, 2 × 10 mL). After filtration, the solvent was removed in vacuo and the product was bulb-to-bulb distilled (0.01 mmHg) to give phosphaalkene **1e** as a yellow oil (3.8 g, 50 %). $[\alpha]_D^{19} = -80.8$ (c = 1.1 in CH_2Cl_2); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 245 ppm; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.73–6.47 (m, 6H), 4.23–4.16 (m, 1H), 3.98–3.94 (m, 1H), 3.90–3.82 (m, 1H), 3.66 (s, 3H), 2.25 (s, 3H), 2.20 (s, 3H), 2.12 (s, 3H), 1.77–1.69 (m, 1H), 1.67 (s, 3H), 1.62 (s, 3H), 0.91 (d, ^3J(H,H) = 7 Hz, 3H), 0.82 ppm (d, ^3J(H,H) = 7 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 203.2 (d, ^1J(P,C) = 48 Hz), 170.8 (d, J(P,C) = 8 Hz), 158.0, 140.0 (d, J(P,C) = 6 Hz), 139.8 (d, J(P,C) = 6 Hz), 137.9, 136.1 (d, ^1J(P,C) = 43 Hz), 135.4 (d, J(P,C) = 15 Hz), 128.1 (d, J(P,C) = 6 Hz), 127.9 (d, J(P,C) = 9 Hz), 112.4, 72.0, 69.9, 55.3, 47.6 (d, J(P,C) = 26 Hz), 32.6, 28.3 (d, J(P,C) = 5 Hz), 28.1, 22.6 (d, J(P,C) = 8 Hz), 22.5 (d, J(P,C) = 8 Hz), 21.2, 19.2, 18.0 ppm; HRMS: *m/z* calcd for $C_{26}H_{34}NO_2P$: 423.2327; found: 423.2322; LRMS (EI): *m/z* (%): 424, 423 (6, 8) [M^+], 410, 409, 408 (6, 30, 100) [M^+−Me].

(*S,E*)-MesP=C(Ph)C(-C$_4$H$_8$-)Ox (1f): MeLi in Et_2O (1.1 M, 2.8 mL, 3.2 mmol) was added to a solution of MesP(SiMe$_3$)$_2$ (0.94 g, 3.2 mmol) in THF (10 mL). The reaction mixture was heated at 55 °C for 1–2 h. $^{31}P\{^1H\}$ NMR analysis of an aliquot removed from the reaction mixture revealed a single resonance (δ = −187 ppm) assigned to be MesP(SiMe$_3$)Li. The solution was cooled to −78 °C and treated with a solution of oxazoline **7** (0.90 g, 3.2 mmol) in THF (5 mL). After warming to room temperature, analysis of an aliquot removed from the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy revealed a singlet resonance that was assigned to be phosphaalkene **1f** (δ = 243 ppm). The reaction mixture was quenched with Me$_3$SiCl (0.34 g, 3.2 mmol), the solvent evaporated in vacuo, and the product extracted into hexanes (3 × 10 mL). The solvent was removed in vacuo and phosphaalkene **1f** was isolated as an impure yellow oil [$^{31}P\{^1H\}$ NMR (121 MHz, THF): δ = 243 ppm]. The solvent was removed in vacuo and **1f** was purified by bulb-to-bulb distillation (0.01 mmHg; 0.82 g, 50 %). $[\alpha]_D^{18} = -41.0$ (c = 1.3 in CH_2Cl_2); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 245 ppm; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.99–6.93 (m, 3H), 6.81–6.77 (m, 2H), 6.62–6.57 (m, 2H), 4.19–4.13 (m, 1H), 3.98–3.93 (m, 1H), 3.87–3.81 (m, 1H), 2.42–2.35 (m, 3H), 2.26 (s, 3H), 2.20 (s, 3H), 2.20–2.13 (m, 1H), 2.11 (s, 3H), 1.87–1.80 (m, 4H), 1.74–1.69 (m, 1H), 0.90 (d, ^3J(H,H) = 7 Hz, 3H), 0.81 ppm (d, ^3J(H,H) = 7 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 200.8 (d, ^1J(P,C) = 47 Hz), 169.4 (d, J(P,C) = 9 Hz), 143.3 (d, J(P,C) = 14 Hz), 140.1 (d, J(P,C) = 7 Hz), 139.9 (d, J(P,C) = 6 Hz), 137.9, 136.0 (d, J(P,C) = 41 Hz), 128.1, 128.0, 126.9, 126.7, 126.6, 126.4, 72.2, 70.0, 59.3 (d, J(P,C) = 23 Hz), 37.9 (d, J(P,C) = 20 Hz), 37.6 (d, J(P,C) = 20 Hz), 32.6, 24.0, 23.9, 22.6 (d, J(P,C) = 10 Hz), 22.5 (d, J(P,C) = 8 Hz), 21.2, 19.3, 18.1 ppm; HRMS: *m/z* calcd for $C_{27}H_{34}PNO$: 419.2387; found: 419.2375; LRMS (EI): *m/z* (%): 419, 418 (45, 5) [M^+], 301, 300 (8, 33) [M^+−Mes].

(*S,E*)-MesP=C(3,5-(CF$_3$)$_2$C$_6$H$_4$)C(-C$_4$H$_8$-)Ox (1g): MeLi in Et_2O (1.1 M, 2.8 mL, 3.2 mmol) was added to a solution of MesP(SiMe$_3$)$_2$ (0.95 g, 3.2 mmol) in THF (10 mL). The reaction mixture was heated at 55 °C for 1–2 h. $^{31}P\{^1H\}$ NMR analysis of an aliquot removed from the reaction mixture revealed a single resonance (δ = −187 ppm) assigned to be MesP(SiMe$_3$)Li. The solution was cooled to −78 °C and treated with a solution of oxazoline **8** (1.3 g, 3.1 mmol) in THF (5 mL). After warming to room temperature, analysis of an aliquot removed from the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy revealed a singlet resonance that was assigned to be phosphaalkene **1g** (δ = 256 ppm). The reaction mixture was quenched with Me$_3$SiCl (0.34 g, 3.2 mmol), the solvent evaporated in vacuo, and the product extracted into hexanes (3 × 10 mL). The solvent was removed in vacuo and phosphaalkene **1g** was isolated as an impure yellow oil [$^{31}P\{^1H\}$ NMR (121 MHz, THF): δ = 256 ppm]. The solvent was removed in vacuo and the phosphaalkene was purified by bulb-to-bulb distillation (0.01 mmHg; 1.2 g, 67 %). $[\alpha]_D^{18} = -56.4$ (c = 1.6 in CH_2Cl_2); $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 254 ppm; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.40 (m, 1H), 7.24–7.19 (m, 2H), 6.63–6.56 (m, 1H), 6.55–6.51 (m, 1H), 4.23–4.18 (m, 1H), 3.97–3.92 (m, 1H), 3.88–3.78 (m, 1H), 2.48–2.33 (m, 3H), 2.22 (s, 3H), 2.13 (s, 3H), 2.12–2.09 (m, 1H), 2.08 (s, 3H), 1.89–1.80 (m, 4H), 1.67–1.58 (m, 1H), 0.89 (d, ^3J(H,H) = 7 Hz, 3H), 0.79 ppm (d, ^3J(H,H) = 7 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 196.9 (d, ^1J(P,C) = 50 Hz), 169.9 (d, J(P,C) = 9 Hz), 144.9 (d, J(P,C) = 14 Hz), 139.8 (d, J(P,C) = 6 Hz), 139.5 (d, J(P,C) = 5 Hz), 138.9,

134.7 (d, J(P,C) = 42 Hz), 130.4 (q, J(F,C) = 33 Hz), 128.4, 128.4, 127.1–126.8 (m), 123.4 (q, ^1J(F,C) = 272 Hz), 120.0–119.7 (m), 72.3, 70.4, 58.8 (d, ^2J(P,C) = 21 Hz), 37.6 (d, J(P,C) = 15 Hz), 37.3 (d, J(P,C) = 20 Hz), 32.8, 37.3 (d, J(P,C) = 20 Hz), 24.0, 23.9, 22.2 (d, J(P,C) = 9 Hz), 22.1 (d, J-(P,C) = 8 Hz), 21.0, 19.0, 18.1 ppm; HRMS: m/z calcd for $C_{29}H_{32}NOPF_6$: 555.2126; found: 555.2127; LRMS (EI): m/z (%): 557, 556, 555 (8, 29, 84) [M^+], 528, 527, 526 (5, 25, 72) [M^+−Et], 513, 512 (5, 15) [M^+−iPr], 488, 487, 486 (3, 7, 8) [M^+−CF_3], 437, 436 (7, 29) [M^+−Mes], 406, 405, 404 (18, 26, 100) [M^+−$C_9H_{12}P$].

(*S*)-(MesP)$_2$C(Ph)=CNCH(*i*Pr)CH$_2$O (3/3′): MeLi (1.5 M, 4.6 mL, 6.9 mmol) was added to a solution of MesP(SiMe$_3$)$_2$ (2.0 g, 6.9 mmol) in THF (20 mL). The reaction mixture was heated at 55 °C for 1–2 h. $^{31}P\{^1H\}$ NMR analysis of an aliquot removed from the reaction mixture suggested quantitative formation of MesP(SiMe$_3$)Li ($\delta = -187$ ppm). The reaction mixture was cooled to −78 °C and treated with a solution of oxazoline **2** (1.5 g, 6.9 mmol) in THF (20 mL). After warming to room temperature, analysis of an aliquot removed from the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy revealed multiple resonances ($\delta = -40$–33 ppm). The solvent was evaporated in vacuo and the product extracted into hexanes (1×20 mL, 2×10 mL). X-Ray crystallography quality crystals were obtained from slow evaporation of the solvent. A mixture of **3** and **3′**: $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta = 32$ (d, ^1J(P,P) = 202 Hz), 32 (d, ^1J(P,P) = 196 Hz), 4 (d, ^1J(P,P) = 202 Hz), 0 ppm (d, ^1J(P,P) = 196 Hz); ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.41$–6.79 (m, 18H), 4.75–4.70 (m, 1H), 4.67–4.63 (m, 1H), 4.54–4.50 (m, 1H), 4.41–4.37 (m, 1H), 3.86–3.80 (m, 1H), 3.48–3.41 (m, 1H), 2.62 (s, 3H), 2.55–2.51 (m, 21H), 2.27 (s, 3H), 2.26 (s, 3H), 2.23 (s, 3H), 2.22 (s, 3H), 2.11–2.03 (m, 1H), 1.80–1.70 (m, 1H), 1.01 (d, ^3J(H,H) = 7 Hz, 3H), 0.95 (d, ^3J(H,H) = 7 Hz, 3H), 0.90 (d, ^3J(H,H) = 7 Hz, 3H), 0.64 ppm (d, ^3J(H,H) = 7 Hz, 3H).

(*S*)-PhC(=O)CMe$_2$Ox (5): *s*BuLi (1.27 M, 51 mL, 65 mmol) was added to a cooled solution (−78 °C) of oxazoline **4** (10.0 g, 64 mmol) and TMEDA (7.4 g, 64 mmol) in THF (1 M). After 1 h at −78 °C, ethyl benzoate (10.7 g, 71 mmol) was added to the reaction mixture. The solution was warmed to room temperature and stirred for 30 min. Subsequently, water (25 mL) and saturated aqueous ammonium chloride (25 mL) were added to the yellow reaction mixture. The aqueous layer was extracted with diethyl ether (3×150 mL). The organic fractions were combined, dried by using sodium sulfate, and concentrated by rotary evaporation in vacuo. The residue was purified by fractional distillation (155–165 °C, 0.2 mmHg) by using a Kugelrohr to give ketone **5** as a colorless oil (8.2 g, 49%). $[\alpha]_D^{22} = -28.1$ ($c = 0.13$ in $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) $\delta =$ 7.98–7.96 (m, 2H), 7.50–7.46 (m, 1H), 7.39–7.35 (m, 2H), 4.11–4.07 (m, 1H), 3.97–3.90 (m, 1H), 3.88–3.83 (m, 1H), 1.84–1.73 (m, 1H) 1.60 (s, 3H), 1.58 (s, 3H), 0.97 (d, ^3J(H,H) = 7 Hz, 3H), 0.87 ppm (d, ^3J(H,H) = 7 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 199.0$, 170.2, 135.8, 132.7, 128.9, 128.4, 72.1, 70.6, 48.3, 32.5, 25.0, 24.9, 19.1, 18.2 ppm; IR (neat, NaCl): 1691, 1661, 1449 cm^{-1}; HRMS: m/z calcd for $C_{16}H_{21}NO_2Na$: 282.1470; found: 282.1469; LRMS (ESI): m/z (%): 283, 282 (15, 100) [M+Na$^+$], 261, 260 (8, 38) [M+H$^+$]; elemental analysis calcd (%) for $C_{16}H_{21}NO_2$: C 74.10, H 8.16, N 5.40; found: C 73.73, H 8.27, N 5.45.

(*S*)-4-OMeC$_6$H$_4$C(=O)CMe$_2$Ox (6): *s*BuLi (1.24 M, 38 mL, 47 mmol) was added to a cooled solution (−78 °C) of oxazoline **4** (7.4 g, 47 mmol) and TMEDA (7.2 mL, 47 mmol) in THF (50 mL). After stirring the reaction mixture at −78 °C for 45 min, a cold solution of methyl 4-methoxybenzoate (8.0 g, 47 mmol) in THF (30 mL) was added and the reaction mixture was stirred for 1 h and warmed to room temperature. The reaction mixture was quenched with a solution of saturated aqueous NH_4Cl (25 mL) and water (25 mL). The aqueous layer was extracted with Et_2O (3×30 mL). The organic fractions were combined, dried by using Na_2SO_4, and the solvent removed by rotary evaporation in vacuo. The yellow oil was purified by bulb-to-bulb distillation under reduced pressure to give ketone **6** (9.9 g, 72%) as a colorless oil. $R_f = 0.26$ (hexanes/EtOAc, 3:1); $[\alpha]_D^{21} = -33.9$ ($c = 0.326$ in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.97$ (d, ^3J(H,H) = 9 Hz, 2H), 6.82 (d, ^3J(H,H) = 9 Hz, 2H), 4.08 (dd, ^3J(H,H) = 9, ^3J(H,H) = 7 Hz, 1H), 3.92–3.83 (m, 2H), 3.80 (s, 3H), 1.84–1.73 (m, 1H), 1.55 (s, 3H), 1.53 (s, 3H), 0.95 (d, ^3J(H,H) = 7 Hz, 3H), 0.85 ppm (d, ^3J(H,H) = 7 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 197.1$, 170.5, 163.1, 131.3, 128.4, 113.5, 72.0, 70.5, 55.5, 48.0, 32.5, 25.1, 25.0, 19.1, 18.2 ppm; IR (neat, NaCl): 2960, 2936, 2904, 2866, 1682, 1656, 1602, 1575, 1511 cm^{-1}; HRMS: m/z calcd for $C_{17}H_{24}NO_3$: 290.1756; found: 290.1752.

(*S*)-HC(CH$_2$)$_4$Ox: A modified literature procedure was used.[26] Cyclopentane carboxylic acid was added (9.1 mL, 83 mmol) to a solution of L-valinol (8.5 g, 83 mmol) in xylenes (0.5 M) and the mixture was heated at reflux by using a Dean–Stark apparatus for 44 h. The reaction mixture was cooled and extracted with aqueous hydrochloric acid (10%) and the aqueous layer was neutralized with aqueous sodium hydroxide (40%). The aqueous layer was extracted with Et_2O (3×60 mL) and the combined organic extracts were dried by using Na_2SO_4. The solvent was removed by rotary evaporation in vacuo, and the crude product was purified by bulb-to-bulb distillation (95 °C, 0.4 mmHg) to give the product as a colorless oil (8.3 g, 55%). $R_f = 0.39$ (hexanes/EtOAc, 3:1); $[\alpha]_D^{22} = -62.5$ ($c =$ 0.607 in $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 4.17$–4.11 (m, 1H), 3.88–3.79 (m, 2H), 2.76–2.65 (m 1H), 1.88–1.83 (m, 2H), 1.77–1.70 (m, 5H), 1.55–1.52 (m, 2H), 0.86 (d, ^3J(H,H) = 7 Hz, 3H), 0.77 ppm (d, ^3J(H,H) = 7 Hz, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): $\delta = 170.7$, 71.8, 69.7, 38.4, 32.6, 30.7, 30.6, 25.9, 18.8, 17.8 ppm; IR (neat, NaCl): 2958, 2872, 1666 cm^{-1}; HRMS: m/z calcd for $C_{11}H_{20}NO$: 182.1545; found: 182.1540.

(*S*)-PhC(=O)C(CH$_2$)$_4$Ox (7): *s*BuLi (1.4 M, 20.0 mL, 28.0 mmol) was added to a solution of (*S*)-2-cyclopentyl-4-isopropyl-4,5-dihydrooxazole (5.0 g, 28 mmol) and TMEDA (4.2 mL, 27.7 mmol) in THF (30 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h, following which cold ethyl benzoate (4.0 g, 27.5 mmol) in THF (15 mL) was added. The reaction mixture was stirred for 1 h and then warmed to room temperature, at which point it was quenched with a solution of saturated aqueous NH_4Cl (50 mL) and water (10 mL). The aqueous layer was extracted with Et_2O (3×50 mL). The organic fractions were combined, dried by using Na_2SO_4, and the solvent removed by rotary evaporation in vacuo. The yellow oil was purified by flash column chromatography on silica (hexanes/EtOAc, 95:5) to obtain ketone **7** as a colorless oil (5.5 g, 70%). $R_f = 0.48$ (hexanes/EtOAc, 3:1); $[\alpha]_D^{22} = -19.9$ ($c = 0.982$ in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.87$–7.84 (m, 2H), 7.32–7.26 (m, 1H), 7.21–7.16 (m, 2H), 3.89–3.86 (m, 1H), 3.74–3.60 (m, 2H), 2.35–2.10 (m, 4H), 1.65–1.46 (m, 5H), 0.77 (d, ^3J(H,H) = 7 Hz, 3H), 0.68 ppm (d, ^3J(H,H) = 7 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 196.5$, 169.3, 135.2, 132.2, 128.7, 127.8, 71.5, 70.2, 58.2, 35.3, 35.2, 32.2, 25.7, 25.5, 18.5, 17.9 ppm; IR (neat, NaCl): 3059, 2958, 2872, 1689, 1659, 1598, 1573 cm^{-1}; HRMS: m/z calcd for $C_{18}H_{24}NO_2$: 286.1807; found: 286.1800.

(*S*)-3,5-(CF$_3$)$_2$C$_6$H$_3$C(=O)C(CH$_2$)$_4$Ox (8): *s*BuLi (1.0 M, 2.0 mL, 2.0 mmol) was added to a solution of oxazoline (*S*)-2-cyclopentyl-4-isopropyl-4,5-dihydrooxazole (0.34 g, 1.9 mmol) and TMEDA (0.3 mL, 1.8 mmol) in THF (19 mL) at −78 °C . After stirring the reaction mixture at −78 °C for 1 h, a cold solution of *N*-methoxy-*N*-methyl-3,5-bis(trifluoromethyl)benzamide (0.56 g, 1.88 mmol)[38] in THF (15 mL) was added. The reaction mixture was stirred for 1 h and warmed to room temperature, at which point it was quenched with a solution of saturated aqueous NH_4Cl (15 mL) and water (15 mL). The aqueous layer was extracted with Et_2O (3×25 mL). The organic fractions were combined, dried by using Na_2SO_4, and the solvent removed by rotary evaporation in vacuo. The yellow oil was purified by flash column chromatography with silica (hexanes/EtOAc, 95:5) to obtain ketone **8** as a colorless oil (0.71 g, 90%). $R_f = 0.63$ (hexanes/EtOAc, 3:1); $[\alpha]_D^{22} = -27.0$ ($c = 1.04$ in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.46$ (s, 2H), 8.00 (s, 1H), 4.15–4.06 (m, 1H), 3.87–3.77 (m, 2H), 2.51–2.23 (m, 4H), 1.91–1.52 (m, 5H), 0.92 (d, ^3J(H,H) = 7 Hz, 3H), 0.81 ppm (d, ^3J(H,H) = 7 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 194.8$, 168.8, 137.4, 132.1 (q, ^2J(F,C) = 34 Hz), 129.3 (q, ^3J(F,C) = 4 Hz), 125.9 (quint, ^3J(F,C) = 4 Hz), 123.2 (q, ^1J(F,C) = 271 Hz), 72.5, 71.2, 58.8, 35.8, 35.6, 32.9, 26.2, 26.1, 19.1, 18.3 ppm; IR (neat, NaCl): 3088, 2962, 2876, 1703, 1661, 1615 cm^{-1}; HRMS: m/z calcd for $C_{20}H_{22}F_6NO_2$: 422.1555; found: 422.1547.

Copolymer [{MesPC(Ph)(CMe$_2$Ox)}$_x${CH$_2$CHPh}$_y$]$_n$ (9a): Styrene (0.80 g, 7.7 mmol), phosphaalkene **1a** (1.50 g, 3.8 mmol) and VAZO 88 (0.03 g, 0.12 mmol) were added to a pyrex tube. The tube was flame-sealed in vacuo and, subsequently, heated at 160 °C in an oven equipped with rocking tray. Over a period of 14 h, the polymerization mixture became in-

creasingly viscous. The tube was removed from the oven and cooled to ambient temperature, at which point the sample was solid and broken in a nitrogen filled glovebox. The contents were dissolved in THF (ca. 3 mL) in the glovebox and transferred to a Schlenk flask (10 mL). The solution was concentrated in vacuo and precipitated with hexanes (5 mL) to give a light yellow solid. This process was repeated four times to give a light-yellow powder that was dried in vacuo for 24 h (0.25 g, 11%). $[\alpha]_D^{22} = -14.0$ ($c = 1.41$ in $CHCl_3$); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -7$ ppm (br s); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.5$–5.8 (br m; aryl H from phosphaalkene and styrene), 4.1–3.3 (br s; methane CH from oxazoline), 3.0–0.5 ppm (br m; CH_3 from phosphaalkene, CH, CH_2 from styrene); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 172.3$, 145.3, 140.2, 138.2, 129.8, 127.9, 125.6, 71.3, 69.2, 45.9, 40.3, 32.3, 25.1, 22.7, 21.0, 18.7, 17.5 ppm; GPC-LLS (THF): $M_n = 7400\ g\,mol^{-1}$; PDI = 1.15; $dn/dc = 0.198$; elemental analysis found: C 87.00, H 8.14, N 1.19, P 2.83.

X-ray crystallography: All single crystals were immersed in oil and mounted on a glass fiber. Data were collected on a Bruker X8 APEX diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation. Structures were solved by direct methods and subsequent Fourier difference techniques. All non-hydrogen atoms were refined anisotropically with hydrogen atoms being included in calculated positions but not refined. All data sets were corrected Lorentz and polarization effects. All calculations were performed by using the SHELXTL[39] crystallographic software package from Bruker-AXS. Additional crystal data and details of the data collection and structure refinement are given in Table 2. CCDC-692226 (**1a**) and CCDC-857554 (**3/3′**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 2. X-ray data collection and refinement details

	3/3′	**1a**
formula	$2 \times C_{31}H_{37}N_1O_1P_2$	$C_{25}H_{32}NOP$
M_r	1003.11	393.49
crystal system	triclinic	hexagonal
space group	$P\bar{1}$	$P6_1$
color	colorless	colorless
a [Å]	8.196(1)	8.697(1)
b [Å]	10.656(1)	8.697(1)
c [Å]	15.571(2)	50.627(8)
α [°]	101.997(9)	90
β [°]	91.31(1)	90
γ [°]	96.89(1)	120
V [Å^3]	1319.4(3)	3316(6)
T [K]	173	173
Z	1	6
$\mu(Mo_{K\alpha})$ [cm^{-1}]	0.190	0.139
crystal size [mm^3]	$0.25 \times 0.25 \times 0.1$	$0.6 \times 0.4 \times 0.3$
calcd density [Mg m^{-3}]	1.262	1.182
$2\theta_{max}$ [°]	56.8	56.4
no. of reflns	21 909	55 634
no. of unique data	11 052	5413
R_{int}	0.0422	0.0704
refln/param. ratio	17.08	20.82
R_1[a]	0.0431; $I > 2\sigma(I)$	0.0471; $I > 2\sigma(I)$
wR_2 (all data)[b]	0.1174	0.1010
GOF	1.005	1.082

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ [b] $wR_2(F^2[\text{all data}]) = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

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