New route to a pyrazoline scaffold featuring original substitutions and its crystal structure

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Abstract Pyrazolines are among the heterocyclic compounds a class that exhibit a range of applications in a wide diversity of fields. We report here a novel approach to the pyrazoline scaffold featuring an unprecedented substitution pattern. This synthesis is carried out from a diazoester and promoted by the addition of a phosphinyl chloride through a putative cyclic phosphinazine. The pyrazoline has been fully spectroscopically characterized and the structure has been further assessed by X-Ray diffraction, as the new compound crystallized from toluene in a monoclinic crystal lattice.

Keywords Phosphorus compounds ● Heterocycles ● Diazo compounds ● Cyclization ● X-Ray structure determination

Introduction

Among the heterocyclic compounds featuring two connected heteroatoms, pyrazolines have been attracting significant interest as they represent a scaffold commonly found in numerous compounds exhibiting activities in a wide range of therapeutic areas such as neurological disorders [1], and cancer [2], promoting their recent recognition as promising pharmacophore to fight emerging diseases and overcome drug resistance [3]. Pyrazolines are also incorporated into derivatives featuring exquisite optoelectronic properties [4, 5], as well as fluorescent scintillators [6]. These applications have promoted the development of various synthetic approaches. The first and most illustrated approach consist in introducing the two nitrogens simultaneously via a hydrazone derivative by addition on a α,β-unsaturated carbonyl in a refluxing polar solvent (EtOH or AcOH). These reaction conditions provide a pyrazoline featuring no substitution on nitrogen, thus generally requiring a further acylation [7, 8], which can occur in situ when the solvent is a carboxylic acid [9, 10].

Alternative reactions to pyrazoline have also been performed. [3+2]-dipolar cycloadditions of nitrileimine with enones [11], or conjugated dienes [12], have proved especially efficient, although mixtures of diastereo- or regioisomers are commonly encountered. Starting from aryl- and sulfonyl-hydrazones, CH activation at allylic positions performed by TEMPO/DIAD [13], or catalyzed by palladium [14], have led to vinyl substituted pyrazolines. Finally, asymmetric syntheses of pyrazolines featuring a quaternary center have been achieved by addition of the saturated nitrogen of a hydrazone on a pendant double bond either through a Wacker type cyclization catalyzed by a palladium–pyrox complex [15], or by iodofunctionnalization in the presence of a chiral thiourea [16]. In the course of our investigation of non-carbene-generating diazo reactivities, we wondered how the N–N connection of the diazo could be transferred into the cyclic structure of a pyrazoline. We report here our recent achievement to perform such a transformation through a cascade reaction process.

Results and Discussion

In order to perform the cyclization of a diazo to a pyrazoline, we postulated that an aza-anion derived from a diazo compound could perform an intramolecular nucleophilic displacement. The coupling of diazo compounds with phosphine has been known since the very early work of Staudinger and Meyer who described the first phosphinazine in 1919 [17].

At that stage, only the phosphinazine derived from diphenyldiazo and triphenylphosphine were found to undergo nitrogen extrusion to lead to the phosphonium ylide upon heating. Indeed, the phosphinazines were shown to be fairly stable compounds due to their mesomeric structures, the heterodiene **1N**, the azo-carbanion **1Z^{C}** and the aza-ylide **1Z^{N}** (Figure 1).

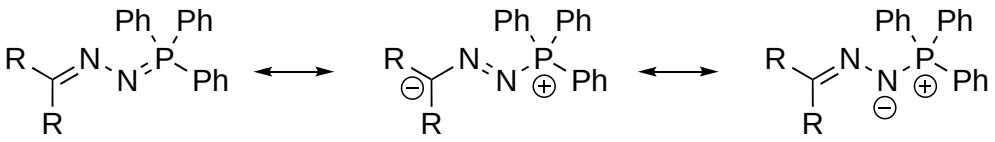

Figure 1: Mesomeric forms of Phosphinazines

Interested in the reactivity of such a polarized heterodiene, we wondered if a cyclic analog featuring a double bond such as **2** could be isolated and how it would react (Figure 2). One possible outcome is the extrusion of nitrogen that leads to the phosphorous ylide, and would parallel the seminal work of Staudinger. Another possibility would correspond to nucleophilic reactivities at carbon or nitrogen that would imply the forms **1Z^{C}** and **1Z^{N}** and may lead to different cyclic structures.

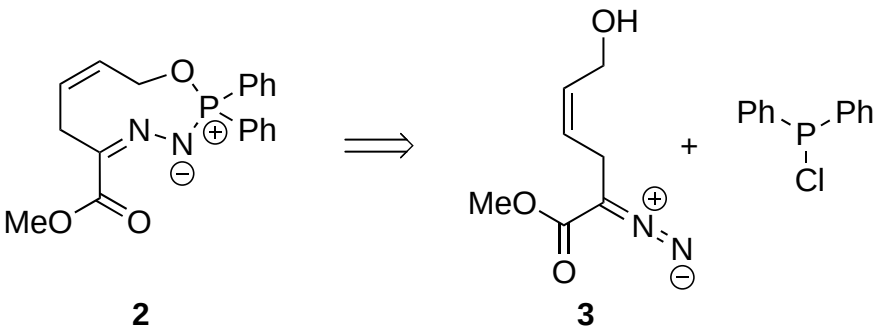

Figure 2: A straightforward access to cyclic phosphinazine to probe its reactivity

In order to reach the cyclic phosphinazine **2**, we attempted to introduce the phosphorous moiety on a diazo containing group. Thus, we treated the diazoalcohol **3** with 2 equivalents of chlorodiphenylphosphine and 2 equivalents of triethylamine in dichloromethane at room temperature. After stirring overnight at room temperature, we observed the formation of a single compound which could be isolated pure after short path flash column chromatography on silica gel.

The ^{31}P NMR signal at a chemical shift of 26.62 ppm is indicative of a P(V), stating the oxidation of phosphorous during the reaction as this could be expected during the formation of the phosphinazine. Furthermore, it also appeared that the obtained product features aromatic signals as the multiplets (corresponding to 10 protons) ranging from 7.95 to 7.45 ppm indicative of an electron withdrawing group connected to the aromatics. More interestingly, 3 vinylic protons are observed at 5.84, 5.00 and 4.96 ppm compared to the 2 of the starting material. Also noteworthy, the internal vinyl proton couples with its allylic neighbor which chemical shift of 4.83 ppm indicates the close proximity of the latter from an electron withdrawing group. The allylic proton also couples with two others in the aliphatic region, at 3.32 and 2.93 ppm with two J^3 constants of 6 and 12 Hz. A strong J^2 constant of 18 Hz is also found within these last two signals indicating a geminal coupling. This assesses the diastereotopic nature of the corresponding protons, and the quaternary nature of the fourth substituent of the carbon bearing them. A singlet at 3.81 ppm confirms the presence of the methoxy group. The HRMS m/z value of the protonated molecular peak of 355.1214 reveals the chemical formula $C_{19}H_{20}N_2O_3P$ (calculated at 355.1212), indicating that the two nitrogens of the starting diazoester are indeed conserved in the obtained product. The ^{13}C NMR spectra showed two low field signals for quaternary carbons at 162.3 and 145.8 ppm corresponding to the carbonyl group of an ester and matching the chemical shift of the iminyl carbon of a hydrazone. Furthermore, this signal also shows a coupling with the phosphorous (*J* 13 Hz) as does the allylic carbon at 63.3 ppm (*J* 4Hz) and the aliphatic carbon at 38.8 ppm (3 Hz). Finally, the $^{1}H\{^{31}P\}$ NMR analysis revealed couplings not only between the phosphorous and the aromatic proton, but also with the allylic proton and the proton at 2.93 ppm. These latter heteronuclear coupling constants were confirmed and quantified by a J-resolved experiment with or without ^{31}P refocusing in the indirect dimension (Figure 3) [18].

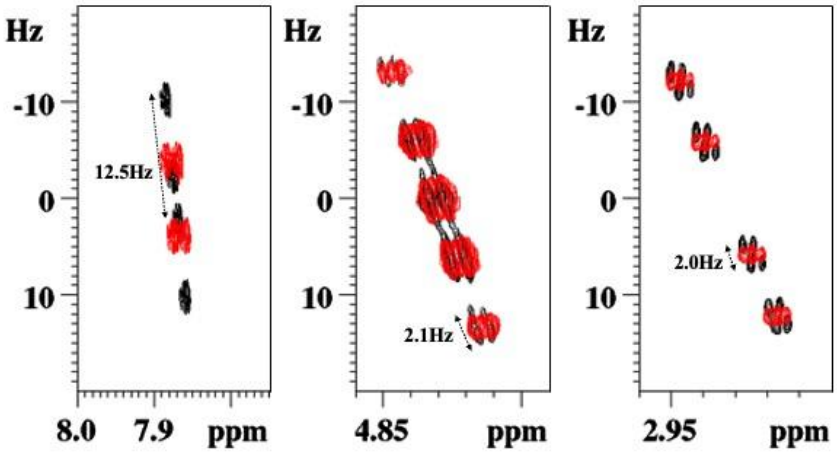

Figure 3: J-resolved spectra with (red) or without (black) refocusing of the ^{1}H-^{31}P coupling constant in the indirect dimension. The additional multiplet structure allows measurement of the heteronuclear J-coupling. (left) Aromatic proton of the phenyl rings, whose coupling constant to the ^{31}P nucleus is 12.5 Hz. (middle) Allylic proton with a 2.1 Hz coupling constant, and (right) aliphatic proton at 2.93 ppm, with a similar weak coupling constant of 2.0 Hz.

All these data are supportive of a structure featuring endocyclic nitrogens, and an exocyclic phosphinic substituent. Thus, it appears that under the reaction conditions the alcohol **3** undergoes a straightforward conversion to the pyrazoline **4** (Figure 4).

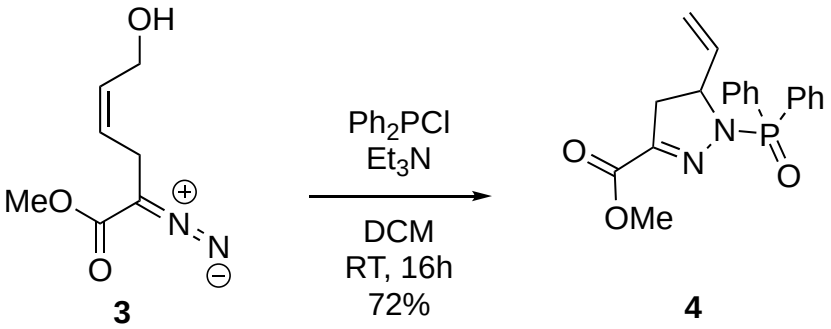

Figure 4: One-pot conversion of a diazo to a pyrazoline

Although no evidence has so far been obtained, we consider that the reaction is likely to proceed through the formation of a phosphinite from the alcohol **3** and the chlorophosphine. The phosphorous would then undergo a nucleophilic addition on the terminal nitrogen of the diazo leading to the cyclic phosphinazine **2**. This would enhance the

nucleophilic character of this nitrogen that would thus undergo a S_N2' process, the formation of a P=O double bond being the driving force of this last step leading to **4** (Figure 5).

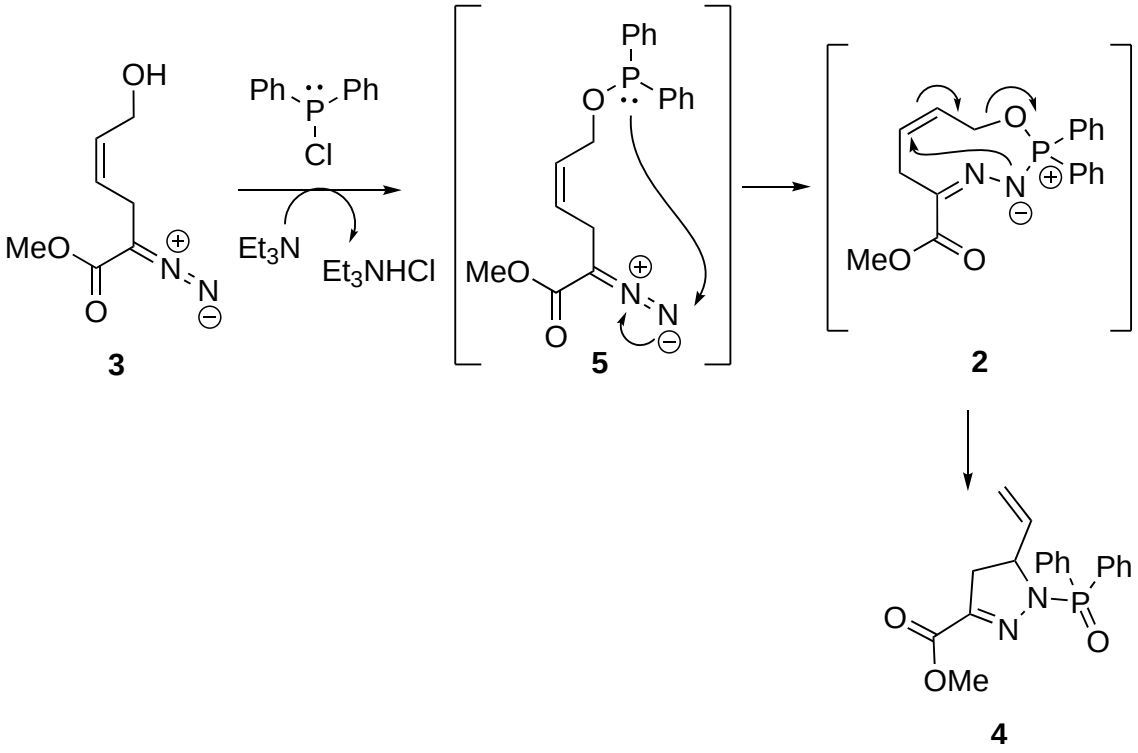

Figure 5: Proposed cascade mechanism for the transformation

This unprecedented access to a pyrazoline scaffold was further confirmed by X-ray diffraction of a monocrystal obtained from slow evaporation of a saturated solution of **4** in toluene. The compounds crystallized in a monoclinic crystal system and P 21/c space group (Figure 6).

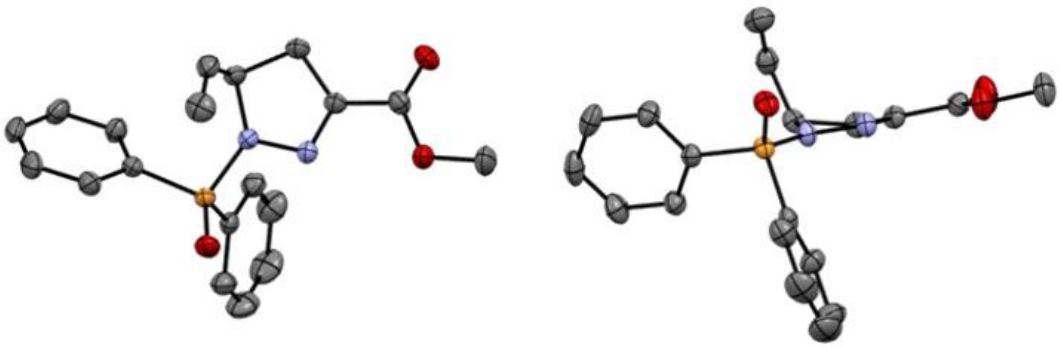

Figure 6: Orthogonal views of the crystal structure of 4

To the best of our knowledge, this represents the sole example of a straight access to phosphinic *N*-substituted pyrazoline as the only other occurrence found in the literature

strictly reports a tautomeric equilibrium between an hydroxypyrazoline **7** and the acyclic phosphonylated hydrazone **6** and thus do not provide any structural details of a such scaffold (Figure 7) [19]. We shall also point out that the crystal structures of only 5 pyrazolines bearing a simple vinyl substituent at the C3 position of the pyrazoline have been described in only two reports, supporting the rare occurrence of the scaffold reported herein [13, 14].

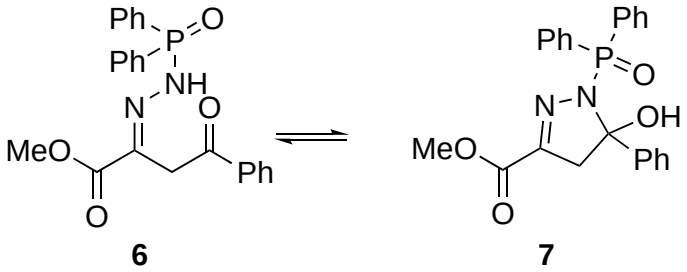

Figure 7: Only precedent of such a N-phosphinic-pyrazoline

The pyrazoline core of **4** exhibits a highly planar geometry, which contrasts with the most structurally related sulfonyl-pyrazoline reported by Chauvin *et al*. [14]. In **4** the C3 carbon bearing the vinyl substituent stands only 0.255 Å above the C=N–N plane, thus 0.18 Å less than the mean value of similar derivatives. Interestingly all atoms of the carboxylate substituent and as well as the phosphorous atom are also embedded in this plane supporting a significant electron delocalization. This contrasts with the structures of sulfonyl pyrazolines where the sulfur stands out of this plane [14].

The plane of the vinyl group and its connected carbon from the pyrazoline make a 78.35 ° angle with the plane of the pyrazoline. This plane crosses one of the phenyl rings of the phosphinic substituent making an angle of 60.96 ° with its plane. The second phenyl ring lies below the plane with its centre standing 3.079 Å below the pyrazoline plane.

The two phenyl rings of the phosphinic moiety form an angle of 75.28 °. All these structural features confer to the molecule a cross-shape with one perfectly flat part and the second with substituents pointing away on each side of the plane.

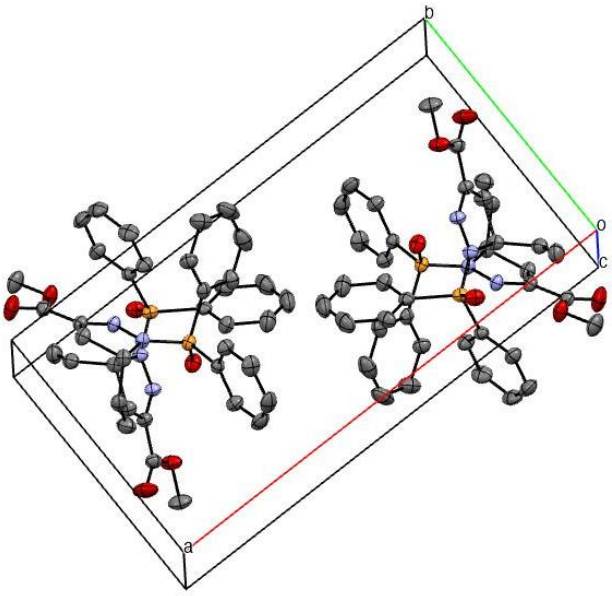

Figure 8: Unit Cell of crystallized **4**

Within the unit cell which contains 4 molecules (Figure 8), it can be viewed that the phosphinic moieties are pointing toward the center of the cell and that the P=O bonds exhibit an alignment that suggest Keesom forces between these permanent dipoles to be the driving force of the packing. The head-to-tail positioning of the pyrazoline may represent another illustration of such Keesom forces. Further London interaction between the phenyl substituents might support the relative position of the phenyl groups within the unit cell.

Conclusion

In conclusion, we have discovered a new route to the scarcely illustrated vinyl-pyrazoline scaffold from a diazo compound through the phosphorous based activation of the latter. This synthetic approach proceeds under very smooth conditions thus contrasting with the usually high temperatures required to access this moiety. Furthermore, the reaction generates very few wastes, and thus represents a sustainable way to access the pyrazoline scaffold. The structure has been thoroughly supported by spectroscopic means; both the scaffold and the unusual substitution pattern of the pyrazoline have been confirmed by X-ray diffraction. The pyrazoline exhibits a limited deviation from planarity and the delocalization toward the substituents is assessed by their coplanarity. The crystal packing is indicative of a strong influence of the P=O dipole in the crystal organization. We are currently investigating

the influence of the substitution pattern on this reaction and generalization of this route to a range of structurally diverse pyrazolines will be reported in due course.

Experimental

General Information

Solvents, Reagents, and General procedures:

All chemicals were purchased from commercial sources (Sigma-Aldrich, Acros, Alfa Aesar and Tokyo Chemical Industry, Fluorochem and BLDPharm) and used as received unless otherwise noted. Solvents used were all commercial grade and used as received with no drying unless otherwise noted. Dry solvents were obtained by solvent purification system (SPS) MBraun SPS-800 from previously degassed solvents, pressurized under argon through two filters columns filled with 4Å molecular sieve. All reactions were performed in oven-dried glassware under argon atmosphere unless otherwise stated. Deuterated solvents for NMR spectroscopic analysis were purchased from Euriso-Top.

4Å Molecular sieve is activated heating to 150°C under high vacuum overnight in a two-necked round-bottomed flask.

Purification by flash column chromatography (FCC) is carried out on a Interchim PuriFlash XS520+ using Interchim PuriFlash Columns Si-HP 30µ unless otherwise indicated.

Analysis:

Reactions were monitored using Merck Silica gel 60 F_{254} glass backed plates. TLC plates were visualized by UV fluorescence (λ= 254, 365 nm), potassium permanganate $KMNO_4$ and/or phosphomolybdic acid (PMA) staining.

Melting points of crystals have been recorded on a Stuart SMP40 automatic melting point apparatus.

NMR experiments were performed in deuterated solvents. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker AVANCE III HD 500 MHz (2013) 2 channels equipped with a Prodigy 5mm BBO, ^{1}H or ^{19}F ATMA cryoprobe optimized for the observation of heteronuclei. The $^{13}C\{^{1}H, ^{31}P\}$ and ^{1}H, ^{31}P J-resolved experiment was acquired on an 800MHz Bruker NEO spectrometer equipped with a QCPI cryogenic probe head. All spectra were recorded at ambient temperature (298 K). Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane and relative to the residual proton (^{1}H) of the deuterated

solvents $CDCl_3$ ($CHCl_3$, δ = 7.26 ppm) for ^{1}H-NMR or the carbon (^{13}C) of solvents $CDCl_3$ (δ = 77.2 ppm) as internal standards. The J-resolved experiment was acquired as two matrices of 16k x 64 complex points for a window of 12ppm x 60Hz.[18] Multiplicity of signals is indicated using the following abbreviations: s (singlet), b (broad), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), dt (doublet of triplet), hept (heptet) and m (multiplet). Coupling constants (J) are given in Hz.

IR spectra were recorded on a Benchtop FTIR Instruments Cary 630 FTIR Spectrometer with an ATR sampling module and frequencies expressed in cm^{-1}.

High resolution mass spectra were acquired on a Waters GCT Premier spectrometer for DC (CH_4) ionization mode or Waters XevoG2QTof for ES ionization mode.

Xray diffraction of monocrystals was acquired at 193K by using phi- and omega- scans on a Bruker-AXS kappa APEX II Quazar diffractometer using a 30 W air-cooled MoK_α microfocus source (λ = 0.71073Å) with focusing multilayer optics. Bruker-AXS softwares were used for structures determination (SAINT and SADABS).

Methyl 1-(diphenylphosphoryl)-5-vinyl-4,5-dihydro-1H-pyrazole-3-carboxylate (4).

To 205 mg of methyl (Z)-2-diazo-6-hydroxyhex-4-enoate **3** (1.2 mmol) in dichloromethane (5 mL) in a round bottom flask under argon at room temperature (25 °C) was added triethylamine (1.2 equiv., 1.44 mmol, 146 mg, 0,21 ml) followed by chlorodiphenylphosphine (1.2 equiv., 1,44 mmol, 319 mg, 0,27 ml). The reaction mixture was further stired for 16h at room temperature, then quenched by an addition of water (5ml). The reaction medium was then extracted with ethyl acetate (3 x 25 ml); the organic phase was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The remaining oil was purified by flash chromatography (dichloromethane/ethyl acetate) yielding 298 mg of a white powder (0.842 mmol, 70%) after removal of the solvents under reduced pressure. Suitable crystals for Xray Diffraction were obtained by slow evaporation of a saturated solution in toluene.

M.P. : 142.1 °C.

^{1}H NMR (500 MHz, $CDCl_3$): 7.90-7.83 (4H, m); 7.60-7.53 (2H, m); 7.52-7.44 (4H, m); 5.84 (1H, ddd, $^3J_{trans}$ 17 $^3J_{cis}$ 10 $^3J_{allyl}$ 8); 4.98 (1H, ddd, $^3J_{trans}$ 17 ^2J 1 $^4J_{allyl}$ 1); 4.98 (1H, ddd, $^3J_{cis}$ 10 ^2J 1 $^4J_{allyl}$ 1); 4.86 (1H, dddddd, ^3J 12 $^3J_{allyl}$ 8 ^3J 7 $^3J_{PH}$ 2 $^4J_{allyl}$ 1 $^4J_{allyl}$ 1); 3.81 (3H, s); 3.32 (1H, dd, ^2J 18 ^3J 12); 2.93 (1H, ddd ^2J 18 ^3J 7 $^4J_{PH}$ 2)

^{13}C NMR (125 MHz, $CDCl_3$): 162.5 (s, C=O); 146.0 (d, $^3J_{PC}$ 13, C=N); 136.5 (s, CH_{Et}); 132.5 (d, $^3J_{PC}$ 8, $2CH_{Ar}$); 132.4 (d, $^4J_{PC}$ 7, $2CH_{Ar}$); 132.4 (d, $^3J_{PC}$ 8, $2CH_{Ar}$); 131.6 (d, $^1J_{PC}$ 62, $C_{Ar\text{-}q}$); 130.6 (d, $^1J_{PC}$ 60, $C_{Ar\text{-}q}$); 128.6 (d, $^2J_{PC}$ 11, $2CH_{Ar}$); 128.5 (d, $^2J_{PC}$ 11, $2CH_{Ar}$); 117.2 (s, CH_{2Et}); 63.5 (d, $^2J_{PC}$ 4, CH_{allyl}); 52.4 (s, OCH_3); 39.0 (d, $^3J_{PC}$ 3, CH_2).

$^{31}P\{^1H\}$ NMR (202 MHz, $CDCl_3$): 26.62

I.R. (ν): 1707, 1569

HRMS (DCI-CH_4): calcd for : $C_{19}H_{20}N_2O_3P$ (MH^+) 355.1212 found : 355.1214.

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