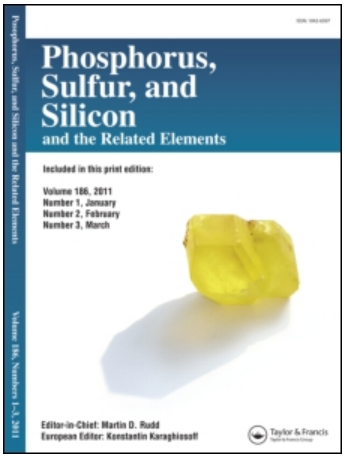

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PHOSPHINIMINES DERIVED FROM PHOSPHOLE DIMERS BY THE STAUDINGER REACTION

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The Staudinger reaction of phenyl azide with the phosphine groups of phosphole dimers gives bis(phenylimino) derivatives. Hydrolysis or methanolysis leads to diphosphine dioxides with retention of configuration at the bridging phosphorus and inversion at the 2-phospholene phosphorus. This reaction is useful in providing access to a new isomeric form of the phosphole oxide dimer framework. Amines catalyze the rearrangement at the 2-phospholene phosphorus to the isomeric form which is commonly produced on dimerization of phosphole oxides. Amides also catalyze the inversion at the 2-phospholene group in the Staudinger product. Both the original and the rearranged Staudinger product were found to be reduced with trichlorosilane to give the same diphosphine.

The two phosphorus atoms in the phosphole dimer framework exhibit quite different properties;[1] the atom in the bridging position (P_8) is strongly influenced by the contracted C—P—C bond angle and by the forced proximity to the double bond, while the atom in the 2-phospholene moiety (P_1) displays normal tertiary phosphine character. We have now found that both phosphine centers react rapidly with phenyl azide in the Staudinger reaction to form phenylimino derivatives. Stereochemical properties of the products, and the unusual stereochemistry of some of their reactions, are described in this report.

Synthesis and Properties of Bis(phosphinimines)

Two bis(phenylimino) derivatives (**2** and **4**) were prepared from phosphole dimers **1** and **3** by reaction with phenyl azide in toluene at 0°C. The imino compounds precipitated from the medium. Since they were sensitive to the atmosphere and also thermally unstable, their properties were studied immediately after their synthesis, without further purification. The thermal instability is derived from the ready occurrence of a retro-cycloaddition process involving the bridging phosphorus. Many examples of this process are known,[1] and it results in the formation of a dihydrophosphindole derivative. In the case of **2** and **4**, the products would be **5** and **6**, respectively. These products have characteristic ^{31}P NMR signals, and in one case (**5**) the identity was confirmed by high resolution mass spectrometry. The fragment presumed to be ejected [RP = NPh] belongs to a class well-known to be unstable unless protected by large substituents. Its fate in this process is uncertain at this time.

The mass spectra of the phosphinimines, not surprisingly, fail to show a peak

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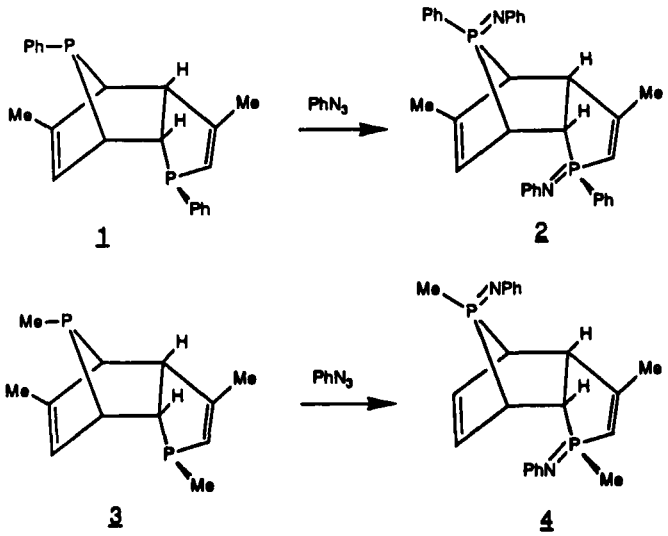
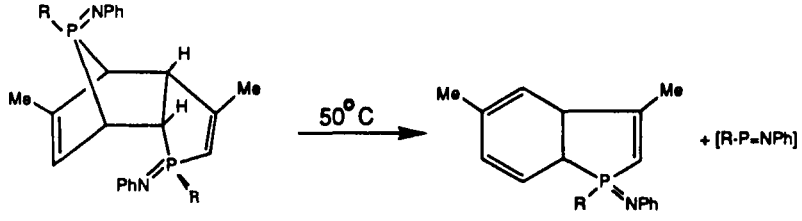


1 2

3 4

for the molecular ion. Various ions from the loss of the bridging phosphorus are present; the base peak from **2** is in fact the dihydrophosphindole ion, and an ion for the ejected fragment $HPhN=PPh^+$ is also prominent (m/z 200, 24%). Similar fragments arise from **4**; here the base peak is m/z 122, $PhN=P^+$, and the dihydrophosphindole ion is 59% of the base.



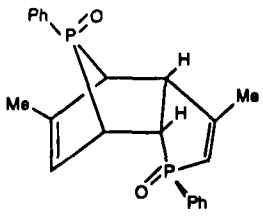
5, R = Ph

6, R = Me

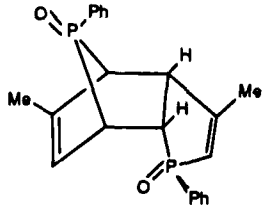
The ^{31}P NMR spectra of the phosphinimines show the expected doublet of doublets, with the bridging P assumed to cause the more downfield signal as is customary in the dimer framework[2] (**2**, δ $^{31}P + 57.3$ and $+71.9$, $^3J_{PP} = 41.5$ Hz; **4**, δ $^{31}P + 65.9$ and $+79.7$, $^3J_{PP} = 41.5$ Hz).

The structures **2** and **4** assigned to the products are those from retention of the configuration at both phosphorus nuclei. This is a reasonable assumption, since all other P(V) conversions occur with retention in the phosphole dimer system,[1a] and Staudinger products of simpler phosphines also form with retention.[3]

Hydrolysis of the imino compounds occurs simply on stirring a chloroform solution containing a small amount of water for a few minutes at room temperature. That the products are dioxides was confirmed by high resolution mass spectrometry, which gave the expected molecular ion. However, the ^{31}P NMR spectra of the dioxides did not match those of previously known structures. Thus, the δ values of the product from the hydrolysis of **2** are

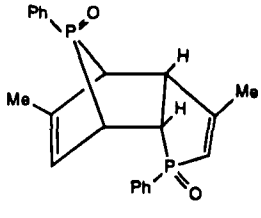


7, δ +55.1, +81.7[36]
$^3J_{PP}$ = 40 .0 Hz



8, δ +57.7, +83.3[4]
$^3J_{PP}$ = 40.4 Hz

^{31}P + 57.1 and +79.4, $^3J_{PP}$ = 36.6 Hz; data for known dioxides are shown below. Since the large value for $^3J_{PP}$ precludes the possibility that *exo* fusion is present,[1c] the only explanation is that a new form isomeric at P_1 has resulted from the imino compound. Of the two possibilities (**9** and **10**), only **9** is allowed from a study of the ^{13}C NMR spectrum of the product. This decision is based on the two-bond



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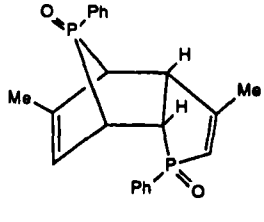
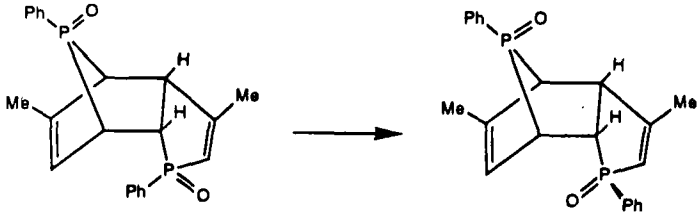
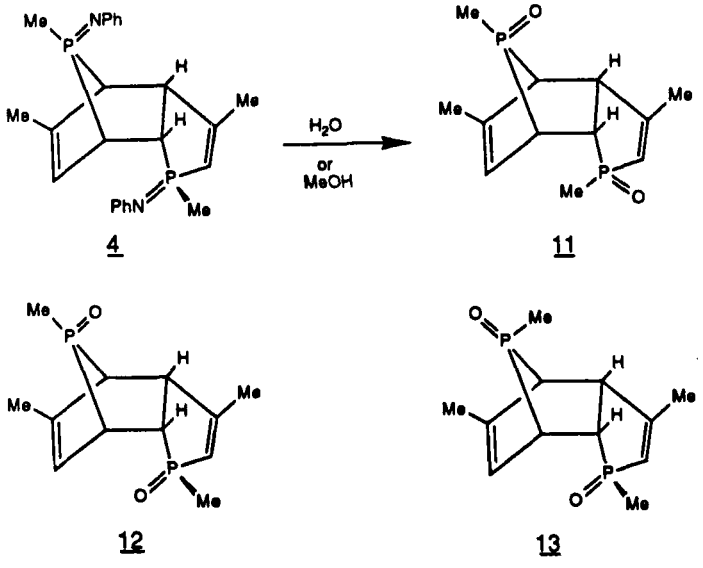


10

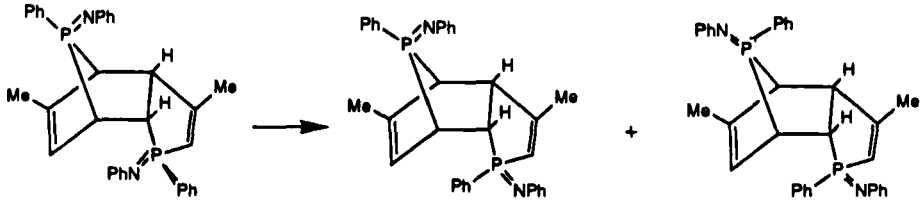
coupling constants for the bridging ^{31}P to C-3a and C-7a. The values are 13.2 and 15.4 Hz, close to those for compound **7** (12.0 and 11.6 Hz, respectively). These couplings are sterically controlled in the 7-phosphanorbornene system and, as noted for phosphine oxides,[2,5] the isomeric compound **8** with *anti*-phenyl at the bridging position would have much larger couplings to C-3a and C-7a. It must therefore be concluded that the hydrolysis of the imino groups of **2** has occurred with stereochemical retention at the angle-constricted bridging phosphorus but with inversion at the 2-phospholene phosphorus (as noted for acyclic phosphinimines[3a]). Further proof of the stereochemical assignments came from the observation that dioxide **9** is quite unstable in water and rearranges to give the known isomer **7**. Triethylamine and diethylamine cause virtually instantaneous rearrangement at room temperature. Phosphinimine **4** on hydrolysis or methanolysis also gives a dioxide (**11**) that is isomeric with the known dioxides



9 7



(**12**, **13**). The Staudinger product **2** isomerizes rapidly at the 2-phospholene position by triethylamine or diethylamine at 0°C. A small amount of another isomer forms, presumably arising from isomerization also at the bridging position. On hydrolysis in a chloroform-water medium at room temperature, **14** rapidly is converted to dioxide **7**, again a result that requires inversion of configuration at the 2-phospholene phosphorus.



2

14, 85 %

$\delta^{31}P$ = +33.6, +60.5

J_{PP} = 36.6 Hz

15, 15 %

$\delta^{31}P$ = +33.6, +79.9

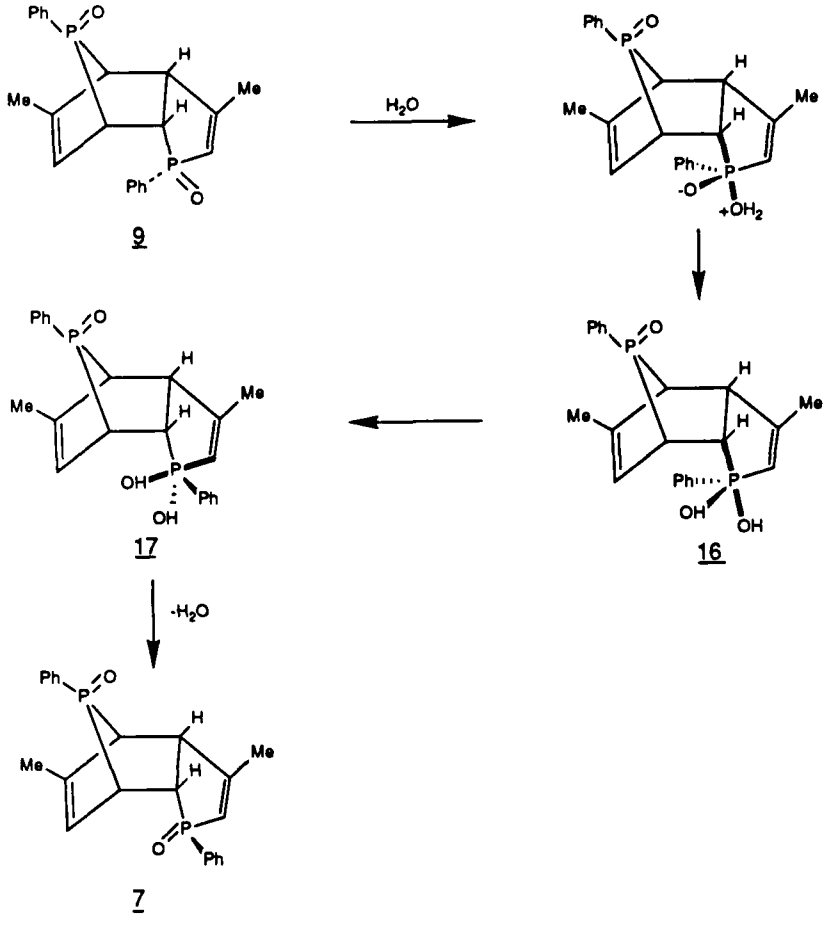
J_{PP} = 36.6 Hz

Trichlorosilane in chloroform at 0–25°C is effective for the reduction of the phosphinimines to the phosphines. It was expected that this reaction as applied to **2** and **14** would provide isomeric phosphines owing to the configurational difference in these substances at P_1. However, both give the same diphosphine, which proved to be identical to the starting compound **1**. Thus, **2** is reduced with retention and **14** with inversion at the P_1 center, and with retention at P_8 in both compounds. Isomerization *via* a P(V) intermediate, known to form in trichlorosilane reductions, has again occurred, and has provided the more stable phosphine. The behavior of phosphine oxide **9** in this process was then explored, since this substance also might be expected to isomerize to the less crowded form. This is indeed the case; reduction of dioxide **9** occurs with retention at P_8 and inversion

at P_1 to regenerate **1**. Up to the present, no unusual chemistry had been encountered at P_1, and only derivatives with the P-substituent *exo* to the ring has been available. These studies now reveal the pronounced tendency for this phosphorus to adapt to steric hindrance effects by isomerization to relieve crowding.

Stereochemical implications

The Staudinger reaction products of phosphole dimers are seen to offer an entry into a previously unknown configuration at the 2-phospholene phosphorus. In all known oxides, the P-substituent has been *syn* to the hydrogens at the ring fusion carbons (C_{3a} and C_{7a}), but hydrolysis of the Staudinger products leads to an *anti* position for this substituent. The instability of this configuration is evident, however, from the great ease of its isomerization to the *syn* arrangement. The instability seen also in the Staudinger product, as reflected in the ease of rearrangement of the phenylimino group from the *anti* to the *syn* orientation relative to the fusion hydrogens, may derive from the same property, the presence of interactions between large substituents on the 2-phospholene



phosphorus when projected toward the molecular framework. The formation of P(V) intermediates (**16**) with nucleophilic species provides a mechanism for isomerization to less crowded P(V) structures (e.g. **17**) which collapse to P(IV) products. The process is illustrated with the oxide isomerization, **9** to **7**.

The amine-promoted rearrangement of the initial phosphinimine from the Staudinger reaction to a more stable form may derive from interactions from a $C_6H_5N=$ group on the *anti* face. Such interactions must exceed those from a C_6H_5 group. The trichlorosilane reductions of **2**, **14**, and **9**, which all give the same phosphine **1**, may be similarly explained. These reductions proceed through P(V) intermediates,[1a] which provide the mechanism for equilibration to the less crowded configuration at P_1.

EXPERIMENTAL

General. Proton-decoupled, Fourier transform NMR spectra were obtained on a JEOL FX90Q spectrometer. Carbon-13 spectra were referenced to internal tetramethylsilane; phosphorus-31 spectra were referenced to external 85% phosphoric acid, with downfield signals given positive signs. High resolution mass spectra were obtained by the Midwest Center for Mass Spectrometry, University of Nebraska–Lincoln. Phosphate dimers **1** and **3** were prepared by a modification of a previously described[1a] procedure. Dimer **1** was prepared by adding 1.28 ml (15.8 mmol) of pyridine and 0.58 ml (5.26 mmol) of trichorosilane to 1.0 g (2.63 mmol) of the corresponding dioxide **7** in 25 ml of degassed benzene. After 4 h of reflux (under nitrogen), the mixture was filtered and the filtrate evaporated, finally under high vacuum, to leave an oily residue of **1** (0.9 g, 98%) that was satisfactory for reaction with phenyl azide. Dimer **3** was prepared similarly. Both dimers were protected with nitrogen during preparation and storage.

Reaction of Phosphole Dimer 1 with Phenyl Azide. The dimer (0.9 g, 2.6 mmol) in 25 ml of dry, deoxygenated toluene was treated at 0°C with a solution of 0.62 g (5.2 mmol) of phenyl azide in 5 ml of toluene. The addition required 15 min; the solution was stirred an additional hour at 0°C, and then for 1 h at room temperature. Gas evolution occurred during the reaction. The precipitated product was filtered off, washed with n-pentane and dried *in vacuo* to give 0.43 g (31%) of bis(phenylimino) compound **2**; ^{31}P NMR ($CDCl_3$) δ +57.3 and +71.9, d of d, $^3J_{PP} = 41.5$ Hz; mass spectrum (M^+ absent), m/z 332 (24%), 331 (100%, $M^+ - PhN{=}PPh$), 330 (72%), 200 (24%, $HPhN{=}PPh^+$), 122 (36%, $Ph{-}N{=}P^+$ or $Ph{-}P{=}N^+$); ^{13}C NMR ($CDCl_3$; partial) δ 37.8 (d of d, $J_{CP_1} = 64.8$, $J_{CP_8} = 14.3$ Hz, C_{7a}), 41.5 (d, $J_{CP_8} = 61.5$ Hz, C_7), 46.6 (d, $J_{CP_8} = 63.7$ Hz, C_4), 55.6 (apparent t, $J_{CP_1} = J_{CP_8} = 13.2$ Hz, C_{3a}), 167.4 (d of d, $J_{CP_1} = 23.1$, $J_{CP_8} = 9.9$ Hz, C_3).

Reaction of Phosphole Dimer 3 with Phenyl Azide. Using the same quantities and conditions as above, dimer **3** gave a crude oily product containing only about 60% of bis-imino compound **4**; ^{31}P NMR ($CDCl_3$) δ +65.9 and +79.7, d of d,

$^3J_{PP} = 41.5$ Hz; mass spectrum (M^+ absent), m/z 270 (20%), 269 (59%, M^+ – MeP=NPh), 268 (62%), 138 (40%, MeP=NPhH$^+$), 122 (100%, PhP=N$^+$).

Isomerization of Bis-Phosphinimine 2. To a solution of 0.43 g (0.811 mmol) of phosphinimine **2** in 25 ml of dry deoxygenated chloroform at 25°C was added dropwise 1.5 ml (10.8 mmol) of triethylamine. The mixture was stirred for 10 min and then evaporated to dryness. The residue consisted of two compounds: major isomer (**14**, 90%) ^{31}P NMR ($CDCl_3$) δ +33.6 and +60.5, $^3J_{PP} = 36.6$ Hz; minor isomer (**15**, 10%) δ +33.6 and +79.9, $^3J_{PP} = 36.6$ Hz. Neither spectrum corresponded to that of **2**, but the mass spectra were very similar. Partial ^{13}C NMR ($CDCl_3$) for **14** δ 40.9 (d of d, $J_{CP_1} = 69.1$, $J_{CP_8} = 13.2$ Hz, C_{7a}), 42.8 (d, $J_{CP_8} = 60.4$ Hz, C_7), 48.0 (d, $J_{CP_8} = 67.0$ Hz, C_4), 54.1 (apparent t, $J_{CP_1} = J_{CP_8} =$ 12.1 Hz, C_{3a}), 161.1 (d of d, $J_{CP_1} = 22.5$, $J_{CP_8} = 10.5$ Hz, C_3).

Hydrolysis of Phosphinimine 2. A solution of 0.35 g (0.66 mmol) of **2** in 20 ml of chloroform was treated with 1 ml of water at room temperature. The mixture was stirred for 10 min and then the chloroform phase was dried ($MgSO_4$) and evaporated to give 0.24 g of residue consisting almost entirely of diphosphine dioxide **9**. Attempts at purifying the sample on chromatographic columns led to isomerization to **7**. The crude sample was used in obtaining spectral data; high resolution mass spectrum, calcd for $C_{22}H_{22}O_2P_2$ (M^+) 380.1097, found m/z 380.1092, low resolution MS, m/z 380 (34%), 256 (100%, M^+ – PhPO), 125 (18%, PhPOH); ^{31}P NMR ($CDCl_3$) δ +57.1 and +79.4, d of d, $^3J_{PP} = 36.6$ Hz; partial ^{13}C NMR ($CDCl_3$) δ 18.7 (d, $J_{CP_8} = 3.3$ Hz, C_5—$\underline{C}H_3$), 19.6 (d, $J_{CP} =$ 18.7 Hz, C_3—$\underline{C}H_3$), 39.1 (d of d, $J_{CP_1} = 70.3$, $J_{CP_8} = 15.4$ Hz, C_{7a}), 41.9 (d, $J_{CP_8} = 60.4$ Hz, C_7), 47.2 (d, $J_{CP_8} = 64.8$ Hz, C_4), 56.1 (apparent t, $J_{CP_1} = J_{CP_8} =$ 13.2 Hz, C_{3a}), 113.8 (d, $J_{CP_1} = 101.1$ Hz, C_2), 168.8 (d of d, $J_{CP_1} = 24.2$, $J_{CP_8} =$ 9.9 Hz, C_3).

The same result was obtained from the reaction of **2** with methanol after 1 day at room temperature.

Hydrolysis of Phosphinimine 14. The reaction was conducted as for **2** on 0.10 g (0.19 mmol) of phosphinimine **14** and provided diphosphine dioxide **7** as indicated by ^{31}P NMR ($CDCl_3$) δ +54.6 and +80.8, d of d, $^3J_{PP} = 36.6$ Hz, which matched a known specimen.

Reaction of Phosphinimine 4 with Methanol. A mixture of 0.10 g (0.246 mmol) of **4** and 0.15 ml (3.7 mmol) of methanol in 0.5 ml of $CDCl_3$ was allowed to stand at room temperature for 12 h. Examination of the solution by ^{31}P NMR revealed only the presence of diphosphine dioxide **11**, δ +67.2 and +88.2, $^3J_{PP} = 41.5$ Hz. High resolution mass spectrum, calcd for $C_{12}H_{18}O_2P_2$ 256.0783; found for M^+, m/z 256.0785; low resolution MS 256 (11%, M^+), 194 (78%, M^+ – MePO), 179 (100%, M^+ – MePO – Me).

Reductions with Trichlorosilane. A 0.1 g sample of the substrate in 0.5 ml of $CHCl_3$ was treated with 0.3 ml of trichlorosilane at 0°C in an NMR tube. The solution was allowed to warm to room temperature. For phosphinimines **2** and

14, the reaction was complete after 20 min; for diphosphine dioxides **9** and **7**, the reaction required 1 h. In every case, the only product observed was determined to be phosphole dimer **1**; ^{31}P NMR[1a] δ +114.2 and +15.7, $^{3}J_{PP} = 24.4$ Hz.

Thermal Decomposition of Phosphinimine 2. A solution of **2** (0.15 g, 0.28 mmol) in 0.5 ml of $CDCl_3$ was sealed under nitrogen in an NMR tube and heated at 55°C. Progress of the decomposition was monitored by ^{31}P NMR; after 2 days, all **2** had decomposed and the major product was dihydrophosphindole derivative **5**, δ ^{31}P + 64.3. The identity of **5** was confirmed by high resolution mass spectrometry, calcd for $C_{22}H_{22}NP$ 331.1490, found m/z 331.1491.

ACKNOWLEDGEMENT

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