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## Phosphorus, Sulfur, and Silicon and the Related Elements

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### An Efficient Synthesis of New Stable Phosphorus Ylides Containing Sulfur and Nitrogen Atoms

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## An Efficient Synthesis of New Stable Phosphorus Ylides Containing Sulfur and Nitrogen Atoms

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*2-acetyl-3-anilinophenyl-2-butenamide, which is readily accessible from the reaction of 4-phenylaminopent-3-en-2-one with phenyl isocyanate, reacted with dialkyl acetylenedicarboxylate in the presence of  $\text{Ph}_3\text{P}$  in the mixture of hexane-ethyl acetate (1:2) as a solvent to give new stable phosphorus ylides. Similarly, 1-naphthalenethiol reacted with acetylenic esters in the presence of  $\text{Ph}_3\text{P}$  to give novel phosphorus ylides.*

**Keywords** Stable phosphorus ylides; 1-naphthalenethiol;  $\beta$ -enamino ketones

### INTRODUCTION

Phosphorus compounds such as phosphorus ylides have attracted considerable attention in recent years in organic synthesis.<sup>1–3</sup> They have been widely used as precursors in many reactions to provide heterocyclic compounds,<sup>4</sup> alkenes,<sup>5</sup> and drugs.<sup>6</sup>

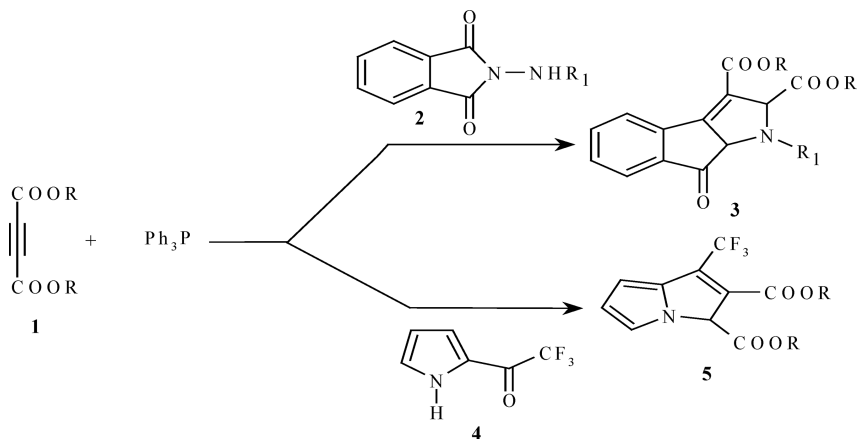
Several methods have been developed for the preparation of phosphorus ylides. These compounds are usually prepared by treatment of a desired phosphonium salt with a base, and usually these salts are synthesized from triphenylphosphine and alkyl halides.<sup>7,8</sup>

Recently, we have synthesized pyrrazoloisindole and pyrrolizine derivatives using stable phosphorus ylides as key intermediates from acetylenic esters, N-aminophthalimide, or 2,2,2-trifluoro-1-(1H-pyrrol-2-yl)ethanone bearing NHR or NH groups by a Michael addition-Wittig olefination sequence<sup>9,10</sup> (Scheme 1).

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SCHEME 1

These reactions start with the Michael addition of the  $\text{Ph}_3\text{P}$  to the carbon-carbon triple bond of dialkyl acetylenedicarboxylate **1** and a sequent protonation of the adduct followed by another Michael addition leading to form stable phosphorus ylides, which then can undergo an intermolecular Wittig reaction to give heterocycles **3** and **5**.

Herein we wish to report a simple and an efficient route for the synthesis of stable phosphorus ylides using triphenylphosphine, dialkyl acetylenedicarboxylate in the presence of 1-naphthalenethiol or anilino-butenamide derivative as a proton source in the mixture of hexane-ethyl acetate (1:2) as a solvent in good to excellent yields.

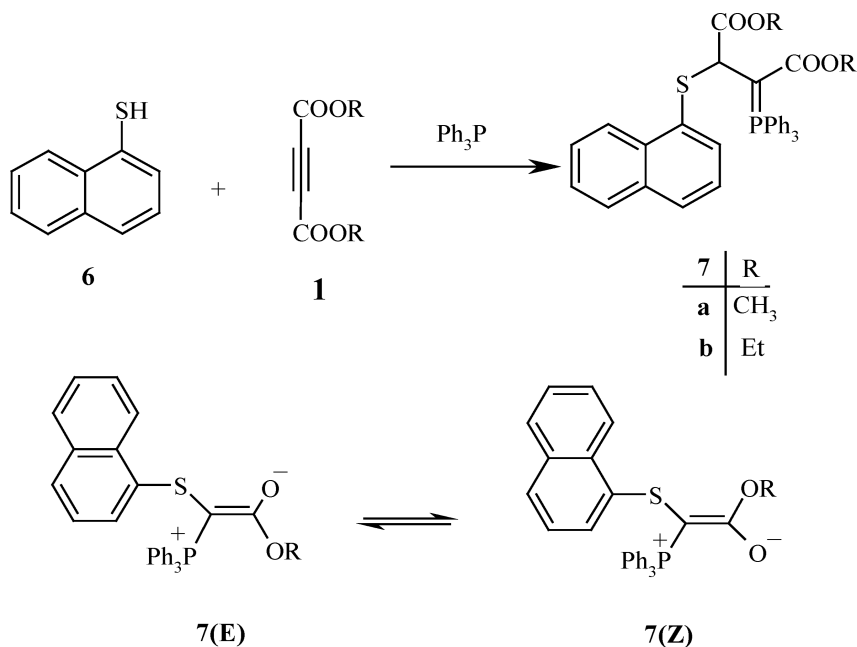
## RESULTS AND DISCUSSION

### Reaction of 1-Naphthalenethiol with Acetylenic Esters

1-naphthalenethiol **6** reacted with dialkyl acetylenedicarboxylate at r.t. in the presence of triphenylphosphine in a hexane-ethyl acetate mixture to give two products, **7a** and **7b** (Scheme 2).

The structures of two products were characterized by their IR, high-field  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra, and elemental analyses.

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of compound **7a** exhibited a mixture of two rotational isomers. The ylide moiety of these compounds was strongly conjugated with the adjacent carbonyl group, and rotation about the partial double bond in **7(E)** and **7(Z)** geometrical isomers was low on the NMR timescale at r.t.

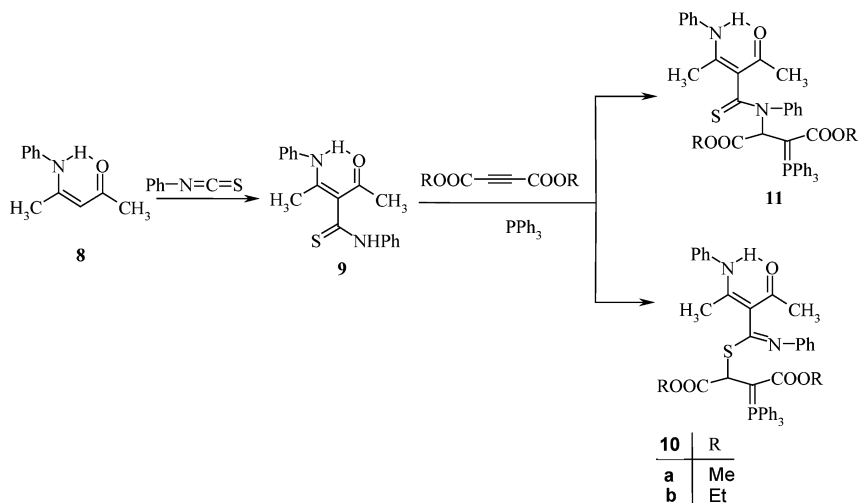


SCHEME 2

The  $^1\text{H}$  NMR spectrum of compound **7a** displayed four sharp lines ( $\delta = 3.14, 3.61, 3.65$ , and  $3.67$  ppm) arising from methoxy protons along with signals for methine protons at  $\delta = 4.29$  and  $4.41$  ppm, which appeared as two doublets ( $^3J_{\text{PH}} = 19.1$  Hz and  $^3J_{\text{PH}} = 18.5$  Hz, respectively) for the major and minor geometrical isomers. The  $^{13}\text{C}$  NMR spectrum of **7a** exhibited signals that were also in agreement with the mixture of two rotational isomers. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of **7b** were similar to those of **7a**, except for the ester groups, which exhibited peaks with appropriate chemical shifts.

### Reaction of 4-Phenylaminopent-3-en-2-One with Acetylenic Esters

$\beta$ -enaminocarbonyl derivatives have been of considerable interest owing to their potential use as 1,3-dielectrophile synthons in organic synthesis. Several methods have been reported for the synthesis of  $\beta$ -enaminoketones using amines and desired 1,3-dicarbonyl systems.<sup>11–14</sup> The functionalization of these compounds by the introduction of different substituents, such as chloroacetylchloride as a bielectrophilic



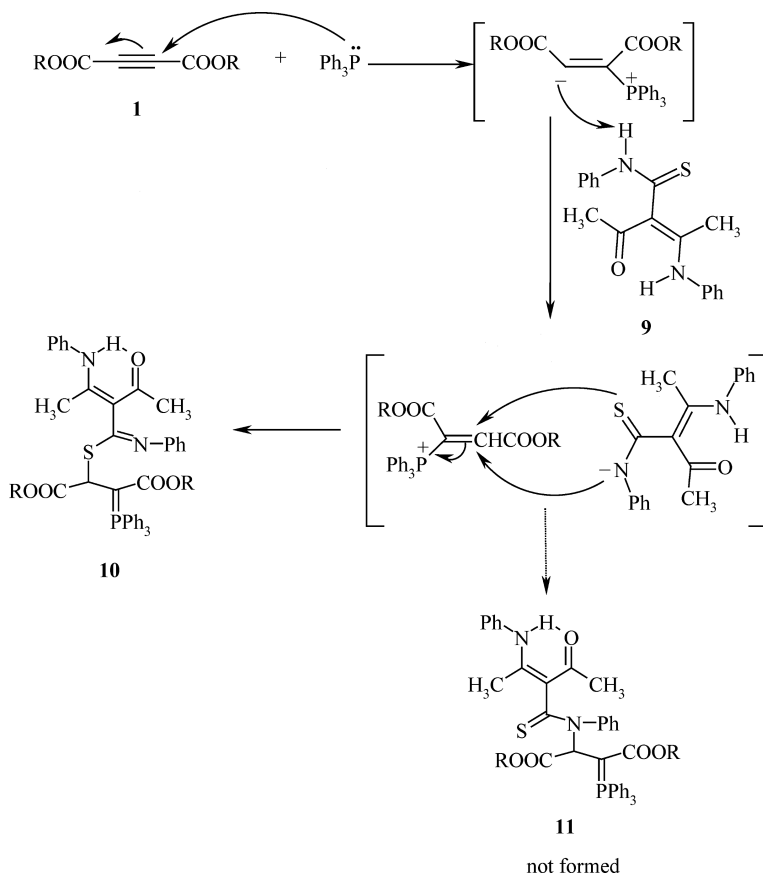
SCHEME 3

on nitrogen and  $\alpha$ -carbon, has been studied and reported in the literature.<sup>15</sup>

Also, we report the reaction of  $\beta$ -enamino ketone **8** with phenyl thioisocyanate yielding corresponding compounds **9** in excellent yields via a sequence of C-thioacylization of enamino tautomer **8** in the presence of montmorillonite K<sub>10</sub> clay (Scheme 3).<sup>16</sup> Compound **9** was further treated with dialkyl acetylenedicarboxylate at r.t. in the presence of triphenylphosphine, and the corresponding phosphorus ylides formed in high yields. The <sup>13</sup>C NMR spectroscopy was applied to distinguish structure **10** from **11**. The NMR spectrum of **10** displayed signals for S=C=N group in  $\delta = 171.07$  ppm, while in the case of compound **11**, the signal of N=C=S group should be appeared at about 180–190 ppm.

Based on the well-established chemistry of trivalent phosphorus compounds, a reasonable reaction mechanism for the formation of compound **10a–b** is depicted in Scheme 4. Phosphorus ylides **10a–b** resulted from the initial addition of Ph<sub>3</sub>P to the acetylenic ester **1** and a concomitant protonation of 1:1 adduct by NH-acid **9**, and then the positively charged ion was attacked by the sulfide anion. It is pertinent to note that in this reaction, compound **11** was not formed. This process shows that in the final step of the mechanism, the sulfide anion acts as a stronger nucleophile than the nitrogen anion.

In conclusion, we have developed a simple and an efficient method for the synthesis of phosphorus ylides via three-component reactions



SCHEME 4

containing  $\text{Ph}_3\text{P}$ , acetylenic esters, and N-H acid in good to excellent yields.

## EXPERIMENTAL

Dialkyl acetylenedicarboxylates and triphenylphosphine were obtained from Merck Chemical Co. (Hohenbrum, Germany) and were used without further purification. Compound **8** was prepared according to the reported procedure in the literature.<sup>17</sup> Melting points were obtained on a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses for C, H, and N were performed using a Heracus CHN-O-Rapid analyzer. IR spectra were measured on a Mattson 1000 FT-IR spectrometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a

BRUKER DRX-500 AVANCE spectrometer at 500 and 125.77 MHz, respectively.

### **Dimethyl 2-(2-Naphtylsulfanyl)-3-(1,1,1-Triphenyl- $\lambda^5$ -Phosphanylidene) Succinate**

At ambient temperature dimethyl acetylenedicarboxylate (0.24 mL, 2.00 mmol) was added dropwise to a stirred solution of triphenylphosphine (0.53 g, 2.00 mmol) and 1-naphthalenethiol (0.32 g, 2.00 mmol) in a mixture of hexane-ethyl acetate (6.00 mL, 1:2). After the addition was complete (approximately 30 min), the mixture was stirred for an additional 1 h and was subsequently filtered. The solid collected in the filter was washed thoroughly with ethyl acetate to give a white powder.

(0.97 g, m.p. 166–168°C, yield 98%); IR (KBr) ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 1741 and 1641 (C=O). Anal. calcd. for  $\text{C}_{34}\text{H}_{29}\text{O}_4\text{PS}$  (564.65): C, 72.32; H, 5.18; S, 5.68%. Found: C, 71.90; H, 5.22; N, 5.79%. Isomer (Z) (50%)  $^1\text{H}$  NMR:  $\delta$  3.14, 3.65 (6H, 2s, 2  $\text{OCH}_3$ ), 4.29 (1H, d,  $^3\text{J}_{\text{PH}}$  19.1 Hz,  $\text{P}=\text{C}-\text{CH}$ ), 7.26–7.70 (44 H, m, arm) (for two rotamers).  $^{13}\text{C}$  NMR:  $\delta$  42.03 (d,  $^1\text{J}_{\text{PC}}$  125.1 Hz,  $\text{P}=\text{C}$ ), 49.13, 52.52 (2  $\text{OCH}_3$ ), 54.20 (d,  $^2\text{J}_{\text{PC}}$  11.0 Hz,  $\text{P}=\text{C}-\text{CH}$ ), 125.57–134.88 (carbons of aromatic rings) (for two rotamers),  $^{18-20}$  165.33 (C–S) (for two rotamers), 169.20 (d,  $^2\text{J}_{\text{PC}}$  13.4 Hz, C=O), 173.00 (d,  $^3\text{J}_{\text{PC}}$  25.2 Hz, C=O). Isomer (E) (50%),  $^1\text{H}$  NMR:  $\delta$  3.61, 3.67 (6H, 2s, 2  $\text{OCH}_3$ ), 4.41 (1H, d,  $^3\text{J}_{\text{PH}}$  18.5 Hz,  $\text{P}=\text{C}-\text{CH}$ ).  $^{13}\text{C}$  NMR:  $\delta$  43.22 (d,  $^1\text{J}_{\text{PC}}$  135.8 Hz,  $\text{P}=\text{C}$ ), 50.35 and 52.55 (2  $\text{OCH}_3$ ), 54.74 (d,  $^2\text{J}_{\text{PC}}$  12.0 Hz,  $\text{P}=\text{C}-\text{CH}$ ), 170.43 (d,  $^2\text{J}_{\text{PC}}$  20.2 Hz, C=O), 172.98 (d,  $^3\text{J}_{\text{PC}}$  37.7 Hz, C=O).

### **Diethyl 2-(2-Naphtylsulphanyl)-3-(1,1,1-Triphenyl- $\lambda^5$ -Phosphanylidene) Succinate**

(1.01 g, m.p. 138–140°C, yield 88%); IR (KBr) ( $\nu_{\max}$ ,  $\text{cm}^{-1}$ ): 1741, 1641 (C=O). Anal. calcd. for  $\text{C}_{36}\text{H}_{33}\text{O}_4\text{PS}$  (592.70): C, 72.95; H, 5.61; S, 5.41%. Found: C, 72.92; H, 5.67; S, 5.66%. Isomer (Z) (50%),  $^1\text{H}$  NMR:  $\delta$  0.43 (3H, t,  $^3\text{J}_{\text{HH}}$  6.9 Hz,  $\text{CH}_3$ ), 1.25 (3H, t,  $^3\text{J}_{\text{HH}}$  7.0 Hz,  $\text{CH}_3$ ), 3.66–4.17 (8 H, m, 4  $\text{OCH}_2$ ) (for two rotamers), 4.44 (1H, d,  $^3\text{J}_{\text{PH}}$  18.8 Hz,  $\text{P}=\text{C}-\text{CH}$ ) (for two rotamers), 7.16–7.78 (44H, m, arm) (for two rotamers).  $^{13}\text{C}$  NMR: 13.95 and 14.21 (2  $\text{CH}_3$ ), 41.70 (d,  $^1\text{J}_{\text{PC}}$  127.3 Hz,  $\text{P}=\text{C}$ ), 54.67 (d,  $^2\text{J}_{\text{PC}}$  13.8 Hz  $\text{P}=\text{C}-\text{CH}$ ), 57.66 and 61.35 (2  $\text{OCH}_2$ ), 125.49–134.97 (carbons of aromatic rings) (for two rotamers), 164.99 (C–S) (for two rotamers), 168.75 (d,  $^2\text{J}_{\text{PC}}$  12.5 Hz, C=O), 172.39 (d,  $^2\text{J}_{\text{PC}}$  25.5 Hz, C=O). Isomer (E) (50%),  $^1\text{H}$  NMR:  $\delta$  1.18 (3H, t,  $^3\text{J}_{\text{HH}}$  7.0 Hz,  $\text{CH}_3$ ), 1.27 (3H, t,  $^3\text{J}_{\text{HH}}$  7.0 Hz,  $\text{CH}_3$ ),  $^{13}\text{C}$  NMR: 14.11 and 14.15 ( $\text{CH}_3$ ), 43.37 (d,  $^1\text{J}_{\text{PC}}$  133.3 Hz,  $\text{P}=\text{C}$ ), 54.90 (d,  $^2\text{J}_{\text{PC}}$  13.7 Hz,  $\text{P}=\text{C}-\text{H}$ ), 58.45 and

61.21 (2 OCH<sub>2</sub>), 170.06 (d, <sup>2</sup>J<sub>PC</sub> 20.5 Hz, C=O), 172.43 (d, <sup>2</sup>J<sub>PC</sub> 37.7 Hz, C=O).

**Dimethyl 2-[[*(E)*-2-Acetyl-3-Aminophenyl-2-Butenimidoyl]-3-(1,1,1-Triphenylphosphanylidene)] Succinate**

(1.3 g, m.p. 138–141°C, yield 91%); IR (KBr) ( $\nu_{\max}$ , cm<sup>-1</sup>). 3478 (NH), 1765 and 1641 (C=O). Anal. calcd. for C<sub>42</sub>H<sub>39</sub>N<sub>2</sub>O<sub>5</sub>SP (714.83): C, 70.57; H, 5.50; N, 3.92%. Found: C, 70.40; H, 5.50; N, 4.00%. Major isomer, (*Z*) (60%), <sup>1</sup>H NMR:  $\delta$  1.23 (6H, s, 2 CH<sub>3</sub>) (for two rotamers), 2.02 (6H, s, 2 CH<sub>3</sub>) (for two rotamers), 3.12 and 3.17 (6H, 2s, 2 OCH<sub>3</sub>), 4.38 (1H, d, <sup>3</sup>J<sub>PH</sub> 14.4 Hz, P=C–CH), 7.11 (1H, brod band, NH), 7.39–7.52 (50H, m, arm) (for two rotamers). <sup>13</sup>C NMR:  $\delta$  14.21 and 21.08 (2 CH<sub>3</sub>), 39.60 (d, <sup>1</sup>J<sub>PC</sub>, 141.2 Hz, P=C), 49.44 and 49.48 (2 OCH<sub>3</sub>), 66.72 (d, <sup>2</sup>J<sub>PC</sub> 15.5 Hz, P=C–CH), 125.08–133.70 (carbons of aromatic rings) (for two rotamers), 169.78 (d, <sup>2</sup>J<sub>PC</sub> 17.0 Hz, C=O), 171.07 (S–C=N) (for two rotamers), 174.80 (d, <sup>3</sup>J<sub>PC</sub> 5.7 Hz, C=O), 181.40 (C=O). Minor isomer, (*E*) (40%), <sup>1</sup>H NMR:  $\delta$  4.09 and 4.11 (6H, 2s, 2 OCH<sub>3</sub>), 4.32 (1H, d, <sup>3</sup>J<sub>PH</sub> 13.2 Hz, P=C–CH), 7.17 (1H, brod band, NH), <sup>13</sup>C NMR:  $\delta$  14.30 and 21.05 (2 CH<sub>3</sub>), 38.90 (d, <sup>1</sup>J<sub>PC</sub> 132.6 Hz, P=C), 50.71 and 50.80 (2 OCH<sub>3</sub>), 66.75 (d, <sup>2</sup>J<sub>PC</sub> 15.7 Hz, P=C–CH), 168.73 (d, <sup>2</sup>J<sub>PC</sub> 12.6 Hz, C=O), 175.11 (d, <sup>3</sup>J<sub>PC</sub> 5.7 Hz, C=O), 182.07 (C=O).

**Diethyl 2-[[*(E)*-2-Acetyl-3-Aminophenyl-2-Butenimidoyl]-3-(1,1,1-Triphenyl- $\lambda^5$ -Phosphanyl Idene)] Succinate**

(1.1 g, m.p. 145–148°C, yield 74%); IR (KBr) ( $\nu_{\max}$ , cm<sup>-1</sup>): 3429 (NH), 1765 and 1641 (C=O). Anal. calcd. for C<sub>44</sub>H<sub>43</sub>N<sub>2</sub>O<sub>5</sub>PS (742.88): C, 71.14; H, 5.83; N, 3.77%. Found: C, 70.68; H, 5.60; N, 3.78%. Major isomer, (*Z*) (62%), <sup>1</sup>H NMR:  $\delta$  0.38 (3H, t, <sup>3</sup>J<sub>HH</sub> 5.2 Hz, CH<sub>3</sub>), 1.24 (6H, t, <sup>3</sup>J<sub>HH</sub> 6.9 Hz, 2CH<sub>3</sub>) (for two rotamers), 1.31 (6H, s, 2 CH<sub>3</sub>) (for two rotamers), 2.03 (6H, s, 2 CH<sub>3</sub>) (for two rotamers), 3.48–4.28 (8H, m, 4 OCH<sub>2</sub>), 4.33 (1H, d, <sup>3</sup>J<sub>PH</sub> 13.5 Hz, P=C–CH), 6.85 (1H, broad band, NH) (for two rotamers), 7.13–7.69 (50H, m, arom) (for two rotamers). <sup>13</sup>C NMR:  $\delta$  14.10 and 14.20 (2 CH<sub>3</sub>), 15.58 (2 CH<sub>3</sub>) (for two rotamers), 21.02 (2CH<sub>3</sub>), 39.41 (d, <sup>1</sup>J<sub>PC</sub> 141.2 Hz, P=C), 60.35 and 61.30 (2 OCH<sub>2</sub>), 66.62 (d, <sup>2</sup>J<sub>PC</sub> 17.9 Hz, P=C–CH), 125.24–133.76 (carbons of aromatic rings) (for two rotamers), 164.98 (C), 168.23 (d, <sup>2</sup>J<sub>PC</sub> 11.8 Hz, C=O), 171.07 (S–C=N) (for two rotamers), 174.16 (d, <sup>3</sup>J<sub>PC</sub> 6.0 Hz, C=O), 182.06 (C=O). Minor isomer, (*E*) (38%), <sup>1</sup>H NMR:  $\delta$  0.24 (3H, t, <sup>3</sup>J<sub>HH</sub> 5.0 Hz, CH<sub>3</sub>), 4.38 (1H, d, <sup>3</sup>J<sub>PH</sub> 14.7 Hz, P=C–CH), <sup>13</sup>C NMR:  $\delta$  13.87 and 14.02 (2 CH<sub>3</sub>), 39.87 (d, <sup>1</sup>J<sub>PC</sub> 141.4 Hz, P=C), 57.94 and 58.80 (2 OCH<sub>2</sub>), 67.75 (d, <sup>2</sup>J<sub>PC</sub> 17.9 Hz, P=C–CH), 175.50 (d, <sup>3</sup>J<sub>PC</sub> 7.9 Hz, C=O), 181.11 (C=O).



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