Uncatalyzed Addition of TMSCN to Acylphosphonates

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Abstract: The cyanosilylations of various alkyl- and arylphosphonates under comparatively mild conditions furnished the trimethylsilyloxycyanophosphonates in high yield. The addition to ketophosphonate functions works without the influence of a catalyst.

Key words: cyanohydrins, addition reactions, phosphorus, nucleophilic additions

The addition of trimethylsilyl cyanide (TMSCN) to carbonyl compounds along with the subsequent hydrolysis in turn produces cyanohydrins.[1] Cyanohydrins are useful intermediates for the synthesis of many interesting compounds with biological properties. The two functional groups (–OH and –CN) can be easily transformed into various compounds.[2] The general route to O-TMS cyanohydrins is the addition of TMSCN to the aldehydes (or ketones), which only occurs in the presence of Lewis acid[3a] and nucleophilic catalysis.[3b,c] When considering the value of O-TMS cyanohydrins, it is not surprising that catalysis was reported hundreds of times so far for this particular transformation, and continue to be reported at the same pace.[4]

Phosphorus analogues of hydroxycarboxylic acids as well as phosphorylated α-hydroxynitriles are interesting as potential biologically active substances, mild water-soluble phosphorylating agents for biological systems, and water-soluble ligands for metal complex catalysis. Only a few methods have been described for the addition of carbon nucleophiles to acylphosphonates,[5] and as far as we know, only two methods describe the synthesis of phosphorylated α-hydroxynitriles. Konovalova et al.[6] obtained these compounds by the reaction of trimethylsilyl diethyl phosphite with esters and nitriles of α-oxocarboxylic acids. Beletskaya[7] reported the reaction of α-, β-, and γ-ketophosphonates with TMSCN to only occur with catalytic Bu_3SnCN at elevated temperatures (50–60 °C, 6–8 h) and acetylphosphonate was only example for α-ketophosphonate. In this present paper, we investigated the scope of the addition reaction of TMSCN to ketophosphonate for the synthesis of α-trimethylsilyloxynitrile, which are interesting precursors in synthetic organic chemistry, in which we found that TMSCN adds to ketophosphonate in high yield without any influence from a catalyst.

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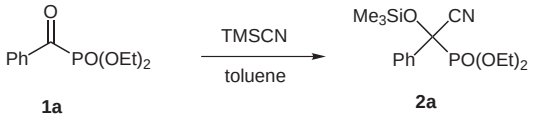
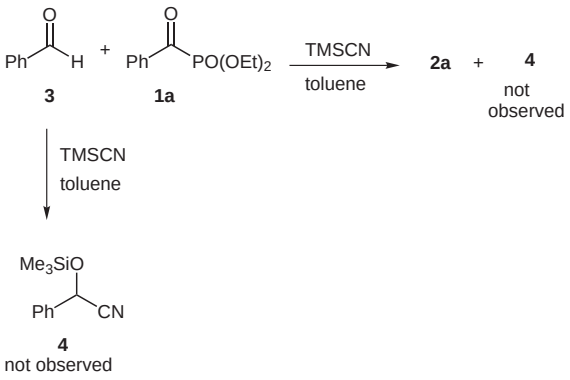
In our previous work we have shown that acylphosphonates are potent acyl anion precursors and that they undergo nucleophile-promoted phosphonate–phosphate rearrangement in order to provide corresponding acyl anion equivalents as reactive intermediates.[8] During our investigations regarding the nature of carbanionic intermediates that are generated via phosphonate–phosphate rearrangement we needed to synthesize compound **2a** (Scheme 1). In an initial reaction, acylphosphonate **1a** was dissolved in 1 mL toluene, and 1.2 mmol (1.2 equiv) of TMSCN was slowly added via a syringe. After the completion of the reaction (15–30 min), a reaction mixture was concentrated under vacuum and purified by column chromatography (ether eluent) to obtain **2a** in 98% yield.



1a **2a**

Scheme 1

After rapid screening with **1a** and **1b**, we found that the reaction indeed proceeds smoothly in various solvents. For example, we observed similar purities in DMF, toluene, CH_2Cl_2, and MeCN. Moreover, neat **1b** reacted with TMSCN providing a quantitative conversion. Although the reaction in DMF provided faster conversions, we chose the toluene as the reaction medium for practical reasons. We initially attributed the enhanced reactivity of acylphosphonates to the presence of a phosphonate moiety that could interact with TMSCN through P=O and activates it to execute an intramolecular attack. Interestingly, Beletskaya[7] reported that the reaction of α-, β-, and γ-ketophosphonates with TMSCN only occurs with catalytic Bu_3SnCN at elevated temperatures (50–60 °C, 6–8 h). This report was in good agreement with our observations. Therefore, we carried out some control experiments prior to proceeding. In two separate experiments, benzaldehyde (**3**) along with a one-to-one mixture of benzaldehyde (**3**) and benzoylphosphonate (**1a**) were reacted with one equivalent of TMSCN. Crude reaction mixtures were inspected for two possible products, namely **2a** and **4**. We observed that there were no traces of the product **4** in both reaction mixtures, whereas **2a** was the single product in the latter reaction (Scheme 2). Although we have no explanation for Belatskaya's report, we did observe **1a** to react with TMSCN without needing a catalyst in 15–30 minutes (<5 min in DMF).

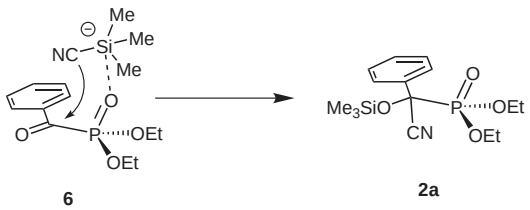


Scheme 2

Shibasaki and co-workers showed that enantioselectivies in chiral Lewis acid, the catalyzed addition of TMSCN to aldehydes was sometimes enhanced by the addition of 'promoters' such as Bu_3PO, $CH_3P(O)Ph_2$, and Ph_3PO.[9] This phosphine oxide activation effect led to the incorporation of phosphine oxide moieties into the catalytic Lewis acid structures as a Lewis acid–Lewid base pair for what has been described as a 'two-center' catalysis. Later, Corey and Ryu[10] investigated the effect of phosphine oxide, and proposed that a reaction between phosphine oxide and TMSCN occurred as follows (Scheme 3).

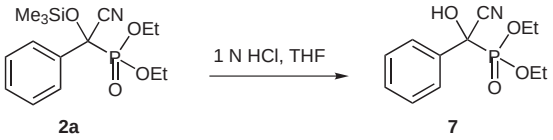
Scheme 3

They supported their proposal with several NMR and IR experiments and identified **5** as a more reactive cyanosilylating reagent than isomeric cyanide. This seems to be in agreement with our initial proposal where a phosphonate moiety activates the TMSCN through an interaction via P=O bond as in **6** to afford **2a** (Scheme 4).



Scheme 4

Several aromatic and aliphatic acylphophonates were reacted with TMSCN in toluene, the results of which are summarized in Table 1. The compound **2i** that was derived from proloylphosphonate **1i** showed a complex spectrum at room temperature due to the restricted rotation.



Scheme 5

From a synthetic point of view, this reaction provides not only biologically active α-hydroxyphosphonates with quaternary carbon but also in a highly functionalized form. These products can be used for the generation of valuable acyl anion equivalents via phosphonate–phosphate rearrangement.[8] As a general extension of this work, we are currently investigating the asymmetric version of this reaction as well as addition reactions with TMS derivatives other than TMSCN.

A highly efficient synthesis of trimethylsilyloxycyanophosphonates was described via the cyanosilylations of various alkyl and arylphosphonates. The cyanosilylations take place under comparatively mild conditions in terms of temperature and reaction time. The high-yield addition of TMSCN to ketophosphonate works without the influence of a catalyst. Acid hydrolysis of the trimethylsilyloxycyanophosphonates can be derived from α-hydroxy-α-cyanophosphonates in high yield.

General Procedure for TMSCN Addition

Acylphosphonate (1 mmol) was dissolved in toluene (1 mL) and TMSCN (1.2 mmol, 1.2 equiv) and slowly added via a syringe (5 min). After the completion of the reaction (15–30 min), the reaction mixture was concentrated under vacuum and (if needed) purified by column chromatography (Et_2O eluent) to obtain **2**.

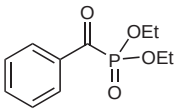
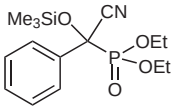
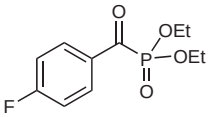
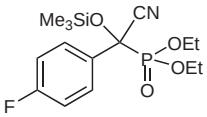
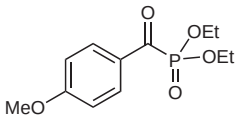
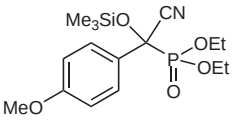
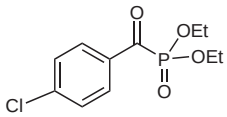
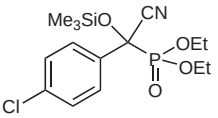
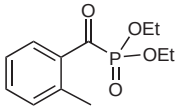
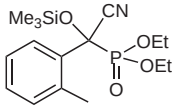
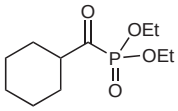
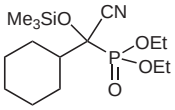
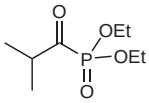
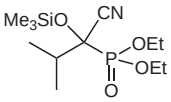
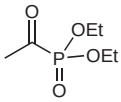
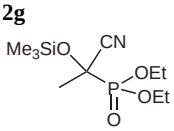
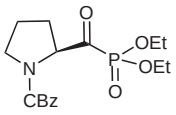
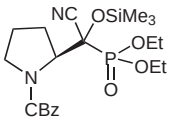
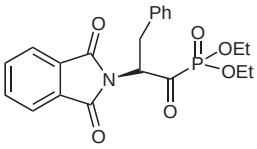
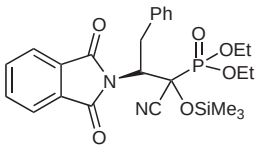
Diethyl Cyano(phenyl)(trimethylsilyloxy)methylphosphonate (2a)

Yield 321 mg (98%); white semisolid. ^{1}H NMR ($CDCl_3$): δ = 0.19 (9 H, s), 1.22 (3 H, dt, *J* = 0.6, 7.1 Hz), 1.35 (3 H, t, *J* = 7.1, 0.5 Hz), 3.90–4.00 (1 H, m), 4.02–4.13 (1 H, m), 4.17–4.28 (2 H, m), 7.37–7.45 (3 H, m), 7.66–7.71 (2 H, m). ^{13}C NMR ($CDCl_3$–CCl_4): δ = 0.98, 16.2 (d, *J* = 5.2 Hz), 16.4 (d, *J* = 5.9 Hz), 64.8 (d, *J* = 7.4 Hz), 65.4 (d, *J* = 7.2 Hz), 73.1 (d, *J* = 176.5 Hz), 117.9, 126.9 (d, *J* = 4.5 Hz), 128.4 (d, *J* = 2.2 Hz), 129.5 (d, *J* = 3.3 Hz), 134.5 (d, *J* = 3.6 Hz). ^{31}P NMR ($CDCl_3$): δ = 11.3. Anal. Calcd for $C_{15}H_{24}NO_4PSi$ (341.41): C, 52.77; H, 7.09; N, 4.10. Found: C, 52.61; H, 7.12; N, 4.28.

Diethyl Cyano(4-fluorophenyl)(trimethylsilyloxy)methylphosphonate (2b)

Yield 351 mg (98%); colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 0.19 (9 H, s), 1.23 (3 H, t, *J* = 7.1 Hz), 1.35 (3 H, t, *J* = 7.39 Hz), 3.95–4.03 (1 H, m), 4.05–4.14 (1 H, m), 4.17–4.28 (2 H, m), 7.08–7.13 (2 H, m), 7.64–7.68 (2 H, m). ^{13}C NMR ($CDCl_3$–CCl_4): δ = 0.96, 16.2 (d, *J* = 5.3 Hz), 16.4 (d, *J* = 5.3 Hz), 64.8 (d, *J* = 7.4 Hz), 65.5 (d, *J* = 7.4 Hz), 72.4 (d, *J* = 178 Hz), 115.4 (dd, *J* = 1.7, 21.1 Hz), 117.7, 128.8 (dd, *J* = 4.0, 8.5 Hz), 130.5 (m), 163.3 (dd, *J* = 2.8, 250 Hz). ^{31}P NMR ($CDCl_3$): δ = 11.1. Anal. Calcd for $C_{15}H_{23}FNO_4PSi$ (359.41): C, 50.13; H, 6.45; N, 3.90. Found: C, 50.22; H, 6.21; N, 4.13.

Table 1 Uncatalyzed Addition of TMSCN to Acylphosphonates

Entry	Acylphosphonate **1**[a]	Product **2**	Yield (%)[b]
1	 **1a**	 **2a**	98
2	 **1b**	 **2b**	98
3	 **1c**	 **2c**	97
4	 **1d**	 **2d**	97
5	 **1e**	 **2e**	98
6	 **1f**	 **2f**	97
7	 **1g**	 **2g**	94
8	 **1h**	 **2h**	87
9	 **1i**	 **2i**	93
10	 **1j**	 **2j**	83

[a] All phosphonates except **1i**,**j** are known.[8,]

[b] Isolated yields. Products of type **2a**–**j** can be quantitatively hydrolyzed to the corresponding alcohols by acidic hydrolysis. For example, compound **2a** was readily hydrolyzed in a mixture of 1 N HCl and THF, in turn affording **7** (Scheme 5).

Diethyl Cyano(4-methoxyphenyl)(trimethylsilyloxy)methylphosphonate (2c)
Yield 360 mg (97%); colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 0.18 (9 H, s), 1.21 (3 H, t, *J* = 7.1 Hz), 1.37 (3 H, t, *J* = 7.1 Hz), 3.83 (3 H, s), 3.86–3.97 (1 H, m), 3.90–4.11 (1 H, m), 4.17–4.31 (2 H, m), 6.91 (2 H, m), 7.58 (2 H, m). ^{13}C NMR ($CDCl_3$–CCl_4): δ = 1.0, 16.2 (d, *J* = 5.2 Hz), 16.4 (d, *J* = 5.6 Hz), 55.3, 64.7 (d, *J* = 7.4 Hz), 65.3 (d, *J* = 7.2 Hz), 72.7 (d, *J* = 179.0 Hz), 113.7 (d, *J* = 1.9 Hz), 118.0, 126.2 (d, *J* = 3.7 Hz), 128.3 (d, *J* = 4.7 Hz), 160.5 (d, *J* = 2.3 Hz). ^{31}P NMR ($CDCl_3$): δ = 11.4. Anal. Calcd for $C_{16}H_{26}NO_5PSi$ (371.44): C, 51.74; H, 7.06; N, 3.77. Found: C, 51.58; H, 7.23; N, 3.88.

Diethyl Cyano(trimethylsilyloxy)(4-chlorophenyl)methylphosphonate (2d)
Yield 363 mg (97%); colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 0.20 (9 H, s), 1.04 (3 H, t, *J* = 7.0 Hz), 1.17 (3 H, t, *J* = 7.0 Hz), 3.73–3.81 (1 H, m), 3.86–3.95 (1 H, m), 3.97–4.09 (2 H, m), 7.19 (2 H, d, *J* = 8.5 Hz), 7.39 (2 H, dd, *J* = 8.6, 2.0 Hz). ^{13}C NMR ($CDCl_3$–CCl_4): δ = 0.8, 15.2, (d, *J* = 5.7 Hz), 15.4, (d, *J* = 5.8 Hz), 63.6 (d, *J* = 6.9 Hz), 64.2 (d, *J* = 7.6 Hz), 70.4. 116.1, 127.1, 127.2, 127.2, 127.5, 132.2, 134.6. ^{31}P NMR ($CDCl_3$): δ = 10.9. Anal. Calcd for $C_{15}H_{23}ClNO_4PSi$ (375.86): C, 47.93; H, 6.17; N, 3.73. Found: C, 47.71; H, 6.33; N, 3.51.

Diethyl Cyano(trimethylsilyloxy)(2-methylphenyl)methylphosphonate (2e)
Yield 348 mg (98%); colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 0.26 (9 H, s), 1.26 (3 H, t, *J* = 6.2 Hz), 1.37 (3 H, t, *J* = 7.0 Hz), 2.69 (3 H, s), 3.91–4.30 (4 H, m), 7.19–7.29 (3 H, m), 7.26 (1 H, d *J* = 7.0 Hz). ^{13}C NMR ($CDCl_3$–CCl_4): δ = 0.863, 15.3 (d, *J* = 5.7 Hz), 15.5 (d, *J* = 5.0 Hz), 20.6, 63.5 (d, *J* = 7.2 Hz), 64.0 (d, *J* = 7.3 Hz), 72.0 (d, *J* = 176 Hz), 116.8, 124.7, 127.0, 127.1, 128.1, 130.9, 131.9. ^{31}P NMR ($CDCl_3$): δ = 11.9. Anal. Calcd for $C_{16}H_{26}NO_4PSi$ (355.44): C, 54.07; H, 7.37; N, 3.94. Found: C, 53.81; H, 7.23; N, 3.68.

Diethyl Cyano(cyclohexyl)methylphosphonate (2f)
Yield 336 mg (97%); colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 0.30 (9 H, s), 1.16–1.30 (5 H, m), 1.40 (6 H, m), 1.68–1.71 (1 H, m), 1.84–2.07 (5 H, m), 4.15–4.33 (4 H, m). ^{13}C NMR ($CDCl_3$): δ = 1.3, 16.4 (2 C, m), 25.8, 26.0, 27.1 (d, *J* = 5.8 Hz), 27.7 (d, *J* = 3.7 Hz), 30.8, 45.2, 65.3 (d, *J* = 7.4 Hz), 64.5 (d, *J* = 7.5 Hz), 74.4 (d, *J* = 175.5 Hz), 117.4 (d, *J* = 2.4 Hz). ^{31}P NMR ($CDCl_3$–CCl_4): δ = 14.0. Anal. Calcd for $C_{15}H_{30}NO_4PSi$ (347.46): C, 51.85; H, 8.70; N, 4.03. Found: C, 51.61; H, 8.62; N, 4.28.

Diethyl 1-Cyano-1-trimethylsilyloxy-2-methylpropylphosphonate (2g)
Yield 288 mg (94%); colorless oil. ^{1}H NMR ($CDCl_3$): δ = 0.29 (9 H, s), 1.10 (3 H, d, *J* = 6.7 Hz), 1.15 (3 H, d, *J* = 6.8 Hz), 1.35–1.41 (6 H, m), 2.14–2.29 (1 H, m), 4.19–4.30 (4 H, m). ^{13}C NMR ($CDCl_3$–CCl_4): δ = 1.4, 16.5 (2 C, m), 17.6 (d, *J* = 6.3 Hz), 18.0 (d, *J* = 3.7 Hz), 36.1, 64.2 (d, *J* = 7.2 Hz), 64.3 (d, *J* = 7.5 Hz), 74.6 (d, *J* = 176 Hz), 117.0 (d, *J* = 3.4 Hz). ^{31}P NMR ($CDCl_3$): δ = 14.20. Anal. Calcd for $C_{12}H_{26}NO_4PSi$ (307.4): C, 46.89; H, 8.53; N, 4.56. Found: C, 46.71; H, 8.37; N, 4.78.

Diethyl Cyano(methyl)(trimethylsilyloxy)methylmhosphonate (2h)
Yield 242 mg (87%); colorless liquid. ^{1}H NMR ($CDCl_3$): δ = 0.27 (9 H, s), 1.31–1.40 (6 H, m), 1.74 (3 H, d, *J* = 14.9 Hz), 4.18–4.29 (4 H, m). ^{13}C NMR ($CDCl_3$–CCl_4): δ = 1.30, 16.4 (2 C, m), 24.8, 64.3 (d, *J* = 7.2 Hz), 64.8 (d, *J* = 7.3 Hz), 66.6 (d, *J* = 182.5 Hz), 118.4. ^{31}P NMR ($CDCl_3$): δ = 13.71. Anal. Calcd for $C_{10}H_{22}NO_4PSi$ (279.35): C, 43.00; H, 7.94; N, 5.01. Found: C, 42.83; H, 7.77; N, 4.78.

(2*S*)-Diethyl {1-[(Benzyloxy)carbonyl]pyrrolidin-2-yl}(cyano)(trimethylsilyloxy)methylphosphonate (2i)
Yield 407 mg (87%); yellow oil; $[\alpha]_D^{25}$ –23 (*c* 1.8, $CHCl_3$). ^{1}H NMR (DMSO, 90 °C): δ = 0.25 and 0.32 (9 H, s), 1.30–1.36 (6 H, m), 1.82–2.23 (4 H, m), 3.34–3.81 (2 H, m), 4.06–4.30 (4 H, m), 4.64–4.67 (1 H, m), 5.05–5.25 (2 H, m), 7.31–7.41 (5 H, m). ^{13}C NMR (DMSO, 90 °C): δ = .074, 0.89, 1.71, 15.6 (d, *J* = 6.2 Hz), 15.9 (d, *J* = 4.8 Hz), 22.9, 26.3, 26.9, 47.0, 47.6, 59.5, 64.4 (d, *J* = 6.9 Hz), 64.7 (d, *J* = 8.1 Hz), 66.6, 72.0, 73.7, 117.5, 127.7, 127.8, 128.3, 136.7, 155.2, 155.5, 169.8. ^{31}P NMR (DMSO): δ = 11.8, 12.1, 13.0. HRMS: *m/z* calcd for $C_{21}H_{33}N_2O_6PSi$: 468.1845. Found: 468.1843.

(2*S*)-Diethyl 1-Cyano-1-trimethylsilyloxy-2-(1,3-dioxoisoindolin-2-yl)-3-phenylphosphonate (2j)
Yield 426 mg (73%); yellow liquid; $[\alpha]_D^{25}$ –136 (*c* 0.7, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ = 0.16 (9 H, s), 1.37–1.46 (6 H, m), 3.48 (1 H, dd, *J* = 14.1, 3.4 Hz), 3.99 (1 H, t, *J* = 13.0 Hz), 4.31–4.43 (4 H, m), 5.07–5.18 (1 H, m), 7.16–7.22 (5 H, m), 7.65–7.86 (4 H, m). ^{13}C NMR ($CDCl_3$–CCl_4): δ = 1.0, 14.1, 16.3, 16.4 (d, *J* = 5.5 Hz), 22.7, 29.7, 31.9, 32.9, 56.4 (d, *J* = 3.1 Hz), 65.4 (d, *J* = 7.7 Hz), 65.6 (d, *J* = 7.1 Hz), 70.4, 72.1, 116.1, 123.2, 123.3, 126.7, 128.5, 128.7, 131.0, 131.9, 133.9, 134.2, 136.8, 167.6, 168.0. ^{31}P NMR ($CDCl_3$): δ = 11.9, 12.4. HRMS: *m/z* calcd for $C_{25}H_{31}N_2O_6PSi$: 514.1689. Found: 514.1687.

General Procedure for the Hydrolysis of 2
Compound **2a** (1 mmol) was dissolved in THF (1 mL), and 1 N HCl (1 mL) was slowly added into the mixture. After the completion of the reaction (TLC, ca. 15 min), the reaction was diluted with Et_2O and washed with brine in order to quantitatively obtain a pure hydrolysis product **7**.

Diethyl Cyano(hydroxy)(phenyl)methylphosphonate (7)
White solid; mp 71–73 °C. ^{1}H NMR ($CDCl_3$): δ = 1.16 (3 H, t, *J* = 7.1 Hz), 1.28 (3 H, t, *J* = 7.1 Hz), 3.96–4.20 (4 H, m), 4.90 (1 H, br s), 7.32–7.42 (3 H, m), 7.61–7.64 (2 H, m). ^{13}C NMR ($CDCl_3$): δ = 16.2 (2 C, m), 65.6 (d, *J* = 7.8 Hz), 65.8 (d, *J* = 7.3 Hz), 71.0 (d, *J* = 166.6 Hz), 117.8 (d, *J* = 3.1 Hz), 126.3 (d, *J* = 3.8 Hz), 128.4 (d, *J* = 2.3 Hz), 129.4 (d, *J* = 3.1 Hz), 133.6 (d, *J* = 4.7 Hz). ^{31}P NMR ($CDCl_3$): δ = 12.04. Anal. Calcd for $C_{12}H_{16}NO_4P$ (269.23): C, 53.53; H, 5.99; N, 5.20. Found: C, 53.34; H, 6.22; N, 4.88.

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