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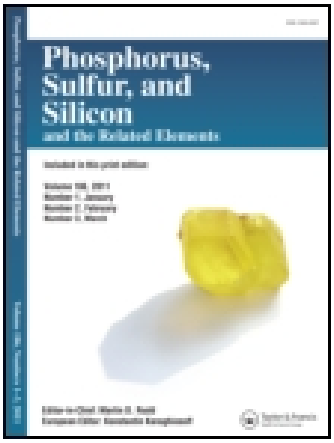

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Regioselective Cycloadditions of Phosphonyl Nitrile Oxides with Vinylphosphonate and Phosphaalkyne

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REGIOSELECTIVE CYCLOADDITIONS OF PHOSPHONYL NITRILE OXIDES WITH VINYLPHOSPHONATE AND PHOSPHAALKYNE

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1,3-Dipolar cycloaddition reactions are important synthetic manipulations allowing the construction of five-membered heterocycles. In this article, we report the cycloaddition of phosphonyl nitrile oxides with vinylphosphonate and phosphaalkyne to form the unexpected 2:1 cycloaddition product with excellent levels of regiocontrol product. The structures of title compounds were confirmed by ^{1}H NMR, ^{31}P NMR, MS, and IR. The mechanism of the cycloaddition was explored using the density functional theory (DFT) method.

Keywords Cycloaddition; dihydroisoxazoles; nitrile oxides

INTRODUCTION

Cycloaddition reactions are important synthetic manipulations for construction of the five-member ring carbocycles and heterocycles.[1–2] The reaction between nitrile oxides and alkenes is of considerable interest in organic synthesis, as the resulting heterocycles are versatile intermediates for the syntheses of natural products and biologically active compounds.[3] Intensive investigations have been undertaken on 1,3-dipolar cycloaddition reactions between nitrile oxide and electron-deficient alkenes, and in most cases 4,5-dihydroisoxazoles were obtained. Although there are several examples of the 1,3-dipolar cycloaddition of electron-deficient nitrile oxide with unsaturated alkenes, the scope and generality of the nitrile oxides remain insufficient. In this article, we report the cycloaddition of phosphonyl nitrile oxides and the formation of an unexpected 2:1 cycloaddition product. It provides a direct route to obtain triphosphonyl-substituted dihydroisoxazolyl dihydroisoxazoles and diphosphonyl-substituted dihydroisoxazolyl dihydroisoxazoles with

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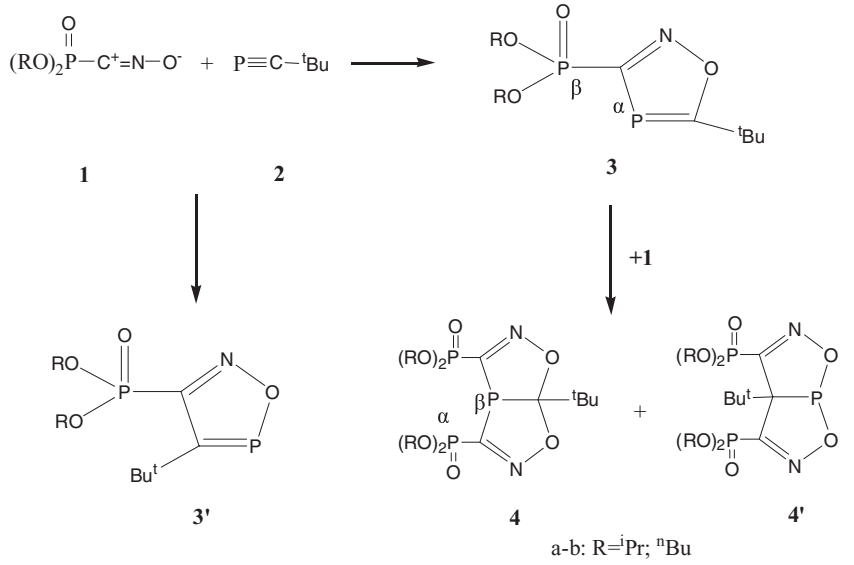
excellent regiocontrol product. We believe that this strategy provides a potentially facile route to a wide range of dihydroisoxazolyl dihydroisoxazoles–based targets.

RESULTS AND DISCUSSION

Cycloaddition of Phosphonyl Nitrile Oxides with Phosphaalkyne

The requisite nitrile oxides **1** were prepared according to the literature from the corresponding hydroximoyl bromides via base-induced dehydrobromidination.[4–6] We first investigated the 1,3-dipolar cycloaddition between nitrile oxide and phosphaalkyne **2**, as shown in Scheme 1. In our initial attempts, we failed to isolate nitrile oxide **1**. Therefore, without purification, nitrile oxide was directly used for the cycloaddition reaction. Tert-butyl phosphaalkyne **2** can react with nitrile oxides **1** to give heteocyclic compounds. However, we found that an unexpected 2:1 cycloaddition product **4** is achieved when threefold excess of tert-butyl phosphaalkyne reacts with phosphonyl nitrile oxides. Its regio isomer **4′** is not obtained. This is because of the steric bulk of the tert-butyl on phosphaalkyne **2** and the highly reactive dipole 1, so only one regio isomer is obtained.



Scheme 1 Cycloaddition of phosphonyl nitrile oxides with phosphaalkyne.

When onefold excess of dibutoxyphosphonyl nitrile oxides **1b** was added, a 1:1 cycloaddition product **3b** was observed from ^{1}H NMR and ^{31}P NMR spectra. From ^{31}P NMR (Figure 1), a doublet at 86.3 ppm is observed, which indicates a typical bivalent phosphorus chemical displacement.[7] It is a chemical displacement of phosphorus atom in isoxazole. Another doublet at 7.5 ppm is the chemical displacement of phosphorus atom in phosphonate. From ^{31}P NMR, a coupling constant of 67.7 Hz can also be observed. In the case of a reverse dipole orientation as represented by the structure **3′**, the $^{\alpha}$P resonances would be expected at a considerably lower field (δ = ca. 160–180).[8]

In addition, from the integration of the hydrogen in ^{1}H NMR, a 1:1 cycloaddition product is also observed. The 1:1 cycloaddition product **3** could not be isolated. After

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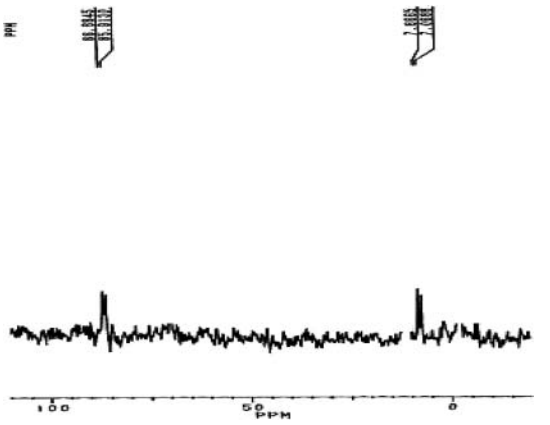

Figure 1 ^{31}P NMR of compound **3**.

another one equivalent of phosphonyl nitrile oxide was added to the reaction, the expected product **4** is formed. We can draw the conclusion that the cycloaddition reaction is completed in two steps. First, a 1:1 cycloaddition product **3** is formed. Second, another phosphonyl nitrile oxide **1** adds to the P=C double bond of **3**, so forming a 2:1 product **4**.

The structure of the 2:1 cycloaddition product **4a** is also confirmed by ^{1}H and ^{31}P NMR. Figure 2 shows a ^{31}P spectrum of compound **4a**. Since the middle-group phosphorus ($^{\beta}$P) is attached to two chemically different phosphorus atoms ($^{\alpha}$P), spin–spin splitting into a 1:2:1 triplet is to be expected in δ 16.1–17.6. Coupling constants of 56.1 Hz can be observed. Likewise, the attachment of the two end-group phosphorus atoms to the lone middle-group phosphorus gives spin–spin splitting into 1:1 doublet at δ 1.05–1.75.

Cycloaddition of Phosphonyl Nitrile Oxides with Alkene

We also examined the scope of phosphonyl nitrile oxides with an electron-deficient alkene. With acrylonitrile, diisopropoxy phosphonyl nitrile oxides **1** showed analogous

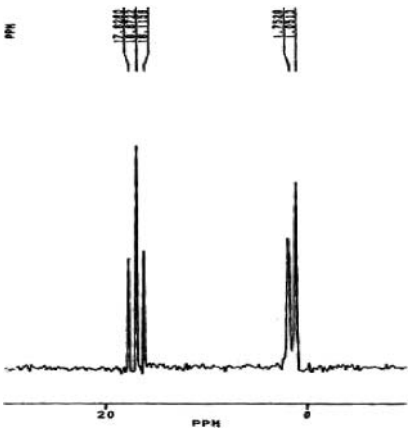

Figure 2 ^{31}P NMR of compound **4a**.

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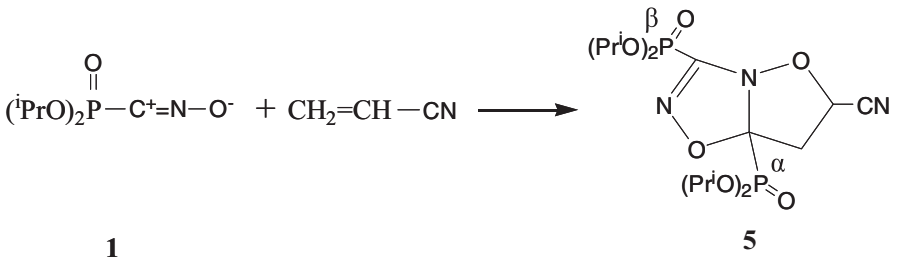
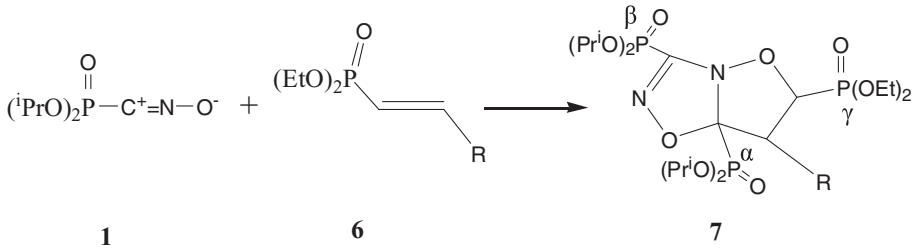


1 **5**

Scheme 2 Cycloaddition of phosphonyl nitrile oxides with acrylonitrile.

behavior. Nitrile oxide **1** reacted regioselectively with acrylonitrile to give an unexpected 2:1 product **5** (shown in Scheme 2).

When reacted with trans-vinylphosphonate, phosphonyl nitrile oxides **1** also showed analogous behavior (shown in Scheme 3). The vinylphosphonate **6** was prepared according to the procedures we previously described.[2h] When diisopropoxy phosphonyl nitrile oxides **1** reacted with β-substituted vinylphosphonate **6**, only the regioselective 2:1 addition product **7** was obtained. Meanwhile, when excessive β-substitute vinylphosphonate **6** was added, only the 2:1 cycloadduct was obtained.



1 **6** **7**

A-F: R= C_6H_5, C_6H_{13}, *p*-$O_2NC_6H_4$, CO_2CH_3, 2,4-$Cl_2C_6H_3$, *m*-$O_2NC_6H_4$

Scheme 3 Cycloaddition of phosphonyl nitrile oxides with vinylphosphonate.

The Mechanism of Cycloaddition

The detailed mechanism has been explored using the density functional theory (DFT) method. Each structure was fully optimized with the B3LYP[9–13] method using the 6-31G* basis set for C, O, and H atoms (Figure 3). Harmonic vibrational frequencies were calculated for each structure. The bond orders reported were Wiberg bond calculated by means of natural bond orbitals (NBO). The charges reported were the Mulliken atomic charges. All calculations were carried out with the Gaussian 03 program package. All relative energies discussed within this context are free energies at 298 K. In order to make the calculations easier, we used methyl instead of isopropyl.

A plausible reaction pathway has been proposed to account for the high reactivity and selectivity of diisopropoxy phosphonyl nitrile oxide. First, a regiospecific 1:1 product was formed. Second, a highly reactive diisopropoxy phosphonyl nitrile oxide can continue reacting with the C=N double bond and give the corresponding cycloadduct. From Figure 3

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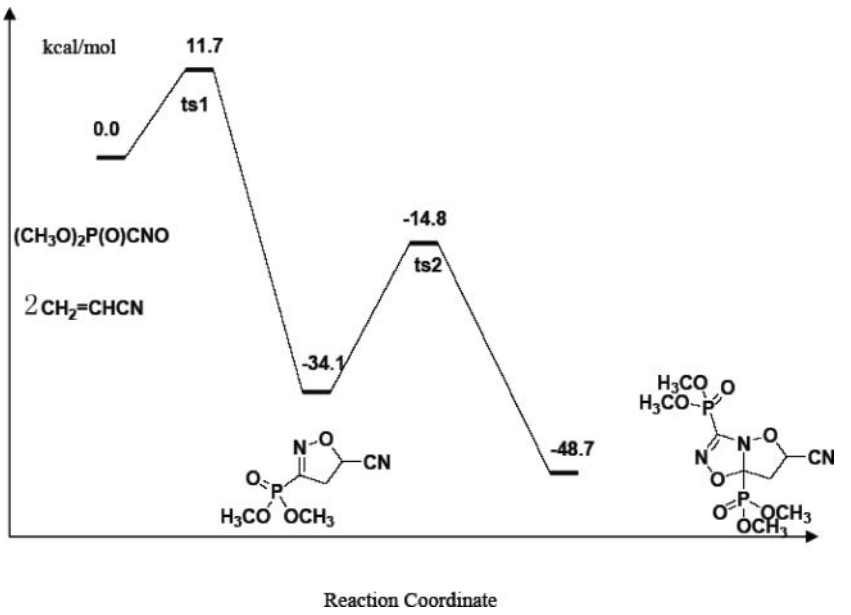

Figure 3 Potential energy surface of the reaction with the B3LYP method. All energies are electronic energies without ZPE (zero point energy) corrections with respect to the reactants. ts1 and ts2 stand for the transition state of the first step and second step.

we can see that the free energy barriers for the first and second steps are 11.7 and −14.6 kcal/mol, respectively. The free energy of the second step is quite low. So the cycloaddition stopped in this step.

CONCLUSIONS

In conclusion, the [3+2] cycloaddition reaction of nitrile oxides with alkynes and alkenes provides a direct route to triphosphonyl-substituted dihydroisoxazolyl dihydroisoxazoles and diphosphonyl-substituted dihydroisoxazolyl dihydroisoxazoles with excellent levels of regiocontrol product. Additionally, an unexpected 2:1 cycloaddition takes place in the presence of Et_3N when phosphonyl hydroximoyl bromides are employed to furnish the dihydroisoxazoles. We believe that this strategy provides a potentially facile route to a wide range of dihydroisoxazolyl dihydroisoxazoles–based targets. The DFT studies of the reactions between nitrile oxides and acrylonitrile reveal that the following mechanism is quite possible: It starts as a normal 1,3-dipolar cycloaddition reaction to produce a regiospecific 1:1 product, then highly reactive diisopropanyl phosphonyl nitrile oxide continue to react with the regiospecific 1:1 product and give the corresponding cycloadduct. Further study is underway to expand the scope of this methodology, as well as to ascertain mechanistic details of the cycloaddition process.

EXPERIMENTAL

Elemental analyses were carried on a Yanaco CHN Corder MT-3 apparatus. ^{1}H, ^{13}C, and ^{31}P NMR spectra were measured by using a Bruker 300 spectrometer with TMS and

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85% H_3PO_4 as the internal and external references, respectively, and with $CDCl_3$ as the solvent. IR spectra were recorded as KBr pellets on a Bruck spectrometer. Mass spectra were acquired in positive ion mode using a Bruker Esquire-LCTM ion trap spectrometer equipped with a gas nebulizer probe, capable of analyzing ions up to m/z 20000. Solvents used were purified and dried by standard procedures.

Procedure for the Synthesis of 4

To a rapidly stirred solution of tert-butyl phosphaacetylene **2** (0.2 mL, 1 M in $Me_3SiOSiMe_3$) and Et_3N (0.15 g) in dry ether (10 mL) under N_2, a solution of compound **1** (0.288 g, 1 mmol) in dry ether (6 mL) was added dropwise at −10°C. The mixture was stirred at room temperature for 24 h. Then, the reaction mixture was filtered to remove triethylamine hydrobromides, and the solvent was evaporated in vacuum. The residue was chromatographed on a silica gel column with petroleum ether:ethyl acetate 1:1 (V:V) to give pure **4a–b** as an oil.

Similar to the synthesis of **4**, compound **3** was obtained as an oil. Yield 43.2%, ^{1}H NMR: 0.87–0.94 (m, 6H), 1.19–1.44 (m, 13H), 1.67–1.68 (m, 4H), 4.17 (m, 4H); ^{31}P NMR: 86.3 (d, J = 67.7 Hz, $^{\alpha}$P), 7.5 (d, J = 67.7 Hz, $^{\beta}$P).

4a: Yield 50.4%, anal. calcd. found (calcd): C 44.27 (44.36), H 7.32 (7.25), N 5.44 (5.44). ^{1}H NMR: 4.78 (m, 4H, C<u>H</u>Me_2), 1.26–1.33 (t, 24H, CH<u>Me</u>$_2$), 1.03 (s, 9H, Me); ^{13}C NMR: 20.1 CH_3), 50.0 (CH), 26.3 (<u>Me</u>C), 36.6 (Me_3<u>C</u>), 130.0 (P—C), 156.0 (C=N); ^{31}P NMR: 1.4 ($^{\alpha}$P), 16.8 ($^{\beta}$P).

4**b:** Yield 76.4%, anal. calcd. found (calcd): C 48.46 (48.42), H 7.92 (7.95), N 4.88 (4.91). ^{1}H NMR: 4.66 (m, 4H, CH), 1.67 (m, 8H, CH_2), 1.28–1.36 (m, 12H, CH_3), 1.08 (s, 9H, C<u>Me</u>$_3$), 0.88–0.95 (t, 12H, Me), ^{31}P NMR: 1.7 ($^{\alpha}$P), 17.6 ($^{\beta}$P).

General Procedure for the Synthesis of 5 and 7

To stirred solution of compound **1** (0.432 g, 1.5 mmol) and alkene (15 mmol) in dry ether (10 mL), a solution of Et_3N (0.2 g, 2 mmol) in dry ether (10 mL) was added dropwise at −10°C. After 30 min, the solution was warmed to ambient temperature. The reaction mixture was stirred continuously for 3 days. After it was filtered, the solvent was evaporated in vacuo. The residue was chromatographed on a silica gel column with petroleum ether:ethyl acetate (1:3) to give pure **5** or **7** as an oil.

5: Yield 22%, anal. calcd. found(calcd): C 43.64 (43.69), H 6.63 (6.68), N 8.95 (8.99), ^{1}H NMR: 5.03–5.12 (dd, J = 35 Hz, 1H, <u>CH</u>CN), 4.53–4.61 (m, 4H, O<u>CH</u>Me_2), 3.53–3.59 (t, J = 7.8 Hz, 2H, <u>CH$_2$</u>CHCN), 0.99–1.23 (m, 24H, OCH<u>Me</u>$_2$); ^{13}C NMR: 22.0 (<u>CH$_3$</u>CH), 50.0 (CH_3<u>CH</u>), 70.0 (<u>CH$_2$</u>), 128.0 (CP), 131.0 (CH), 148.0 (PC=N), 151.0 (CN); ^{31}P NMR: 0.6 ($^{\alpha}$P), −3.4 ($^{\beta}$P).

7a: Yield 19.6%, anal. calcd. found(calcd): C 47.72 (47.71), H 6.79 (6.93), N 4.29 (4.28), ^{1}H NMR: 7.32 (m,5H), 5.89–6.03 (dd, J = 30 Hz, 1H), 4.69 (m,4H), 4.12–4.22 (m,5H), 1.20–1.39 (m, 30H), ^{13}C NMR: 15.0 (CH_2<u>CH$_3$</u>), 22.3 (CH_3), 22.6 (CH_3), 30.6 (CH), 49.0 (CPh), 50.0 (CH), 56.0 (<u>CH$_2$</u>CH_3), 82.0 (CHP), 92.0 (PC—N), 160.0 (PC=N), 126.2, 128.5, 129.6, 143.7 (C_{arom}); ^{31}P NMR: 0.9 ($^{\alpha}$P), −3.2 ($^{\beta}$P), 18.5 ($^{\gamma}$P).

7b: Yield 31.4%, anal. calcd. found(calcd): C 46.98 (47.13), H 8.13 (8.06), N 4.28 (4.23). ^{1}H NMR: 4.65–4.75 (m, 5H), 3.99–4.10 (m, 5H), 1.08–1.41 (m, 40H), 0.73–0.76 (m, 3H), ^{13}C NMR: 14.2 (CH_2<u>CH$_3$</u>), 20.3 (CH_2), 22.3 (CH_2), 22.6 (CH_3), 27.4 (CH_2),

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30.4 (CH_2), 32.4(CH_2), 62.3 ($\underline{CH_2}CH_3$), 80.1 (CHO), 82.5 (PC−O), 92.4 (PCN), 160.0 (PC=N); ^{31}P NMR: 1.1 ($^{\alpha}$P), −3.1 ($^{\beta}$P), 19.2 ($^{\gamma}$P).

7c: Yield 56.1%, anal. calcd. found(calcd): C 44.59 (44.64), H 6.35 (6.34), N 5.98 (6.01), ^{1}H NMR: 8.19–8.23 (d, J = 15 Hz, 2H), 7.51–7.55 (d, J = 22 Hz, 2H), 6.06 (dd, J = 35 Hz, 1H), 4.83 (m, 4H), 4.21 (m, 5H), 1.23–1.37 (m, 30H), ^{13}C NMR: 14.1 ($CH_2\underline{CH_3}$), 22.4 (CH_3), 22.5 (CH_3), 30.5 (CH), 62.4 ($\underline{CH_2}CH_3$), 71.5 (CH), 83.3 (CHP), 92.0 (PC−O), 123.2, 127.5, 145.7, 154.6 (C_{arom}), 162.0 (PC=N); ^{31}P NMR: 0.5 ($^{\alpha}$P), −3.3 ($^{\beta}$P), 17.7 ($^{\gamma}$P).

7d: Yield 78.8%, anal. calcd. found(calcd): C 41.49 (41.51), H 6.80 (6.81), N 4.38 (4.40), ^{1}H NMR: 5.31–5.45 (dd, J = 18 Hz, 1H), 4.77 (m, 4H), 4.13–4.20 (m, 5H), 3.75–3.77 (s, 3H), 1.27–1.37 (m, 30H),^{13}C NMR: 14.5 ($CH_2\underline{CH_3}$), 22.4 (CH_3), 32.5 (CH), 50.7 (OCH_3), 62.7 ($\underline{CH_2}CH_3$), 72.1 (CHO), 79.2 (PCHO), 88.6 (PC−N), 162.5 (PC=N), 175.4 (C=O); ^{31}P NMR: 0.03 ($^{\alpha}$P), −3.3 ($^{\beta}$P), 17.7 ($^{\gamma}$P); IR:3268 2957 1739 1649 1579 1490 1439 1204 924 769cm^{-1}; ESI-MS: 637.3 $[M+H]^+$.

7e: Yield 56.1%, anal. calcd. found(calcd): C 43.1 (43.16), H 5.96 (5.99), N 3.85 (3.87), ^{1}H NMR: 7.24–7.37 (m, 3H), 6.19–6.32 (dd, J = 27 Hz, 1H), 4.67–4.87 (m, 4H), 4.15–4.31 (m, 5H), 1.20–1.39 (m, 30H), ^{13}C NMR: 14.6 ($CH_2\underline{CH_3}$), 22.3 (CH_3), 22.5 (CH_3), 61.7 ($\underline{CH_2}CH_3$), 72.2 (CHO), 82.8 (PCHO), 91.6 (PC−N), 162.0 (PC=N), 126.6, 128.8, 131.8, 132.7, 147.4 (C_{arom}); ^{31}P NMR: 0.9 ($^{\alpha}$P), −3.2 ($^{\beta}$P), 18.5 ($^{\gamma}$P).

7f: Yield 35.3%, anal. calcd. found(calcd): C 44.65 (44.64), H 6.37 (6.34), N 6.03 (6.01),^{1}H NMR: 8.14–8.18 (d, J = 27 Hz, 2H), 7.54–7.66 (dd, J = 24 Hz, 2H), 5.95–6.09 (dd, J = 22Hz, 1H), 4.69 (m, 4H), 4.14–4.36 (m, 5H), 1.21–1.35 (m, 30H), ^{13}C NMR: 14.7 ($CH_2\underline{CH_3}$), 22.3 (CH_3), 22.5 (CH_3), 30.2 (CH), 62.7 ($\underline{CH_2}CH_3$), 72.0 (CHP), 85.4 (PCH−O), 90.3 (PCO), 161.0 (PC=N), 120.2, 122.5, 127.6, 129.3, 147.7, 149.2 (C_{arom}); ^{31}P NMR: 0.5 ($^{\alpha}$P), −3.4 ($^{\beta}$P), 17.6 ($^{\gamma}$P); ESI-MS: 700.5 $[M+H]^+$.

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