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Synthesis of New Dibenzo[*c.e*][1,2]oxaphosphorine 2-oxide Containing Diols Based on Diethanolamine

Yana Bykov,[1] Sebastian Wagner,[1] Olaf Walter,[1] Manfred Döring,[1] Oliver Fischer,[2] Doris Pospiech,[2] Thomas Köppl,[3] and Volker Altstädt[3]

[1]*Institute of Catalysis Research and Technology, Karlsruhe Institute of Technology, Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

[2]*Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden, Germany*

[3]*Department of Polymer Engineering, University of Bayreuth, Universitätsstr. 30, 95447 Bayreuth, Germany*

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ABSTRACT: *Different approaches were applied to obtain new diol compounds based on dibenzo[c.e][1,2]oxaphosphorine 2-oxide (DOPO, **1**) and diethanolamine (DEolA). Of four processes investigated, a four-step synthesis of **1** containing propionic acid amide of DEolA proved to be the most efficient one. In addition, the intramolecular amine salt of the DOPO derivative with a ring-opened structure was obtained by reinvestigation of the reaction of DOPO with DEolA and paraformaldehyde. The Atherton–Todd reaction of **1** and DEolA was investigated as well.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 23:146–153, 2012; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20763

Correspondence to: Yana Bykov; e-mail: yana.bykov@kit.edu, Manfred Döring; e-mail: manfred.doering@kit.edu.

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INTRODUCTION

Commercially available dibenzo[*c.e*][1,2] oxaphosphorine 2-oxide (DOPO, **1**) and its derivatives are applied as ligands in coordination chemistry [1] and, additionally, they are known to be versatile and environmentally friendly substances used to render a broad range of polymers flame retardant [2–4]. They can be incorporated into the polymer matrix as either nonreactive additives [5–7] or reactive comonomers [8–10]. For a long time, the synthesis of such functionalized DOPO derivatives and the study of their flame-retardant properties have been of great interest to both industry and academia [11,12]. The synthesis of DOPO-containing molecules with alcohol functionalities is especially attractive for chemical connection of **1** with the polymer backbone, for example, as comonomers in polyesters [13–15] or polyurethanes [16].

This article will present the synthesis of novel diethanolamine (DEolA) derivatives possessing one or more DOPO units. Such compounds are expected to benefit from a phosphorus–nitrogen synergism supporting their flame retardancy. This was already reported for other phosphorus–nitrogen systems, for example, flame retardants for cellulose [17]. The

synthesis of DOPO derivatives containing nitrogen functionalities is of interest since synergistic systems often allow for a reduced flame-retardant load while maintaining high efficiency.

Three alternative approaches for achieving the goal of connecting **1** and DEolA were investigated and compared. The first strategy was a Kabachnik–Fields reaction, the second approach was an Atherton–Todd reaction, and the third one was the synthesis of DOPO containing propionic acid amide of DEolA.

RESULTS AND DISCUSSION

The connection of **1** to DEolA through a methylene group by a Kabachnik–Fields approach was described in a US patent in 1988 [18]. The authors report that the reaction between **1** and DEolA with paraformaldehyde in water as a solvent yields a "material, which is very viscous, colorless, and transparent" (**2**) (Scheme 1). However, when repeating the synthesis in accordance with the published procedure, a white precipitate was obtained by concentration of the reaction mixture in vacuum. Spectroscopic data, namely, ^{1}H NMR (a broad signal at 10.9 ppm in DMSO) and ESI MS (a peak $[M - H]^-$ at $m/z = 350$ in the negative measurement) revealed the formation of an intramolecular amine salt of ring-opened DOPO (**3**) via hydrolysis of **2**. A similar phenomenon was observed by Keglevich et al. during a study of the Kabachnik–Fields reaction of **1** under microwave conditions [19]. Moreover, the intermolecular amine salt **4** was obtained by the stirring of 6*H*-dibenz[*c*, *e*][1,2]oxaphosphorin-6-propanoic acid methyl ester 6-oxide (DOPAcMe, **5**; synthesized by the Michael-like addition of **1** to methyl acrylate in the presence of triethylamine [20]) with diethylamine under air (Scheme 2). This confirms that **1** easily hydrolyzes in the presence of a base to yield a ring-opened salt. The structures of **3** and **4** were confirmed by X-ray diffraction (XRD) of single crystals (Fig. 1).

To reverse the hydrolysis reaction, substance **3** was heated to 120°C in vacuum and, indeed, the formation of the target molecule **2** was observed (Scheme 1). However, partial decomposition occurs under these conditions, which is reflected by the appearance of additional signals in the ^{31}P NMR and ^{1}H NMR spectra.

Even though the described synthesis was not reproducible [18] and prevention of the ring opening was reported to be unsuccessful [19], we were still able to obtain the target molecule **2**. Nonetheless, the synthesis of **2** remains inefficient. Therefore, it was decided to connect DOPO and DEolA directly as an alternative approach.

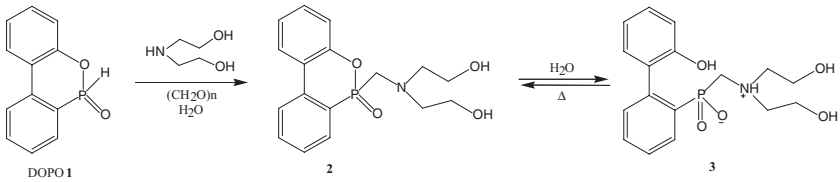
In an attempt to synthesize new OH-functionalized DOPO derivatives, the Atherton–Todd reaction was taken, a reaction known to be an effective way for the synthesis of phosphoramidates from phosphorus compounds containing reactive P—H bonds, such as phosphites and phosphonites [21,22]. Recently, the synthesis of new phosphoramidates with ethanolamine and bis(2-hydroxyethyl)amine using the Atherton–Todd approach was reported in the literature [23,24]. The results presented suggest a selective reactivity of primary as well as secondary amines in the presence of primary alcohols in this reaction. However, such selectivity was not observed in our work. The synthesis of DOPO–DEolA (**6**) using the Atherton–Todd reaction according to Scheme 2 yielded a mixture of different products. Moreover, ^{31}P NMR spectroscopy (signals at 11–12 ppm related to the DOPO-O compounds vs. signals at 16–17 ppm related to the DOPO-N compounds in $CDCl_3$) demonstrates that most of these compounds resulted from the reaction of hydroxyl groups of DEolA with **1**. This can be explained by the fact that the selectivity is strongly dependent on the nature of the phosphorus atom and its reactivity.

Using 3 equiv of **1** in the same reaction caused a complete conversion of DEolA, yielding compound **7** with all three functionalities of DEolA connected to a DOPO unit (Scheme 3).

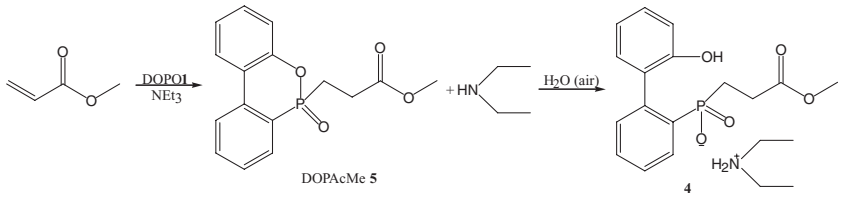
Although the selective amination of **1** with DEolA via the Atherton–Todd reaction was not successful, the synthesis of an alternative molecule was investigated. The aim was to access the DOPO-containing propionic acid amide of DEolA (**8**).

Aminolysis of DOPAcMe (**5**) was performed under an inert atmosphere without any solvent using ammonium hydrochloride as a catalyst (Scheme 4, reaction I). The desired compound **8** was obtained in good yields. However, side products were present in the reaction mixture. ^{31}P NMR spectroscopy (signals at 37 ppm in $CDCl_3$) suggests that a partial transesterification with the hydroxyl groups of DEolA and DOPO took place. The resulting compounds are presented in Fig. 2. Unfortunately, separation of these compounds was not possible.

Another path to access DOPAcDEolA (**8**) is a two-step synthesis shown in Scheme 4 (route II). For this purpose, *N*,*N*-bis(2-hydroxyethyl)acrylamide (AcDEolA, **9**) has to be obtained (Scheme 4, reaction IIa). In the following step, **1** is to react with **9** in a Michael-type reaction [25,26] and to ultimately yield the desired molecule **8** (Scheme 4, reaction IIb). The intermediate AcDEolA (**9**) can be synthesized in



SCHEME 1 Synthesis of compounds **2** and **3**.



SCHEME 2 Synthesis of compounds **4** and **5**.

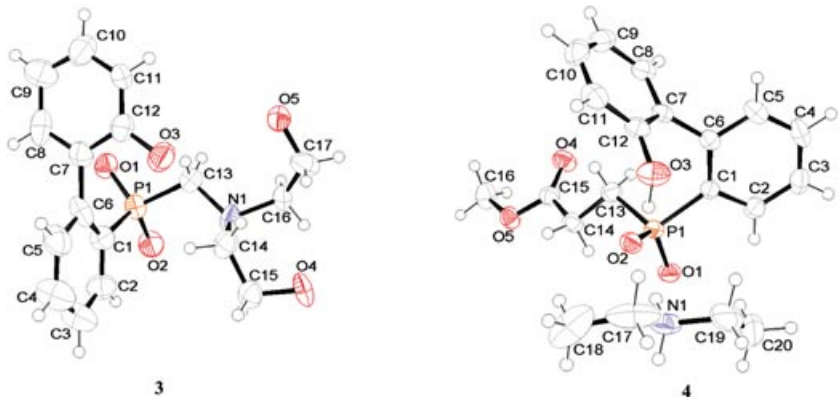
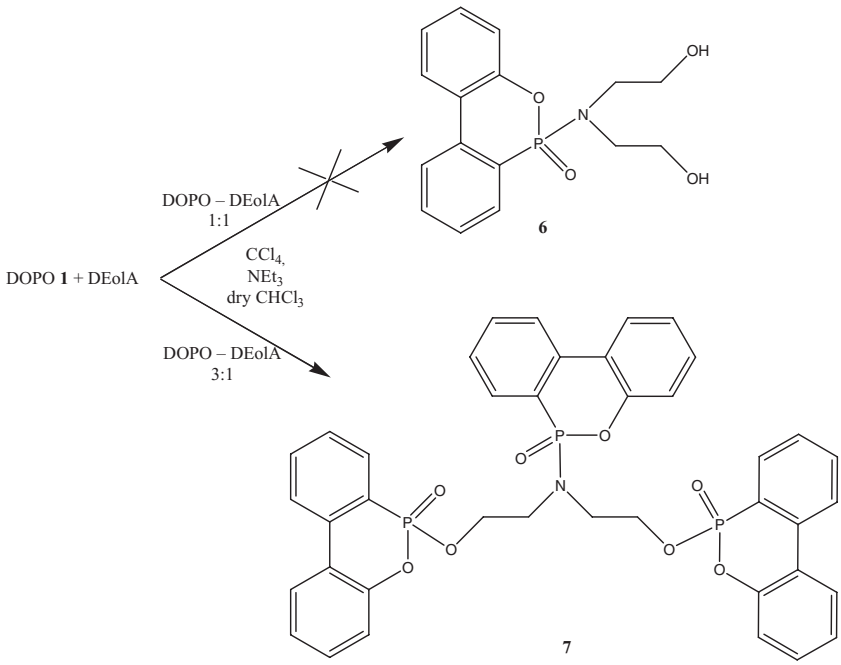
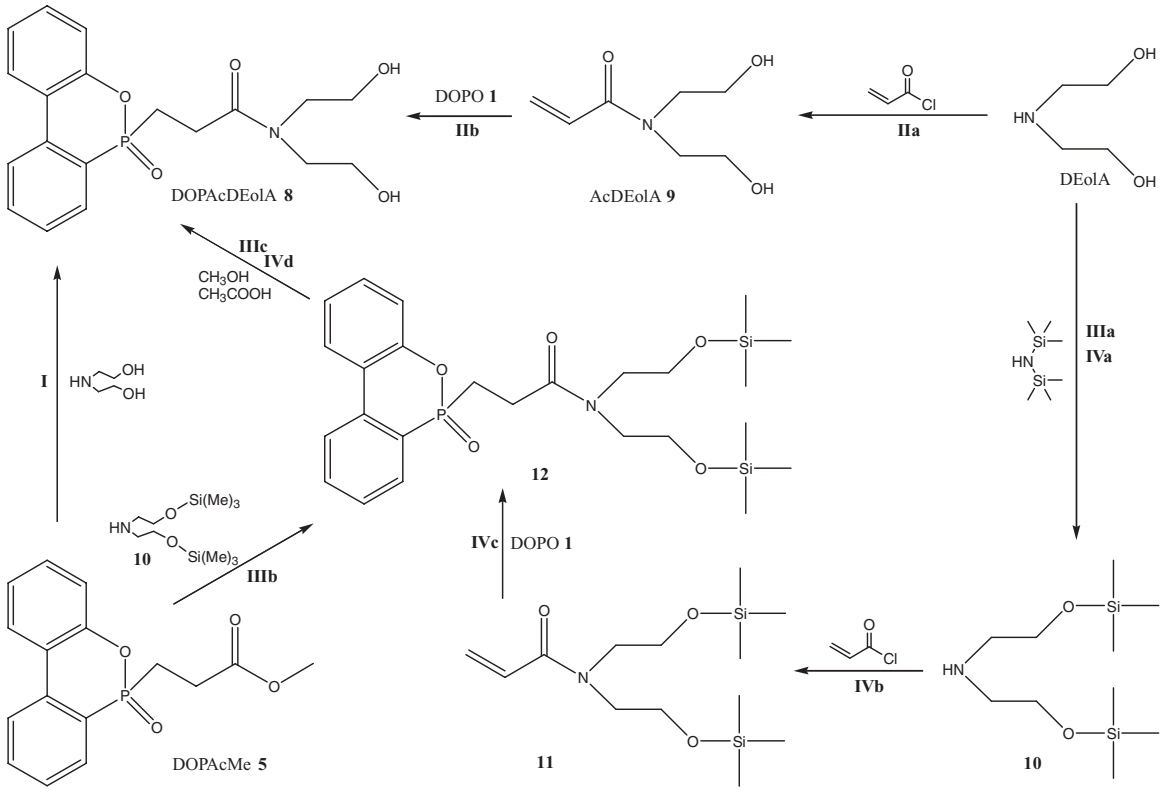


FIGURE 1 Molecular structures of compounds **3** and **4** validated by X-ray analysis.



SCHEME 3 Atherton–Todd reaction of DOPO (**1**) with DEolA.



SCHEME 4 Synthesis of DOPAcDEolA (**8**). I: DEolA, NH_4Cl, 120°C. IIa: (a) AcCl, NEt_3, CH_2Cl_2, 5°C; (b) Na_2CO_3, MeOH, H_2O, r.t. IIb: DOPO, NEt_3, dry toluene, reflux. IIIa (IVa): hexamethyldisilazane, reflux. IIIb: **10**, NH_4Cl, dry toluene, reflux. IIIc (IVd): CH_3OH, CH_3COOH, reflux. IVb: AcCl, NEt_3, dry *n*-pentane, 5°C; IVc: DOPO, NEt_3, dry toluene, reflux.

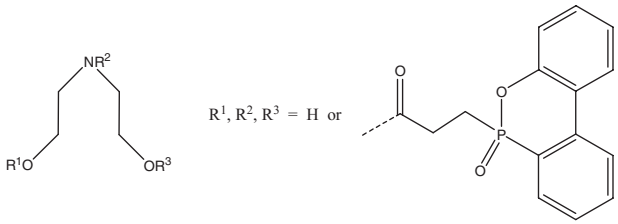


FIGURE 2 Possible products in the reaction of DOPAcMe with DEolA (Scheme 4, reaction I).

two steps: reaction of DEolA with 3 equiv of acryloyl chloride followed by a selective hydrolysis of the hydroxyl groups using sodium carbonate [27]. The described method was slightly modified, and AcDEolA (**9**) was synthesized successfully. However, complete polymerization of this very reactive substance occurs during a few hours at room temperature. This, in turn, means that it is not possible to apply AcDEolA (**9**) in a Michael-type addition without obtaining polymers as side products. The use of stabilization agents was not desirable because of the problematic separation and purification of the final product.

Coming back to the idea of the aminolysis of DOPAcMe (**5**) with DEolA, it was decided to mask the hydroxyl functionalities of the latter with protection groups to prevent the transesterification reaction. Applying a synthesis described in the literature [28], we were able to solely protect the hydroxyl groups of DEolA with hexamethyldisilizane, leaving the secondary amine unaffected and yielding the desired product **10** (Scheme 4, reaction IIIa). Aminolysis of **10** with DOPAcMe (**5**) (Scheme 4, reaction IIIb) reached 50% conversion after only 24 h.

Finally, route IV in Scheme 4 demonstrates the most efficient way to obtain the desired product DOPAcDEolA (**8**). The synthesis includes four steps. After protection of DEolA with trimethylsilyl groups [28] (Scheme 4, reaction IVa), followed a nucleophilic substitution of acryloyl chloride with **10** (Scheme 4, reaction IVb); the product (**11**) was obtained at a yield of 92%. The Michael-like addition of **1** to the double bond of compound **11** was carried out according to the synthesis described for DOPAcMe (**5**), using triethylamine as a catalyst (Scheme 4, reaction IVc). The trimethylsilyl groups are very sensitive to air and moisture, which is why

the analytical data of **12** tend to reveal traces of the hydrolyzed compound. Total deprotection of the hydroxyl groups occurred very smoothly by reflux in methanol in the presence of acetic acid (Scheme 4, reaction IVd). DOPAcDEolA (**8**) was obtained in a quantitative yield. For compound **8**, the ^{13}C NMR signals of C=O, C—O, and C—N were doubled, and in the ^{1}H NMR spectrum, all methylene groups appeared as multiplets. This fact can be explained by the formation of hydrogen bonds and by a partial double bond character of the amidic C—N bond, which restricts the rotation around the C—N axis. The structure and purity of DOPAcDEolA (**8**) were additionally confirmed by HR-MS and elemental analysis, respectively.

To summarize our results, the intramolecular amine salt of the DOPO derivative with an opened ring (**3**) was described. It was formed by the addition of water to compound **2** in the presence of a base. The reverse ring-closing reaction was also demonstrated. It was shown that the addition of **1** to the amine group of DEolA using the Atherton–Todd reaction is not selective because of the similar reactivities of all three functional groups of DEolA and the very reactive phosphorus center. On the other hand, substance **7**, containing three DOPO units, was successfully synthesized using 3 equiv of **1**. Finally, the synthesis of the new DOPO compound containing a diol functionality (**8**) was developed and described. Of the four approaches investigated, one was found to be the most efficient. All four steps of this route provide the corresponding products **10, 11, 12**, and **8** at very high yields. This successful synthesis demonstrates a novel pathway to OH-functionalized phosphorus-containing compounds that can be incorporated as reactive flame retardants in the polymers.

EXPERIMENTAL

Materials and Instruments

Unless stated otherwise, solvents and chemicals were obtained from commercial sources and used without any further purification. NMR spectra were recorded with a Bruker-Analytical BZH 250/52 (250 MHz) and a Varian INOVA-400 (400 MHz). Chemical shifts are reported as δ values relative to the solvent peak. Trimethylsilane was used as a standard. All ^{31}P NMR spectra were measured in a proton-decoupled manner. All ^{13}C NMR spectra were measured in a proton-decoupled and phosphorus-coupled manner. ^{1}H proton spectra were measured by a phosphorus-coupled process. Melting points were uncorrected and measured with a Büchi B-545. High-resolution mass spectrometry (HR MS) analyses were performed on a MicroMass GCT (time of flight (TOF); electron ionization (EI), 70 eV) and Bruker micrOTOF (Nano ESI Offline). IR spectra were recorded with a Varian 660-IR (FT-IR).

Crystallographic Data

XRD measurements were performed using a Siemens SMART CCD 1000 diffractometer with monochromated Mo Kα-irradiation collecting a full sphere of data in the θ ranging from 1.57 to 28.34°. Frames were collected with an irradiation time of 20 s (**3**) or 10 s (**4**) per frame and using the ω-scan technique with $\Delta\omega = 0.45°$. Data were corrected to Lorentz and polarization effects, and an empirical adsorption correction with SADABS [29] was applied. The structures were solved by direct methods and refined to an optimum R1 value with SHELX-97 [30]. Visualization for evaluation was performed with xpma [31], and figures were created with ORTEP [32].

Cambridge Crystallographic Data Centre (CCDC) numbers 811746 and 811747 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033; or deposit@ccdc.cam.ac.uk).

((Bis(2-hydroxyethyl)ammonio)methyl)(2′-hydroxy-[1,1′-biphenyl]-2-yl)phosphinate (3)

DOPO (**1**) (20.0 g, 92.0 mmol) and DEolA (9.7 g, 92.0 mmol) were dissolved in 40 mL of distilled water in a three-neck flask equipped with a reflux condenser, a thermometer, and an addition funnel. The reaction mixture was heated to 80°C using an oil bath, and paraformaldehyde (3.10 g) was added in a dropwise manner during a period of 5 min. The reaction mixture was refluxed for 1 h, cooled down to room temperature, and then concentrated in vacuum using a rotary evaporator to yield a white precipitate. After filtration, followed by washing with distilled water and drying in air, the product **3** was obtained as a white solid (15.2 g, 43.0 mmol, 47%): mp: 151–153°C; ^{31}P NMR (101 MHz, DMSO-d_6) δ 14.4 ppm; ^{13}C NMR (63 MHz, DMSO-d_6) δ 154.5 (s, 1C), 141.5 (d, J = 9.8 Hz, 1C), 136.9 (d, J = 125.5 Hz, 1C—P),133.0 (d, J = 2.9 Hz, 1C), 132.0–131.4 (m, 3C), 130.4 (s, 1C), 129.1 (s, 1C), 126.7 (d, J = 10.9 Hz, 1C), 120.3 (s, 2C), 57.0 (s, 2C—O), 55.3 (s, 2C—N), 52.3 ppm (d, J = 89.0 Hz, 1C—P); ^{1}H NMR (250 MHz, DMSO-d_6) δ10.67 (broad, 1H, O—H), 8.01 (m, 1H),

7.47 (m, 2H), 7.26 (m, 1H), 7.10 (m, 2H), 6.93 (m, 2H), 5.37 (broad, 3H, $2CH_2O$—H and N—H), 3.52 (m, 4H, $2O—CH_2$), 3.12 (m, 4H, $2N—CH_2$), 2.89–2.68 ppm (m, 2H, $P—CH_2$); IR (KBr) ν 3622 (m, O—H), 3209 (vs, O—H), 3077 (m, C_{aryl}—H), 294 and 2923 (m, C—H), 2869 and 2828 (m, C—N), 1606 (m, C=C), 1449 (s, $P—C_{aryl}$), 1180 (vs, P—O), 1093 (s, C—O), 1053 (s, C—N), 1035 (vs, P—O), 765 (s, C—H bend); HRMS (ESI) calcd. for $[^{12}C_{17}H_{22}NO_5P] + H^+$ 352.1308, found 352.1354.

Structural details for **3**: Reflections collected/unique/observed ($I > 2\sigma$): 23,502/4529/800 [R(int) = 0.8426]; parameters refined: 221; formula $C_{17}H_{22}NO_5P$, MM 351.33 g/mol; T = 200(2) K; monoclinic, $C2/c$ (no. 15, Z = 8); a = 2951.0(5)) pm; b = 1012.2(15) pm; c = 1226.2(18) pm; α = 90°; β = 111.33(4)°; γ = 90°; V 3411(9) × 10^6 pm^3; ρ (calcd.) = 1.368 g/cm^3; absorption coefficient = 0.188 mm^{-1}; F(000) = 1488; Goof ($F2$) = 0.788; crystal size 0.2 × 0.3 × 0.04 mm^3; index ranges $-39 \le h \le 39$, $-13 \le k \le 13$, $-16 \le l \le 16$; completeness to θ = 29.70: 93.6%; $R1$ ($I > 2\sigma$) = 0.1342, $wR2$ = 0.3842 (all data); largest difference peak and hole: 0.429 and −0.640 × 10^{-6} e/pm^{-3}. CCDC 811746.

Diethylammonium(2′-hydroxy-[1,1′-biphenyl]-2-yl)(3-oxobutyl)phosphinate (4)

DOPAcMe (**5**) [20] (5.0 g, 16.5 mmol) and diethylamine (2.4 g, 33.0 mmol) were stirred in a round-bottom flask at room temperature for 10 days. The addition of 20 mL of acetonitrile and stirring of the solution over a period of 30 min gave a white precipitate. After recrystallization from acetonitrile and drying in air, the product **4** was obtained as white crystals (4.10 g, 10.4 mmol, 63%): mp: 128–130°C; ^{31}P NMR (101 MHz, DMSO-d_6) δ 23.5 ppm; ^{13}C NMR (63 MHz, DMSO-d_6) δ 73.1 (d, J = 17.1 Hz, 1C=O), 155.0 (s, 1C), 141.8 (d, J = 9.8 Hz, 1C), 138.0 (d, J = 113.8 Hz, 1C—P),134.9 (d, J = 2.6 Hz, 1C), 131.6 (d, J = 6.7 Hz, 1C), 131.4 (d, J = 9.8 Hz, 1C), 130.8 (s, 1C), 129.4 (d, J = 1.9 Hz, 1C), 128.6 (s, 1C), 126.1 (d, J = 9.9 Hz, 1C), 121.2 (s, 1C), 120.0 (s, 1C), 51.1 (s, 1C—O), 41.1 (s, 2C—N), 27.9 (s, 1C—C=O), 25.6 (d, J = 98.3 Hz, 1C—P), 10.9 ppm (s, $2CH_3$); ^{1}H NMR (250 MHz, DMSO-d_6) δ 12.17 (2H), 8.95 (1H), 7.96 (m, 1H), 7.37 (m, 2H), 7.19 (m, 1H), 6.98 (m, 2H), 6.83 (m, 2H), 3.42 (s, 3H, $O—CH_3$), 2.89 (q, J = 7.2 Hz, 4H, $2N—CH_2$), 2.04 (m, 2H, $CH_2—C=O$), 1.86 (m, 2H, $P—CH_2$), 1.18 (t, J = 7.2 Hz, 6H, $2CH_3$); IR (KBr) ν 3447 (m, O—H, N—H), 1731 (vs, C=O), 1456 (m, $P—C_{aryl}$), 1233 (s, C—O), 1160 (s, P—O), 1053 (m, C—N), 1025 (s, P—O), 762 (s, C—H bend); HRMS (ESI) calcd. for $[^{12}C_{20}H_{28}NO_5P] + H^+$ 394.1778, found 394.1820; Anal. calcd. for $C_{20}H_{28}NO_5P$: C, 61.06; H, 7.17; N, 3.56; P, 7.87. Found: C, 61.34; H, 6.97; N, 3.49; P, 7.94%.

Structural details for **4**: Reflections collected/unique/observed ($I > 2\sigma$): 27,526/5137/3116 [R(int) = 0.0606]; parameters refined: 263; formula $C_{20}H_{28}NO_5P$, MM 393.40 g/mol; T = 200(2) K; monoclinic, $P2(1)/c$ (no. 14, Z = 4); a = 1248.0 (3) pm; b = 828.1 (2) pm; c = 2082.0 (5) pm; α = 90°; β = 104.064 (4)°; γ = 90°; V 2087.2 (9) × 10^6 pm^3; ρ (calcd.) = 1.252 g/cm^3; absorption coefficient = 0.161 mm^{-1}; F(000) = 840; Goof ($F2$) = 0.960; crystal size 0.3 × 0.3 × 0.35 mm^3; index ranges $-16 \le h \le 16$, $-10 \le k \le 11$, $-27 \le l \le 27$; completeness to θ = 28.38: 92.2%; $R1$ ($I > 2\sigma$) = 0.0527, $wR2$ = 0.1388 (all data); the largest difference peak and hole: 0.400 and −0.284 × 10^{-6} e/pm^{-3}. CCDC 811747.

6-((Bis(2-hydroxyethyl)amino)methyl)-6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide (2)

Heating of compound **3** (1.0 g, 2.8 mmol) using an oil bath at 120°C for 2 h while stirring in vacuum (3 mbar) gave the product **2** as a transparent gum-like substance (806 mg, 2.4 mmol, 86%): mp: 45–47°C; ^{31}P NMR (101 MHz, DMSO-d_6) δ 33.4 ppm; ^{13}C NMR (63 MHz, DMSO-d_6) δ 148.9 (d, J = 8.3 Hz, 1C), 134.9 (d, J = 5.7 Hz, 1C), 133.3 (d, J = 2.0 Hz, 1C), 130.7 (d, J = 10.5 Hz, 1C), 130.6 (s, 1C), 128.4 (d, J = 12.6 Hz, 1C), 125.5 (s, 1C), 124.5 (s, 1C), 124.1 (d, J = 113.3 Hz, 1C—P), 123.8 (d, J = 9.0 Hz, 1C), 121.5 (d, J = 10.0 Hz, 1C), 119.8 (d, J = 5.7 Hz, 1C), 59.0 (s, 2C—O), 57.8/57.7 (s, 2C—N), 53.2 ppm (d, J = 116.3 Hz, 1C—P); ^{1}H NMR (250 MHz, DMSO-d_6) 8.18 (m, 2H), 8.01 (m, 1H), 7.78 (m, 1H), 7.59 (m, 1H), 7.45 (m, 1H), 7.28 (m, 2H), 4.36 (m, 2H, 2O—H), 3.38 (m, 2H, $P—CH_2$), 3.26 (m, 4H, $2O—CH_2$), 2.64 ppm (m, 4H, $2N—CH_2$); IR (KBr) ν 3381 (vs, O—H), 3063 (m, C_{aryl}—H), 2945 (s, C—H), 2881 (s, C—N), 1594 (m, C=C), 1477 (s, CH_2), 1448 (s, $P—C_{aryl}$), 1431 (s, OH), 1202 (vs, P=O), 1038 (s, C—O), 917 (m, P—O), 757 (vs, C—H bend); HRMS (ESI) calcd. for $[^{12}C_{17}H_{20}NO_4P] + H^+$ 334.1203, found 334.1249.

6,6′-((((6-Oxido-6H-dibenzo[c,e][1,2]oxaphosphinine-6-yl)azanediyl)bis(ethane-2,1-diyl))bis(oxy))bis(6H-dibenzo[c,e][1,2]oxaphosphinine 6-oxide) (7)

A flame-dried three-neck flask with a condenser, a thermometer, and an addition funnel was flooded with argon and charged with **1** (30.9 g, 143 mmol), carbon tetrachloride (23.0 g, 150 mmol), and 200 mL of dry chloroform. The reaction mixture was cooled

to 5°C with an ice bath. The addition funnel was charged with triethylamine (15.5 g, 150 mmol) and DEolA (5.00 g, 47.5 mmol) dissolved in 50 mL of dry chloroform. The triethylamine mixture was added in a dropwise manner under vigorous stirring. The reaction temperature was not allowed to exceed 10°C. After 1 h, the addition was complete and the NMR analysis indicated complete conversion of the starting material. The reaction mixture was washed three times with 50 mL water to remove triethylamine hydrochloride. The organic phase was isolated, dried over $MgSO_4$, and filtered over a small pad of aluminum oxide (basic). The solvent was removed in vacuum. The spectroscopically pure product **7** was obtained as a brown solid (24.5 g, 32.8 mmol, 69%) mp 81–83°C; ^{31}P NMR (101 MHz, $CDCl_3$) δ17.17 (P–N), 11.01/10.97 (P—O) ppm; ^{13}C NMR (63 MHz, DMSO-d_6) δ 149.7 (d, J = 7.9 Hz, 3C—O), 137.1 (d, J = 7.0 Hz, 1C), 136.8 (d, J = 7.0 Hz, 2C), 134.7 (s, 2C), 133.6 (s, 1C), 131.5 (s, 2C), 131.1 (s, 1C), 130.4/129.6 (d, J = 9.4 Hz, 3C), 126.5 (d, J = 4.3 Hz, 3C), 125.9 (s, 1C), 125.7 (s, 2C), 125.4 (d, J = 11.4 Hz, 3C), 124.8 (s, 1C), 123.9/123.8 (d, J = 177.9 Hz, 3C—P), 122.6 (d, J = 11.6 Hz, 2C), 121.7/121.2 (d, J = 11.4 Hz, 3C), 120.5–120.4 (m, 3C), 64.4–64.2 (m, 3C), 45.4–45.3 ppm (m, 3C); ^{1}H NMR (250 MHz, DMSO-d_6) δ 8.20—8.09 (m, 6H,), 7.86–7.77 (m, 4H), 7.67 (t, J = 7.7 Hz, 1H), 7.60–7.53 (m, 2H), 7.43–7.14 (m, 10H), 7.00–6.88 (m, 1H), 4.00–3.99 (m, 4H), 3.06–2.97 ppm (m, 4H); IR (KBr) ν 3063 (m, C_{aryl}—H), 2955 (m, C—H), 1596 (m, C=C), 1477 (vs, P—C_{aryl}), 1448 and 1431 (s, CH_2), 1272, 1240, and 1204 (vs, P=O), 1005 (vs, P—N), 919 (vs, P—O), 754 (vs, C—H bend) cm^{-1}; HRMS (ESI) calcd. for [$^{12}C_{40}H_{32}NO_8P_3$] + H^+ 748.1414, found 748.1697.

N,N-Bis(2-((trimethylsilyl)oxy)ethyl)acrylamide (11)

DEolA-2-TMS (**10**) [28] (75.0 g, 301 mmol) and triethylamine (33.5 g, 331 mmol) were dissolved in 400 mL of dry *n*-pentane in a three-neck flask equipped with a reflux condenser, a mechanical stirrer, an addition funnel, and an argon gas inlet. The reaction mixture was cooled with an ice bath under an argon atmosphere, and a solution of acryloyl chloride (27.3 g, 301 mmol) in 100 mL of dry *n*-pentane was added in a dropwise manner over a period of 30 min under vigorous stirring. The reaction mixture was stirred for 30 min at room temperature. The formed triethylamine hydrochloride was filtered off and washed thoroughly with *n*-pentane. The organic phase was concentrated in vacuum to yield the spectroscopically pure product **11** as a yellow oil (84.0 g, 277 mmol, 92%): ^{13}C NMR (63 MHz, $CDCl_3$) δ 166.7 (s, 1C=O), 128.1 (s, 1CH=C), 127.3 (s, 1CH_2=C), 60.6/60.4 (s, 2C—O), 51.3/49.6 (s, 2C—N), −0.7/ − 0.8 ppm (s, 6C—Si); ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.66 (dd, J = 10.4 Hz, J = 16.8 Hz, 1H), 6.31 (dd, J = 16.8 Hz, J = 2.0 Hz, 1H), 5.64 (dd, J = 10.4 Hz, J = 2.0 Hz, 1H), 3.85–3.66 (m, 4H, 2O—CH_2), 3.66–3.42 (m, 4H, 2N—CH_2), 0.08 ppm (s, 18H, 6Si—CH_3); IR (KBr) ν 2958 (vs, C=C—H), 2901, (m, C—H), 2869 (m, C—N), 1654 (vs, C=O), 1615 (s, C=C), 1471, 1445 and 1428 (s, CH_2 and CH_3), 1252 (vs, C—O), 1102 (vs, Si–O), 931 and 877 (s-vs, C=C—H), 841 (vs, Si—C), 748 (s, C—H bend); HRMS (EI) calcd. for [$^{12}C_{13}H_{29}NO_3Si_2$]$^+$ 303.1686, found 303.1763.

3-(6-Oxido-6H-dibenzo[c,e][1,2]oxaphosphinine-6-yl)-N,N-bis(2-((trimethylsilyl)oxy)ethyl)-propanamide (12)

DOPO (**1**) (57.0 g, 264 mmol) and triethylamine (3.03 g, 3.00 mmol) were dissolved in 100 mL of dry toluene at 85°C in a three-neck flask equipped with a condenser, an addition funnel, and an argon gas inlet. A solution of AcDEolA-2-TMS (**11**) (80.0 g, 264 mmol) in 50 mL of dry toluene was added to the reaction mixture over a period of 15 min under stirring in an argon atmosphere at the same temperature. The reaction mixture was refluxed overnight and then cooled to room temperature. The solvent was removed in vacuum, and the residue was dried in high vacuum at 10^{-3} mbar at 95°C for 3 h. The product **12** was obtained quantitatively as a white, very viscous oil (135 g, 261 mmol, 99%): ^{31}P NMR (101 MHz, $CDCl_3$) δ 39.1 ppm; ^{13}C NMR (63 MHz, $CDCl_3$) δ 170.9 (d, J = 17.4 Hz, 1C=O), 148.8 (d, J = 8.1 Hz, 1C), 135.5 (d, J = 6.0 Hz, 1C), 133.2 (d, J = 3.8 Hz, 1C), 130.5 (s, 1C), 129.8 (d, J = 11.0 Hz, 1C), 128.3 (d, J = 13.3 Hz, 1C), 125.1 (s, 1C), 124.6 (s, 1C), 124.3 (d, J = 120.4 Hz, 1C—P), 123.8 (d, J = 9.5 Hz, 1C), 122.2 (d, J = 11.0 Hz, 1C), 120.3 (d, J = 5.9 Hz, 1C), 60.3/59.8 (s, 2C—O), 50.9/48.8 (s, 2C—N), 25.2 (d, J = 1.8 Hz, 1C—C=O), 24.0 (d, J = 99.1 Hz, 1C—P), −0.7/ − 0.8 ppm (s, 6C—Si); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.92 (m, 3H), 7.68 (m, 1H), 7.50 (m, 1H), 7.36 (m, 1H), 7.22 (m, 2H), 3.64 (m, 4H, 2O—CH_2), 3.45 (m, 4H, 2N—CH_2), 2.77 (m, 2H, P—CH_2), 2.40 (m, 2H, O=C—CH_2), 0.06 ppm (m, 18H, 6Si—CH_3); HRMS (ESI) calcd. for [$^{12}C_{25}H_{38}NO_5PSi_2$] + H^+ 520.2871, found 520.2099.

N,N-Bis(2-hydroxyethyl)-3-(6-oxido-6H-dibenzo[c,e][1,2]oxaphosphinine-6-yl)propanamide (8)

DOPAcDEolA-2-TMS (**12**) (144 g, 277 mmol), acetic acid (8.30 g, 139 mmol), and 100 mL of methanol

were charged in a round-bottom flask equipped with a condenser. The reaction mixture was refluxed overnight. The solvent was removed in vacuum, and the residue was dried in high vacuum at 10^{-3} mbar at 100°C for 8 h. The hot, viscous mass was poured into an aluminum mould and cooled to room temperature. The transparent glass-like solid was crushed and then ground in a blender to give the product **8** as a white powder in a quantitative yield (103 g, 274 mmol, 99%): mp 47–50°C; ^{31}P NMR (101 MHz, $CDCl_3$) δ 39.9 ppm; ^{13}C NMR (63 MHz, $CDCl_3$) δ 172.2/172.0 (s, 1C=O), 148.4 (d, J = 8.0 Hz, 1C), 135.2 (d, J = 6.1 Hz, 1C), 133.4 (s, 1C), 130.5 (s, 1C), 129.8 (d, J = 11.2 Hz, 1C), 128.4 (d, J = 13.5 Hz, 1C), 125.0 (s, 1C), 124.6 (s, 1C), 123.7 (d, J = 9.6 Hz, 1C), 123.6 (d, J = 121.9 Hz, 1C—P), 121.9 (d, J = 11.0 Hz, 1C), 120.1 (d, J = 5.9 Hz, 1C), 60.1/59.8 (s, 2C—O), 51.7/50.2 (s, 2C—N), 25.3 (d, J = 2.2 Hz, 1C—C=O), 23.7 ppm (d, J = 98.5 Hz, 1C—P); ^{1}H NMR (250 MHz, $CDCl_3$) 7.85 (m, 3H), 7.63 (m, 1H), 7.46 (m, 1H), 7.30 (m, 1H), 7.17 (m, 2H), 5.67 (broad, 2H, $2CH_2O$—H), 3.67–3.56 (m, 4H, $2O-CH_2$), 3.50–3.26 (m, 4H, $2N-CH_2$), 2.86–2.56 (m, 2H, $P-CH_2$), 2.49–2.16 ppm (m, 2H, $O=C-CH_2$); IR (KBr) ν 3389 (s, O—H), 3064 (w, C_{aryl}—H), 2923 (m, C—H), 2865 (m, C—N), 1638 (vs, C=O), 1477 (s, $P-C_{aryl}$), 1447 (m, CH_2), 1430 (s, OH), 1229 and 1203 (vs, P=O), 1044 (m, C—O), 912 (m, P—O), 758 (vs, C—H bend); HRMS (ESI) calcd. for $[^{12}C_{19}H_{22}NO_5P] + H^+$ 376.1308, found 376.1381; Anal. calcd. for $C_{19}H_{22}NO_5P$: C, 60.80; H, 5.91; N, 3.73; P, 8.25. Found: C, 60.28; H, 5.88; N, 3.62; P, 8.12%.

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