Phosphine-Catalyzed Synthesis of Unsymmetrical 1,3-Bis- and Trisphosphorus Ligands

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Abstract: Phosphine-catalyzed umpolung γ-additions of phosphorus pronucleophiles on alkynes bearing phosphinoyl (P=O) or phosphinothioyl (P=S) moieties have been explored. The reaction leads to bis- or trisphosphorus subunits that can be useful for the preparation of chelating ligands.

Key words: addition reactions, catalysis, umpolung, chelates, phosphorus

Among known metal chelating subunits, phosphorus-based functions are of considerable importance in coordination chemistry.[1] Because of their strong metal ion complexing ability, bis- and trisphosphorus compounds are commonly used as efficient bi- or tridentate ligands for metal sequestration. In this context, new and efficient synthetic methods for the preparation of this important class of organophosphorus products are of key interest.[2]

In connection with our efforts to develop new synthetic routes to bisphosphorus actinide ligands,[3] we have recently described the phosphine-catalyzed α-P-addition on phosphinoyl alkynes, leading to P–C–P backbones[4] (Scheme 1, upper part). In this paper, we would like to report the extension of this process to the preparation of 1,3-diphosphane oxides **4**. The designed route to compounds **4** involves a Bu_3P-catalyzed γ-addition of phosphorus pronucleophiles on activated alkynes **1**, as the key step (Scheme 1, lower part). Phosphines are known to impart the electronic character to the γ-carbon of acetylenic esters and promote C–C,[5] C–O,[6] or C–N[7] bond formation in the presence of various pronucleophiles. Following our results on the Bu_3P-catalyzed α-C–P bond formation,[4] we envisaged that such chemistry could be extended to γ-P-addition by using the appropriate phosphorus-based pronucleophiles and alkynes. Thus, reaction of 1-(phosphane oxide)-propyne **1** with *H*-phosphane oxide pronucleophiles in the presence of catalytic amounts of Bu_3P should generate 1,3-diphosphoryl(phosphonyl, phosphinyl)-propenes **2** and **3** whose double bond could be hydrogenated to afford the desired products **4**.

This synthetic route, based on phosphine-catalyzed umpolung γ-addition, allows the control of the nature of the two phosphorus moieties and therefore is well adapted to the preparation of unsymmetrical 1,3-bisphosphorus compounds. The latter are usually difficult to synthesize by classical methods.[8]

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The preparation of the starting alkynes **1** was achieved using a conventional route (Scheme 2). Compounds **1a**,**b** were obtained by reaction of propynyl magnesium bromide on the corresponding phosphinic chloride at –78 °C.

With the objective to synthesize mixed 1,3-phosphinoyl/phosphinothioyl P(O)/P(S) ligands, we also prepared the sulfur containing alkyne **1c** that will be used as model substrate. Alkyne **1c** was obtained in satisfactory yield by reacting **1a** with Lawesson's reagent (Scheme 2).

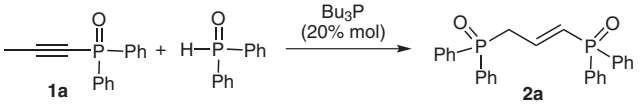
To study the γ-P-addition, the reaction of diphenylphosphine oxide with alkyne **1a** was chosen as the model reaction (Scheme 3).

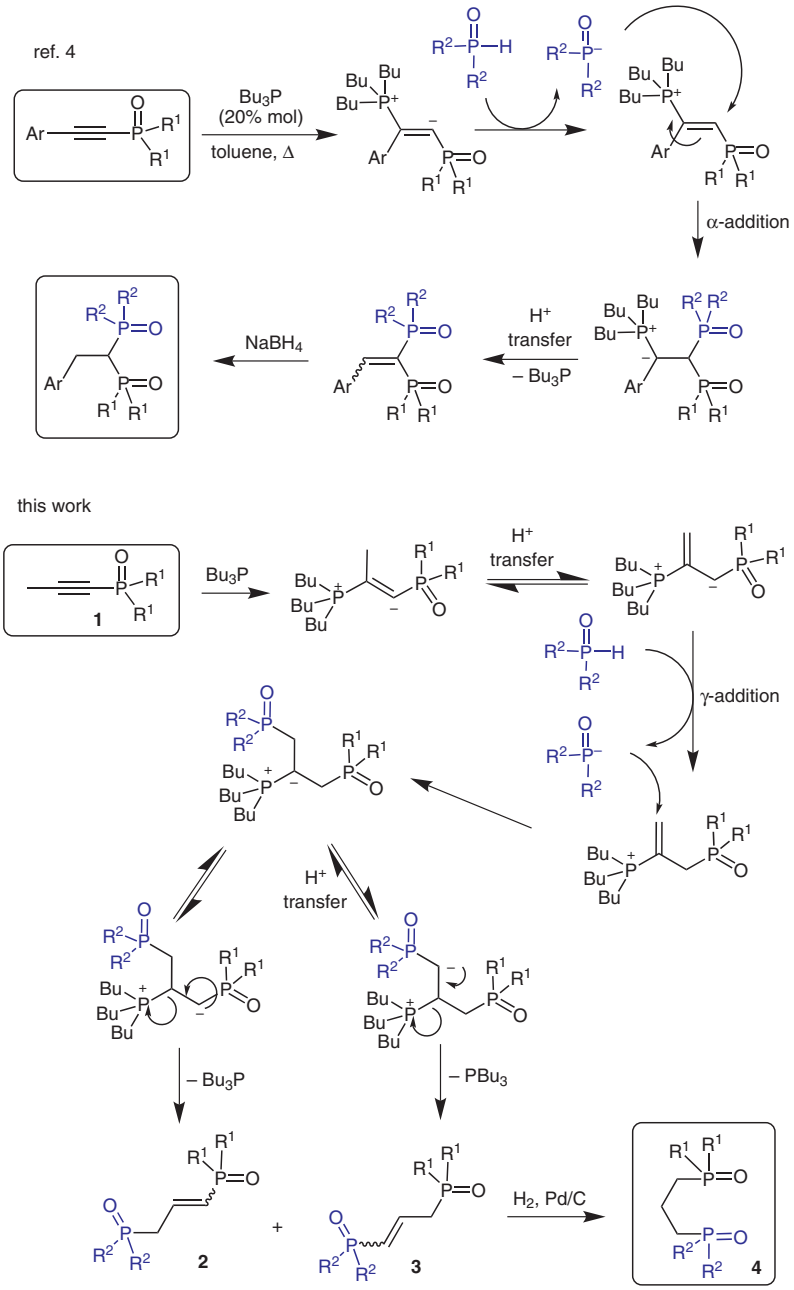
Our first attempts showed that the γ-P-addition was trickier compared to the α-P-addition reaction (Table 1). Indeed, prolonged heating of reactants in the presence of 20 mol% of the phosphine catalyst afforded only traces of the desired product (entries 1 and 2, Table 1). After numerous unsuccessful attempts, microwave irradiation in 2-PrOH was found to be the most efficient method to obtain good yields of product **2a** (entry 7, Table 1).

To look at the scope and limitations of this new reaction we ran a series of γ-additions under the optimized conditions (Scheme 4, Table 2). The reaction generated, in each case, a mixture of *Z*- and *E*-isomers of γ-adducts **2** and **3** in moderate to good yields. It has to be pointed out that compounds **2** and **3** were not formed in the absence of Bu_3P. The only products observed in this case are classical Michael adducts resulting from the 1,4-addition of *H*-phosphane oxide.

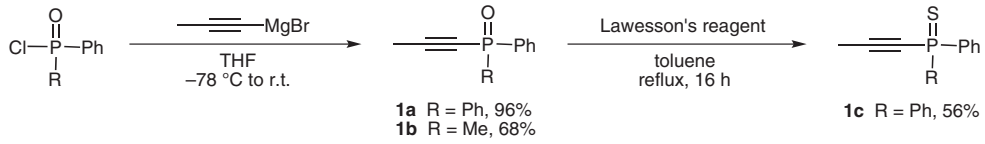
After isolation by flash chromatography of **2** and **3** from the crude product, the mixture of isomers (**2/3**) was subjected to hydrogenation to afford a single product **4** in high yield. However, in the case of sulfur-containing compounds **2g/3g**, hydrogenation proceeded less readily and required 1.5 equivalents of Pd/C and high pressure (50 bar) to generate the expected product **4g**. Notably was that the mixture of isomers **2h/3h** failed to react, even under these forcing conditions.

Overall, the double bond incorporated in the skeleton of **2** and **3** was found to display very poor reactivity and functionalization attempts using, for example, Michael addition reactions with amines, Rli, or RMgX were unsuccessful.





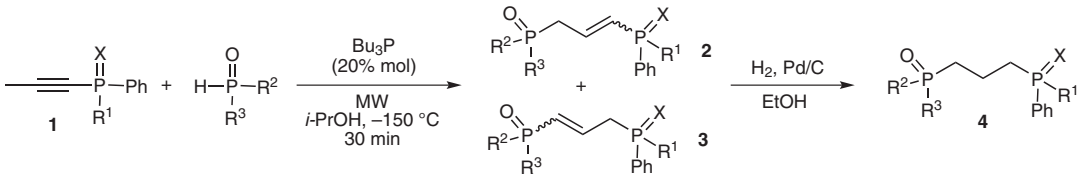
Scheme 1 Routes to unsymmetrical phosphorus ligands using phosphine-catalyzed umpolung additions



Scheme 2 Preparation of compounds **1**

Scheme 3 Model reaction under investigation

The same strategy was also applied to the preparation of trisphosphane oxide **4h** starting from bisalkyne **1d** which was prepared by double addition of propynyl magnesium bromide on dichlorophenylphosphine oxide (Scheme 5). Compound **1d** was then reacted with 3 equivalents of diethylphosphite under microwave irradiation. The reaction resulted in double γ-P-addition of $HP(O)(OEt)_2$ on **1d**. Catalytic hydrogenation of the crude mixture finally afforded the desired trisphosphane oxide **4h** in satisfactory yield.

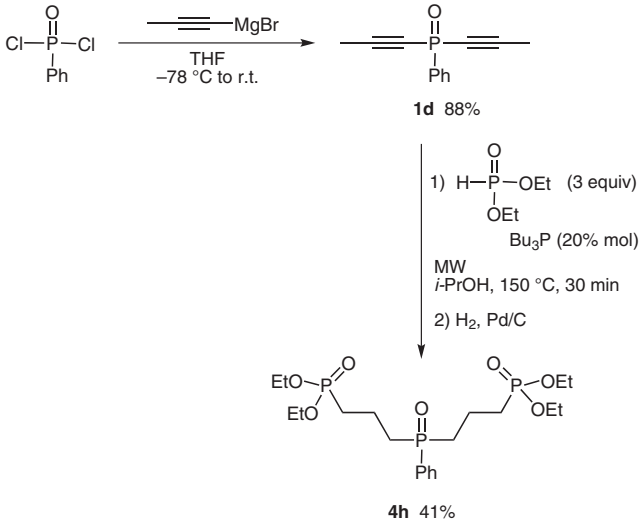


Scheme 4 Preparation of unsymmetrical bisphosphorus ligands **4**

Table 1 Optimization of the Model Reaction[a]

Entry	Conditions	Yield of **2a** (%)[b]
1	EtOH, 80 °C, 6 h	traces
2	toluene, 110 °C, 6 h	traces
3	EtOH, MW, 150 °C, 30 min	27
4	DME, MW, 150 °C, 30 min	traces
5	MeCN, MW, 150 °C, 30 min	traces
6	*t*-BuOH, MW, 150 °C, 30 min	traces
7	*i*-PrOH, MW, 150 °C, 30 min	72

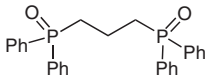
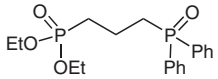
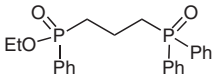
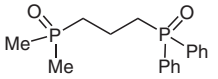
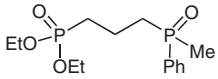
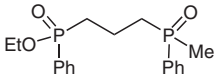
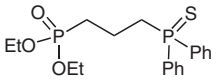
[a] Reactions were conducted with 1.1 equiv of $Ph_2P(O)H$ at 0.1 M.
[b] Isolated yields.



Scheme 5 Preparation of trisphosphorus ligand **4h**

In conclusion, we have developed a new method for the synthesis of symmetrical or unsymmetrical 1,3-phosphane oxides compounds using γ-P-addition on activated propynes. The reaction proceeds under microwave irradiation within 30 minutes, and the resulting mixture of isomers was successfully reduced to the final products by hydrogenation.[9] This method is complementary to others known procedures but only requires two steps and is straightforward for the synthesis of 1,3-phosphane oxides. This reaction may also be used for the preparation of unsymmetrical 1,3-bisphosphines that are of interest in catalysis by complete reduction of products **2** and **3**.[10]

Table 2 Scope of the Reaction

Entry	R	R′	R″	X	Yield (%)[a] of **2** and **3** (2:3 ratio)	Product **4** (yield, %)[a]
1	Ph	Ph	Ph	O	**2a** 72 (–)	 **4a** 96
2	Ph	OEt	OEt	O	**2b/3b** 74 (50:50)	 **4b** 90
3	Ph	OEt	Ph	O	**2c/3c** 78 (56:44)	 **4c** 89
4	Ph	Me	Me	O	**2d/3d** 25 (72:28)	 **4d** 94
5	Me	OEt	OEt	O	**2e/3e** 45 (37:63)	 **4e** 99
6	Me	OEt	Ph	O	**2f/3f** 49 (18:82)	 **4f** 99
7	Ph	OEt	OEt	S	**2g/3g** 26 (58:42)	 **4g** 90
8	Ph	Ph	Ph	S	**2h/3h** 34 (50:50)	no reaction

[a] Isolated yields.

Acknowledgment

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(9) **General Procedure for the Preparation of Compounds 1**
To a soln of phosphoric chloride (5.5 mmol) in dry THF propynylmagnesium bromide (10 mL, 5 mmol, 0.5 M in THF) was added dropwise under Ar at –78 °C. The mixture was stirred at this temperature for 2 h, diluted with Et_2O, washed with a sat. soln of NH_4Cl and brine, dried over $MgSO_4$, filtered, and concentrated under vacuum. The crude residue was purified by column chromatography on SiO_2 (eluent: EtOAc–cyclohexane = 8:2).
Compound **1a**: white solid, mp 89–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.11 (d, *J* = 3.6 Hz, 3 H), 7.43–7.48 (m, 6 H), 7.79–7.85 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.02 (d, *J* = 3 Hz), 75.33 (d, *J* = 174 Hz), 105.46 (d, *J* = 32 Hz), 128.44 (t, *J* = 10 Hz), 130.81 (d, *J* = 12 Hz), 132.01 (d, *J* = 3 Hz), 133.20 (d, *J* = 121 Hz) ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 7.76 ppm. MS (ESI/TOF): *m/z* = 241 $[M + H]^+$.
Compound **1b**: white solid, mp 67–68 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.86 (d, *J* = 14.4 Hz, 3 H), 2.04 (d, *J* = 3.6 Hz, 3H), 7.47-7.56 (m, 3H), 7.81-7.87 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 4.77 (d, *J* = 3 Hz), 20.53 (d, *J* = 86 Hz), 75.22 (d, *J* = 167 Hz), 103.2 (d, *J* = 32 Hz), 128.56 (d, *J* = 13 Hz), 129.85 (d, *J* = 11 Hz), 131.99 (d, *J* = 3 Hz), 133.54 (d, *J* = 118 Hz) ppm. ^{31}P NMR (160 MHz, $CDCl_3$) δ = 10.17 ppm. MS (ESI/TOF): *m/z* = 179 $[M + H]^+$.
Compound **1c**: white solid, mp 93–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.12 (d, *J* = 4 Hz, 3 H), 7.41–7.48 (m, 6 H), 7.89–7.92 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.39 (d, *J* = 3 Hz), 73.25 (d, *J* = 158 Hz), 106.07 (d, *J* = 28 Hz), 128.52 (d, *J* = 14 Hz), 130.73 (d, *J* = 12 Hz), 131.66 (d, *J* = 3 Hz), 133.83 (d, *J* = 97 Hz) ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 19.69 ppm. MS (ESI/TOF): *m/z* = 257 $[M + H]^+$.
Compound **1d**: white solid, mp 85–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.88 (d, *J* = 4.0 Hz, 6 H), 7.31–7.41 (m, 3 H), 7.77 (dd, *J* = 7.2, 15.6 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 4.76 (d, *J* = 4 Hz), 74.85 (d, *J* = 102 Hz), 103.42 (d, *J* = 39 Hz), 128.47 (d, *J* = 15 Hz), 129.92 (d, *J* = 12 Hz), 132.35 (d, *J* = 3 Hz), 132.97 (d, *J* = 141 Hz) ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = –20.76 ppm. MS (ESI/TOF): *m/z* = 203 $[M + H]^+$.

General Procedure for γ-P-Addition Reaction
The mixture of compound **1** (1 equiv), phosphorus pronucleophiles (1.2 equiv), and tributylphosphine (0.2 equiv) in 2-PrOH was irradiated under microwave for 30 min at 150 °C. The solvent was evaporated under vacuum, and the product was purified by column chromatography on SiO_2 (eluent: acetone).
Compound **2a**: white solid, mp 87–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.36 (dd, *J* = 7.6 Hz, *J* = 15.2 Hz, 2 H), 6.34–6.46 (m, 1 H), 6.47–6.60 (m, 1 H), 7.33–7.56 (m, 16 H), 7.69–7.75 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.61 (d, *J* = 17 Hz), 37.25 (d, *J* = 17 Hz), 128.45 (d, *J* = 12 Hz), 128.76 (d, *J* = 12 Hz), 129.44 (d, *J* = 10 Hz), 130.86 (d, *J* = 10 Hz), 131.25 (d, *J* = 10 Hz), 131.76 (d, *J* = 3 Hz), 131.61, 132.12 (d, *J* = 2 Hz), 132.19, 132.66, 140.17–140.30 (m)ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 23.38, 23.42, 28.96, 29.00 ppm. MS (ESI/TOF): *m/z* = 443 $[M + H]^+$.

General Procedure for Hydrogenation of Compounds 2 and 3
A mixture of **2** and **3** was hydrogenated using Pd/C (0.03 equiv of 10% Pd/C) catalyst in EtOH at r.t. for 24 h. After filtration, the residue was washed with EtOH (3×). The combined organic phases were evaporated to give desired product.
Compound **4a**: white solid, mp 142–144 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.91–2.02 (m, 2 H), 2.43–2.50 (m, 4 H), 7.35–7.46 (m, 12 H), 7.63–7.66 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.85, 29.95 (dd, *J* = 11, 71 Hz), 128.59 (d, *J* = 12 Hz), 130.61 (d, *J* = 9 Hz), 131.68 (d, *J* = 3 Hz), 132.53 (d, *J* = 98 Hz) ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 32.52 ppm. MS (ESI/TOF): *m/z* = 445 $[M + H]^+$. HRMS: *m/z* calcd for $C_{27}H_{26}O_2NaP_2$: 467.1306; found: 467.1312.
Compound **4b**: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, *J* = 7.2 Hz, 6 H), 1.81–1.95 (m, 4 H), 2.38–2.43 (m, 2 H), 3.98–4.03 (m, 4 H), 7.43–7.51 (m, 6 H), 7.69–7.75 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.29, 16.33 (d, 6 H), 26.26 (dd, *J* = 14, 140 Hz), 30.00 (d, *J* = 84 Hz), 128.62 (d, *J* = 11 Hz), 130.68 (d, *J* = 10 Hz), 131.73 (d, *J* = 2 Hz), 132.61 (d, *J* = 98 Hz) ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 30.58, 32.01 ppm. MS (ESI/TOF): *m/z* = 381 $[M + H]^+$. HRMS: *m/z* calcd for $C_{19}H_{26}O_4NaP_2$: 403.1204; found: 403.1211.
Compound **4c**: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.18–1.24 (m, 3 H), 1.75–2.08 (m, 4 H), 2.35–2.46 (m, 2H); 3.74–3.80 (m, 1 H), 3.95–4.02 (m, 1 H), 7.39–7.51 (m, 9 H), 7.63–7.72 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.63, 16.35 (d, *J* = 6 Hz), 30.15 (dd, *J* = 14, 100 Hz), 60.51 (d, *J* = 6 Hz), 128.58 (d, *J* = 12 Hz), 130.67 (d, *J* = 9 Hz), 131.50 (d, *J* = 10 Hz), 131.68 (s, l), 132.22–132.27 (m)ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 32.17, 43.68 ppm. MS (ESI/TOF): *m/z* = 413 $[M + H]^+$. HRMS: *m/z* calcd for $C_{23}H_{26}O_3NaP_2$: 435.1255; found: 435.1258.
Compound **4d**: white solid, mp 145–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.37 (d, *J* = 12.0 Hz, 6 H), 1.85–1.94 (m, 4 H), 2,37–4,48 (m, 2 H), 7.40–7.47 (m, 6 H), 7.69 (t, *J* = 8.8 Hz, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.85, 16.03 (d, *J* = 68 Hz), 22.12, 30.24 (dd, *J* = 12, 71 Hz), 31.77–31.83 (m), 32.43 (d, *J* = 13 Hz), 128.68 (d, *J* = 12 Hz), 130.62 (d, *J* = 9 Hz), 131.84 (d, *J* = 2 Hz), 132.83 ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 32.45, 43.33 ppm. MS (ESI/TOF): *m/z* = 321 $[M + H]^+$. HRMS: *m/z* calcd for $C_{17}H_{22}O_2NaP_2$: 343.0993; found: 343.0995.

Compound **4e**: yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.05–1.17 (m, 6 H), 1.58 (d, *J* = 11.2 Hz, 3 H), 1.65–1.96 (m, 6 H), 3.85–3.92 (m, 4 H), 7.35–7.40 (m, 3 H), 7.58 (s, l, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.29 (d, *J* = 4 Hz), 16.17 (d, *J* = 70 Hz), 16.27 (t, *J* = 5 Hz), 26.24 (dd, *J* = 13, 140 Hz), 31.55–32.69 (m), 61.39 (d, *J* = 6.4 Hz), 128.58 (d, *J* = 10 Hz), 128.58 (d, *J* = 11 Hz), 129.90 (d, *J* = 8 Hz), 131.62, 133.05 (d, *J* = 97 Hz)ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 30.42, 36.84 ppm. MS (ESI/TOF): *m/z* = 319 [M + H]$^+$. HRMS: *m/z* calcd for $C_{14}H_{24}O_4NaP_2$: 341.1048; found: 341.1046.

Compound **4f**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.03–1.17 (m, 3 H), 1.53 (t, *J* = 12.8 Hz, 3 H), 1.58–1.98 (m, 6 H), 3.61–3.71 (m, 1 H), 3.83–3.93 (m, 1 H), 7.26–7.42 (m, 6 H), 7.48–7.62 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.53–14.65 (m), 15.54, 15.76, 16.22–16.46 (m), 29.67 (t, *J* = 14 Hz), 30.67 (t, *J* = 14 Hz), 31.70 (t, *J* = 12 Hz), 32.39 (t, *J* = 12 Hz), 57.46, 60.34–60.45 (m), 128.42–128.62 (m), 129.57 (d, *J* = 20 Hz), 129.83 (d, *J* = 9 Hz), 130.79 (d, *J* = 20 Hz), 131.38 (d, *J* = 10 Hz), 131.51–131.61 (m), 132.16–132.35 (m), 132.44 (d, *J* = 20 Hz), 133.39 (d, *J* = 20 Hz)ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 36.74 (d, *J* = 3.4 Hz), 36.85, 43.27 (d, *J* = 3.5 Hz), 43.44 ppm. MS (ESI/TOF): *m/z* = 351 [M + H]$^+$. HRMS: *m/z* calcd for $C_{18}H_{24}O_3NaP_2$: 373.1098; found: 373.1097.

Compound **4g**: dark oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.08–1.49 (m, 8 H), 1.71–2.09 (m, 4 H), 3.88–4.16 (m, 4 H), 7.28–7.60 (m, 6 H), 7.63–8.87 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.98, 16.38 (d, *J* = 5 Hz), 19.68, 22.64, 29.30, 29.40, 29.64, 31.86, 61.59 (d, *J* = 6 Hz), 128.40, 128.55, 128.67, 130.45, 131.00 (d, *J* = 11 Hz), 131.50, 131.87 (d, *J* = 11 Hz), 133.67 ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 30.66, 42.12 ppm. MS (ESI/TOF): *m/z* = 397 [M + H]$^+$. HRMS: *m/z* calcd for $C_{19}H_{26}O_3NaP_2S$: 419.0976; found: 419.0981.

Compound **4h**: colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, *J* = 6.8 Hz, 6 H), 1.28 (t, *J* = 6.8 Hz, 6 H), 1.72–1.96 (m, 12 H), 3.96–4.10 (m, 8 H), 7.47–7.54 (m, 3 H), 7.67–7.72 (m, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.14 (t, *J* = 4 Hz), 16.34 (t, *J* = 6 Hz), 26.34 (dd, *J* = 14, 140 Hz), 30.37 (dd, *J* = 14, 68 Hz), 61.52 (d, *J* = 6 Hz), 128.76 (d, *J* = 11 Hz), 130.41 (d, *J* = 9 Hz), 131.28 (d, *J* = 92 Hz), 131.82 (d, *J* = 3 Hz) ppm. ^{31}P NMR (160 MHz, $CDCl_3$): δ = 30.45, 30.48, 39.71 ppm. MS (ESI/TOF): *m/z* = 483 [M + H]$^+$. HRMS: *m/z* calcd for $C_{20}H_{37}O_7NaP_3$: 505.1650; found: 505.1645.

(10) Benn, R. F.; Briggs, J. C.; McAuliffe, C. A. *J. Chem. Soc., Dalton Trans.* **1984**, 293.

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