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Zirconium-Promoted Ring Opening. A Useful New Methodology

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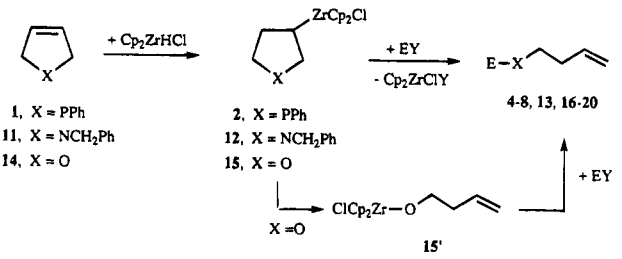
*Summary: Hydrozirconation of phosphorus-, nitrogen-, or oxygen-containing unsaturated five membered rings such as phospholene (**1**), 1-benzyl-3-pyrroline (**11**), 2,5-dihydrofuran (**14**), or 2,3-dihydrofuran (**21**) followed by addition of various electrophiles lead via ring opening to a variety of acyclic unsaturated phosphanes **4**–**8**, **13**, **16**, and **20** or to the corresponding alcohol **17**, ether **18**, or ester **19**.*

Considerable effort has recently been directed toward the use of organozirconium derivatives as intermediates in organic synthesis. These compounds appear to be useful reagents for a variety of applications:[1] reductive coupling reactions of unsaturated organic molecules, carbon–carbon or carbon–hydrogen bond formation, halogenolysis, carbonylation, acylation, catalytic hydrogenation, etc. Moreover, main group heterocycles can be prepared by metallacycle transfer from zirconium.[2] Nevertheless, to our knowledge, no general method[3] of ring opening induced by an *exocyclic* zirconium group has ever been reported till now, despite the obvious synthetic potential of this reaction.

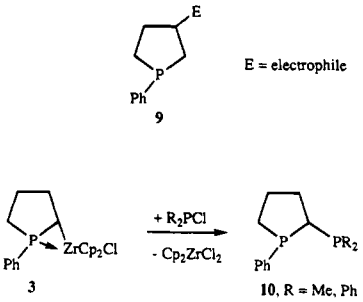
In this note we wish to report a useful general selective ring opening reaction which can be applied to phosphorus-, nitrogen-, or oxygen-containing unsaturated five membered rings.

We initiated our studies by examining the hydrozirconation of phospholene **1** by means of Cp_2ZrHCl. It was demonstrated[4] that zirconation takes place on the carbon atom in the β position relative to phosphorus with the formation of **2** provided that the hydrozirconation reaction was carried out at room temperature (Scheme 1).

Scheme 1



Scheme 2



Treatment of **2** with a variety of organic or phosphorus electrophiles leads, via elimination of Cp_2ZrClX (X = Cl, CF_3SO_3), to unsymmetrical functionalized acyclic phosphorus derivatives **4**–**8**[5] (Table 1) obtained in excellent yield. It is of particular interest in a synthetic context that no compound **9** resulting from the direct grafting in β position of the electrophile is formed. The key role played by the phosphorus lone pair can be pointed out since the reaction of the α-zirconated phospholane **3**—in which the phosphorus lone pair is engaged in a dative bond with Cp_2ZrCl—with chlorophosphanes R_2PCl (R = Me, Ph) leads to the exchange reaction products **10** (Scheme 2).[4]

A similar ring opening occurs with nitrogen-containing heterocycles. 1-Benzyl-3-pyrroline (**11**) treated with Cp_2ZrHCl gives the β-zircona-substituted cyclic species **12**;[6] further addition of diphenylchlorophosphane undergoes the formation of the linear aminophosphane **13** (Table 1).

Such reactions can be extended to the ring cleavage of the corresponding oxygen-containing heterocycles such as 2,5-dihydrofuran (**14**). Reaction of **14** with Cp_2-

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(1) For reviews see for example: (a) Annby, U.; Karlsson, S. *Acta Chem. Scand.* **1993**, *47*, 425. (b) Labinger, J. A. *Comprehensive Organic Chemistry* **1991**, *3*, 667, Chap. 3, Ed. Fleming I., Pergamon Press. (c) Negishi, E. *Ibid.* **1991**, *9*, 1163, Chap. 5, Ed. Paquette L. A., Pergamon Press. (d) Ryabov, A. D. *Chem. Rev.* **1990**, 403. (e) Karlsson, S.; Hallberg, A.; Gronowitz, S. *J. Organomet. Chem.* **1991**, *403*, 133. (f) Erker, G.; Aulbach, M.; Mena, M.; Pfaff, R.; Sosna, F. *Chemica Scripta* **1989**, *29*, 451. (g) Negishi, E. *Ibid.* **1989**, *29*, 457. (h) Negishi, E.; Takahashi, T. *Synthesis* **1988**, 1. (i) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. (j) Negishi, E. *Acc. Chem. Res.* **1987**, *20*, 65. (k) Erker, G. *Acc. Chem. Res.* **1984**, *17*, 103.

(2) (a) Binger, P.; Wettling, T.; Schneider, R.; Zurmühlen, F.; Bergsträsser, U.; Hoffmann, J.; Maas, G.; Regitz, M. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 207. (b) Fisher, R. A.; Nielsen, R. B.; Davis, W. M.; Buchwald, S. L. *J. Am. Chem. Soc.* **1991**, *113*, 165 and ref. included. (c) Buchwald, S. L.; Fisher, R. A.; Foxman, B. M. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 771. (d) Douglas, T.; Theopold, K. H. *Angew. Chem. Int. Ed. Eng.* **1989**, *28*, 1367. (e) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310.

(3) It was already mentioned that hydrozirconation of dihydropyran leads to the acyclic compound $Cp_2ZrClO(CH_2)_3CH{=}CH_2$. Wipf, P.; Smitrovich, H. J. *J. Org. Chem.* **1991**, *56*, 6494.

(4) Zablocka, M.; Boutonnet, F.; Igau, A.; Dahan, F.; Majoral, J.-P.; Pietrusiewicz, K. M. *Angew. Chem. Int. Ed. Engl.* **1993**, *12*, 1735.

(5) It can be noted that direct addition of an electrophile such as $[H_2C{=}NMe_2]I$, CF_3SO_3Me, or CF_3SO_3H to phospholene **1** gives rise to the corresponding phosphonium salts $Ph(E)P^+CH_2CH{=}CHCH_2X^-$ (E = H_2CNMe_2, Me, H; X = I, CF_3SO_3). Hydrozirconation of these salts does not take place.

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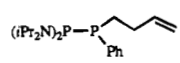
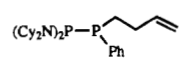
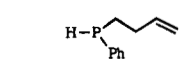
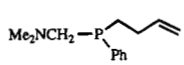
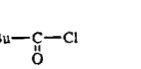
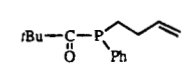
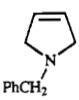
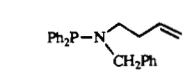
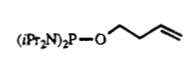
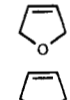
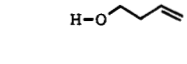
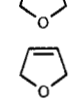
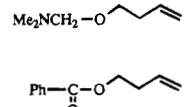
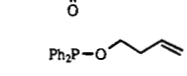
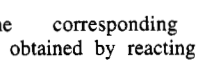
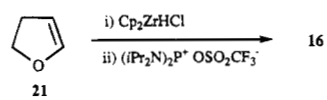
Table 1. Zirconium-Promoted Ring Opening of Compounds 1, 11, 14

Substrate	Electrophile EY	Product (% isolated yield)
 1	$(iPr_2N)_2P^+ OSO_2CF_3^-$	 4 (95)
 1	$(Cy_2N)_2P^+ OSO_2CF_3^-$	 5 (95)
 1	$HOSO_2CF_3$	 6 (90)
 1	$[H_2C{=}NMe_2]Cl$	 7 (80)
 1		 8 (80)
 11	Ph_2PCl	 13* (50)
 14	$(iPr_2N)_2P^+ OSO_2CF_3^-$	 16 (75)
 14	$HOSO_2CF_3$	 17 (90)
 14	$[H_2C{=}NMe_2]Cl$	 18 (90)
 14		 19 (60)
 14	Ph_2PCl	 20 (75)

* **13** was isolated as the corresponding sulfide $Ph_2P(S)N(CH_2CH_2CH{=}CH_2)CH_2Ph$, **22**, obtained by reacting **13** with sulfur.

Scheme 3



ZrHCl and then electrophiles like phosphenium salts $(R_2N)_2P^+CF_3SO_3^-$ (R = iPr, cyclohexyl), Eschenmoser's salt $[H_2C{=}NMe_2]Cl$, and triflic acid, leads to acyclic species **16**–**20** (Table 1). Here, it was not possible to isolate the transient expected β-zirconated ring system **15**. Due to the oxophilicity of zirconium, migration of $ZrCp_2Cl$ to oxygen rapidly occurs, giving rise to the linear derivative **15′**, which was isolated and fully characterized.[6] Experiments conducted with a vinyl cyclic system, 2,3-dihydrofuran (**21**) lead to similar results. Hydrozirconation of **21** followed by, for example, addition of phosphenium salt $(iPr_2N)_2P^+CF_3SO_3^-$ gave **16** (Scheme 3).

Therefore, it appears that the ring opening process necessitates *the preliminary β-zirconation* of the phosphorus, nitrogen, or oxygen heterocycles. Concomitant attack of the electrophile on the heteroatom of the ring and nucleophilic attack of the anion X^- (X = CF_3SO_3, Cl) on the Zr center may be ascribed for the ring opening, the transient resulting β-anionic cyclic system being highly unstable.[7]

The foregoing results clearly demonstrate the synthetic generality and operational simplicity of this new ring opening method. Applications of this methodology to other cyclic compounds and to problems of synthetic interest are underway.

Experimental Section

Synthesis of Compounds 4–8, 13, and 16–20. General Procedure. To a suspension of Cp_2ZrHCl (0.9 mmol, 232 mg) in 5 mL of THF at −20 °C was added dropwise a solution of **1**, **11**, or **14** (1 mmol) in 5 mL of THF. After stirring from 15 min to 1 h at −20 °C, the solution is allowed to warm up at room temperature, stirred for an additional 1 h, and then cooled at −78 °C. To this solution was added the electrophile (0.9 mmol). The resulting mixture was stirred for 20 min at −78 °C and then allowed to warm up slowly at room temperature (2 h). Evaporation of the solvent followed by extraction with pentane (3 × 20 mL) gave compounds **4–8**, **13**, **16–20**.

Compound 4. $^{31}P\{^1H\}$ NMR (δ, C_6D_6): −48.3 (d, $^1J_{PP}$ = 125.4 Hz, PPh), 71.7 (d, $^1J_{PP}$ = 125.4 Hz, PN*i*Pr). $^{13}C\{^1H\}$ NMR (δ, C_6D_6): 24.3, 24.4, 24.5, 24.7 (s, CH_3), 27.2 (dd, $^1J_{CP}$ = 27.6 Hz, $^2J_{CP}$ = 16.3 Hz, CH_2P), 32.0 (dd, $^2J_{CP}$ = 14.7 Hz, $^3J_{CP}$ = 9.9 Hz, $CH_2CH{=}$), 48.9 (dd, $^2J_{CP}$ = 8.5 Hz, $^3J_{CP}$ = 8.5 Hz, CHN), 114.3 (s, $=CH_2$), 128.2 (s, *p*-Ph), 128.6 (s, *m*-Ph), 136.1 (dd, $^2J_{CP}$ = 19.0 Hz, $^3J_{CP}$ = 7.7 Hz, *o*-Ph), 137.6 (dd, $^1J_{CP}$ = 17.6 Hz, $^2J_{CP}$ = 8.3 Hz, *i*-Ph), 139.5 (d, $^3J_{CP}$ = 11.5 Hz, CH=) ppm. ^1H NMR (δ, THF-d_8): 0.73 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3), 1.06 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 1.15 (d, $^3J_{HH}$ = 6.6 Hz, 3H, CH_3), 1.17 (d, $^3J_{HH}$ = 6.7 Hz, 6H, CH_3), 1.22 (d, $^3J_{HH}$ = 5.1 Hz, 3H, CH_3), 1.26 (d, $^3J_{HH}$ = 5.2 Hz, 6H, CH_3), 1.85–2.35 (m, 4H, CH_2), 3.60 (m, 4H, HCN), 4.96 (m, 2H, $=CH_2$), 5.88 (m, 1H, CH=), 7.06–7.93 (m, 5H, Ph). Mass spectrum: *m/z* 394 $[M]^+$. Anal. Calcd for $C_{22}H_{40}N_2P_2$: C, 66.98; H, 10.22. Found: C, 66.91; H, 10.16.

Compound 5. $^{31}P\{^1H\}$ NMR (C_6D_6): −47.6 (d, $^1J_{PP}$ = 130.6 Hz, PPh), 78.9 (d, $^1J_{PP}$ = 130.6 Hz, PNCy). $^{13}C\{^1H\}$ NMR (δ, C_6D_6): 25.4–28.6 and 34.2–37.2 (m, CH_2), 59.64 (m, CH-cyclohexyl), 114.7 (s, $=CH_2$), 128.6 (s, *p*-Ph), 129.6 (s, *m*-Ph), 137.0 (dd, $^2J_{CP}$ = 18.8 Hz, $^3J_{CP}$ = 7.9 Hz, *o*-Ph), 138.7 (dd, $^1J_{CP}$ = 21.7 Hz, $^2J_{CP}$ = 11.9 Hz, *i*-Ph), 140.0 (d, $^3J_{CP}$ = 11.0 Hz, CH=). ^1H NMR (δ, THF-d_6): 1.01–2.05 (m, 44H, CH_2), 3.22 (m, 4H, HCN), 4.95 (m, 2H, $=CH_2$), 5.87 (m, 1H, CH=), 7.10 −7.16 (m, 2H, Ph) 7.87–7.91 (m, 3H, Ph). Mass spectrum: *m/z* 555 $[M]^+$. Anal. Calcd for $C_{34}H_{56}N_2P_2$: C, 73.61; H, 10.18. Found: C, 73.44; H, 10.11.

Compound 6. ^{31}P NMR (δ, CD_2Cl_2): −53.0 (d, $^1J_{PH}$ = 211.4 Hz). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 23.2 (d, $^1J_{CP}$ = 13.0 Hz, CH_2P), 32.5 (d, $^2J_{CP}$ = 7.4 Hz, $CH_2CH{=}$), 115.4 (s, $=CH_2$), 128.7 (s, *p*-Ph), 129.1 (d, $^3J_{CP}$ = 5.8 Hz, *m*-Ph), 134.3 (d, $^2J_{CP}$ = 15.7 Hz, *o*-Ph), 139.0 (d, $^3J_{CP}$ = 7.3 Hz, CH=) (*i*-Ph not detected). ^1H NMR (δ, CD_2Cl_2): 2.04 (m, 2H, CH_2), 2.39 (m, 2H, CH_2), 4.89 (m, 2H, $=CH_2$), 5.57 (m, 1H, CH=), 7.05–7.47 (m, 5H, Ph). Mass spectrum: *m/z* 164 $[M]^+$. Anal. Calcd for $C_{10}H_{13}P$: C, 73.15; H, 7.98. Found: C, 73.01; H, 7.90.

Compound 7. $^{31}P\{^1H\}$ NMR (δ, CD_2Cl_2): −39.5 (s). $^{13}C\{^1H\}$ NMR (δ, CD_2Cl_2): 26.5 (d, $^1J_{CP}$ = 7.8 Hz, CH_2P), 29.7 (d, $^2J_{CP}$ = 16.1 Hz, $CH_2CH{=}$), 44.3 (d, $^3J_{CP}$ = 6.5 Hz, NCH_3), 59.2 (d, $^1J_{CP}$ = 20.1 Hz, NCH_2P), 115.3 (s, $=CH_2$), 129.3 (d, $^3J_{CP}$ = 8.5 Hz, *m*-Ph), 130.7 (s, *p*-Ph), 133.3 (d, $^2J_{CP}$ = 20.8 Hz, *o*-Ph),

(6) Selected data for compounds **12** and **15′**. **Compound 12.** $PhCH_2NC_\alpha H_2C_\beta H(ZrCp_2Cl)C_\gamma H_2C_\delta H_2$. $^{13}C\{^1H\}$ NMR (δ, C_6D_6) 35.9 (s, γ-CH_2), 56.9 (s, δ-CH_2), 60.6 (s, CHZr), 61.3 and 63.1 (s, α, ϵ-CH_2), 113.0, 113.1 (s, Cp), 127.4 (s, *p*-Ph), 128.98 (s, *m*-Ph), 129.36 (s, *o*-Ph), 141.40 (s, *i*-Ph). ^1H NMR (δ, C_6D_6) 1.88 (m, 2H, γ-CH_2), 2.31 (m, 2H, δ-CH_2), 2.73 (m, 2H, α-CH_2), 3.59 (m, 3H, ϵ-CH_2 and CHZr), 5.92, 5.89 (s, 10H, Cp), 7.11–7.45 (m, 5H, Ph). **Compound 15′.** $^{13}C\{^1H\}$ NMR (δ, C_6D_6): 38.7 (s, $CH_2CH{=}$), 75.3 (s, CH_2OZr), 113.9 (s, Cp), 116.8 (s, $=CH_2$), 136.6 (s, CH=) ppm. ^1H NMR (δ, C_6D_6): 2.09 (m, 2H, CH_2-CH=), 3.86 (t, $^3J_{HH}$ = 6.7 Hz, 2H, CH_2OZr), 5.06 (m, 2H, $=CH_2$), 5.75 (m, 1H, CH=).

(7) It can be noted that the zirconium-promoted ring opening of cyclopentene was found to proceed inefficiently.

137.8 (d, $^3J_{CP}h$ = 12.6 Hz, CH=) (*i*-Ph not detected). ^1H NMR (δ, CD_2Cl_2): 2.12 (m, 4H, CH_2), 2.68 (d, $^4J_{HP}$ = 4.4 Hz, 3H, NCH_3), 2.87 (d, $^4J_{HP}$ = 4.5 Hz, 3H, NCH_3), 3.54 (d, $^2J_{HP}$ = 2.8 Hz, 2H, NCH_2P), 5.02 (m, 2H, $=CH_2$), 5.84 (m, 1H, =CH), 7.45−7.75 (m, 5H, Ph). Mass spectrum: *m/z* 222 $[M]^+$. Anal. Calcd for $C_{13}H_{20}NP$: C, 70.56; H, 9.11. Found: C, 70.41; H, 8.98.

Compound 8. $^{31}P\{^1H\}$ NMR (δ, C_6D_6): −7.1 (s). $^{13}C\{^1H\}$ NMR (δ, C_6D_6): 26.0 (d, $^1J_{CP}$ = 8.7 Hz, CH_2P), 27.4 (d, $^3J_{CP}$ = 5.6 Hz, CCH_3), 28.2 (d, $^2J_{CP}$ = 21.9 Hz, CCH_3), 30.8 (d, $^2J_{CP}$ = 18.5 Hz, CH_2CH=), 115.2 (s, $=CH_2$), 129.4 (d, $^3J_{CP}$ = 8.6 Hz, *m*-Ph), 130.24 (s, *p*-Ph), 135.4 (d, $^2J_{CP}$ = 20.3 Hz, *o*-Ph), 139.3 (d, $^3J_{CP}$ = 13.1 Hz, CH=), 168.5 (d, $^1J_{CP}$ = 49.9 Hz, C=O) (*i*-Ph not detected). ^1H NMR (δ, C_6D_6): 1.01 (s, 9H, CH_3), 2.08 (m, 2H, CH_2), 2.31 (m, 2H, CH_2), 4.94 (m, 2H, $=CH_2$), 5.76 (dtt, $^3J_{HHtrans}$ = 17.0 Hz, $^3J_{HHcis}$ = 10.1 Hz, $^3J_{HH}$ = 5.8 Hz, 1H, CH=), 7.00−7.50 (m, 5H, Ph). Mass spectrum: *m/z* 249 $[M + 1]^+$. Anal. Calcd for $C_{15}H_{21}OP$: C, 72.55; H, 8.52. Found: C, 72.42; H, 8.44.

Compound 13. Treatment of **13** with sulfur gave **22**. $^{31}P\{^1H\}$ NMR (δ, C_6D_6): 68.6 (s, PS). $^{13}C\{^1H\}$ NMR (δ, C_6D_6): 33.17 (s, CH_2CH), 47.5 (s, CH_2N), 51.1 (s, CH_2N), 116.71 (s, $=CH_2$), 128.72 (s, *m*-Ph), 129.02 (s, *p*-Ph), 129.44 (s, *o*-Bz), 131.84 (s, CH=), 133.04 (d, $^2J_{CP}$ = 11.1 Hz, *o*-Ph), 136.0 (s, *i*-Bz) (*i*-Ph not detected). ^1H NMR (δ, C_6D_6) 2.12 (dt, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 8.0 Hz, 2H, CH_2C=), 3.01 (m, 2H, CH_2NP), 4.23 (m, 2H, NCH_2Ph), 4.70 (m, 2H, $=CH_2$), 5.25 (ddt, $^3J_{HHtrans}$ = 16.1 Hz, $^3J_{HHcis}$ = 10.6 Hz, $^3J_{HH}$ = 6.9 Hz, 1H, CH=), 6.99−8.19 (m, 15H, Ph). Mass spectrum: *m/z* 378 $[M + 1]^+$. Anal. Calcd for $C_{23}H_{24}NPS$: C, 73.12; H, 6.36. Found: C, 73.01; H, 6.27.

Compound 16. $^{31}P\{^1H\}$ NMR (δ, C_6D_6): 122.1 (s). $^{13}C\{^1H\}$ NMR (δ, C_6D_6): 24.4, 24.5, 25.0, 25.2 (s, CH_3), 37.1 (d, $^3J_{CP}$ = 8.7 Hz, CH_2CH=), 45.5 (d, $^2J_{CP}$ = 13.0 Hz, HCN), 64.6 (d, $^2J_{CP}$ = 21.8 Hz, CH_2OP), 116.6 (s, $=CH_2$), 136.4 (s, CH=). ^1H NMR (δ, C_6D_6): 1.18, 1.22 (d, $^3J_{HH}$ = 6.8 Hz, 12H, CH_3), 2.32 (m, 2H, CH_2CH=), 3.51 (d, sept, $^3J_{HP}$ = 10.6 Hz, $^3J_{HH}$ = 6.8 Hz, 4H, CHN), 3.61 (dt, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 6.8 Hz, 2H, CH_2OP), 5.04 (m, 2H, $=CH_2$), 5.87 (m, 1H, CH=). Mass spectrum: *m/z* 303 $[M + 1]^+$. Anal. Calcd for $C_{16}H_{35}N_2OP$: C, 63.54; H, 11.67. Found: C, 63.44; H, 11.55.

Compound 18. $^{13}C\{^1H\}$ NMR (δ, C_6D_6): 26.1 (s, CH_2CH=), 41.9 (s, NCH_3), 68.4 (s, CH_2O), 89.9 (s, OCH_2N), 116.9 (s, $=CH_2$), 136.2 (s, CH=). ^1H NMR (δ, C_6D_6): 2.22 (m, 2H, CH_2-CH=), 2.25 (s, 6H, NCH_3), 3.31 (t, $^3J_{HH}$ = 6.7 Hz, 2H, CH_2O), 3.86 (s, 2H, OCH_2N), 5.02 (m, 2H, $=CH_2$), 5.79 (m, 1H, CH=). Mass spectrum: *m/z* 129 $[M]^+$. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.91; H, 6.81.

Compound 19. $^{13}C\{^1H\}$ NMR (δ, C_6D_6): 33.8 (s, CH_2CH=), 64.3 (s, CH_2O), 117.5 (s, $=CH_2$), 128.9 (s, *m*-Ph), 130.3 (s, *o*-Ph), 131.1 (s, *i*-Ph), 133.3 (s, *p*-Ph), 135.4 (s, =CH), 166.6 (s, C=O). ^1H NMR (δ, C_6D_6): 2.18 (dt, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2CH=), 4.15 (t, $^3J_{HH}$ = 6.6 Hz, 2H, CH_2O), 4.96 (m, 2H, $=CH_2$), 5.63 (m, 1H, CH=), 6.81−8.14 (m, 5H, Ph). Mass spectrum: *m/z* 176 $[M]^+$. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 74.91; H, 6.81.

Compound 20. $^{31}P\{^1H\}$ NMR (δ, C_6D_6): 111.8 (s). $^{13}C\{^1H\}$ NMR (δ, C_6D_6): 36.7 (d, $^3J_{CP}$ = 7.8 Hz, CH_2CH=), 69.9 (d, $^2J_{CP}$ = 19.6 Hz, CH_2OP), 117.4 (s, $=CH_2$), 129.0 (d, $^3J_{CP}$ = 6.8 Hz, *m*-Ph), 129.9 (s, *p*-Ph), 131.1 (d, $^2J_{CP}$ = 21.8 Hz, *o*-Ph), 135.4 (s, CH=), 143.5 (d, $^1J_{CP}$ = 18.7 Hz, *i*-Ph). ^1H NMR (δ, C_6D_6): 2.26 (dt, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 6.7 Hz, 2H, CH_2CH=), 3.77 (dt, $^3J_{HH}$ = 6.7 Hz, $^3J_{HP}$ = 9.1 Hz, 2H, CH_2OP), 4.96 (m, 2H, $=CH_2$), 5.76 (ddt, $^3J_{HHtrans}$ = 16.9 Hz, $^3J_{HHcis}$ = 10.6 Hz, $^3J_{HH}$ = 6.7 Hz, 1H, CH=), 6.96−7.64 (m, 5H, Ph). Mass spectrum: *m/z* 256 $[M]^+$. Anal. Calcd for $C_{16}H_{17}OP$: C, 74.98; H, 6.69. Found: C, 74.72; H, 6.57.

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