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Reactions of Sterically Protected Phosphaalkenes with Some Boron Reagents

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ABSTRACT: *The reactions of sterically protected phosphaalkenes with some boron reagents, such as boron hydrides, were carried out leading to hydroboration products depending on the substrates and boron reagents.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 187–196, 1999

INTRODUCTION

Sterically protected organophosphorus compounds are of current interest because of their unusual structures and reactivities [1]. By utilizing a sterically bulky substituent, such as the 2,4,6-tri-*t*-butylphenyl group (abbreviated to the Ar group), we have been successful in preparation and characterization of diphosphenes (R–P=P–R) [2] and phosphaalkenes (R–P=C<) [3,4]. Among various kinds of their reactivities, only a little is known on the reaction of such double bonds with boron reagents. Ionkin et al. reported on the reaction of 2-(dialkylamino)-1-phenylphosphaethenes with dialkylboranes [5]. We now report the reactions of some sterically protected phosphaalkenes **1, 2, 3**, and **4**, carrying the Ar group or 2,4-di-*t*-butyl-6-methylphenyl (abbreviated to the Dbt group), with some boron reagents.

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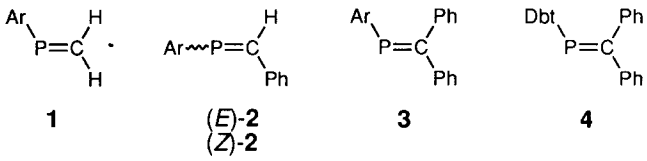
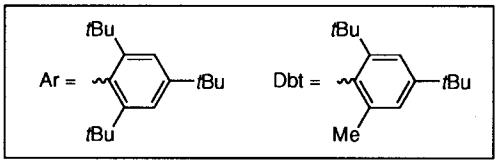
RESULTS AND DISCUSSION

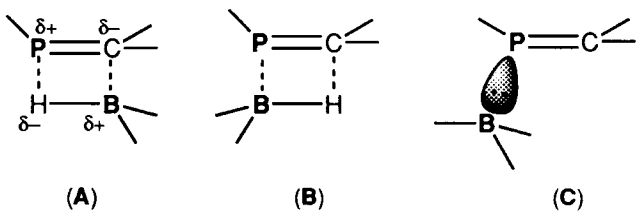
There are two possible modes for the reactions of the P=C bonding with hydroboration reagents (normal



1 (*E*)-**2** (*Z*)-**2** **3** **4**



mode of type A and reversed mode of type B) in addition to coordination of the lone-pair electrons to boron (type C), as shown in Figure 1. According to the results on the hydroboration reaction with olefins, the reaction modes are controlled by both steric and electronic effects [6]. Furthermore, theoretical



(**A**) (**B**) (**C**)

FIGURE 1 Some modes of reactions of phosphaalkenes with boranes: (A) hydroboration of normal type, (B) hydroboration of reversed type, and (C) coordination.

calculations by Ermolaeva and Ionkin indicate that borane adopts coordination with the lone-pair electrons of the phosphorus atoms of the phosphaalkene (type C) rather than forming an intermediate of hydroboration reaction (type A or B) [7].

Reaction of Phosphaalkenes with Catecholborane **5**

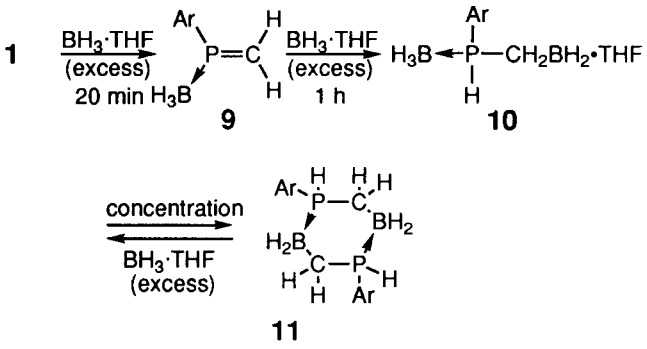
When phosphaalkene **1** [8] was allowed to react with catecholborane (**5**) [9], hydroboration proceeded only in the presence of $ClRh(PPh_3)_3$ [10] as a catalyst at room temperature for 2 hours to give **6**, as shown in Scheme 1. No reaction of **1** proceeded in the absence of the catalyst. When (*E*)-**2** [4,11] was employed as a substrate, hydroboration proceeded to give **7a** and **7b**, together with benzylphosphine **8** [12]. It seemed likely that two diastereomers **7a** and **7b** had been formed with the ^{31}P NMR peak ratio of **7a**:**7b**:**8** = 2:1:4. The phosphine **8** seemed to be a hydrolyzed product of **7**. It is interesting to note that the product ratio was almost the same even if the reaction was conducted with (**Z**)-**2** [13], indicating that the reaction is not stereospecific. The *E*-isomer reacted with **5** more sluggishly than the *Z*-isomer, indicating that the reaction site of (*Z*)-**2** is more hindered than that of (*E*)-**2**, as has been determined by X-ray analyses [3,4], and thus the energy release during the reaction of (*Z*)-**2** is smaller than that of (*E*)-**2**. Furthermore, if **3** [4,14] was used as a substrate, no reaction with **5** proceeded, suggesting that the bulkiness caused by the two phenyl groups within **5** is detrimental for the hydroboration reaction with **5**.

Reaction of Phosphaalkenes with $BH_3 \cdot THF$

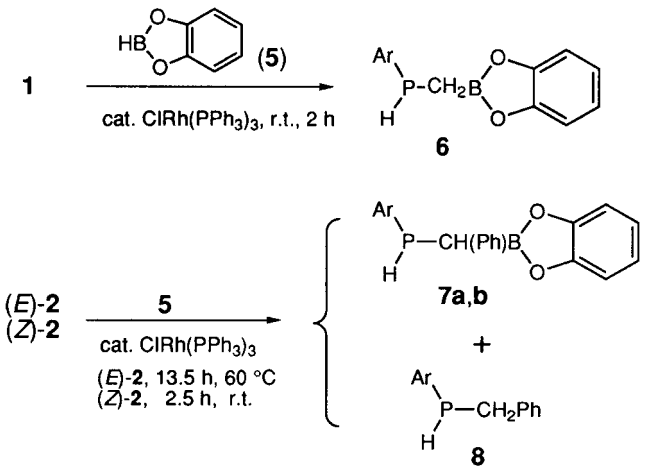
Reaction of phosphaalkenes with sterically less bulky boron hydrides was attempted in place of catecholborane **5**, as follows. When phosphaalkene **1** was allowed to react with the THF complex of borane, $BH_3 \cdot THF$ [15], the formation of phosphine–borane complex **9** was observed after 20 minutes, with the observation of $\delta_P = 256.5$, as monitored by the ^{31}P NMR analysis, and then the hydroboration reaction seemed to proceed to give **10** after 1 hour, as evidenced by the appearance of broad signals at $\delta_P = -6.4$ (br. d, $J_{PH} = 398.2$ Hz). It is known that $^1J_{PH}$ for phosphine–borane is about 400 Hz [16] and that the ^{31}P NMR signal becomes broad upon complex formation [17]. The compound **10**, however, dimerized upon concentration to give **11**. The process appeared to be reversible, because **10** was formed again, when $BH_3 \cdot THF$ was added to **11**, as shown in Scheme 2, according to the NMR studies.

Similarly, starting from (*E*)-**2**, (*E*)-**12** was formed after 4 hours and then slowly changed to **13e** in 4 days. Upon concentration of **13e**, however, it dimerized to **14e**, together with the formation of a trace amount of **14z** and the phosphine–borane complex **15**. Again, **13e** was regenerated when excess $BH_3 \cdot THF$ was added to **14e**, as shown in Scheme 3.

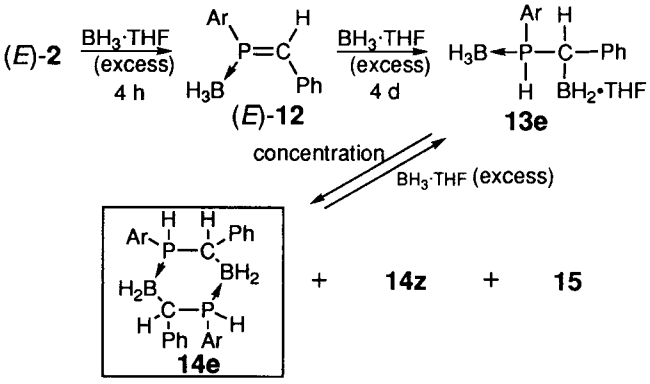
When (*Z*)-**2** was employed as a substrate, (*Z*)-**12** was formed after 7.5 hours, and similarly, it was con-



SCHEME 2



SCHEME 1

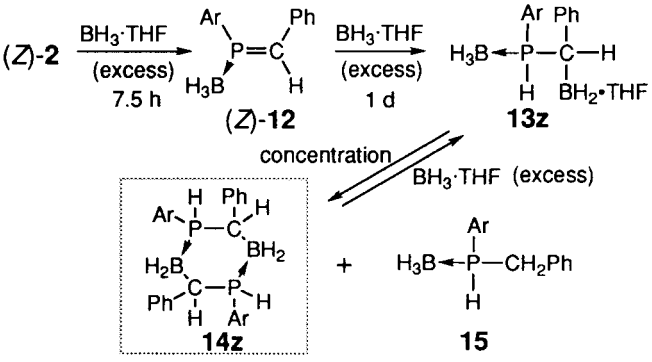


SCHEME 3

verted to **13z** after 1 day. Upon concentration of **13z**, however, it dimerized to **14z**, together with the formation of **15** as a major product. Similarly, **13z** was regenerated when excess $BH_3 \cdot THF$ was added to **14z**, as shown in Scheme 4. The difference between the results on the formation of the dimers from (*E*)-**2** and (*Z*)-**2** might be explainable if the steric hindrance within **14e** and **14z** is taken into account, as depicted in Figure 2. It seems likely that the less hindered **14e** is more easily formed than **14z**, which suffers from the repulsion between the Ar and the Ph groups. The formation of a similar six-membered ring compound, consisting of the two PCB units and the two P–B coordination bonds, has been reported by Ionkin *et al.* [5].

On the other hand, when **3** was employed as a substrate for the reaction with excess $BH_3 \cdot THF$, no reaction was observed, even at 60°C, probably because of the steric effect caused by the two phenyl groups. However, if **4** was employed for the reaction, hydroboration proceeded to give **16** or **17**, with δ_P = 31.0 (Chart 2), suggesting that hydroboration takes place even though the diphenylmethylene group is attached to the phosphorus, if the bulkiness around the phosphorus atom is slightly released, such as by the Dbt group [18].

Furthermore, the hydroboration products of **5** with **6** and **7** formed the corresponding phosphine–borane complexes **18** and **19**, respectively, in the presence of $BH_3 \cdot THF$, as shown in Scheme 5.



SCHEME 4

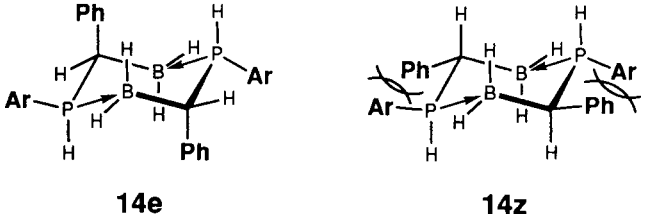


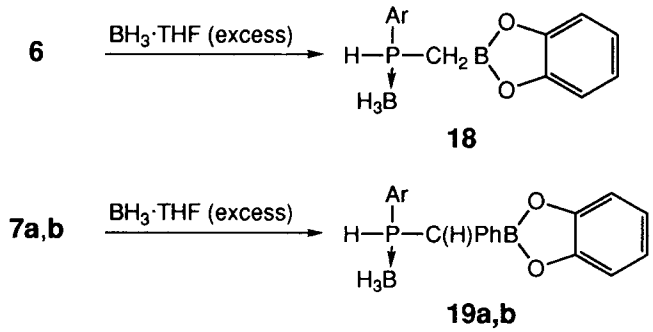
FIGURE 2 Steric hindrance within **14e** and **14z**.

Decomplexation of Phosphine–Borane Complexes with Diethylamine

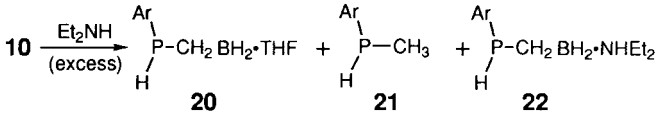
It is well known that trialkylphosphines form the corresponding phosphine–borane complexes by reaction with boranes and that the phosphines are regenerated by reaction with amines, such as diethylamine [19].

When phosphine–borane complex **10** was allowed to react with diethylamine, **20** was formed together with **21** [20] and a trace amount of **22**, as shown in Scheme 6. The product ratio of **20** and **21** was 14:3, according to the peaks of the ^{31}P NMR spectra. Furthermore, the dimer **11** also gave **22** by the reaction with diethylamine, but no **20** was formed. Furthermore, phosphaalkene–borane complexes, **9**, (*E*)-**12**, and (*Z*)-**12**, regenerated **1**, (*E*)-**2**, and (*Z*)-**2**, respectively, upon addition of diethylamine.

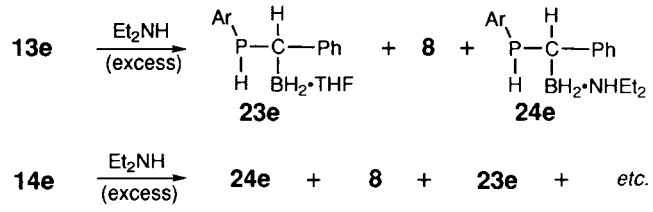
When **13e** was allowed to react with diethylamine, **23e** was obtained together with trace amounts of **8** and **24e**, as shown in Scheme 7. Furthermore, under similar conditions, the dimer **14e** gave **24e** as a major product, together with **23e** and **8**, where the ratio of **24e**:**23e**:**8** was 7:2:2.



SCHEME 5



SCHEME 6



SCHEME 7

On the other hand, when **13z** was allowed to react with diethylamine, **23z** was obtained as a major product, together with a trace amount of **8**, as shown in Scheme 8. However, in the case of the dimer **14z**, the reaction gave **8** as the major product, together with a trace amount of **23z** and several unidentified products.

When catecholborane complex **18** was allowed to react with diethylamine, **6** was regenerated, together with **21**, while **19** did not give **7** but rather gave **8**, probably because a carbanionic function at the benzylic position in **19** might have been formed and then gave **8** even in the presence of a secondary amine.

Oxidative Workup of Hydroboration Products

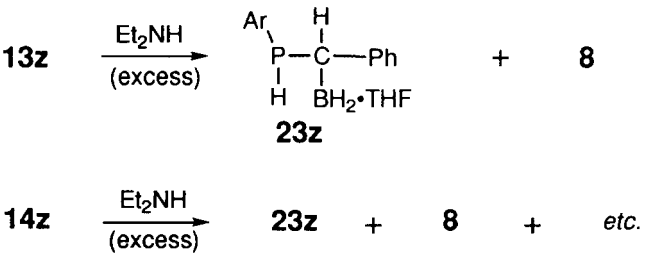
It is quite common that oxidation of the hydroboration products give the corresponding alcohols [6]. Thus, attempts were made to oxidize the hydroboration products **6, 10,** and the dimer **11,** as well as **13e, 13z,** and their dimers **14e** and **14z**, as shown in Scheme 9. The catecholborane adduct **6** gave **25** in 32% yield, together with phosphine oxide **26** in 16% yield, under the oxidative conditions with hydrogen peroxide in the presence of sodium hydroxide. The $BH_3 \cdot THF$ complex **10** also gave **25** and **26** in 20% and 6% yield, respectively. Similar reaction products were obtained when dimer **11** was used as a substrate to give **25** in 37% yield and **26** in 8% yield. The compounds **25** and **26** might be the oxidation products of the corresponding phosphines **27** (Chart 3) and **21**, respectively, indicating that under these conditions, the further oxidation reaction of the phosphines takes place to afford phosphine oxides.

Nevertheless, when **13e** was employed as a substrate, **28** was obtained in 76% isolated yield from (*E*)-**2**, but no alcoholic products were obtained. Similarly, the dimeric product **14e** gave **28** in 63% yield without formation of **29** (Chart 3). The phosphine oxide **28** might be the oxidized product of phosphine **8**, indicating that the C–B bond is not oxidatively cleaved but rather hydrolyzed, even in a basic medium as depicted in Scheme 10. Similarly, both **13z** and **14z** gave **28** in 66% and 61% yields, respectively.

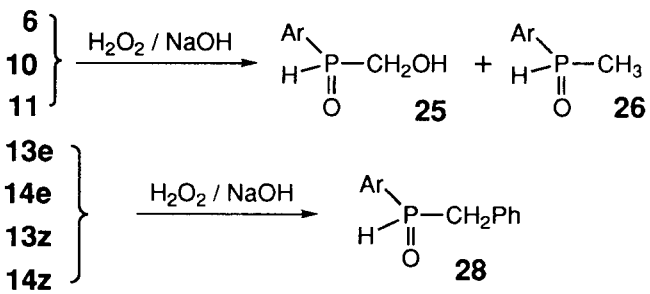
In summary, phosphaalkenes reacted with boron reagents in various modes, coordination, and hydroboration, depending on the substituents of the phosphorus and boron atoms, indicating that steric factors plays an important role in controlling the reactions. The reactions of boranes with phosphaalkenes are not so simple as those of well-defined hydroboration reactions with olefins.

EXPERIMENTAL

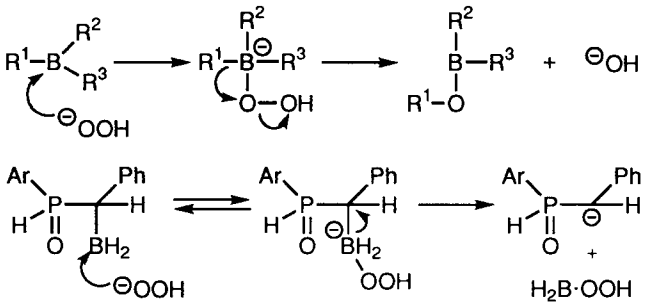
All experiments were carried out under an argon atmosphere with dry solvents, unless otherwise specified. All melting points were determined with a Yanagimoto MP-J3 micromelting point apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were measured by use of a Bruker AC-200P spectrometer. ^{31}P NMR spectra were obtained with a Bruker AC-200P spectrometer using 85% H_3PO_4 as an external standard. IR spectra were recorded on a Horiba FT-300 spectrometer. MS spectra were obtained with a Hitachi M-2500S or a JEOL HX-110, DX-303, or AX-500 spectrometer. Elemental microanalyses were performed at the Instrumental Analysis Center of Chemistry, Graduate School of Science, Tohoku University.



SCHEME 8



SCHEME 9



SCHEME 10

Preparation of Phosphaalkenes

Phosphaalkenes, **1, 2,** and **3**, were prepared according to the procedures reported previously [3,8,11,13,14]. Compound **4** was prepared by a method similar to that reported in the literature [21], but it was not stable enough to be fully characterized. **4**: ^{31}P NMR (81 MHz, $CDCl_3$) δ = 238.3.

Reaction of **1** *with Catecholborane* **5**

Phosphaalkene **1** (50.0 mg, 0.172 mmol) was dissolved in THF (10.0 mL) together with chlorotris(triphenylphosphine)rhodium (14.1 mg, 14.8 μmol) and to the solution was added catecholborane (**5**, 0.40 mL, 3.68 mmol). The reaction was monitored by ^{31}P NMR spectroscopy to indicate that **6** was formed in 2 hours at room temperature. The THF solution of **6** was used without purification. **6**: ^{31}P NMR (81 MHz, THF-C_6D_6) δ = −82.5 (d, J_{PH} = 224.4 Hz). The reaction of **1** (32.3 mg, 0.111 mmol) with **5** (0.05 mL, 0.46 mmol) in THF (10.0 mL) did not proceed in the absence of the rhodium catalyst even at 60°C, according to the ^{31}P NMR monitoring of the reaction.

Reaction of **3** *with* **5**

Very similarly, **3** (72.0 mg, 0.163 mmol) was allowed to react with **5** (0.021 mL, 0.193 mmol) in THF (5.0 mL) in the presence of chlorotris(triphenylphosphine)rhodium (11.8 mg, 12.4 μmol) at room temperature; however, no reaction proceeded according to the ^{31}P NMR monitoring. The starting **3** (66.5 mg, 0.150 mmol) was obtained after chromatographic treatment in 92% recovery.

Reaction of (*E*)-**2** *with* **5**

Similarly, (*E*)-**2** (194.9 mg, 0.532 mmol) was allowed to react with **5** (0.12 mL, 1.10 mmol) in the presence of chlorotris(triphenylphosphine)rhodium (25.1 mg, 26.3 μmol) in THF (10.0 mL) at 60°C. Monitoring by ^{31}P NMR spectroscopy indicated that **7a, 7b,** and **8** were formed after 13.5 hours in a ratio of 2:1:4. The THF solution of **7a,b** was used for further reaction without purification. **7a**: ^{31}P NMR (81 MHz, THF–C_6D_6) δ = −47.7 (d, J_{PH} = 218.1 Hz). **7b**: ^{31}P NMR (81 MHz, THF–C_6D_6) δ = −38.1 (d, J_{PH} = 222.7 Hz). **8**: ^{31}P NMR (81 MHz, THF–C_6D_6) δ = −62.5 (d, J_{PH} = 219.9 Hz).

Preparation of **8** *by an Alternative Method*

A THF solution (30 mL) of 2,4,6-tri-*t*-butylphenylphosphine (0.540 g, 1.94 mmol) was allowed to react with *t*-butyllithium (1.3 mL, 2.08 mmol) at −78°C, and the mixture was stirred for 10 minutes. Benzyl bromide (0.25 mL, 2.06 mmol) was added to the above solution that was then stirred for 2 hours. After hexane (10 mL) had been added to the reaction mixture, it was submitted to flash column chromatography using hexane as an eluent to afford **8** (0.511 g, 1.39 mmol) in 72% yield. **8**: Colorless prisms, mp 75.5–76.0°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.36 (9H, s, *p*-*t*-Bu), 1.61 (18H, s, *o*-*t*-Bu), 2.7–3.0 (2H, m, CH_2), 4.99 (1H, ddd, $^1J_{PH}$ = 222.7 Hz, $^3J_{PH}$ = 6.8 Hz and $^3J_{PH}$ = 9.7 Hz, PH), 7.0–7.3 (5H, m, Ph), and 7.42 (2H, s, *m*-Ar); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 31.4 (s, *p*-CMe_3), 33.6 (s, *o*-CMe_3), 33.7 (s, *o′*-CMe_3), 35.0 (s, *p*-CMe_3), 35.0 (d, $^1J_{PC}$ = 15.8 Hz, CH_2), 38.4 (s, *o*-CMe_3), 122.1 (d, J_{PC} = 3.7 Hz, *m*-Ar), 125.8 (d, J_{PC} = 2.3 Hz, *p*-Ph), 128.4 (d, J_{PC} = 3.0 Hz, *m*-Ph), 128.5 (d, J_{PC} = 3.8 Hz, *o*-Ph), 132.8 (d, J_{PC} = 32.9 Hz, *ipso*-Ar), 139.6 (d, J_{PC} = 5.6 Hz, *ipso*-Ph), 149.3 (s, *p*-Ar), and 154.6 (d, J_{PC} = 7.7 Hz, *o*-Ar); ^{31}P NMR (81 MHz, $CDCl_3$) δ = −62.6 (d, J_{PH} = 222.8 Hz); MS (70 eV) *m/z* (rel. intensity) 367 (M^+–1; 33), 277 (M^+–CH_2Ph; 100), and 57 (*t*-Bu^+; 13) [12]. Found: C, 81.49; H, 9.83%. Calcd for $C_{25}H_{37}P$: C, 81.48; H, 10.12%.

Reaction of (*Z*)-**2** *with* **5**

Very similarly, (*Z*)-**2** (77.6 mg, 0.212 mmol) was allowed to react with **5** (0.10 mL, 0.92 mmol) in the presence of chlorotris(triphenylphosphine)rhodium (25.1 mg, 26.3 μmol) in THF (3 mL) at room temperature. Monitoring by ^{31}P NMR spectroscopy indicated that **7** and **8** were formed after 2.5 hours in a ratio of 2:1:4.

Reaction of **1** *with* $BH_3 \cdot THF$

To a THF solution of **1** (151.5 mg, 0.522 mmol) was added $BH_3 \cdot$ THF (1 mol/L, 10.0 mL, 10.0 mmol) and, according to ^{31}P NMR spectroscopic monitoring, it was observed that **9** was formed after 20 minutes at room temperature. After an additional 40 minutes of stirring, formation of **10** was observed. The THF solution of **9** and **10** thus obtained was used for further reactions immediately after preparation and without any purification. **9**: ^{31}P{^{1}H} NMR (81 MHz, THF–C_6D_6) δ = 256.5. **10**: ^{31}P NMR (81 MHz, THF–C_6D_6) δ = −6.4 (br. d, J_{PH} = 398.2 Hz).

Preparation of **11** *and the Reaction with* $BH_3 \cdot THF$

A mixture of a THF solution of **10**, prepared from **1** (107.1 mg, 0.369 mmol), and $BH_3 \cdot$ THF (1 mol/L, 7.4

mL, 7.4 mmol) was concentrated at room temperature to afford **11**, according to the ^{31}P NMR study. Into the THF solution of **11** was again added an excess amount of $BH_3 \cdot THF$ (1 mol/L, 4.0 mL, 4.0 mmol) at room temperature to regenerate **10**. **11**: $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 30.8 (s, *p*-CMe_3), 31.9 (s, *o*-CMe_3), 35.1 (s, *p*-CMe_3), 37.5 (s, *o*-CMe_3), 119.7 (s, *m*-Ar), 123.5 (s, *m′*-Ar), 131.8 (s, *ipso*-Ar), 147.6 (s, *o*-Ar), 148.2 (s, *o′*-Ar), and 150.3 (s, *p*-Ar); ^{31}P NMR (81 MHz, C_6D_6) δ = −16.8 (br. d, J_{PH} = 393.6 Hz); MS (70 eV) *m/z* (rel. intensity) 607 (M^+–1; 0.5), 549 (M^+–*t*-Bu+2; 5), 493 (M^+–2*t*-Bu–1; 3), 363 (M^+-Ar; 5), and 57 (*t*-Bu^+; 100).

Reaction of (*E*)-**2** *with* $BH_3 \cdot THF$

To a THF solution of (*E*)-**2** (89.3 mg, 0.244 mmol) was added $BH_3 \cdot THF$ (1 mol/L, 5.0 mL, 5.0 mmol). ^{31}P NMR monitoring of the reaction indicated that (*E*)-**12** was formed after 4 hours stirring and that **13e** was formed as the major product in 4 days. The THF solution of (*E*)-**12** and **13e** thus obtained was used for the further reaction without any purification. (*E*)-**12**: $^{31}P\{^1H\}$ NMR (81 MHz, THF–C_6D_6) δ = 214.5. **13e**: ^{31}P NMR (81 MHz, THF–C_6D_6) δ = −0.6 (br. d, J_{PH} = 370.7 Hz).

Preparation of **14e** *and the Reaction with* $BH_3 \cdot THF$

A THF solution of **13e**, prepared from (*E*)-**2** (98.5 mg, 0.269 mmol), was subjected to ^{31}P NMR spectroscopic investigation, and, after evaporation of the solvent, formation of **14e** as a major product was confirmed by the ^{31}P NMR spectrum, a trace amount of **14z** and **15** also being detected. Into the THF solution of **14e** was added an excess amount of $BH_3 \cdot THF$ (1 mol/L, 4.0 mL, 4.0 mmol) at room temperature to regenerate **13e**. **14e**: ^{31}P NMR (81 MHz, C_6D_6) δ = 3.3 (br. d, J_{PH} = 378.4 Hz).

Reaction of (*Z*)-**2** *with* $BH_3 \cdot THF$

To a THF solution of (*Z*)-**2** (75.4 mg, 0.206 mmol) was added $BH_3 \cdot THF$ (1 mol/L, 4.5 mL, 4.5 mmol). ^{31}P NMR monitoring of the reaction indicated that (*Z*)-**12** was formed after 7.5 hours stirring and that **13z** was formed as the major product after 24 hours. The THF solution of (*Z*)-**12** and **13z** thus obtained was used for the further reaction without any purification. (*Z*)-**12**: ^{31}P NMR (81 MHz, THF–C_6D_6) δ = 201.6. **13z**: ^{31}P NMR (81 MHz, THF–C_6D_6) δ = 14.0 (br. d, J_{PH} = 373.8 Hz).

Preparation of **14z** *and the Reaction with* $BH_3 \cdot THF$

A THF solution of **13z**, prepared from (*Z*)-**2** (51.9 mg, 0.142 mmol), was subjected to ^{31}P NMR spectroscopic inspection, and, after evaporation of the solvent, formation of **14z** was confirmed by the ^{31}P NMR spectrum together with **15** [δ_P = 6.9 (br. d, J_{PH} = 383.7 Hz)], in a peak ratio of 1:2. Into the THF solution of **14z** was added an excess amount of $BH_3 \cdot THF$ (1 mol/L, 3.5 mL, 3.5 mmol) at room temperature to regenerate **13z**. **14z**: ^{31}P NMR (81 MHz, C_6D_6) δ = 8.3 (br. d, J_{PH} = 392.4 Hz).

Preparation of **15**

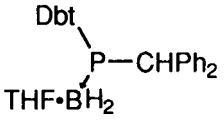
A THF solution of **8** (52.5 mg, 0.142 mmol) was allowed to react with $BH_3 \cdot THF$ (1 mol/L, 3.0 mL, 3.0 mmol) at room temperature for 18.5 hours to give a solution of **15**. The solvent was evaporated to give **15**: ^{31}P NMR (81 MHz, C_6D_6) δ = 7.4 (br. d, J_{PH} = 382.9 Hz).

Reaction of **3** *with* $BH_3 \cdot THF$

An attempted reaction of **3** (102.0 mg, 0.230 mmol) with $BH_3 \cdot THF$ (1 mol/L, 5.5 mL, 5.5 mmol) in THF (7.0 mL) at 60°C for 15 hours did not occur.

Reaction of **4** *with* $BH_3 \cdot THF$

The ^{31}P NMR spectrum of the reaction mixture of **4** (18.5 mg, 46.2 μmol) with $BH_3 \cdot THF$ (1 mol/L, 1.0 mL, 1.0 mmol), carried out at room temperature for 22 hours, gave a peak δ = 31.0 that could be assignable to either **16** or **17**, and no change was observed upon concentration.



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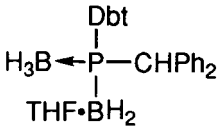

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Reaction of **6** *with* $BH_3 \cdot THF$

To a THF solution (10 mL) of **6**, prepared from **1** (125.7 mg, 0.433 mmol), was added $BH_3 \cdot THF$ (1 mol/L, 4.5 mL, 4.5 mmol) dropwise to form **18** after 8.5 hours at room temperature. The THF solution of **18** was used for further reactions without any purification. **18**: ^{31}P NMR (81 MHz, C_6D_6) δ = −14.8 (br. d, J_{PH} = 379.9 Hz).

Reaction of **7** *with* $BH_3 \cdot THF$

Into a THF solution of **7** (10.0 mL), prepared from (*E*)-**2** (194.9 mg, 0.532 mmol), was added $BH_3 \cdot$ THF solution (1 mol/L, 8.0 mL, 8.0 mmol), and the reaction was monitored by ^{31}P NMR spectroscopy to indicate that **19** was formed after 3 hours at room temperature. The THF solution of **19** was used for the further reactions without purification. **19**: ^{31}P NMR (81 MHz, THF–C_6D_6) δ = 15.8 (br. d, J_{PH} = 382.7 Hz).

Reaction of **10** *with Diethylamine*

A THF solution of **10**, prepared from **1** (151.5 mg, 0.522 mmol), was allowed to react with an excess amount of diethylamine at room temperature to give **20** as a major product according to the ^{31}P NMR spectrum, together with **21** [20] and a trace amount of **22**. The ratio of the products of **20** and **21** was 14:3. **20**: ^{31}P NMR (81 MHz, THF-C_6D_6) δ = −71.5 (d, J_{PH} = 230.2 Hz).

Preparation of **21** *by an Alternative Method*

A THF solution (30 mL) of 2,4,6-tri-*t*-butylphenylphosphine (1.03 g, 3.71 mmol) was allowed to react with *t*-butyllithium (2.6 mL, 3.80 mmol) at −78°C, and the mixture was stirred further. Methyl iodide (0.24 mL, 3.84 mmol) was added to the above solution. After flash column chromatography using hexane as an eluent **21** (0.564 g, 1.93 mmol) was obtained in 52% yield. **21**: Colorless prisms, mp 71–72°C; ^1H NMR (200 MHz, $CDCl_3$) δ = 1.09 (3H, dd, $^2J_{PH}$ = 5.0 Hz and $^3J_{HH}$ = 7.0 Hz, PMe), 1.30 (9H, s, *p*-*t*-Bu), 1.58 (18H, s, *o*-*t*-Bu), 5.04 (1H, dq, $^1J_{PH}$ = 226.3 Hz and $^3J_{HH}$ = 7.0 Hz, PH), and 7.39 (2H, d, $^4J_{PH}$ = 2.1 Hz, *m*-Ar); $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$) δ = 11.3 (s, J_{PC} = 14.5 Hz, PMe), 31.3 (s, *p*-CMe_3), 33.5 (s, *o*-CMe_3), 33.6 (s, *o*′-CMe_3), 34.9 (s, *p*-CMe_3), 38.4 (s, *o*-CMe_3), 122.1 (d, J_{PC} = 4.2 Hz, *m*-Ar), 135.2 (s, *ipso*-Ph), 149.0 (s, *p*-Ar), and 154.3 (d, J_{PC} = 8.0 Hz, *o*-Ar); ^{31}P NMR (81 MHz, $CDCl_3$) δ = −90.7 (d, J_{PH} = 225.3 Hz) [20]; IR (KBr) 2399, 1595, 1535, 1473, 1458, 1410, 1390, 1362, 1281, 1238, 1209, 1190, 1007, 924, 901, 877, 843, 752, 699, 463, and 422 cm^{-1}; MS (70 eV) *m*/*z* (rel intensity) 291 (M^+–1; 100), 277 (M^+–CH_3; 100), and 57 (*t*-Bu^+; 27). HRMS (70 eV). Found: *m*/*z* 292.2316. Calcd for $C_{18}H_{31}P$: M, 292.2320.

Reaction of **11** *with Diethylamine*

A THF solution of **11**, prepared from **1** (151.5 mg, 0.522 mmol), was concentrated and then allowed to react with an excess amount of diethylamine at room temperature in THF to give **22** as a major product according to the ^{31}P NMR spectrum. **22**: ^{31}P NMR (81 MHz, C_6D_6) δ = −81.8 (d, J_{PH} = 227.7 Hz).

Reaction of **9** *with Diethylamine*

A THF solution of **9**, prepared from **1** (151.5 mg, 0.522 mmol), was allowed to react with an excess amount of diethylamine at room temperature in THF to regenerate **1** according to the ^{31}P NMR spectrum. **1**: $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$) δ = 288.8.

Reaction of (*E*)-**12** *with Diethylamine*

A THF solution of (*E*)-**12**, prepared from (*E*)-**2** (75.4 mg, 0.206 mmol), was allowed to react with an excess amount of diethylamine at room temperature in THF to regenerate (*E*)-**2** according to the ^{31}P NMR spectrum. (*E*)-**2**: ^{31}P NMR (81 MHz, $CDCl_3$) δ = 259.7 (d, J_{PH} = 26.9 Hz).

Reaction of (*Z*)-**12** *with Diethylamine*

A THF solution of (*Z*)-**12**, prepared from (*Z*)-**2** (75.4 mg, 0.206 mmol), was allowed to react with an excess amount of diethylamine at room temperature in THF to regenerate (*Z*)-**2** according to the ^{31}P NMR spectrum. (*Z*)-**2**: ^{31}P NMR (81 MHz, $CDCl_3$) δ = 241.6 (d, J_{PH} = 39.1 Hz).

Reaction of **13e** *with Diethylamine*

A THF solution of **13e**, prepared from (*E*)-**2** (89.3 mg, 0.244 mmol), was allowed to react with an excess amount of diethylamine at room temperature in THF to give **23e** as a major product according to the ^{31}P NMR spectrum, together with a trace amount of **8** and **24e**. **23e**: ^{31}P NMR (81 MHz, THF–C_6D_6) δ = −51.8 (d, J_{PH} = 213.6 Hz).

Reaction of **14e** *with Diethylamine*

A THF solution of **14e**, prepared from (*E*)-**2** (89.3 mg, 0.244 mmol), was allowed to react with an excess amount of diethylamine at room temperature in THF to give **24e** as a major product according to the ^{31}P NMR spectrum, together with **23e** and **8** in a ratio of 7:2:2. **24e**: ^{31}P NMR (81 MHz, C_6D_6) δ = −55.6 (d, J_{PH} = 216.8 Hz).

Reaction of **13z** *with Diethylamine*

A THF solution of **13z**, prepared from (*Z*)-**2** (75.4 mg, 0.206 mmol), was allowed to react with an excess

amount of diethylamine at room temperature in THF to give **23z** as a major product according to the ^{31}P NMR spectrum, together with a trace amount of **8**. **23z**: ^{31}P NMR (81 MHz, THF–C_6D_6) $\delta = -25.2$ (d, $J_{PH} = 230.4$ Hz).

Reaction of **14z** *with Diethylamine*

A THF solution of **14z**, prepared from (*Z*)-**2** (75.4 mg, 0.206 mmol), was allowed to react with an excess amount of diethylamine at room temperature in THF to give **8** as a major product according to the ^{31}P NMR spectrum, together with a trace amount of **23z**.

Reaction of **18** *with Diethylamine*

A THF solution of **18** in THF (14.5 mL), prepared from **1** (125.7 mg, 0.433 mmol), was concentrated and was allowed to react with diethylamine. The reaction mixture was submitted to ^{31}P NMR monitoring to indicate the formation of **6** and **21**.

Reaction of **19** *with Diethylamine*

A THF solution of **19** in THF (15.0 mL), prepared from (*E*)-**2** (194.9 mg, 0.532 mmol), was allowed to react with excess amount of diethylamine. The reaction mixture was submitted to ^{31}P NMR monitoring to indicate the formation of **8**.

Oxidative Workup of **6**

A THF solution of **6** in THF (15.0 mL), prepared from **1** (51.4 mg, 0.177 mmol), was cooled at 0°C, and to it was added a 3 M aqueous solution of NaOH (35 mL) and a 30% aqueous solution of hydrogen peroxide (25 mL). Then the solution was warmed to room temperature and stirred for 1.5 hours, extracted with diethyl ether, and the organic layer separated and washed with aqueous sodium hydrogen carbonate, saturated NaCl, and dried ($MgSO_4$). The solvent was evaporated, and the residue was submitted to silica-gel column chromatography to give **25** (18.1 mg, 55.9 μmol) and **26** (8.9 mg, 28.9 μmol) in 32% and 16% yields, respectively. **25**: Colorless needles, mp 154–155°C (decomp); ^1H NMR (200 MHz, $CDCl_3$) $\delta = 1.30$ (9H, s, *p*-*t*-Bu), 1.56 (18H, s, *o*-*t*-Bu), 3.66 (2H, br. d, $^2J_{PH} = 13.2$ Hz, C<u>H</u>H), 4.5–4.3 (1H, m, CH<u>H</u>), 5.94 (1H, br. s, OH), 7.44 (2H, d, $^4J_{PH} = 3.7$ Hz, *m*-Ar), and 7.95 (1H, dd, $^1J_{PH} = 498.0$ Hz and $^3J_{HH} = 4.9$ Hz, PH); ^{13}C {^1H} NMR (50 MHz, $CDCl_3$) $\delta = 30.9$ (s, *p*-C<u>Me</u>$_3$), 33.7 (s, *o*-C<u>Me</u>$_3$), 35.0 (s, *p*-<u>C</u>Me$_3$), 38.4 (s, *o*-<u>C</u>Me$_3$), 38.5 (s, *o′*-<u>C</u>Me$_3$), 64.7 (d, $J_{PC} = 77.5$ Hz, CH_2), 123.5 (d, $J_{PC} = 11.6$ Hz, *m*-Ar), 124.1 (d, $J_{PC} = 87.3$ Hz, *ipso*-Ar), 153.3 (d, $J_{PC} = 8.3$ Hz, *p*-Ar), and 156.6 (d, $J_{PC} = 8.3$ Hz, *o*-Ar); ^{31}P NMR (81 MHz, $CDCl_3$) $\delta = 24.3$ (d, $J_{PH} = 498.5$ Hz); IR (KBr) 3269, 2962, 1595, 1527, 1471, 1458, 1408, 1367, 1290, 1240, 1198, 1161, 1128, 1061, 1041, 1024, 960, 879, 818, 768, 706, 685, 648, 609, 511, 451, and 430 cm^{-1}; MS (70 eV) *m*/*z* (rel. intensity) 323 (M^+–1;2), 293 (M^+–CH_2OH; 100), 279 (M^+–CH_2OH–CH_3 + 1; 12), and 57 (*t*-Bu^+; 74). HRMS (70 eV). Found: *m*/*z* 324.2223. Calcd for $C_{19}H_{33}O_2P$: M, 324.2218. **26**: Colorless prisms, mp 109.5–110.5°C; ^1H NMR (200 MHz, $CDCl_3$) $\delta = 1.31$ (9H, s, *p*-*t*-Bu), 1.57 (18H, s, *o*-*t*-Bu), 1.70 (3H, dd, $^2J_{PH} = 12.5$ Hz and $^3J_{HH} = 4.1$ Hz, PMe), 7.46 (2H, d, $^4J_{PH} = 3.9$ Hz, *m*-Ar), and 8.14 (1H, dq, $^1J_{PH} = 487.3$ Hz and $^3J_{HH} = 4.1$ Hz, PH); ^{13}C {^1H} NMR (50 MHz, $CDCl_3$) $\delta = 19.9$ (s, $J_{PC} = 70.7$ Hz, PMe), 31.0 (s, *p*-C<u>Me</u>$_3$), 33.8 (s, *o*-C<u>Me</u>$_3$), 34.9 (s, *p*-<u>C</u>Me$_3$), 38.5 (s, *o*-<u>C</u>Me$_3$), 38.6 (s, *o′*-<u>C</u>Me$_3$), 123.5 (d, $J_{PC} = 12.1$ Hz, *m*-Ar), 128.2 (s, *ipso*-Ar), 152.7 (s, *p*-Ar), and 155.6 (d, $J_{PC} = 7.6$ Hz, *o*-Ar); ^{31}P NMR (81 MHz, $CDCl_3$) $\delta = 15.9$ (d, $J_{PH} = 483.7$ Hz); IR (KBr) 2488, 1593, 1525, 1469, 1398, 1365, 1288, 1238, 1182, 1055, 997, 877, 822, 725, 600, 513, 420, and 407 cm^{-1}; MS (70 eV) *m*/*z* (rel. intensity) 307 (M^+–1; 100), 293 (M^+–CH_3; 56), 252 (M^+–*t*-Bu + 1; 59), 237 (M^+–*t*-Bu–CH_3 + 1; 30), and 57 (*t*-Bu^+; 60). HRMS (70 eV). Found: *m*/*z* 308.2262. Calcd for $C_{19}H_{33}OP$: M, 308.2262.

Oxidative Workup of **10**

A THF solution of **10** in THF (4.0 mL), prepared from **1** (54.5 mg, 0.188 mmol), was cooled at 0°C, and to it was added a 3 M aqueous solution of NaOH (35 mL) and a 30% aqueous solution of hydrogen peroxide (25 mL). Then the solution was warmed to room temperature and stirred for 3.5 hours then extracted with diethyl ether. The organic layer was separated and washed with aqueous sodium hydrogen carbonate, saturated NaCl, and dried ($MgSO_4$). The solvent was evaporated, and the residue was submitted to silica-gel column chromatography to give **25** (12.4 mg, 38.2 μmol) and **26** (3.4 mg, 11.0 μmol) in 20% and 6% yields, respectively.

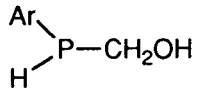
Oxidation of **11**

A THF solution of **11** in THF (15.0 mL), prepared from **1** (490.9 mg, 1.69 mmol), was cooled at 0°C, and to it was added a 3 M aqueous solution of NaOH (60 mL) and a 30% aqueous solution of hydrogen peroxide (40 mL). Then the solution was warmed to room temperature and stirred for 3.5 hours, extracted with diethyl ether, and the organic layer was separated and washed with aqueous sodium hydro-

gen carbonate, saturated NaCl, and dried ($MgSO_4$). The solvent was evaporated, and the residue was submitted to silica-gel column chromatography and reversed HPLC to give **25** (204.8 mg, 0.631 mmol) and **26** (41.8 mg, 0.136 mmol) in 37% and 8% yields, respectively.

Oxidation of **13e**

A THF solution of **13e** in THF (4.0 mL), prepared from (*E*)-**2** (59.6 mg, 0.163 mmol), was cooled at 0°C, and to it was added a 3 M aqueous solution of NaOH (35 mL) and a 30% aqueous solution of hydrogen peroxide (25 mL). Then the solution was warmed to room temperature and stirred for 2 hours, extracted with diethyl ether, and the organic layer was separated and washed with aqueous sodium hydrogen carbonate, saturated NaCl, and dried ($MgSO_4$). The solvent was evaporated, and the residue was submitted to silica-gel column chromatography to give **28** (47.3 mg, 0.123 mmol) in 76% yield. **28**: Colorless oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ = 1.31 (9H, s, *p*-*t*-Bu), 1.41 (18H, s, *o*-*t*-Bu), 3.2–3.4 (2H, m, CH_2), 6.2–6.4 (2H, m, *o*-Ph), 6.9–7.1 (3H, m, *m*-Ph, and *p*-Ph), 7.31 (2H, br. s, *m*-Ar), and 7.59 (1H, ddd, $^1J_{PH}$ = 494.7 Hz, $^3J_{HH}$ = 5.7 Hz, and $^3J_{HH}$ = 3.1 Hz, PH); ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$) δ = 31.1 (s, *p*-C$\underline{Me}_3$), 33.6 (s, *o*-C$\underline{Me}_3$), 34.9 (d, J_{PC} = 1.1 Hz, *o*-$\underline{C}Me_3$), 38.5 (s, *p*-$\underline{C}Me_3$), 42.0 (d, $^1J_{PC}$ = 63.3 Hz, CH_2), 122.8 (d, J_{PC} = 11.9 Hz, *m*-Ar), 124.7 (s, *ipso*-Ar), 126.5 (d, J_{PC} = 4.2 Hz, *p*-Ph), 128.2 (d, J_{PC} = 3.7 Hz, *m*-Ph), 129.1 (d, J_{PC} = 5.9 Hz, *o*-Ph), 132.3 (d, J_{PC} = 5.0 Hz, *ipso*-Ph), 153.0 (d, J_{PC} = 3.4 Hz, *p*-Ar), and 156.8 (s, *o*-Ar); ^{31}P NMR (81 MHz, $CDCl_3$) δ = 27.8 (dt, $^1J_{PH}$ = 494.9 Hz and $^2J_{PH}$ = 14.8 Hz); IR (Neat) 2440, 1591, 1527, 1489, 1471, 1462, 1400, 1365, 1279, 1230, 1203, 1172, 1124, 1072, 1049, 1030, 978, 908, 879, 789, 777, 700, 650, 606, 519, 484, and 478 cm^{-1}; MS (70 eV) *m*/*z* (rel. intensity) 383 (M^+–1; 5), 327 (M^+–*t*-Bu; 3), 307 (M^+–Ph; 2), and 293 (M^+–CH_2Ph; 100). HRMS (70 eV). Found: *m*/*z* 384.2579. Calcd for $C_{25}H_{37}OP$: M, 384.2582.



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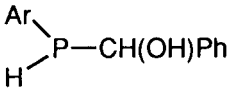

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Oxidation of **14e**

A THF solution of **14e** in THF (4.0 mL), prepared from (*E*)-**2** (58.6 mg, 0.160 mmol), was cooled at 0°C, and to it was added 3 M aqueous solution of NaOH (35 mL) and a 30% aqueous solution of hydrogen peroxide (25 mL). Then the solution was warmed to room temperature and stirred for 4.5 hours, extracted with diethyl ether, and the organic layer was separated and washed with aqueous sodium hydrogen carbonate, saturated NaCl, and dried ($MgSO_4$). The solvent was evaporated, and the residue was submitted to silica-gel column chromatography to give **28** (39.0 mg, 0.101 mmol) in 63% yield.

Oxidation of **13z**

A THF solution of **13z** in THF (4.0 mL), prepared from (*E*)-**2** (47.9 mg, 0.131 mmol), was cooled at 0°C, and to it was added a 3 M aqueous solution of NaOH (35 mL) and a 30% aqueous solution of hydrogen peroxide (25 mL). Then the solution was warmed to room temperature and stirred for 4.5 hours, extracted with diethyl ether, and the organic layer was separated and washed with aqueous sodium hydrogen carbonate, saturated NaCl, and dried ($MgSO_4$). The solvent was evaporated, and the residue was submitted to silica-gel column chromatography to give **28** (33.1 mg, 86.1 μmol) in 66% yield.

Oxidation of **14z**

A THF solution of **14z** in THF (4.0 mL), prepared from (*Z*)-**2** (53.7 mg, 0.147 mmol), was cooled at 0°C, and to it was added a 3 M aqueous solution of NaOH (35 mL) and a 30% aqueous solution of hydrogen peroxide (25 mL). Then the solution was warmed to room temperature and stirred for 16 hours, extracted with diethyl ether, and the organic layer was separated and washed with aqueous sodium hydrogen carbonate, saturated NaCl, and dried ($MgSO_4$). The solvent was evaporated and the residue was submitted to silica-gel column chromatography to give **28** (34.7 mg, 90.2 μmol) in 61% yield.

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