# A New Tetratertiary Phosphine Ligand and Its Use in Pd-Catalyzed Allylic Substitution

Dorothée Laurenti, Marie Feuerstein, Gérard Pèpe,[‡] Henri Doucet, and Maurice Santelli*,[†]

*Laboratoire de Synthèse Organique, UMR−CNRS 6009, Faculté de St-Jérôme, 13397 Marseille Cedex 20, France*

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*m.santelli@lso.u-3mrs.fr*

A new tetraphosphine, the *cis-cis-cis*-1,2,3,4-tetrakis(diphenylphosphinomethyl)cyclopentane (Tedicyp) **1** has been synthesized, characterized, and used in Pd-catalyzed allylic substitutions. The Tedicyp was easily prepared in seven steps from the commercially available himic anhydride. The structure of the complex Tedicyp−borane was determined by X-ray analysis. The tetraphosphine in combination with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ affords a very efficient catalyst for allylic substitution of several allylic acetates. Under mild conditions, very high turnover numbers and turnover frequencies have been obtained.

## Introduction

The transition-metal-mediated allylic substitution reaction is known as an efficient synthetic tool for the elaboration of carbon−carbon and carbon−heteroatom bonds.[1] In this area, the palladium-catalyzed allylic alkylation constitutes the most useful reaction.[2] The increasing importance of such transition metal-catalyzed reactions has run parallel to the development of new ligands, and diphosphine ligands have been widely used for this purpose. Recently, extensive efforts have been devoted to the design of new polypodal ligands.[3] In particular, transition-metal complexes of tripodal phosphines have begun to attract interest because of their potential as catalysts in several homogeneous reactions.[4] In contrast, tetraphosphine ligands have been poorly exploited in homogeneous catalysis.[5]

We wish to report here the preparation and the use in palladium-catalyzed allylic substitution of the new tetrapodal phosphine ligand, *cis-cis-cis*-1,2,3,4-tetrakis-(diphenylphosphinomethyl)cyclopentane or Tedicyp **1**, in which four diphenylphosphino groups are stereospecifically bound to the same face of the cyclopentane ring.

**Preparation and Characterization of Tedicyp 1.** Tedicyp was prepared in seven steps from the commercially available starting material himic anhydride **2** as illustrated in Scheme 1. Reduction of the anhydride **2** with $LiAlH_4$ gave diol **3** in 74% yield.[6] Treatment with methoxypropene afforded, in quantitative yield, the tricyclic compound **4** which was submitted to ozonolysis followed by reduction with $NaBH_4$ to give **5** in 86% yield.[7] Exposure of **5** to water in tetrahydrofuran in the presence of a strong acidic cation-exchange resin led to tetraol **6**.[8] Treatment of **6** with an excess of tosyl chloride in pyridine afforded the expected tetratosylate **7** in 60−65% yield along with bicyclic ether **8** (20−25%).[9] The desired tetraphosphane Tedicyp **1** was prepared in excellent yield employing established procedures.[10] As **1** is air-sensitive and requires protection for handling and storage, borane was added before workup. The Tedicyp−borane complex **9** was obtained in 82% yield. Deboronation was carried out by treatment with diethylamine.[11] When borane was not added before workup, Tedicyp was partially oxidized and, finally, the tetrakis phosphonoyl derivative **10** was isolated in 66% yield.

The stereochemical identity of **1** was verified by an X-ray crystal structure determination of Tedicyp−borane complex **9**. The salient finding is the severe deviation from the idealized planar symmetry ($C_s$). The boranato-

[†]To whom correspondence should be addressed.

[‡] Address X-ray correspondence to this author. E-mail: pepe@luminy.univ-mrs.fr.

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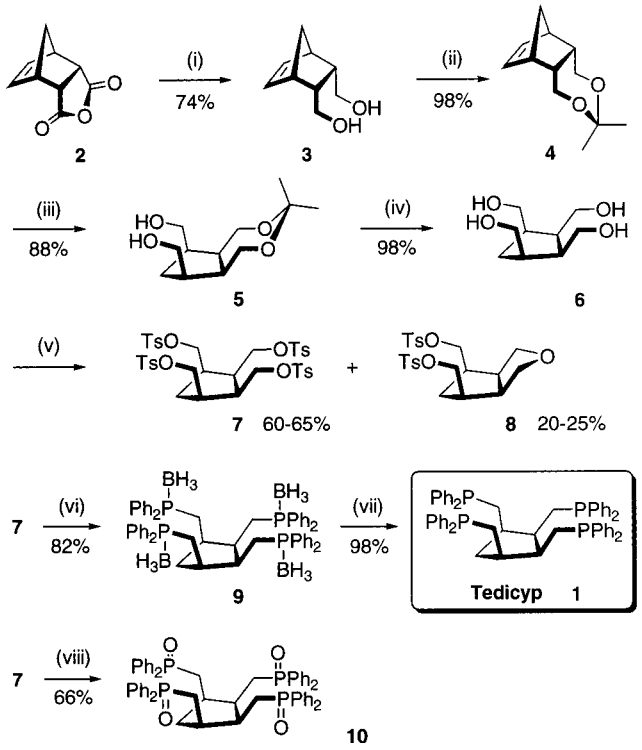
**Scheme 1**[a]

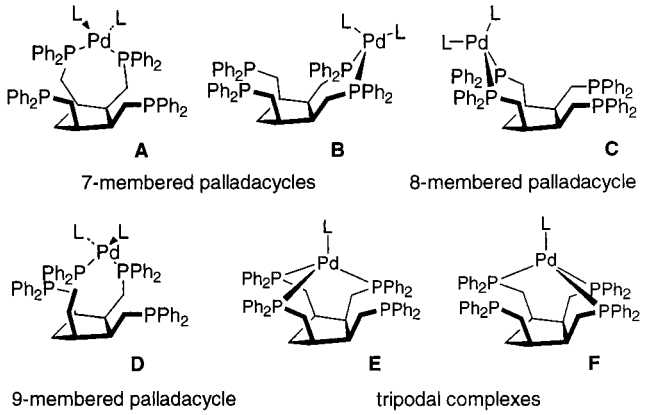



[a] (i) $LiAlH_4$, THF, 65 °C, 3 h; (ii) MeC(OMe)$CH_2$, cat. *p*-TsOH·$H_2O$, rt, 2 h; (iii) $O_3-O_2$, $CH_2Cl_2$, −60 °C then $NaBH_4$, EtOH, rt, overnight; (iv) Amberlite IR-120(H), $H_2O$−THF, 65 °C, 2 h; (v) *p*-TsCl (1.5 equiv), pyridine, −20 °C, 5 h; (vi) $ClPPh_2$−Li, THF, rt, 5 h then $BH_3$·THF, THF, 0 °C, 1.5 h; (vii) $Et_2NH$, 55−60 °C, 10 h; (viii) $ClPPh_2$ − Li, THF, rt, 5 h, then $H_2O_2$.

diphenylphosphanylmethyl groups were alternatively in pseudoequatorial and pseudoaxial positions, displaying a gear effect.[12]

**Complexes Structure.** The chelate ring size has an important effect on transition-metal-catalyzed reactions particularly in palladium chemistry.[13] We can expect a great reactivity of the Pd−Tedicyp complex resulting from the possibility for the metal atom to exchange ligand in the way to increase "chelate effect". According to the tetrahedral structure of Pd(0) complexes,[14] a tetradentate ligand such as Tedicyp may exhibit six possible coordination modes, four built with two diphenylphosphino groups (Chart 1, **A**−**D)** and two with three diphenylphosphino groups (Chart 2, **E**, **F)**. Coordination modes of Tedicyp to Pd(II) should be simpler, and only two phosphine functions should be coordinated simultaneously. We tried to get some information on the structure of this palladium−Tedicyp complex by $^{31}P$ NMR analysis. Addition of 1 equiv of Tedicyp to 0.5 equiv of the dimer $[PdCl(C_3H_5)]_2$ gave a clean spectrum in $^{31}P$ NMR which possesses two broad signals at 19 and 25 ppm (vs $H_3PO_4$). The characteristic signals of the free phosphine at −16.3 and −17.7 ppm were not observed. Addition of 1 equiv of Tedicyp to 1 equiv of $[PdCl(C_3H_5)]_2$ gave an identical $^{31}P$ NMR spectrum. Addition of 2 equiv of Tedicyp to 0.5 equiv of $[PdCl(C_3H_5)]_2$ led to a more complicated spectrum. Mainly four signals of free phosphines at −16.9, −18.2, −19.3, and −20.9 ppm and some broad peaks between 40 and 10 ppm were observed in $^{31}P$ NMR. In the first case, addition of 1 equiv of Tedicyp to 0.5 equiv of Pd complex, the broad signals produced at 19 and 25 ppm suggest that this complex is involved in a succession of equilibriums due to a fast coordination−dissociation process of the four phosphines of the ligand. The absence of peaks of free phosphines probably comes from the equilibrium rate which seems to be of the order of the NMR time scale. Similar results have already been described, for example $Pd(PPh_3)_3$ is largely dissociated, and the equilibrium rate is of the order of the NMR time scale even at low temperature.[15]

**Chart 1**




**Allylic Substitutions.** Our aim was to obtain complexes capable of very high turnover numbers in catalysis. To evaluate the catalytic potential of Tedicyp, we decided to investigate the palladium-catalyzed allylic substitution of allyl acetate **11** with sodium dimethyl malonate as a test reaction.

Our first objective was to compare the catalysts prepared with $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ associated with a monophosphine ($PPh_3$) or diphosphines such as 1,2-bis(diphenylphosphino)ethane (dppe) or 1,4-bis(diphenylphosphino)-butane (dppb) and our tetraphosphine **1**. The addition of sodium dimethyl malonate to allyl acetate in the presence of 0.1% catalyst led to 93% conversion when $PPh_3$ was used as ligand and complete conversion with dppe, dppb, or tedicyp (Table 1, entries 2−5). In the presence of 0.01% catalyst, only 1% conversion was observed with $PPh_3$ and 49−50% with dppe and dppb as ligands (Table 1, entries 6−8). With Tedicyp, the conversion was complete (Table 1, entry 9). A similar tendency was observed in the presence of 0.001% catalyst, 16% conversion with dppe and complete conversion with Tedicyp were obtained (Table 1, entries 10 and 11). Finally, we tried to reach the limits of Tedicyp−palladium complex for this reaction and we obtained a conversion of 98% after 14 days in the presence of 0.00001% catalyst (ratio substrate/catalyst of 10 000 000) when the reaction was conducted at 50 °C (Table 1, entry 14).

These results prompted us to investigate the allylation of dimethyl malonate with substituted allyl acetates.

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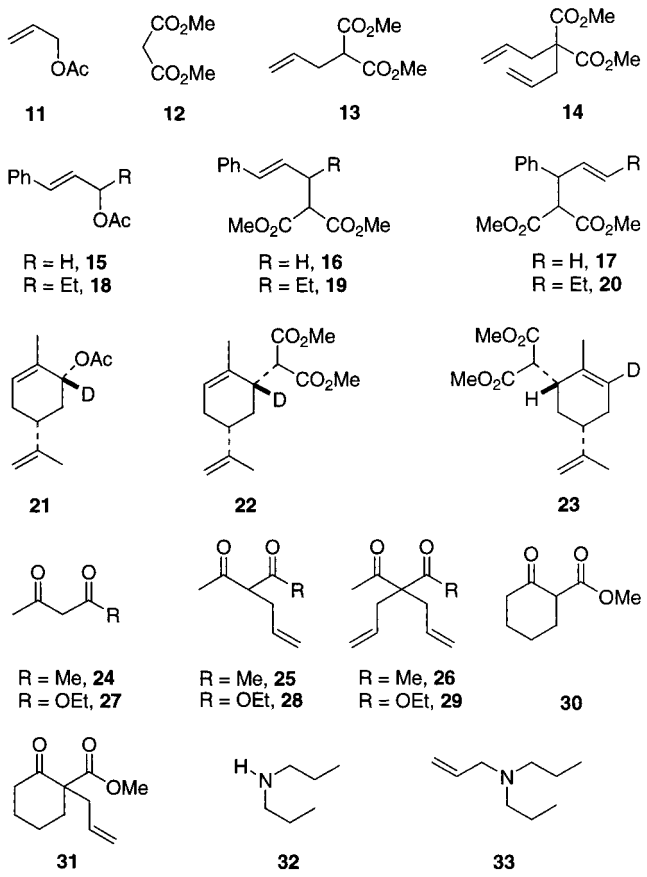
**Table 1. Pd-Catalyzed Allyl Acetate Reactions with Sodium Dimethyl Malonate[a]**

| entry | ligand | ratio ligand/Pd[b] | ratio substrate/catalyst | reaction time (h) | conversion (%) | ratio **13**/**14** | turnover frequency ($h^{-1}$)[d] | turnover number |
|---|---|---|---|---|---|---|---|---|
| 1 | - | - | 1 000 | 3 | 0 | - | 0 | 0 |
| 2 | $PPh_3$ | 2 | 1 000 | 3 | 93 | 4:1 | 310 | 930 |
| 3 | dppe | 2 | 1 000 | 3 | 100 | 3.5:1 | 333 | 1000 |
| 4 | dppb | 2 | 1 000 | 3 | 100 | 2.6:1 | 333 | 1000 |
| 5 | **1** | 1 | 1 000 | 3 | 100 | 4.9:1 | 333 | 1000 |
| 6 | $PPh_3$ | 4 | 10 000 | 3 | 1 | 1:0 | 33 | 100 |
| 7 | dppe | 2 | 10 000 | 3 | 50 | 7.3:1 | 1666 | 5 000 |
| 8 | dppb | 2 | 10 000 | 3 | 49 | 4.9:1 | 1633 | 4 900 |
| 9 | **1** | 1 | 10 000 | 3 | 100 | 4.9:1 | 3333 | 10 000 |
| 10 | dppe | 2 | 100 000 | 24 | 16 | 7.3:1 | 830 | 16 000 |
| 11 | **1** | 1 | 100 000 | 24 | 99 | 4.6:1 | 12 000 | 99 000 |
| 12 | 1 | 1 | 1 000 000 | 19 | 74 | 7.7:1 | 39 000[e] | 740 000 |
| 13 | 1 | 1 | 10 000 000 | 60 | 56 | 11.5:1 | 175 000[e] | 5 600 000 |
| 14 | 1 | 1 | 10 000 000 | 340 | 98[c] | 4.9:1 | 190 000[e] | 9 800 000 |

[a] Allyl acetate **11**, 1 equiv; dimethyl malonate **12**, 2 equiv; sodium hydride, 2 equiv; THF; rt. [b] $[ClPd(\eta^3\text{-}C_3H_5)]_2$. [c] 50 °C. [d] TOF calculated between initial time and 3 h. [e] Calculated after 19 h.

**Scheme 2**




When we used cinnamyl acetate **15** in the presence of 0.1% catalyst (Table 2, entry 1), complete conversion was observed, and a turnover number of 3400 was obtained with 0.01 mol % catalyst (Table 2, entry 3). We noted a good regioselectivity for the alkylation of cinnamyl acetate in favor of the linear isomer. Lower turnover numbers were observed in the course of the alkylation of hindered *E*-3-acetoxy-1-phenyl-1-pentene **18** (Table 2, entries 4 and 5). The major isomer **19** obtained for this reaction corresponds to the addition to the carbon in position 3; only 10% of the regioisomer **20** are observed. Hayashi had reported that the alkylation of this substrate by sodium dimethyl malonate in similar reaction conditions and in the presence of tetrakis(triphenylphosphine)palladium(0) occurred in low yield (4%). In contrast, the use of the palladium−dppe system proceeded in very good yields.[16] Addition to deuterated chiral carveyl acetate **21** led to an equimolecular mixture of the two isomers **22** and **23** (Table 2, entry 6).[17]

Addition to the anions of pentane-2,4-dione and ethyl acetoacetate led mainly to the dialkylated products **26** and **29** in good yield in the presence of 0.1% catalyst (Table 3, entries 1 and 2). The reaction of 2-carbomethoxycyclohexanone anion with allyl acetate occurred with high turnover numbers (Table 3, entry 3).[18] Finally the use of Tedicyp−Pd complex provides a convenient access to tertiary amines. Addition of dipropylamine **32** to allyl acetate, led to the addition product **33** in good yield.[19] With a ratio substrate/catalyst of 300000 the conversion was 84% after 90 h, and a turnover number of 680000 can be obtained with a ratio substrate/catalyst of 1000000 (Table 3, entries 5 and 6).

In conclusion, use of the complex Tedicyp−Pd obtained by addition of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ to Tedicyp **1** provides a convenient catalyst for the allylic substitution reaction. This catalyst is much more efficient than the complex formed with triphenylphosphine ligand. This efficiency probably comes from the presence of the four diphenylphosphinoalkyl groups stereospecifically bound to the same face of the cyclopentane ring which probably increases the coordination of the ligand to the metal and prevent precipitation of the catalyst. Such catalyst gives rates of ca. 6000 kg·$h^{-1}$ of dimethyl allylmalonate **13** per mol of palladium under mild conditions or 56 kg·$h^{-1}$ of **13** per gram of palladium (in one batch, one mol of catalyst affords the production of 1 685 tons of **13**!). These results represent an inexpensive, efficient, and environmentally friendly synthesis. Further applications of the ligand Tedicyp will be reported in due course.

## Experimental Section

**General.** All reactions were run under argon in oven-dried glassware. $^1H$ (400 or 200 MHz) and $^{13}C$ NMR (100 or 50 MHz) spectra were recorded in $CDCl_3$ solutions. Chemical shift ($\delta$) are reported in ppm relative to TMS. Flash chromatography was performed on silica gel (230−400 mesh) and TLC on silica gel.

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**Table 2. Pd−Tedicyp[a]-Catalyzed Allylation Reactions of Sodium Dimethyl Malonate[b]**

| entry | allylic derivative | ratio substrate/catalyst | reaction time (h) and reaction temp. (°C) | conversion (%) | ratio of product | turnover frequency ($h^{-1}$)[d] | turnover number |
|---|---|---|---|---|---|---|---|
| 1 | **15** | 1 000 | 90, 25 | 100 | **16**:**17** = 9:1 | 53 | 1 000 |
| 2 | **15**[c] | 1 000 | 15, 25 | 100 | **16**:**17** = 9:1 | 67 | 1 000 |
| 3 | **15** | 10 000 | 15, 25 | 34 | **16**:**17** = 9:1 | 227 | 3 400 |
| 4 | **18** | 100 | 20, 40 | 65 | **19**:**20** = 4.9:1 | 3.4 | 65 |
| 5 | **18** | 100 | 90, 55 | 100 | **19**:**20** = 9:1 | 4.1[e] | 100 |
| 6 | **21** | 100 | 24, 25 | 58 | **22**:**23** = 1:1 | 2.4[e] | 58 |

[a] $[ClPd(\eta^3\text{-}C_3H_5)]_2$:Tedicyp = 1:2 (mol/mol). [b] Allyl derivative, 1 equiv; dimethyl malonate, 2 equiv; sodium hydride, 2 equiv; THF. [c] **15**, 1 equiv; dimethyl malonate, 5 equiv; sodium hydride, 4.5 equiv; THF. [d] TOF calculated between initial time and 15 h. [e] Calculated after 24 h.

**Table 3. Pd-Catalyzed Allyl Acetate Reactions with Nucleophilic Reagents[a]**

| entry | nucleo. | ratio substrate/catalyst | reaction time (h) | conversion (%) | ratio of product or product | turnover frequency ($h^{-1}$)[e] | turnover number |
|---|---|---|---|---|---|---|---|
| 1 | **24**[b] | 1 000 | 20 | 100 | **26**:**25** = 19:1 | 50[f] | 1 000 |
| 2 | **27**[b] | 1 000 | 40 | 100 | **29**:**28** = 24:1 | 30 | 1 000 |
| 3 | **30**[c] | 10 000 | 48 | 100 | **31** | 341 | 10 000 |
| 4 | **32**[d] | 30 000 | 90 | 99 | **33** | 1100 | 29 700 |
| 5 | **32**[d] | 300 000 | 90 | 84 | **33** | 6875 | 270 000 |
| 6 | **32**[d] | 1 000 000 | 136 | 68 | **33** | 8125 | 680 000 |

[a] $[ClPd(\eta^3\text{-}C_3H_5)]_2$:Tedicyp = 1:2 (mol/mol). [b] Allyl acetate, 1 equiv; **24** or **27**, 2 equiv; sodium hydride, 2 equiv; THF; 25 °C. [c] Allyl acetate, 1 equiv; **30**, 1.2 equiv; sodium hydride, 1 equiv; THF, 25 °C. [d] Allyl acetate, 1 equiv; **32**, 2 equiv, 25 °C. [e] TOF calculated between initial time and 24 h. [f] Calculated after 24 h.

**Material.** *endo*,*endo*-Bis(hydroxymethyl)norborn-2-ene (**3**) was prepared by a known procedure.[20]

**(1*R**,2*S**,8*R**,9*S**)-5,5-Dimethyl-4,6-dioxatricyclo-[7.2.1.0$^{2,8}$]dodec-10-ene (4).**[21] To a solution of diol **3** (12 g, 77.9 mmol) in $CH_2Cl_2$ (300 mL) were added 2-methoxypropene (14.7 mL, 156 mmol) and a catalytic amount of *p*-TsOH. After stirring at room temperature for 2 h, some crystals of $K_2CO_3$ were added, and the solution was stirred, filtered, and concentrated in vacuo. The crude product was recrystallized from petroleum ether yielding **4** (14.8 g, 76.3 mmol, 98%) as white crystals: mp 45 °C; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 6.04 (2H, t, $J$ = 1.7 Hz), 3.62 (2H, dd, $J$ = 13.0, 4.0 Hz), 3.31 (2H, td, $J$ = 13.0, 11.1 Hz), 2.58 (4H, m), 1.42 (2H, t, $J$ = 1.7 Hz), 1.27 (3H, s), 1.26 (3H, s); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 134.9 (d), 101.1 (s), 65.0 (t), 51.4 (t), 45.5 (d), 45.1 (d), 29.9 (q), 19.6 (q).

**(1*R**,7*S**,8*S**,10*R**)-8,10-Bis(hydroxymethyl)-4,4-dimethyl-3,5-dioxabicyclo[5.3.0]decane (5).**[7] Ozone in oxygen was bubbled through a solution of **4** (5.0 g, 25.8 mmol) in 300 mL of $CH_2Cl_2$ at −60 °C. The reaction was monitored by TLC (MeOH/$CH_2Cl_2$, 2/98). Then argon was purged through to remove the excess of ozone, followed by addition of a suspension of $NaBH_4$ (3 g, 77.4 mmol) in EtOH (50 mL). The stirred solution was allowed to reach room-temperature overnight. The reaction mixture was filtered on Celite and, after concentration, chromatographed on silica gel (MeOH−$CH_2Cl_2$, 5:95) to give **5** (5.2 g, 22.6 mmol, 88%) as white crystals, mp 150 °C; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 3.86−3.46 (8H, m), 2.27 (4H, br. s), 1.79−1.62 (2H, m), 1.32 (6H, s); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 102.1 (s), 63.1 (t), 60.8 (t), 45.1 (d), 42.8 (d), 29.7 (t), 24.7 (q), 24.5 (q).

**(1*R**,2*R**,3*S**,4*S**)-1,2,3,4-Tetrakis(hydroxymethyl)cyclopentane (6).**[8] To a solution of **5** (4.6 g, 20 mmol), water (20 mL), and THF (50 mL) under argon was added beads of Amberlite IR-120 (1 g), the reaction mixture was refluxed for 2 h and then cooled to room temperature. After filtration, the crude product was concentrated in vacuo. Toluene (25 mL) was added and then removed by rotary evaporation. This operation was repeated twice, and the crude product (oil) was used for the following tosylation step. Purification for analysis was accomplished by chromatography on silica gel (MeOH−$CH_2Cl_2$, 1:3). $^1$H NMR (200 MHz, DMSO-$d_6$) $\delta$ 4.55 (2H, t, $J$ = 4.8 Hz), 4.49 (2H, t, $J$ = 5.1 Hz), 3.52−3.25 (8H, m), 2.14−2.01 (4H, m), 1.84−1.74 (1H, m), 1.09−0.99 (1H, m); $^{13}$C NMR (50 MHz, DMSO-$d_6$) $\delta$ 62.8 (t), 58.5 (t), 45.5 (d), 42.4 (d), 31.5 (t).

**(1*R**,2*R**,3*S**,4*S**)-1,2,3,4-Tetrakis(((tolyl-4-sulfonyl)-oxy)methyl)cyclopentane (7).**[22] A solution of crude tetraol **6** (1.31 g, 6.9 mmol) in anhydrous pyridine (27.6 mL)($c$ = 0.25 mmol/mL) was cooled to −20 °C. Tosyl chloride (7.9 g, 41.4 mmol) was added, and the mixture was stirred at −20 °C for 5 h. The mixture was poured on ice and acidified (pH ∼ 1) by addition of diluted HCl followed by vigorous extraction with $CH_2Cl_2$. The combined organic layers were washed with brine, dried ($MgSO_4$), and evaporated. The crude oil was crystallized in $Et_2O$−$CH_2Cl_2$, (1:2) to give white crystals: mp 145 °C, or chromatographed on silica gel ($CH_2Cl_2$)(3.38 g, 4.48 mmol, 65%); $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.72 (4H, d, $J$ = 8.3 Hz), 7.70 (4H, d, $J$ = 8.3 Hz), 7.35 (4H, d, $J$ = 8.3 Hz), 7.34 (4H, d, $J$ = 8.3 Hz), 4.05−3.85 (8H, m), 2.45 (6H, s), 2.44 (6H, s), 2.44−2.35 (4H, m), 2.0−1.80 (1H, m), 1.05 (1H, m); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 145.4 (s), 145.2 (s), 132.5 (s), 132.1 (s), 130.2 (d), 130.1 (d), 130.0 (d), 128.0 (d), 127.9 (d), 69.8 (t), 66.7 (t), 41.6 (d), 38.9 (d), 30.9 (t), 21.8 (q). Anal. Calcd for $C_{37}H_{42}O_{12}S_4$: C, 55.09; H, 5.21. Found: C, 54.79; H, 5.22.

**(1*R**,2*R**,4*S**,5*S**)-2,4-Bis(((tolyl-4-sulfonyl)oxy)methyl)-7-oxabicyclo[3.3.0]octane (8).** This byproduct was isolated by chromatography of the reaction mixture (0.83 g, 1.72 mmol, 25%). Mp: 155 °C; $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 7.72 (4H, dd, $J$ = 8.3 Hz), 7.32 (4H, d, $J$ = 8.3 Hz), 4.05−3.85 (4H, m), 3.48−3.34 (4H, m), 2.72 (2H, br. s), 2.41 (6H, s), 2.40−2.27 (2H, m), 1.65 (1H, m), 1.16 (1H, m); $^{13}$C NMR (50 MHz, DMSO-$d_6$) $\delta$ 144.8 (s), 132.4 (s), 129.7 (d), 127.6 (d), 70.0 (t), 68.3 (t), 44.3 (d), 40.5 (d), 30.9 (t), 21.4 (q). Anal. Calcd for $C_{23}H_{28}O_7S_2$: C, 57.50; H, 5.83. Found: C, 57.41; H, 5.85.

**(1*R**,2*R**,3*S**,4*S**)-1,2,3,4-Tetrakis((boranatodiphenylphosphanyl)methyl)cyclopentane (9).** One piece of Li (1 g, 0.14 atom.g) was hammer-wrought to give a foil which was cut in narrow band and put in anhydrous THF (50 mL) under argon. The suspension was stirred at 0 °C and chlorodiphenylphosphine (10 mL, 55.7 mmol) was slowly added. The mixture was then stirred at room temperature for 3 h to give a solution of diphenylphosphide lithium ($c$ = 0.93 mmol/mL). Tetratosylate **7** (1.0 g, 1.24 mmol) was added to THF (10 mL) under argon. The solution was stirred at 0 °C, and 21.5 mL of the solution of phosphide lithium was slowly added. The

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solution was allowed to reach room temperature and stirred for 5 h and then cooled to 0 °C. A solution of borane in THF (1 M, 28 mL, 28 mmol) was added. The reaction mixture was poured on ice and extracted with $CH_2Cl_2$ (3 × 200 mL). The combined organic layers were washed with brine, dried ($MgSO_4$), and evaporated. The crude oil was chromatographed on silica gel (AcOEt−PE, 1:4) to give white crystals (0.93 g, 1.0 mmol, 82%): mp 149 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.74−7.59 (16H, m), 7.48−7.38 (16H, m), 7.35−7.28 (8H, m), 2.45 (2H, m), 2.14 (4H, m), 2.00 (2H, m), 1.76 (4H, dt, $J$ = 12.5, 10.2 Hz), 1.27 (2H, m), 1.21−0.5 (12H, m); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 133.0 (d, $|^1J|_{P,C}$ = 9.0 Hz), 132.7 (d, $|^1J|_{P,C}$ = 9.0 Hz), 132.55 (d, $|^1J|_{P,C}$ = 9.0 Hz), 132.4 (d, $|^1J|_{P,C}$ = 10.0 Hz), 131.7 (d, $|^2J|_{P,C}$ = 16.0 Hz), 131.3 (br. s), 129.3 (d, $|^3J|_{P,C}$ = 10.0 Hz), 129.1 (d, $|^1J|_{P,C}$ = 10.0 Hz), 129.0 (d, $|^1J|_{P,C}$ = 10.0 Hz), 128.7 (d, $|^1J|_{P,C}$ = 10.0 Hz), 43.2 (d, br. s), 37.1 (t), 36.2 (d, br.s), 29.2 (t, br. d, $|^1J|_{P,C}$ = 34.1 Hz), 21.9 (t, $|^1J|_{P,C}$ = 35.1 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 16.7, 15.4.

**(1*R**,2*R**,3*S**,4*S**)-1,2,3,4-Tetrakis((diphenylphosphanyl)methyl)cyclopentane (1).** Borane−phosphine **9** (1 g, 1 mmol) was added to anhydrous diethylamine and the solution was heated at 55−60 °C for 10 h. The amine was removed in vacuo. This operation was repeated twice. The crude product was chromatographed on silica gel ($Et_2O$−PE, 1:20) to give white crystals (0.90 g, 0.98 mmol, 98%), mp 79 °C. The white crystals are not air stable and were stored under argon. $^1$H NMR (400 MHz, THF-$d_8$) $\delta$ 7.71−7.23 (40H, m) 2.91−2.52 (2H, m), 2.38−1.72 (10H, m), 1.25 (2H, m); $^{13}$C NMR (100 MHz, THF-$d_8$) $\delta$ 141.6 (s, $|^1J|_{P,C}$ = 15.1 Hz), 141.1 (s, $|^1J|_{P,C}$ = 14.1 Hz), 140.0 (s, $|^1J|_{P,C}$ = 15.0 Hz), 139.4 (s, $|^1J|_{P,C}$ = 16.0 Hz), 134.6 (d, $|J|_{P,C}$ = 20.1 Hz), 134.5 (d, $|J|_{P,C}$ = 19.1 Hz), 133.5 (d, $|J|_{P,C}$ = 17.0 Hz), 133.3 (d, $|J|_{P,C}$ = 18.0 Hz), 129.6 (d, $|J|_{P,C}$ = 14.0 Hz), 129.3−129.0, 128.9 (d, $|J|_{P,C}$ = 15.0), 45.4 (t, $|^2J|_{P,C}$ = 8.6 Hz), 45.2 (d, $|^2J|_{P,C}$ = 8.7 Hz), 40.4 (t, $|^2J|_{P,C}$ = 8.75 Hz), 40.3 (t, $|^2J|_{P,C}$ = 9.2 Hz), 39.1 (d, $|^2J|_{P,C}$ = 13.3 Hz), 33.2 (d, $|^1J|_{P,C}$ = 10 Hz), 26.5 (t, $|^1J|_{P,C}$ = 12.9 Hz); $^{31}$P NMR (162 MHz, THF-$d_8$) $\delta$ −16.3, −17.7.

**(1*R**,2*R**,3*S**,4*S**)-1,2,3,4-Tetrakis((diphenylphosphinoyl)methyl)cyclopentane (10).** Procedure as in the synthesis of **9** with the exception that borane solution was not added. To the crude material in THF was added excess $H_2O_2$. The mixture was stirred at room temperature for 4 days. After usual workup, **10** was purified by chromatography on silica gel (MeOH−$CH_2Cl_2$, 5:95)(0.76 g, 0.82 mmol, 66%). White crystals, mp 165 °C; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.79−7.62 (16H, m), 7.50−7.35 (16H, m), 7.32−7.28 (8H, m), 2.85 (2H, br t, $J$ = 12.9 Hz), 2.28 (4H, d, $J$ = 11.9 Hz), 2.26−2.15 (2H, m), 2.10−2.05 (2H, m), 1.88 (2H, br q, $J$ = 12.9 Hz), 1.60 (1H, dt, $J$ = 13.8, 7.5 Hz), 1.36 (1H, dt, $J$ = 13.8, 10.2 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 134.3 ($|^1J|_{P,C}$ = 13.0 Hz), 133.3 ($|^1J|_{P,C}$, m), 131.94 ($|^1J|_{P,C}$ = 5 Hz), 131.62 ($|^1J|_{P,C}$ = 5 Hz), 131.27−131.0 (m), 129.0−128.6 (m), 41.9 (d, $|^2J|_{P,C}$ = 10.0 Hz), 38.0 (t), 35.2 (d), 33.0 (t, $|^1J|_{P,C}$ = 69.9 Hz), 27.1 (t, $|^1J|_{P,C}$ = 70.0 Hz); $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 32.2; HRMS calcd for $C_{57}H_{54}O_4P_4$ 926.2972, found 926.2965. Anal. Calcd for $C_{57}H_{54}O_4P_4$: C, 73.86; H, 5.87. Found: C, 73.54; H, 5.82.

**Preparation of the Pd−Tedicyp Catalyst.** An oven-dried 40-mL Schlenk tube, equipped with a magnetic stirring bar, a serum cap, and a stopcock under argon atmosphere, was charged with [Pd($\eta^3$-$C_3H_5$)Cl]$_2$ (4.2 mg, 11.6 $\mu$mol) and Tedicyp (20 mg, 23.2 $\mu$mol). Anhydrous THF (10 mL) was added, and then the solution was stirred at room temperature for 10 min. Concentration of the catalyst solution was 2.32 $\mu$mol/mL. $^{31}$P NMR (162 MHz, $CDCl_3$) $\delta$ 25 ($w$ = 80 Hz), 19.4 ($w$ = 110 Hz).

**General Procedure for the Allylic Alkylation Reaction.** To a solution of catalyst in anhydrous THF in a Schlenk tube under argon atmosphere was added allylic acetate. The solution was stirred at room temperature for 10 mn, and the nucleophilic reagent was added. The progress of the reaction was monitored by GC. The mixture was submitted to the usual workup.

**Dimethyl Allylmalonate (13) and Dimethyl Diallylmalonate (14).** To 1 mL of a solution of Pd−Tedicyp catalyst ($C$ = 2.32 $10^{-3}$ $\mu$mol/mL) in anhydrous THF was added allyl acetate **11** (2.5 mL, 23.2 mmol), and the mixture was stirred at room temperature for 10 min. In an other Schlenk tube under argon atmosphere, dimethylmalonate **12** (5.32 mL, 46.4 mmol) was added dropwise to a solution of NaH (1.11 g, 46.2 mmol), in anhydrous THF (100 mL), and the mixture was stirred at room temperature for 30 min.. The resulting anion was transferred to the solution of catalyst. The mixture was stirred at 55 °C during 14 days. Diethyl ether (200 mL) and water (20 mL) were added. After extraction with diethyl ether, the combined organic layers were dried ($MgSO_4$), and evaporated. The product was purified by chromatography on silica gel ($Et_2O$−PE, 5:95) to give **13** and **14** (ratio **13**/**14**, 4.9:1) in 95% yield (3.94 g, 22.1 mmol). **13**, $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 5.71 (1H, ddt, $J$ = 17.0, 10.1, 6.8 Hz), 5.08 (1H, dd, $J$ = 17.0, 1.6 Hz), 5.02 (1H, dd, $J$ = 10.1, 1.6 Hz), 3.68 (6H, s), 3.41 (1H, t, $J$ = 7.5 Hz), 2.59 (2H, dd, $J$ = 7.5, 6.8 Hz); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 169.9, 133.9, 117.7, 52.6, 51.4, 32.9. **14**, $^1$H NMR (200 MHz, $CDCl_3$) $\delta$ 5.65 (2H, ddt, $J$ = 17.0, 10.1, 6.8 Hz), 5.08 (2H, dd, $J$ = 17.0, 1.6 Hz), 5.02 (2H, dd, $J$ = 10.1, 1.6 Hz), 3.68 (6H, s), 2.65 (4H, d, $J$ = 6.8 Hz).

**Methyl 3-Ethyl-2-methoxycarbonyl-5-phenyl-4-pentenoate (19) and Methyl 2-Methoxycarbonyl-3-phenyl-4-heptenoate (20).** Inseparable mixture. **19**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.35−7.15 (5H, m), 6.45 (1H, d, $J$ = 15.7 Hz), 6.00 (1H, dd, $J$ = 15.7, 9.6 Hz), 3.70 (3H, s) 3.65 (3H, s), 3.49 (1H, d, $J$ = 4.0 Hz)$_2$), 2.87 (1H, dtd, $J$ = 9.6, 9.4, 4.0 Hz), 1.3 (2H, dq, $J$ = 9.4, 7.3 Hz), 0.9 (3H, t, $J$ = 7.3 Hz); $^{13}$C NMR (50 MHz, $CDCl_3$) $\delta$ 168.7, 137.1, 134.8, 129.4, 128.5, 127.4, 126.3, 56.9, 52.5, 52.3, 45.3, 25.9, 11.8. **20**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 5.6−5.5 (2H, m), 4.0−3.8 (2H, m), the other signals are masked by those of compound **19**. Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. Found: C, 70.02; H, 7.18.

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**Supporting Information Available:** Crystal structure refinement data for compound **9** including tables of atomic coordinates, thermal parameters, and bond lengths and angles, and the labeled structure. $^{31}$P NMR spectra for **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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