JOC The Journal of Organic Chemistry

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Two-Fold Modification of the Phenyl Substituent in Phenylphosphonic Acid Monoester Monoamides

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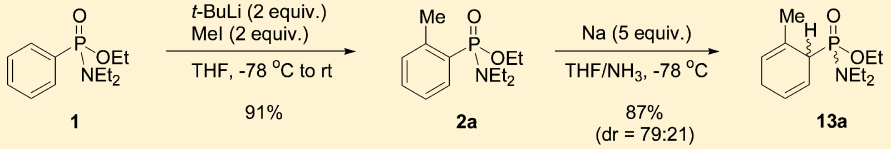
Supporting Information



ABSTRACT: Phenylphosphonic acid ethyl ester *N*,*N*-diethylamide was subjected to a double modification of its phenyl substituent through directed *ortho*-metalation followed by dearomatization of the aryl substituent under Birch reduction conditions. Application of the same methodology to a diastereomerically pure phenylphosphonic acid monoester monoamide led to the formation of *P*-stereogenic cyclohexadienyl-phosphonic acid derivatives. The method offers a simple and efficient modification of phenyl substituent in organophosphorus compounds.

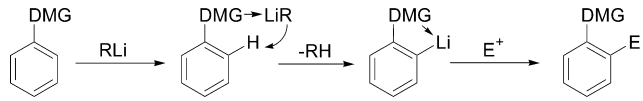
INTRODUCTION

Most strategies for the construction of organophosphorus compounds are based on the sequential attachment of the desired substituents at phosphorus atoms through classical transformations such as nucleophilic substitution at electrophilic phosphorus atoms,[1−4] nucleophilic substitution with a phosphorus nucleophile,[5−8] transition-metal-catalyzed coupling reactions,[9−11] or additions of organophosphorus reagents to multiple bonds.[12−15] However, this means that the synthesis of an analogue requires at least partial repetition of the synthetic sequence, and this obviously raises the synthetic workload and total cost significantly. A rational solution to this problem might be to modify the substituents that are already present in a simple and accessible organophosphorus compound so as to give new and more highly functionalized compounds in fewer steps. In such a case, the organophosphorus compound can then be regarded as the starting point of a synthetic pathway wherein the number of new compounds available is limited only by flexibility of the elaboration methodology. Organophosphorus compounds that already possess appropriate functional groups can be modified by functional group interconversions (FGI),[16−19] but those lacking functional groups require modification of the carbon skeleton.[20−22] Such skeletal modification is particularly interesting because it can profoundly alter the nature of the molecule.

When considering the modification of an arene fragment, Directed *ortho*-Metalation (DoM) is a very attractive process because it provides a potential for introducing many functionalities into the position *ortho* to the directing group in the substrate (Scheme 1). A broad range of functional groups can direct the attack of a base toward the *ortho* position, and among them amido and alkoxy groups direct very powerfully.[23−25]

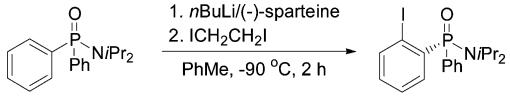
The use of DoM protocols is widespread in organic chemistry but has received little attention in organophosphorus chemistry so far.[26−30] This is generally attributed to the weak ability of the phosphorus-containing groups to interact with the incoming base. Nevertheless, an interesting application of a DoM protocol has been reported by Lopez Ortiz and coworkers, who have presented the desymmetrization of diphenylphosphinic amides with a chiral base using a DoM strategy (Scheme 2).[31]

Scheme 1



DMG = $CONR_2$, oxazoline, $CH(OR)_2$ etc.

Scheme 2



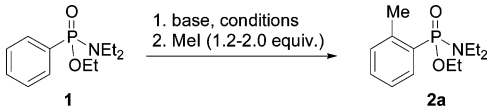
86% (63% ee)

In the course of a research project to modify aryl substituents in arylphosphorus compounds, we have already described the Birch dearomatization of a phenyl substituent in phosphineboranes[32] and in phosphine oxides.[33] In the latter case the product (1,4-cyclohexadien-3-yl)phosphine oxides have been successfully used by our group to prepare 1,2-bis(phosphinoyl)-cyclohexenes through sequential one-pot double bond isomerization-Michael addition of secondary phosphine oxides.[34] We also found that functionalization of the phenyl substituent in

Received: July 31, 2012
Published: August 29, 2012

dx.doi.org/10.1021/jo301526k | J. Org. Chem. 2012, 77, 8244−8256

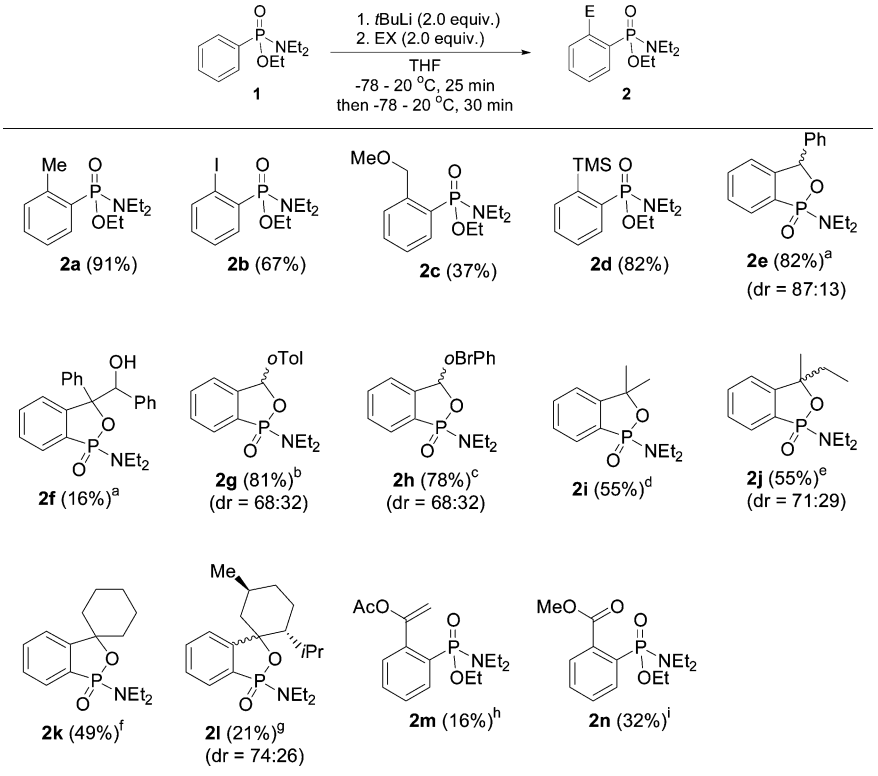
Table 1. Optimization of DoM Reaction on 1



entry	deprotonation conditions[a]	alkylation conditions[a]	GC yield of **2a**
1	LDA (1.0), THF, −78−20 °C, 30 min	MeI (1.2), −78−20 °C, 15 min	no reaction
2	*n*BuLi (1.2)/*i*Pr$_2$NH (1.2), THF, −78−20 °C, 1 h	MeI (1.2), −78−20 °C, 2 h	no reaction
3	*n*BuLi (1.2), THF, −78−20 °C, 2 h	MeI (1.2), −78−20 °C, 24 h	no reaction
4	*s*BuLi (1.2), THF, −78−20 °C, 2 h	MeI (1.2), −78−20 °C, 24 h	no reaction
5	*t*BuLi (1.2), THF, −78−20 °C, 2 h	MeI (1.2), −78−20 °C, 15 min	68%
6	*t*BuLi (1.3), THF, −78−20 °C, 2 h	MeI (1.2), −78−20 °C, 24 h	65%
7	*t*BuLi (2.0), THF, −78−20 °C, 1 h	MeI (1.2), −78−20 °C, 30 min	82%
8	*t*BuLi (2.0), THF, −78−20 °C, 45 min	MeI (2.0), −78−20 °C, 30 min	71%
9	**tBuLi (2.0), THF, −78−20 °C, 25 min**	**MeI (2.0), −78−20 °C, 30 min**	**83%**
10	*t*BuLi (2.0), THF, −78−20 °C, 15 min	MeI (2.0), −78−20 °C, 30 min	73%
11	*t*BuLi (2.0), Et$_2$O, −78−20 °C, 25 min	MeI (2.0), −78−20 °C, 1 h	68%
12	*t*BuLi (2.0), TMEDA (2.0), Et$_2$O, −78−20 °C, 25 min	MeI (2.0), −78−20 °C, 1 h	61%

[a]The number of equivalents of reactants is given in brackets.

Table 2. *ortho*-Functionalization of 1 with Different Electrophiles



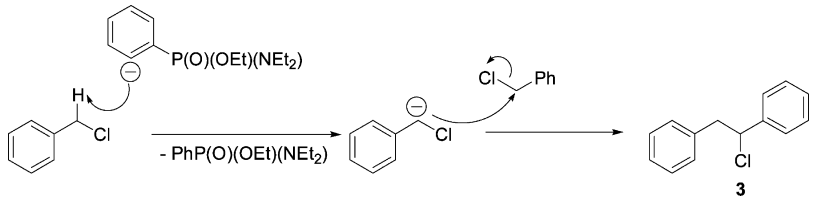
[a]Benzaldehyde was used. [b]*o*-Tolualdehyde was used. [c]*o*-Bromobenzaldehyde was used. [d]Acetone was used. [e]Butanone was used. [f]Cyclohexanone was used. [g]L-Menthone was used. [h]Acetyl chloride was used. [i]Methyl chloroformate was used.

phenylphosphine-boranes and phenylphosphine oxides through *in situ* dearomatization-alkylation can lead to the formation of *α*-substituted (1,4-cyclohexadien-3-yl)phosphine derivatives.[35]

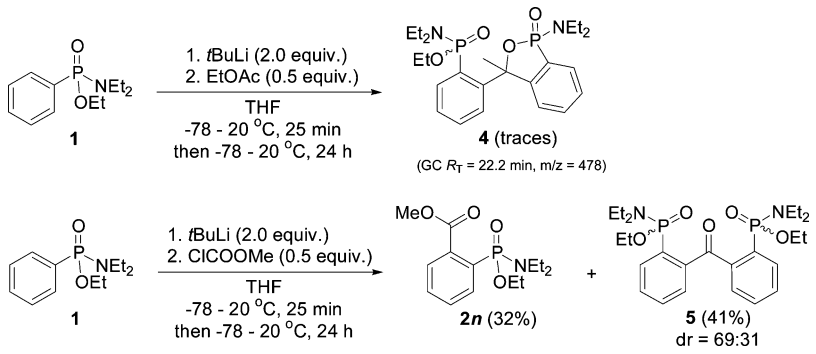
All the data presented so far clearly show the utility of Birch reduction for the modification of aryl substituents in phosphine derivatives, so we were curious to see if other classes of organophosphorus compounds, especially those possessing phosphorus-heteroatom bonds, would be stable enough under Birch reduction conditions to allow the dearomatization of arene substituent. We were particularly interested in dearomatization of arylphosphinic acid monoester monoamides because some of them can be prepared in enantiomerically pure form.[36] Most nonchiral, racemic, or *P*-stereogenic arylphosphonic acid derivatives possess simple phenyl groups at phosphorus because of the ready accessibility of dichlorophenylphosphine or its oxide. Assuming that the -P(O)(OR)(NR$_2$) functionality should exhibit some directing metalation group (DMG) properties, we suspected that it might be a good starting point for demonstrating how easy and profound the modification of a phenyl substituent using a combination of DoM methodology and Birch reduction can be.

dx.doi.org/10.1021/jo301526k | J. Org. Chem. 2012, 77, 8244−8256

Scheme 3



Scheme 4



RESULTS AND DISCUSSION

The initial experiments were undertaken on the model compound phenylphosphonic acid ethyl ester *N*,*N*-diethylamide (**1**) to provide insight into the D*o*M process (Table 1).

The first experiment performed using LDA as the base failed to produce any products according to GC−MS of the reaction mixture (Table 1, entry 1). The same failure was observed when LDA was generated *in situ* from iPr$_2$NH and *n*-butyllithium (Table 1, entry 2). Similarly, neither *n*-butyllithium nor *sec*-butyllithium gave the *ortho*-alkylation product **2a** (or any other product: Table 1, entries 3 and 4), but *t*BuLi gave **2a** in 68% yield after just 15 min according to GC−MS analysis (Table 1, entry 5). These results suggest that the first three bases are insufficiently strong to promote the *ortho*-deprotonation step of **1**. Prolonging the methylation before the quench had no effect on the yield of the product (Table 1, entry 6), but the yield of **2a** rose to 82% when the amount of base was increased to 2.0 equiv (Table 1, entry 7). We also tested the influence of the duration of the deprotonation step on the yield of product, and it appeared that the highest yields were obtained when deprotonation was carried out for 25 min (Table 1, entry 9). Both shortening and prolonging the deprotonation time caused a decrease of product yield to a similar degree (Table 1, entries 8 and 10). The reasons seem likely to be slow deprotonation in the first case and degradation of the carbanion in the second case.

For comparison, the D*o*M reaction was also performed in Et$_2$O as a solvent (Table 1, entries 11 and 12) but failed to give a better result.

Bearing in mind that the bases used here possess some nucleophilic character, we were wary of the potential formation of phosphinic amides. These are the products of nucleophilic substitution of the phosphorus ester moiety. Interestingly, no traces of such products were detected in the reaction mixture, even with *n*BuLi and *s*BuLi; these failed to engage in the D*o*M reaction and should therefore remain intact in the reaction mixture.

Once the optimization of the D*o*M reaction was complete, we attempted to estimate its scope and limits by reacting **1** with a range of electrophiles (Table 2).

It seems that the success of the *ortho*-functionalization of **1** depends strongly on the nature of the electrophile. We observed a clean formation of *ortho*-functionalization products **2a**, **2b**, and **2d** with methyl iodide, iodine, and chlorotrimethylsilane, respectively. Under the reaction conditions, these reactants can only undergo nucleophilic substitution with a carbanion. In the case of chloromethyl methyl ether, the deprotonation of a methylene carbon atom is highly possible and a low yield of **2c** is observed. Further, attempted reactions of **1** with alkyl halides possessing active hydrogens such as ethyl bromide, allyl bromide, benzyl chloride, ethyl chloroacetate, or chloroacetonitrile failed to produce the corresponding *ortho*-functionalized compounds (data not shown). In the case of benzyl chloride the only product isolated from the reaction mixture was 1,2-diphenylchloroethane **3**, which is the product of benzylation of the carbanion formed by deprotonation of benzyl chloride (Scheme 3).

These results show that the -P(O)(OEt)(NEt$_2$) function constitutes a weakly stabilizing directed metalation group, which means that the carbanion formed by deprotonation of **1** should be regarded as a "hard nucleophile" that is inclined to behave as a base.

Aldehydes and ketones, which represent a very different type of electrophiles, exhibited quite interesting reactivity upon treatment with the carbanion of **1**. The products had cyclic 2-oxa-1-phosphaindan-1-oxide structures (compounds **2e**−**l**) and therefore showed that the primary *ortho*-functionalization product undergoes intramolecular substitution of alkoxy group at phosphorus. This process was observed for every aldehyde or ketone used in the reaction except for formaldehyde and acetaldehyde, which failed to react with **1**. Interestingly, the reaction between **1** and benzaldehyde also afforded a side product **2f**; this arose from *in situ* deprotonation of **2e** followed by addition of excess benzaldehyde present in the reaction mixture to the carbanion. This product type was

dx.doi.org/10.1021/jo301526k | J. Org. Chem. 2012, 77, 8244−8256

obtained only in the case when benzaldehyde was the electrophile.

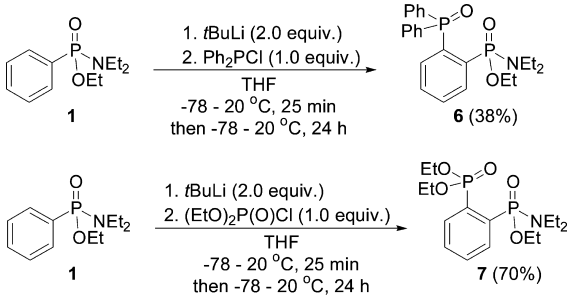
L-Menthone was used in the reaction with **1** to check whether incoming chirality can influence the diastereoselectivity of the reaction. However, the diastereomeric ratio of **2*n*** obtained in this case was almost the same as for other aldehydes and unsymmetrically substituted ketones but the yield was significantly lower.

Acetyl chloride and methyl chloroformate, another class of carbonyl electrophiles, used to modify **1** afforded the corresponding *ortho*-functionalized products **2m** and **2n** in 16% and 32% yields, respectively. Compound **2m** had an unusual structure whose formation can be easily explained by *ortho*-acylation of **1** followed by deprotonation of acyl group and *O*-acylation of the formed anion with excess acetyl chloride.

Unlike aldehydes and ketones, the more highly functionalizable acetyl chloride and methyl chloroformate can theoretically enter into 2-fold and 3-fold substitution/additions at the carbonyl group so that reaction with **1** could lead to the formation of bulky di- or triphosphorus compounds. Acetyl chloride failed to give any products when treated with 2-fold excess of **1**, but ethyl acetate afforded traces of the diphosphorus compound **4** under the same reaction conditions (Scheme 4).

Among all compounds listed in the Table 1 compound **2d** is probably the most interesting because it was formed by reaction of **1** with the very bulky trimethylsilyl chloride. The implication is that, provided no side reactions with the electrophile take place, the *ortho*-functionalization can occur with bulky electrophiles. We therefore assumed that phosphorus electrophiles could give rise to 1,2-bis(phosphorus-substituted)-benzenes. To verify this, the *ortho*-functionalization of **1** with chlorodiphenylphosphine and diethyl chlorophosphate was attempted (Scheme 5).

Scheme 5



In both cases we were pleased to find that reaction of **1** with phosphorus electrophiles led to the formation of the corresponding *ortho*-functionalized compounds in fair to good yields. In the reaction of **1** with chlorodiphenylphosphine we obtained the corresponding oxidized product **6** rather than P(III) compound. This probably arose from oxidation of the primary product during the workup. On the other hand, reaction of **1** with diethyl chlorophosphate under the same reaction conditions led to the formation of the expected product in good yield.

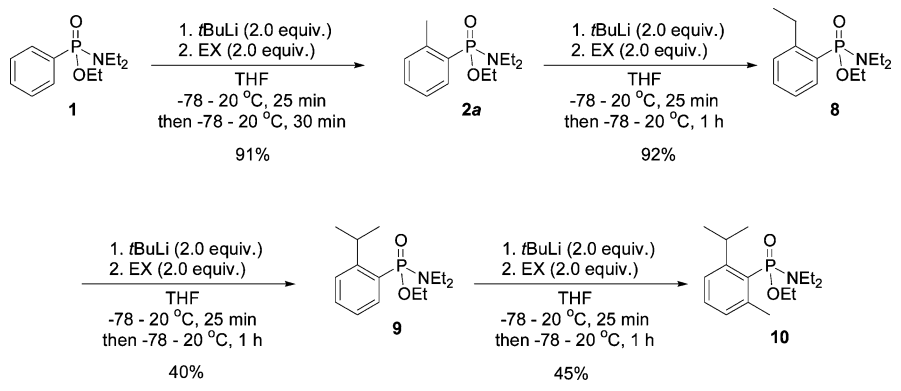
ortho-Functionalization of **1** appeared to be quite electrophile-specific, which makes the scope of the reaction somewhat narrow. We attempted to alleviate this problem through a multistep functionalization of the starting compound: the first step is the standard *ortho*-functionalization, and the second step involves a further functionalization of the newly introduced *ortho*-substituent in the next ones. Under ideal circumstances this would be nicely demonstrated by stepwise methylation of **2a**, up to a compound possessing a *tert*-butyl substituent in the *ortho* position (Scheme 6).

Experimentally we found that deprotonation of **2a** under the standard reaction conditions is an efficient process that affords the corresponding *ortho*-ethyl compound **8** in 92% yield after treatment with methyl iodide. A further cycle involving deprotonation of **8** followed by methylation of the product carbanion then afforded the corresponding *o*-isopropyl compound **9** in fair yield. However, the attempted synthesis of *o*-*tert*-butyl-substituted compound gave compound **10** instead. This suggests that the tertiary isopropyl proton is inaccessible to the bulky *tert*-butyllithium because of steric constrains, so the deprotonation switches back to the aryl site at the 6 position.

The results presented so far clearly show the utility of the DoM methodology for modifications of **1**. If a *P*-stereogenic organophosphorus compound is available, this method can offer a fast and efficient way to prepare various aryl-substituted nonracemic *P*-stereogenic compounds. We have found that phenylphosphonic acid L-menthyl ester *N*,*N*-diethylamide **11** can be prepared in diastereomerically pure form from L-menthyl phenylphosphinate under Appel conditions.[14] In the next step, we attempted the *ortho*-functionalization of **11** under the conditions developed above (Table 3).

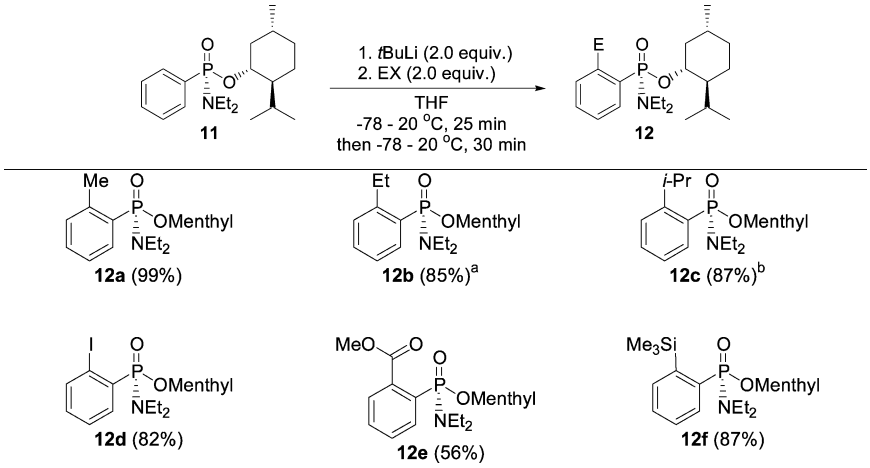
ortho-Functionalization of the diastereomerically pure compound **11** appeared to be as efficient as in the case of racemic **1**; *ortho*-methylation of diastereomerically pure **11** afforded **12a** almost quantitatively. Similarly, *ortho*-iodination, methoxycarbonylation, and silylation afforded the correspond-

Scheme 6



dx.doi.org/10.1021/jo301526k | J. Org. Chem. 2012, 77, 8244−8256

Table 3. *ortho*-Functionalization of 11

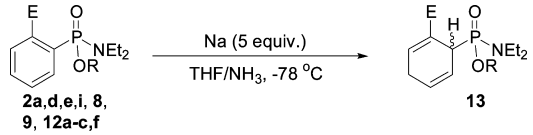


[a]Obtained by methylation of **12a**. [b]Obtained by methylation of **12b**.

ing *ortho*-substituted arylphosphonic acid derivatives **12d–f** efficiently. As with **1**, exhaustive methylation of **11** was attempted. We were pleased to find that methylation of **12a** afforded **12b** in good yield. The latter compound underwent smooth methylation in the presence of *t*-BuLi to yield *o*-isopropyl-substituted *P*-stereogenic arylphosphonic acid derivative **12c**.

Once a set of *ortho*-functionalized arylphosphonic acid derivatives was prepared, we decided to test the behavior of some of them under Birch reduction conditions. For the initial test reactions, we chose compounds lacking additional reactive functional groups, so as to avoid unwanted side processes that might take place under reductive conditions (Table 4).

Table 4. Birch Reduction of Arylphosphonic Acid Monoester Monoamides



entry	substrate	-E	-OR	products
1	**2a**	Me	OEt	**13a** (87%, dr = 79:21)
2	**2d**[a]	$SiMe_3$	OEt	**13b** (89%, dr = 65:35)
3	**2e**[a]	-CH(Ph)O-		complex mixture
4	**2i**	$-C(CH3)_2O-$		complex mixture
5	**8**	Et	OEt	**13c** (80%, dr = 57:43)
6	**9**	*i*-Pr	OEt	**13d** (76%, dr = 77:23)
7	**12a**	Me	O-menthyl	**13e** (99%, dr = 81:19)
8	**12b**	Et	O-menthyl	**13f** (77%, dr = 68:32)
9	**12c**	*i*-Pr	O-menthyl	**13g** (63%, dr = 74:26)
10	**12f**	$SiMe_3$	O-menthyl	**13h** (79%, dr = 91:9)

[a]The reaction was performed with 2.5 equiv of sodium.

We were pleased to find that Birch reduction of the aryl fragment was observed in most cases as an exclusive process. The chiral phosphorus center in the substrate should give rise to the formation of diastereoisomers during Birch reduction, and this ratio should be close to 50:50 due to the nature of a reactant. Indeed, Birch reduction of **2a** afforded **13a** in very good yield as a mixture of two diastereoisomers but in a ratio of 79:21, so it appears that the arrangement of the phosphorus substituents drives the preferential formation of one diastereomer. The crowded compound **2d**, possessing trimethylsilyl substituent in the *ortho* position afforded a 65:35 mixture of two diastereoisomers in 89% yield. Similarly, *o*-ethyl and *o*-isopropyl derivatives **8** and **9** yielded a mixtures of two diastereoisomers. Interestingly, a comparison of the four increasingly hindered compounds **2a**, **8**, **9**, and **2d** reveals that increasing the steric crowding about phosphorus does not raise the diastereoselectivity of dearomatization; rather the best diastereomeric ratio was observed for the smallest (methyl) substituent with the worst being found for the *o*-ethyl-substituted compound.

While the *ortho*-substituted compounds **2a**, **2d**, **8**, and **9** underwent clean dearomatization of the arene fragment, attempted Birch reductions of the benzoxaphospholes **2e** and **2i** failed to give clean conversions. In both cases we observed the formation of complex reaction mixtures containing many products although Birch reduction products could be detected among these in minor amounts.

Finally, we attempted the Birch reduction of some diastereomerically pure arylphosphonic acid derivatives **12a–c,f**. It appeared that dearomatization of the arene fragment proceeded with diastereoselectivities that were similar to the racemic substrates. However, **12b** and **12f** showed diastereoselectivities slightly better than those of the racemic analogues (Table 4, entries 8 and 10).

■ SUMMARY

Both transformations presented in this paper, namely *ortho*-functionalization using D*o*M methodology and Birch reduction, are very classical organic transformations that have many applications in organic synthesis. However, despite their utility, these two processes are rarely used in organophosphorus chemistry. It is clear that combining these reactions will provide a powerful tool for the extensive structural modifications of aryl fragments in arylphosphonic acid derivatives.

■ EXPERIMENTAL SECTION

All reactions were performed under an argon atmosphere by using Schlenk techniques. Only dry solvents were used, and the glassware was heated under vacuum prior to use. All chemicals were used as received unless otherwise noted. Solvents for chromatography and crystallization were distilled once before use, and solvents for

dx.doi.org/10.1021/jo301526k | J. Org. Chem. 2012, 77, 8244–8256

extraction were used as received. Tetrahydrofurane and diethyl ether were dried over sodium/benzophenone ketyl.

Analytics and Instruments. The NMR spectra was recorded on 500 MHz spectrometer in $CDCl_3$ as a solvent at room temperature unless otherwise noted. Chemical shifts (δ) are reported in ppm relative to residual solvent peak. Mass spectra were recorded in electron ionization (EI) mode and GC was recorded using following parameters: pressure 97.9 kPa, total flow 19.5 mL/min, column flow 1.5 mL/min, linear velocity 44.9 cm/s, split 10, temperature program (70 °C hold 3 min, 70−340 °C/12 °C/min hold 9.5 min, total 35 min) or pressure 65 kPa, total flow 23.9 mL/min, column flow 1.2 mL/min, linear velocity 36.8 cm/s, split 20, temperature program (80 °C hold 3 min, 80−250 °C/20 °C/min hold 5 min, 250−300 °C/10 °C/min hold 30.5 min, total 50 min). HPLC-HRMS was performed using reversed phase stationary phase with water/methanol 80:20 as eluent, electronspray ionization (ESI), and IT-TOF detector. Thin-layer chromatography (TLC) was performed with precoated silica gel plates and visualized by UV light or $KMnO_4$ solution. The reaction mixtures were purified by column chromatography over silica gel (60−240 mesh).

Phenylphosphonic acid ethyl ester *N*,*N*-diethylamide **1**[37] and phenylphosphonic acid L-menthyl ester *N*,*N*-diethylamide **11**[36] were prepared according to the literature procedures.

General Procedure for *ortho*-Functionalization of Phenylphosphonic Acid Monoester Monoamide Using DoM Methodology. In a flame-dried Schlenk tube (50 mL) equipped with magnetic stirrer and inert gas inlet was placed substrate **1** or **11** (0.5 mmol) in 10 mL THF. The mixture was cooled to −78 °C and *tert*-butyllithium (0.588 mL, 1.0 mmol, 1.7 M solution in pentane) was added at once. The mixture was allowed to warm to room temperature for 25 min and then was cooled again to −78 °C. An electrophile (1.0 mmol) was added at once, and the mixture was allowed to warm to room temperature over 30 min. The reaction was quenched by addition of saturated NH_4Cl solution (10 mL) and extracted with DCM (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography using $CHCl_3$/MeOH (v/v = 15:1) as eluent.

***o*-Tolylphosphonic Acid Ethyl Ester *N*,*N*-Diethylamide (2a).** This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and methyl iodide (0.062 mL, 1.0 mmol): yield 0.116 g (91%); pale yellow oil; R_f = 0.79 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.38 (t, $J_{H,H}$ = 7.1 Hz, 3H), 2.57 (s, 3H), 2.98−3.09 (m, 2H), 3.10−3.21 (m, 2H), 3.99−4.07 (m, 1H), 4.10−4.20 (m, 1H), 7.16−7.23 (m, 2H), 7.32−7.37 (m, 1H), 7.70−7.76 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.0, 16.3 (d, $J_{P,C}$ = 7.3 Hz), 21.1 (d, $J_{P,C}$ = 3.6 Hz), 38.7 (d, $J_{P,C}$ = 5.5 Hz), 59.6 (d, $J_{P,C}$ = 5.5 Hz), 125.0 (d, $J_{P,C}$ = 12.7 Hz), 129.6 (d, $J_{P,C}$ = 174.4 Hz), 131.3 (d, $J_{P,C}$ = 14.5 Hz), 131.4 (d, $J_{P,C}$ = 1.8 Hz), 132.9 (d, $J_{P,C}$ = 8.2 Hz), 142.0 (d, $J_{P,C}$ = 10.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 22.64 ppm; GC t_R = 12.76 min; GC−MS (EI, 70 eV) m/z = 255 (M^+) (8), 240 (41), 183 (25), 156 (12), 155 (100), 91 (48); HPLC t_R = 2.60 min; HRMS calcd for $C_{13}H_{22}NO_2P$ [M + H$^+$]: 256.1461; found: 256.1455.

***o*-Iodophenylphosphonic Acid Ethyl Ester *N*,*N*-Diethylamide (2b).** This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and iodine (0.254 g, 1.0 mmol): yield 0.123 g (67%); yellow oil; R_f = 0.78 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (t, $J_{H,H}$ = 7.0 Hz, 6H), 1.40 (t, $J_{H,H}$ = 7.0 Hz, 3H), 2.99−3.07 (m, 2H), 3.21−3.29 (m, 2H), 4.02−4.07 (m, 1H), 4.12−4.21 (m, 1H), 7.06−7.12 (m, 1H), 7.34−7.40 (m, 1H), 7.85−7.91 (m, 1H), 7.94−7.99 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.0 (d, $J_{P,C}$ = 1.7 Hz), 16.2 (d, $J_{P,C}$ = 6.9 Hz), 39.3 (d, $J_{P,C}$ = 5.2 Hz), 59.9 (d, $J_{P,C}$ = 5.8 Hz), 98.1 (d, $J_{P,C}$ = 7.5 Hz), 127.2 (d, $J_{P,C}$ = 12.1 Hz), 132.2 (d, $J_{P,C}$ = 2.9 Hz), 135.1 (d, $J_{P,C}$ = 6.9 Hz), 135.3 (d, $J_{P,C}$ = 181.6 Hz), 141.5 (d, $J_{P,C}$ = 12.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 20.44; GC t_R = 13.48 min; GC−MS (EI, 70 eV) m/z = 367 (M^+) (8), 353 (13), 352 (100), 324 (30), 295 (33), 267 (96), 240 (15), 141 (38), 140 (44), 139 (17), 125 (16), 92 (14); HPLC t_R = 2.62 min; HRMS calcd for $C_{12}H_{19}INO_2P$ [M + H$^+$]: 368.0271; found: 368.0289.

***o*-(Methoxymethyl)phenylphosphonic Acid Ethyl Ester *N*,*N*-Diethylamide (2c).** This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and chloromethyl methyl ether (0.076 mL, 1.0 mmol): yield 0.053 g (37%); colorless oil; R_f = 0.68 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (t, $J_{H,H}$ = 7.0 Hz, 6H), 1.38 (t, $J_{H,H}$ = 7.1 Hz, 3H), 2.99−3.21 (m, 4H), 3.45 (s, 3H), 3.99−4.08 (m, 1H), 4.10−4.19 (m, 1H), 4.77−4.87 (m, 2H), 7.27−7.31 (m, 1H), 7.46−7.51 (m, 1H), 7.61−7.65 (m, 1H), 7.71−7.77 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.0 (d, $J_{P,C}$ = 1.8 Hz), 16.3 (d, $J_{P,C}$ = 6.4 Hz), 38.7 (d, $J_{P,C}$ = 4.8 Hz), 58.5, 59.8 (d, $J_{P,C}$ = 5.5 Hz), 71.9 (d, $J_{P,C}$ = 4.5 Hz), 126.4 (d, $J_{P,C}$ = 13.6 Hz), 127.6 (d, $J_{P,C}$ = 13.6 Hz), 128.2 (d, $J_{P,C}$ = 173.5 Hz), 131.6 (d, $J_{P,C}$ = 2.7 Hz), 132.6 (d, $J_{P,C}$ = 8.2 Hz), 142.5 (d, $J_{P,C}$ = 10.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 21.92; GC t_R = 8.37 min; GC−MS (EI, 70 eV) m/z = 285 (M^+) (9), 270 (58), 224 (11), 197 (73), 185 (44), 169 (100), 155 (14), 153 (59), 151 (11), 105 (12), 91 (29), 90 (13), 89 (14); HPLC t_R = 1.85 min; HRMS calcd for $C_{14}H_{24}NO_3P$ [M + H$^+$]: 286.1567; found: 286.1570.

***o*-(Trimethylsilyl)phenylphosphonic Acid Ethyl Ester *N*,*N*-Diethylamide (2d).** This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and chlorotrimethylsilane (0.127 mL, 1.0 mmol): yield 0.128 g (82%); colorless liquid; R_f = 0.87 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.41 (s, 9H), 1.07 (t, $J_{H,H}$ = 7.2 Hz, 6H), 1.34 (t, $J_{H,H}$ = 7.1 Hz, 3H), 2.99−3.22 (m, 4H), 3.96−4.12 (m, 2H), 7.34−7.45 (m, 2H), 7.65−7.75 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 1.3, 14.0 (d, $J_{P,C}$ = 2.3 Hz), 16.2 (d, $J_{P,C}$ = 7.5 Hz), 39.0 (d, $J_{P,C}$ = 4.6 Hz), 60.1 (d, $J_{P,C}$ = 5.8 Hz), 128.0 (d, $J_{P,C}$ = 13.8 Hz), 130.2 (d, $J_{P,C}$ = 3.5 Hz), 132.4 (d, $J_{P,C}$ = 12.7 Hz), 135.9 (d, $J_{P,C}$ = 18.4 Hz), 136.4 (d, $J_{P,C}$ = 174.7 Hz), 145.2 (d, $J_{P,C}$ = 19.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 25.96; GC t_R = 11.21 min; GC−MS (EI, 70 eV) m/z = 313 (M^+) (0.2), 299 (22), 298 (100), 271 (11), 270 (56), 242 (13), 213 (30), 198 (15), 197 (92), 183 (12), 179 (15), 135 (18), 133 (12), 121 (16), 107 (13), 91 (10); HPLC t_R = 8.80 min; HRMS calcd for $C_{15}H_{28}NO_2PSi$ [M + H$^+$]: 314.1700; found: 314.1680.

***N*,*N*-Diethyl-3-phenyl-1,3-dihydro-2,1-benzoxaphosphol-1-amine 1-Oxide (2e).** This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and benzaldehyde (0.102 mL, 1.0 mmol): yield of two diastereoizomers (dr = 87:13) 0.123 g (82%). Major diastereomer was isolated in pure form.

Major Diastereomer. Yield 0.068 g (45%); yellow solid; mp = 102.0−103.9 °C; R_f = 0.69 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 (t, $J_{H,H}$ = 7.0 Hz, 6H), 3.01−3.15 (m, 4H), 6.21 (d, $J_{P,H}$ = 9.7 Hz, 1H), 7.10−7.15 (m, 1H), 7.24−7.37 (m, 3H), 7.40−7.51 (m, 4H), 7.65−7.73 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.5 (d, $J_{P,C}$ = 1.8 Hz), 38.9 (d, $J_{P,C}$ = 5.5 Hz), 82.7 (d, $J_{P,C}$ = 1.8 Hz), 123.5 (d, $J_{P,C}$ = 12.7 Hz), 125.6 (d, $J_{P,C}$ = 161.7 Hz), 126.9, 127.2 (d, $J_{P,C}$ = 11.8 Hz), 128.6, 128.8, 128.9 (d, $J_{P,C}$ = 13.6 Hz), 132.3 (d, $J_{P,C}$ = 2.7 Hz), 139.3 (d, $J_{P,C}$ = 1.8 Hz), 147.3 (d, $J_{P,C}$ = 22.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 38.82; GC t_R = 19.10 min; GC−MS (EI, 70 eV) m/z = 301 (M^+) (6), 287 (18), 286 (95), 230 (15), 229 (100), 166 (29), 165 (58); HPLC t_R = 1.62 min; HRMS calcd for $C_{17}H_{20}NO_2P$ [M + H$^+$]: 302.1304; found: 302.1276.

***N*,*N*-Diethyl-3-phenyl-3-(hydroxy(phenyl)methyl)-1,3-dihydro-2,1-benzoxaphosphol-1-amine 1-Oxide (2f).** This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and benzaldehyde (0.102 mL, 1.0 mmol): yield 0.034 g (16%); pale yellow solid; mp = 167.1−168.8 °C; R_f = 0.60 ($CHCl_3$/MeOH = 30:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (t, $J_{H,H}$ = 7.1 Hz, 6H), 2.82−2.99 (m, 4H), 5.29 (s, 1H), 7.12−7.22 (m, 5H), 7.25−7.32 (m, 3H), 7.47−7.52 (m, 1H), 7.53−7.57 (m, 2H), 7.59−7.67 (m, 2H), 7.81−7.84 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.2 (d, $J_{P,C}$ = 2.7 Hz), 38.4 (d, $J_{P,C}$ = 5.5 Hz), 80.6, 91.3, 124.7 (d, $J_{P,C}$ = 13.6 Hz), 126.3, 127.2 (d, $J_{P,C}$ = 161.7 Hz), 127.38, 127.39 (d, $J_{P,C}$ = 11.8 Hz), 127.8, 128.0, 128.1, 128.5, 129.1 (d, $J_{P,C}$ = 13.6 Hz), 132.1 (d, $J_{P,C}$ = 2.7 Hz), 138.1, 139.1 (d, $J_{P,C}$ = 4.5 Hz), 147.2 (d, $J_{P,C}$ = 20.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 37.80; GC t_R = 15.51 min; GC−MS (EI, 70 eV) m/z = 407 (M^+) (0.2), 287 (16), 286 (90), 230 (15), 228

dx.doi.org/10.1021/jo301526k | J. Org. Chem. 2012, 77, 8244−8256

(100), 166 (38), 165 (78), 164 (12), 152 (10); $C_{24}H_{26}NO_3P$ (407.17): calcd C 70.75, H 6.43, N 3.44; found C 70.89, H 6.60, N 3.62.

***N,N*-Diethyl-3-*o*-tolyl-1,3-dihydro-2,1-benzoxaphosphol-1-amine 1-Oxide (2g).** This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and *o*-tolualdehyde (0.115 mL, 1.0 mmol): yield of two diastereoizomers (dr = 68:32) 0.128 g (81%). Isolated as a mixture of diastereomers.

Major Diastereomer. R_f = 0.61 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.10 (t, $J_{H,H}$ = 7.1 Hz, 6H), 2.50 (s, 3H), 2.91−3.14 (m, 4H), 6.50 (d, $J_{P,H}$ = 8.5 Hz, 1H), 7.15−7.26 (m, 4H), 7.43−7.46 (m, 2H), 7.50−7.54 (m, 1H), 7.67−7.73 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.4 (d, $J_{P,C}$ = 1.8 Hz), 19.3, 38.7 (d, $J_{P,C}$ = 5.5 Hz), 79.5 (d, $J_{P,C}$ = 1.8 Hz), 123.1 (d, $J_{P,C}$ = 12.7 Hz), 126.1 (d, $J_{P,C}$ = 162.6 Hz), 126.4, 127.1 (d, $J_{P,C}$ = 11.8 Hz), 127.8, 128.4, 128.6 (d, $J_{P,C}$ = 13.6 Hz), 130.4, 132.1 (d, $J_{P,C}$ = 2.7 Hz), 135.6, 136.9 (d, $J_{P,C}$ = 1.8 Hz), 147.0 (d, $J_{P,C}$ = 22.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 38.23; GC t_R = 11.41 min; GC−MS (EI, 70 eV) m/z = 315 (M^+) (16), 300 (45), 244 (16), 243 (95), 180 (40), 179 (80), 178 (100), 165 (40), 152 (15); HPLC t_R = 1.93 min; HRMS calcd for $C_{18}H_{22}NO_2P$ [M + H^+]: 316.1461; found: 316.1425.

Minor Diastereomer. R_f = 0.61 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (t, $J_{H,H}$ = 7.1 Hz, 6H), 2.57 (s, 3H), 2.91−3.14 (m, 4H), 6.83 (d, $J_{P,H}$ = 7.83, 1H), 7.04−7.15 (m, 4H), 7.40−7.46 (m, 2H), 7.47−7.50 (m, 1H), 7.67−7.73 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.2 (d, $J_{P,C}$ = 1.8 Hz), 19.1, 38.8 (d, $J_{P,C}$ = 4.2 Hz), 77.9 (d, $J_{P,C}$ = 2.7 Hz), 124.1 (d, $J_{P,C}$ = 13.2 Hz), 125.7, 126.7, 127.1 (d, $J_{P,C}$ = 11.8 Hz), 127.7 (d, $J_{P,C}$ = 160.8 Hz), 128.8 (d, $J_{P,C}$ = 13.6 Hz), 129.0, 130.7, 131.7 (d, $J_{P,C}$ = 2.7 Hz), 135.9 (d, $J_{P,C}$ = 4.5 Hz), 138.5, 145.8 (d, $J_{P,C}$ = 20.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 37.13; GC t_R = 11.65 min; GC−MS (EI, 70 eV) m/z = 315 (M^+) (15), 301 (11), 300 (63), 244 (17), 243 (100), 180 (29), 179 (66), 178 (80), 165 (39), 152 (15), 151 (10), 136 (11); HPLC t_R = 2.24 min; HRMS calcd for $C_{18}H_{22}NO_2P$ [M + H^+]: 316.1461; found: 316.1425.

***N,N*-Diethyl-3-(*o*-bromophenyl)-1,3-dihydro-2,1-benzoxaphosphol-1-amine 1-Oxide (2h).** This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and *o*-bromobenzaldehyde (0.117 mL, 1.0 mmol): yield of two diastereoizomers (dr = 68:32) 0.148 g (78%). Major diastereomer was isolated in pure form.

Major Diastereomer. Yield 0.080 g (42%); white solid; mp = 105.3−106.5 °C; R_f = 0.66 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (t, $J_{H,H}$ = 6.9 Hz, 6H), 3.00−3.15 (m, 4H), 6.78 (d, $J_{P,H}$ = 9.5 Hz, 1H), 7.09−7.14 (m, 1H), 7.20−7.26 (m, 1H), 7.37−7.50 (m, 4H), 7.54−7.57 (m,1H), 7.64−7.69 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.5 (d, $J_{P,C}$ = 1.8 Hz), 38.9 (d, $J_{P,C}$ = 5.5 Hz), 80.7 (d, $J_{P,C}$ = 2.4 Hz), 121.8, 123.4 (d, $J_{P,C}$ = 13.2 Hz), 125.2 (d, $J_{P,C}$ = 162.5 Hz), 127.3 (d, $J_{P,C}$ = 11.8 Hz), 128.4, 129.12, 129.12 (d, $J_{P,C}$ = 6.4 Hz), 129.9, 132.5 (d, $J_{P,C}$ = 3.1 Hz), 132.6, 138.9 (d, $J_{P,C}$ = 2.6 Hz), 146.9 (d, $J_{P,C}$ = 21.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ = 39.61; GC t_R = 12.12 min; GC−MS (EI, 70 eV) m/z = 380 (M^+) (0.7), 367 (10), 366 (56), 365 (10), 364 (56), 309 (61), 307 (62), 300 (11), 229 (12), 227 (12), 199 (25), 181 (21), 166 (17), 165 (100), 164 (42), 163 (35), 152 (34), 151 (13), 129 (11); HPLC t_R = 2.12 min; HRMS calcd for $C_{17}H_{19}BrNO_2P$ [M + H^+]: 380.0409; found: 380.0397.

Minor Diastereomer. R_f = 0.63 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (t, $J_{H,H}$ = 7.1 Hz, 6H), 3.01−3.14 (m, 4H), 6.79 (d, $J_{P,H}$ = 9.4 Hz, 1H), 6.99−7.01 (m, 1H), 7.22−7.24 (m, 1H), 7.45−7.53 (m, 4H), 7.66−7.69 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.4 (d, $J_{P,C}$ = 9.9 Hz), 38.9 (d, $J_{P,C}$ = 4.3 Hz), 79.6 (d, $J_{P,C}$ = 3.6 Hz), 124.0 (d, $J_{P,C}$ = 13.5 Hz), 125.0, 127.1 (d, $J_{P,C}$ = 160.8 Hz), 127.1 (d, $J_{P,C}$ = 12.0 Hz), 127.6, 129.0 (d, $J_{P,C}$ = 8.2 Hz), 129.1, 130.5, 132.2 (d, $J_{P,C}$ = 2.7 Hz), 133.4, 137.8 (d, $J_{P,C}$ = 6.4 Hz), 146.0 (d, $J_{P,C}$ = 20.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 37.06; GC t_R = 12.78 min; GC−MS (EI, 70 eV) m/z = 380 (M^+) (0.5), 367 (11), 366 (62), 365 (11), 364 (61), 309 (65), 307 (66), 300 (13), 229 (14), 227 (13), 199 (25), 181 (22), 16 (18), 165 (100), 164 (41), 163 (40), 153 (12), 152 (38), 151 (13), 139 (11); HPLC t_R = 2.89 min; HRMS calcd for $C_{17}H_{19}BrNO_2P$ [M + H^+]: 380.0409; found: 380.0397.

***N,N*-Diethyl-3,3-dimethyl-1,3-dihydro-2,1-benzoxaphosphol-1-amine 1-Oxide (2i).** This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and acetone (0.073 mL, 1.0 mmol): yield 0.070 g (55%); yellow pasty oil; R_f = 0.68 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.10 (t, $J_{H,H}$ = 7.1, 6H), 1.65 (s, 3H), 1.70 (s, 3H), 2.97−3.15 (m, 4H), 7.26−7.29 (m, 1H), 7.40−7.45 (m, 1H), 7.52−7.56 (m, 1H), 7.57−7.62 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.5 (d, $J_{P,C}$ = 1.7 Hz), 28.4 (d, $J_{P,C}$ = 5.8 Hz), 31.1, 38.8 (d, $J_{P,C}$ = 5.8 Hz), 84.0 (d, $J_{P,C}$ = 1.7 Hz), 121.4 (d, $J_{P,C}$ = 13.8 Hz), 125.9 (d, $J_{P,C}$ = 160.9 Hz), 127.3 (d, $J_{P,C}$ = 12.1 Hz), 128.4 (d, $J_{P,C}$ = 13.8 Hz), 132.2 (d, $J_{P,C}$ = 2.9 Hz), 152.7 (d, $J_{P,C}$ = 21.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.09; GC t_R = 14.22 min; GC−MS (EI, 70 eV) m/z = 253 (M^+) (8), 239 (14), 238 (100), 195 (13), 181 (42), 167 (10), 164 (10), 163 (70), 149 (13), 133 (21), 132 (10), 131 (85), 129 (10), 116 (27), 115 (41), 91 (26); HPLC t_R = 1.50 min; HRMS calcd for $C_{13}H_{20}NO_2P$ [M + H^+]: 254.1304; found: 254.1285.

***N,N*-Diethyl-3-ethyl-3-methyl-1,3-dihydro-2,1-benzoxaphosphol-1-amine 1-Oxide (2j).** This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and 2-butanone (0.090 mL, 1.0 mmol): yield of two diastereoizomers (dr = 71:29) 0.073 g (55%). Major diastereomer was isolated in pure form.

Major Diastereomer. Yield 0.036 g (27%); colorless oil; R_f = 0.66 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.87 (t, $J_{H,H}$ = 7.3 Hz, 3H), 1.08 (t, $J_{H,-H}$ = 7.1 Hz, 6H), 1.59 (s, 3H), 1.84−2.03 (m, 2H), 2.94−3.11 (m, 4H), 7.19−7.22 (m, 1H), 7.38−7.43 (m, 1H), 7.49−7.53 (m, 1H), 7.56−7.61 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 8.4, 14.5 (d, $J_{P,C}$ = 1.8 Hz), 26.6 (d, $J_{P,C}$ = 5.4 Hz), 35.8, 38.8 (d, $J_{P,C}$ = 5.8 Hz), 87.0 (d, $J_{P,C}$ = 1.8 Hz), 121.6 (d, $J_{P,C}$ = 14.0 Hz), 126.6 (d, $J_{P,C}$ = 161.2 Hz), 127.2 (d, $J_{P,C}$ = 11.8 Hz), 128.4 (d, $J_{P,C}$ = 13.6 Hz), 132.0 (d, $J_{P,C}$ = 3.6 Hz), 151.5 (d, $J_{P,C}$ = 21.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.54; GC t_R = 8.78 min; GC−MS (EI, 70 eV) m/z = 267 (M^+) (12), 253 (14), 252 (96), 238 (29), 209 (10), 195 (42), 177 (34), 167 (13), 166 (18), 149 (42), 146 (13), 145 (100), 133 (12), 131 (17), 130 (19), 129 (24), 128 (17), 116 (14), 115 (35), 103 (15), 91 (38); HPLC t_R = 1.60 min; HRMS calcd for $C_{14}H_{22}NO_2P$ [M + H^+]: 268.1461; found: 268.1421.

Minor Diastereomer. R_f = 0.61 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (t, $J_{H,H}$ = 7.2 Hz, 3H), 1.11 (t, $J_{H,H}$ = 7.4, 6H) 1.64 (s, 3H), 1.96−2.06 (m, 2H), 2.99−3.18 (m, 4H), 7.22−7.25 (m, 1H), 7.38−7.44 (m, 1H), 7.50−7.56 (m, 1H), 7.56−7.63 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 8.3, 14.5 (d, $J_{P,C}$ = 1.8 Hz), 28.1, 33.9 (d, $J_{P,C}$ = 5.5 Hz), 38.7 (d, $J_{P,C}$ = 5.5 Hz), 86.4 (d, $J_{P,C}$ = 1.8 Hz), 121.6 (d, $J_{P,C}$ = 13.6 Hz), 126.4 (d, $J_{P,C}$ = 161.7 Hz), 127.3 (d, $J_{P,C}$ = 11.8 Hz), 128.2 (d, $J_{P,C}$ = 14.5 Hz), 131.3 (d, $J_{P,C}$ = 2.7 Hz), 152.6 (d, $J_{P,C}$ = 20.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.30; GC t_R = 8.93 min; GC−MS (EI, 70 eV) m/z = 267 (M^+) (11), 266 (60), 224 (38), 210 (14), 209 (100), 197 (17), 196 (42), 182 (13), 153 (30), 140 (17), 139 (38), 126 (14), 125 (60), 120 (15), 106 (19), 104 (10), 91 (16), 83 (23); HPLC t_R = 1.90 min; HRMS calcd for $C_{14}H_{22}NO_2P$ [M + H^+]: 268.1461; found: 268.1448.

***N,N*-Diethyl-3-spiro(cyclohexyl)-1,3-dihydro-2,1-benzoxaphosphol-1-amine 1-Oxide (2k).** This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and cyclohexanone (0.103 mL, 1.0 mmol): yield 0.072 g (49%); pale yellow solid; mp = 74.0−75.8 °C; R_f = 0.68 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01−1.11 (m, 6H), 1.23−1.36 (m, 1H), 1.61−1.92 (m, 9H), 2.88−3.11 (m, 4H), 7.19−7.24 (m, 1H), 7.33−7.40 (m, 1H), 7.44−7.50 (m, 1H), 7.51−7.57 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.4, 21.9, 22.2, 24.9, 36.8 (d, $J_{P,C}$ = 4.5 Hz), 38.7 (d, $J_{P,C}$ = 6.4 Hz), 39.2, 85.6, 121.5 (d, $J_{P,C}$ = 13.6 Hz), 126.0 (d, $J_{P,C}$ = 161.3 Hz), 127.2 (d, $J_{P,C}$ = 12.0 Hz), 128.4 (d, $J_{P,C}$ = 13.6 Hz), 131.9 (d, $J_{P,C}$ = 2.7 Hz), 152.5 (d, $J_{P,C}$ = 21.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.04; GC t_R = 10.19 min; GC−MS (EI, 70 eV) m/z = 293 (M^+) (17), 279 (18), 278 (100), 260 (14), 235 (12), 233 (32), 222 (23), 221 (38), 203 (22), 185 (16), 183 (25), 171 (10), 165 (53), 155 (12), 153 (13), 152 (12), 149 (18), 141 (18), 137 (31), 133 (16), 131 (11), 129 (33), 128 (39), 127 (13), 116 (26), 109 (14), 103 (11), 102 (14), 91 (34), 89 (14); HPLC t_R = 2.23 min; HRMS calcd for $C_{16}H_{24}NO_2P$ [M + H^+]: 294.1617; found: 294.1588.

dx.doi.org/10.1021/jo301526k | J. Org. Chem. 2012, 77, 8244−8256

_N,N_-Diethyl-3-spiro((2_R_,5_S_)-2-isopropyl-5-methylcyclohexyl)-1,3-dihydro-2,1-benzoxaphosphol-1-amine 1-Oxide (2l). This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and L-menthone (0.172 mL, 1.0 mmol): yield of two diastereomers (dr = 74:26) 0.037 g (21%). Major diastereomer was isolated in pure form.

Major Diastereomer. Yield 0.021 g (12%); white solid; mp = 75.0−76.2 °C; R_f = 0.71 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.65 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.91 (d, $J_{H,H}$ = 6.5 Hz, 3H), 0.92 (d, $J_{H,H}$ = 6.9 Hz, 3H), 1.06−1.17 (m, 1H), 1.11 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.35−1.52 (m, 2H), 1.58−1.75 (m, 4H), 1.88−2.01 (m, 2H), 2.9−3.02 (m, 2H), 3.05−3.16 (m, 2H), 7.19−7.23 (m, 1H), 7.39−7.44 (m, 1H), 7.5−7.56 (m, 1H), 7.57−7.62 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.5, 18.4, 22.0, 22.8, 24.2, 26.1, 28.7, 34.9, 39.0 (d, $J_{P,C}$ = 6.4 Hz), 48.9 (d, $J_{P,C}$ = 3.6 Hz), 50.1 (d, $J_{P,C}$ = 1.8 Hz), 90.3, 121.5 (d, $J_{P,C}$ = 14.5 Hz), 126.7 (d, $J_{P,C}$ = 156.2 Hz), 127.4 (d, $J_{P,C}$ = 6.6 Hz), 128.4 (d, $J_{P,C}$ = 13.6 Hz), 132.2 (d, $J_{P,C}$ = 2.7 Hz), 151.7 (d, $J_{P,C}$ = 22.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.55; GC t_R = 10.40 min; GC−MS (EI, 70 eV) m/z = 349 (M^+) (51), 335 (15), 334 (56), 307 (23), 306 (97), 292 (11), 278 (19), 276 (11), 275 (14), 265 (10), 264 (52), 240 (20), 239 (18), 238 (100), 236 (16), 235 (30), 233 (42), 225 (16), 222 (28), 219 (19), 217 (15), 215 (23), 214 (13), 213 (51), 212 (56), 211 (12), 210 (32), 201 (12), 199 (17), 198 (10), 197 (43), 194 (12), 193 (18), 192 (13), 183 (18), 182 (17), 179 (10), 175 (17), 171 (10), 167 (18), 166 (22), 165 (96), 164 (22), 163 (12), 157 (29), 155 (20), 154 (15), 153 (25), 152 (20), 151 (17), 149 (39), 147 (10), 145 (14), 144 (10), 143 (35), 142 (18), 141 (33), 138 (12), 137 (44), 136 (10), 134 (15), 133 (22), 131 (22), 130 (14), 129 (50), 128 (65), 127 (22), 123 (12), 122 (14), 121 (10), 118 (10), 117 (19), 116 (28), 115 (62), 109 (16), 105 (15), 103 (16), 102 (15), 95 (13), 92 (10), 91 (48), 83 (15), 81 (12); HPLC t_R = 6.78 min; HRMS calcd for $C_{20}H_{32}NO_2P$ [M + H^+]: 350.2243; found: 350.2224.

Minor Diastereomer. R_f = 0.70 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.89 (d, $J_{H,H}$ = 6.4 Hz, 6H), 1.03−1.16 (m, 1H), 1.12 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.35−1.43 (m, 2H), 1.58−1.71 (m, 4H), 1.85−1.93 (m, 2H), 2.91−3.18 (m, 4H), 7.19−7.25 (m, 1H), 7.38−7.44 (m, 1H), 7.5−7.55 (m, 1H), 7.58−7.65 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.2 (d, $J_{P,C}$ = 2.7 Hz), 19.1, 21.9, 22.1, 24.1, 27.0, 28.9, 34.8, 37.9 (d, $J_{P,C}$ = 5.5 Hz), 48.1 (d, $J_{P,C}$ = 6.4 Hz), 51.1, 90.0, 121.5 (d, $J_{P,C}$ = 13.6 Hz), 126.9 (d, $J_{P,C}$ = 125.7 Hz), 127.6 (d, $J_{P,C}$ = 11.8 Hz), 128.1 (d, $J_{P,C}$ = 13.6 Hz), 132.1 (d, $J_{P,C}$ = 2.7 Hz), 153.2 (d, $J_{P,C}$ = 20.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.94; GC t_R = 10.61 min; GC−MS (EI, 70 eV) m/z = 349 (M^+) (27), 336 (11), 335 (20), 334 (72), 316 (12), 315 (10), 307 (24), 306 (84), 292 (15), 280 (15), 279 (12), 278 (26), 277 (51), 276 (16), 275 (22), 265 (13), 264 (36), 263 (10), 261 (11), 260 (10), 259 (14), 257 (11), 254 (11), 253 (11), 252 (10), 250 (15), 247 (12), 241 (11), 240 (21), 239 (19), 238 (85), 236 (18), 235 (40), 234 (20), 233 (54), 229 (10), 227 (10), 226 (10), 225 (18), 224 (12), 222 (33), 221 (16), 220 (14), 219 (25), 218 (11), 217 (23), 216 (10), 215 (31), 214 (19), 213 (74), 212 (100), 211 (16), 210 (27), 209 (13), 208 (15), 207 (24), 205 (12), 203 (13), 201 (19), 200 (10), 199 (26), 198 (17), 197 (69), 196 (14), 195 (13), 194 (14), 193 (25), 192 (13), 191 (18), 189 (17), 187 (12), 185 (12), 184 (11), 183 (26), 182 (16), 181 (15), 180 (15), 179 (20), 178 (12), 177 (12), 176 (12), 175 (21), 173 (12), 172 (10), 171 (21), 170 (13), 169 (16), 168 (17), 167 (32), 166 (26), 165 (76), 164 (21), 163 (23), 162 (11), 159 (13), 158 (14), 157 (44), 156 (15), 155 (30), 154 (23), 153 (37), 152 (26), 151 (25), 150 (21), 149 (90), 147 (14), 146 (11), 145 (25), 144 (18), 143 (58), 142 (28), 141 (53), 139 (13), 138 (33), 137 (43), 136 (15), 135 (21), 134 (23), 133 (36), 132 (13), 131 (34), 130 (20), 129 (74), 128 (88), 127 (30), 123 (18), 122 (21), 121 (18), 120 (10), 119 (15), 118 (14), 117 (29), 116 (43), 115 (90), 109 (20), 108 (14), 107 (12), 106 (11), 105 (24), 104 (17), 103 (22), 102 (20), 101 (11), 97 (11), 96 (12), 95 (19), 94 (11), 93 (14), 92 (15), 91 (66), 90 (13), 89 (18), 85 (10), 84 (13), 83 (26), 81 (18), 80 (14); HPLC t_R = 6.94 min; HRMS calcd for $C_{20}H_{32}NO_2P$ [M + H^+]: 350.2243; found: 350.2224.

***o*-(1-Acetoxyvinyl)phenylphosphonic Acid Ethyl Ester *N,N*-Diethylamide (2m).** This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and acetyl chloride (0.071 mL, 1.0 mmol); yield 0.026 g (16%); yellow oil; R_f = 0.74 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12 (t, $J_{H,H}$ = 7.2 Hz, 6H), 1.39 (t, $J_{H,H}$ = 7.11 Hz, 3H), 2.21 (s, 3H), 2.97−3.08 (m, 2H), 3.14−3.24 (m, 2H), 3.99−4.08 (m, 1H), 4.18−4.27 (m, 1H), 5.16 (q, $J_{H,H}$ = 1.89 Hz, 2H), 7.35−7.41 (m, 1H), 7.44−7.49 (m, 1H), 7.54−7.58 (m, 1H), 7.74−7.79 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.5 (d, $J_{P,C}$ = 1.8 Hz), 16.1 (d, $J_{P,C}$ = 8.2 Hz), 21.4, 39.6 (d, $J_{P,C}$ = 5.5 Hz), 59.5 (d, $J_{P,C}$ = 6.4 Hz), 105.4, 128.3 (d, $J_{P,C}$ = 13.6 Hz), 128.9 (d, $J_{P,C}$ = 175.3 Hz), 131.3 (d, $J_{P,C}$ = 6.4 Hz), 131.3 (d, $J_{P,C}$ = 3.6 Hz), 133.0 (d, $J_{P,C}$ = 8.6 Hz), 139.5 (d, $J_{P,C}$ = 9.1 Hz), 154.0 (d, $J_{P,C}$ = 4.5 Hz), 169.3; ^{31}P NMR (202 MHz, $CDCl_3$) δ 22.60; GC t_R = 15.12 min; GC−MS (EI, 70 eV) m/z = 325 (M^+) (2), 283 (11), 282 (60), 254 (41), 226 (16), 222 (39), 212 (20), 211 (52), 184 (22), 183 (100), 182 (22), 166 (19), 165 (100), 151 (10), 137 (45), 118 (30), 109 (21), 102 (12), 101 (13), 91 (15), 90 (25), 89 (12). $C_{16}H_{24}NO_4P$ (325.14): calcd C 59.07, H 7.44, N 4.31; found C 59.31, H 7.55, N 4.32.

***o*-(Methoxycarbonyl)phenylphosphonic Acid Ethyl Ester *N,N*-Diethylamide (2n).** This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and methyl chloroformate (0.077 mL, 1.0 mmol): yield 0.048 g (32%); pale yellow oil; R_f = 0.4 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.33 (t, $J_{H,H}$ = 7.2 Hz, 3H), 2.98−3.11 (m, 2H), 3.11−3.23 (m, 2H), 3.90 (s, 3H), 3.95−4.04 (m, 1H), 4.04−4.14 (m, 1H), 7.46−7.51 (m, 2H), 7.58−7.61 (m, 1H), 7.77−7.83 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.9 (d, $J_{P,C}$ = 1.8 Hz), 16.1 (d, $J_{P,C}$ = 7.3 Hz), 38.7 (d, $J_{P,C}$ = 4.5 Hz), 52.6, 59.9 (d, $J_{P,C}$ = 5.5 Hz), 128.9 (d, $J_{P,C}$ = 11.8 Hz), 129.9 (d, $J_{P,C}$ = 12.7 Hz), 130.2 (d, $J_{P,C}$ = 172.6 Hz), 131.0 (d, $J_{P,C}$ = 2.7 Hz), 132.9 (d, $J_{P,C}$ = 7.3 Hz), 136.4 (d, $J_{P,C}$ = 8.2 Hz), 169.0 (d, $J_{P,C}$ = 4.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 20.39; GC t_R = 14.66 min; GC−MS (EI, 70 eV) m/z = 299 (M^+) (0.4), 227 (59), 199 (100), 185 (13), 167 (53), 141 (11), 92 (14); HPLC t_R = 1.66 min; HRMS calcd for $C_{14}H_{22}NO_4P$ [M + H^+]: 300.1359; found: 300.1364.

2,2′-Bis(ethoxy-*N*,*N*-diethylamidophosphoryl)-benzophenone (5). This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and methyl chloroformate (0.019 mL, 0.25 mmol) except that the reaction time was 24 h: yield of two diastereoizomers (dr = 69:31) 0.052 g (41%). Isolated as a mixture of diastereomers.

Major Diastereomer. R_F = 0.67 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (t, $J_{H,H}$ = 7.27 Hz, 12H), 1.30 (t, $J_{H,H}$ = 7.1 Hz, 6H), 3.01−3.13 (m, 4H), 3.22−3.34 (m, 4H), 3.92−4.04 (m, 2H), 4.05−4.15 (m, 2H), 7.39−7.53 (m, 6H), 7.91−7.98 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.1 (d, $J_{P,C}$ = 2.0 Hz), 16.1 (d, $J_{P,C}$ = 7.3 Hz), 38.9 (d, $J_{P,C}$ = 5.5 Hz), 59.1 (d, $J_{P,C}$ = 5.5 Hz), 129.5 (d, $J_{P,C}$ = 12.4 Hz), 130.3 (d, $J_{P,C}$ = 12.0 Hz), 131.1 (d, $J_{P,C}$ = 168.9 Hz), 133.1 (d, $J_{P,C}$ = 6.5 Hz), 143.3 (d, $J_{P,C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 19.82; GC t_R = 25.05 min; GC−MS (EI, 70 eV) m/z = 438 (19), 437 (83), 436 (25), 366 (11), 337 (16), 336 (28), 310 (18), 309 (51), 308 (38), 307 (29), 306 (19), 291 (17), 290 (10), 258 (11), 245 (11), 228 (16), 227 (100), 216 (24), 212 (11), 211 (13), 199 (21), 183 (14), 183 (19), 180 (19), 153 (16), 152 (28); HPLC t_R = 4.25 min; HRMS calcd for $C_{25}H_{38}N_2O_5P_2$ [M + H^+]: 509.2329; found: 509.2342.

Minor Diastereomer. R_f = 0.62 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (t, $J_{H,H}$ = 7.1 Hz, 12H), 1.17 (t, $J_{H,H}$ = 7.1 Hz, 6H), 3.12−3.35 (m, 8H), 3.90−4.02 (m, 2H), 4.05−4.15 (m, 2H), 7.39−7.53 (m, 6H), 7.91−7.98 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.1 (d, $J_{P,C}$ = 2.5 Hz), 15.9 (d, $J_{P,C}$ = 7.3 Hz), 38.8 (d, $J_{P,C}$ = 5.5 Hz), 59.5 (d, $J_{P,C}$ = 6.4 Hz), 129.7 (d, $J_{P,C}$ = 12.7 Hz), 131.0 (d, $J_{P,C}$ = 173.5 Hz), 130.4 (d, $J_{P,C}$ = 6.3 Hz), 133.1 (d, $J_{P,C}$ = 8.2 Hz), 143.7 (d, $J_{P,C}$ = 10.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 20.81; GC t_R = 25.61 min; GC−MS (EI, 70 eV) m/z = 438 (19), 437 (79), 436 (23), 408 (12), 380 (11), 366 (11), 336 (20), 310 (18), 309 (47), 308 (34), 307 (31), 306 (21), 291 (15), 258 (14), 253 (11), 245 (10), 228 (17), 227 (100), 216 (22), 212 (10), 211 (15), 199 (21), 183 (14), 182 (27), 180 (20), 154 (17), 152 (29), 151 (11); HPLC t_R = 3.83 min; HRMS calcd for $C_{25}H_{38}N_2O_5P_2$ [M + H^+]: 509.2329; found: 509.2342.

dx.doi.org/10.1021/jo301526k | J. Org. Chem. 2012, 77, 8244−8256

***o*-(Diphenylphosphinoyl)phenylphosphonic Acid Ethyl Ester *N,N*-Diethylamide (6).** This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and chlorodiphenylphosphine (0.090 mL, 0.5 mmol): yield 0.084 g (38%); white solid; mp = 55.3−56.7 °C; R_f = 0.54 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (t, $J_{H,H}$ = 7.1 Hz, 3H), 0.99 (t, $J_{H,H}$ = 7.1 Hz, 6H), 3.00−3.12 (m, 2H), 3.17−3.29 (m, 2H), 3.63−3.74 (m, 1H), 3.78−3.88 (m, 1H), 7.30−7.44 (m, 6H), 7.45−7.51 (m, 2H), 7.55−7.62 (m, 5H), 8.02−8.09 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.9, 15.5 (d, $J_{P,C}$ = 6.4 Hz), 38.7 (d, $J_{P,C}$ = 5.5 Hz), 59.7 (d, $J_{P,C}$ = 6.4 Hz), 128.1 (d, $J_{P,C}$ = 12.7 Hz), 130.7 (d, $J_{P,C}$ = 122.6 Hz), 130.7 (d, $J_{P,C}$ = 122.6 Hz), 131.2, 131.7 (d, $J_{P,C}$ = 10.0 Hz), 132.0 (d, $J_{P,C}$ = 9.1 Hz), 134.1 (dd, $J_{P,C}$ = 7.3 Hz, $J_{P,C}$ = 18.2 Hz), 134.7 (dd, $J_{P,C}$ = 10.0 Hz, $J_{P,C}$ = 10.5 Hz), 134.9 (dd, $J_{P,C}$ = 11.8 Hz, $J_{P,C}$ = 14.5 Hz), 135.5 (dd, $J_{P,C}$ = 12.7 Hz, $J_{P,C}$ = 13.6 Hz), 137.4 (dd, $J_{P,C}$ = 9.1 Hz, $J_{P,C}$ = 175.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 20.92 (d, $J_{P,P}$ = 7.5 Hz), 32.79 (d, $J_{P,P}$ = 7.5 Hz); GC t_R = 26.59 min; GC−MS (EI, 70 eV) *m*/*z* = 441 (M^+) (0.3), 370 (43), 369 (49), 342 (20), 341 (100), 293 (38), 277 (20), 263 (29), 199 (42), 187 (17), 183 (16), 152 (21), 107 (28), 77 (18), 72 (14), 44 (10), 29 (12); HPLC t_R = 2.20 min; HRMS calcd for $C_{24}H_{29}NO_3P_2$ [M + H$^+$]: 442.1695; found: 442.1686.

***o*-(Diethylphosphoryl)phenylphosphonic Acid Ethyl Ester *N,N*-Diethylamide (7).** This compound was prepared according to General Procedure from **1** (0.120 g, 0.5 mmol) and diethyl chlorophosphate (0.072 mL, 0.5 mmol): yield 0.132 g (70%); colorless oil; R_f = 0.67 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.09 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.34 (t, $J_{H,H}$ = 7.1 Hz, 3H), 1.37 (t, $J_{H,H}$ = 7.0 Hz, 3H), 1.39 (t, $J_{H,H}$ = 7.1 Hz, 3H), 3.03−3.14 (m, 2H), 3.21−3.32 (m, 2H), 4.06−4.29 (m, 6H), 7.51−7.57 (m, 2H), 7.86−7.93 (m, 1H), 8.12−8.19 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.4 (d, $J_{P,C}$ = 1.8 Hz), 16.1 (d, $J_{P,C}$ = 7.3 Hz), 16.3 (d, $J_{P,C}$ = 6.4 Hz), 16.4 (d, $J_{P,C}$ = 6.4 Hz), 39.6 (d, $J_{P,C}$ = 4.5 Hz), 59.9 (d, $J_{P,C}$ = 6.4 Hz), 62.1 (d, $J_{P,C}$ = 5.5 Hz), 62.7 (d, $J_{P,C}$ = 5.5 Hz), 130.6 (dd, $J_{P,C}$ = 2.7 Hz, $J_{P,C}$ = 13.6 Hz), 131.3 (dd, $J_{P,C}$ = 2.7 Hz, $J_{P,C}$ = 13.6 Hz), 131.6 (dd, $J_{P,C}$ = 10.9 Hz, $J_{P,C}$ = 187.1 Hz), 133.8 (dd, $J_{P,C}$ = 10.0 Hz, $J_{P,C}$ = 14.5 Hz), 135.0 (dd, $J_{P,C}$ = 12.7 Hz, $J_{P,C}$ = 166.2 Hz), 135.7 (dd, $J_{P,C}$ = 9.1 Hz, $J_{P,C}$ = 13.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 16.62 (d, $J_{P,P}$ = 13.8 Hz), 21.42 (d, $J_{P,P}$ = 13.8 Hz); GC t_R = 13.51 min; GC−MS (EI, 70 eV) *m*/*z* = 377 (M^+) (0.4), 306 (17), 305 (29), 277 (55), 249 (40), 221 (100), 204 (10), 203 (54), 158 (11), 141 (20), 139 (24), 105 (15); HPLC t_R = 1.57 min; HRMS calcd for $C_{16}H_{29}NO_5P_2$ [M + H$^+$]: 378.1594; found: 378.1577.

***o*-Tolylphosphonic Acid L-Menthyl Ester *N,N*-Diethylamide (12a).** This compound was prepared according to General Procedure from **11** (0.120 g, 0.5 mmol) and methyl iodide (0.062 mL, 1.0 mmol): yield 0.181 g (99%); yellow oil; R_f = 0.81 ($CHCl_3$/MeOH = 15:1); $[\alpha]_D$ = −48.30 (*c* 1.47, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.71 (d, $J_{H,H}$ = 6.6 Hz, 3H), 0.82−0.89 (m, 1H), 0.86 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.93 (d, $J_{H,H}$ = 6.6 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.00−1.09 (m, 1H), 1.21 (q, $J_{H,H}$ = 11.7 Hz, 1H), 1.36−1.52 (m, 2H), 1.64−1.71 (m, 2H), 2.08−2.21 (m, 2H), 2.56 (s, 3H), 2.92−3.03 (m, 2H), 3.14−3.25 (m, 2H), 4.29−4.38 (m, 1H), 7.15−7.21 (m, 2H), 7.31−7.36 (m, 1H), 7.83−7.89 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.4 (d, $J_{P,C}$ = 1.8 Hz), 15.4, 21.0 (d, $J_{P,C}$ = 4.5 Hz), 21.2, 22.2, 22.7, 25.4, 31.5, 34.1, 38.3 (d, $J_{P,C}$ = 5.5 Hz), 43.1, 48.9 (d, $J_{P,C}$ = 5.5 Hz), 74.7 (d, $J_{P,C}$ = 6.4 Hz), 124.9 (d, $J_{P,C}$ = 12.7 Hz), 130.3 (d, $J_{P,C}$ = 175.5 Hz), 131.0, 131.1 (d, $J_{P,C}$ = 2.7 Hz), 133.4 (d, $J_{P,C}$ = 7.3 Hz), 141.7 (d, $J_{P,C}$ = 10.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 18.54; GC t_R = 9.85 min; GC−MS (EI, 70 eV) *m*/*z* = 365 (M^+) (0.4), 229 (13), 228 (100), 212 (53), 95 (10), 91 (15); HPLC t_R = 22.90 min; HRMS calcd for $C_{21}H_{36}NO_2P$ [M + H$^+$]: 366.2556; found: 366.2568.

***o*-Iodophenylphosphonic Acid L-Menthyl Ester *N,N*-Diethylamide (12d).** This compound was prepared according to General Procedure from **11** (0.120 g, 0.5 mmol) and iodine (0.254 g, 1.0 mmol): yield 0.196 g (82%); pale yellow oil; R_f = 0.78 ($CHCl_3$/MeOH = 15:1); $[\alpha]_D$ = −56.27 (*c* 1.12, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.66 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.79−0.87 (m, 1H), 0.83 (d, $J_{H,H}$ = 7.1 Hz, 3H), 0.91 (d, $J_{H,H}$ = 6.6 Hz, 3H), 0.94−1.07 (m, 1H), 0.97 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.15−1.22 (m, 1H), 1.34−1.5 (m, 2H), 1.59−1.69 (m, 2H), 2.07−2.18 (m, 2H), 2.94−3.07 (m, 2H), 3.20−3.33 (m, 2H), 4.26−4.36 (m, 1H), 7.01−7.09 (m, 1H), 7.31−7.38 (m, 1H), 7.89−8.02 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.4 (d, $J_{P,C}$ = 1.8 Hz), 15.4, 21.1, 22.1, 22.7, 25.4, 31.5, 34.0, 39.0 (d, $J_{P,C}$ = 5.5 Hz), 43.0, 48.8 (d, $J_{P,C}$ = 5.5 Hz), 75.4 (d, $J_{P,C}$ = 6.4 Hz), 98.4 (d, $J_{P,C}$ = 7.3 Hz), 127.1 (d, $J_{P,C}$ = 11.8 Hz), 131.9 (d, $J_{P,C}$ = 2.7 Hz), 135.6 (d, $J_{P,C}$ = 6.4 Hz), 135.7 (d, $J_{P,C}$ = 181.6 Hz), 141.4 (d, $J_{P,C}$ = 12.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 16.89; GC t_R = 11.40 min; GC−MS (EI, 70 eV) *m*/*z* = 477 (M^+) (0.3), 341 (11), 340 (100), 324 (50), 95 (26), 83 (11), 81 (23); HPLC t_R = 24.10 min; HRMS calcd for $C_{20}H_{33}INO_2P$ [M + H$^+$]: 478.1366; found: 478.1395.

***o*-(Methoxycarbonyl)phenylphosphonic acid L-Menthyl Ester *N,N*-Diethylamide (12e).** This compound was prepared according to General Procedure from **11** (0.120 g, 0.5 mmol) and methyl chloroformate (0.077 mL, 1.0 mmol): yield 0.121 g (56%); colorless oil; R_f = 0.7 ($CHCl_3$/MeOH = 15:1); $[\alpha]_D$ = −28.07 (*c* 1.28, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.60 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.81−0.87 (m, 1H), 0.83 (d, $J_{H,H}$ = 7.1 Hz, 3H), 0.92 (d, $J_{H,H}$ = 6.6 Hz, 3H), 0.95−1.05 (m, 1H), 0.97 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.19 (q, J_{H-H} = 11.7 Hz, 1H), 1.30−1.37 (m, 1H), 1.40−1.50 (m, 1H), 1.60−1.69 (m, 2H), 1.98−2.06 (m, 1H), 2.20−2.27 (m, 1H), 3.17−3.28 (m, 2H), 3.18−3.29 (m, 2H), 3.91 (s, 3H), 4.25−4.35 (m, 1H), 7.44−7.51 (m, 2H), 7.54−7.58 (m, 1H), 7.87−7.92 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.5 (d, $J_{P,C}$ = 1.9 Hz), 15.4, 21.1, 22.1, 22.7, 25.3, 31.6, 34.1, 38.4 (d, $J_{P,C}$ = 5.5 Hz), 43.1, 48.9 (d, $J_{P,C}$ = 5.5 Hz), 52.6, 75.8 (d, $J_{P,C}$ = 6.4 Hz), 128.5 (d, $J_{P,C}$ = 11.8 Hz), 129.7 (d, $J_{P,C}$ = 12.7 Hz), 130.7 (d, $J_{P,C}$ = 2.7 Hz), 131.1 (d, $J_{P,C}$ = 172.6 Hz), 133.3 (d, $J_{P,C}$ = 7.3 Hz), 136.5 (d, $J_{P,C}$ = 9.1 Hz), 169.2 (d, $J_{P,C}$ = 4.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 16.87; GC t_R = 9.91 min; GC−MS (EI, 70 eV) *m*/*z* = 409 (M^+) (0.1), 243 (15), 242 (100), 241 (45), 226 (61), 212 (10), 151 (10), 133 (19), 95 (15), 83 (14), 81 (15); HPLC t_R = 11.75 min; HRMS calcd for $C_{22}H_{36}NO_4P$ [M + H$^+$]: 410.2455; found: 410.2442.

***o*-(Trimethylsilyl)phenylphosphonic Acid L-Menthyl Ester *N,N*-Diethylamide (12f).** This compound was prepared according to General Procedure from **11** (0.120 g, 0.5 mmol) and chlorotrimethylsilane (0.127 mL, 1.0 mmol): yield 0.184 g (87%); colorless oil; R_f = 0.87 ($CHCl_3$/MeOH = 15:1); $[\alpha]_D$ = −60.51 (*c* 1.02, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.20 (d, $J_{H,H}$ = 7.0 Hz, 3H), 0.39 (s, 9H), 0.71 (d, $J_{H,H}$ = 7.1 Hz, 3H), 0.79−0.88 (m, 2H), 0.87 (d, $J_{H,H}$ = 6.6 Hz, 3H), 0.98 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.15 (q, $J_{H,H}$ = 11.7 Hz, 1H), 1.23−1.29 (m, 1H), 1.32−1.43 (m, 1H), 1.51−1.60 (m, 2H), 1.72−1.80 (m, 1H), 2.34−2.40 (m, 1H), 2.94−3.11 (m, 4H), 3.96−4.04 (m, 1H), 7.29−7.39 (m, 2H), 7.65−7.73 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 1.4, 13.8 (d, $J_{P,C}$ = 2.7 Hz), 14.8, 20.9, 21.9, 22.6, 25.3, 31.5, 34.1, 38.6 (d, $J_{P,C}$ = 5.5 Hz), 43.5, 48.6 (d, $J_{P,C}$ = 7.2 Hz), 76.2 (d, $J_{P,C}$ = 5.5 Hz), 127.8 (d, $J_{P,C}$ = 13.6 Hz), 130.0 (d, $J_{P,C}$ = 2.9 Hz), 133.2 (d, $J_{P,C}$ = 10.6 Hz), 135.3 (d, $J_{P,C}$ = 18.3 Hz), 137.0 (d, $J_{P,C}$ = 172.3 Hz), 145.5 (d, $J_{P,C}$ = 21.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 23.24; GC t_R = 13.36 min; GC−MS (EI, 70 eV) *m*/*z* = 423 (M^+) (0.1), 271 (19), 270 (100), 197 (40), 83 (10); $C_{23}H_{42}NO_2PSi$ (423.64): calcd C 65.21, H 9.99, N 3.31; found C 65.25, H 9.96, N 3.32.

Synthesis of 8 by Deprotonation-Methylation of 2a. In a flame-dried Schlenk tube (50 mL) equipped with magnetic stirrer and inert gas inlet was placed **2a** (0.127 g, 0.25 mmol) in 5 mL THF. The mixture was cooled to −78 °C, and *tert*-butyllithium (0.300 mL, 0.5 mmol, 1.7 M solution in pentane) was added at once. The mixture was allowed to warm to room temperature for 25 min and then was cooled again to −78 °C. Methyl iodide (0.031 mL, 0.5 mmol) was added at once, and the mixture was allowed to warm to room temperature over 1 h. The reaction was quenched by addition of saturated NH_4Cl solution (10 mL) and extracted with DCM (3 × 20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography using $CHCl_3$/MeOH (v/v = 15:1) as eluent yielding **8** (0.062 g, 92%).

***o*-(Ethyl)phenylphosphonic Acid Ethyl Ester *N,N*-Diethylamide (8).** Yellow oil; R_f = 0.76 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.28 (t, $J_{H,H}$ = 7.5 Hz, 3H), 1.39 (t, $J_{H,H}$ = 7.1 Hz, 3H), 2.89−3.02 (m, 2H), 3.02−3.22 (m, 4H), 3.97−4.08 (m, 1H), 4.11−4.22 (m, 1H), 7.16−7.23 (m, 1H),

dx.doi.org/10.1021/jo301526k | J. Org. Chem. 2012, 77, 8244−8256

7.27−7.33 (m, 1H), 7.37−7.43 (m, 1H), 7.68−7.75 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.1 (d, $J_{P,C}$ = 2.3 Hz), 15.4 (d, $J_{P,C}$ = 1.2 Hz), 16.3 (d, $J_{P,C}$ = 6.9 Hz), 26.8 (d, $J_{P,C}$ = 4.0 Hz), 38.8 (d, $J_{P,C}$ = 5.2 Hz), 59.6 (d, $J_{P,C}$ = 6.3 Hz), 125.0 (d, $J_{P,C}$ = 13.8 Hz), 129.2 (d, $J_{P,C}$ = 174.1 Hz), 129.5 (d, $J_{P,C}$ = 13.8 Hz), 131.6 (d, $J_{P,C}$ = 2.9 Hz), 132.9 (d, $J_{P,C}$ = 9.2 Hz), 148.3 (d, $J_{P,C}$ = 11.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 23.41; GC t_R = 7.88 min; GC−MS (EI, 70 eV) m/z = 269 (M^+) (22), 254 (33), 240 (15), 226 (12), 197 (26), 170 (15), 169 (100), 151 (22), 149 (21), 133 (52), 105 (13), 103 (13), 91 (13); HPLC t_R = 3.27 min; HRMS calcd for $C_{14}H_{24}NO_2P$ [M + H^+]: 270.1617; found: 270.1613.

Synthesis of *o*-(Isopropyl)phenylphosphonic Acid Ethyl Ester *N,N*-Diethylamide (9) by Deprotonation-Methylation of 8. The synthesis was performed analogously to that described above using **8** (0.062 g, 0.24 mmol), *t*-BuLi (0.28 mL, 0.48 mmol, 1.7 M in pentane), and methyl iodide (0.030 mL, 0.48 mmol): yield 0.027 g (40%); pale yellow oil; R_f = 0.8 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.24 (d, $J_{H,H}$ = 6.8 Hz, 3H), 1.29 (d, $J_{H,H}$ = 6.7, 3H), 1.39 (t, $J_{H,H}$ = 7.1, 3H), 3.00−3.22 (m, 4H), 3.76 (h, $J_{H,H}$ = 6.7 Hz, 1H), 3.98−4.10 (m, 1H), 4.11−4.24 (m, 1H), 7.14−7.21 (m, 1H), 7.37−7.47 (m, 2H), 7.67−7.75 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.2 (d, $J_{P,C}$ = 2.3 Hz), 16.3 (d, $J_{P,C}$ = 7.5 Hz), 23.8, 24.6, 30.7 (d, $J_{P,C}$ = 4.6 Hz), 38.8 (d, $J_{P,C}$ = 5.2 Hz), 59.5 (d, $J_{P,C}$ = 6.3 Hz), 125.0 (d, $J_{P,C}$ = 13.8 Hz), 126.7 (d, $J_{P,C}$ = 13.8 Hz), 128.6 (d, $J_{P,C}$ = 174.7 Hz), 131.7 (d, $J_{P,C}$ = 2.9 Hz), 132.7 (d, $J_{P,C}$ = 9.2 Hz), 153.4 (d, $J_{P,C}$ = 12.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 23.55; GC t_R = 12.93 min; GC−MS (EI, 70 eV) m/z = 283 (M^+) (19), 268 (32), 254 (10), 240 (27%), 212 (13%), 211 (32), 184 (16), 183 (76), 181 (15), 167 (21), 165 (17), 163 (29), 149 (33), 148 (11), 147 (100), 145 (12), 133 (20), 121 (11), 117 (14), 116 (16), 115 (26), 103 (16), 91 (30); HPLC t_R = 4.22 min; HRMS calcd for $C_{15}H_{26}NO_2P$ [M + H^+]: 284.1774; found: 284.1777.

Synthesis of (2-Isopropyl-6-methylphenyl)phosphonic Acid Ethyl Ester *N,N*-Diethylamide (10) by Deprotonation-Methylation of 9. The synthesis was performed analogously to that described above using **9** (0.051 g, 0.18 mmol), *t*-BuLi (0.21 mL, 0.36 mmol, 1.7 M in pentane), and methyl iodide (0.023 mL, 0.36 mmol): yield 0.024 g (45%); pale yellow oil; R_f = 0.92 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (t, $J_{H,H}$ = 7.2 Hz, 6H), 1.19 (d, $J_{H,H}$ = 6.8 Hz, 3H), 1.23 (d, $J_{H,H}$ = 6.5 Hz, 3H), 1.33 (t, $J_{H,H}$ = 7.1 Hz, 3H), 2.57−2.60 (m, 3H), 2.93−3.20 (m, 4H), 3.75 (h, $J_{H,H}$ = 6.5 Hz, 1H), 3.98−4.11 (m, 2H), 6.98−7.03 (m, 1H), 7.22−7.31 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.0 (d, $J_{P,C}$ = 2.7 Hz), 16.4 (d, $J_{P,C}$ = 7.3 Hz), 24.4 (d, $J_{P,C}$ = 2.7 Hz), 24.5, 25.0, 30.3 (d, $J_{P,C}$ = 3.6 Hz), 38.5 (d, $J_{P,C}$ = 5.5 Hz), 60.0 (d, $J_{P,C}$ = 5.5 Hz), 124.6 (d, $J_{P,C}$ = 13.6 Hz), 126.9 (d, $J_{P,C}$ = 167.1 Hz), 129.5 (d, $J_{P,C}$ = 14.5 Hz), 131.1 (d, $J_{P,C}$ = 3.6 Hz), 142.8 (d, $J_{P,C}$ = 10.9 Hz), 155.3 (d, $J_{P,C}$ = 11.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 26.24; GC t_R = 8.15 min; GC−MS (EI, 70 eV) m/z = 297 (M^+) (46), 283 (14), 282 (84), 268 (11), 254 (50), 240 (12), 226 (28), 225 (61), 198 (23), 197 (100), 196 (15), 195 (36), 183 (14), 181 (46), 179 (25), 177 (47), 165 (11), 163 (34), 162 (10), 161 (73), 149 (19), 147 (16), 133 (41), 132 (11), 130 (13), 129 (17), 128 (15), 119 (10), 117 (27), 116 (20), 115 (46), 105 (18), 103 (10), 92 (10), 91 (56); HPLC t_R = 4.90 min; HRMS calcd for $C_{16}H_{28}NO_2P$ [M + H^+]: 298.1930; found: 298.1907.

Synthesis of (*o*-Ethylphenyl)phosphonic Acid L-Menthyl Ester *N,N*-Diethylamide (12b) by Deprotonation-Methylation of 12a. The synthesis was performed analogously to that described above using **12a** (0.090 g, 0.25 mmol), *t*-BuLi (0.29 mL, 0.49 mmol, 1.7 M in pentane), and methyl iodide (0.031 mL, 0.49 mmol): yield 0.079 g (85%); yellow oil; R_f = 0.68 ($CHCl_3$/MeOH = 15:1); $[\alpha]_D$ = −49.66 (*c* 1.39, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.70 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.83−0.89 (m, 1H), 0.85 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.93 (d, $J_{H,H}$ = 6.6 Hz, 3H), 0.96 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.00−1.07 (m, 1H), 1.21 (q, $J_{H,H}$ = 11.7 Hz, 1H), 1.26 (t, $J_{H,H}$ = 7.6 Hz, 3H), 1.35−1.51 (m, 2H), 1.64−1.71 (m, 2H), 2.08−2.22 (m, 2H), 2.89−3.11 (m, 4H), 3.13−3.23 (m, 2H), 4.29−4.38 (m, 1H), 7.16−7.21 (m, 1H), 7.27−7.31 (m, 1H), 7.37−7.42 (m, 1H), 7.84−7.89 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.6 (d, $J_{P,C}$ = 1.9 Hz), 14.9, 15.5, 21.2, 22.2, 22.8, 25.4, 26.4 (d, $J_{P,C}$ = 4.5 Hz), 31.6, 34.2, 38.4 (d, $J_{P,C}$ = 4.5 Hz), 43.3 (d, $J_{P,C}$ = 1.8 Hz), 49.0 (d, $J_{P,C}$ = 5.4 Hz), 75.0 (d, $J_{P,C}$ = 7.2 Hz), 124.8 (d, $J_{P,C}$ = 13.2 Hz), 128.8 (d, $J_{P,C}$ = 14.5 Hz), 130.0 (d, $J_{P,C}$ = 175.3 Hz), 131.2 (d, $J_{P,C}$ = 2.7 Hz), 133.5 (d, $J_{P,C}$ = 7.3 Hz), 147.8 (d, $J_{P,C}$ = 12.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 18.75; GC t_R = 9.91 min; GC−MS (EI, 70 eV) m/z = 379 (M^+) (2), 272 (29), 212 (10), 200 (10), 199 (100), 167 (34), 166 (10), 95 (17), 81 (15); HPLC t_R = 3.34 min; HRMS calcd for $C_{22}H_{38}NO_2P$ [M + H^+]: 380.2713; found: 380.2726.

Synthesis of (*o*-Isopropylphenyl)phosphonic Acid L-Menthyl Ester *N,N*-Diethylamide (12c) by Deprotonation-Methylation of 12b. The synthesis was performed analogously to that described above using **12b** (0.079 g, 0.21 mmol), *t*-BuLi (0.25 mL, 0.42 mmol, 1.7 M in pentane), and methyl iodide (0.027 mL, 0.49 mmol): yield 0.071 g (87%); yellow oil; R_f = 0.72 ($CHCl_3$/MeOH = 15:1); $[\alpha]_D$ = −43.54 (*c* 1.17, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.72 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.85 (d, $J_{H,H}$ = 7.3 Hz, 3H), 0.88−0.96 (m, 2H), 0.95 (d, $J_{H,H}$ = 6.6 Hz, 3H), 0.99 (t, $J_{H,H}$ = 7.0 Hz, 6H), 1.18−1.35 (m, 1H), 1.23 (d, $J_{H,H}$ = 6.6 Hz, 3H), 1.28 (d, $J_{H,H}$ = 6.9 Hz, 3H), 1.35−1.42 (m, 1H), 1.44−1.52 (m, 1H), 1.65−1.71 (m, 2H), 2.07−2.15 (m, 1H), 2.18−2.25 (m, 1H), 2.95−3.05 (m, 2H), 3.11−3.19 (m, 2H), 3.71−3.82 (m, 1H), 4.32−4.41 (m, 1H), 7.15−7.20 (m, 1H), 7.37−7.46 (m, 2H), 7.82−7.88 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.8 (d, $J_{P,C}$ = 2.7 Hz), 15.5, 21.2, 22.2, 22.8, 23.6, 25.1, 25.4, 30.3 (d, $J_{P,C}$ = 4.5 Hz), 31.6, 34.2, 38.5 (d, $J_{P,C}$ = 4.5 Hz), 43.3, 49.0 (d, $J_{P,C}$ = 5.5 Hz), 75.3 (d, $J_{P,C}$ = 7.3 Hz), 124.9 (d, $J_{P,C}$ = 12.7 Hz), 126.5 (d, $J_{P,C}$ = 13.6 Hz), 129.6 (d, $J_{P,C}$ = 176.2 Hz), 131.4 (d, $J_{P,C}$ = 3.6 Hz), 133.3 (d, $J_{P,C}$ = 7.3 Hz), 153.1 (d, $J_{P,C}$ = 12.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 18.86; GC t_R = 13.54 min; GC−MS (EI, 70 eV) m/z = 393 (M^+) (1), 257 (18), 256 (100), 255 (23), 240 (54), 212 (11), 165 (10), 163 (14), 149 (11), 147 (38), 95 (21), 91 (12), 83 (31), 81 (23). $C_{23}H_{40}NO_2P$ (393.28): calcd C 70.19, H 10.24, N 3.56; found C 70.41, H 10.26, N 3.49.

General Procedure of Birch Reduction of Some Arylphosphonic Acid Derivatives. Through a flame-dried three-necked 100 mL round-bottom flask, immersed in an acetone−dry ice bath and equipped with magnetic stirrer, inert gas inlet, and coldfinger with dry ice−acetone mixture, was passed gaseous ammonia until 15 mL of it was condensed. Then, sodium (1.25−2.5 mmol) was added, and the mixture was allowed to stir at −78 °C for 15 min. Once all sodium was dissolved, a solution of phosphonic acid monoester monoamide (0.5 mmol) in THF (5 mL) was added at once, and the mixture was allowed to stir at −78 °C for 5 min. The reaction was quenched by addition of solid NH_4Cl (0.5 g), ammonia was removed from the reaction mixture under water pump, the residue was filtered, the solids were washed with DCM (2 × 10 mL), and the filtrate was concentrated using a rotary evaporator. The residue was purified by flash column chromatography using $CHCl_3$/MeOH (v/v = 15:1) as eluent.

(2-Methyl-1,4-cyclohexadien-3-yl)phosphonic Acid Ethyl Ester *N,N*-Diethylamide (13a). This compound was prepared according to General Procedure from **2a** (0.128 g, 0.5 mmol) and sodium (0.058 g, 2.50 mmol): yield of two diastereomers (dr = 79:21) 0.112 g (87%). Isolated as a mixture of diastereomers.

Major Diastereomer. R_f = 0.64 ($CHCl_3$/MeOH = 15:1); NMR (500 MHz, $CDCl_3$) δ 1.06 (t, $J_{H,H}$ = 6.9 Hz, 6H), 1.30 (t, $J_{H,H}$ = 6.9 Hz, 3H), 1.90 (s, 3H), 2.59−2.84 (m, 2H), 2.99−3.15 (m, 4H), 3.16−3.27 (m, 1H), 3.81−3.91 (m, 1H), 4.04−4.14 (m, 1H), 5.57−5.62 (m, 1H), 5.67−5.73 (m, 1H), 5.81−5.88 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.2 (d, $J_{P,C}$ = 1.8 Hz), 16.2 (d, $J_{P,C}$ = 7.3 Hz), 23.5, 27.3 (d, $J_{P,C}$ = 7.3 Hz), 38.9 (d, $J_{P,C}$ = 3.6 Hz), 43.2 (d, $J_{P,C}$ = 127.2 Hz), 59.1 (d, $J_{P,C}$ = 7.3 Hz), 122.2 (d, $J_{P,C}$ = 10.0 Hz), 122.6 (d, $J_{P,C}$ = 10.9 Hz), 127.2 (d, $J_{P,C}$ = 10.9 Hz), 128.9 (d, $J_{P,C}$ = 8.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.25; GC t_R = 12.24 min; GC−MS (EI, 70 eV) m/z = 257 (M^+) (0.1), 165 (25), 150 (24), 136 (71), 122 (12), 108 (11), 93 (12), 91 (27), 77 (20), 72 (22), 65 (17), 58 (100), 44 (25), 42 (12), 29 (15); HPLC t_R = 2.20 min; HRMS calcd for $C_{13}H_{24}NO_2P$ [M + H^+]: 258.1617; found: 258.1606.

Minor Diastereomer. R_f = 0.61 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07 (t, $J_{H,H}$ = 7.2 Hz, 6H), 1.30 (t, $J_{H,H}$ = 6.9 Hz, 3H), 1.87 (s, 3H), 2.59−2.85 (m, 2H), 2.98−3.15 (m, 4H), 3.16−

dx.doi.org/10.1021/jo301526k | *J. Org. Chem.* 2012, 77, 8244−8256

3.28 (m, 1H), 3.80−3.91 (m, 1H), 4.04−4.13 (m, 1H), 5.52−5.56 (m, 1H), 5.77−5.91 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.4 (d, $J_{P,C}$ = 1.8 Hz) 16.2 (d, $J_{P,C}$ = 7.5 Hz), 23.4, 27.3 (d, $J_{P,C}$ = 7.3 Hz), 39.2 (d, $J_{P,C}$ = 3.6 Hz), 44.0 (d, $J_{P,C}$ = 126,25 Hz), 59.6 (d, $J_{P,C}$ = 7.3 Hz), 122.5 (d, $J_{P,C}$ = 10.0 Hz), 122.7 (d, $J_{P,C}$ = 10.9 Hz), 126.8 (d, $J_{P,C}$ = 10.9 Hz), 129.1 (d, $J_{P,C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.09; GC t_R = 12.27 min; GC−MS (EI, 70 eV) m/z = 257 (M^+) (0.1), 165 (25), 150 (24), 136 (71), 122 (12), 108 (11), 93 (12), 91 (27), 77 (20), 72 (22), 65 (17), 58 (100), 44 (25), 42 (12), 29 (15); HPLC t_R = 2.60 min; HRMS calcd for $C_{13}H_{24}NO_2P$ [M + H^+]: 258.1617; found: 258.1606.

(2-Trimethylsilyl-1,4-cyclohexadien-3-yl)phosphonic Acid Ethyl Ester *N,N*-Diethylamide (13b). This compound was prepared according to General Procedure from **2d** (0.157 g, 0.5 mmol) and sodium (0.029 g, 1.25 mmol): yield of two diastereomers (dr = 65:35) 0.140 g (89%). Isolated as a mixture of two diastereomers.

Major Diastereomer. R_f = 0.66 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.15 (s, 9H), 1.05 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.31 (t, $J_{H,H}$ = 6.9 Hz, 3H), 2.57−2.92 (m, 2H), 2.95−3.18 (m, 3H), 3.34−3.44 (m, 1H), 3.42−3.60 (m, 1H), 3.81−3.93 (m, 1H), 4.11−4.22 (m, 1H), 5.70−5.75 (m, 1H), 5.86−5.92 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ −0.4, 14.4 (d, $J_{P,C}$ = 1.8 Hz), 16.4 (d, $J_{P,C}$ = 6.4 Hz), 28.4 (d, $J_{P,C}$ = 7.3 Hz), 39.4 (d, $J_{P,C}$ = 2.7 Hz), 42.7 (d, $J_{P,C}$ = 128.1 Hz), 59.8 (d, $J_{P,C}$ = 7.3 Hz), 123.4 (d, $J_{P,C}$ = 10.0 Hz), 126.7 (d, $J_{P,C}$ = 10.9 Hz), 135.2 (d, $J_{P,C}$ = 8.2 Hz), 137.6 (d, $J_{P,C}$ = 10.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 28.17; GC t_R = 12.54 min; GC−MS (EI, 70 eV) m/z = 316 (M^+) (0.1), 165 (51), 150 (52), 137 (17), 136 (100), 135 (19), 122 (17), 121 (29), 108 (12); HPLC t_R = 7.40 min; HRMS calcd for $C_{15}H_{30}NO_2PSi$ [M + H^+]: 316.1856; found: 316.1835.

Minor Diastereomer. R_f = 0.62 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.15 (s, 9H), 1.09 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.30 (t, $J_{H,H}$ = 6.9 Hz, 3H), 2.57−2.92 (m, 2H), 2.95−3.18 (m, 3H), 3.34−3.44 (m, 1H), 3.42−3.60 (m, 1H), 3.81−3.93 (m, 1H), 3.97−4.06 (m, 1H), 5.92−5.97 (m, 1H), 6.14−6.19 (m, 1H), 6.26−6.30 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ −0.5, 14.3 (d, $J_{P,C}$ = 1.8 Hz), 16.1 (d, $J_{P,C}$ = 7.3 Hz), 28.5 (d, $J_{P,C}$ = 7.3 Hz), 39.1 (d, $J_{P,C}$ = 3.6 Hz), 40.4 (d, $J_{P,C}$ = 128.1 Hz), 59.1 (d, $J_{P,C}$ = 7.3 Hz), 122.6 (d, $J_{P,C}$ = 10.0 Hz), 128.2 (d, $J_{P,C}$ = 11.8 Hz), 134.1 (d, $J_{P,C}$ = 8.2 Hz), 138.5 (d, $J_{P,C}$ = 10.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.50; GC t_R = 12.67 min; GC−MS (EI, 70 eV) m/z = 316 (M^+) (0.1), 165 (68), 150 (70), 137 (21), 136 (100), 135 (23), 122 (23), 121 (35), 120 (11), 108 (15), 107 (10), 80 (12); HPLC t_R = 7.43 min; HRMS calcd for $C_{13}H_{24}NO_2PSi$ [M + H^+]: 316.1856; found: 316.1848.

(2-Ethyl-1,4-cyclohexadien-3-yl)phosphonic Acid Ethyl Ester *N,N*-Diethylamide (13c). This compound was prepared according to General Procedure from **8** (0.134 g, 0.5 mmol) and sodium (0.058 g, 2.50 mmol): yield of two diastereomers (dr = 57:43) 0.108 g (80%). Isolated as a mixture of two diastereomers.

Major Diastereomer. R_f = 0.66 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.07 (t, $J_{H,H}$ = 7.2 Hz, 6H), 1.30 (t, $J_{H,H}$ = 6.9 Hz, 3H), 2.11−2.25 (m, 2H), 2.63−2.88 (m, 2H), 2.96−3.16 (m, 4H), 3.26−3.38 (m, 1H), 3.80−3.92 (m, 1H), 4.03−4.13 (m, 1H), 5.59−5.65 (m, 1H), 5.70−5.77 (m, 1H), 5.81−5.92 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 12.2 (d, $J_{P,C}$ = 1.8 Hz), 14.3 (d, $J_{P,C}$ = 1.9 Hz), 16.2 (d, $J_{P,C}$ = 7.3 Hz), 27.3 (d, $J_{P,C}$ = 7.3 Hz), 28.8, 39.0 (d, $J_{P,C}$ = 3.6 Hz), 41.7 (d, $J_{P,C}$ = 127.2 Hz), 59.2 (d, $J_{P,C}$ = 7.3 Hz), 120.5 (d, $J_{P,C}$ = 18.2 Hz), 122.5 (d, $J_{P,C}$ = 9.1 Hz), 127.4 (d, $J_{P,C}$ = 10.9 Hz), 134.6 (d, $J_{P,C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.29; GC t_R = 12.67 min; GC−MS (EI, 70 eV) m/z = 271 (M^+) (0.1), 165 (24), 150 (27), 136 (64), 122 (12), 108 (10), 91 (16), 80 (10), 79 (28), 77 (14), 72 (23), 65 (12), 58 (100), 44 (23), 42 (10), 29 (29); HPLC t_R = 2.70 min; HRMS calcd for $C_{14}H_{26}NO_2P$ [M + H^+]: 272.1774; found: 272.1774.

Minor Diastereomer. R_f = 0.66 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03 (t, $J_{H,H}$ = 7.4 Hz, 3H), 1.07 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.28 (t, $J_{H,H}$ = 6.9 Hz, 3H), 2.27−2.43 (m, 2H), 2.63−2.88 (m, 2H), 2.96−3.16 (m, 4H), 3.26−3.38 (m, 1H), 3.80−3.92 (m, 1H), 4.03−4.13 (m, 1H), 5.54−5.58 (m, 1H), 5.81−5.92 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 12.2 (d, $J_{P,C}$ = 1.8 Hz), 14.5 (d, $J_{P,C}$ = 1.8 Hz), 16.3 (d, $J_{P,C}$ = 7.3 Hz), 27.3 (d, $J_{P,C}$ = 7.3 Hz), 28.7, 39.4 (d, $J_{P,C}$ = 3.6 Hz), 42.5 (d, $J_{P,C}$ = 126.3 Hz), 59.7 (d, $J_{P,C}$ = 8.2 Hz), 120.6 (d, $J_{P,C}$ = 18.2 Hz), 122.8 (d, $J_{P,C}$ = 10.0 Hz), 127.2 (d, $J_{P,C}$ = 10.9 Hz), 134.9 (d, $J_{P,C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.23; GC t_R = 12.78 min; GC−MS (EI, 70 eV) m/z = 271 (M^+) (0.1), 165 (22), 150 (28), 136 (45), 122 (10), 105 (13), 77 (10), 73 (11), 72 (41), 58 (100), 44 (26), 43 (43), 42 (10), 41 (18), 27 (14); HPLC t_R = 3.40 min; HRMS calcd for $C_{14}H_{26}NO_2P$ [M + H^+]: 272.1774; found: 272.1774.

(2-Isopropyl-1,4-cyclohexadien-3-yl)phosphonic Acid Ethyl Ester *N,N*-Diethylamide (13d). This compound was prepared according to General Procedure from **9** (0.142 g, 0.5 mmol) and sodium (0.058 g, 2.50 mmol): yield of two diastereomers (dr = 77:23) 0.108 g (76%). Isolated as a mixture of two diastereomers.

Major Diastereomer. R_f = 0.70 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (d, $J_{H,H}$ = 6.6 Hz, 3H), 1.07 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.08 (d, $J_{H,H}$ = 6.6 Hz, 3H), 1.29 (t, $J_{H,H}$ = 7.1 Hz, 3H), 2.61−2.74 (m, 3H), 2.96−3.16 (m, 4H), 3.34−3.44 (m, 1H), 3.80−3.90 (m, 1H), 4.03−4.13 (m, 1H), 5.61−5.66 (m, 1H), 5.72−5.78 (m, 1H), 5.82−5.87 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.3 (d, $J_{P,C}$ = 1.8 Hz), 16.2 (d, $J_{P,C}$ = 7.3 Hz), 20.6, 22.9 (d, $J_{P,C}$ = 2.7 Hz), 27.3 (d, $J_{P,C}$ = 7.3 Hz), 31.5, 39.1 (d, $J_{P,C}$ = 3.6 Hz), 41.4 (d, $J_{P,C}$ = 127.2 Hz), 59.1 (d, $J_{P,C}$ = 8.2 Hz), 118.7 (d, $J_{P,C}$ = 10.9 Hz), 122.9 (d, $J_{P,C}$ = 10.0 Hz), 127.6 (d, $J_{P,C}$ = 10.9 Hz), 139.5 (d, $J_{P,C}$ = 8.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.23; GC t_R = 7.89 min; GC−MS (EI, 70 eV) m/z = 285 (M^+) (0.4), 165 (53), 150 (63), 137 (13), 136 (100), 122 (20), 120 (10), 108 (13), 105 (27), 91 (14), 80 (12); HPLC t_R = 3.40 min; HRMS calcd for $C_{15}H_{28}NO_2P$ [M + H^+]: 286.1930; found: 286.1925.

Minor Diastereomer. R_f = 0.70 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (d, $J_{H,H}$ = 6.7 Hz, 3H), 1.07 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.09 (d, $J_{H,H}$ = 6.7 Hz, 3H), 1.29 (t, $J_{H,H}$ = 7.1 Hz, 3H), 2.75−2.88 (m, 3H), 2.96−3.16 (m, 4H), 3.34−3.44 (m, 1H), 3.80−3.90 (m, 1H), 4.03−4.13 (m, 1H), 5.56−5.61 (m, 1H), 5.82−5.92 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.5 (d, $J_{P,C}$ = 1.8 Hz), 16.3 (d, $J_{P,C}$ = 6.4 Hz), 20.5, 22.9 (d, $J_{P,C}$ = 2.7 Hz), 27.4 (d, $J_{P,C}$ = 7.3 Hz), 31.4, 39.5 (d, $J_{P,C}$ = 3.6 Hz), 42.1 (d, $J_{P,C}$ = 126.3 Hz), 59.7 (d, $J_{P,C}$ = 7.3 Hz), 118.7 (d, $J_{P,C}$ = 10.0 Hz), 123.0 (d, $J_{P,C}$ = 10.0 Hz), 127.4 (d, $J_{P,C}$ = 10.9 Hz), 139.5 (d, $J_{P,C}$ = 8.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 29.30; GC t_R = 7.86 min; GC−MS (EI, 70 eV) m/z = 285 (M^+) (0.1), 165 (44), 150 (46), 137 (11), 136 (100), 122 (16), 108 (12), 105 (20), 91 (14), 80 (11); HPLC t_R = 4.40 min; HRMS calcd for $C_{15}H_{28}NO_2P$ [M + H^+]: 286.1930; found: 286.1925.

(2-Methyl-1,4-cyclohexadien-3-yl)phosphonic Acid L-Menthyl Ester *N,N*-Diethylamide (13e). This compound was prepared according to General Procedure from **12a** (0.128 g, 0.5 mmol) and sodium (0.058 g, 2.50 mmol): yield of two diastereomers (dr = 81:19) 0.182 g (99%). Major diastereomer was isolated in pure form.

Major Diastereomer. Colorless oil; R_f = 0.74 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.91 (d, $J_{H,H}$ = 6.6 Hz, 3H), 0.93 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.89−1.02 (m, 2H), 1.05 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.11 (q, J_{H-H} = 11.6 Hz, 1H), 1.30−1.36 (m, 1H), 1.40−1.49 (m, 1H), 1.63−1.69 (m, 2H), 1.94 (s, 3H), 2.11−2.24 (m, 2H), 2.65−2.78 (m, 2H), 3.02−3.15 (m, 4H), 3.18−3.30 (m, 1H), 4.26−4.33 (m, 1H), 5.55−5.59 (m, 1H), 5.76−5.83 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.0 (d, $J_{P,C}$ = 2.7 Hz), 15.7, 21.2, 22.1, 22.8, 23.7, 25.7, 27.4 (d, $J_{P,C}$ = 6.4 Hz), 31.5, 34.2, 38.9 (d, $J_{P,C}$ = 3.6 Hz), 43.2, 44.7 (d, $J_{P,C}$ = 128.1 Hz), 49.0 (d, $J_{P,C}$ = 5.5 Hz), 75.5 (d, $J_{P,C}$ = 8.2 Hz), 122.0 (d, $J_{P,C}$ = 11.8 Hz), 123.3 (d, $J_{P,C}$ = 10.0 Hz), 126.0 (d, $J_{P,C}$ = 10.9 Hz), 129.5 (d, $J_{P,C}$ = 8.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 25.76; GC t_R = 13.51 min; GC−MS (EI, 70 eV) m/z = 367 (M^+) (0.1), 139 (23), 138 (48), 137 (19), 136 (14), 122 (22), 97 (15), 95 (20), 93 (15), 92 (15), 91 (27), 83 (100), 81 (24); $C_{21}H_{38}NO_2P$ (367.26): calcd C 68.63, H 10.42, N 3.81; found C 68.59, H 10.19, N 3.62.

Minor Diastereomer. R_f = 0.78 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.70 (d, $J_{H,H}$ = 6.6 Hz, 3H), 0.82 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.87 (d, $J_{H,H}$ = 7.3 Hz, 3H), 0.83−0.93 (m, 2H), 0.97 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.22 (q, $J_{H,H}$ = 11.4 Hz, 1H), 1.34−1.52 (m, 1H), 1.57−1.72 (m, 1H), 1.78−1.94 (m, 2H), 2.05−2.32 (m, 2H), 2.56 (s, 3H), 2.64−2.75 (m, 2H), 2.93−3.26 (m, 5H), 4.28−4.37 (m, 1H), 5.51−5.57 (m, 1H), 5.79−5.89 (m, 2H); ^{13}C NMR (126 MHz,

dx.doi.org/10.1021/jo301526k | J. Org. Chem. 2012, 77, 8244−8256

$CDCl_3$) δ 13.5 (d, $J_{P,C}$ = 1.8 Hz), 15.5, 21.2, 22.1, 22.2, 22.8, 25.5, 27.4 (d, $J_{P,C}$ = 6.4 Hz), 31.6, 34.2, 38.4 (d, $J_{P,C}$ = 5.5 Hz), 43.2, 45.1 (d, $J_{P,C}$ = 127.2 Hz), 49.0 (d, $J_{P,C}$ = 5.5 Hz), 74.9 (d, $J_{P,C}$ = 7.3 Hz), 122.8 (d, $J_{P,C}$ = 11.8 Hz), 126.5 (d, $J_{P,C}$ = 10.0 Hz), 129.4 (d, $J_{P,C}$ = 10.0 Hz), 131.0 (d, $J_{P,C}$ = 11.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 26.56; GC t_R = 13.63 min; GC–MS (EI, 70 eV) m/z = 367 (M^+) (0.1), 139 (24), 138 (36), 137 (11), 136 (13), 122 (13), 97 (14), 95 (16), 93 (10), 92 (17), 91 (24), 83 (100), 81 (21).

(2-Ethyl-1,4-cyclohexadien-3-yl)phosphonic Acid L-Menthyl Ester *N,N*-Diethylamide (13f). This compound was prepared according to General Procedure from **12b** (0.128 g, 0.5 mmol) and sodium (0.058 g, 2.50 mmol): yield of two diastereomers (dr = 68:32) 0.147 g (77%). Isolated as a mixture of two diastereomers.

Major Diastereomer. R_f = 0.79 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.85 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.91 (d, $J_{H,H}$ = 6.6 Hz, 3H), 0.92 (t, $J_{H,H}$ = 7.3 Hz, 6H), 0.92–1.00 (m, 1H), 0.93 (d, $J_{H,H}$ = 6.9 Hz, 3H), 1.00–1.07 (m, 1H), 1.05 (t, $J_{H,H}$ = 7.1 Hz, 3H), 1.23–1.39 (m, 1H), 1.40–1.51 (m, 1H), 1.61–1.72 (m, 2H), 1.92–1.95 (m, 1H), 2.08–2.30 (m, 2H), 2.66–2.77 (m, 2H), 2.91–3.15 (m, 6H), 3.16–3.30 (m, 1H), 4.25–4.38 (m, 1H), 5.55–5.59 (m, 1H), 5.76–5.82 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 12.1, 14.0 (d, $J_{P,C}$ = 2.7 Hz), 15.7, 21.2, 22.1, 22.8, 23.7, 25.7, 27.4 (d, $J_{P,C}$ = 4.5 Hz), 31.5, 34.2, 38.9 (d, $J_{P,C}$ = 3.6 Hz), 43.2 (d, $J_{P,C}$ = 1.8 Hz), 44.7 (d, $J_{P,C}$ = 127.2 Hz), 49.0 (d, $J_{P,C}$ = 6.4 Hz), 75.6 (d, $J_{P,C}$ = 8.2 Hz), 122.1 (d, $J_{P,C}$ = 10.9 Hz), 126.1 (d, $J_{P,C}$ = 10.9 Hz), 129.4 (d, $J_{P,C}$ = 9.1 Hz), 133.5 (d, $J_{P,C}$ = 7.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 25.87; GC t_R = 13.68 min; GC–MS (EI, 70 eV) m/z = 381 (M^+) (0.1), 139 (25), 138 (56), 137 (26), 136 (15), 122 (28), 97 (15), 95 (15), 91 (18), 83 (100), 81 (21).

Minor Diastereomer. R_f = 0.79 ($CHCl_3$/MeOH = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.90 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.90 (t, $J_{H,H}$ = 7.3 Hz, 6H), 0.91 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.92–1.00 (m, 1H), 1.00–1.07 (m, 1H), 1.07 (t, $J_{H,H}$ = 7.1 Hz, 3H), 1.23–1.39 (m, 1H), 1.40–1.51 (m, 1H), 1.61–1.72 (m, 2H), 1.88–1.92 (m, 1H), 2.08–2.30 (m, 2H), 2.66–2.77 (m, 2H), 2.91–3.15 (m, 6H), 3.16–3.30 (m, 1H), 4.25–4.38 (m, 1H), 5.51–5.55 (m, 1H), 5.82–5.88 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 12.2, 14.1 (d, $J_{P,C}$ = 1.8 Hz), 15.6, 21.2, 22.2, 22.8, 23.8, 25.5, 27.4 (d, $J_{P,C}$ = 5.5 Hz), 31.5, 34.1, 39.2 (d, $J_{P,C}$ = 3.4 Hz), 43.2 (d, $J_{P,C}$ = 1.8 Hz), 45.1 (d, $J_{P,C}$ = 127.2 Hz), 49.1 (d, $J_{P,C}$ = 6.4 Hz), 75.9 (d, $J_{P,C}$ = 8.2 Hz), 123.2 (d, $J_{P,C}$ = 10.0 Hz), 126.5 (d, $J_{P,C}$ = 10.9 Hz), 129.5 (d, $J_{P,C}$ = 9.1 Hz), 133.5 (d, $J_{P,C}$ = 7.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 26.66; GC t_R = 13.79 min; GC–MS (EI, 70 eV) m/z = 381 (M^+) (0.1), 139 (25), 138 (53), 137 (23), 136 (15), 122 (25), 97 (15), 95 (16), 91 (19), 83 (100), 81 (22). $C_{22}H_{40}NO_2P$ (381.53): calcd C 69.26, H 10.57, N 3.67; found C 69.51, H 10.29, N 3.69.

(2-Isopropyl-1,4-cyclohexadien-3-yl)phosphonic Acid L-Menthyl Ester *N,N*-Diethylamide (13g). This compound was prepared according to General Procedure from **12c** (0.128 g, 0.5 mmol) and sodium (0.058 g, 2.50 mmol): yield of two diastereomers (dr = 74:26) 0.124 g (63%). Isolated as a mixture of two diastereomers.

Major Diastereomer. R_f = 0.78 ($CHCl_3$/MeOH = 30:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.87–0.94 (m, 1H), 0.90 (d, $J_{H,H}$ = 6.6 Hz, 3H), 0.92 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.99 (d, $J_{H,H}$ = 6.6 Hz, 3H), 1.02–1.14 (m, 2H), 1.05 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.08 (d, $J_{H,H}$ = 6.9 Hz, 3H), 1.14–1.34 (m, 1H), 1.36–1.50 (m, 1H), 1.60–1.71 (m, 2H), 2.09–2.24 (m, 2H), 2.66–2.88 (m, 2H), 2.94–3.14 (m, 5H), 3.32–3.47 (m, 1H), 4.20–4.30 (m, 1H), 5.53–5.63 (m, 1H), 5.76–5.84 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.1 (d, $J_{P,C}$ = 1.8 Hz), 15.6, 20.5, 21.2, 22.1, 22.7, 23.0 (d, $J_{P,C}$ = 2.7 Hz), 25.6, 27.4 (d, $J_{P,C}$ = 7.3 Hz), 31.5, 31.6, 34.2 (d, $J_{P,C}$ = 1.8 Hz), 39.2 (d, $J_{P,C}$ = 3.6 Hz), 42.5 (d, $J_{P,C}$ = 127.2 Hz), 43.2, 48.9 (d, $J_{P,C}$ = 6.4 Hz), 75.5 (d, $J_{P,C}$ = 8.2 Hz), 118.3 (d, $J_{P,C}$ = 11.8 Hz), 123.6 (d, $J_{P,C}$ = 10.0 Hz), 126.9 (d, $J_{P,C}$ = 10.0 Hz), 139.8 (d, $J_{P,C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 26.07; GC t_R = 11.57 min; GC–MS (EI, 70 eV) m/z = 395 (M^+) (0.1), 139 (26), 138 (64), 137 (26), 136 (16), 122 (32), 120 (15), 105 (15), 97 (15), 95 (11), 83 (100), 81 (19), 79 (18), 73 (10), 72 (17), 69 (26), 58 (15), 57 (32), 55 (37), 44 (11), 43 (53), 41 (27); HPLC t_R = 20.00 min; HRMS calcd for $C_{23}H_{42}NO_2P$ [M + H^+]: 396.3026; found: 396.3051.

Minor Diastereomer. R_f = 0.78 ($CHCl_3$/MeOH = 30:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.81 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.87–0.95 (m, 1H), 0.90 (d, $J_{H,H}$ = 7.3 Hz, 3H), 0.94 (d, $J_{H,H}$ = 6.6 Hz, 3H), 0.98 (d, $J_{H,H}$ = 6.9 Hz, 3H), 1.02–1.15 (m, 2H), 1.08 (t, $J_{H,H}$ = 7.2 Hz, 6H), 1.22 (d, $J_{H,H}$ = 6.9 Hz, 3H), 1.21–1.36 (m, 1H), 1.36–1.50 (m, 1H), 1.61–1.72 (m, 2H), 2.06–2.30 (m, 2H), 2.66–2.79 (m, 2H), 2.96–3.20 (m, 5H), 3.30–3.43 (m, 1H), 4.24–4.33 (m, 1H), 5.55–5.60 (m, 1H), 5.85–5.90 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.2 (d, $J_{P,C}$ = 2.7 Hz), 15.6, 20.4, 21.2, 22.2, 22.7, 22.8 (d, $J_{P,C}$ = 3.6 Hz), 25.2, 27.5 (d, $J_{P,C}$ = 7.3 Hz), 31.3, 31.5, 34.1, 39.4 (d, $J_{P,C}$ = 2.7 Hz), 43.1 (d, $J_{P,C}$ = 128.1 Hz), 43.6, 49.1 (d, $J_{P,C}$ = 6.4 Hz), 75.7 (d, $J_{P,C}$ = 8.2 Hz), 118.7 (d, $J_{P,C}$ = 10.9 Hz), 123.3 (d, $J_{P,C}$ = 10.0 Hz), 127.2 (d, $J_{P,C}$ = 10.0 Hz), 140.1 (d, $J_{P,C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 26.77; GC t_R = 11.62 min; GC–MS (EI, 70 eV) m/z = 395 (M^+) (0.1), 139 (26), 138 (61), 137 (23), 136 (16), 122 (30), 120 (14), 105 (15), 97 (14), 95 (11), 83 (100), 81 (18), 79 (17), 72 (15), 69 (26), 58 (14), 57 (32), 55 (37), 44 (11), 43 (50), 41 (27); HPLC t_R = 20.00 min; HRMS calcd for $C_{23}H_{42}NO_2P$ [M + H^+]: 396.3026; found: 396.3051.

(2-Trimetrylsilyl-1,4-cyclohexadien-3-yl)phosphonic Acid L-Menthyl Ester *N,N*-Diethylamide (13h). This compound was prepared according to General Procedure from **12f** (0.128 g, 0.5 mmol) and sodium (0.058 g, 2.50 mmol): yield 0.168 g (79%). Only the major diastereomer was isolated from the reaction mixture.

Major Diastereomer. Pale yellow oil; R_f = 0.84 ($CHCl_3$/MeOH = 30:1); $[\alpha]_D$ = 3.23 (*c* 0.65, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.17 (s, 9H), 0.78 (d, $J_{H,H}$ = 6.9 Hz, 3H), 0.87 (d, $J_{H,H}$ = 7.3 Hz, 3H), 0.89 (d, $J_{H,H}$ = 6.6 Hz, 3H), 0.90–1.07 (m, 3H), 1.09 (t, $J_{H,H}$ = 7.1 Hz, 6H), 1.19–1.27 (m, 1H), 1.35–1.44 (m, 1H), 1.59–1.67 (m, 2H), 2.04–2.11 (m, 1H), 2.17–2.27 (m, 1H), 2.60–2.83 (m, 2H), 3.08–3.15 (m, 4H), 3.36–3.46 (m, 1H), 4.16–4.24 (m, 1H), 5.82–5.92 (m, 2H), 6.15–6.19 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ −0.3, 14.2 (d, $J_{P,C}$ = 1.8 Hz), 15.8, 21.2, 22.2, 22.7, 24.6, 28.4 (d, $J_{P,C}$ = 7.3 Hz), 31.5, 34.1, 39.3 (d, $J_{P,C}$ = 3.6 Hz), 42.9, 43.9 (d, $J_{P,C}$ = 129.9 Hz), 49.1 (d, $J_{P,C}$ = 5.5 Hz), 75.0 (d, $J_{P,C}$ = 8.2 Hz), 123.8 (d, $J_{P,C}$ = 9.1 Hz), 126.4 (d, $J_{P,C}$ = 10.9 Hz), 135.7 (d, $J_{P,C}$ = 8.2 Hz), 137.5 (d, $J_{P,C}$ = 10.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 25.95; GC t_R = 13.54 min; GC–MS (EI, 70 eV) m/z = 139 (34), 138 (62), 137 (26), 136 (12), 135 (17), 122 (20), 120 (10), 97 (15), 95 (12), 83 (100), 81 (19); $C_{23}H_{44}NO_2PSi$ (425.67): calcd C 64.90, H 10.42, N 3.29; found C 65.01, H 10.60, N 3.30.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H, ^{13}C, ^{31}P, and GC–MS spectra of pure compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the National Research Centre (research grant No. N N204 3539 40) is kindly acknowledged. Authors are grateful to Dr. Duncan Carmichael for his guidance during the preparation of manuscript.

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