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Substitution of Secondary Benzylic Phosphates with Diarylmethyl Anions

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ABSTRACT

Substitution of diethyl and diphenyl benzylic phosphates, Alk-CH(Ar^1)OP(O)$(OR)_2$ (R = Et, Ph; Alk = Me, Et, *i*-Pr; Ar^1 = aryl), with the anions derived from Ar^2CH_2 (Ph_2CH_2,9*H*-xanthene and fluorene) and *n*-BuLi at −15 °C was studied. For phosphates with Me as an Alk, diethyl phosphates produced Me-CH(Ar^1)$CH(Ar^2)_2$ (Ar^1 = 4-halo-, 4-CN, 4-Me-, 2-Me, 2-Br-, 3-MeO-phenyl and 2-naphthyl). However, an unwanted substitution at the Et group competed with phosphates of Alk = Et- and *i*-Pr. Fortunately, the corresponding diphenyl phosphates cleanly underwent the desired substitution. Two enantioenriched phosphates, MeCH(Ph)OP(O)$(OEt)_2$ and EtCH(Ph)OP(O)$(OPh)_2$, proceeded with complete inversion of the stereochemistry.

1. Introduction

Recently, we reported that the substitution of secondary allylic and propargylic phosphates **1** and **2** with Ar_2CHLi (Ar: aryl) proceeded with inversion of the stereochemistry to afford **4** and **5**, respectively (Scheme 1, eq. 1) [1]. Then, the substitution was extended to secondary alkyl phosphates **3**, in which the diphenyl phosphate group was the optimized leaving group to produce **6** with the reactivity comparable to those of **1** and **2** (Scheme 1, eq. 2) [2]. The aryl groups in these products would shape sterically and electronically specific spaces that would create performance materials and ligands binding to transition metal catalysts. In this context, we were interested in the substitution of secondary benzylic phosphates **7** (Scheme 1, eq. 3). Three aryl groups and one stereogenic carbon in a tiny space of the products **8** would provide a specific space that is distinctly different from those of **4**, **5**, and **6**. On the other hand, this class of structure is involved in quebecol [3] and lasofoxifene [4], which are a potential antioxidant and an estrogen receptor modulator, respectively. Previously, substitutions of benzylic ammonium salt [5], chloride [6] and bromides [7], with the Ph_2CH anion have been published, however, the results are insufficient to show a scope of the substrates/Ar_2CH anions. The Ni-catalyzed diarylation of alkenylarenes [4c] also produces compounds of type **8**. Since the preparation of substrates and the scope of substrates/reagents are different from those of the present substitution, these reactions would be complementary. In addition, phosphate group have been utilized for C–C bond forming reactions at benzylic carbons [8], showing the high potency as the leaving group. However, structures of the products are rather simpler than that of **8**.

The aryl and alkyl groups in **7** (abbreviated as Ar^1 and Alk) are influencers to the present substitution, but degree of the influence was uncertain. Consequently, we studied the substitution of diethyl and diphenyl phosphates with Ar_2CHLi. Furthermore, the stereochemical outcome was evaluated by using enantioenriched phosphates. Herein, we report results of these studies.

2. Results and discussion

Diethyl and diphenyl phosphates that possess a Me, Et, or *i*-Pr substituent as Alk in **7** were prepared from the corresponding ketone by reduction with $NaBH_4$ and subsequent phosphorylation with ClP(O)$(OEt)_2$ or ClP(O)$(OPh)_2$ (Scheme 2). Enantioenriched alcohol (*R*)-**10a** (>98% ee) was obtained from a company and transferred to (*R*)-**7a**, while (*S*)-**7d** (86% ee as determined by chiral HPLC) was synthesized by the asymmetric transfer hydrogenation [9] of ketone **9c** followed by phosphorylation (Scheme 2). The Ph_2CHLi anion was prepared from Ph_2CH_2 and *n*-BuLi in THF at 0 °C

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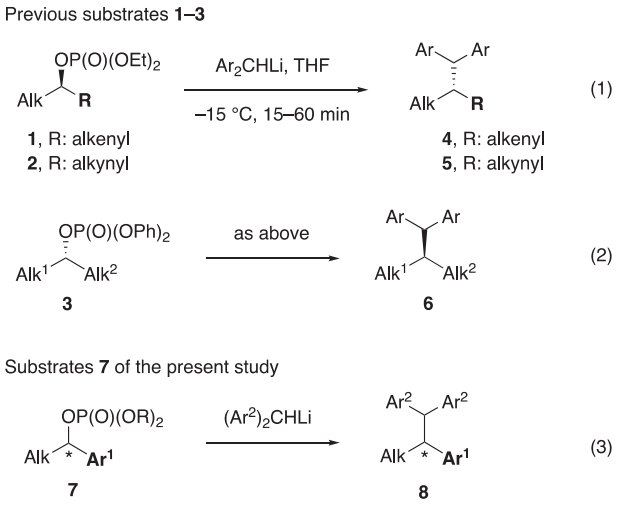
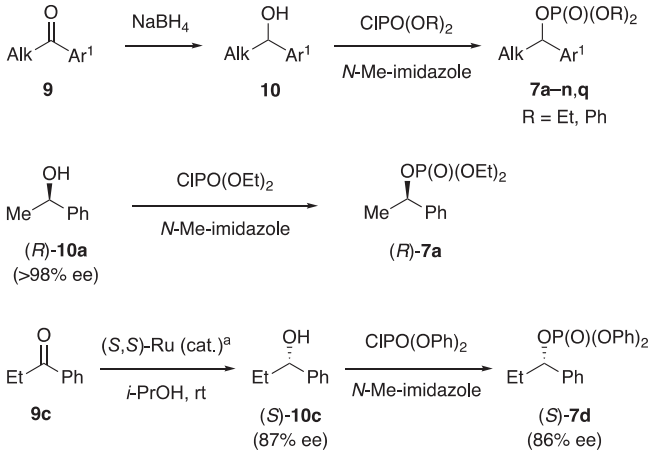


Scheme 1. Previous and present substrates for the substitution with diarylmethyllithiums.



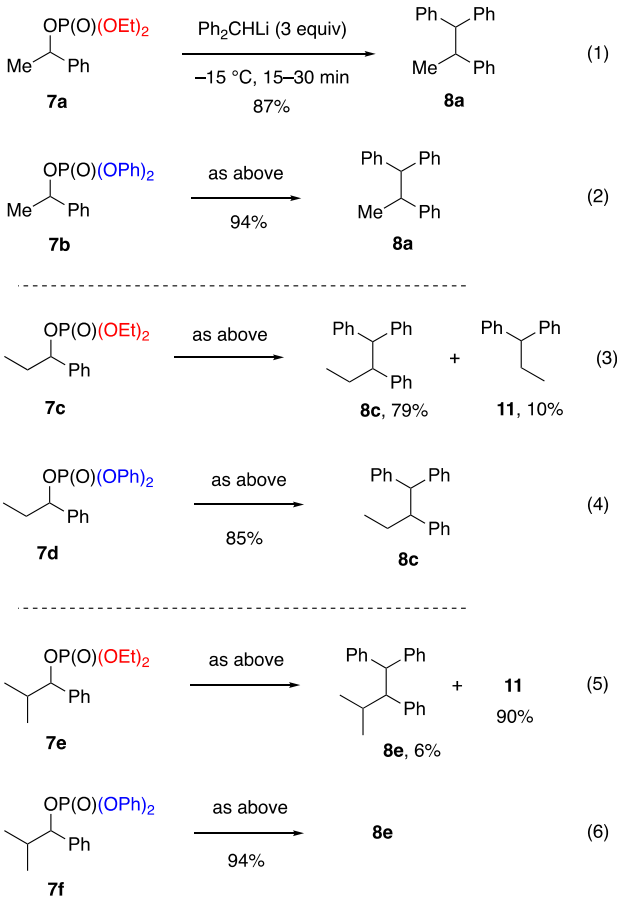
Scheme 2. Synthesis of phosphates. [a] RuCl[(*S*,*S*)-TsDPEN](*p*-cymene).

to rt for 15 min, and used for the substitution, which was carried out at −15 °C or −15 to 0 °C for 15–30 min.

Racemic diethyl phosphate **7a** afforded **8a** in 87% yield (Scheme 3, Eq. (1)). Similarly, diphenyl phosphate **7b** produced **8a** in a comparable yield (Eq. (2)). We also attempted a substitution of the corresponding Boc ester (MeCPh(H)-OBoc) with Ph_2CHLi in the presence or absence of a palladium catalyst, but the corresponding alcohol was produced in vain.

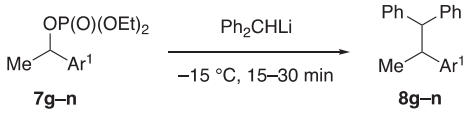
Next, diethyl phosphate **7c** possessing the Et substituent was subjected to the substitution with Ph_2CHLi to afford a mixture of **8c** and **11** in 79% and 10% yields, respectively (Eq. (3)), indicating that the relative reactivity of the benzylic carbon was slightly decreased by the ethyl substituent. A worse result was the substitution of diethyl phosphate **7e**, in which the substitution at the benzylic carbon was substantially blocked by the *i*-Pr group, giving **11** as a major product (Eq. (5)). In contrast, the diphenyl phosphates **7d** and **7f** afforded the desired products **8c** and **8e**, respectively, in good yields [2] (Eqs. (4) and (6)).

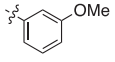
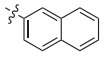
The protocol mentioned above was applied to several benzylic phosphates **7g**–**n** in racemic forms to evaluate the effect of different substituents on the reactivity (Table 1). In all entries, the diethyl phosphate group was used as the leaving group, and the substitutions were carried out at −15 °C for 15 min. Phosphates



Scheme 3. Preliminary study of the substitution with Ph_2CHLi.[a] [a] Generated from Ph_2CH_2 and *n*-BuLi.

Table 1
Reaction of benzylic phosphates with Ph_2CHLi.[a]



entry	Ar^1	Phosphate	product	yield
1	 X = F	**7g**	**8g**	91%
2	X = Cl	**7h**	**8h**	89%
3	X = Br	**7i**	**8i**	79%
4	X = CN	**7j**	**8j**	86%
5	X = Me	**7k**	**8k**	86%
6		**7l**	**8l**	80%
7		**7m**	**8m**	72%
8		**7n**	**8n**	86%

[a] Three equiv of Ph_2CHLi were used.

7g–**i** possessing the halogen atoms at the 4-position of the phenyl group were as reactive as **7a**, and produced **8g**–**i** in 79–91% yields

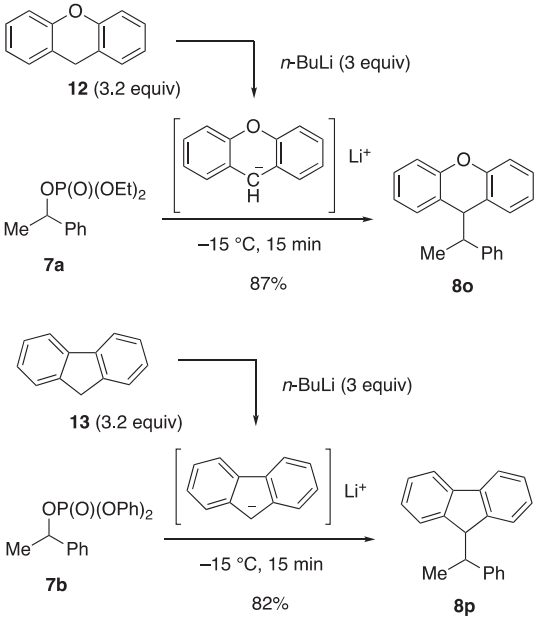
(entries 1–3). The CN group on the phenyl ring did not affect the reactivity, producing **8j** in 86% yield (entry 4). 4- and 2-Tolyl phosphates **7k** and **7ℓ** were good substrates as well to produce **8k** and **8ℓ** in 86% and 80% yields, respectively, indicating that the methyl group at the 2-position was not a severe obstacle (entries 5 and 6). Phosphate **7m** with the electron-donating MeO substituent was transformed to **8m** in 72% yield (entry 7). 2-Naphtyl phosphate **7n** also underwent the substitution to furnish **8n** in 86% yield (entry 8). In contrast to these substrates, diethyl phosphates from MeCH(Ar)OH (Ar = 4-methoxyphenyl, naphthalen-1-yl, and 2-furyl) could not be prepared because of their instability during isolation or routine purification by chromatography. In all cases, the substitution at the Et group did not take place as **11** was not observed in the ^{1}H NMR spectra.

Diarylmethyl anions participated in the substitution as summarized in Scheme 4. Thus, 9*H*-xanthene (**12**) was changed to the anion with *n*-BuLi and the substitution with **7a** afforded **8o** in a good yield. Similarly, the anion derived from fluorene (**13**) produced **8p**.

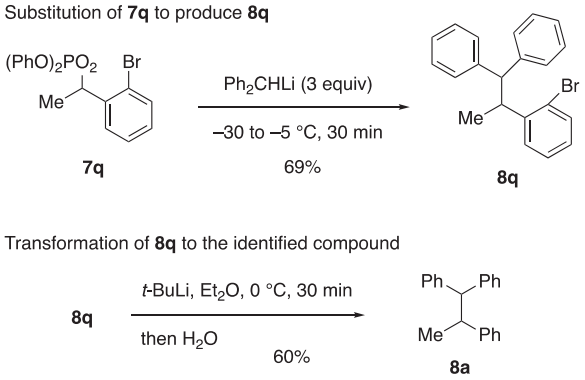
o-Br substituted benzylic phosphate **7q** was not an exception, and produced **8q** in 69% yield (Scheme 5). Although the chemical shifts and integrations in ^{1}H and ^{13}C NMR spectra supported the structure, the C*H*$_3$ signal in the ^{1}H NMR spectrum did not appear as expected doublet, but unusually as a broad singlet. The methyl and methine carbons in the ^{13}C NMR spectrum were seen as somewhat broad singlets. Because of the unusual NMR spectra, the structure of the substitution product (**8q**) was further confirmed by changing to the unambiguously-identified **8a** by the lithium-bromine exchange followed by protonolysis. It is likely that the rotations around the single bonds in **8q** are substantially restricted, and that a specific chiral space for chiral ligands is produced. Such a chiral space would be The bromine atom on the phenyl ring would be substituted by heteroatom groups such as phosphorus and nitrogen groups and 1-acetylenes for further functionalization.

To clarify the stereochemistry of the substitution, (*R*)-**7a** and (*S*)-**7d** were prepared by the methods summarized in Scheme 2, and subjected to the substitution with Ph$_2$CHLi (Scheme 6). The substitution of (*R*)-**7a** gave (*R*)-**8a**, and the enantiomeric purity of 99% ee was determined by chiral HPLC analysis. The *R* configuration was established by comparing the specific rotation with the published data [5], and 100% enantiospecificity (es) [10] of the substitution was calculated from the enantiomeric excess (ee), thus unambiguously confirming the complete inversion of the substitution reaction. Similarly, the substitution of (*S*)-**7d** proceeded with inversion to produce (*S*)-**8c** in 86% yield with 100% es. The absolute configuration was determined by the specific rotation: $[\alpha]_{364}^{21}$ −22 (*c* 0.89, CHCl$_3$) and $[\alpha]_{364}^{21}$ −51 (*c* 0.94, EtOH); lit [11]. $[\alpha]_{364}^{21}$ −21.8 (*c* 2.2, CHCl$_3$) and $[\alpha]_{364}^{21}$ −65.7 (*c* 1, EtOH).

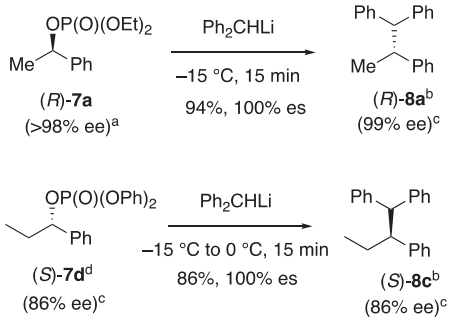
As mentioned in the introduction, similar substitutions have been reported. Here, the present substitution is compared with those reactions. The substitution of ammonium salt (*R*)-**14** with Ph$_2$CHLi afforded (*R*)-**8a** in 65% yield with 100% es (Scheme 7, Eq. (1)) [5]. The ammonium leaving group was prepared from the *primary* benzyl amines [12] by Eschweiler-Clarke reaction [13] followed by quaternarization with MeI. By analogy with the results



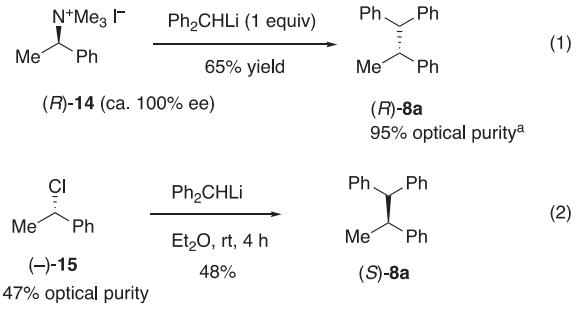
Scheme 4. Substitution reaction of **7a** with diarylmethyl anions.



Scheme 5. Substitution of **7q** with Ph$_2$CHLi.



Scheme 6. Study on the stereochemistry. [a] Described on a summary sheet by TCI. [b] The configuration was determined based on the specific rotation. [c] Determined by chiral HPLC analysis. [d] Prepared by the asymmetric reduction.



Scheme 7. Literature substitution with Ph$_2$CHLi. [a] Based on the maximum value ($[\alpha]_D^{23}$ +30.99 (acetone)) after five recrystallizations.[5]

mentioned above in Eqs. (3) and (5) of Scheme 3, Ph_2CHLi might attack the methyl carbon of the ammonium group when a substituent at the benzyl carbon is larger than the methyl group. However, quaternarization of the nitrogen atom with the phenyl group or a bulky alkyl group would be difficult. Enantioenriched benzylic chloride (−)-**15** is also a good substrate for the substitution with Ph_2CH anion (equiv not given, Eq. (2)) [6]. Unfortunately, the reported enantiomeric purity of (*S*)-**8a** is ambiguous [14]. Furthermore, long reaction times for the synthesis of the enantioenriched chloride from the benzylic alcohol with $POCl_3$ seems synthetically less convenient [15], whereas the cyclopropenone-catalyzed conversion of alcohols with $(COCl)_2$ [16] and the reaction of organoboranes with trichloroisocyanuric acid [17] are at the research level [18]. The substitution of the corresponding benzylic bromide with Ph_2CHK in liq. NH_3 was concluded to proceed via the radical mechanism [7]. In contrast, *sec*-benzylic alcohols in enantioenriched forms are available by several methods [19], and hence the present method is advantageous to the methods via the benzylic ammonium salt and chloride.

3. Conclusions

The substitution of benzylic phosphates **7**, Alk-CH(Ar^1)$OP(O)(OR)_2$, with lithium anions derived from Ph_2CH_2, 9*H*-xanthene and fluorene with *n*-BuLi was studied to find that diethyl phosphates (R = Et) possessing the Me substituent as an Alk group produced the desired products, whereas diphenyl phosphates (R = Ph) were suited for **7** possessing Et or *i*-Pr groups as an Alk group, bigger groups than Me. Two phosphates of $MeCH(Ph)OP(O)(OEt)_2$ and $EtCH(Ph)OP(O)(OPh)_2$ derived from the corresponding enantioenriched alcohols proceeded with complete inversion of the stereochemistry.

4. Experimental

4.1. General

The ^1H (300, 400 MHz) and ^{13}C NMR (75, 100 MHz) spectroscopic data were recorded in $CDCl_3$ using Me_4Si (δ = 0 ppm) and the centerline of the triplet (δ = 77.1 ppm), respectively, as internal standards. Signal patterns are indicated as br s (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Coupling constants (*J*) are given in Hertz (Hz). Chemical shifts of carbons are accompanied by minus (for C and CH_2) and plus (for CH and CH_3) signs of the attached proton test (APT) experiment. High-resolution mass spectroscopy (HRMS) was performed with a double-focusing mass spectrometer with an ionization mode of positive FAB or EI as indicated for each compound. The following solvents were distilled before use: THF (from Na/benzophenone), Et_2O (from Na/benzophenone) and CH_2Cl_2 (from CaH_2). Products were purified by chromatography on silica gel (Kanto, spherical silica gel 60N). (*R*)-(+)-1-Phenylethyl alcohol ((*R*)-**10a**) (>98% ee) was purchased from TCI.

4.2. Synthesis of benzylic phosphates

4.2.1. General procedure for reduction of ketones and subsequent phosphorylation

To an ice-cold solution of an alkyl aryl ketone (1 equiv) in MeOH was added $NaBH_4$ (ca. 1.5 equiv) portionwise. The mixture was stirred at rt for 30–60 min and diluted with saturated NH_4Cl. The resulting mixture was extracted with EtOAc repeatedly. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The alcohol thus obtained was passed through a short column of silica gel (hexane/EtOAc).

To an ice-cold solution of a benzylic alcohol (1 equiv) in CH_2Cl_2 were added *N*-methylimidazole (1.2–2 equiv) and diethyl or diphenyl chlorophosphate (1.1–1.5 equiv). The solution was stirred at rt and diluted with saturated $NaHCO_3$ with vigorous stirring. The resulting mixture was extracted with EtOAc several times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The residual oil was purified by chromatography on silica gel (hexane/EtOAc) to give the phosphate.

4.2.2. Diethyl (1-phenylethyl) phosphate (*7a*)

According to the general procedure for the reduction/phosphorylation of ketones, acetophenone (**9a**) (0.50 mL, 4.30 mmol) was reduced with $NaBH_4$ (247 mg, 6.54 mmol) in MeOH (8 mL) at rt for 1 h to afford alcohol **10a**, which was converted to phosphate **7a** (938 mg, 85% yield) with diethyl chlorophosphate (1.25 mL, 8.69 mmol) and *N*-methylimidazole (0.85 mL, 10.8 mmol) in CH_2Cl_2 (10 mL) at rt for 12 h: liquid; R_f 0.07 (hexane/EtOAc 2:1); IR (neat) 1455, 1263, 1029, 980 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.18 (dt, J = 1.2, 7.0 Hz, 3 H), 1.28 (dt, J = 1.2, 7.0 Hz, 3 H), 1.63 (d, J = 6.4 Hz, 3 H), 3.88–4.17 (m, 4 H), 5.48 (dq, J = 7.5, 6.4 Hz, 1 H), 7.26–7.42 (m, 5 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ 15.9 (+) (d, J = 7 Hz), 16.0 (+) (d, J = 7 Hz), 24.2 (+) (d, J = 5 Hz), 63.5 (−) (d, J = 6 Hz), 76.7 (+) (d, J = 6 Hz), 125.8 (+), 128.1 (+), 128.4 (+), 141.7 (−) (d, J = 5 Hz); HRMS (FAB^+): m/z calcd for $C_{12}H_{20}O_4P$ [$(M+H)^+$] 259.1099, found 259.1094. The ^1H and ^{13}C NMR spectra were consistent with those reported [8a,20].

4.2.3. (*R*)-Diethyl (1-phenylethyl) phosphate ((*R*)-*7a*)

According to the general procedure for the phosphorylation of alcohols, a mixture of (*R*)-**10a** (>98% ee, 0.24 mL, 1.99 mmol) (purchased from TCI, Jpn), diethyl chlorophosphate (0.43 mL, 2.99 mmol) and *N*-methylimidazole (0.28 mL, 3.55 mmol) in CH_2Cl_2 (2 mL) was stirred at rt for 12 h to give phosphate (*R*)-**7a** (484 mg, 94% yield): The ^1H and ^{13}C NMR spectra were consistent with those of the racemic phosphate **7a**.

4.2.4. Diethyl (1-phenylpropyl) phosphate (*7c*)

According to the general procedure for the reduction/phosphorylation of ketones, propiophenone (**9c**) (251 mg, 1.87 mmol) was reduced with $NaBH_4$ (114 mg, 3.02 mmol) in MeOH (2 mL) at rt for 30 min to afford alcohol **10c**, which was subjected to phosphorylation with diethyl chlorophosphate (0.405 mL, 2.82 mmol) and *N*-methylimidazole (0.270 mL, 3.42 mmol) in CH_2Cl_2 (2 mL) at rt for 12 h to afford phosphate **7c** (331 mg, 65% yield over two steps): liquid; R_f 0.24 (hexane/EtOAc 1:1); ^1H NMR (300 MHz, $CDCl_3$) δ 0.91 (t, J = 7.2 Hz, 3 H), 1.13 (dt, J = 1.2, 7.2 Hz, 3 H), 1.25 (dt, J = 1.2, 7.2 Hz, 3 H), 1.76–2.00 (m, 2 H), 3.79–4.15 (m, 4 H), 5.21 (q, J = 6.9 Hz, 1 H), 7.26–7.38 (m, 5 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ 9.7 (+), 15.9 (+) (d, J = 7 Hz), 16.0 (+) (d, J = 7 Hz), 31.0 (−) (d, J = 6 Hz), 63.47 (−) (d, J = 6 Hz), 63.55 (−) (d, J = 6 Hz), 81.9 (+) (d, J = 6 Hz), 126.5 (+), 128.1 (+), 128.4 (+), 140.4 (−) (d, J = 3 Hz). The literature ^1H NMR data (coupling constants) was slightly revised, while the ^{13}C NMR data was consistent with the literature data [21].

4.2.5. (*S*)-Diphenyl (1-phenylpropyl) phosphate [(*S*)-*7d*]

A mixture of RuCl[(*S*,*S*)-TsDPEN](*p*-cymene) (42 mg, 0.066 mmol) and KOH (ca. 103 mg, 1.84 mmol) in CH_2Cl_2 (5 mL) was stirred at rt for 30 min and washed with H_2O several times. The CH_2Cl_2 solution was transferred to another flask with CH_2Cl_2. The solution was dried over CaH_2. The resulting mixture was filtered and then concentrated to afford a purple solid. The solid was diluted with *i*-PrOH (5 mL) and propiophenone (**9c**) (0.400 mL, 3.01 mmol) in *i*-PrOH (5 mL) was added. After being stirred at rt for 6 h, the mixture was concentrated to afford a residue, which was

purified by chromatography on silica gel (hexane/EtOAc 9:1) to give alcohol (*S*)-**10c** (321 mg, 78%): 87% ee by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 99/1, 1.0 mL/min, 35 °C, t_R/min = 19.9 (*S*-isomer, minor), 20.7 (*R*-isomer, major)); liquid; R_f 0.38 (hexane/EtOAc 4:1); $[\alpha]_D^{23}$ −37 (*c* 1.03, hexane); lit [22]. $[\alpha]_D^{26}$ −49.0 (*c* 1.01, hexane) for (*S*)-**10c** of 95% ee); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.92 (t, J = 7.5 Hz, 3 H), 1.68–1.92 (m, 3 H), 4.60 (dt, J = 2.9, 6.6 Hz, 1 H), 7.25–7.42 (m, 5 H). The ^{1}H NMR spectrum was identical with that reported [22].

According to the general procedure for the phosphorylation of alcohols, the above alcohol (187 mg, 1.37 mmol) was subjected to phosphorylation with diphenyl chlorophosphate (0.426 mL, 2.06 mmol) and *N*-methylimidazole (0.195 mL, 2.47 mmol) in CH_2Cl_2 (3 mL) at rt for 3 h to afford diphenyl phosphate (*S*)-**7d** (413 mg, 82%): 86% ee by HPLC (Chiralpak AD-H, hexane/*i*-PrOH = 70/30, 1.0 mL/min, 35 °C, t_R/min = 9.3 (*R*-isomer, minor), 19.8 (*S*-isomer, major); liquid; R_f 0.38 (hexane/EtOAc 4:1); $[\alpha]_D^{23}$ −21 (*c* 0.98, $CHCl_3$); IR (neat) 1591, 1490, 1192, 1012 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, J = 7.6 Hz, 3 H), 1.83–1.96 (m, 1 H), 1.97–2.10 (m, 1 H), 5.45 (q, J = 7.1 Hz, 1 H), 6.94–6.99 (m, 2 H), 7.07–7.38 (m, 13 H); ^{13}C–APT NMR (100 MHz, $CDCl_3$) δ 9.5 (+), 30.7 (−) (d, J = 7 Hz), 84.01 (+) (d, J = 7 Hz), 119.9 (+) (d, J = 5 Hz), 120.1 (+) (d, J = 5 Hz), 125.0 (+) (d, J = 5 Hz), 126.5 (+), 128.31 (+), 128.34 (+), 129.5 (+), 129.6 (+), 139.3 (−) (d, J = 4 Hz), 150.4 (−) (d, J = 7 Hz), 150.5 (−) (d, J = 7 Hz); HRMS (FAB$^+$): m/z calcd for $C_{21}H_{21}O_4PNa$ [(M+Na)$^+$] 391.1075, found 391.1067.

4.2.6. 2-Methyl-1-phenylpropyl diphenyl phosphate (*7f*)

According to the general procedure for the reduction/phosphorylation of ketones, isobutyrophenone (**9e**) (287 mg, 1.94 mmol) was reduced with $NaBH_4$ (88 mg, 2.33 mmol) in MeOH (2 mL) at rt for 30 min to afford the corresponding alcohol **10e**, which was converted to diphenyl phosphate **7f** (519 mg, 70% yield from the ketone) with diphenyl chlorophosphate (0.420 mL, 2.03 mmol) and *N*-methylimidazole (0.183 mL, 2.32 mmol) in CH_2Cl_2 (2 mL) at rt for 12 h: liquid; R_f 0.75 (hexane/EtOAc 1:1); IR (neat) 1591, 1490, 1192, 1012, 953 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.77 (d, J = 6.9 Hz, 3 H), 0.98 (d, J = 6.6 Hz, 3 H), 2.07–2.24 (m, 1 H), 5.22 (t, J = 7.5 Hz, 1 H), 6.93 (dm, J = 7.5 Hz, 2 H), 7.04–7.36 (m, 13 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ 18.4 (+) (d, J = 7 Hz), 34.8 (+) (d, J = 7 Hz), 87.9 (+) (d, J = 7 Hz), 120.0 (+) (d, J = 5 Hz), 120.2 (+) (d, J = 5 Hz), 125.0 (+) (d, J = 1 Hz), 125.2 (+) (d, J = 1 Hz), 127.2 (+), 128.2 (+), 128.3 (+), 129.5 (+), 129.7 (+), 138.5 (−) (d, J = 2 Hz), 150.5 (−) (d, J = 7 Hz), 150.7 (−) (d, J = 7 Hz); HRMS (EI$^+$): m/z calcd for $C_{22}H_{23}O_4P$ [M$^+$] 382.1334, found 382.1326.

4.2.7. Diethyl (1-(4-fluorophenyl)ethyl) phosphate (*7g*)

According to the general procedure for the reduction/phosphorylation of ketones, 4-fluorophenyl methyl ketone (**9g**) (217 mg, 1.57 mmol) was reduced with $NaBH_4$ (89 mg, 2.36 mmol) in MeOH (2 mL) at rt for 30 min to afford the corresponding alcohol, which was subjected to phosphorylation with diethyl chlorophosphate (0.34 mL, 2.36 mmol) and *N*-methylimidazole (0.225 mL, 2.85 mmol) in CH_2Cl_2 (2 mL) at rt for 13 h to afford phosphate **7g** (353 mg, 81% yield over two steps): liquid; R_f 0.28 (hexane/EtOAc 1:1); IR (neat) 1606, 1513, 1265, 1225, 1031, 982 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20 (dt, J = 1.2, 7.2 Hz, 3 H), 1.30 (dt, J = 1.2, 7.2 Hz, 3 H), 1.62 (d, J = 6.6 Hz, 3 H), 3.88–4.17 (m, 4 H), 5.47 (quint., J = 6.6 Hz, 1 H), 7.05 (t, J = 8.8 Hz, 2 H), 7.37 (dd, J = 8.8, 5.1 Hz, 2 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ 16.0 (+) (d, J = 7 Hz), 16.1 (+) (d, J = 7 Hz), 24.2 (+) (d, J = 5 Hz), 63.6 (−) (d, J = 6 Hz), 63.7 (−) (d, J = 6 Hz), 76.0 (+) (d, J = 6 Hz), 115.4 (+) (d, J = 21 Hz), 127.7 (+) (d, J = 8 Hz), 137.6 (−) (dd, J = 5, 3 Hz), 162.5 (−) (d, J = 245 Hz); HRMS (EI$^+$): m/z calcd for $C_{12}H_{18}FO_4P$ [M$^+$] 276.0927, found 276.0920.

4.2.8. 1-(4-Chlorophenyl)ethyl diethyl phosphate (*7h*)

According to the general procedure for the reduction/phosphorylation of ketones, 4-chlorophenyl methyl ketone (**9h**) (398 mg, 2.58 mmol) was reduced with $NaBH_4$ (148 mg, 3.92 mmol) in MeOH (2 mL) at rt for 30 min to afford the corresponding alcohol, which was subjected to phosphorylation with diethyl chlorophosphate (0.50 mL, 2.96 mmol) and *N*-methylimidazole (0.33 mL, 4.18 mmol) in CH_2Cl_2 (2 mL) at rt for 13 h to afford phosphate **7h** (621 mg, 91% yield over two steps): liquid; R_f 0.33 (hexane/EtOAc 1:1); IR (neat) 1600, 1493, 1263, 981, 835 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 (dt, J = 0.9, 7.2 Hz, 3 H), 1.30 (dt, J = 0.9, 7.2 Hz, 3 H), 1.61 (d, J = 6.4 Hz, 3 H), 3.90–4.18 (m, 4 H), 5.45 (dq, J = 7.5, 6.4 Hz, 1 H), 7.33 (s, 4 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ 16.0 (+) (d, J = 6 Hz), 16.1 (+) (d, J = 6 Hz), 24.2 (+) (d, J = 5 Hz), 63.66 (−) (d, J = 6 Hz), 63.70 (−) (d, J = 6 Hz), 75.8 (+) (d, J = 5 Hz), 127.3 (+), 128.6 (+), 133.8 (−), 140.3 (−) (d, J = 5 Hz); HRMS (EI$^+$): m/z calcd for $C_{12}H_{18}ClO_4P$ [M$^+$] 292.0631, found 292.0632.

4.2.9. 1-(4-Bromophenyl)ethyl diethyl phosphate (*7i*)

According to the general procedure for the reduction/phosphorylation of ketones, 4-bromophenyl methyl ketone (**9i**) (247 mg, 1.24 mmol) in MeOH (2 mL) was reduced with $NaBH_4$ (71 mg, 1.88 mmol) at rt for 30 min to afford the corresponding alcohol, which was converted to phosphate **7i** (346 mg, 80% yield over two steps) with diethyl chlorophosphate (0.27 mL, 1.88 mmol) and *N*-methylimidazole (0.18 mL, 2.28 mmol) in CH_2Cl_2 (2 mL) at rt for 13 h: liquid; R_f 0.28 (hexane/EtOAc 1:1); IR (neat) 1489, 1265, 1031, 982, 824 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.21 (dt, J = 1.0, 7.1 Hz, 3 H), 1.30 (dt, J = 1.0, 7.1 Hz, 3 H), 1.60 (d, J = 6.6 Hz, 3 H), 3.90–4.17 (m, 4 H), 5.43 (quint., J = 7.1 Hz, 1 H), 7.26 (d, J = 8.5 Hz, 2 H), 7.49 (d, J = 8.5 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 16.0 (+) (d, J = 7 Hz), 16.1 (+) (d, J = 7 Hz), 24.2 (+) (d, J = 5 Hz), 63.71 (−) (d, J = 6 Hz), 63.73 (−) (d, J = 6 Hz), 75.9 (+) (d, J = 5 Hz), 122.0 (−), 127.6 (+), 131.7 (+), 140.8 (−) (d, J = 5 Hz); HRMS (EI$^+$): m/z calcd for $C_{12}H_{18}BrO_4P$ [M$^+$] 336.0126, found 336.0127.

4.2.10. Diethyl (1-(4-cyanophenyl)ethyl) phosphate (*7j*)

According to the general procedure for the reduction/phosphorylation of ketones, 4-acetylbenzonitrile (**9j**) (230 mg, 1.58 mmol) was reduced with $NaBH_4$ (90 mg, 2.58 mmol) in MeOH (2 mL) at rt for 30 min to afford the corresponding alcohol, which was subjected to phosphorylation with diethyl chlorophosphate (0.341 mL, 2.37 mmol) and *N*-methylimidazole (0.224 mL, 2.76 mmol) in CH_2Cl_2 (2 mL) at rt for 12 h to give phosphate **7j** (336 mg, 75% yield over two steps): liquid; R_f 0.13 (hexane/EtOAc 1:1); IR (neat) 2229, 1269, 1029, 982, 841 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.23 (t, J = 7.2 Hz, 3 H), 1.32 (t, J = 7.2 Hz, 3 H), 1.63 (d, J = 6.8 Hz, 3 H), 3.94–4.20 (m, 4 H), 5.51 (quint., J = 6.8 Hz, 1 H), 7.50 (d, J = 8.3 Hz, 2 H), 7.67 (d, J = 8.3 Hz, 2 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ 16.0 (+) (d, J = 7 Hz), 16.1 (+) (d, J = 7 Hz), 24.2 (+) (d, J = 5 Hz), 63.85 (−) (d, J = 6 Hz), 63.91 (−) (d, J = 6 Hz), 75.5 (+) (d, J = 5 Hz), 111.9 (−), 118.6 (−), 126.4 (+), 132.4 (+), 147.0 (−) (d, J = 5 Hz); HRMS (EI$^+$): m/z calcd for $C_{13}H_{18}NO_4P$ [M$^+$] 283.0973, found 283.0975.

4.2.11. Diethyl (1-(p-tolyl)ethyl) phosphate (*7k*)

According to the general procedure for the reduction/phosphorylation of ketones, methyl *p*-tolyl ketone **9k** (249 mg, 1.86 mmol) was reduced with $NaBH_4$ (105 mg, 2.77 mmol) at rt for 30 min to give the corresponding alcohol, which was subjected to phosphorylation with diethyl chlorophosphate (0.400 mL, 2.78 mmol) and *N*-methylimidazole (0.265 mL, 3.36 mmol) in CH_2Cl_2 (2 mL) at rt for 12 h to afford phosphate **7k** (365 mg, 73% yield over two steps): liquid; R_f 0.35 (hexane/EtOAc 1:1); IR (neat) 1263, 1041, 980, 819 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20 (dt, J = 1.1, 7.1 Hz, 3 H), 1.29 (dt, J = 1.1, 7.1 Hz, 3 H), 1.62 (d, J = 6.6 Hz, 3 H), 2.34 (s, 3 H),

3.88–4.16 (m, 4 H), 5.45 (quint., J = 7.1 Hz, 1 H), 7.16 (d, J = 7.8 Hz, 2 H), 7.28 (d, J = 7.8 Hz, 2 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ 15.9 (+) (d, J = 7 Hz), 16.1 (+) (d, J = 7 Hz), 21.2 (+), 24.1 (+) (d, J = 5 Hz), 63.5 (−) (d, J = 6 Hz), 76.6 (+) (d, J = 6 Hz), 125.9 (+), 129.1 (+), 137.9 (−), 138.7 (−) (d, J = 5 Hz); HRMS (EI$^+$): m/z calcd for $C_{13}H_{21}O_4P$ [M$^+$] 272.1177, found 272.1177.

4.2.12. Diethyl (1-(o-tolyl)ethyl) phosphate (**7ℓ**)

According to the general procedure for the reduction/phosphorylation of ketones, methyl *o*-tolyl ketone **9ℓ** (258 mg, 1.92 mmol) was subjected to reduction with $NaBH_4$ (113 mg, 2.99 mmol) in MeOH (2 mL) at rt for 30 min to afford the corresponding alcohol, which was converted to phosphate **7ℓ** (418 mg, 80% yield over two steps) with diethyl chlorophosphate (0.415 mL, 2.89 mmol) and *N*-methylimidazole (0.275 mL, 3.49 mmol) in CH_2Cl_2 (2 mL) at rt for 12 h: liquid; R_f 0.28 (hexane/EtOAc 1:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18 (dt, J = 1.2, 7.2 Hz, 3 H), 1.27 (dt, J = 1.2, 7.2 Hz, 3 H), 1.59 (d, J = 6.5 Hz, 3 H), 2.37 (s, 3 H), 3.88–4.16 (m, 4 H), 5.71 (dq, J = 6.5, 7.2 Hz, 1 H), 7.10–7.28 (m, 3 H), 7.47 (dd, J = 7.2, 1.8 Hz, 1 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ 16.0 (+) (d, J = 7 Hz), 16.1 (+) (d, J = 7 Hz), 19.1 (+), 23.6 (+) (d, J = 5 Hz), 63.6 (−) (d, J = 6 Hz), 73.6 (+) (d, J = 5 Hz), 125.5 (+), 126.3 (+), 127.8 (+), 130.4 (+), 134.0 (−), 140.2 (−) (d, J = 5 Hz). The ^{1}H and ^{13}C NMR spectra were consistent with those reported [20a].

4.2.13. Diethyl (1-(3-methoxyphenyl)ethyl) phosphate (**7m**)

According to the general procedure for the reduction/phosphorylation of ketones, 3-methoxyphenyl methyl ketone (**9m**) (1.51 g, 10.1 mmol) was reduced with $NaBH_4$ (523 mg, 13.8 mmol) in MeOH (10 mL) at rt for 30 min to afford the corresponding alcohol (1.48 g, 96% yield) after chromatography on silica gel. A mixture of the alcohol (454 mmol, 2.98 mmol), diethyl chlorophosphate (0.644 mL, 4.48 mmol), and *N*-methylimidazole (0.424 mL, 5.38 mmol) in CH_2Cl_2 (2 mL) was stirred at rt for 12 h to produce phosphate **7m** (639 mg, 74% yield): liquid; R_f 0.30 (hexane/EtOAc 1:1); IR (neat) 1603, 1489, 1263, 1033, 985 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (dt, J = 1.0, 7.1 Hz, 3 H), 1.29 (dt, J = 1.0, 7.1 Hz, 3 H), 1.62 (d, J = 6.5 Hz, 3 H), 3.82 (s, 3 H), 3.91–4.16 (m, 4 H), 5.45 (dq, J = 6.9, 6.5 Hz, 1 H), 6.84 (dm, J = 8.0 Hz, 1 H), 6.91–6.98 (m, 2 H), 7.27 (t, J = 8.0 Hz, 1 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ 16.0 (+) (d, J = 7 Hz), 16.1 (+) (d, J = 7 Hz), 24.3 (+) (d, J = 5 Hz), 55.3 (+), 63.6 (−) (d, J = 7 Hz), 76.5 (+) (d, J = 5 Hz), 111.4 (+), 113.5 (+), 118.1 (+), 129.5 (−), 143.4 (−) (d, J = 5 Hz), 159.7 (−); HRMS (EI$^+$): m/z calcd for $C_{13}H_{21}O_5P$ [M$^+$] 288.1127, found 288.1127.

4.2.14. Diethyl (1-(naphthalen-2-yl)ethyl) phosphate (**7n**)

According to the general procedure for the reduction/phosphorylation of ketones, methyl 2-naphthyl ketone (**9n**) (256 mg, 1.50 mmol) was reduced with $NaBH_4$ (87 mg, 2.29 mmol) in MeOH (2 mL) at rt for 30 min to afford the corresponding alcohol, which was converted with diethyl chlorophosphate (0.325 mL, 2.26 mmol) and *N*-methylimidazole (0.215 mL, 2.73 mmol) in CH_2Cl_2 (2 mL) at rt for 12 h to phosphate **7n** (356 mg, 77% yield over two steps): liquid; R_f 0.35 (hexane/EtOAc 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (dt, J = 1.0, 7.1 Hz, 3 H), 1.29 (dt, J = 1.0, 7.1 Hz, 3 H), 1.72 (d, J = 6.5 Hz, 3 H), 3.89–3.99 (m, 2 H), 3.99–4.17 (m, 2 H), 5.65 (quint., J = 6.9 Hz, 1 H), 7.43–7.57 (m, 3 H), 7.80–7.89 (m, 4 H); ^{13}C–APT NMR (100 MHz, $CDCl_3$) δ 15.8 (+) (d, J = 7 Hz), 15.9 (+) (d, J = 7 Hz), 24.1 (+) (d, J = 5 Hz), 63.42 (−) (d, J = 6 Hz), 63.44 (−) (d, J = 6 Hz), 76.6 (+) (d, J = 6 Hz), 123.6 (+), 124.7 (+), 126.0 (+), 126.1 (+), 127.5 (+), 127.9 (+), 128.2 (+), 132.9 (−), 133.0 (−), 138.9 (−) (d, J = 5 Hz); The ^{1}H and ^{13}C NMR spectra were consistent with those reported [21].

4.2.15. 1-(2-Bromophenyl)ethyl diphenyl phosphate (**7q**)

To ice-cold solution of 2-bromobenzaldehyde (1.51 g, 8.16 mmol) in THF (30 mL) was added MeMgCl (1.0 M in THF, 12.0 mL, 12.0 mmol) dropwise. The solution was warmed slowly to rt over 5 h, and diluted with saturated NH_4Cl. The resulting mixture was extracted with EtOAc four times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated to give the corresponding alcohol **10q** (1.47 g, 90%): liquid; R_f 0.40 (hexane/EtOAc 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (d, J = 6.4 Hz, 3 H), 2.07 (br s, 1 H), 5.24 (q, J = 6.4 Hz, 1 H), 7.13 (dt, J = 1.8, 7.6 Hz, 1 H), 7.34 (t, J = 7.6 Hz, 1 H), 7.51 (dd, J = 7.6, 1.0 Hz, 1 H), 7.59 (dd, J = 7.6, 1.8 Hz, 1 H). The ^{1}H spectra was identical with that reported [23].

According to the general procedure for the phosphorylation of alcohols, **10q** (1.47 g, 7.31 mmol) was subjected to phosphorylation with diphenyl chlorophosphate (2.27 mL, 11.0 mmol) and *N*-methylimidazole (1.04 mL, 13.2 mmol) in CH_2Cl_2 (20 mL) at rt for 2 h to afford diphenyl phosphate **7q** (2.79 g, 88%): liquid; R_f 0.41 (hexane/EtOAc 4:1); IR (neat) 1490, 1291, 1190, 957 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.62 (t, J = 6.4 Hz, 3 H), 6.03–6.11 (m, 1 H), 7.11–7.19 (m, 6 H), 7.24–7.34 (m, 6 H), 7.47(dd, J = 8.0, 1.8 Hz, 1 H), 7.51 (dd, J = 8.0, 1.2 Hz, 1 H); ^{13}C–APT NMR (100 MHz, $CDCl_3$) δ 23.4 (+) (d, J = 5 Hz), 77.4 (+) (m), 119.97 (+) (d, J = 5 Hz), 119.99 (+) (d, J = 5 Hz), 120.8 (−), 125.2 (+), 127.0 (+), 127.8 (+), 129.4 (+), 129.6 (+), 132.6 (+), 140.4 (−) (d, J = 5 Hz), 150.38 (d, J = 7 Hz), 150.40 (−) (d, J = 8 Hz); HRMS (FAB$^+$): m/z calcd for $C_{20}H_{19}BrO_4P$ [(M+H)$^+$] 433.0204, found 433.0213.

4.3. Substitution of benzylic phosphates with the anions of diarylmethanes

4.3.1. General procedure

To an ice-cold solution of a diarylmethane (3.2–3.5 equiv) in THF was added a solution of *n*-BuLi (3 equiv) in hexane dropwise. The solution was stirred at 0 °C–rt for 15 min and cooled to −15 °C. A solution of a phosphate (1 equiv) in THF was added to the solution dropwise. The solution was stirred at −15 °C for a specific period of time (usually 15 min) and diluted with saturated NH_4Cl. The resulting mixture was extracted with EtOAc several times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated. The residual oil was purified by chromatography on silica gel to afford the corresponding product.

4.3.2. Propane-1,1,2-triyltribenzene (**8a**)

According to the general procedure for the substitution, phosphate **7a** (24 mg, 0.091 mmol) in THF (0.5 mL) was added to a mixture of *n*-BuLi (1.60 M in hexane, 0.19 mL, 0.304 mmol) and Ph_2CH_2 (54 mg, 0.322 mmol) in THF (0.5 mL) at −15 °C and the solution was stirred at −15 °C for 15 min to afford **8a** (22 mg, 87% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (d, J = 6.8 Hz, 3 H), 3.58 (dq, J = 11.4, 6.8 Hz, 1 H), 4.05 (d, J = 11.4 Hz, 1 H), 6.92–7.42 (m, 15 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2 (+), 44.4 (+), 59.5 (+), 125.7 (+), 125.8 (+), 126.3 (+), 127.7 (+), 128.1 (+), 128.2 (+), 128.27 (+), 128.34 (+), 128.6 (+), 143.9 (−), 144.2 (−), 145.9 (−). The ^{1}H and ^{13}C NMR spectra were consistent with the reported data [24].

4.3.3. (R)-Propane-1,1,2-triyltribenzene ((R)-**8a**)

According to the general procedure for the substitution, phosphate (*R*)-**7a** (>98% ee, 52 mg, 0201 mmol) in THF (1 mL) was added to a mixture of Ph_2CH_2 (115 mg, 0.684 mmol) and *n*-BuLi (1.60 M in hexane, 0.38 mL, 0.608 mmol) in THF (1 mL) at −15 °C and the solution was stirred at −15 °C for 15 min to afford (*R*)-**8a** (51 mg, 94% yield): 99% ee as determined by HPLC analysis (Chiralcel OJ-H, hexane/*i*-PrOH = 99/1, 0.5 mL/min, 33 °C, t_R (min) = 24.4 (minor (*S*)-isomer), 31.3 (major (*R*)-isomer)); $[\alpha]_D^{21}$ +29 (*c* 0.71, acetone); cf. lit [5]. $[\alpha]_D^{23}$ +30.99 (*c* 2.42, acetone) for (*R*)-**8a**; R_f 0.86 (hexane/

EtOAc 1:1). The ^{1}H and ^{13}C NMR spectra were consistent with those of the above racemic compound.

4.3.4. Butane-1,1,2-triyltribenzene (**8c**)

According to the general procedure for the substitution, phosphate **7c** (53 mg, 0.195 mmol) in THF (1 mL) was added to a mixture of Ph_2CH_2 (110 mg, 0.654 mmol) and *n*-BuLi (1.60 M in hexane, 0.37 mL, 0.59 mmol) in THF (1 mL) at −15 °C and the solution was stirred at −15 °C for 15 min to afford **8c** (44 mg, 79% yield) and Ph_2CHEt (**11**) (4 mg, 10%). Product **8c**: solids; mp 76–77 °C; IR (nujol) 1599, 1584, 1493, 751, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.66 (t, J = 7.4 Hz, 3 H), 1.46 (ddq, J = 13.8, 11.4, 7.4 Hz, 1 H), 1.70 (ddq, J = 13.8, 3.2, 7.4 Hz, 1 H), 3.32 (dt, J = 3.2, 11.4 Hz, 1 H), 4.12 (d, J = 11.4 Hz, 1 H), 6.93 (tt, J = 7.2, 1.6 Hz, 1 H), 7.01–7.07 (m, 3 H), 7.09–7.16 (m, 6 H), 7.15–7.22 (m, 1 H), 7.28–7.34 (m, 2 H), 7.38–7.43 (m, 2 H); ^{13}C–APT NMR (100 MHz, $CDCl_3$) δ 12.1 (+), 27.9 (−), 52.0 (+), 58.6 (+), 125.6 (+), 125.8 (+), 126.3 (+), 127.95 (+), 128.00 (+), 128.2 (+), 128.3 (+), 128.6 (+), 128.7 (+), 143.4 (−), 144.0 (−), 144.4 (−); HRMS (EI$^+$): m/z calcd for $C_{22}H_{22}$ [M$^+$] 286.1722, found 286.1723. The ^{1}H NMR spectrum of **11** was consistent with the literature data [2].

4.3.5. (*S*)-Butane-1,1,2-triyltribenzene [(*S*)-**8c**]

According to the general procedure for the substitution, diphenyl phosphate (*S*)-**7d** (86% ee, 195 mg, 0.529 mmol) in THF (1 mL) was added to a mixture of Ph_2CH_2 (0.281 mL, 1.69 mmol) and *n*-BuLi (1.55 M in hexane, 1.06 mL, 1.64 mmol) in THF (4 mL) at −15 °C and the solution was warmed to 0 °C over 30 min to afford (*S*)-**8c** (131 mg, 86%): 86% ee by HPLC (Chiralcel OJ-H, hexane/*i*-PrOH = 99.5/0.5, 1.0 mL/min, 35 °C, t_R/min = 12.7 (*S*-isomer, major), 19.3 (*R*-isomer, minor)); solids; mp 87–88 °C; R_f 0.30 (hexane only); $[\alpha]^{21}_{364}$ −22, $[\alpha]^{21}_{436}$ +0, $[\alpha]^{21}_{546}$ +6 (*c* 0.89, $CHCl_3$); $[\alpha]^{21}_{364}$ −51, $[\alpha]^{21}_{436}$ −19 (*c* 0.94, EtOH); lit [11]. $[\alpha]^{21}_{364}$ −21.8, $[\alpha]^{21}_{436}$ +0, $[\alpha]^{21}_{546}$ +4.0 (*c* 2.2, $CHCl_3$); $[\alpha]^{21}_{364}$ −65.7, $[\alpha]^{21}_{436}$ −25.2 (*c* 1, EtOH).

4.3.6. (3-Methylbutane-1,1,2-triyl)tribenzene (**8e**)

According to the general procedure for the substitution, diphenyl phosphate **7f** (76 mg, 0.199 mmol) in THF (1 mL) was added to a mixture of Ph_2CH_2 (117 mg, 0.695 mmol) and *n*-BuLi (1.60 M in hexane, 0.37 mL, 0.59 mmol) in THF (1 mL) at −15 °C, and the solution was stirred at −15 °C for 15 min to afford **8e** (56 mg, 94% yield): solids; mp 114–115 °C; R_f 0.90 (hexane/EtOAc 2:1); IR (nujol) 1598, 1071, 1031, 741, 700 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.72 (d, J = 6.9 Hz, 3 H), 0.79 (d, J = 6.9 Hz, 3 H), 1.83 (d of sept., J = 3.0, 6.9 Hz, 1 H), 3.55 (dd, J = 12.3, 3.0 Hz, 1 H), 4.44 (d, J = 12.3 Hz, 1 H), 6.89 (tt, J = 7.2, 1.2 Hz, 1 H), 6.98–7.22 (m, 10 H), 7.29 (t, J = 7.8 Hz, 2 H), 7.42 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.9 (+), 22.6 (+), 28.5 (+), 54.1 (+), 54.7 (+), 125.6 (+), 125.8 (+), 126.3 (+), 127.3 (+), 128.0 (+), 128.1 (+), 128.4 (+), 128.8 (+), 130.3 (+), 139.3 (−), 144.1 (−), 144.7 (−); HRMS (EI$^+$): m/z calcd for $C_{23}H_{24}$ [M$^+$] 300.1878, found 300.1875.

4.3.7. (2-(4-Fluorophenyl)propane-1,1-diyl)dibenzene (**8g**)

According to the general procedure for the substitution, phosphate **7g** (55 mg, 0.20 mmol) in THF (1 mL) was added to a mixture of Ph_2CH_2 (110 mg, 0.654 mmol) and *n*-BuLi (1.60 M in hexane, 0.37 mL, 0.59 mmol) in THF (1 mL) at −15 °C and the solution was stirred at −15 °C for 15 min to give **8g** (52 mg, 91% yield): solids; mp 76–78 °C; R_f 0.92 (hexane/EtOAc 1:1); IR (nujol) 1597, 1509, 1221, 833, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.17 (d, J = 6.8 Hz, 3 H), 3.57 (dq, J = 11.4, 6.8 Hz, 1 H), 3.98 (d, J = 11.4 Hz, 1 H), 6.82 (t, J = 8.0 Hz, 2 H), 6.96 (t, J = 6.5 Hz, 1 H), 7.02–7.12 (m, 6 H), 7.18 (t, J = 7.8 Hz, 1 H), 7.29 (t, J = 7.1 Hz, 2 H), 7.38 (d, J = 7.7 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2 (+), 43.7 (+), 59.8 (+), 114.9 (+) (d, J = 21 Hz), 125.9 (+), 126.4 (+), 128.15 (+), 128.21 (+), 128.27 (+), 128.7 (+), 129.0 (+) (d, J = 8 Hz), 141.6 (−) (d, J = 3 Hz), 143.7 (−), 144.0 (−), 161.0 (d, J = 242 Hz); HRMS (EI$^+$): m/z calcd for $C_{21}H_{19}F$ [M$^+$] 290.1471, found 290.1472.

4.3.8. (2-(4-Chlorophenyl)propane-1,1-diyl)dibenzene (**8h**)

According to the general procedure for the substitution, phosphate **7h** (58 mg, 0.20 mmol) in THF (1 mL) was added to a mixture of Ph_2CH_2 (109 mg, 0.644 mmol) and *n*-BuLi (1.60 M in hexane, 0.37 mL, 0.59 mmol) in THF (1 mL) at −15 °C and the solution was stirred at −15 °C for 15 min to furnish **8h** (54 mg, 89% yield): solids; mp 93–94 °C; R_f 0.85 (hexane/EtOAc 1:1); IR (nujol) 1596, 1491, 1093, 1011, 745, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (d, J = 6.8 Hz, 3 H), 3.56 (dq, J = 11.4, 6.8 Hz, 1 H), 3.99 (d, J = 11.4 Hz, 1 H), 6.97 (tt, J = 6.8, 1.6 Hz, 1 H), 7.03–7.13 (m, 8 H), 7.18 (t, J = 7.4 Hz, 1 H), 7.30 (d, J = 7.8 Hz, 2 H), 7.37 (d, J = 7.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1 (+), 43.9 (+), 59.4 (+), 125.9 (+), 126.4 (+), 128.17 (+), 128.21 (+), 128.24 (+), 128.29 (+), 128.7 (+), 129.0 (+), 131.4 (−), 143.6 (−), 143.9 (−), 144.5 (−); HRMS (EI$^+$): m/z calcd for $C_{21}H_{19}Cl$ [M$^+$] 306.1175, found 306.1181.

4.3.9. (2-(4-Bromophenyl)propane-1,1-diyl)dibenzene (**8i**)

According to the general procedure for the substitution, phosphate **7i** (46 mg, 0.137 mmol) in THF (1 mL) was added to a mixture of Ph_2CH_2 (74 mg, 0.44 mmol) and *n*-BuLi (1.63 M in hexane, 0.250 mL, 0.408 mmol) in THF (1 mL) at −15 °C and the solution was stirred at −15 °C for 15 min to give **8i** (38 mg, 79% yield): solids; mp 94–95 °C; R_f 0.90 (hexane/EtOAc 2:1); IR (nujol) 1489, 1071, 1007, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (d, J = 6.8 Hz, 3 H), 3.55 (dq, J = 11.4, 6.8 Hz, 1 H), 3.99 (d, J = 11.4 Hz, 1 H), 6.94–7.02 (m, 3 H), 7.03–7.12 (m, 4 H), 7.17 (t, J = 7.8 Hz, 1 H), 7.25 (d, J = 8.3 Hz, 2 H), 7.29 (t, J = 7.5 Hz, 2 H), 7.37 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1 (+), 43.9 (+), 59.3 (+), 119.5 (−), 125.9 (+), 126.4 (+), 128.15 (+), 128.22 (+), 128.7 (+), 129.4 (+), 131.2 (+), 143.5 (−), 143.8 (−), 145.0 (−); HRMS (EI$^+$): m/z calcd for $C_{21}H_{19}Br$ [M$^+$] 350.0670, found 350.0674.

4.3.10. 4-(1,1-Diphenylpropan-2-yl)benzonitrile (**8j**)

According to the general procedure for the substitution, phosphate **7j** (56 mg, 0.20 mmol) in THF (1 mL) was added to a mixture of Ph_2CH_2 (112 mg, 0.666 mmol) and *n*-BuLi (1.60 M in hexane, 0.37 mL, 0.59 mmol) in THF (1 mL) at −15 °C and the mixture was stirred at −15 °C for 15 min to afford **8j** (51 mg, 86% yield): liquid; R_f 0.87 (hexane/EtOAc 1:1); IR (neat) 2226, 1606, 1494, 1451, 704 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.19 (d, J = 6.6 Hz, 3 H), 3.64 (dq, J = 11.5, 6.6 Hz, 1 H), 4.01 (d, J = 11.5 Hz, 1 H), 6.94–7.46 (m, 14 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7 (+), 44.7 (+), 59.1 (+), 109.6 (−), 119.1 (−), 126.1 (+), 126.6 (+), 128.0 (+), 128.1 (+), 128.3 (+), 128.5 (+), 128.8 (+), 132.0 (+), 143.0 (−), 143.2 (−), 151.7 (−); HRMS (EI$^+$): m/z calcd for $C_{22}H_{19}N$ [M$^+$] 297.1517, found 297.1515.

4.3.11. (2-(p-Tolyl)propane-1,1-diyl)dibenzene (**8k**)

According to the general procedure for the substitution, phosphate **7k** (52 mg, 0.19 mmol) in THF (1 mL) was added to a mixture of Ph_2CH_2 (108 mg, 0.64 mmol) and *n*-BuLi (1.60 M in hexane, 0.36 mL, 0.58 mmol) in THF (1 mL) at −15 °C and the solution was stirred at −15 °C for 15 min to give **8k** (47 mg, 86% yield): solids; mp 52–54 °C; R_f 0.88 (hexane/EtOAc 2:1); IR (nujol) 1596, 1513, 1491, 1071, 810 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.16 (dd, J = 6.9, 2.0 Hz, 3 H), 2.19 (s, 3 H), 3.49–3.60 (m, 1 H), 4.04 (d, J = 11.4 Hz, 1 H), 6.90–7.19 (m, 10 H), 7.27 (dt, J = 1.5, 7.4 Hz, 2 H), 7.37 (t, J = 7.9 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0 (+), 22.4 (+), 43.9 (+), 59.4 (+), 125.7 (+), 126.3 (+), 127.5 (+), 128.1 (+), 128.28 (+), 128.32 (+), 128.6 (+), 128.9 (+), 135.1 (−), 142.9 (−), 144.1 (−), 144.4 (−); HRMS (EI$^+$): m/z calcd for $C_{22}H_{22}$ [M$^+$] 286.1722, found 286.1724.

*4.3.12. (2-(o-Tolyl)propane-1,1-diyl)dibenzene (**8ℓ**)*

According to the general procedure for the substitution, phosphate **7ℓ** (38 mg, 0.14 mmol) in THF (1 mL) was added to a mixture of Ph_2CH_2 (77 mg, 0.458 mmol) and *n*-BuLi (1.63 M in hexane, 0.36 mL, 0.42 mmol) in THF (1 mL) at −15 °C, and the solution was stirred at −15 °C for 15 min to afford **8ℓ** (32 mg, 80% yield): liquid; R_f 0.90 (hexane/EtOAc 2:1); IR (neat) 1601, 1494, 1451, 760, 701 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.12 (d, J = 6.9 Hz, 3 H), 2.27 (s, 3 H), 3.83 (dq, J = 11.4, 6.9 Hz, 1 H), 4.19 (d, J = 11.4 Hz, 1 H), 6.91–7.13 (m, 8 H), 7.15–7.36 (m, 4 H), 7.40 (dd, J = 8.7, 0.6 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.8 (+), 21.7 (+), 38.8 (+), 58.5 (+), 125.5 (+), 125.7 (+), 126.07 (+), 126.11 (+), 126.3 (+), 128.0 (+), 128.1 (+), 128.5 (+), 128.6 (+), 130.2 (+), 135.2 (−), 143.9 (−), 144.2 (−), 144.3 (−); HRMS (EI^+): m/z calcd for $C_{22}H_{22}$ [M^+] 286.1722, found 286.1723.

*4.3.13. (2-(3-Methoxyphenyl)propane-1,1-diyl)dibenzene (**8m**)*

According to the general procedure for the substitution, phosphate **7m** (57 mg, 0.20 mmol) in THF (1 mL) was added to a mixture of Ph_2CH_2 (109 mg, 0.648 mmol) and *n*-BuLi (1.60 M in hexane, 0.37 mL, 0.59 mmol) in THF (1 mL) at −15 °C and the solution was stirred at −15 °C for 15 min to afford **8m** (43 mg, 72% yield): liquid; R_f 0.78 (hexane/EtOAc 1:1); IR (neat) 1600, 1493, 1451, 1261, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (d, J = 6.8 Hz, 3 H), 3.55 (dq, J = 11.4, 6.8 Hz, 1 H), 3.67 (s, 3 H), 4.03 (d, J = 11.4 Hz, 1 H), 6.58 (dd, J = 8.1, 2.4 Hz, 1 H), 6.67 (s, 1 H), 6.75 (d, J = 7.6 Hz, 1 H), 6.92–7.21 (m, 7 H), 7.29 (t, J = 7.4 Hz, 2 H), 7.37 (t, J = 7.5 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1 (+), 44.4 (+), 55.1 (+), 59.4 (+), 110.9 (+), 113.8 (+), 120.2 (+), 125.8 (+), 126.3 (+), 128.1 (+), 128.2 (+), 128.3 (+), 128.6 (+), 129.1 (+), 143.9 (−), 144.2 (−), 147.6 (−), 159.3 (−); HRMS (EI^+): m/z calcd for $C_{22}H_{22}O$ [M^+] 302.1671, found 302.1672.

*4.3.14. 2-(1,1-Diphenylpropan-2-yl)naphthalene (**8n**)*

According to the general procedure for the substitution, phosphate **8n** (59 mg, 0.19 mmol) in THF (1 mL) was added to a mixture of Ph_2CH_2 (108 mg, 0.642 mmol) and *n*-BuLi (1.60 M in hexane, 0.36 mL, 0.58 mmol) in THF (1 mL) at −15 °C and the solution was stirred at −15 °C for 15 min to give **8n** (53 mg, 86% yield): solids; mp 69–70 °C; R_f 0.90 (hexane/EtOAc 1:1); IR (nujol) 1599, 1493, 813, 743, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.26 (d, J = 6.9 Hz, 3 H), 3.77 (dq, J = 11.4, 6.9 Hz, 1 H), 4.20 (d, J = 11.4 Hz, 1 H), 6.90 (tt, J = 7.3, 1.2 Hz, 1 H), 7.01 (t, J = 7.9 Hz, 2 H), 7.14–7.23 (m, 3 H), 7.29–7.42 (m, 5 H), 7.43 (d, J = 7.9 Hz, 2 H), 7.58 (s, 1 H), 7.65 (d, J = 8.5 Hz, 1 H), 7.68–7.74 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.4 (+), 44.4 (+), 59.2 (+), 125.1 (+), 125.7 (+), 125.8 (+), 126.2 (+), 126.3 (+), 126.4 (+), 127.57 (+), 127.59 (+), 127.8 (+), 128.1 (+), 128.2 (+), 128.3 (+), 128.7 (+), 132.1 (−), 133.5 (−), 143.5 (−), 143.8 (−), 144.3 (−); HRMS (EI^+): m/z calcd for $C_{25}H_{22}$ [M^+] 322.1722, found 322.1723.

*4.3.15. 9-(1-Phenylethyl)-9H-xanthene (**8o**)*

According to the general procedure for the substitution, phosphate **7a** (36 mg, 0.14 mmol) in THF (1 mL) was added to a mixture of 9*H*-xanthene (**12**) (82 mg, 0.45 mmol) and *n*-BuLi (1.60 M in hexane, 0.26 mL, 0.42 mmol) in THF (1 mL) at −15 °C and the solution was stirred at −15 °C for 15 min to afford **8o** (35 mg, 87% yield): liquid; R_f 0.81 (hexane/EtOAc 2:1); IR (neat) 1601, 1576, 1478, 1457, 1255, 760 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.12 (t, J = 7.2 Hz, 3 H), 3.07 (quint., J = 5.0 Hz, 1 H), 4.08 (d, J = 5.0 Hz, 1 H), 6.67 (d, J = 7.6 Hz, 1 H), 6.78–6.85 (m, 2 H), 6.92 (t, J = 7.2 Hz, 1 H), 6.96–7.07 (m, 4 H), 7.13–7.23 (m, 5 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.8 (+), 47.3 (+), 48.7 (+), 116.1 (+), 116.2 (+), 122.5 (+), 122.8 (+), 123.1 (−), 124.5 (−), 126.4 (+), 127.6 (+), 127.7 (+), 127.9 (+), 128.3 (+), 129.1 (+), 129.7 (+), 143.3 (−), 153.0 (−), 153.1 (−); HRMS (EI^+): m/z calcd for $C_{21}H_{18}O$ [M^+] 286.1358, found 286.1358.

*4.3.16. 9-(1-Phenylethyl)-9H-fluorene (**8p**)*

According to the general procedure for the substitution, phosphate **7b** (300 mg, 0.847 mmol) in THF (1 mL) was added to a mixture of fluorene (**13**) (450 mg, 2.71 mmol) and *n*-BuLi (1.57 M in hexane, 1.62 mL, 2.54 mmol) in THF (4 mL) at −15 °C and the solution was stirred at −15 °C for 15 min to afford **8p** (187 mg, 82%): mp 88–89 °C; R_f = 0.29 (hexane only); IR (neat) 1496, 1449, 740, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.94 (d, J = 7.2 Hz, 6 H), 3.69 (dq, J = 4.4, 7.2 Hz, 1 H), 4.31 (d, J = 4.4 Hz, 1 H), 6.83 (d, J = 7.6 Hz, 1 H), 7.12 (d, J = 7.6 Hz, 1 H), 7.25–7.41 (m, 8 H), 7.50 (d, J = 7.6 Hz, 1 H), 7.70–7.76 (m, 2 H); ^{13}C–APT NMR (100 MHz, $CDCl_3$) δ 13.9 (+), 41.9 (+), 54.2 (+), 119.6 (+), 119.7 (+), 124.3 (+), 125.7 (+), 126.2 (+), 126.3 (+), 126.8 (+), 127.0 (+), 127.1 (+), 128.1 (+), 128.2 (+), 141.4 (−), 141.8 (−), 144.55 (−), 144.61 (−), 146.5 (−); HRMS (FAB^+): m/z calcd for $C_{21}H_{18}$ [M^+] 270.1409, found 270.1408.

*4.3.17. (2-(2-Bromophenyl)propane-1,1-diyl)dibenzene (**8q**)*

According to the general procedure for the substitution, diphenyl phosphate **7q** (250 mg, 0.579 mmol) in THF (1 mL) was added to a mixture of Ph_2CH_2 (0.308 mL, 1.85 mmol) and *n*-BuLi (1.55 M in hexane, 1.08 mL, 1.67 mmol) in THF (5 mL) at −30 °C, and the solution was warmed to −5 °C over 30 min to afford **8q** (141 mg, 69%): liquid; R_f 0.20 (hexane only); IR (neat) 1494, 1022, 751, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.06–1.15 (pseudo s, 3 H), 4.21 (br s, 2 H), 6.86–6.91 (m, 1 H), 6.93–6.99 (m, 1 H), 7.04–7.14 (m, 3 H), 7.15–7.21 (m, 3 H), 7.23–7.33 (m, 3 H), 7.36–7.44 (m, 3 H); ^{13}C–APT NMR (100 MHz, $CDCl_3$) δ 21.5 (+), 42.2 (+), 58.1 (+), 124.9 (−), 125.9 (+), 126.5 (+), 127.3 (+), 127.6 (+), 128.1 (+), 128.2 (+), 128.4 (+), 128.7 (+), 132.8 (+), 143.5 (−), 144.0 (−), 144.8 (−); HRMS (FAB^+): m/z calcd for $C_{21}H_{19}BrNa$ [$(M+Na)^+$] 373.0568, found 373.0574.

*4.3.18. Conversion of **8q** to identified compound **8a***

To ice-cold solution of bromide **8q** (30 mg, 0.085 mmol) in Et_2O (1 mL) was added *t*-BuLi (1.61 M in pentane, 0.11 mL, 0.18 mmol) dropwise. The solution was stirred at 0 °C for 30 min, and diluted with saturated NH_4Cl. The resulting mixture was extracted with EtOAc three times. The combined extracts were washed with brine, dried over $MgSO_4$, and concentrated to give **8a** (14 mg, 60%). The ^1H NMR spectrum was consistent with the data of **8a** obtained from **7a** (*vide supra*).

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2019.03.050.

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