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Room-Temperature Negishi Reaction of Trisubstituted Vinyl Phosphates for the Synthesis of Tetrasubstituted Alkenes

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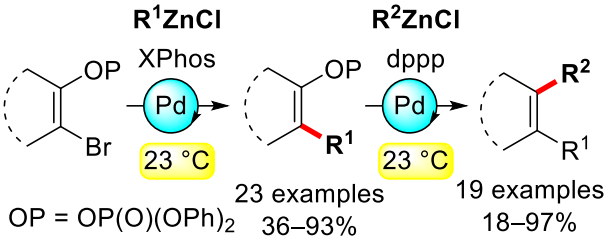
Abstract

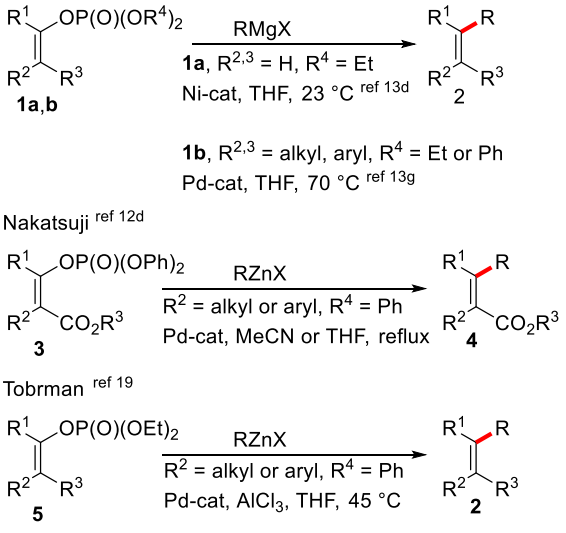


The present study investigated the ability of bromovinyl phosphates to react with organozinc reagents at room temperature during palladium-catalyzed reactions. It was determined that both the bromine atom and the phosphate group were successfully substituted by means of the reaction with the organozinc reagents, thereby allowing for the synthesis of cyclic and acyclic tetrasubstituted double bonds. The low stability of the organozinc compounds in an acidic environment was exploited to accomplish the synthesis of alkenes using a one-pot, two-step experimental setup.

Introduction

The intentional construction of a single C–C bond remains the principal focus of organic synthesis. More specifically, cross-coupling-based reactions are frequently used to synthesize C–C bonds. This synthesis is usually achieved via the reaction between electrophilic and nucleophilic templates. It has previously been determined that a diverse range of electrophilic templates can be used in cross-coupling reactions. Among them, organohalides represent the most commonly used electrophilic template.[1] In recent years, it has been found that activated C–H,[2] C–N,[2b,3] and C–S[2b,4] bonds can also be used as efficient reaction partners in cross-coupling chemistry.

In addition to the above-mentioned templates, the cross-coupling reactions of activated C–O bonds[3b,5] remain popular in relation to the synthesis of a C–C bond. In terms of the other possibilities for C–O bond activation, phosphates, especially vinyl phosphates, have been found to have a number of practical applications. For instance, in 1999, Aggarwal synthesized (+)-Anatoxin-a,[6] while Fuwa reported the total synthesis of gambieric acid A,[7] (+)-neopeltolide,[8] and the C15–C38 fragment of okadaic acid.[9] The widespread use of vinyl phosphates in organic synthesis can be attributed to their high availability, good stability under various conditions, and good reactivity in cross-coupling reactions.[10] For these reasons, phosphates have previously been coupled with

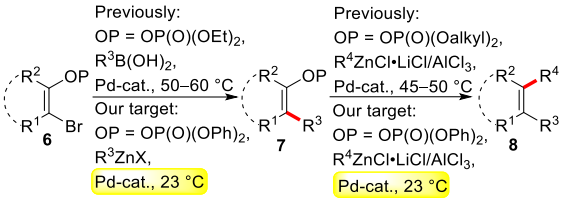


Scheme 1 Recent examples of the transition-metal-catalyzed cross-coupling reactions of vinyl phosphates.

organoaluminium,[11] boronic acids,[12] Grignard reagents,[13] organozinc reagents,[12c,12d,13g,14] and alkenes.[15] It is important to note that the applications of phosphates are not limited to cross-coupling reactions with alkenes, as the phosphate group can also be used as a directing group[16] as an electrophilic partner for C–H activation[17] and for the purposes of carbonylation.[18]

The ability of the phosphate group to react with organometallic reagents during cross-coupling reactions is influenced by a number of factors. Aside from the effects of the utilized catalyst and ligand, the steric effects of vinyl phosphates as well as the degree of nucleophilicity of the utilized organometallic reagents represent the two major factors that affect the course of cross-coupling reactions. For instance, Grignard reagents react with the unhindered vinyl phosphates **1a** at room temperature[13d,13e] (Scheme 1). Yet, the use of sterically demanding vinyl phosphates, such as trisubstituted vinyl phosphates **1b**, leads to an increase in the reaction temperature.[13g] A similar phenomenon can be observed in the case of certain organozinc reagents, whereby trisubstituted (diphenyl)vinyl phosphates **3** react with organozinc reagents in refluxing acetonitrile or tetrahydrofuran (THF).[12d] We have previously determined that aluminum chloride decreases the reaction temperature during the cross-coupling reaction of the trisubstituted vinyl phosphates **5** with organozinc reagents to 45 °C.[19a,e]

The apparent inability of trisubstituted vinyl phosphates to react with organozinc reagents at ambient temperature conflicts with reports of the Negishi reaction being conducted at room temperature.[20] During our recent synthetic efforts to conduct transition-metal-catalyzed reactions in the pursuit of organic synthesis[19] we decided to investigate the ability of trisubstituted vinyl phosphate to react with organozinc reagents at room temperature. The strategy proposed for the synthesis of tetrasubstituted alkenes begins with the preparation of the trisubstituted vinyl phosphates **7** (Scheme 2). Based on our previous report,[19a,e] we chose the cyclic bromovinyl phosphates **6** as the starting substrates. However, this type of bromovinyl phosphate was only coupled with boronic acid in the temperature range 50–60 °C.[19a,b,e] Therefore, we decided to improve its performance through the use of organozinc reagents.



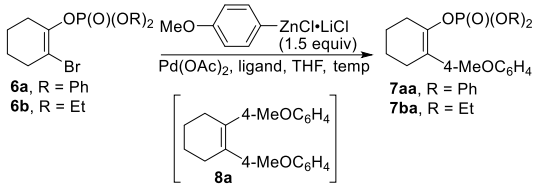
Scheme 2 Proposed strategy for the synthesis of tetrasubstituted alkenes via a double Negishi reaction at room temperature.

Results and discussion

A brief investigation of the reaction between the bromocyclohexenyl phosphate **6a** and 4-methoxyphenylzinc chloride in the presence of palladium acetate showed that only the negligible conversion of the **6a** into the phosphate **7aa** was achieved (Table 1, entry 1). Interestingly, substantially higher conversions of the phosphate **6a** were achieved when the Buchwald-type ligands were used, while the bidentate 1,3-bis(diphenylphosphino)propane (dppp) ligand proved unable to catalyze the reaction (Table 1, entries 2–7). It is important to note that all the above-mentioned reactions were contaminated by the formation of the undesired symmetrically substituted cyclohexadiene **8a** (Table 1, note e). Unfortunately, the cyclohexene **8a** could not be separated from the homocoupling reaction product, which meant that the yield of the **8a** was not determined. No cyclohexene **8a** was formed during the cross-coupling reaction of the diethyl phosphate **6b** (Table 1, entries 4 and 6). The use of the 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) ligand proved fruitful, as the almost quantitative conversion of the starting phosphate **6a** was observed (Table 1, entry 8). Reducing the amount of 4-

methoxyphenylzinc chloride allowed for the complete conversion of the phosphate **6a** by avoiding the formation of a symmetrical product **8a**. Moreover, it also allowed for the almost quantitative isolation of product **7aa**. Similar results were obtained in reactions carried out at 40 °C and 23 °C (Table 1, entries 9–11).

Table 1 Optimization of the Negishi reaction between the phosphates **6a** and **6b** and 4-methoxyphenylzinc chloride.



Entry	6	Ligand[a]	Temp (°C)	7, Conv. (%)
1	**6a**	PPh_3	60	**7aa**, 18
2	**6a**	SPhos	60	**7aa**, 61 (47[b,e])
3	**6a**	DavePhos	60	**7aa**, 83[e]
4	**6b**	DavePhos	60	**7ba**, 100 (72[b])
5	**6a**	RuPhos	60	**7aa**, 49 (38[b,e])
6	**6b**	RuPhos	60	**7ba**, 100 (69[b])
7	**6a**	dppp	60	**7aa**, –[c,e]
8	**6a**	XPhos	60	**7aa**, 96[e]
9	**6a**	XPhos	60	**7aa**, 100 (91[b,d])
10	**6a**	XPhos	40	**7aa**, 100 (88[b,d])
11	**6a**	XPhos	23	**7aa**, 100 (91[b,d])

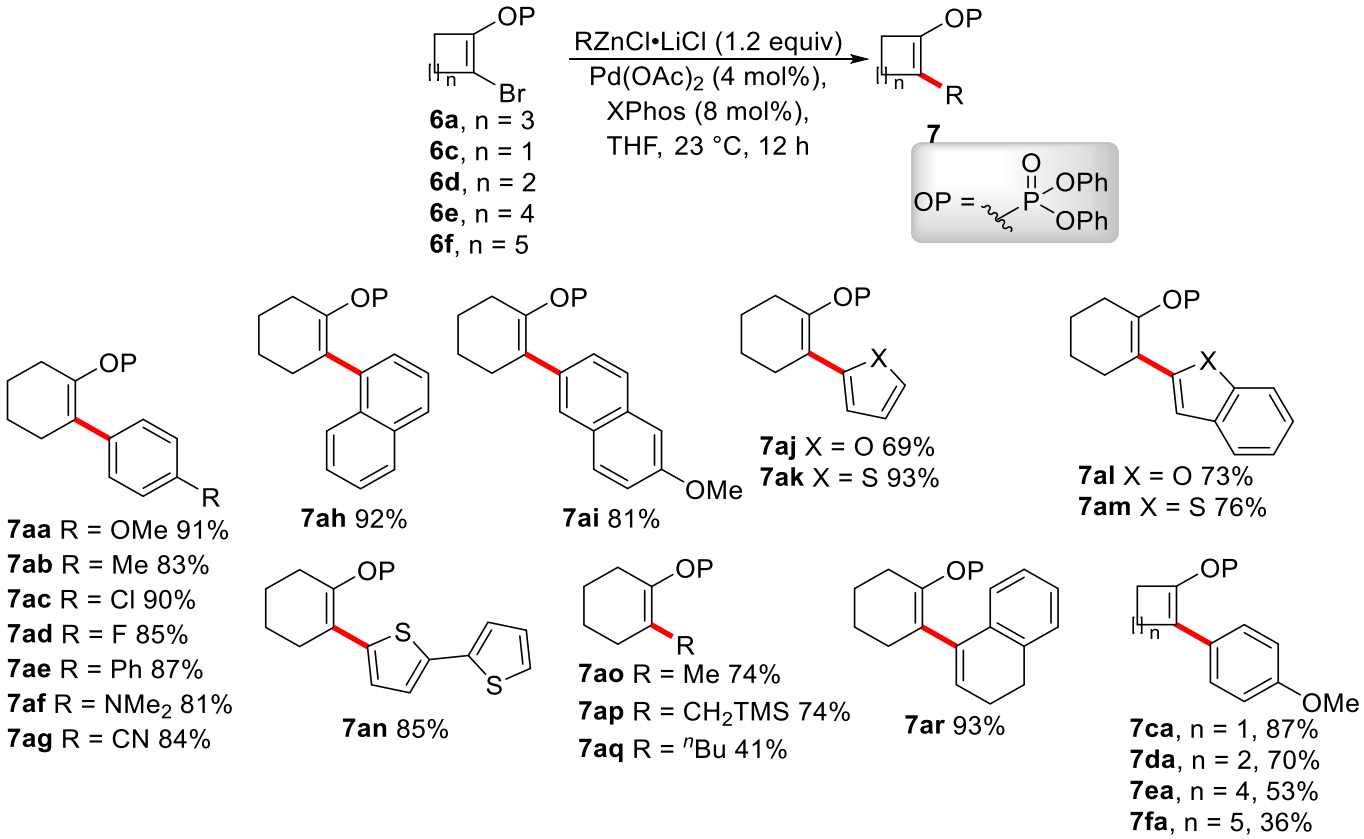
[a]Typical reaction conditions: A solution of organozinc chloride was added to a mixture of $Pd(OAc)_2$ (4 mol%) and ligand (8 mol%) in dry THF. The resultant mixture was stirred at the indicated temperature for 12 h. [b]Isolated yield. [c]Formation of phosphate **7aa** was not observed. The product of biscoupling **8a** was formed in this case. [d]1.2 equiv. of 4-methoxyphenylzinc chloride was used. [e]A significant amount of the symmetrically substituted cyclohexadiene **8a** was formed.

The ability of the diphenyl phosphate **6a** to provide a trace amount of the phosphate group substitution product **8a** indicates that this phosphate should be the substrate of choice when exploring the extent of the Negishi reactions of the bromovinyl phosphates **6a** and **6c**–**6f** with various organozinc reagents. In addition to the electron-neutral substituents **7ab** and **7ae**, the developed methodology allowed for the smooth introduction of the para-substituted phenyl ring with the electron-donating **7af** and the electron-withdrawing **7ag** groups as well as of the halogen atoms **7ac** and **7ad** in excellent isolated yields (Scheme 3). Excellent reactivity was also observed in the case of the 1-naphthyl- and 2-naphthylzinc chlorides **7ah** and **7ai**, although the heteroaromatic organozinc reagents yielded the products **7aj**–**7an** in good yields. Aliphatic and alkenyl substituents **7ao**, **7ap**, **7aq** and **7ar** are also introducible via this method. The scope of the bromine atom substitution at room temperature was extended to the cyclic bromovinyl phosphates **6c**–**6f**. The results showed that the best isolated yields of the cyclic phosphates were obtained in the case of the 4–6-membered carbocycles **7ca**, **7da** and **7aa**, while moderate isolated yields were provided by the cycloheptene and cyclooctene derivatives **7ea** and**7fa**.

With the phosphates **7** having been obtained, we optimized the phosphate substitution reaction. Thus, the starting compound **7aa** was treated with 4-tolylzinc chloride under different reaction conditions (Table 2). In accordance with previous reports, the phosphate **7aa** coupled with the organozinc reagent in the presence of $Pd(OAc)_2$ and the dppp ligand at 60 °C, thereby affording the product **8b** in a 96% yield, although the same reaction yielded no product when performed at 45 °C and 23 °C (Table 2, entries 1–3). The use of aluminum chloride as an additive gave the alkene **8b** in an 81% isolated yield, thereby maintaining the quantitative conversion. The use of two equivalents of 4-tolylzinc chloride increased the yield of the alkene **8b** to 86% (Table 2, entries 4–6). The other tested ligands proved to be less efficient (Table 2, entries 7 and 8).

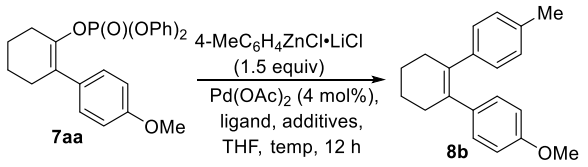
The reaction conditions developed for phosphate substitution at room temperature (Table 2, entry 6) were also applied to other organozinc reagents (Scheme 4). Uniformly high isolated yields of the cyclohexenes **8b**–**8f** were obtained in the case of the substituted phenyl ring bearing halogen atoms as well as electron-donating and electron-withdrawing groups. A similar reactivity pattern was observed for the 2-furyl- **8h** and 2-thienylzinc chloride **8i** as well as for the fused analogues **8j** and **8k**. The 2-naphthyl- **8m** and 1-naphthylzinc

chloride **8n** also coupled with the phosphate **6aa**, although the latter substrate required the addition of DPEPhos as well as heating to 45 °C to achieve the complete conversion of the starting phosphate **7aa**. This result indicated that the incomplete conversion of the phosphate **7aa** during the reaction with the 1-naphthylzinc chloride was the result of steric factors. To verify this hypothesis, we reacted the phosphate **7aa** with 2-tolylzinc chloride. The incomplete conversion of the **7aa** was observed when the reaction was performed in the presence of the dppp ligand at 23 °C. The use of the DPEPhos ligand as well as the heating of the reaction mixture to 45 °C resulted in the complete conversion of the phosphate **7aa** while the product **8o** was isolated in a 96% yield. A similarly positive result was obtained in relation to the aliphatic organozinc reagent. Analogous to the first cross-coupling reaction, the other cyclic phosphates, namely **7ca**, **7da**, **7ea** and **7fa** reacted with 4-methoxyphenylzinc



Scheme 3 Substitution of the bromine atom via the Negishi reaction at room temperature.

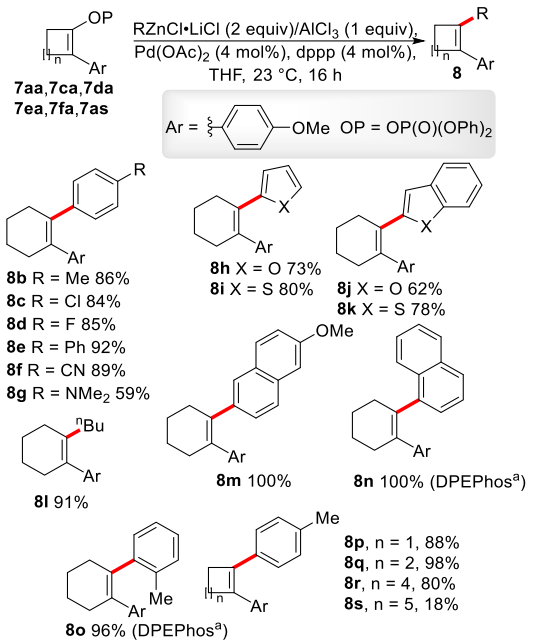
Table 2 Optimization of the Negishi reaction between the phosphate **7aa** and 4-tolylzinc chloride.



Entry	Ligand[a]	Additives	Temp (°C)	Conv. (%)
1	dppp	–	60	100 (96[b])
2	dppp	–	45	0
3	dppp	–	23	0
4	dppp	$AlCl_3$	45	95 (79[b])
5	dppp	$AlCl_3$	23	100 (81[b])
6	dppp	$AlCl_3$	23	100 (86[b,c])
7	RuPhos	$AlCl_3$	45	67
8	DPEPhos	$AlCl_3$	45	74

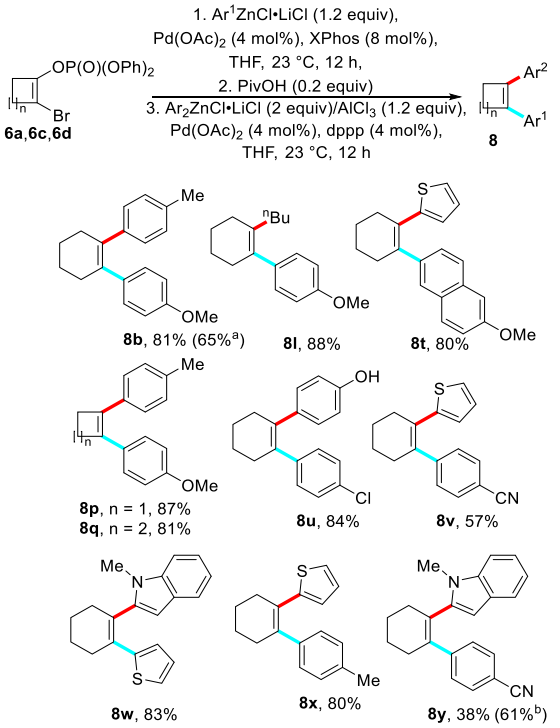
[a]Typical reaction conditions: A solution of organozinc reagent (1.5 equiv.) was added to a mixture of $Pd(OAc)_2$ (4 mol%), ligand (4 mol% for the bidentate ligand, 8 mol% for the monodentate ligand), and phosphate (1.0 equiv.). The resultant mixture was stirred at the temperatures and for the time periods indicated in the table. [b]Isolated yield. [c]2 equiv of 4-tolylzinc chloride was used.

chloride at 23 °C, thereby yielding the corresponding alkenes **8p**–**8s**.

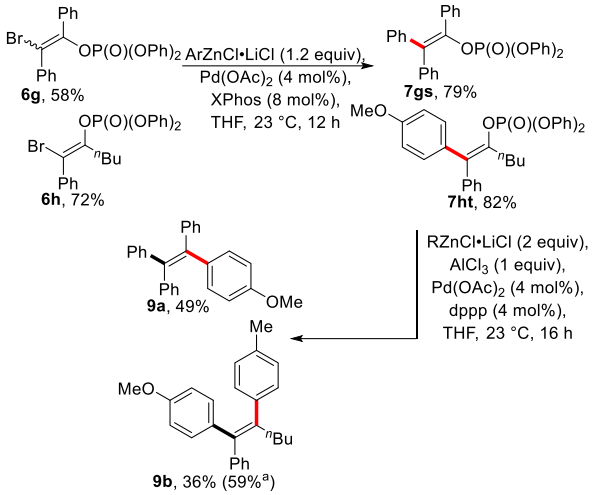


Scheme 4 The scope of the phosphate substitution by the aluminum chloride promoted the Negishi reaction at room temperature. [a]The reaction was catalyzed by $Pd(OAc)_2$/DPEPhos at 45 °C.

Inspired by the known properties of the organozinc reagents, we developed a simple one-pot, two-step procedure for the preparation of tetrasubstituted cyclic alkenes. In doing so, we exploited the low stability of organozinc compounds in an acidic environment. Thus, the phosphates **6a**,**6c** and **6d** reacted with 1.2 equiv. of aryl/heteroarylzinc chloride under the catalysis of $Pd(OAc)_2$/XPhos in THF at 23 °C. At the end of the reaction, the excess organozinc reagent was quenched with 0.2 equiv of pivalic acid, while the second Negishi reaction completed the synthesis of the alkenes **8** in excellent isolated yields (Scheme 5). It is important to note, that palladium acetate and the dppp ligand must be added in order to accomplish the one-pot synthesis of the cyclic alkene **8b** in high isolated yield. Indeed, performing the second Negishi reaction without the addition of palladium acetate and the dppp ligand inhibited the second reaction and the formation of alkene **8b** was not observed in the crude reaction mixture. Moreover, the addition of only the dppp ligand reduced the isolated yield of alkene **8b** to 65%. The other cyclohexene derivatives namely **8l**, **8t**, **8u**, **8w** and **8x** with electron-rich or electron-neutral phenyl groups as well as 2-thienyl and 1-methyl-2-indolyl moiety were prepared in similarly high isolated yields. The introduction of an electron-poor substituent during first step significantly reduced the isolated yield of the alkenes **8v** and **8y** although some improvement was obtained when the reaction mixture was heated to 45 °C. The developed one-pot methodology was also successfully used for the preparation of the four- and five-membered cyclic alkenes **8p** and **8q**.



Scheme 5 The one-pot, two-step synthesis of 1,2-disubstituted cyclohexenes. [a]Only the dppp ligand was added during the second cross-coupling reaction. [b]The reaction was performed at 45 °C.



Scheme 6 Double Negishi reaction of phosphates **6g** and **6h**. [a]The reaction was catalyzed by $Pd(OAc)_2$/DPEPhos at 45 °C

Using the methodology developed for the conversion of cyclic bromovinyl phosphates we also investigated the behavior of acyclic bromovinyl phosphates. The easily available acyclic bromovinyl phosphate **6g** was smoothly converted into the trisubstituted vinyl phosphate **7gs** in a 79% isolated yield. However, the second Negishi reaction gave the alkene **9a** in only a 49% isolated yield. A similar reactivity pattern was identified in relation to the asymmetrically substituted vinyl phosphate **6h**. In addition, we observed the formation of the alkene **9b** as a single stereoisomer by ^{1}H NMR spectroscopy.

Conclusions

In conclusion, we have demonstrated that bromovinyl phosphates can be used as double electrophilic templates for the synthesis of tetrasubstituted alkenes by means of a double Negishi reaction performed at room temperature. The bromine atom was substituted by the $Pd(OA)_2$/XPhos ligand, while the phosphate group smoothly coupled with the organozinc reagents in the presence of the $Pd(OA)_2$/dppp catalyst. Both reactions were performed in dry THF at 23 °C. The bromine atom and phosphate group substitution can be combined in a one-pot, two-step procedure in order to synthesize a tetrasubstituted double bond that requires only the separation of the final product.

Experimental section

General Information

All reactions were performed under argon atmosphere. NMR spectra were measured on Varian MercuryPlus 300 (^{1}H, 300.13 MHz; ^{13}C, 75.46 MHz), Agilent 400MR DD2 (^{1}H, 400.13 MHz; ^{13}C, 100.61 MHz) or Bruker Avance III 500 (^{31}P, 202.45 MHz) spectrometer at 298 K. Chemical shifts of ^{31}P NMR spectra are referenced to the signal of 85% H_3PO_4 that was assigned the chemical shift of 0. Mass spectra were measured on ZAB-SEQ (VG Analytical). The dry and degassed THF was prepared by PureSolv MD7. Silica gel (Merck, Silica Gel 60, 40–63 µm or Merck Silica Gel 60, 63-200 µm) was used for column chromatography. *n*-BuLi (2.5 M solution in hexane), and other compounds were purchased from Sigma-Aldrich, FLuorochem and Acros Organics. Concentration of BuLi was determined by titration using menthol and 1,10-phenanthroline before use.

General procedure for the preparation of phosphates 6

To a solution of HMDS (1.2 equiv) in THF (0.5 mL/mmol) cooled to 0 °C was dropwise added BuLi (1.2 equiv) and the reaction mixture was stirred at 0 °C for 10 minutes. The resultant LiHMDS was cooled to -78 °C and a solution of α-bromoketone (1.0 equiv) in dry THF (1 mL/mmol) was dropwise added. The reaction mixture was stirred at -78 °C for 30 minutes followed by addition of diphenyl chlorophosphate (1.3 equiv) and the mixture was allowed warmed up to ambient temperature. Then the solution was stirred at 23 °C for 4 hours, the crude reaction mixture was quenched with water (5 mL/mmol), water layer was extracted with diethyl ether (3x10 mL/mmol) and the organic layer was washed with brine (5 mL/mmol) and dried over $MgSO_4$. The solvents were evaporated under reduce pressure and column chromatography afforded the pure product.

*2-Bromocyclohex-1-en-1-yl diphenyl phosphate (***6a***).* L-selectride (26.7 mL, 26.7 mmol, 1 M in THF) was added to a solution of cyclohex-2-enone (4.24 g, 24.2 mmol) in THF (60 mL) cooled to -78 °C. The resultant mixture was stirred at -78 °C for 1 h. Then diphenyl chlorophosphate (4.1 mL, 19.8 mmol) was added and the reaction mixture was stirred at 23 °C for 4 h. The crude mixture was quenched with water (200 mL), water layer was extracted with diethyl ether (3x200 mL), washed with brine (100 mL) and the organic layer was dried over $MgSO_4$. The solvents were evaporated under reduce pressure and column chromatography (Hexane:EtOAc 6:1, R_f = ≈0.3) afforded 6.94 g (70 %) of the title compound as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.33 (m, 4H), 7.31–7.28 (m, 4H), 7.23–7.19 (m, 2H), 2.51 (s, 2H), 2.44 (s, 2H), 1.78–1.71 (m, 2H), 1.71–1.64 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.5 (d, *J* = 7.6 Hz), 144.5 (d, *J* = 7,2 Hz),

129.9, 125.6, 120.3 (d, *J* = 4.7 Hz), 108.6 (d, *J* = 10.2 Hz), 34.3, 29.2, 23.7, 22.5. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.92. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{18}BrO_4P$ 409.0199; Found 409.0202.

*2-Bromocyclohex-1-en-1-yl diethyl phosphate (***6b***).* Prepared according to the general procedure starting from HMDS (2.0 g, 12.4 mmol), BuLi (4.41 mL, 12.4 mmol, 2.57 M), THF (5 mL). Then a solution of 2-bromocyclohexanone (1.83 g, 10.3 mmol) in dry THF (5 mL) was dropwise added to a solution of LiHMDS cooled to 0 °C. The reaction mixture was stirred at 0 °C for 30 minutes followed by addition of diethyl chlorophosphate (2.0 mL, 13.8 mmol). Column chromatography (Hexane:EtOAc 3:1, R_f = ≈0.3) afforded 1.71 g (53 %) of the title compound as a light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.27–4.16 (m, 4H), 2.53–2.42 (m, 4H), 1.79–1.65 (m, 4H), 1.39–1.30 (m, 6H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 144.4 (d, *J* = 6.6 Hz), 107.5 (d, *J* = 9.8 Hz), 64.5 (d, *J* = 6.3 Hz), 34.3 (d, *J* = 0.7 Hz), 29.1 (d, *J* = 0.9 Hz), 23.8, 22.5, 16.1 (d, *J* = 7.0 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.67. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{18}BrO_4P$ 313.0199; Found 313.0201.

*2-Bromocyclobut-1-en-1-yl diphenyl phosphate (***6c***).* Prepared according to the general procedure from HMDS (1.93 g, 12.0 mmol), BuLi (4.55 mL, 10.92 mmol, 2.4 M), THF (8 mL), 2-bromocyclobutanone (1.46 g, 9.80 mmol), THF (10 mL), and diphenyl chlorophosphate (2.7 mL, 13.0 mmol). Column chromatography (Hexane:EtOAc 6:1, R_f = ≈0.3) afforded 1.104 g (30 %) of the title compound as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.9 Hz, 1H), 7.32–7.18 (m, 1H), 2.95–2.83 (m, 1H), 2.52–2.41 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.2 (d, *J* = 7.4 Hz), 140.3 (d, *J* = 8.0 Hz), 130.0, 125.9, 120.1 (d, *J* = 4.9 Hz), 90.9 (d, *J* = 12.9 Hz), 33.6, 28.6. ^{31}P NMR (202 MHz, $CDCl_3$) δ -18.37. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}BrO_4P$ 380.9886; Found 380.9873.

*2-Bromocyclopent-1-en-1-yl diphenyl phosphate (***6d***).* L-selectride (5.3 mL, 5.3 mmol, 1 M in THF) was added to a solution of cyclopent-2-enone (0.77 g, 4.80 mmol) in THF (15 mL) cooled to -78 °C. The resultant mixture was stirred at -78 °C for 1 h. Then diphenyl chlorophosphate (0.81 mL, 3.9 mmol) was added and the reaction mixture was stirred at 23 °C for 4 h. The crude mixture was quenched with conc. NH_4Cl solution (50 mL), water layer was extracted with diethyl ether (3x50 mL), washed with brine (100 mL) and the organic layer was dried over $MgSO_4$. The solvents were evaporated under reduce pressure and column chromatography (Hexane:EtOAc 6:1, R_f = ≈0.3) afforded 1.89 g (63 %) of the title compound as a light yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (t, *J* = 7.7 Hz, 4H), 7.31–7.24 (m, 4H), 7.21 (t, *J* = 7.5 Hz, 2H), 2.66–2.50 (m, 4H), 2.02 (p, *J* = 7.7 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.3 (d, *J* = 7.5 Hz), 146.3 (d, *J* = 6.5 Hz), 129.9, 125.7, 120.2, 103.3 (d, *J* = 11.2 Hz), 34.7, 30.3, 20.0. ^{31}P NMR (202 MHz, $CDCl_3$) δ -19.89. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{16}BrO_4P$ 395.0042; Found 395.0037.

*2-Bromocyclohept-1-en-1-yl diphenyl phosphate (***6e***).* Prepared according to the general procedure starting from HMDS (1.20 g, 7.4 mmol), BuLi (3.1 mL, 7.44 mmol, 2.4 M), THF (6 mL), 2-bromocycloheptanone (1.18 g, 6.2 mmol), THF (6 mL), and diphenyl chlorophosphate (1.67 g, 8.1 mmol). Column chromatography (Hexane:EtOAc 6:1, R_f = ≈0.3) afforded 0.44 g (17 %) of the title compound as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.31 (m, 4H), 7.30–7.24 (m, 4H), 7.24–7.17 (m, 2H), 2.71–2.63 (m, 2H), 2.61–2.53 (m, 2H), 1.73–1.61 (m, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.47 (d, *J* = 7.6 Hz), 148.44 (d, *J* = 8.3 Hz), 129.74, 125.49 (d, *J* = 1.2 Hz), 120.28 (d, *J* = 5.0 Hz), 112.25 (d, *J* = 10.2 Hz), 37.21, 32.56, 29.77, 25.44 (d, *J* = 1.7 Hz), 24.23 (d, *J* = 0.9 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.87. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{20}BrO_4P$ 423.0355; Found 423.0347.

*2-Bromocyclooct-1-en-1-yl diphenyl phosphate (***6f***).* Prepared according to the general procedure starting from HMDS (1.29 g, 8.0 mmol), BuLi (3.3 mL, 7.92 mmol, 2.4 M), THF (6 mL), 2-bromocyclooctanone (1.37 g, 6.68 mmol), THF (6 mL), and diphenyl chlorophosphate (1.80 mL, 8.68 mmol). Column chromatography (Hexane:EtOAc 6:1, R_f = ≈0.3) afforded 1.53 g (52 %) of the title compound as a yellow solid, mp = 55.8–58.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.8 Hz, 4H), 7.31–7.27 (m, 4H), 7.23–7.15 (m, 2H), 2.63–2.58 (m, 2H), 2.58–2.51 (m, 2H), 1.74–1.60 (m, 4H), 1.52 (s, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.5 (d, *J* = 7.5 Hz), 146.0 (d, *J* = 7.8 Hz), 129.8, 125.5, 120.3 (d, *J* = 4.9 Hz), 111.1 (d, *J* = 9.9 Hz), 35.4, 30.9, 28.5, 28.3 (d, *J* = 2.3 Hz), 26.3, 25.5. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.93. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}BrO_4P$ 437.0512; Found 437.0494.

*2-Bromo-1,2-diphenylvinyl diphenyl phosphate (***6g***).* Prepared according to the general procedure starting from HMDS (1.19 g, 7,37 mmol), BuLi (3.1 mL, 7.44 mmol, 2.4 M), THF (6 mL), desyl bromide (1.70 g, 6.18 mmol), THF (6 mL), and diphenyl chlorophosphate (1.66 mL, 8.0 mmol). Column chromatography (Hexane:EtOAc 6:1, R_f = ≈0.3) afforded 1.83 g (58 %) of the title compound as a gray solid, mp = 75.0-80.0 and 97.0-97.8 °C. According to ^{13}C NMR the title compound was isolated as a single stereoisomer. The double bond stereoselectivity was not determined but by analogy with previous report[21] we reasoned that a *trans*-stereoisomer is formed. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.7 Hz, 1H), 7.23–7.18 (m, 1H), 7.19–7.13 (m, 1H), 7.13–7.08 (m, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.5 (d, *J* = 7.4 Hz), 145.7 (d, *J* = 8.4 Hz), 137.4, 133.0, 130.3 (d, *J* = 1.5 Hz), 129.8, 129.7, 129.2, 128.5, 128.2, 128.1, 125.4, 120.2 (d, *J* = 5.0 Hz), 113.1 (d, *J* = 10.0 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.88. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{20}BrO_4P$ 507.0355; Found 507.0329.

*(Z)-1-Bromo-1-phenylhex-1-en-2-yl diphenyl phosphate (**6h**).* To a solution of 1,1-dibromohex-1-en-2-yl diphenyl phosphate (1.273 g, 2.60 mmol), phenylboronic acid (0.44 g, 3.61 mmol), $Pd(OAc)_2$ (11.7 mg) and PPh_3 (41.0 mg) in

toluene (10 mL) was added K_3PO_4 (3.6 mL, 2M in water) and the reaction mixture was placed in an oil bath at 45 °C and stirred for 12 h. Column chromatography (Hexane:EtOAc 6:1, R_f = ≈0.4) afforded 0.918 g (72%) of the title compound as an yellow solid, mp = 59–62 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.29 (m, 8H), 7.24–7.19 (m, 2H), 2.41–2.34 (m, 2H), 1.49–1.39 (m, 2H), 1.20–1.07 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.6 (d, *J* = 7.4 Hz), 148.3 (d, *J* = 8.1 Hz), 137.6, 129.8, 129.5 (d, *J* = 1.6 Hz), 128.7, 128.5, 125.5, 120.2 (d, *J* = 5.0 Hz), 109.7 (d, *J* = 10.0 Hz), 31.6, 29.0, 21.9, 13.6. ^{31}P NMR (202 MHz, $CDCl_3$) δ -18.44. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{24}BrO_4P$ 487.0668; Found 487.0673.

General procedure for the Negishi reaction of bromovinyl phosphates 6 (GP1)

Organozinc chloride (1.2 equiv) was added to a solution of phosphate **6**, $Pd(OAc)_2$ (4 mol%) and XPhos (8 mol%) in THF (1 mL). The resultant mixture was stirred at 23 °C for 12 hours, afterthat the reaction mixture was quenched with tartaric acid (10 mL, 1M solution in water). The water layer was extracted with diethyl ether (3x15 mL), the organic layer was dried over $MgSO_4$ and the solvents were removed under reduce pressure. The product was isolated by column chromatography (Hexane:EtOAc 6:1, R_f = ≈0.3).

*2-(4-Methoxyphenyl)cyclohex-1-en-1-yl diphenyl phosphate (**7aa**).* Prepared according to GP1 starting from phosphate **6a** (132.8 mg, 0.32 mmol), 4-methoxyphenylzinc chloride (0.79 mL, 0.40 mmol, 0.5 M), $Pd(OAc)_2$ (2.9 mg) and XPhos (12.3 mg), yield 129.0 mg (91%), white solid, mp = 74.5–77.0 °C. *Large scale preparation:* phosphate **6a** (6.73 g, 16.45 mmol), 4-methoxyphenylzinc chloride (40.3 mL, 19.75 mmol, 0.49 M), $Pd(OAc)_2$ (0.15 g, 0.67 mmol) and XPhos (0.63 g, 1.32 mmol), hexane:EtOAc (4:1, R_f = ≈0.3), yield 5.08 g (71%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.25 (m, 4H), 7.22 (d, *J* = 8 Hz, 2H), 7.20–7.14 (m, 2H), 7.06–7.02 (m, 4H), 6.76 (d, *J* = 8 Hz, 2H), 3.81 (s, 3H), 2.56 (s, 2H), 2.40 (s, 2H), 1.88–1.81 (m, 2H), 1.78–1.71 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.3, 150.6 (d, *J* = 7.4 Hz), 142.5 (d, *J* = 8.4 Hz), 131.2, 129.6, 129.4, 125.1, 123.6 (d, *J* = 8.6 Hz), 120.0 (d, *J* = 5.0 Hz), 113.4, 55.2, 30.7, 28.3, 23.1, 22.5. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.55. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{25}O_5P$ 437.1512; Found 437.1513.

*2-(4-Methoxyphenyl)cyclohex-1-en-1-yl diethyl phosphate (**7ba**).* Prepared according to modified GP1 starting from phosphate **6b** (114.9 g, 0.37 mmol), 4-methoxyphenylzinc chloride (1.2 mL, 0.6 mmol, 0.5 M), $Pd(OAc)_2$ (3.3 mg) and RuPhos (13.6 mg), and the reaction mixture was placed in an oil bath at 60 °C and stirred for 12 h, hexane:EtOAc (4:1, R_f = ≈0.3), yield 86.0 mg (69 %), colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.9 Hz, 2H), 3.94–3.72 (m, 7H), 2.51–2.41 (m, 2H), 2.37–2.30 (m, 2H), 1.85–1.75 (m, 2H), 1.75–1.66 (m, 2H), 1.17 (dd, *J* = 7.0, 1.0 Hz, 6H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.2, 142.4 (d, *J* = 8.2 Hz), 131.8 (d, *J* = 1.6 Hz), 129.5 (d, *J* = 0.9 Hz), 122.4 (d, *J* = 8.1 Hz), 113.2, 63.7 (d, *J* = 6.1 Hz), 55.3, 30.4 (d, *J* = 0.8 Hz), 28.3 (d, *J* = 0.7 Hz), 23.0, 22.5, 16.0 (d, *J* = 7.2 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -6.23. HRMS (APCI) m/z: $[M+H]^+$ Calcd For $C_{17}H_{25}O_5P$ 341.1512; Found 341.1512.

*2-(4-tolyl)cyclohex-1-en-1-yl diphenyl phosphate (**7ab**).* Prepared according to GP1 starting from phosphate **6a** (213.8 mg, 0.52 mmol), 4-tolylzinc chloride (1.3 mL, 0.65 mmol, 0.5 M), $Pd(OAc)_2$ (4.7 mg) and XPhos (20.0 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 182.7 mg (83%), yellow solid, mp = 47–50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.20 (m, 4H), 7.17–7.10 (m, 4H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.97 (d, *J* = 8.2 Hz, 4H), 2.56–2.46 (m, 2H), 2.42–2.33 (m, 2H), 2.31 (s, 3H), 1.85–1.75 (m, 2H), 1.75–1.64 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.5 (d, *J* = 7.5 Hz), 142.5 (d, *J* = 8.4 Hz), 136.3, 135.9, 129.5, 128.7, 128.2, 125.0, 123.9 (d, *J* = 8.6 Hz), 120.0 (d, *J* = 5.1 Hz), 30.6, 28.2, 23.0, 22.4, 21.2. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.54. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{25}O_4P$ 421.1563; Found 421.1564.

*2-(4-Chlorophenyl)cyclohex-1-en-1-yl diphenyl phosphate (**7ac**).* Prepared according to GP1 starting from phosphate **6a** (198.3 mg, 0.48 mmol), 4-chlorophenylzinc chloride (1.20 mL, 0.58 mmol, 0.48 M), $Pd(OAc)_2$ (4.4 mg) and XPhos (18.5 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 191.7 mg (90%), yellow solid, mp = 59–65 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.29 (m, 1H), 7.29–7.22 (m, 4H), 7.23–7.10 (m, 6H), 7.02–6.96 (m, 3H), 2.56–2.47 (m, 2H), 2.36–2.28 (m, 2H), 1.86–1.76 (m, 2H), 1.77–1.66 (m, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.4 (d, *J* = 7.5 Hz), 143.2 (d, *J* = 8.3 Hz), 137.2, 132.5, 129.7, 129.6, 128.2, 125.2, 123.1 (d, *J* = 8.7 Hz), 119.9 (d, *J* = 5.0 Hz), 30.5, 28.2, 23.0, 22.3. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.63. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{22}ClO_4P$ 441.1017; Found 441.1019.

*2-(4-fluorophenyl)cyclohex-1-en-1-yl diphenyl phosphate (**7ad**).* Prepared according to GP1 starting from phosphate **6a** (205.1 mg, 0.50 mmol), 4-fluorophenylzinc chloride (1.4 mL, 0.62 mmol, 0.44 M), $Pd(OAc)_2$ (4.5 mg) and XPhos (19.1 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 180.3 mg (85%), white solid, mp = 53–54.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.22 (m, 4H), 7.22–7.10 (m, 4H), 7.04–6.96 (m, 4H), 6.90–6.81 (m, 2H), 2.62–2.44 (m, 2H), 2.42–2.26 (m, 2H), 1.86–1.76 (m, 2H), 1.76–1.67 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.6 (d, *J* = 246.4 Hz), 150.4 (d, *J* = 7.1 Hz), 143.0 (d, *J* = 9.1 Hz), 134.6, 129.9 (dd, *J* = 1.0, 8.1 Hz), 129.6, 125.2, 123.1 (d, *J* = 8.1 Hz), 119.9 (d, J = 5.1 Hz), 114.8 (d, *J* = 21.2 Hz), 30.6, 28.2, 23.0, 22.3. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.57. ^{19}F NMR (471 MHz, $CDCl_3$, $CFCl_3$) δ -115, 96. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{22}FO_4P$ 425.1313; Found 425.1313.

*2-(Biphenyl-4-yl)cyclohex-1-en-1-yl diphenyl phosphate (**7ae**).* Prepared according to GP1 starting from phosphate **6a** (216.8 mg, 0.53 mmol), biphenyl-4-ylzinc chloride (1.7 mL, 0.65 mmol, 0.38 M), $Pd(OAc)_2$ (4.8 mg) and XPhos (20.2 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 221.0 mg

(87%), off-white solid, mp = 86–90 °C ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 4H), 7.37–7.30 (m, 3H), 7.21 (t, *J* = 7.7 Hz, 4H), 7.09 (t, *J* = 7.3 Hz, 2H), 6.99 (d, *J* = 7.9 Hz, 3H), 2.60–2.50 (m, 2H), 2.47–2.36 (m, 2H), 1.88–1.78 (m, 2H), 1.79–1.69 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.5 (d, *J* = 7.4 Hz), 143.0 (d, *J* = 8.4 Hz), 141.0, 139.5, 137.9, 129.6, 128.8, 127.2, 127.0, 126.7, 125.1, 123.6 (d, *J* = 8.8 Hz), 120.0 (d, *J* = 5.2 Hz), 30.5, 28.3, 23.1, 22.4. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.57. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{27}O_4P$ 483.1720; Found 483.1719.

*2-[4-(N,N-Dimethylamino)phenyl]cyclohex-1-en-1-yl diphenyl phosphate (***7af***).* Prepared according to GP1 starting from phosphate **6a** (219.9 mg, 0.54 mmol), 4-(*N*,*N*-dimethylamino)phenylzinc chloride (1.5 mL, 0.66 mmol, 0.44 M), $Pd(OAc)_2$ (4.8 mg) and XPhos (20.5 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 195.4 mg (81%), yellow solid, mp = 50.0–53.0. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25–7.20 (m, 4H), 7.16 (d, *J* = 8.3 Hz, 2H), 7.14–7.09 (m, 2H), 7.03–6.98 (m, 4H), 6.60 (d, *J* = 8.4 Hz, 2H), 2.92 (s, 6H), 2.51 (s, 2H), 2.36 (s, 2H), 1.82–1.76 (m, 2H), 1.72–1.67 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.6 (d, *J* = 7.5 Hz), 149.4, 141.9 (d, *J* = 8.4 Hz), 129.5, 129.0, 126.9, 125.0, 123.7 (d, *J* = 8.6 Hz), 120.1 (d, *J* = 5.0 Hz), 112.2, 40.6, 30.5, 28.4, 23.2, 22.6. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.41. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{28}NO_4P$ 450.1829; Found 450.1829.

*2-(4-Cyanophenyl)cyclohex-1-en-1-yl diphenyl phosphate (***7ag***).* Prepared according to GP1 starting from phosphate **6a** (188.3 mg, 0.46 mmol), 4-cyanophenylzinc chloride (2.8 mL, 0.56 mmol, 0.2 M), $Pd(OAc)_2$ (4.1 mg) and XPhos (17.6 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 167.2 mg (84%), colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.34 (m, 2H), 7.29–7.24 (m, 7H), 7.21–7.15 (m, 2H), 7.02–6.98 (m, 3H), 2.60–2.48 (m, 2H), 2.38–2.31 (m, 2H), 1.88–1.80 (m, 2H), 1.78–1.70 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.3 (d, *J* = 7.6 Hz), 144.2 (d, *J* = 8.2 Hz), 143.6, 131.7, 129.7, 129.0, 125.4, 122.7 (d, *J* = 8.6 Hz), 119.8 (d, *J* = 5.1 Hz), 119.0, 110.3, 30.0, 28.2, 22.8, 22.2. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.78. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{22}NO_4P$ 432.1359; Found 432.1360.

*2-(Naphthalen-1-yl)cyclohex-1-en-1-yl diphenyl phosphate (***7ah***).* Prepared according to GP1 starting from phosphate **6a** (207.7 mg, 0.51 mmol), 1-naphthylzinc chloride (1.4 mL, 0.62 mmol, 0.44 M), $Pd(OAc)_2$ (4.6 mg) and XPhos (19.4 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 212.1 mg (92%), colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.81 (m, 2H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.50–7.44 (m, 2H), 7.44–7.35 (m, 1H), 7.35–7.29 (m, 1H), 7.13–6.98 (m, 6H), 6.76–6.68 (m, 2H), 6.68–6.62 (m, 2H), 2.71–2.59 (m, 2H), 2.50–2.35 (m, 2H), 2.01–1.91 (m, 2H), 1.87–1.79 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.2 (d, *J* = 7.6 Hz), 143.9 (d, *J* = 8.0 Hz), 137.0 (d, *J* = 1.4 Hz), 133.7, 131.0, 129.4, 128.3, 127.3, 126.0 (d, *J* = 1.1 Hz), 126.0, 125.7, 125.6, 125.5, 125.0, 123.0 (d, *J* = 8.8 Hz), 119.7 (d, *J* = 9.7 Hz), 119.7, 31.5, 28.0, 23.3, 22.5. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.89. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{25}O_4P$ 457.1563; Found 457.1564.

*2-(6-Methoxynaphthalen-2-yl)cyclohex-1-en-1-yl diphenyl phosphate (***7ai***).*Prepared according to GP1 starting from phosphate **6a** (194.1 mg, 0.47 mmol), 6-methoxynaphthalen-2-ylzinc chloride (2.85 mL, 0.57 mmol, 0.2 M), $Pd(OAc)_2$ (4.3 mg) and XPhos (18.1 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 187.4 mg (81%), white solid, mp = 106.0–108.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62–7.56 (m, 3H), 7.35 (dd, *J* = 8.5 Hz, 1.5 Hz, 1H), 7.12–7.00 (m, 8H), 6.90–6.86 (m, 4H), 3.93 (s, 3H), 2.60–2.54 (m, 2H), 2.48–2.42 (m, 2H), 1.88–1.82 (m, 2H), 1.79–1.72 (m, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.6, 150.4 (d, *J* = 12.7 Hz), 143.0 (d, *J* = 8.3 Hz), 134.2, 133.5, 129.6, 129.5, 128.8, 127.4, 126.9, 126.4, 125.0, 124.1 (d, *J* = 8.9 Hz), 129.9 (d, *J* = 4.9 Hz), 118.6, 105.6, 55.4, 30.8, 28.3, 23.1, 22.5. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.51. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{27}O_5P$ 487.1669; Found 487.1670.

*2-(2-Furyl)cyclohex-1-en-1-yl diphenyl phosphate (***7aj***).* Prepared according to GP1 starting from phosphate **6a** (206.0 mg, 0.50 mmol), 2-furylzinc chloride (1.75 mL, 0.61 mmol, 0.35 M), $Pd(OAc)_2$ (4.5 mg) and XPhos (19.2 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 138.0 mg (69%), colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.26 (m, 5H), 7.25–7.15 (m, 6H), 6.50 (d, *J* = 3.4 Hz, 1H), 6.31 (dd, *J* = 3.3, 1.9 Hz, 1H), 2.66–2.55 (m, 2H), 2.55–2.46 (m, 2H), 1.80–1.73 (m, 2H), 1.71–1.63 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 150.5 (d, *J* = 7.3 Hz), 142.7 (d, *J* = 8.5 Hz), 140.7, 129.7 (d, *J* = 0.6 Hz), 125.4, 120.1, 120.1, 113.9 (d, *J* = 9.1 Hz), 111.2, 109.1, 28.5, 25.4, 22.7, 21.7. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.69., HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{21}O_5P$ 397.1199; Found 397.1200.

*(2-(2-Thienyl)cyclohex-1-en-1-yl) diphenyl phosphate (***7ak***).*Prepared according to GP1 starting from phosphate **6a** (199.1 mg, 0.49 mmol), 2-thienylzinc chloride (0.94 mL, 0.58 mmol, 0.62 M), $Pd(OAc)_2$ (4.4 mg) and XPhos (18.6 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 186.1 mg (93%), brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.27 (m, 4H), 7.25–7.13 (m, 7H), 7.10 (d, *J* = 3.7 Hz, 1H), 6.95 (dd, *J* = 5.1, 3.8 Hz, 1H), 2.70–2.63 (m, 2H), 2.60–2.51 (m, 2H), 1.81–1.71 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.6 (d, *J* = 7.2 Hz), 143.0 (d, *J* = 7.9 Hz), 139.6, 129.7, 126.2, 125.4, 125.1, 124.9, 120.2 (d, *J* = 5.2 Hz), 116.2 (d, *J* = 9.5 Hz), 28.9, 28.6, 22.8, 22.3. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.77. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{21}O_4PS$ 413.0971; Found 413.0971.

*2-(Benzofuran-2-yl)cyclohex-1-en-1-yl diphenyl phosphate (***7al***).* Prepared according to GP1 starting from phosphate **6a** (187.2 mg, 0.46 mmol), 2-benzofuran-2-ylzinc chloride (1.85 mL, 0.56 mmol, 0.3 M), $Pd(OAc)_2$ (4.1 mg) and XPhos (17.4 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 149.2 mg (73%), off-white solid, mp = 63.0–64.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.40 (m, 1H), 7.37–7.27 (m, 5H), 7.26–7.20 (m, 5H), 7.20–7.13 (m, 3H), 6.76 (s, 1H), 2.69–2.60 (m, 4H), 1.85–1.77 (m, 2H), 1.77–1.69 (m,

2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 153.7, 152.6 (d, *J* = 2.6 Hz), 150.5 (d, *J* = 7.3 Hz), 145.5 (d, *J* = 8.2 Hz), 129.8, 128.8, 125.4, 123.9, 122.5, 120.9, 120.1, 120.0, 113.9 (d, *J* = 9.0 Hz), 110.9, 105.6, 28.8, 25.6, 22.6, 21.7. ^{31}P NMR (202 MHz, $CDCl_3$) δ -18.03. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{23}O_5P$ 447.1356; Found 447.1353.

*2-(2-Thianaphthenyl)cyclohex-1-en-1-yl diphenyl phosphate (***7am***).* Prepared according to GP1 starting from phosphate **6a** (197.7 mg, 0.48 mmol), 2-thianaphthenylzinc chloride (2.1 mL, 0.59 mmol, 0.28 M), $Pd(OAc)_2$ (4.7 mg) and XPhos (19.9 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 170.0 mg (76%), brown solid, mp = 57.6–69.5 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.3 Hz, 1H), 7.32–7.22 (m, 8H), 7.22–7.17 (m, 4H), 7.14 (t, *J* = 7.5 Hz, 2H), 2.70 (s, 2H), 2.60 (s, 2H), 1.87–1.72 (m, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) 150.5 (d, *J* = 7.3 Hz), 144.9 (d, *J* = 7.7 Hz), 139.9, 139.2, 129.7, 125.4, 124.0 (d, *J* = 5.2 Hz), 123.3, 121.9, 121.6, 120.1 (d, *J* = 5.0 Hz), 116.4 (d, *J* = 9.4 Hz), 29.0, 28.8, 22.7, 22.2. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.98. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{23}O_4PS$ 463.1127; Found 463.1128.

*2-(2,2'-Bithiophen-5-yl)cyclohex-1-en-1-yl diphenyl phosphate (***7an***).* Prepared according to GP1 starting from phosphate **6a** (219.2 mg, 0.54 mmol), 2,2'-bithiophen-5-ylzinc chloride (2.0 mL, 0.66 mmol, 0.33 M), $Pd(OAc)_2$ (4.8 mg) and XPhos (20.4 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 224.5 (85%), orange solid, mp = 65.7–71.0 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.33–7.27 (m, 4H), 7.25–7.22 (m, 4H), 7.19–7.14 (m, 3H), 7.03 (d, *J* = 3.0 Hz, 1H), 7.01–6.95 (m, 3H), 2.68 (s, 2H), 2.53 (s, 2H), 1.80–1.70 (m, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 150.6 (d, *J* = 7.2 Hz), 143.3 (d, *J* = 7.5 Hz), 138.5, 137.6, 136.7, 129.8, 127.8, 125.6, 125.4, 124.2, 123.4, 123.0, 120.3 (d, *J* = 4.9 Hz), 120.1 (d, *J* = 5.0 Hz), 115.9 (d, *J* = 9.5 Hz), 28.6, 28.5, 22.8, 22.2. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.92. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{23}O_4PS_2$ 495.0848; Found 495.0850.

*2-Methylcyclohex-1-en-1-yl diphenyl phosphate (***7ao***).* Prepared according to GP1 starting from phosphate **6a** (217.6 mg, 0.53 mmol), methylzinc chloride (1.45 mL, 0.64 mmol, 0.44 M), $Pd(OAc)_2$ (4.8 mg) and XPhos (20.3 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 134.8 mg (74%), colourless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.8 Hz, 4H), 7.25 (d, *J* = 8.1 Hz, 4H), 7.18 (t, *J* = 7.3 Hz, 2H), 2.31 (s, 2H), 2.00 (s, 2H), 1.72–1.65 (m, 2H), 1.58 (s, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 150.7 (d, *J* = 7.4 Hz), 141.6 (d, *J* = 9.1 Hz), 129.8, 125.3, 120.1 (d, *J* = 4.9 Hz), 119.7 (d, *J* = 7.6 Hz), 30.4, 27.9, 23.4, 22.2, 16.2. ^{31}P NMR (202 MHz, $CDCl_3$) δ -16.52. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}O_4P$ 345.1250; Found 345.1253.

*Diphenyl 2-[(trimethylsilyl)methyl]cyclohex-1-en-1-yl phosphate (***7ap***).* Prepared according to GP1 starting from phosphate **6a** (189.9 mg, 0.46 mmol), trimethylsilylmethylzinc chloride (0.82 mL, 0.57 mmol, 0.69 M), $Pd(OAc)_2$ (4.2 mg) and XPhos (17.7 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 142.6 mg (74%), yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.7 Hz, 4H), 7.25 (d, *J* = 7.7 Hz, 4H), 7.18 (t, *J* = 7.3 Hz, 2H), 2.38 (s, 2H), 1.98 (s, 2H), 1.73–1.63 (m, 2H), 1.59–1.50 (m, 2H), 1.47 (s, 2H), -0.04 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 150.7 (d, *J* = 7.4 Hz), 139.5 (d, *J* = 8.5 Hz), 129.7, 125.2, 121.4 (d, *J* = 8.7 Hz), 120.2 (d, *J* = 5.0 Hz), 30.9, 27.8, 23.5, 22.4, 20.9 (d, *J* = 1.4 Hz), -0.8. ^{31}P NMR (202 MHz, $CDCl_3$) δ -16.60. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{29}O_4PSi$ 439.1465; Found 439.1468.

*2-Butylcyclohex-1-en-1-yl diphenyl phosphate (***7aq***).* Prepared according to GP1 starting from phosphate **6a** (207.9 mg, 0.51 mmol), n-butylzinc chloride (1.3 mL, 0.61 mmol, 0.47 M), $Pd(OAc)_2$ (4.7 mg) and XPhos (19.4 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 79.9 mg (41%), yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.7 Hz, 4H), 7.32–7.27 (m, 4H), 7.23 (t, *J* = 7.4 Hz, 2H), 2.40 (s, 2H), 2.10–1.98 (m, 4H), 1.78–1.68 (m, 2H), 1.64–1.56 (m, 2H), 1.38–1.27 (m, 2H), 1.27–1.16 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 150.7 (d, *J* = 7.4 Hz), 141.5 (d, *J* = 8.8 Hz), 129.7, 125.3, 123.7 (d, *J* = 8.4 Hz), 120.2 (d, *J* = 4.9 Hz), 29.9, 29.6, 28.04, 27.97, 23.3, 22.7, 22.3, 14.0. ^{31}P NMR (202 MHz, $CDCl_3$) δ -16.79. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}O_4P$ 387.1720; Found 387.1721.

*2-(3,4-Dihydronaphthalen-1-yl)cyclohex-1-en-1-yl diphenyl phosphate (***7ar***).* Prepared according to GP1 starting from phosphate **6a** (221.8 mg, 0.54 mmol), 3,4-dihydronaphth-1-ylzinc chloride (1.9 mL, 0.67 mmol, 0.35 M), $Pd(OAc)_2$ (4.9 mg) and XPhos (20.6 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 232.2 mg (93%), colourless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.23–7.15 (m, 6H), 7.15–7.07 (m, 4H), 7.02 (d, *J* = 8.1 Hz, 4H), 5.93 (t, *J* = 4.5 Hz, 1H), 2.68 (s, 2H), 2.57–2.48 (m, 2H), 2.30–2.07 (m, 4H), 1.85 (p, *J* = 6.2 Hz, 2H), 1.77–1.64 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 150.5 (d, *J* = 7.7 Hz), 143.5 (d, *J* = 8.4 Hz), 136.2, 135.7 (d, *J* = 1.6 Hz), 133.6 (d, *J* = 1.0 Hz), 129.6, 127.6, 127.4 (d, *J* = 1.4 Hz), 126.8, 126.5, 125.1, 124.2, 123.2 (d, *J* = 8.5 Hz), 120.0 (d, *J* = 4.9 Hz), 30.0, 28.1, 27.8, 23.2, 23.0, 22.3. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.53. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{27}O_4P$ 459.1720; Found 459.1706.

*2-(4-Methoxyphenyl)cyclobut-1-en-1-yl diphenyl phosphate (***7ca***).* Prepared according to GP1 starting from phosphate **6c** (205.4 mg, 0.54 mmol), 4-methoxyphenylzinc chloride (1.5 mL, 0.68 mmol, 0.45 M), $Pd(OAc)_2$ (4.8 mg) and XPhos (20.5 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 191.8 mg (87%), off-white solid, mp = 79–81 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.7 Hz, 4H), 7.34–7.29 (m, 6H), 7.26 (t, *J* = 7.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H), 2.99 (s, 2H), 2.44 (s, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.8, 150.4 (d, *J* = 7.3 Hz), 131.7 (d, *J* = 8.7 Hz), 129.9, 127.6, 125.7, 125.4, 122.2 (d, *J* = 11.3 Hz), 120.2 (d, *J* = 5.0 Hz), 113.8, 55.3, 31.2, 21.0. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.49. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{21}O_5P$ 409.1199; Found 409.1180.

*2-(4-Methoxyphenyl)cyclopent-1-en-1-yl diphenyl phosphate (***7da***).* Prepared according to GP1 starting from

phosphate **6d** (300.9 mg, 0.76 mmol), 4-methoxyphenylzinc chloride (2.1 mL, 0.95 mmol, 0.45 M), $Pd(OAc)_2$ (6.8 mg) and XPhos (28.9 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 224.4 mg (70%), off-white solid, mp = 75.6–77.1 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 4H), 7.27–7.16 (m, 6H), 6.75 (d, *J* = 8.7 Hz, 2H), 3.79 (s, 3H), 2.89 (t, *J* = 7.5 Hz, 2H), 2.75–2.65 (m, 2H), 1.99 (p, *J* = 7.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.4, 150.5 (d, *J* = 7.4 Hz), 142.7 (d, *J* = 7.5 Hz), 129.8, 128.4, 126.8, 125.5, 120.9 (d, *J* = 9.5 Hz), 120.2 (d, *J* = 4.9 Hz), 113.5, 55.2, 32.9, 31.3, 19.3. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.39. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}O_5P$ 423.1356; Found 423.1333.

*2-(4-Methoxyphenyl)cyclohept-1-en-1-yl diphenyl phosphate (**7ea**).* Prepared according to GP1 starting from phosphate **6e** (182.8 mg, 0.43 mmol), 4-methoxyphenylzinc chloride (1.2 mL, 0.54 mmol, 0.45 M), $Pd(OAc)_2$ (3.9 mg) and XPhos (16.5 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 102.3 mg (53%), yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.26–7.20 (m, 4H), 7.17–7.10 (m, 4H), 7.00–6.94 (m, 4H), 6.75–6.68 (m, 2H), 3.76 (s, 3H), 2.74–2.65 (m, 2H), 2.48–2.40 (m, 2H), 1.82–1.65 (m, 7H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 158.1, 150.5 (d, *J* = 7.4 Hz), 146.7 (d, *J* = 9.4 Hz), 133.0 (d, *J* = 2.0 Hz), 129.6 (d, *J* = 0.5 Hz), 129.3, 129.3, 129.0 (d, *J* = 8.7 Hz), 125.0, 119.9 (d, *J* = 5.1 Hz), 113.3, 55.2, 33.7, 33.3, 31.4, 26.4, 24.9. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.53. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{27}O_5P$ 451.1669; Found 451.1647.

*2-(4-Methoxyphenyl)cyclooct-1-en-1-yl diphenyl phosphate (**7fa**).*

Prepared according to GP1 starting from phosphate **6f** (356.7 mg, 0.82 mmol), 4-methoxyphenylzinc chloride (2.2 mL, 0.99 mmol, 0.45 M), $Pd(OAc)_2$ (7.3 mg) and XPhos (31.1 mg), hexane:EtOAc (4:1, R_f = ≈0.3), yield 137.3 mg (36%), yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.26–7.20 (m, 4H), 7.16 (d, *J* = 8.8 Hz, 2H), 7.14–7.09 (m, 2H), 6.98–6.93 (m, 4H), 6.74 (d, *J* = 8.8 Hz, 2H), 3.76 (s, 3H), 2.70–2.62 (m, 2H), 2.48–2.38 (m, 2H), 1.81–1.70 (m, 2H), 1.65–1.52 (m, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 158.2, 150.5 (d, *J* = 7.5 Hz), 143.9 (d, *J* = 8.7 Hz), 131.4, 129.8 (d, *J* = 1.3 Hz), 129.5, 126.3 (d, *J* = 8.3 Hz), 125.0 (d, *J* = 1.1 Hz), 119.9 (d, *J* = 5.1 Hz), 113.4, 55.1, 32.8, 30.4, 28.9 (d, *J* = 2.5 Hz), 28.6 (d, *J* = 1.4 Hz), 26.6, 26.2.^{31}P NMR (202 MHz, $CDCl_3$) δ -17.51. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{29}O_5P$ 465.1825; Found 465.1809.

*Diphenyl (1,2,2-triphenylvinyl) phosphate (**7gs**).* Prepared according to GP1 starting from phosphate **6g** (1.06 g, 2.09 mmol), phenylzinc chloride (5.0 mL, 2.50 mmol, 0.5 M), $Pd(OAc)_2$ (19.0 mg) and XPhos (80.0 mg) in THF (3mL), hexane:EtOAc (4:1, R_f = ≈0.3), yield 0.836 g (79%), yellow solid, mp = 109.5–110.8 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 6.8 Hz, 2H), 7.38 (d, *J* = 7.0 Hz, 2H), 7.28–7.12 (m, 11H), 7.12–7.06 (m, 5H), 7.04–6.99 (m, 2H), 6.81 (d, *J* = 8.5 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 150.5 (d, *J* = 7.4 Hz), 143.8 (d, *J* = 8.8 Hz), 139.6, 139.2, 134.6, 131.2 (d, *J* = 8.8 Hz), 130.7, 130.5, 129.9, 129.5, 128.7, 128.2, 128.0, 127.9, 127.4, 127.0, 125.1, 120.0 (d, *J* = 5.0 Hz). ^{31}P NMR (202 MHz, $CDCl_3$) δ -16.89. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{25}O_4P$ 505.1563; Found 505.1544.

*(Z)-1-(4-methoxyphenyl)-1-phenylhex-1-en-2-yl diphenyl phosphate (**7ht**).* Prepared according to GP1 starting from phosphate **6h** (0.763 g, 1.57 mmol), 4-methoxyphenylzinc chloride (4.33 mL, 1.90 mmol, 0.44 M), $Pd(OAc)_2$ (14.0 mg) and XPhos (80.0 mg), hexane:EtOAc (6:1, R_f = ≈0.3), yield 0.664 g (82%), yellow solid, mp. = 70-74 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.22 (m, 7H), 7.20–7.10 (m, 6H), 7.04–6.97 (m, 4H), 6.67 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 2.51–2.43 (m, 2H), 1.58–1.49 (m, 2H), 1.25–1.16 (m, 2H), 0.76 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.4, 150.6 (d, *J* = 7.3 Hz), 146.1 (d, *J* = 9.1 Hz), 140.2, 131.2 (d, *J* = 2.0 Hz), 131.0, 129.8 (d, *J* = 1.4 Hz), 129.6, 128.2, 127.1, 125.0, 119.9 (d, *J* = 5.1 Hz), 113.2, 55.1, 31.7, 29.3, 21.9, 13.7. ^{31}P NMR (202 MHz, $CDCl_3$) δ -17.94. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{31}H_{31}O_5P$ 515.1982; Found 515.1980.

*General procedure for the Negishi reaction of bromovinyl phosphates **7** (GP2)*

A solution of $AlCl_3$ (1 equiv, 0.5M solution in THF) was added to a mixture of phosphate **7**, $Pd(OAc)_2$ (4 mol %) and dppp (4 mol %) at 23 °C. The resultant mixture was stirred at 23 °C for 2 minutes and then a solution of organozinc chloride (2.0 equiv) was added and the reaction mixture was stirred at 23 °C for 12 hours. Then the mixture was quenched by tartaric acid (10 mL, 1M solution in water). The water layer was extracted with diethyl ether (3x15 mL), the organic layer was dried over $MgSO_4$ and the solvents were removed under reduce pressure. The product was isolated by column chromatography.

General procedure for one-pot two step synthesis of 1,2-disubstituted cyclohexenes (GP3)

Organozinc chloride (1.2 equiv) was added to a solution of phosphate **6a**, $Pd(OAc)_2$ (4 mol %) and XPhos (8 mol %) in THF (1 mL). The resultant mixture was stirred at 23 °C for 12 h, afterthat the residual organozinc chloride was quenched by addition of a solution of pivalic acid (0.2 equiv) in dry THF (1 mL). Then the crude reaction mixture was stirred at 23 °C for 5 min, followed by addition of $Pd(OAc)_2$ (4 mol%) and dppp (4 mol%). The solution was stirred at 23 °C for 5 min and organozinc chloride (2 equiv) and $AlCl_3$ (1.2 equiv, 0.5M solution of in THF) were added and the reaction mixture was stirred at 23 °C for 12 h. Then the mixture was quenched by tartaric acid (10 mL, 1M solution in water). The water layer was extracted with diethyl ether (3x15 mL), the organic layer was dried over $MgSO_4$ and the solvents were removed under reduce pressure. The product was isolated by column chromatography.

*4-Methoxy-4''-methyl-3',4',5',6'-tetrahydro-1,1':2',1''-terphenyl (**8b**).* It was prepared according to GP2 starting from phosphate **7aa** (205.2 mg, 0.47 mmol), 4-tolylzinc

chloride (1.9 mL, 0.95 mmol, 0.5 M), $Pd(OAc)_2$ (4.2 mg), dppp (7.8 mg) and $AlCl_3$ (0.94 mL, 0.47 mmol), hexane:DCM (9:1 → 4:1, R_f = ≈0.4), yield 112.0 mg (86%), white solid, mp = 52.0–55.4 °C. The title compound was also prepared following GP3 starting from phosphate **6a** (496.3 mg, 1.21 mmol), 4-methoxyphenylzinc chloride (3 mL, 1.50 mmol, 0.5 M), $Pd(OAc)_2$ (10.9 mg), XPhos (46.3 mg), PivOH (25 mg), $Pd(OAc)_2$ (10.9 mg), dppp (20.0 mg), 4-tolylzinc chloride (4.9 mL, 2.45 mmol, 0.5 M) and $AlCl_3$ (2.9 mL), 273.6 mg (81%).^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95–6.85 (m, 6H), 6.65 (d, *J* = 8.5 Hz, 2H), 3.73 (s, 3H), 2.43 (s, 4H), 2.24 (s, 3H), 1.82 (s, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 157.4, 141.1, 136.5, 135.0, 134.3, 134.0, 130.1, 128.9, 128.4 113.0, 55.1, 32.1, 23.4, 21.1. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{22}O$ 278.1671; Found 278.1662.

*4-Chloro-4''-methoxy-3',4',5',6'-tetrahydro-1,1':2',1''-terphenyl (**8c**).* Prepared according to GP2 starting from phosphate **7aa** (202.4 mg, 0.46 mmol), 4-chlorophenylzinc chloride (1.93 mL, 0.93 mmol, 0.48 M), $Pd(OAc)_2$ (4.2 mg), dppp (7.6 mg) and $AlCl_3$ (0.93 mL, 0.46 mmol), hexane:DCM (9:1 → 4:1, R_f = ≈0.4), yield 116.3 mg (84%), light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 2.41 (s, 4H), 1.82 (s, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.6, 142.5, 135.8, 135.2, 133.2, 131.2, 130.4, 130.0, 127.8, 113.1, 55.1, 32.0, 31.8, 23.2. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}ClO$ 299.1197; Found 299.1182.

*4-Fluoro-4''-methoxy-3',4',5',6'-tetrahydro-1,1':2',1''-terphenyl (**8d**).* Prepared according to GP2 starting from phosphate **7aa** (210.9 mg, 0.48 mmol), 4-fluorophenylzinc chloride (2.2 mL, 0.97 mmol, 0.44 M), $Pd(OAc)_2$ (4.3 mg), dppp (8.0 mg) and $AlCl_3$ (0.97 mL, 0.48 mmol), hexane:DCM (9:1 → 4:1, R_f = ≈0.4), yield 116.2 mg (85%), white solid, mp = 74.1–75.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (dd, *J* = 8.4, 5.7 Hz, 2H), 6.88 (d, *J* = 8.3 Hz, 2H), 6.79 (t, *J* = 8.6 Hz, 2H), 6.65 (d, *J* = 8.3 Hz, 2H), 3.73 (s, 3H), 2.41 (s, 4H), 1.82 (s, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 160.9 (d, *J* = 244.4 Hz), 157.6, 140.0 (*J* = 3.8 Hz), 136.0, 134.8, 133.4, 130.5 (d, *J* = 7.6 Hz), 130.0, 114.5 (*J* = 21.4 Hz), 113.1, 55.1, 32.1, 32.0, 23.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -117.59. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}FO$ 283.1493; Found 283.1476.

*4-Methoxy-3',4',5',6'-tetrahydro-1,1':2',1'':4'',1'''-quaterphenyl (**8e**).* Prepared according to GP2 starting from phosphate **7aa** (195.8 mg, 0.45 mmol), 4-biphenylzinc chloride (2.4 mL, 0.91 mmol, 0.38 M), $Pd(OAc)_2$ (4.0 mg), dppp (7.4 mg) and $AlCl_3$ (0.90 mL, 0.45 mmol), hexane:DCM (9:1 → 4:1, R_f = ≈0.4), yield 140.9 mg (92%), white solid, mp = 88.8–93.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.0 Hz, 2H), 7.44–7.31 (m, 4H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.6 Hz, 2H), 6.66 (d, *J* = 8.6 Hz, 2H), 3.72 (s, 3H), 2.53–2.42 (m, 4H), 1.85 (s, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 157.6, 143.2, 140.9, 138.1, 136.2, 134.7, 133.9, 130.1, 129.5, 128.7, 127.0, 126.9, 126.3, 113.1, 55.1, 32.2, 31.9, 23.4. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{24}O$ 341.1900; Found 341.1887.

*4''-Methoxy-3',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-4-carbonitrile (**8f**).* Prepared according to GP2 starting from phosphate **7aa** (204.6 mg, 0.47 mmol), 4-cyanophenylzinc chloride (4.8 mL, 0.96 mmol, 0.2 M), $Pd(OAc)_2$ (4.2 mg), dppp (7.7 mg) and $AlCl_3$ (0.94 mL, 0.47 mmol), hexane:EtOAc (20:1, R_f = ≈0.1), yield 121.1 mg (89%), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.85 (d, *J* = 7.9 Hz, 2H), 6.65 (d, *J* = 8.0 Hz, 2H), 3.73 (s, 3H), 2.61–2.29 (m, 4H), 1.83 (s, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.0, 149.3, 137.1, 135.2, 133.0, 131.6, 130.0, 129.9, 119.3, 113.3, 109.1, 55.1, 32.1, 31.4, 23.1. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{19}NO$ 290.1539; Found 290.1522.

*4''-Methoxy-N,N-dimethyl-3',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-4-amine (**8g**).* Prepared according to GP2 starting from phosphate **7aa** (191.4 mg, 0.44 mmol), 4-*N*,*N*-dimethylaminophenylzinc chloride (2 mL, 0.88 mmol, 0.44 M), $Pd(OAc)_2$ (3.9 mg), dppp (7.2 mg) and $AlCl_3$ (0.88 mL, 0.44 mmol). hexane:EtOAc (20:1, R_f = ≈0.2), yield 79.1 mg (59%), yellow solid, mp = 62.5–65.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.51 (d, *J* = 8.8 Hz, 2H), 3.73 (s, 3H), 2.87 (s, 6H), 2.42 (s, 4H), 1.80 (s, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 157.2, 148.4, 136.9, 133.9, 132.7, 132.2, 130.1, 129.7, 113.0, 111.9, 55.1, 40.6, 32.1, 31.9, 23.5. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{25}NO$ 308.2009; Found 308.1998.

*2-(4'-Methoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)furan (**8h**).* Prepared according to GP2 starting from phosphate **7aa** (210.0 mg, 0.48 mmol), 2-furylzinc chloride (2.75 mL, 0.96 mmol, 0.35 M), $Pd(OAc)_2$ (4.3 mg), dppp (7.9 mg) and $AlCl_3$ (0.96 mL, 0.48 mmol), hexane:DCM (9:1 → 4:1, R_f = ≈0.4), yield 89.4 mg (73%), white solid. mp = 50.4–51.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (s, 1H), 7.04 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.18–6.12 (m, 1H), 5.45 (d, *J* = 3.2 Hz, 1H), 3.81 (s, 3H), 2.52 (s, 2H), 2.38 (s, 2H), 1.78 (s, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.3, 155.2, 140.0, 137.1, 136.0, 129.1, 123.9, 113.8, 110.6, 107.3, 55.2, 33.5, 27.3, 23.1, 22.6. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}O_2$ 255.1380; Found 255.1368.

*2-(4'-Methoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)thiophene (**8i**).* Prepared according to GP2 starting from phosphate **7aa** (200.1 mg, 0.46 mmol), 2-thienylzinc chloride (1.5 mL, 0.93 mmol, 0.62 M), $Pd(OAc)_2$ (4.1 mg), dppp (7.6 mg) and $AlCl_3$ (0.92 mL, 0.46 mmol), hexane:DCM (9:1 → 4:1, R_f = ≈0.4), yield 99.0 mg (80%), white solid, mp = 61.0–64.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.85 (d, *J* = 8.5 Hz, 2H), 6.81–6.78 (m, 1H), 6.68 (d, *J* = 3 Hz, 1H), 3.81 (s, 3H), 2.59–2.53 (m, 2H), 2.44–2.38 (m, 2H), 1.87–1.76 (m, 4H). $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 158.6, 145.7, 136.5, 136.3, 130.0, 126.7, 125.9, 124.8, 124.1, 114.0, 55.2, 33.9, 31.3, 23.2, 23.0. HRMS (APCI)

m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}OS$ 271.1151; Found 271.1142.

*2-(4'-Methoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)benzofuran (***8j***).* Prepared according to GP2 starting from phosphate **7aa** (195.3 mg, 0.45 mmol), 2-benzofurylzinc chloride (3 mL, 0.90 mmol, 0.3 M), $Pd(OAc)_2$ (4.0 mg), dppp (7.4 mg) and $AlCl_3$ (0.89 mL, 0.45 mmol), hexane:DCM (9:1 → 4:1, R_f = ≈0.4), yield 84.0 mg (62%), white solid, mp = 72.0–76.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.11–7.06 (m, 3H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.86 (s, 1H), 3.82 (s, 3H), 2.62 (s, 2H), 2.45 (s, 2H), 1.88–1.77 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.5, 157.4, 153.6, 139.6, 136.6, 129.1, 128.9, 124.0, 123.3, 122.3, 120.5, 113.8, 110.7, 104.0, 55.3, 33.7, 27.6, 23.0, 22.6. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{20}O_2$ 305.1536; Found 305.1530.

*2-(4'-Methoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)thianaphthene (***8k***).* Prepared according to GP2 starting from phosphate **7aa** (204.0 mg, 0.47 mmol), 2-benzothiophenylzinc chloride (3.4 mL, 0.95 mmol, 0.28 M), $Pd(OAc)_2$ (4.2 mg), dppp (7.7 mg) and $AlCl_3$ (0.93 mL, 0.47 mmol), hexane:DCM (9:1 → 4:1, R_f = ≈0.4), yield 116.3 mg (78%), white solid. mp = 88.2–91.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 12.1, 7.9 Hz, 2H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 8.6 Hz, 2H), 6.95 (s, 1H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.80 (s, 3H), 2.61 (s, 2H), 2.44 (s, 2H), 1.90–1.75 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.8, 146.0, 139.8, 139.4, 138.6, 135.8, 130.1, 127.1, 123.8, 123.6, 123.0, 121.8, 121.4, 113.9, 55.2, 34.0, 31.3, 23.2, 23.0. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{20}OS$ 321.1308; Found 321.1295.

*6-^{n}Butyl-4'-methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl (***8l***).* Prepared according to GP2 starting from phosphate **7aa** (197.5 mg, 0.45 mmol), *n*-butylzinc chloride (1.93 mL, 0.91 mmol, 0.47 M), $Pd(OAc)_2$ (4.1 mg), dppp (7.5 mg) and $AlCl_3$ (0.91 mL, 0.46 mmol), hexane:DCM (9:1 → 4:1, R_f = ≈0.4), yield 100.8 mg (91%), colorless oil. The title compound was also prepared according to GP3 starting from phosphate **6a** (153.2 mg, 0.37 mmol), 4-methoxyphenylzinc chloride (1.01 mL, 0.48 mmol, 0.48 M), $Pd(OAc)_2$ (3.4 mg), XPhos (14.3 mg), PivOH (7.6 mg), $Pd(OAc)_2$ (3.4 mg), dppp (6.2 mg), *n*-butylzinc chloride (1.6 mL, 0.75 mmol, 0.47 M) and $AlCl_3$ (0.75 mL, 0.38 mmol), 100.8 mg (91%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.7 Hz, 4H), 7.32–7.27 (m, 4H), 7.23 (t, *J* = 7.4 Hz, 2H), 2.40 (s, 2H), 2.10–1.98 (m, 4H), 1.78–1.68 (m, 2H), 1.64–1.56 (m, 2H), 1.38–1.27 (m, 2H), 1.27–1.16 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.7, 137.2, 133.3, 132.2, 129.4, 113.3, 55.2, 34.0, 32.7, 30.7, 28.8, 23.7, 23.2, 22.7, 14.1. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{24}O$ 245.1900; Found 245.1891.

*2-Methoxy-6-(4'-methoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)naphthalene (***8m***).* Prepared according to GP2 starting from phosphate **7aa** (202.6 mg, 0.46 mmol), 6-methoxy-2-naphthylzinc chloride (4.65 mL, 0.93 mmol, 0.2 M), $Pd(OAc)_2$ (4.2 mg), dppp (7.6 mg) and $AlCl_3$ (0.93 mL, 0.46 mmol), hexane:DCM (9:1 → 2:1, R_f = ≈0.3), yield 159.9 mg (100%), yellow solid, mp = 71.9–75.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 9.0 Hz, 1H), 7.47 (s, 1H), 7.43 (d, *J* = 8.5 Hz, 1H), 7.09–7.00 (m, 3H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.61 (d, *J* = 8.3 Hz, 2H), 3.88 (s, 3H), 3.68 (s, 3H), 2.54 (s, 2H), 2.48 (s, 2H), 1.86 (s, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.5, 157.3, 139.6, 136.3, 134.5, 134.2, 132.8, 130.2, 129.3, 128.9, 128.8, 127.0, 125.3, 118.3, 113.1, 105.5, 55.3, 55.1, 32.19, 32.15, 23.5, 23.4. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{24}O_2$ 345.1849; Found 345.1837.

*1-(4'-Methoxy-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)naphthalene (***8n***).* Prepared according to modified GP2 starting from phosphate **7aa** (208.1 mg, 0.48 mmol), 1-naphthylzinc chloride (2.2 mL, 0.97 mmol, 0.44 M), $Pd(OAc)_2$ (4.3 mg), DPEPhos (10.3 mg), $AlCl_3$ (0.95 mL, 0.48 mmol) and the reaction mixture was placed in an oil bath at 45 °C and stirred for 12 h, hexane:DCM (9:1 → 4:1, R_f = ≈0.4), yield 149.9 mg (100%), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.45–7.37 (m, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.0 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 2H), 6.46 (d, *J* = 8.5 Hz, 2H), 3.59 (s, 3H), 2.61–2.48 (m, 3H), 2.40–2.28 (m, 1H), 2.03–1.83 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.4, 142.4, 136.0, 135.8, 133.7, 133.6, 131.6, 128.8, 128.3, 126.5, 126.2, 125.9, 125.52, 125.50, 125.3, 54.9, 33.1, 31.8, 23.6, 23.3. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{22}O$ 315.1743; Found 315.1733.

*4-Methoxy-2''-methyl-3',4',5',6'-tetrahydro-1,1':2',1''-terphenyl (***8o***).* Prepared according to modified GP2 starting from phosphate **7aa** (203.1 mg, 0.47 mmol), 2-tolylzinc chloride (2.4 mL, 0.96 mmol, 0.4 M), $Pd(OAc)_2$ (4.2 mg), DPEPhos (10.0 mg) and $AlCl_3$ (0.93 mL, 0.47 mmol) and the reaction mixture was placed in an oil bath at 45 °C and stirred for 12 h, hexane:DCM (4:1, R_f = 0.4), yield 125.0 mg (96%), white solid, mp = 37.8–38.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06–6.95 (m, 4H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 8.8 Hz, 2H), 3.69 (s, 3H), 2.59–2.47 (m, 1H), 2.41–2.20 (m, 3H), 2.05 (s, 3H), 1.90–1.76 (m, 4H).^{13}C{^{1}H}NMR (101 MHz, $CDCl_3$) δ 157.4, 143.7, 135.9, 134.9, 134.3, 134.0, 129.7, 129.4, 129.2, 126.0, 125.2, 112.7, 55.0, 32.4, 31.3, 23.5, 23.2, 19.5. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{22}O$ 279.1743; Found 279.1755.

*1-Methoxy-4-(2-(4-tolyl)cyclobut-1-en-1-yl)benzene (***8p***).* Prepared according to GP2 starting from phosphate **7ca** (181.3 mg, 0.44 mmol), 4-tolylzinc chloride (1.78 mL, 0.89 mmol, 0.5 M), $Pd(OAc)_2$ (4.0 mg), dppp (7.3 mg) and $AlCl_3$ (0.89 mL, 0.45 mmol), hexane:DCM (9:1 → 4:1, R_f = 0.4), yield 97.3 mg (88%), white solid, mp = 74.0–75.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 3.82 (s, 3H), 2.73 (s, 4H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.9, 137.4, 137.0, 136.7, 133.7, 129.3, 129.0, 127.4, 125.9, 113.7, 55.3, 26.8, 26.7, 21.4, in accordance with reference.[19b]

*1-Methoxy-4-(2-(4-tolyl)cyclopent-1-en-1-yl)benzene (**8q**).* Prepared according to GP2 starting from phosphate **7da** (105.7 mg, 0.25 mmol), 4-tolylzinc chloride (1.0 mL, 0.50 mmol, 0.5 M), $Pd(OAc)_2$ (2.2 mg), dppp (4.1 mg) and $AlCl_3$ (0.50 mL, 0.25 mmol), hexane:DCM (9:1 → 4:1, R_f = 0.4), yield 65.1 mg (98%), white solid, mp = 50.0–54.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 2H), 6.75 (d, *J* = 8.1 Hz, 2H), 3.77 (s, 3H), 2.86 (t, *J* = 7.4 Hz, 4H), 2.30 (s, 3H), 2.01 (p, *J* = 7.4 Hz, 2H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.2, 136.2, 136.2, 136.0, 135.8, 131.0, 129.3, 128.8, 128.0, 113.4, 55.2, 39.2, 39.0, 22.0, 21.2. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{20}O$ 265.1587; Found 265.1578.

*1-(4-Methoxyphenyl)-2-(4-tolyl)cyclohept-1-ene (**8r**).* It was prepared according to GP2 starting from phosphate **7ea** (28.0 mg, 0.062 mmol), 4-tolylzinc chloride (0.25 mL, 0.13 mmol, 0.5 M), $Pd(OAc)_2$ (0.6 mg), dppp (1.0 mg) and $AlCl_3$ (0.13 mL, 0.07 mmol), hexane:DCM (9:1 → 4:1, R_f = 0.4), yield 14.5 mg (80%), white solid, mp = 68.4–70.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92–6.83 (m, 6H), 6.63 (d, *J* = 8.6 Hz, 2H), 3.72 (s, 3H), 2.70–2.59 (m, 4H), 2.23 (s, 3H), 1.89 (p, *J* = 5.8 Hz, 2H), 1.77–1.63 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.3, 142.4, 140.2, 140.0, 137.8, 134.7, 130.0, 128.9, 128.3, 113.0, 55.1, 36.9, 32.8, 26.7, 21.1. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{24}O$ 293.1900; Found 293.1885.

*1-(4-Methoxyphenyl)-2-(4-tolyl)cyclooct-1-ene (**8s**).* Prepared according to GP2 starting from phosphate **7fa** (49.7 mg, 0.11 mmol), 4-tolylzinc chloride (0.43 mL, 0.22 mmol, 0.5 M), $Pd(OAc)_2$ (1.0 mg), dppp (1.8 mg) and $AlCl_3$ (0.21 mL, 0.11 mmol). hexane:DCM (9:1 → 4:1, R_f = 0.4), yield 6.0 mg (18%), colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95–6.89 (m, 6H), 6.63 (d, *J* = 9.2 Hz, 2H), 3.72 (s, 3H), 2.67–2.58 (m, 4H), 2.22 (s, 3H), 1.81–1.57 (m, 8H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 157.3, 141.6, 137.3, 137.0, 136.9, 134.8, 130.1, 129.0, 128.3, 112.9, 55.0, 34.2, 34.1, 29.8, 29.7, 26.9, 26.8, 21.1. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{26}O$ 307.2056; Found 307.2037.

*2-(2-(6-Methoxynaphthalen-2-yl)cyclohex-1-en-1-yl)thiophene (**8t**).* Prepared according to GP3 starting from phosphate **6a** (160.1 mg, 0.39 mmol), 2-thienylzinc chloride (0.76 mL, 0.47 mmol, 0.62 M), $Pd(OAc)_2$ (3.5 mg), XPhos (14.9 mg), PivOH (8.0 mg), $Pd(OAc)_2$ (3.5 mg), dppp (6.4 mg), 6-methoxy-2-naphthylzinc chloride (3.91 mL, 0.78 mmol, 0.2 M) and $AlCl_3$ (0.78 mL, 0.39 mmol), hexane:DCM (9:1 → 4:1, R_f = 0.4), 100.0 mg (80%), light yellow solid, mp = 99.5–101.8 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72–7.67 (m, 2H), 7.63 (s, 1H), 7.24 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.18–7.13 (m, 2H), 6.99–6.95 (m, 1H), 6.78–6.75 (m, 1H), 6.70 (d, *J* = 3.5 Hz, 1H), 3.96 (s, 3H), 2.69–2.61 (m, 2H), 2.58–2.50 (m, 2H), 1.98–1.83 (m, 4H).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.6, 145.5, 139.5, 136.6, 133.5, 129.5, 129.2, 128.2, 127.3, 127.1, 126.8, 125.9, 125.1, 124.2, 118.6, 105.7, 55.3, 33.9, 31.4, 23.2, 23.1. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{20}OS$ 321.1308; Found 321.1295.

*4''-chloro-3',4',5',6'-tetrahydro-[1,1':2',1''-terphenyl]-4-ol (**8u**).* Prepared according to modified GP3 starting from phosphate **6a** (116.1 mg, 0.28 mmol), 4-chlorophenylzinc chloride (0.71 mL, 0.34 mmol, 0.48 M), $Pd(OAc)_2$ (2.5 mg), XPhos (10.8 mg), PivOH (5.7 mg), $Pd(OAc)_2$ (2.5 mg), dppp (4.6 mg), (4-((*tert*-butyldimethylsilyl)oxy)phenyl)zinc chloride (1.72 mL, 0.57 mmol, 0.33 M) and $AlCl_3$ (0.68 mL, 0.34 mmol) and the reaction mixture was stirred at 23 °C for 12 h Then the mixture was quenched by tartaric acid (10 mL, 1M solution in water). The water layer was extracted with diethyl ether (3x15 mL), the organic layer was dried over $MgSO_4$ and the solvents were removed under reduce pressure. The crude product was dissolved in THF (5 mL) and TBAF (0.3 mL, 1M in THF) was added. The resultant mixture was stirred for 1 h at 23 °C. Then the crude reaction mixture was diluted with ether (30 mL), the organic phase was washed with HCl (2 mL, 1M aqueous solution), water (1x10 mL) and brine (1x10 mL). The organic phase was dried over $MgSO_4$, concentrated under reduce pressure and the product was isolate by column chromatography, hexane:EtOAc (9:1 → 6:1, R_f = 0.5), 67.9 mg (84%), colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 6.58 (d, *J* = 8.6 Hz, 2H), 4.48 (s, 1H), 2.40 (s, 4H), 1.81 (s, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 153.6, 142.5, 136.1, 135.2, 133.4, 131.3, 130.4, 130.2, 127.8, 114.7, 32.1, 31.8, 23.2. HRMS (APCI) m/z: $[M-H]^-$ Calcd for $C_{18}H_{17}ClO$ 283.0895; Found 283.0898.

*6'-(thiophen-2-yl)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (**8v**).* Prepared according to GP3 starting from phosphate **6a** (108.5 mg, 0.27 mmol), 4-cyanophenylzinc chloride (1.33 mL, 0.32 mmol, 0.24 M), $Pd(OAc)_2$ (2.4 mg), XPhos (10.0 mg), PivOH (5.5 mg), $Pd(OAc)_2$ (2.4 mg), dppp (4.4 mg), 2-thienylzinc chloride (1.07 mL, 0.54 mmol, 0.5 M) and $AlCl_3$ (0.64 mL, 0.32 mmol), hexane:DCM (9:1 → 2:1, R_f = 0.8), 40.0 mg (57%), white solid, mp = 120–124 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.05 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.77 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.56 (dd, *J* = 3.7, 1.2 Hz, 1H), 2.57–2.50 (m, 2H), 2.43–2.33 (m, 2H), 1.87–1.76 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.3, 144.5, 135.1, 132.2, 129.8, 129.1, 126.3, 125.8, 124.6, 119.1, 110.2, 32.8, 31.9, 22.9, 22.7. HRMS (APCI) m/z: $[M-H]^-$ Calcd for $C_{17}H_{15}NS$ 264.0852; Found 264.0853.

*1-methyl-2-(2-(thiophen-2-yl)cyclohex-1-en-1-yl)-1H-indole (**8w**).* Prepared according to GP3 starting from phosphate **6a** (105.7 mg, 0.26 mmol), 2-thienylzinc chloride (0,63 mL, 0.32 mmol, 0.5 M), $Pd(OAc)_2$ (2.3 mg), XPhos (9.9 mg), PivOH (5.3 mg), $Pd(OAc)_2$ (2.3 mg), dppp (4.2 mg), 2-(*N*-methylindol)zinc chloride (1.4 mL, 0.53 mmol, 0.38 M) and $AlCl_3$ (0.62 mL, 0.31 mmol), hexane:DCM (100:0 → 9:1, R_f = 0.2), 62.9 mg (83%), white solid, mp = 79–82 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 1H), 7.29–7.26 (m, 1H), 7.22–7.16 (m, 1H), 7.11 (t, *J* = 7.2 Hz, 1H), 6.99 (dd, *J* = 5.1, 1.1 Hz, 1H), 6.77 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.70 (d, *J* = 3.7 Hz, 1H), 6.38 (s, 1H), 3.36 (s, 3H), 2.69 (s, 2H), 2.43 (s, 2H), 1.91–1.79 (m, 4H). ^{13}C{^{1}H}

NMR (126 MHz, $CDCl_3$) δ 144.3, 141.7, 137.1, 132.0, 128.4, 126.2, 126.1, 125.4, 124.7, 121.1, 120.5, 119.4, 109.6, 100.2, 34.0, 30.5, 29.7, 23.0, 22.8. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{19}NS$ 294.1311; Found 294.1317.

*2-(4'-methyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-yl)thiophene (**8x**).* Prepared according to GP3 starting from phosphate **6a** (126.6 mg, 0.31 mmol), 4-tolylzinc chloride (0.79 mL, 0.37 mmol, 0.47 M), $Pd(OAc)_2$ (2.8 mg), XPhos (11.8 mg), PivOH (6.3 mg), $Pd(OAc)_2$ (2.8 mg), dppp (5.1 mg), 2-thienylzinc chloride (1.25 mL, 0.63 mmol, 0.50 M) and $AlCl_3$ (0.74 mL, 0.37 mmol), hexane:DCM (100:0 → 9:1, R_f = 0.5), 63.0 mg (80%), white solid, mp = 46–48 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.99 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.77 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.65 (dd, *J* = 3.7, 1.2 Hz, 1H), 2.60–2.50 (m, 2H), 2.43–2.37 (m, 3H), 2.34 (s, 3H), 1.86–1.75 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 145.6, 141.2, 136.7, 136.3, 129.2, 128.7, 126.6, 125.9, 124.8, 124.0, 33.8, 31.4, 23.2, 23.0, 21.3. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{18}S$ 255.1202; Found 255.1204.

*6'-(1-methyl-1H-indol-2-yl)-2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carbonitrile (**8y**).* Prepared according to modified GP3 starting from phosphate **6a** (137.1 mg, 0.34 mmol), 4-cyanophenylzinc chloride (1.68 mL, 0.40 mmol, 0.24 M), $Pd(OAc)_2$ (3.0 mg), XPhos (12.8 mg), PivOH (6.9 mg), $Pd(OAc)_2$ (3.0 mg), dppp (5.5 mg), 2-(*N*-methylindol)zinc chloride (1.8 mL, 0.68 mmol, 0.38 M) and $AlCl_3$ (0.80 mL, 0.40 mmol), hexane:DCM (9:1 → 2:1, R_f = 0.5), 39.5 mg (38%), white solid, mp = 122–124 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.14–7.09 (m, 4H), 7.08–7.04 (m, 1H), 6.27 (s, 1H), 3.22 (s, 3H), 2.57–2.51 (m, 2H), 2.50–2.44 (m, 2H), 1.95–1.83 (m, 4H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 147.8, 141.3, 137.5, 136.9, 131.7, 129.1, 128.6, 127.9, 121.2, 120.2, 119.6, 118.9, 109.9, 109.4, 101.0, 32.9, 30.9, 30.3, 23.0, 22.7. HRMS (APCI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}N_2$ 313.1699; Found 313.1703.

*2-(4-Methoxyphenyl)-1,1,2-triphenylethene (**9a**).* Prepared according to GP2 starting from phosphate **7gs** (205.9 mg, 0.41 mmol), 4-methoxyphenylzinc chloride (1.71 mL, 0.82 mmol, 0.48 M), $Pd(OAc)_2$ (3.7 mg), dppp (6.7 mg) and $AlCl_3$ (0.82 mL, 0.41 mmol), hexane:DCM (9:1 → 4:1, R_f = 0.4), 72.0 mg (49%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14–7.06 (m, 9H), 7.06–6.99 (m, 6H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 8.7 Hz, 2H), 3.73 (s, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 158.1, 144.1, 144.0, 140.6, 140.1, 136.1, 132.5, 131.4, 131.4, 131.4, 127.7, 127.6, 126.4, 126.3, 113.1, 55.1, in accordance with ref.[22]

*(Z)-1-methoxy-4-(1-phenyl-2-(p-tolyl)hex-1-en-1-yl)benzene (**9b**).* Prepared according to modified GP2 starting from phosphate **7ht** (87.7 mg, 0.17 mmol), 4-tolylzinc chloride (0.73 mL, 0.37 mmol, 0.40 M), $Pd(OAc)_2$ (1.5 mg), DPEPhos (3.7 mg) and $AlCl_3$ (0.34 mL, 0.17 mmol), hexane:DCM (9:1 → 4:1, R_f = 0.4), 22.0 mg (36%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37–7.29 (m, 2H), 7.27–7.19 (m, 3H), 7.03–6.94 (m, 4H), 6.81–6.75 (m, 2H), 6.58–6.51 (m, 2H), 3.69 (s, 3H), 2.44–2.32 (m, 2H), 2.28 (s, 3H), 1.35–1.11 (m, 4H), 0.76 (t, *J* = 7.1 Hz, 3H), in accordance with ref.[19e]

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge via the Internet at http://pubs.acs.org. Experimental procedures, characterizations of new compounds, NMR spectra data.

Conflicts of interest

There are no conflicts to declare.

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