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Aryl group – a leaving group in arylphosphine oxides

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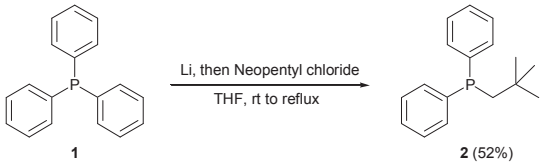
ABSTRACT

The treatment of triphenylphosphine oxide with organometallic reagents leads to the substitution of up to three phenyl substituents with the incoming carbon nucleophile. The replacement of the phenyl/aryl group in tertiary diarylalkylphosphine oxides or even aryldialkylphosphine oxides was also observed. Naphthyl-substituted phosphine oxides undergo Michael-type addition at the naphthyl group when treated with organolithium reagent.

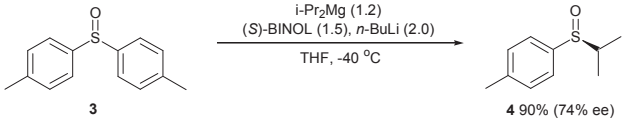
1. Introduction

Modification of the carbon chain in organic molecules through nucleophilic substitution requires the presence of a good leaving group in the molecule which could be replaced by a carbon nucleophile during the reaction. The same trend is observed in phosphorus chemistry, where the organophosphorus compounds possessing a leaving group at the phosphorus atom undergo nucleophilic substitution.[1] Carbon-based groups are regarded as substitution-resistant although the aryl substituents in arylphosphines[2] or phosphine oxides[3] could be replaced through reductive cleavage of *P*-aryl bond with an alkali metal (Scheme 1).



Scheme 1. Replacement of phenyl by reductive cleavage of *P*-aryl bond.

Except for a few observations, the nucleophilic substitution of phenyl (aryl) group in arylphosphorus compounds has never been a subject to intensive research studies.[4] In fact, there is little known about phenyl/aryl group substitution in organic chemistry in general, although a few examples of this kind of transformation can be found in organosulfur chemistry where a treatment of diarylsulfoxides with Grignard (Scheme 2)[5] or organolithium[6] reagents led to substitution of an aryl group.



Scheme 2. Nucleophilic substitution of aryl group in sulfoxides.

The substitution of phenyl/aryl group at phosphorus may be of high importance due to the high availability of arylphosphorus compounds, including triphenylphosphine and its derivatives. With the developed method in hand, the synthesis of new phosphines and derivatives could be achieved by simple replacement of aryl substituents. This approach is much more flexible and convenient compared to the tedious preparation of reactive organophosphorus precursors (halides or esters).

In the course of our research topic, related to the modification of aryl substituent in arylphosphorus compounds, we primarily were interested in the synthetic activation of aryl groups through the dearomatization under Birch reduction conditions[7] or *ortho*-functionalization using directed *ortho*-metallation (DoM)[8] methodology. Considering the results obtained so far we were curious if arylphosphines and their derivatives could be good substrates for

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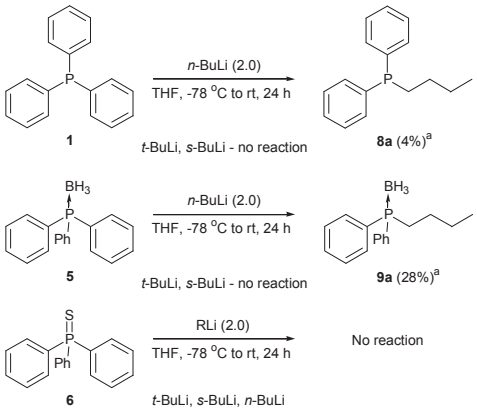
0040-4020/

the nucleophilic substitution at phosphorus in the case where aryl group is the only potential leaving group. Theoretically, such a substitution could take place in the case where the incoming nucleophile has higher pKa value than the leaving aryl anion. In practice, this process would require the use of the very strong carbon nucleophiles.

2. Results and discussion

Among the available arylphosphorus compounds triphenylphosphine **1** and its derivatives appeared to be very suitable substrates for the test reactions. The symmetrical nature of these molecules exclude the problem of competitive substitution of two different aryl groups. The substitution of phenyl groups in **1** and its derivatives using commercially available organolithium compounds have been checked first (Scheme 3).



Scheme 3. Substitution of phenyl group in **1**, **5** and **6**.

A reaction of triphenylphosphine **1**, triphenylphosphine-borane **5** or triphenylphosphine sulfide **6** with commercially available *t*-BuLi, *s*-BuLi or *n*-BuLi generally failed to produce the corresponding products, except reactions of **1** and **5** with *n*-BuLi where the formation of substitution products **8a** and **9a** was observed to a limited extent.

The case of triphenylphosphine oxide **7** was different (Scheme 4, Table 1).

A reaction of triphenylphosphine oxide **7** with 1.1 equivalent of *t*-BuLi afforded *t*-butyldiphenylphosphine oxide **10a** in 76% yield after 2.5 h (Table 1, entry 10). The use of a higher excess of this organolithium reagent led to a decrease of the yield of **10a** and the formation of phosphafluorene oxide **12**, a formal intramolecular cyclization product, has been observed (Table 1, entry 12). A reaction of **7** with *s*-BuLi was solvent-dependent; in THF, the formation of both substitution and cyclization products **10b** and **12** has been observed, whereas in Et_2O the exclusive formation of the desired product **10b** was detected (Table 1, entries 13 and 14). A similar solvent dependence was observed for the reaction of **7** with *n*-BuLi (Table 1, entries 15 and 16). Here however, a reaction in Et_2O led to the formation of **11a** as a side product, which is formally

Table 1
Substitution in triphenylphosphine **1** and derivatives

Nr	RLi (equiv)	Products		
		10	**11**	**12**
1[a]	***t*-BuLi (1.1)**	**10a (76%)**[b]	—	—
2[c]	*t*-BuLi (2.0)	**10a** (51%)[b]	—	—
3[c]	*t*-BuLi (3.0)	**10a** (10%)[b]	—	46%[b]
4	*s*-BuLi (2.0)	**10b** (54%)[b]	—	26%[b]
5[c]	***s*-BuLi (2.0)**	**10b (86%)**[b]	—	—
6	***n*-BuLi (2.0)**	**10c (97%)**	—	—
7[c]	*n*-BuLi (2.0)	**10c** (85%)[b]	**11a** (8%)[b]	—
8	MeLi (2.0)	**10d** (65%)[b]	**11b** (30%)[b]	—
9[c]	**MeLi (1.0)**	**10d** (89%)[b]	**11b** (9%)[b]	—
10[c]	MeLi (3.0)	**10d** (56%)[b]	**11b** (20%)[b]	—
11	$TMSCH_2Li$ (2.0)	**10e** (80%)[b], **10d** (8%)[a]	—	—
12	***i*-BuLi (2.0)**	**10f** (91%)	—	—

[a] The reaction was run for 5 h.
[b] Yields based on NMR analysis of product mixtures.
[c] Reaction performed in Et_2O.

a product of substitution of two phenyl groups. This trend was even more expressed in the case methyllithium (Table 1, entries 16–18). The use of 2 equivalents of organometallic reagent led to the formation of both monosubstitution and disubstitution products **10d** and **11b** in ca. 2:1 ratio. The selectivity of this particular reaction could be shifted towards monosubstitution product **10d** by lowering the amount of an organometallic reagent. On the other hand, an increase in the amount of methyllithium failed to shift the selectivity towards di- or trisubstitution product.

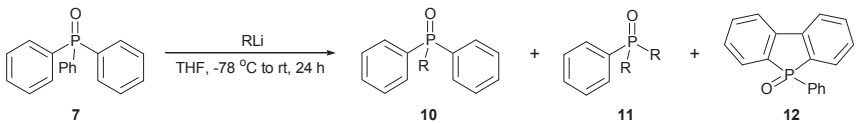
Surprisingly, the problem of overalkylation is not observed using $TMSCH_2Li$, which afforded a mixture of two monoalkylation products (Table 1, entry 20). The formation of **10d** as a side product can be easily explained by the hydrolytic cleavage of the carbon-silicon bond during the aqueous work-up.

The number of commercially available organolithium compounds is relatively low but these reagents could be obtained from the corresponding alkyl/aryl halides using halogen-metal exchange process. In the next step, a set of substitution reactions of **7** with in situ generated organolithium compounds has been performed (Scheme 5, Table 2).

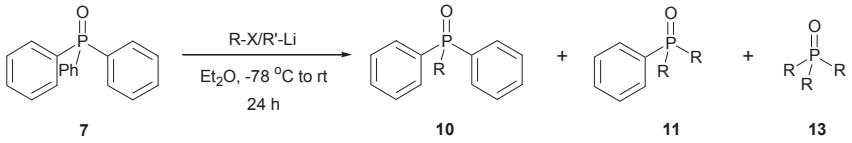
In the case where organometallic species were generated smoothly the substitution went effectively affording the corresponding monosubstitution products **10g** and **10j** (Table 2, entries 1 and 4). The case of aryllithium reagents derived from *m*-iodotoluene and *m*-iodoanisole was different as here the formation of mixtures of mono, di and trisubstitution products has been observed (Table 2, entries 5 and 6). This suggests, that at least for aryllithium reagents the steric crowd generated by the reagent influences the degree of substitution.

Regarding the commercial availability, Grignard reagents are much better candidates for the nucleophilic substitution of phenyl group in triphenylphosphine oxide although they generally exhibit lower reactivity towards nucleophilic substitution. To check the utility of these reagents in phenyl group substitution a set of reactions of **7** with Grignard reagents has been performed (Scheme 6, Table 3).

In accordance with expectations, Grignard reagents appeared to be far less reactive than the corresponding organolithium reagents.



Scheme 4. Substitution in triphenylphosphine **1** and derivatives.

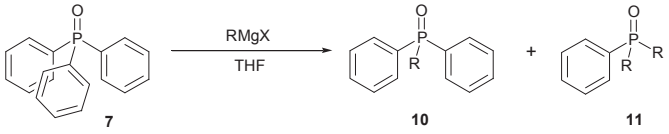


Scheme 5. Substitution of **7** with in situ generated organolithium compounds.

Table 2
Substitution of **7** with in situ generated organolithium compounds

Nr	R-X/R′-Li (equiv)[a]	Products		
		10	**11**	**13**
1	c-HexBr (2.0)/*t*-BuLi (4.0)	**10g** (47%)	—	—
2	1-NpBr (2.0)/*n*-BuLi (2.0)	**10h** (9%)[b]	—	—
3	*o*-AnBr (2.0)/*n*-BuLi (2.0)	**10i** (8%)[b]	—	—
4	*o*-TolI (2.0)/*n*-BuLi (2.0)	**10j** (69%)[b]	—	—
5	*m*-TolI (2.0)/*n*-BuLi (2.0)	**10k** (16%)[b]	**11c** (22%)[b]	**13a** (12%)[b]
6	*m*-AnI (2.0)/*n*-BuLi (2.0)	**10l** (38%)[b]	**11d** (28%)[b]	**13b** (5%)[b]

[a] The halide was stirred with alkyllithium reagent for 2 h prior to the addition of $Ph_3P(O)$.
[b] Yields based on NMR analysis of product mixtures.



Scheme 6. Substitution of **7** with Grignard reagents.

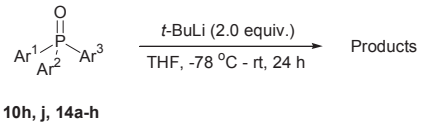
Table 3
Substitution of **7** with Grignard reagents

Nr	Grignard reagent (equiv)	Conditions	Products[a]	
			10	**11**
1	MeMgBr (1.5)	rt, 24 h	**10d** (51%)	**11b** (10%)
2	MeMgBr (3.0)	rt, 24 h	**10d** (44%)	**11b** (50%)
3	MeMgBr (5.0)	rt, 24 h	**10d** (45%)	**11b** (40%)
4	EtMgBr (2.0)	rt, 24 h	**10m** (10%)	—
5	EtMgBr (2.0)	60 °C, 24 h	**10m** (85%)	**11e** (5%)
6	BnMgCl (2.0)	60 °C, 24 h	**10n** (traces)	—
7	*c*-HexMgCl (2.0)	60 °C, 24 h	No reaction	
8	*t*-BuMgCl (2.0)	60 °C, 24 h	No reaction	
9	*o*-TolMgCl (2.0)	60 °C, 24 h	No reaction	
10	*o*-AnMgBr (2.0)	60 °C, 24 h	No reaction	
11	*p*-TolMgCl (2.0)	60 °C, 24 h	**10o** (59%)	**11f** (18%)
12	*m*-AnMgBr (2.0)	60 °C, 24 h	**10l** (47%)	**11d** (15%)

[a] Yields in brackets were calculated based on NMR analysis of product mixtures.

Compound **7** treated with a slight excess of MeMgBr afforded monosubstitution product **10d** with moderate yield along with some disubstitution product **11b** (Table 3, entry 1). An increased amount of Grignard reagent failed to improve the yield of monosubstitution product. Instead, the selectivity of the reaction has been shifted towards disubstitution reaction (Table 3, entries 2 and 3). With EtMgBr the outcome of the reaction run at room temperature was even worse but at 60 °C the reaction afforded predominantly monosubstitution product (Table 3, entries 4 and 5). It seems also, that the reaction of **7** with Grignard reagents is sensitive to the steric factors which might be a consequence of lower reactivity of these compounds; thus, a reaction of **7** with *c*-HexMgCl, *t*-BuMgCl, *o*-TolMgCl and *o*-AnMgBr failed to produce the corresponding substitution products (Table 3, entries 7–10) which is in sharp contrast to a reaction of the same phosphine oxide with *t*-BuLi (Table 1, entry 10) or *o*-TolI/*n*-BuLi (Table 2, entry 4). On the other hand, less crowded *p*-TolMgCl and *m*-AnMgBr afforded monosubstituted phosphine oxides **10o** and **10l**, respectively, along with disubstitution products **11f** and **11d** when heated at 60 °C for a longer time.

The experiments conducted so far showed that at least in case of triphenylphosphine oxide **7** a substitution of phenyl group might take place which should be taken into account once a reaction of these compounds with organometallic compounds is conducted. To answer the question of generality of the discussed reaction a set of reactions of the differently substituted triarylphosphine oxides with *t*-BuLi as the nucleophile was performed (Scheme 7, Table 4).



Scheme 7. Substitution of triarylphosphine oxides with *t*-BuLi.

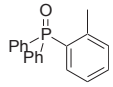
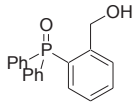
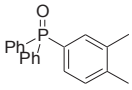
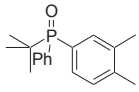
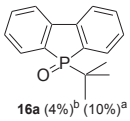
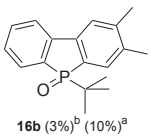
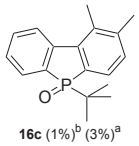
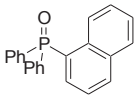
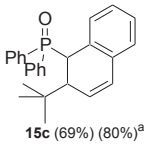
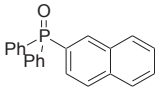
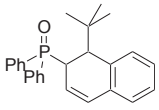
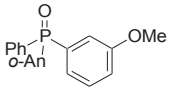
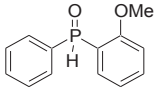
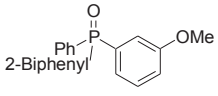
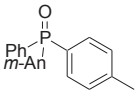
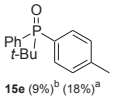
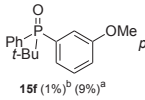
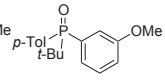
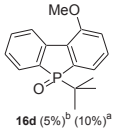
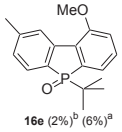
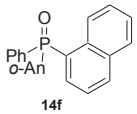
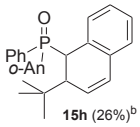
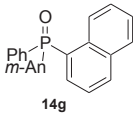
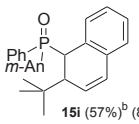
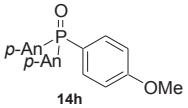
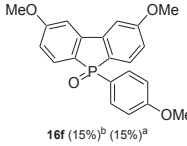
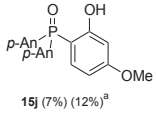
The reactivity of triarylphosphine oxides **10h**, **j**, **14a**–**h** towards *t*-BuLi appeared to be more complex compared to the parent triphenylphosphine oxide **7**. Phosphine oxides with *ortho*-alkyl-substituted aryl groups underwent the deprotonation of benzylic hydrogens rather than substitution at phosphorus (Table 4, entry 1). Phosphine oxides with *m*- and *p*-substituted aryl groups tend to undergo substitution reaction but, due to a similar electronic character, each aryl group could be replaced leading to a mixture of compounds (Table 4, entries 2 and 7). Moreover, the presence of an excess of organometallic reagent in the reaction mixture forced *ortho*-deprotonation of the formed products, which then underwent an intramolecular cyclization leading to the formation of dibenzophospholane oxides.

Interesting cases were the phosphine oxides **10h**, **14b**, **f** and **g** possessing naphthyl substituents at phosphorus. In all cases these substrates acted as Michael acceptors yielding exclusively the corresponding 1,4-addition products in moderate to good yields through the partial dearomatization of the naphthyl ring (Table 4, entries 3, 4, 8 and 9). The addition of *t*-BuLi to an unsymmetrically substituted naphthylphosphine oxides **14f** and **g** creates two new stereocenters so the formation of up to 4 pair of enantiomers should be expected. Luckily, only two diastereomers were observed (albeit with low *de*) which suggest the *trans* orientation of two substituents in dihydronaphthyl moiety.

In one case, a reaction between the symmetrical triarylphosphine oxide **14h** with *t*-BuLi was examined (Table 4, entry 10). The presence of methoxy group in *para* position changed the reaction pathway completely. Instead of substitution of aryl group, the only process was *ortho*-deprotonation followed by the intramolecular cyclization (**16f**) or oxidation (**15j**) of the carbanion.

In the case of phosphine oxides **14a** and **e** the formation of complex mixtures of products, including dibenzophospholanes **16a**–**e**, was observed. Attempted separation of these mixtures failed, therefore it was decided to prepare these compounds using alternative pathways (Scheme 8).

Table 4
Substitution of triarylphosphine oxides with *t*-BuLi

Nr	Substrate	Products
1	 **10j**	 **15a** (35%) (62%)[a]
2	 **14a**	 **15b** (5%)[b] (18%)[a]  **16a** (4%)[b] (10%)[a]  **16b** (3%)[b] (10%)[a]  **16c** (1%)[b] (3%)[a]
3	 **10h**	 **15c** (69%) (80%)[a]
4	 **14b**	 **15d** (58%) (65%)[a]
5	 **14c**	 **17** (25%) (73%)[a]
6	 **14d**	No reaction
7	 **14e**	 **15e** (9%)[b] (18%)[a]  **15f** (1%)[b] (9%)[a]  **15g** (6%)[b] (12%)[a]  **16d** (5%)[b] (10%)[a]  **16e** (2%)[b] (6%)[a]
8	 **14f**	 de = 20% **15h** (26%)[b] (53%)[a]
9	 **14g**	 de = 0% **15i** (57%)[b] (80%)[a]
10	 **14h**	 **16f** (15%)[b] (15%)[a]  **15j** (7%) (12%)[a]

[a]Conversion based on NMR analysis of reaction mixtures.
[b]Yields based on NMR analysis of product mixtures.

Phosphine oxides **15b** and **15e** were obtained from the corresponding secondary phosphine oxide **18** through copper-catalyzed coupling with aryl iodides whereas phosphine oxides **15f** and **15g** were obtained using copper catalysis. Phosphine oxides **15b**, **15f** and **15g** were then subjected to reaction with a base affording dibenzophospholane oxides **16b**–**e** in low to good yields. The analytical data of the obtained **15b**, **15e**–**g** and **16b**–**e** were identical in both cases.

The case of triarylphosphine oxides shows that the substitution of aryl groups can be achieved in the presence of strong nucleophiles like organolithium compounds. Regarding this, it would be interesting to compare the reactivity of secondary diarylphosphine oxides under the same reaction conditions (Scheme 9). Surprisingly, the main reaction product in all cases was diphenyl(α-hydroxy)ethylphosphine oxide **21**, the formation of which could be explained in terms of degradation of THF under basic conditions. Deprotonation of α-CH_2 group in THF furnishes the corresponding carbanion which undergoes fragmentation into ethene and acetaldehyde. The latter undergoes addition reaction with an anion derived from secondary phosphine oxide yielding the final **21**.

Following the course of the research project it appeared interesting to establish, whether diphenylalkylphosphine oxides would undergo phenyl group substitution when treated with organometallic species (Scheme 10, Table 5).

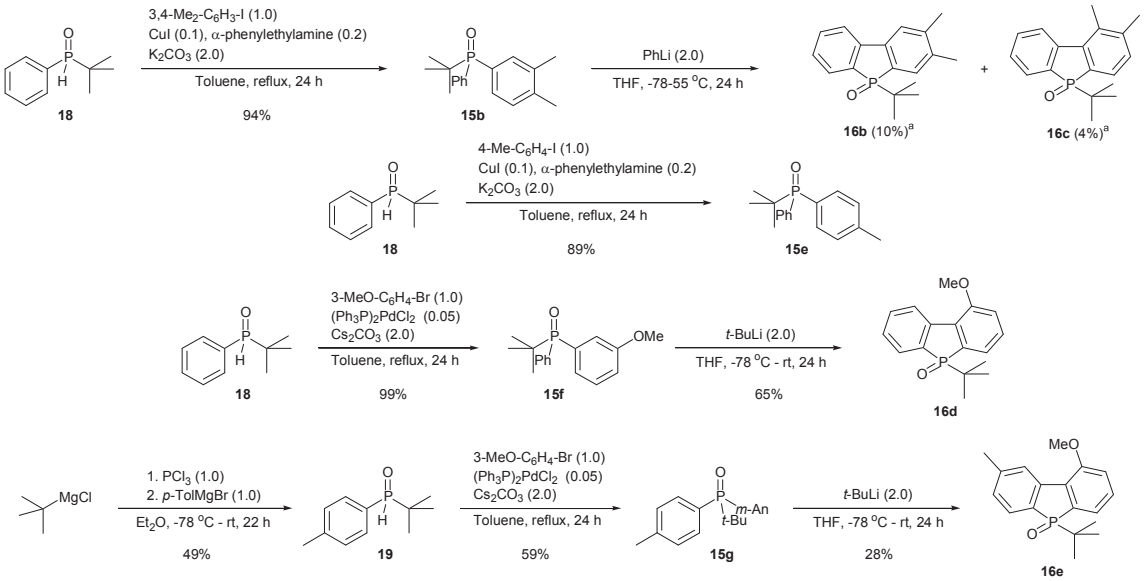
When diphenyl(*t*-butyl)phosphine oxide **10a** was treated with different organolithium compounds, it underwent two general reactions: substitution of the phenyl group in case of less bulky organolithium compounds *n*-BuLi and MeLi (Table 5, entries 1 and 5) and *ortho*-deprotonation-cyclization with the more bulky *s*-BuLi, *t*-BuLi and $TMSCH_2Li$ (Table 5, entries 2–4). Surely, the use of the sterically demanding nucleophiles makes their attack at electrophilic phosphorus impossible thus favouring *ortho*-deprotonation followed by intramolecular cyclization of the formed carbanion.

As it could be expected, phosphine oxide **10d** was much less reactive towards the phenyl group substitution compared to triphenylphosphine oxide **7** or diphenyl(*t*-butyl)phosphine oxide **10a** due to the presence of acidic α protons. Nevertheless, primary organolithium compounds underwent this reaction to some extent and methyllithium appeared to be the best nucleophile. The treatment of **10d** with *s*-BuLi afforded the corresponding substitution product **22d** in only 8% yield and *t*-BuLi failed to produce the desired product.

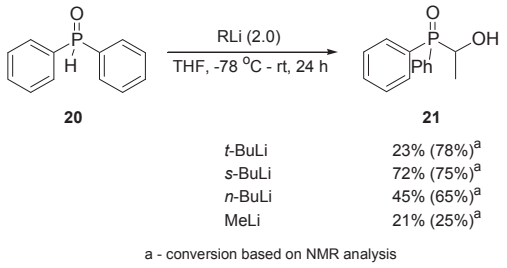
The results described so far lead to the conclusion that the treatment of triaryl and diarylalkylphosphine oxides with organolithium compounds does not necessarily lead to deprotonation of acidic hydrogen atoms. Under optimized reaction conditions substitution of phenyl/aryl group might be a dominant process. To gain insight into the reactivity of other phosphine oxides against organolithium compounds a set of reactions using phospholane and phospholene oxides has been performed (Scheme 11).

Both 2- and 3-phospholene oxides were inactive towards *t*- and *s*-BuLi or, more probably, they acted as proton donors. A treatment of 3-phospholene oxide **23** with *n*-BuLi afforded a mixture of compounds. The most striking observation here was the reaction of methyllithium with both **23** and **25**. With **23**, the main product appeared to be dimethyl(4-but-1-enyl)phosphine oxide **24**. These compounds could be formed only through substitution of both phenyl and alkenyl groups with MeLi. With **25**, the only product was phenylmethyl(2-but-1-enyl)phosphine oxide **26** and this compound could be obtained only through opening of phospholene ring with MeLi.

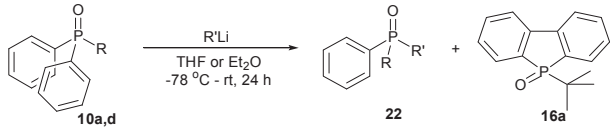
In contrast to the phospholene oxides **23** and **25**, phospholane oxide **27** appeared to be more tolerant to different organolithium compounds. Its reaction with both *t*-BuLi and *s*-BuLi afforded substitution products **28** and **30** along with 2-hydroxyphospholane oxide **29** which was most probably obtained by oxidation of the corresponding α-carbanion. In both cases the conversion of the



Scheme 8. The synthesis of **15b**, **15e**–**g** and **16b**–**e**.



Scheme 9. Reaction of **20** with organolithium compounds.



Scheme 10. Substitution of phenyl group in **10a**, **d**.

substrate varied about 80% and the ratio of both products was about 1:1. This suggests that under the reaction conditions both nucleophilic substitution of phenyl group and deprotonation of CH_2 group operated.

Table 5
Substitution of phenyl group in **10a**, **d**

Nr	Compound	R′Li (equiv)	Products	
			22	**16a**
1	**10a** (R=*t*-Bu)	*n*-BuLi (2.0)	**22a** (44%)[b]	—
2	**10a** (R=*t*-Bu)	*s*-BuLi (2.0)	—	89%[a]
3	**10a** (R=*t*-Bu)	*t*-BuLi (2.0)	—	51%[a]
4	**10a** (R=*t*-Bu)	$TMSCH_2Li$ (2.0)	—	56%[b]
5	**10a** (R=*t*-Bu)	MeLi (2.0)	**22b** (53%)[a] (7%)[b]	—
6	**10d** (R=Me)	*n*-BuLi (2.0)	**22c** (21%)[b]	—
7	**10d** (R=Me)	*s*-BuLi (2.0)	**22d** (8%)[b]	—
8	**10d** (R=Me)	*t*-BuLi (2.0)	No reaction	
9	**10d** (R=Me)	$TMSCH_2Li$ (2.0)	**22e** (5%)[b]	—
10	10d (R=Me)	MeLi (2.0)	11b (45%)[b]	

[a] Conversion based on NMR analysis of reaction mixtures.
[b] Yields based on NMR analysis of product mixtures.

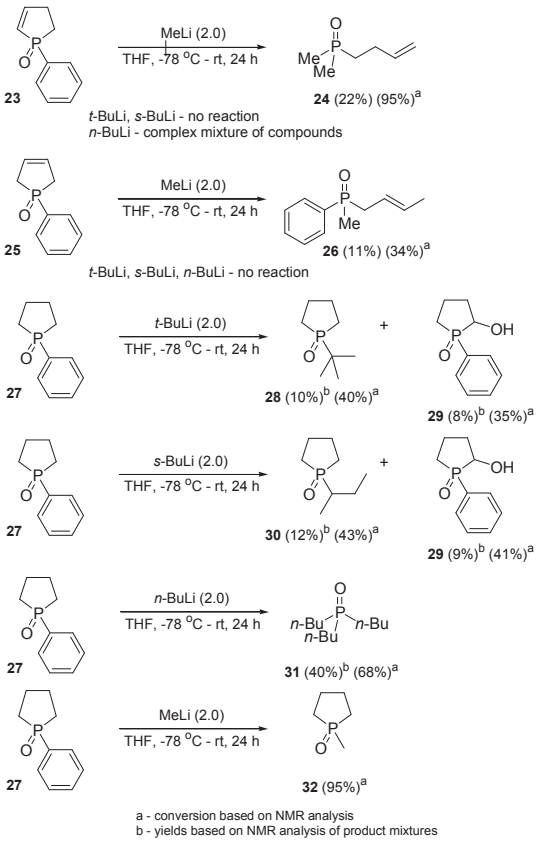
The less sterically crowded *n*-BuLi and MeLi underwent smoothly a reaction with phospholane oxide **27**. The use of *n*-BuLi led to the formation of tributylphosphine oxide **31** in moderate yield and good conversion. The presence of this product suggests that nucleophilic substitution of the phenyl group was followed by the ring opening with an excess of organolithium reagent. In the case of MeLi the only observed product was 1-methylphospholane oxide **32**. NMR analysis of the reaction mixture showed no other products in the reaction mixture. However, attempted isolations of this compound either by simple aqueous work-up or using SPE technique failed, probably due to the volatility of **32** and its solubility in water.

3. Conclusions

Organophosphorus compounds possessing aryl groups at phosphorus are very common molecules in organic chemistry, which is a consequence of their stability and synthetic availability. On the other hand, placement of aryl group at phosphorus limits the number of the pathways for possible modifications and practically eliminates its removal and its substitution would require the use of a very strong nucleophile. The results discussed herein show that phenyl/aryl group, usually regarded as irreplaceable substituents, are labile in the presence of the strong nucleophiles. Moreover, phenyl substitution with organolithium compounds could be achieved even in the presence of acidic hydrogen atoms, like in diarylalkylphosphine oxides or phospholane oxide **27**. These observations raise questions about the nature of the interactions between the substrate and organolithium compound and the selectivity of nucleophilic substitution over deprotonation reaction.

4. Experimental part

All reactions were performed under an argon atmosphere by using Schlenk techniques. Only dry solvents were used, and the glassware was heated under vacuum prior to use. Solvents for chromatography were distilled once before use, and solvents for extraction were used as received. Tetrahydrofurane and diethyl ether were dried over sodium/benzophenone ketyl. Triphenylphosphine, MeLi, *n*-BuLi, *iso*-BuLi, *s*-BuLi, *t*-BuLi, $(TMS)CH_2Li$, EtMgBr, BnMgCl, *p*-TolMgBr, cyclohexyl bromide, 1-naphthyl



Scheme 11. Reactivity of phospholene and phospholane oxides towards organolithium compounds.

bromide, *o*-anisyl bromide, 2-iodotoluene, 3-iodotoluene, *m*-anisyl iodide were commercially available and used as received. The starting compounds: triphenylphosphine-borane (**5**),[9] triphenylphosphine sulfide (**6**),[10] triphenylphosphine oxide (**7**),[11] diphenyl-*o*-tolylphosphine oxide (**10j**),[12] 1-naphthyldiphenylphosphine oxide (**10h**),[13] 2-naphthyldiphenylphosphine oxide (**14b**),[13] *m*-anisyl(*o*-anisyl)phenylphosphine oxide (**14c**),[14] *m*-anisyl(2-biphenyl) phenylphosphine oxide (**14d**),[14] *m*-anisylphenyl(*p*-tolyl)phosphine oxide (**14e**),[14] *o*-anisyl(1-naphthyl)phenylphosphine oxide (**14f**),[14] *m*-anisyl(1-naphthyl)phenylphosphine oxide (**14g**),[14] tri(*p*-anisyl) phosphine oxide (**14h**),[14] diphenylphosphine oxide (**18**),[7b] diphenylmethylphosphine oxide (**10d**),[15] 1-phenylphosphol-2-ene oxide (**21**),[16] 1-phenylphosphol-3-ene oxide (**23**)[17] and 1-phenylphospholane oxide (**25**)[18] were prepared according to the literature procedures.

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

4.1. General procedure for the reaction of triphenylphosphine derivatives and other substrates with organometallic compounds

Method A. In a flame-dried Schlenk tube (50 mL) equipped with magnetic stirrer and an inert gas inlet substrate (0.5 mmol) was dissolved in 10 mL THF. The mixture was cooled to −78 °C and commercial organolithium or Grignard reagent (1.0 mmol) was added at once. The mixture was allowed to warm to room temperature over 24 h. The reaction was quenched by addition of saturated NH_4Cl solution (10 mL) and extracted with DCM (3×20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated under the reduced pressure. The residue was purified by flash column chromatography.

Method B. In a flame-dried Schlenk tube (50 mL) equipped with magnetic stirrer and an inert gas inlet aryl or alkyl halide (1.0 mmol) was dissolved in 10 mL Et_2O. The mixture was cooled to −78 °C and organolithium (1.0 mmol) was added gradually. After the mixture was stirred for 2 h, the reaction was allowed to warm to room temperature and the substrate (0.5 mmol) was added. The mixture was stirred for 24 h. The reaction was quenched by addition of saturated NH_4Cl solution (10 mL) and extracted with DCM (3×20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography.

*4.1.1. Diphenyl(n-butyl)phosphine (**8a**).* This compound was prepared according to general procedure (*Method A*) from triphenylphosphine (**1**) (0.131 g, 0.499 mmol) and *n*-butyllithium (0.625 mL, 0.999 mmol, 1.6 M solution in hexanes): yield 0.005 g (4%); yellow oil; [Found: C, 79.02; H, 7.67. $C_{16}H_{19}P$ requires C, 79.31; H, 7.90%]; R_f (CH_3Cl/MeOH=20:1) 0.58; δ_H (500 MHz, $CDCl_3$) 0.91 (3H, t, *J* 7.1 Hz), 1.41–1.48 (4H, m), 2.04–2.10 (2H, m), 7.31–7.36 (6H, m), 7.41–7.46 (4H, m); δ_C (126 MHz, $CDCl_3$) 13.8, 24.3 (d, *J* 12.7 Hz), 27.6 (d, *J* 10.0 Hz), 28.0 (d, *J* 15.4 Hz), 128.4 (d, *J* 6.4 Hz), 128.5, 132.7 (d, *J* 18.2 Hz); δ_P (202 MHz, $CDCl_3$) −15.89; GC t_R=11.13 min; GC–MS (EI, 70 eV) *m*/*z*=242 (19, M^+), 200 (37), 199 (100), 183 (40), 152 (11), 121 (14), 109 (17), 108 (46), 107 (26), 91 (32%). Analytical data are in accordance with those reported in the literature.[19]

*4.1.2. Diphenyl(n-butyl)phosphine-borane (**9a**).* This compound was prepared according to general procedure (*Method A*) from triphenylphosphine-borane (**5**) (0.138 g, 0.500 mmol) and *n*-butyllithium (0.625 mL, 1.000 mmol, 1.6 M solution in hexanes): yield 0.036 g (28%). Isolated as a mixture with starting material. R_f (Hexane/AcOEt=6:1) 0.72; δ_H (500 MHz, $CDCl_3$) 0.62–1.66 (3H, m), 0.90 (3H, t, *J* 7.3 Hz), 1.37–1.45 (2H, m), 1.46–1.55 (2H, m), 2.17–2.24 (2H, m), 7.42–7.53 (6H, m), 7.65–7.70 (4H, m); δ_C (126 MHz, $CDCl_3$) 13.6, 24.3 (d, *J* 14.5 Hz), 25.0, 25.4 (d, *J* 37.2 Hz), 128.6 (d, *J* 10.0 Hz), 129.2 (d, *J* 58.1 Hz), 129.7 (d, *J* 55.4 Hz), 131.0 (d, *J* 2.7 Hz), 131.2 (d, *J* 2.7 Hz), 132.1 (d, *J* 9.1 Hz), 133.2 (d, *J* 9.1 Hz); δ_P (202 MHz, $CDCl_3$) 15.82 GC t_R=11.15 min; GC–MS (EI, 70 eV) *m*/*z*=242 (19), 200 (37), 199 (100), 185 (10), 183 (41), 152 (12), 121 (14), 109 (18), 108 (48), 107 (27), 91 (32%). Analytical data are in accordance with those reported in the literature.[20]

*4.1.3. Diphenyl(t-butyl)phosphine oxide (**10a**).* This compound was prepared according to general procedure (*Method A*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol) and *tert*-butyllithium (0.323 mL, 0.549 mmol, 1.7 M solution in pentane) except that the reaction time was 2.5 h: yield 0.098 g (76%); white solid; mp 124.2–126.0 °C; [Found: C, 74.61; H, 7.58. $C_{16}H_{19}OP$ requires C, 74.40; H, 7.41%]; R_f (CH_3Cl/MeOH=20:1) 0.81; δ_H (500 MHz, $CDCl_3$) 1.26 (9H, d, *J* 14.8 Hz), 7.46–7.55 (6H, m), 7.94–7.99 (4H, m); δ_C (126 MHz, $CDCl_3$) 25.2, 33.9 (d, *J* 70.8 Hz),

128.2 (d, *J* 10.9 Hz), 131.1 (d, *J* 90.8 Hz), 131.4 (d, *J* 2.7 Hz), 132.2 (d, *J* 7.3 Hz); δ_P (202 MHz, $CDCl_3$) 39.27; GC t_R=9.68 min; GC–MS (EI, 70 eV) *m*/*z*=258 (0.20, M^+), 203 (14), 202 (100), 201 (25), 155 (36), 125 (11%). Analytical data are in accordance with those reported in the literature.[21]

*4.1.4. 1-Phenyldibenzophospholane oxide (**12**).* This compound was prepared according to general procedure (*Method A*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol) and *tert*-butyllithium (0.881 mL, 1.498 mmol, 1.7 M solution in pentane): yield 0.064 g (46%); white solid; mp 164.8–165.4 °C; [Found: C, 77.97; H, 4.50. $C_{18}H_{13}OP$ requires C, 78.25; H, 4.74%]; R_f (CH_3Cl/MeOH=15:1) 0.70; δ_H (500 MHz, $CDCl_3$) 7.37–7.43 (4H, m), 7.48–7.52 (1H, m), 7.58–7.62 (2H, m), 7.64–7.69 (2H, m), 7.70–7.76 (2H, m), 7.82–7.86 (2H, m); δ_C (126 MHz, $CDCl_3$) 121.2 (d, *J* 10.0 Hz), 126.7 (d, *J* 12.7 Hz), 129.5 (d, *J* 10.9 Hz), 129.9 (d, *J* 9.1 Hz), 130.8 (d, *J* 103.5 Hz), 131.0 (d, *J* 10.9 Hz), 132.1 (d, *J* 3.6 Hz), 132.9 (d, *J* 107.2 Hz), 133.4 (d, *J* 1.8 Hz), 141.8 (d, *J* 21.8 Hz); δ_P (202 MHz, $CDCl_3$) 33.66; GC t_R=16.73 min; GC–MS (EI, 70 eV) *m*/*z*=276 (0.24, M^+), 274 (15), 219 (14), 218 (100), 217 (20), 200 (20), 199 (82), 152 (30), 140 (42%). Analytical data are in accordance with those reported in the literature.[22]

*4.1.5. Diphenyl(s-butyl)phosphine oxide (**10b**).* This compound was prepared according to general procedure (*Method A*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol) and *sec*-butyllithium (0.714 mL, 0.999 mmol, 1.4 M solution in cyclohexane): yield 0.111 g (86%); white solid; mp 89.4–90.3 °C; [Found: C, 74.50; H, 7.54. $C_{16}H_{19}OP$ requires C, 74.40; H, 7.41%]; R_f (CH_3Cl/MeOH=20:1) 0.52; δ_H (500 MHz, $CDCl_3$) 0.96 (3H, t, *J* 7.5 Hz), 1.15 (3H, dd, *J* 7.1, 16.9 Hz), 1.40–1.49 (1H, m), 1.66–1.78 (1H, m), 2.21–2.31 (1H, m), 7.40–7.50 (6H, m), 7.73–7.81 (4H, m); δ_C (126 MHz, $CDCl_3$) 11.5 (d, *J* 2.7 Hz), 12.2 (d, *J* 13.6 Hz), 22.1 (d, *J* 1.8 Hz), 33.7 (d, *J* 72.7 Hz), 128.4 (d, *J* 11.8 Hz), 128.5 (d, *J* 10.9 Hz), 130.9 (d, *J* 8.2 Hz), 131.3 (d, *J* 2.7 Hz), 131.4 (d, *J* 2.7 Hz), 132.40 (d, *J* 93.6 Hz), 132.43 (d, *J* 93.6 Hz); δ_P (202 MHz, $CDCl_3$) 36.83; GC t_R=9.94 min; GC–MS (EI, 70 eV) *m*/*z*=258 (10, M^+), 257 (25), 230 (34), 229 (20), 203 (11), 202 (71), 201 (100), 183 (10), 155 (31), 154 (45), 125 (16%). Analytical data are in accordance with those reported in the literature.[23]

*4.1.6. Diphenyl(n-butyl)phosphine oxide (**10c**).* This compound was prepared according to general procedure (*Method A*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol) and *n*-butyllithium (0.625 mL, 0.999 mmol, 1.6 M solution in hexanes): yield 0.125 g (97%); white solid; mp 86.6–87.1 °C; [Found: C, 74.21; H, 7.30. $C_{16}H_{19}OP$ requires C, 74.40; H, 7.41%]; R_f (CH_3Cl/MeOH=15:1) 0.60; δ_H (500 MHz, $CDCl_3$) 0.88 (3H, t, *J* 7.3 Hz), 1.37–1.45 (2H, m), 1.55–1.64 (2H, m), 2.22–2.29 (2H, m), 7.43–7.53 (6H, m), 7.70–7.77 (4H, m); δ_C (126 MHz, $CDCl_3$) 13.6, 23.4 (d, *J* 3.6 Hz), 24.1 (d, *J* 15.4 Hz), 29.4 (d, *J* 72.7 Hz), 128.6 (d, *J* 10.9 Hz), 130.7 (d, *J* 10.0 Hz), 131.6 (d, *J* 2.7 Hz), 133.1 (d, *J* 98.1 Hz); δ_P (202 MHz, $CDCl_3$) 32.62; GC t_R=9.94 min; GC–MS (EI, 70 eV) *m*/*z*=258 (2, M^+), 216 (60), 215 (100), 202 (19), 201 (33), 155 (11), 125 (18%). Analytical data are in accordance with those reported in the literature.[24]

*4.1.7. Di-n-butylphenylphosphine oxide (**11a**).* This compound was prepared according to general procedure (*Method A*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol) and *n*-butyllithium (0.625 mL, 0.999 mmol, 1.6 M solution in hexanes): yield 0.010 g (8%); pale yellow crystals; mp 52.4–54.5 °C; [Found: C, 70.65; H, 9.89. $C_{14}H_{23}OP$ requires C, 70.56; H, 9.73%]; R_f (CH_3Cl/MeOH=20:1) 0.70; δ_H (500 MHz, $CDCl_3$) 0.84 (6H, t, *J* 7.3 Hz), 1.27–1.45 (6H, m), 1.51–1.63 (2H, m), 1.76–1.87 (2H, m), 1.88–2.01 (2H, m), 7.41–7.51 (3H, m), 7.62–7.70 (2H, m); δ_C (126 MHz, $CDCl_3$) 13.5, 23.4 (d, *J* 3.6 Hz), 24.0 (d, *J* 14.5 Hz), 29.6 (d, *J* 68.1 Hz), 128.5 (d, *J* 10.9 Hz), 130.3 (d, *J* 8.2 Hz), 131.3 (d, *J* 2.7 Hz), 132.6 (d, *J* 91.7 Hz); δ_P (202 MHz, $CDCl_3$) 40.55; GC t_R=8.85 min; GC–MS (EI, 70 eV) *m*/*z*=238 (0.84, M^+), 209 (16), 182 (19), 154 (100), 140 (48), 125 (42), 91 (29%). Analytical data are in accordance with those reported in the literature.[25]

*4.1.8. Methyldiphenylphosphine oxide (**10d**).* This compound was prepared according to general procedure (*Method A*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol) and methyllithium (0.313 mL, 0.499 mmol, 1.6 M solution in diethyl ether) except that reaction performed in Et_2O: yield 0.096 g (89%); white solid; mp 107.2–107.8 °C; [Found: C, 72.38; H, 6.15. $C_{13}H_{13}OP$ requires C, 72.21; H, 6.06%]; R_f (CH_3Cl/MeOH=15:1) 0.60; δ_H (500 MHz, $CDCl_3$) 2.03 (3H, d, *J* 13.2 Hz), 7.44–7.59 (4H, m), 7.50–7.55 (2H, m), 7.70–7.76 (4H, m); δ_C (126 MHz, $CDCl_3$) 16.5 (d, *J* 73.6 Hz), 128.6 (d, *J* 11.8 Hz), 130.5 (d, *J* 9.1 Hz), 131.7 (d, *J* 2.7 Hz), 134.0 (d, *J* 100.8 Hz); δ_P (202 MHz, $CDCl_3$) 29.93; GC t_R=13.90 min; GC–MS (EI, 70 eV) *m*/*z*=216 (25, M^+), 215 (100), 201 (60), 139 (12), 91 (12), 77 (56), 51 (44), 50 (10%). Analytical data are in accordance with those reported in the literature.[26]

*4.1.9. Dimethylphenylphosphine oxide (**11b**).* This compound was prepared according to general procedure (*Method A*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol) and methyllithium (0.313 mL, 0.499 mmol, 1.6 M solution in diethyl ether) except that reaction performed in Et_2O: yield 0.007 g (9%); white solid; mp 118.0–120.0 °C; [Found: C, 62.29; H, 7.09. $C_8H_{11}OP$ requires C, 62.33; H, 7.19%]; R_f (CH_3Cl/MeOH=20:1) 0.58; δ_H (500 MHz, $CDCl_3$) 1.74 (6H, d, *J* 13.2 Hz), 7.47–7.57 (3H, m), 7.71–7.77 (2H, m); δ_C (126 MHz, $CDCl_3$) 18.1 (d, *J* 71.8 Hz), 128.7 (d, *J* 11.8 Hz), 129.6 (d, *J* 9.1 Hz), 131.6 (d, *J* 2.7 Hz), 134.7 (d, *J* 99.0 Hz); δ_P (202 MHz, $CDCl_3$) 33.89; GC t_R=6.75 min; GC–MS (EI, 70 eV) *m*/*z*=154 (65, M^+), 139 (100), 92 (10), 91 (45%). Analytical data are in accordance with those reported in the literature.[7b]

*4.1.10. (Trimethylsilylmethyl)diphenylphosphine oxide (**10e**).* This compound was prepared according to general procedure (*Method A*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol) and (trimethylsilyl)methyllithium (0.999 mL, 0.999 mmol, 1 M solution in pentane): yield 0.115 g (80%); white solid; mp 99.6–100.3 °C; [Found: C, 66.66; H, 7.11. $C_{16}H_{21}OPSi$ requires C, 66.63; H, 7.34%]; R_f (CH_3Cl/MeOH=15:1) 0.58; δ_H (500 MHz, $CDCl_3$) 0.04 (9H, s), 1.75 (2H, d, *J* 14.8 Hz), 7.40–7.49 (6H, m), 7.74–7.79 (4H, m); δ_C (126 MHz, $CDCl_3$) 0.2 (d, *J* 2.7 Hz), 18.7 (d, *J* 62.7 Hz), 128.4 (d, *J* 11.8 Hz), 130.4 (d, *J* 9.1 Hz), 131.1 (d, *J* 2.7 Hz), 136.2 (d, *J* 99.0 Hz); δ_P (202 MHz, $CDCl_3$) 30.62; GC t_R=9.53 min; GC–MS (EI, 70 eV) *m*/*z*=288 (0.03, M^+), 216 (25), 215 (100), 201 (60), 139 (11), 91 (11%). Analytical data are in accordance with those reported in the literature.[27]

*4.1.11. Diphenyl(i-butyl)phosphine oxide (**10f**).* This compound was prepared according to general procedure (*Method A*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol) and *iso*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in heptane): yield 0.118 g (91%); pale yellow solid; mp 129.9–130.7 °C; [Found: C, 74.56; H, 7.40. $C_{16}H_{19}OP$ requires C, 74.40; H, 7.41%]; R_f (CH_3Cl/MeOH=15:1) 0.64; δ_H (500 MHz, $CDCl_3$) 1.02 (6H, d, *J* 6.6 Hz), 2.12–2.26 (3H, m), 7.44–7.51 (6H, m), 7.73–7.79 (4H, m); δ_C (126 MHz, $CDCl_3$) 23.6 (d, *J* 4.5 Hz), 24.7 (d, *J* 9.1 Hz), 38.3 (d, *J* 70.8 Hz), 128.6 (d, *J* 10.9 Hz), 130.6 (d, *J* 9.1 Hz), 131.5 (d, *J* 2.7 Hz), 133.8 (d, *J* 98.1 Hz); δ_P (202 MHz, $CDCl_3$) 31.17; GC t_R=11.68 min; GC–MS (EI, 70 eV) *m*/*z*=258 (10, M^+), 257 (29), 216 (34), 215 (100), 202 (26), 201 (39), 155 (13), 140 (29), 125 (23), 91 (13%). Analytical data are in accordance with those reported in the literature.[28]

*4.1.12. Cyclohexyldiphenylphosphine oxide (**10g**).* This compound was prepared according to general procedure (*Method B*) from

triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol), cyclohexyl bromide (0.122 mL, 0.999 mmol) and *t*-butyllithium (1.175 mL, 1.998 mmol, 1.7 M solution in pentane): yield 0.067 g (47%); pale yellow powder; mp 165.7–165.9 °C; [Found: C, 75.89; H, 7.24. $C_{18}H_{21}OP$ requires C, 76.04; H, 7.44%]; R_f (CH_3Cl/MeOH=20:1) 0.56; δ_H (500 MHz, $CDCl_3$) 1.20–1.32 (3H, m), 1.49–1.60 (2H, m), 1.66–1.77 (3H, m), 1.78–1.85 (2H, m), 2.20–2.29 (1H, m), 7.44–7.54 (6H, m), 7.75–7.82 (4H, m); δ_C (126 MHz, $CDCl_3$) 24.7 (d, *J* 2.7 Hz), 25.7, 26.3 (d, *J* 13.6 Hz), 37.1 (d, *J* 72.7 Hz), 128.5 (d, *J* 10.9 Hz), 131.0 (d, *J* 9.1 Hz), 131.4 (d, *J* 2.7 Hz), 132.0 (d, *J* 94.5 Hz); δ_P (202 MHz, $CDCl_3$) 34.67; GC t_R=10.32 min; GC–MS (EI, 70 eV) *m*/*z*=162 (80), 161 (16), 131 (36), 120 (53), 103 (13), 91 (50), 88 (100%). Analytical data are in accordance with those reported in the literature.[21]

*4.1.13. (Naphth-1-yl)diphenylphosphine oxide (**10h**).* This compound was prepared according to general procedure (*Method B*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol), 1-naphthyl bromide (0.140 mL, 0.999 mmol) and *n*-butyllithium (1.249 mL, 1.998 mmol, 1.6 M solution in hexanes): yield 0.015 g (9%); brown powder; mp 183.8–184.7 °C; [Found: C, 80.63; H, 4.96. $C_{22}H_{17}OP$ requires C, 80.48; H, 5.22%]; R_f (CH_3Cl/MeOH=15:1) 0.85; δ_H (500 MHz, $CDCl_3$) 7.28–7.58 (10H, m), 7.65–7.73 (4H, m), 7.87–7.91 (1H, m), 7.99–8.04 (1H, m), 8.57–8.62 (1H, m); δ_C (126 MHz, $CDCl_3$) 124.1 (d, *J* 14.5 Hz), 126.5, 127.3, 127.5 (d, *J* 5.5 Hz), 128.6 (d, *J* 12.7 Hz), 128.72, 128.78 (d, *J* 102.6 Hz), 131.9 (d, *J* 2.7 Hz), 132.0 (d, *J* 10.0 Hz), 132.8 (d, *J* 104.5 Hz), 133.3 (d, *J* 3.6 Hz), 133.7 (d, *J* 9.1 Hz), 133.8 (d, *J* 9.1 Hz); δ_P (202 MHz, $CDCl_3$) 32.39; GC t_R=18.43 min; GC–MS (EI, 70 eV) *m*/*z*=328 (30, M^+), 327 (100), 249 (32), 202 (16), 127 (10%). Analytical data are in accordance with those reported in the literature.[24]

*4.1.14. o-Anisyldiphenylphosphine oxide (**10i**).* This compound was prepared according to general procedure (*Method B*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol), *o*-anisyl bromide (0.125 mL, 0.999 mmol) and *n*-butyllithium (0.624 mL, 0.999 mmol, 1.6 M solution in hexanes): yield 0.012 g (8%); pale yellow solid; mp 164.2–166.6 °C; [Found: C, 74.40; H, 5.40. $C_{19}H_{17}O_2P$ requires C, 74.02; H, 5.56%]; R_f (CH_3Cl/MeOH=15:1) 0.38; δ_H (500 MHz, $CDCl_3$) 3.53 (3H, s), 6.87–6.92 (1H, m), 7.02–7.08 (1H, m), 7.37–7.43 (4H, m), 7.45–7.54 (3H, m), 7.66–7.72 (4H, m), 7.73–7.79 (1H, m); δ_C (126 MHz, $CDCl_3$) 55.1, 111.3 (d, *J* 6.4 Hz), 120.1 (d, *J* 103.5 Hz), 120.8 (d, *J* 11.8 Hz), 128.0 (d, *J* 12.7 Hz), 131.3 (d, *J* 3.6 Hz), 131.7 (d, *J* 10.9 Hz), 133.1 (d, *J* 108.1 Hz), 134.2 (d, *J* 1.8 Hz), 134.8 (d, *J* 7.3 Hz), 160.7 (d, *J* 2.7 Hz); δ_P (202 MHz, $CDCl_3$) 27.33; GC t_R=21.57 min; GC–MS (EI, 70 eV) *m*/*z*=308 (58, M^+), 307 (32), 291 (13), 290 (36), 289 (12), 279 (17), 277 (39), 229 (13), 218 (13), 217 (97), 201 (23), 200 (14), 199 (100), 183 (23), 153 (14), 152 (48), 139 (15), 115 (12), 91 (40), 77 (64), 51 (36), 47 (19%). Analytical data are in accordance with those reported in the literature.[14]

*4.1.15. Diphenyl(o-tolyl)phosphine oxide (**10j**).* This compound was prepared according to general procedure (*Method B*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol), 2-iodotoluene (0.127 mL, 0.999 mmol) and *n*-butyllithium (0.624 mL, 0.999 mmol, 1.6 M solution in hexanes): yield 0.101 g (69%); white solid; mp 121.5–122.9 °C; [Found: C, 78.35; H, 5.95. $C_{19}H_{17}OP$ requires C, 78.07; H, 5.86%]; R_f (CH_3Cl/MeOH=15:1) 0.68; δ_H (500 MHz, $CDCl_3$) 2.45 (3H, s), 6.99–7.05 (1H, m), 7.10–7.15 (1H, m), 7.27–7.30 (1H, m), 7.39–7.44 (1H, m), 7.45–7.49 (4H, m), 7.52–7.57 (2H, m), 7.62–7.68 (4H, m); δ_C (126 MHz, $CDCl_3$) 21.6 (d, *J* 5.5 Hz), 125.1 (d, *J* 12.7 Hz), 128.5 (d, *J* 11.8 Hz), 130.7 (d, *J* 103.5 Hz), 131.7 (d, *J* 2.7 Hz), 131.8 (d, *J* 10.0 Hz), 132.1 (d, *J* 2.7 Hz), 132.6 (d, *J* 103.5 Hz), 133.4 (d, *J* 12.7 Hz), 143.2 (d, *J* 7.3 Hz); δ_P (202 MHz, $CDCl_3$) 31.82; GC t_R=20.03 min; GC–MS (EI, 70 eV) *m*/*z*=292 (35, M^+), 291 (100), 213 (16), 166 (14), 165 (25), 77 (13), 65 (10), 51 (12), 47 (13%). Analytical data are in accordance with those reported in the literature.[14]

*4.1.16. Diphenyl(m-tolyl)phosphine oxide (**10k**).* This compound was prepared according to general procedure (*Method B*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol), 3-iodotoluene (0.128 mL, 0.999 mmol) and *n*-butyllithium (0.624 mL, 0.999 mmol, 1.6 M solution in hexanes): yield 0.023 g (16%); pale yellow solid; mp 122.7–123.3 °C; [Found: C, 78.23; H, 5.96. $C_{19}H_{17}OP$ requires C, 78.07; H, 5.86%]. Isolated as a mixture of monosubstituted **10k**, disubstituted **11c** and trisubstituted products **13a**; R_f (CH_3Cl/MeOH=30:1) 0.63; δ_H (500 MHz, $CDCl_3$) 2.37 (3H, s), 7.32–7.41 (3H, m), 7.44–7.50 (4H, m), 7.52–7.60 (3H, m), 7.65–7.70 (4H, m); δ_C (126 MHz, $CDCl_3$) 21.4, 128.3 (d, *J* 12.7 Hz), 128.4 (d, *J* 11.8 Hz), 129.1 (d, *J* 10.9 Hz), 131.8 (d, *J* 2.7 Hz), 132.1 (d, *J* 9.1 Hz), 132.5 (d, *J* 9.1 Hz), 132.6 (d, *J* 103.5 Hz), 132.7 (d, *J* 2.7 Hz), 138.4 (d, *J* 11.8 Hz); δ_P (202 MHz, $CDCl_3$) 29.29; GC t_R=20.89 min; GC–MS (EI, 70 eV) *m*/*z*=292 (39, M^+), 291 (100), 215 (10), 213 (13), 199 (15), 152 (10), 91 (11%). Analytical data are in accordance with those reported in the literature.[24]

*4.1.17. Phenyldi(m-tolyl)phosphine oxide (**11c**).* This compound was prepared according to general procedure (*Method B*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol), 3-iodotoluene (0.128 mL, 0.999 mmol) and *n*-butyllithium (0.624 mL, 0.999 mmol, 1.6 M solution in hexanes): yield 0.034 g (22%); pale yellow solid; mp 97.4–98.8 °C; [Found: C, 78.66; H, 6.48. $C_{20}H_{19}OP$ requires C, 78.41; H, 6.25%]. Isolated as a mixture of monosubstituted **10k**, disubstituted **11c** and trisubstituted products **13a**; R_f (CH_3Cl/MeOH=30:1) 0.60; δ_H (500 MHz, $CDCl_3$) 2.36 (6H, s), 7.30–7.40 (6H, m), 7.43–7.48 (2H, m), 7.51–7.60 (3H, m), 7.64–7.70 (2H, m); δ_C (126 MHz, $CDCl_3$) 21.4, 128.2 (d, *J* 12.7 Hz), 128.4 (d, *J* 11.8 Hz), 129.1 (d, *J* 10.0 Hz), 131.8 (d, *J* 2.7 Hz), 132.0 (d, *J* 10.0 Hz), 132.3 (d, *J* 103.5 Hz), 132.4 (d, *J* 10.0 Hz), 132.66 (d, *J* 2.7 Hz), 132.71 (d, *J* 103.5 Hz), 138.4 (d, *J* 11.8 Hz); δ_P (202 MHz, $CDCl_3$) 29.45; GC t_R=21.45 min; GC–MS (EI, 70 eV) *m*/*z*=306 (45, M^+), 305 (100), 213 (21), 165 (13), 91 (18%). Analytical data are in accordance with those reported in the literature.[29]

*4.1.18. Tri(m-tolyl)phosphine oxide (**13a**).* This compound was prepared according to general procedure (*Method B*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol), 3-iodotoluene (0.128 mL, 0.999 mmol) and *n*-butyllithium (0.624 mL, 0.999 mmol, 1.6 M solution in hexanes): yield 0.019 g (12%); pale yellow solid; mp 107.2–107.8 °C; [Found: C, 78.87; H, 6.73. $C_{21}H_{21}OP$ requires C, 78.73; H, 6.61%]. Isolated as a mixture of monosubstituted **10k**, disubstituted **11c** and trisubstituted products 13a; R_f (CH_3Cl/MeOH=30:1) 0.67; δ_H (500 MHz, $CDCl_3$) 2.37 (9H, s), 7.30–7.41 (9H, m), 7.55–7.61 (3H, m); δ_C (126 MHz, $CDCl_3$) 21.4, 128.2 (d, *J* 12.7 Hz), 129.1 (d, *J* 10.0 Hz), 132.45 (d, *J* 10.0 Hz), 132.49 (d, *J* 103.5 Hz), 132.6 (d, *J* 3.6 Hz), 138.4 (d, *J* 11.8 Hz); δ_P (202 MHz, $CDCl_3$) 29.51; GC t_R=18.08 min; GC–MS (EI, 70 eV) *m*/*z*=320 (50, M^+), 319 (100), 229 (12), 227 (22), 165 (13), 91 (21), 65 (22%). Analytical data are in accordance with those reported in the literature.[30]

*4.1.19. m-Anisyldiphenylphosphine oxide (**10l**).* This compound was prepared according to general procedure (*Method B*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol), *m*-anisyl iodide (0.119 mL, 0.999 mmol) and *n*-butyllithium (0.624 mL, 0.999 mmol, 1.6 M solution in hexanes): yield 0.059 g (38%); brown solid; mp 102.6–103.1 °C; [Found: C, 74.16; H, 5.23. $C_{19}H_{17}O_2P$ requires C, 74.02; H, 5.56%]; R_f (CH_3Cl/MeOH=20:1) 0.46; δ_H (500 MHz, $CDCl_3$) 3.81 (3H, s), 7.06–7.09 (1H, m), 7.12–7.18 (1H, m), 7.27–7.31 (1H, m), 7.35–7.40 (1H, m), 7.45–7.50 (4H, m), 7.53–7.58 (2H, m), 7.65–7.70 (4H, m); δ_C (126 MHz, $CDCl_3$) 55.4, 116.7 (d, *J* 10.9 Hz),

118.2 (d, *J* 2.7 Hz), 124.3 (d, *J* 10.0 Hz), 128.5 (d, *J* 11.8 Hz), 129.6 (d, *J* 13.6 Hz), 131.9 (d, *J* 2.7 Hz), 132.1 (d, *J* 10.0 Hz), 132.5 (d, *J* 104.5 Hz), 133.8 (d, *J* 103.5 Hz), 159.5 (d, *J* 15.4 Hz); δ_P (202 MHz, $CDCl_3$) 29.44; GC t_R=15.91 min; GC–MS (EI, 70 eV) *m*/*z*=308 (36, M^+), 307 (100), 199 (15), 183 (10%). Analytical data are in accordance with those reported in the literature.[31]

*4.1.20. Di(m-anisyl)phenylphosphine oxide (**11d**).* This compound was prepared according to general procedure (*Method B*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol), *m*-anisyl iodide (0.119 mL, 0.999 mmol) and *n*-butyllithium (0.624 mL, 0.999 mmol, 1.6 M solution in hexanes): yield 0.047 g (28%); white solid; mp 84.3–84.8 °C; [Found: C, 70.82; H, 5.54. $C_{20}H_{19}O_3P$ requires C, 71.00; H, 5.66%]; R_f (CH_3Cl/MeOH=20:1) 0.44; δ_H (500 MHz, $CDCl_3$) 3.81 (6H, s), 7.06–7.09 (2H, m), 7.12–7.17 (2H, m), 7.27–7.31 (2H, m), 7.34–7.39 (2H, m), 7.44–7.49 (2H, m), 7.53–7.57 (1H, m), 7.65–7.70 (2H, m); δ_C (126 MHz, $CDCl_3$) 55.4, 116.7 (d, *J* 10.9 Hz), 118.2 (d, *J* 2.7 Hz), 124.3 (d, *J* 10.0 Hz), 128.5 (d, *J* 12.7 Hz), 129.6 (d, *J* 14.5 Hz), 132.0 (d, *J* 2.7 Hz), 132.0 (d, *J* 9.1 Hz), 132.4 (d, *J* 104.5 Hz), 133.7 (d, *J* 103.5 Hz), 159.5 (d, *J* 14.5 Hz); δ_P (202 MHz, $CDCl_3$) 29.69; GC t_R=17.29 min; GC–MS (EI, 70 eV) *m*/*z*=338 (44, M^+), 337 (100), 229 (20), 92 (15%). Analytical data are in accordance with those reported in the literature.[32]

*4.1.21. Tri(m-anisyl)phosphine oxide (**13b**).* This compound was prepared according to general procedure (*Method B*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol), *m*-anisyl iodide (0.119 mL, 0.999 mmol) and *n*-butyllithium (0.624 mL, 0.999 mmol, 1.6 M solution in hexanes): yield 0.009 g (5%); white crystals; mp 149.2–151.1 °C; [Found: C, 68.52; H, 5.84. $C_{21}H_{21}O_4P$ requires C, 68.47; H, 5.75%]; R_f (CH_3Cl/MeOH=20:1) 0.62; δ_H (500 MHz, $CDCl_3$) 3.80 (9H, s), 7.06–7.09 (3H, m), 7.12–7.17 (3H, m), 7.26–7.31 (3H, m), 7.34–7.38 (3H, m); δ_C (126 MHz, $CDCl_3$) 55.4, 116.7 (d, *J* 10.9 Hz), 118.2 (d, *J* 2.7 Hz), 124.3 (d, *J* 10.0 Hz), 129.6 (d, *J* 14.5 Hz), 133.7 (d, *J* 103.5 Hz), 159.6 (d, *J* 15.4 Hz); δ_P (202 MHz, $CDCl_3$) 29.83; GC t_R=18.36 min; GC–MS (EI, 70 eV) *m*/*z*=368 (52, M^+), 367 (100), 261 (10), 259 (20), 92 (13), 77 (19), 64 (11%). Analytical data are in accordance with those reported in the literature.[33]

*4.1.22. Ethyldiphenylphosphine oxide (**10m**).* This compound was prepared according to general procedure (*Method A*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol) and ethylmagnesium bromide (0.333 mL, 0.999 mmol, 3.0 M solution in diethyl ether) except that reaction performed in 60 °C: yield 0.098 g (85%); white solid; mp 120.4–120.7 °C; [Found: C, 73.29; H, 6.49. $C_{14}H_{15}OP$ requires C, 73.03; H, 6.57%]; R_f (CH_3Cl/MeOH=20:1) 0.73; δ_H (500 MHz, $CDCl_3$) 1.20 (3H, dt, *J* 7.7, 17.3 Hz), 2.25–2.32 (2H, m), 7.44–7.49 (4H, m), 7.50–7.55 (2H, m), 7.70–7.77 (4H, m); δ_C (126 MHz, $CDCl_3$) 5.5 (d, *J* 5.5 Hz), 22.6 (d, *J* 73.6 Hz), 128.6 (d, *J* 11.8 Hz), 130.8 (d, *J* 9.1 Hz), 131.7 (d, *J* 2.7 Hz), 132.6 (d, *J* 98.1 Hz); δ_P (202 MHz, $CDCl_3$) 34.41; GC t_R=9.59 min; GC–MS (EI, 70 eV) *m*/*z*=230 (2.7, M^+), 202 (74), 201 (100%). Analytical data are in accordance with those reported in the literature.[34]

*4.1.23. Diethylphenylphosphine oxide (**11e**).* This compound was prepared according to general procedure (*Method A*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol) and ethylmagnesium bromide (0.333 mL, 0.999 mmol, 3.0 M solution in diethyl ether) except that reaction performed in 60 °C: yield 0.005 g (5%); yellow oil; [Found: C, 66.19; H, 8.57. $C_{10}H_{15}OP$ requires C, 65.92; H, 8.30%]; R_f (CH_3Cl/MeOH=15:1) 0.51; δ_H (500 MHz, $CDCl_3$) 1.14 (6H, dt, *J* 7.6, 17.0 Hz), 1.86–1.96 (2H, m), 1.98–2.10 (2H, m), 7.48–7.58 (3H, m), 7.67–7.74 (2H, m); δ_C (126 MHz, $CDCl_3$) 5.5 (d, *J* 5.5 Hz), 22.1 (d, *J* 69.0 Hz), 128.7 (d, *J* 10.9 Hz), 130.6 (d, *J* 8.2 Hz), 131.7 (d, *J* 1.8 Hz); δ_P (202 MHz, $CDCl_3$) 45.19; GC t_R=7.40 min; GC–MS (EI, 70 eV) *m*/*z*=182 (3, M^+), 154 (92), 153 (100), 126 (10), 125 (69), 109 (11%). Analytical data are in accordance with those reported in the literature.[25]

*4.1.24. Diphenyl(p-tolyl)phosphine oxide (**10o**).* This compound was prepared according to general procedure (*Method A*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol) and *para*-tolylmagnesium bromide (0.999 mL, 0.999 mmol, 1.0 M solution in THF) except that reaction performed in 60 °C: yield 0.086 g (59%); white crystals; mp 131.1–133.2 °C; [Found: C, 78.26; H, 5.97. $C_{19}H_{17}OP$ requires C, 78.07; H, 5.86%]; R_f (CH_3Cl/MeOH=20:1) 0.69; δ_H (500 MHz, $CDCl_3$) 2.41 (3H, s), 7.24–7.30 (2H, m), 7.43–7.48 (4H, m), 7.51–7.59 (4H, m), 7.63–7.70 (4H, m); δ_C (126 MHz, $CDCl_3$) 21.6, 128.4 (d, *J* 12.7 Hz), 129.1 (d, *J* 106.3 Hz), 129.2 (d, *J* 12.7 Hz), 131.8 (d, *J* 2.7 Hz), 132.0 (d, *J* 10.0 Hz), 132.1 (d, *J* 10.0 Hz), 132.8 (d, *J* 103.5 Hz), 142.4 (d, *J* 2.7 Hz); δ_P (202 MHz, $CDCl_3$) 29.19; GC t_R=12.70 min; GC–MS (EI, 70 eV) *m*/*z*=292 (37, M^+), 292 (37), 291 (100), 215 (13), 213 (14), 199 (19), 183 (11), 152 (11), 91 (10%). Analytical data are in accordance with those reported in the literature.[24]

*Phenyldi(p-tolyl)phosphine oxide (**11f**).* This compound was prepared according to general procedure (*Method A*) from triphenylphosphine oxide (**7**) (0.139 g, 0.499 mmol) and *para*-tolylmagnesium bromide (0.999 mL, 0.999 mmol, 1.0 M solution in THF) except that reaction performed in 60 °C: yield 0.028 g (18%); white crystals; mp 80.3–82.4 °C; [Found: C, 78.56; H, 6.47. $C_{20}H_{19}OP$ requires C, 78.41; H, 6.25%]; R_f (CH_3Cl/MeOH=20:1) 0.75; δ_H (500 MHz, $CDCl_3$) 2.37 (6H, s), 7.21–7.26 (4H, m), 7.39–7.44 (2H, m), 7.47–7.57 (5H, m), 7.61–7.68 (2H, m); δ_C (126 MHz, $CDCl_3$) 21.5, 128.3 (d, *J* 11.8 Hz), 129.1 (d, *J* 12.7 Hz), 129.3 (d, *J* 107.2 Hz), 131.6 (d, *J* 2.7 Hz), 131.9 (d, *J* 8.2 Hz), 132.0 (d, *J* 10.0 Hz), 133.0 (d, *J* 103.5 Hz), 142.2 (d, *J* 2.7 Hz); δ_P (202 MHz, $CDCl_3$) 29.23; GC t_R=13.24 min; GC–MS (EI, 70 eV) *m*/*z*=306 (39, M^+), 305 (100), 213 (21), 199 (10), 165 (13), 91 (16%). Analytical data are in accordance with those reported in the literature.[24]

*4.1.25. (2-(Hydroxymethyl)phenyl)diphenylphosphine oxide (**15a**).* This compound was prepared according to general procedure (*Method A*) from diphenyl-*o*-tolylphosphine oxide (**10j**) (0.146 g, 0.499 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield 0.054 g (35%); white sticky solid; [Found: C, 73.86; H, 5.47. $C_{19}H_{17}O_2P$ requires C, 74.02; H, 5.56%]; R_f (CH_3Cl) 0.38; δ_H (500 MHz, $CDCl_3$) 4.59 (2H, s), 5.78 (1H, br s), 7.00–7.07 (1H, m), 7.23–7.31 (1H, m), 7.44–7.56 (7H, m), 7.56–7.65 (5H, m); δ_C (126 MHz, $CDCl_3$) 64.6 (d, *J* 4.5 Hz), 127.2 (d, *J* 12.7 Hz), 128.7 (d, *J* 11.8 Hz), 131.2 (d, *J* 101.7 Hz), 131.6 (d, *J* 10.0 Hz), 131.7 (d, *J* 105.4 Hz), 132.0 (d, *J* 10.0 Hz), 132.3 (d, *J* 2.7 Hz), 132.8 (d, *J* 2.7 Hz), 133.7 (d, *J* 12.7 Hz), 146.6 (d, *J* 8.2 Hz); δ_P (202 MHz, $CDCl_3$) 34.93; GC t_R=18.78 min; GC–MS (EI, 70 eV) *m*/*z*=308 (3, M^+), 307 (21), 291 (26), 290 (100), 289 (25), 279 (22), 277 (19), 241 (7), 229 (11), 214 (8), 213 (8), 212 (26), 202 (15), 201 (14), 199 (22), 183 (32), 166 (15), 165 (39), 152 (30), 127 (7), 123 (8), 122 (11), 106 (8), 105 (17), 77 (44), 51 (25), 47 (56%). Analytical data are in accordance with those reported in the literature.[35]

*4.1.26. t-Butylphenyl(3,4-dimethylphenyl)phosphine oxide (**15b**).* This compound was prepared according to general procedure (*Method A*) from diphenyl(3,4-dimethylphenyl)phosphine oxide (**14a**) (0.153 g, 0.499 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield 0.007 g (5%); white solid. Isolated as a mixture of **16a**, **16b** and **16c**. The same compound was prepared from *t*-butylphenylphosphine oxide **18** through copper-catalyzed coupling with 3,4-dimethyliodobenzene. White solid; mp 154.3–155.9 °C; R_f (CH_3Cl) 0.13; δ_H (500 MHz, $CDCl_3$) 1.24 (9H, d, *J* 14.8 Hz), 2.31 (3H, s), 2.31 (3H, s), 7.21–7.24 (1H, m), 7.43–7.52 (3H, m), 7.61–7.66 (1H, m), 7.73–7.77 (1H, m), 7.92–7.96 (2H, m); δ_C (126 MHz, $CDCl_3$) 19.81, 19.84, 25.2, 33.9 (d, *J* 70.8 Hz), 128.07 (d, *J* 92.6 Hz), 128.10 (d, *J* 10.9 Hz), 129.37 (d, *J* 5.5 Hz), 129.45 (d, *J* 1.8 Hz),

131.2 (d, *J* 2.7 Hz), 131.6 (d, *J* 89.9 Hz), 132.1 (d, *J* 8.2 Hz), 133.4 (d, *J* 8.2 Hz), 136.8 (d, *J* 10.9 Hz), 140.5 (d, *J* 2.7 Hz); δ_P (202 MHz, $CDCl_3$) 38.73; GC t_R=14.83 min; GC–MS (EI, 70 eV) *m*/*z*=286 (1, M^+), 231 (17), 230 (100), 229 (56), 183 (29), 153 (10), 106 (12), 105 (21), 91 (13), 79 (11), 77 (18), 47 (12%).

*4.1.27. 1-t-Butyldibenzophospholane oxide (**16a**).* This compound was prepared according to general procedure (*Method A*) from *tert*-butyldiphenylphosphine oxide (**10a**) (0.129 g, 0.499 mmol) and *sec*-butyllithium (0.714 mL, 0.999 mmol, 1.4 M solution in cyclohexane): yield 0.114 g (89%); yellow oil; [Found: C, 74.97; H, 6.64. $C_{16}H_{17}OP$ requires C, 74.99; H, 6.69%]; R_f (CH_3Cl/MeOH=15:1) 0.64; δ_H (500 MHz, $CDCl_3$) 1.20 (9H, d, *J* 15.5 Hz), 7.39–7.44 (2H, m), 7.56–7.60 (2H, m), 7.77–7.80 (2H, m), 7.82–7.86 (2H, m); δ_C (126 MHz, $CDCl_3$) 23.9, 32.9 (d, *J* 70.8 Hz), 121.1 (d, *J* 9.1 Hz), 128.8 (d, *J* 10.0 Hz), 130.2 (d, *J* 9.1 Hz), 130.4 (d, *J* 95.4 Hz), 133.0 (d, *J* 1.8 Hz), 142.2 (d, *J* 19.1 Hz); δ_P (202 MHz, $CDCl_3$) 54.16; GC t_R=12.46 min; GC–MS (EI, 70 eV) *m*/*z*=256 (6, M^+), 201 (13), 200 (100), 199 (38), 152 (30%). Analytical data are in accordance with those reported in the literature.[36]

*4.1.28. 1-t-Butyl-3,4-dimethyldibenzophospholane oxide (**16b**).* This compound was prepared according to general procedure (*Method A*) from diphenyl(3,4-dimethylphenyl)phosphine oxide (**14a**) (0.153 g, 0.499 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield 0.004 g (3%). Isolated as a mixture of **15b**, **16a**, **16c**. The same compound was prepared from *t*-butylphenylphosphine oxide **18** through copper-catalyzed coupling with 3,4-dimethyliodobenzene followed by reaction with PhLi. R_f (CH_3Cl) 0.13; δ_H (500 MHz, $CDCl_3$) 1.15 (9H, d, *J* 15.1 Hz), 2.43 (3H, s), 2.64 (3H, s), 7.37–7.42 (1H, m), 7.53–7.56 (1H, m), 7.56–7.62 (2H, m), 7.85–7.90 (1H, m), 8.04–8.07 (1H, m); δ_C (126 MHz, $CDCl_3$) 17.7, 21.4, 24.0, 32.8 (d, *J* 71.8 Hz), 125.6 (d, *J* 10.0 Hz), 127.4 (d, *J* 8.2 Hz), 127.6 (d, *J* 10.0 Hz), 129.2 (d, *J* 96.3 Hz), 130.1 (d, *J* 10.9 Hz), 130.4 (d, *J* 8.2 Hz), 131.8 (d, *J* 93.6 Hz), 132.7 (d, *J* 1.8 Hz), 133.8 (d, *J* 9.1 Hz), 140.5 (d, *J* 19.1 Hz), 142.9 (d, *J* 1.8 Hz), 144.0 (d, *J* 19.1 Hz); δ_P (202 MHz, $CDCl_3$) 51.07; GC t_R=12.52 min; GC–MS (EI, 70 eV) *m*/*z*=284 (8, M^+), 229 (17), 228 (100), 227 (22), 213 (19), 179 (9), 178 (10), 165 (22%).

*4.1.29. 1-t-Butyl-4,5-dimethyldibenzophospholane oxide (**16c**).* This compound was prepared according to general procedure (*Method A*) from diphenyl(3,4-dimethylphenyl)phosphine oxide (**14a**) (0.153 g, 0.499 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield 0.001 g (1%). Isolated as a mixture of **15b**, **16a**, **16b**. The same compound was prepared from *t*-butylphenylphosphine oxide **18** through copper-catalyzed coupling with 3,4-dimethyliodobenzene followed by reaction with PhLi. R_f (CH_3Cl) 0.13; δ_H (500 MHz, $CDCl_3$) 1.18 (9H, d, *J* 15.5 Hz), 2.33 (3H, s), 2.36 (3H, s), 7.19–7.22 (1H, m), 7.33–7.38 (1H, m), 7.40–7.43 (1H, m), 7.51–7.55 (1H, m), 7.70–7.74 (1H, m), 8.08–8.10 (1H, m); δ_C (126 MHz, $CDCl_3$) 19.9, 20.5, 24.1, 120.6 (d, *J* 9.1 Hz), 122.3 (d, *J* 10.0 Hz), 122.9 (d, *J* 10.0 Hz), 128.2 (d, *J* 10.9 Hz), 129.9 (d, *J* 10.9 Hz), 131.1 (d, *J* 9.1 Hz), 132.8 (d, *J* 1.8 Hz), 140.1 (d, *J* 19.1 Hz), 142.4 (d, *J* 19.9 Hz), 142.7 (d, *J* 1.8 Hz); δ_P (202 MHz, $CDCl_3$) 54.17; GC t_R=12.21 min; GC–MS (EI, 70 eV) *m*/*z*=284 (10, M^+), 256 (20), 241 (11), 229 (17), 228 (100), 227 (25), 213 (17), 178 (9), 165 (20%).

*4.1.30. Diphenyl(2-t-butyl-1,2-dihydronaphth-1-yl)phosphine oxide (**15c**).* This compound was prepared according to general procedure (*Method A*) from 1-naphthyldiphenylphosphine oxide (**10h**) (0.164 g, 0.499 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield 0.133 g (69%); pale yellow sticky solid; [Found: C, 80.67; H, 6.94. $C_{26}H_{27}OP$ requires C, 80.80; H, 7.04%]; R_f (CH_3Cl) 0.26; δ_H (500 MHz, $CDCl_3$) 0.85 (9H, s), 2.94 (1H, dd, *J* 6.3, 19.9 Hz), 3.99 (1H, d, *J* 18.6 Hz), 5.70 (1H, dd, *J* 6.0, 9.8 Hz), 6.15 (1H, d, *J* 9.8 Hz), 6.41 (1H, dd, *J* 1.9, 7.3 Hz), 6.80–6.85 (1H, m), 6.89 (1H, d, *J* 7.6 Hz); δ_C (126 MHz, $CDCl_3$) 27.0, 36.7 (d, *J* 14.5 Hz), 41.6 (d, *J* 1.8 Hz), 42.5 (d, *J* 62.7 Hz), 126.2 (d, *J* 3.6 Hz), 126.6 (d, *J* 3.6 Hz), 127.2 (d, *J* 3.6 Hz), 127.4 (d, *J* 10.9 Hz), 127.8 (d, *J* 1.8 Hz), 128.0, 128.3 (d, *J* 11.8 Hz), 129.2 (d, *J* 4.5 Hz), 129.3 (d, *J* 5.5 Hz), 131.4 (d, *J* 2.7 Hz), 131.7 (d, *J* 1.8 Hz), 131.9 (d, *J* 8.2 Hz), 132.3 (d, *J* 8.2 Hz), 134.9 (d, *J* 4.5 Hz); δ_P (202 MHz, $CDCl_3$) 32.40; GC t_R=22.10 min; GC–MS (EI, 70 eV) *m*/*z*=386 (3, M^+), 385 (23), 384 (96), 383 (68), 370 (27), 369 (100), 342 (36), 329 (8), 328 (53), 327 (72), 249 (22), 213 (9), 203 (10), 202 (49), 201 (98), 199 (10), 183 (21), 173 (28), 171 (8), 165 (19), 153 (16), 152 (28), 129 (10), 128 (25), 127 (11), 115 (9), 78 (17), 77 (51), 57 (18), 51 (21), 47 (25%).

*4.1.31. Diphenyl(1-t-butyl-1,2-dihydronaphth-2-yl)phosphine oxide (**15d**).* This compound was prepared according to general procedure (*Method A*) from 2-naphthyldiphenylphosphine oxide (**14b**) (0.164 g, 0.499 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield 0.112 g (58%); pale yellow sticky solid; [Found: C, 80.70; H, 6.90. $C_{26}H_{27}OP$ requires C, 80.80; H, 7.04%]; R_f (CH_3Cl) 0.21; δ_H (500 MHz, $CDCl_3$) 0.90 (9H, s), 3.16 (1H, d, *J* 17.8 Hz), 3.72 (1H, dd, *J* 6.0, 24.0 Hz), 5.73–5.79 (1H, m), 6.35–6.40 (1H, m), 6.67–6.70 (1H, m), 6.80–6.83 (1H, m), 6.91–6.95 (2H, m), 7.11–7.16 (2H, m), 7.24–7.29 (1H, m), 7.42–7.47 (2H, m), 7.47–7.53 (1H, m), 7.57–7.62 (2H, m), 7.75–7.81 (2H, m); δ_C (126 MHz, $CDCl_3$) 28.0, 36.6 (d, *J* 15.4 Hz), 38.6 (d, *J* 63.6 Hz), 45.3 (d, *J* 2.7 Hz), 122.4 (d, *J* 8.2 Hz), 125.7 (d, *J* 1.8 Hz), 126.6 (d, *J* 6.4 Hz), 127.2 (d, *J* 10.9 Hz), 128.4 (d, *J* 10.9 Hz), 129.7 (d, *J* 94.5 Hz), 131.33, 131.34 (d, *J* 4.5 Hz), 131.36 (d, *J* 9.1 Hz), 131.4, 131.7 (d, *J* 2.7 Hz), 132.0 (d, *J* 8.2 Hz), 132.2 (d, *J* 95.4 Hz), 132.8 (d, *J* 2.7 Hz), 133.5 (d, *J* 4.5 Hz); δ_P (202 MHz, $CDCl_3$) 30.36; GC t_R=20.41 min; GC–MS (EI, 70 eV) *m*/*z*=386 (1, M^+), 329 (1), 202 (57), 201 (100), 155 (10), 128 (29), 77 (16), 57 (20), 47 (7%). Analytical data are in accordance with those reported in the literature.[37]

*4.1.32. o-Anisylphenylphosphine oxide (**17**).* This compound was prepared according to general procedure (*Method A*) from *m*-anisyl-*o*-anisylphenylphosphine oxide (**14c**) (0.169 g, 0.499 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield 0.029 g (25%); white solid; mp 91–93 °C; [Found: C, 67.07; H, 5.45. $C_{13}H_{13}O_2P$ requires C, 67.24; H, 5.64%]; R_f (CH_3Cl/MeOH=15:1) 0.73; δ_H (200 MHz, $CDCl_3$) 3.80 (3H, s), 6.87–6.99 (1H, m), 7.07–7.19 (1H, m), 7.43–7.61 (4H, m), 7.70–7.89 (3H, m), 8.19 (1H, d, *J* 499,48 Hz); δ_C (50 MHz, $CDCl_3$) 55.5, 110.7 (d, *J* 5.9 Hz), 121.0 (d, *J* 12.0 Hz), 128.4 (d, *J* 12.9 Hz), 130.4 (d, *J* 11.7 Hz), 131.9 (d, *J* 3.1 Hz), 132.9 (d, *J* 7.3 Hz), 134.3 (d, *J* 1.9 Hz); δ_P (161.5 MHz, $CDCl_3$) 14.51; GC t_R=21.59 min; GC–MS (EI, 70 eV) *m*/*z*=232 (27, M^+), 231 (10), 214 (13), 213 (25), 201 (37), 199 (16), 196 (35), 183 (30), 167 (17), 166 (16), 165 (18), 153 (12), 152 (29), 141 (100), 139 (13), 137 (13), 125 (13), 107 (15), 92 (22), 91 (60%); HRMS calcd for $C_{13}H_{14}O_2P$ [$M+H^+$]: 233.0726; found: 233.0731. Analytical data are in accordance with those reported in the literature.[38]

*4.1.33. t-Butylphenyl(p-tolyl)phosphine oxide (**15e**).* This compound was prepared according to general procedure (*Method A*) from *m*-anisylphenyl-*p*-tolylphosphine oxide (**14e**) (0.161 g, 0.499 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield 0.012 g (9%). Isolated as a mixture of **15f**, **15g**, **16d** and **16e**. The same compound was prepared from *t*-butylphenylphosphine oxide **18** through copper-catalyzed coupling with 4-iodotoluene. Pale yellow solid; mp 107.9–109.2 °C; R_f (CH_3Cl) 0.13; δ_H (500 MHz, $CDCl_3$) 1.24 (9H, d, *J* 14.8 Hz), 2.41 (3H, s), 7.26–7.32 (2H, m), 7.43–7.51 (3H, m), 7.82–7.87 (2H, m), 7.92–7.97 (2H, m); δ_C (126 MHz, $CDCl_3$) 21.5, 25.2, 33.9 (d, *J* 70.8 Hz), 127.8 (d, *J* 94.5 Hz), 128.2 (d, *J* 10.9 Hz), 129.0 (d, *J* 11.8 Hz), 131.3 (d, *J* 2.7 Hz), 131.5 (d, *J* 90.8 Hz), 132.15 (d, *J* 8.2 Hz), 132.2 (d, *J* 8.2 Hz), 141.8 (d, *J* 2.7 Hz); δ_P (202 MHz, $CDCl_3$) 38.87; GC t_R=10.42 min; GC–MS (EI,

70 eV) *m*/*z*=217 (14), 216 (100), 215 (41), 169 (30), 139 (10), 92 (8), 91 (28), 77 (10), 65 (14), 47 (25%).

*4.1.34. m-Anisyl(t-butyl)phenylphosphine oxide (**15f**).* This compound was prepared according to general procedure (*Method A*) from *m*-anisylphenyl-*p*-tolylphosphine oxide (**14e**) (0.161 g, 0.499 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield 0.001 g (1%). Isolated as a mixture of **15e**, **15g**, **16d** and **16e**. The same compound was prepared from *t*-butylphenylphosphine oxide **18** through palladium-catalyzed coupling with 3-bromoanizole. Yellow oil; R_f (CH_3Cl) 0.13; δ_H (500 MHz, $CDCl_3$) 1.18 (9H, d, *J* 15.1 Hz), 3.75 (3H, s), 6.96–6.99 (1H, m), 7.29–7.34 (1H, m), 7.37–7.46 (4H, m), 7.46–7.50 (1H, m), 7.86–7.91 (2H, m); δ_C (126 MHz, $CDCl_3$) 25.0, 33.7 (d, *J* 70.8 Hz), 55.2, 117.2 (d, *J* 2.7 Hz), 117.4 (d, *J* 8.2 Hz), 123.9 (d, *J* 8.2 Hz), 128.0 (d, *J* 10.9 Hz), 129.1 (d, *J* 12.7 Hz), 130.9 (d, *J* 90.8 Hz), 131.3 (d, *J* 2.7 Hz), 131.9 (d, *J* 8.2 Hz), 132.3 (d, *J* 89.9 Hz), 159.2 (d, *J* 13.6 Hz); δ_P (202 MHz, $CDCl_3$) 38.79; GC t_R=14.88 min; GC–MS (EI, 70 eV) *m*/*z*=288 (3, M^+), 233 (15), 232 (100), 231 (34), 230 (16), 229 (10), 185 (19), 170 (12), 108 (24), 92 (11), 78 (12), 77 (34), 57 (10), 51 (10), 47 (20%).

*4.1.35. m-Anisyl(t-butyl)(p-tolyl)phosphine oxide (**15g**).* This compound was prepared according to general procedure (*Method A*) from *m*-anisylphenyl-*p*-tolylphosphine oxide (**14e**) (0.161 g, 0.499 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield 0.009 g (6%); colorless oil. Isolated as a mixture of **15e**, **15f**, **16d** and **16e**. The same compound was prepared from *t*-butyl(*p*-tolyl)phosphine oxide **19** through palladium-catalyzed coupling with 3-bromoanizole. Yellow oil; R_f (CH_3Cl) 0.13; δ_H (500 MHz, $CDCl_3$) 1.20 (9H, d, *J* 14.8 Hz), 2.34 (3H, s), 3.79 (3H, s), 6.98–7.01 (1H, m), 7.22–7.26 (2H, m), 7.31–7.36 (1H, m), 7.42–7.46 (1H, m), 7.48–7.52 (1H, m), 7.78–7.83 (2H, m); δ_C (126 MHz, $CDCl_3$) 21.3, 25.1, 33.8 (d, *J* 70.8 Hz), 55.2, 117.2 (d, *J* 2.7 Hz), 117.3 (d, *J* 9.1 Hz), 123.9 (d, *J* 8.2 Hz), 127.6 (d, *J* 92.6 Hz), 128.9 (d, *J* 10.9 Hz), 129.1 (d, *J* 12.7 Hz), 132.0 (d, *J* 8.2 Hz), 132.7 (d, *J* 89.0 Hz), 141.7 (d, *J* 2.7 Hz), 159.2 (d, *J* 13.6 Hz); δ_P (202 MHz, $CDCl_3$) 39.01; GC t_R=11.39 min; GC–MS (EI, 70 eV) *m*/*z*=302 (3, M^+), 247 (15), 246 (100), 245 (55), 199 (21), 184 (9), 155 (6), 152 (6), 139 (10), 108 (16), 92 (13), 91 (20), 78 (9), 77 (19), 65 (11), 57 (8), 47 (15%).

*4.1.36. 1-t-Butyl-5-methoxydibenzophospholane oxide (**16d**).* This compound was prepared according to general procedure (*Method A*) from *m*-anisylphenyl-*p*-tolylphosphine oxide (**14e**) (0.161 g, 0.499 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield 0.007 g (5%); pale yellow sticky solid. Isolated as a mixture of **15e**, **15f**, **15g** and **16e**. The same compound was prepared from *t*-butylphenylphosphine oxide **18** through palladium-catalyzed coupling with 3-bromoanizole followed by reaction with *t*-BuLi. Yellow pasty solid; R_f (CH_3Cl) 0.06; δ_H (500 MHz, $CDCl_3$) 1.16 (9H, d, *J* 15.5 Hz), 4.00 (3H, s), 7.11 (1H, d, *J* 8.5 Hz), 7.33–7.40 (2H, m), 7.42–7.45 (1H, m), 7.52–7.56 (1H, m), 7.79–7.83 (1H, m), 8.36–8.39 (1H, m); δ_C (126 MHz, $CDCl_3$) 23.9, 32.8 (d, *J* 70.8 Hz), 55.4, 115.5 (d, *J* 2.7 Hz), 122.0 (d, *J* 8.2 Hz), 126.4 (d, *J* 9.1 Hz), 127.6 (d, *J* 10.0 Hz), 128.2 (d, *J* 10.9 Hz), 129.7 (d, *J* 8.2 Hz), 129.8 (d, *J* 11.8 Hz), 129.9 (d, *J* 96.3 Hz), 132.5 (d, *J* 92.6 Hz), 132.9 (d, *J* 1.8 Hz), 141.6 (d, *J* 19.1 Hz), 156.8 (d, *J* 11.8 Hz); δ_P (202 MHz, $CDCl_3$) 53.75; GC t_R=12.28 min; GC–MS (EI, 70 eV) *m*/*z*=286 (11, M^+), 231 (15), 230 (100), 229 (13), 215 (14), 214 (6), 199 (6), 186 (9), 168 (9), 157 (13), 139 (8), 133 (10), 57 (9%).

*4.1.37. 1-t-Butyl-5-methoxy-7-methyldibenzophospholane oxide (**16e**).* This compound was prepared according to general procedure (*Method A*) from *m*-anisylphenyl-*p*-tolylphosphine oxide (**14e**) (0.161 g, 0.499 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield 0.003 g (2%). Isolated as a mixture of **15e**, **15f**, **15g** and **16d**. The same compound was prepared from *t*-butyl(*p*-tolyl)phosphine oxide **19** through palladium-catalyzed coupling with 3-bromoanizole followed by reaction with *t*-BuLi. Colorless sticky oil; R_f (CH_3Cl) 0.06; δ_H (500 MHz, $CDCl_3$) 1.15 (9H, d, *J* 15.5 Hz), 2.46 (3H, s), 4.02 (3H, s), 7.10–7.14 (1H, m), 7.17–7.20 (1H, m), 7.35–7.40 (1H, m), 7.41–7.45 (1H, m), 7.68–7.72 (1H, m), 8.18–8.21 (1H, m); δ_C (126 MHz, $CDCl_3$) 22.1, 23.9, 32.8 (d, *J* 70.8 Hz), 55.4, 115.5 (d, *J* 1.9 Hz), 122.0 (d, *J* 9.1 Hz), 126.7 (d, *J* 98.1 Hz), 127.2 (d, *J* 10.0 Hz), 128.4 (d, *J* 10.9 Hz), 129.6 (d, *J* 9.1 Hz), 129.7 (d, *J* 20.0 Hz), 129.8 (d, *J* 11.8 Hz), 133.0 (d, *J* 93.6 Hz), 141.9 (d, *J* 20.0 Hz), 143.4 (d, *J* 1.8 Hz), 156.7 (d, *J* 12.7 Hz); δ_P (202 MHz, $CDCl_3$) 53.40; GC t_R=12.64 min; GC–MS (EI, 70 eV) *m*/*z*=300 (13, M^+), 245 (16), 244 (100), 243 (20), 229 (12), 213 (6), 200 (9), 182 (9), 171 (7%).

*4.1.38. o-Anisylphenyl(2-tert-butyl-1,2-dihydronaphth-1-yl)phosphine oxide (**15h**).* This compound was prepared according to general procedure (*Method A*) from *o*-anisyl-1-naphthylphenylphosphine oxide (**14f**) (0.179 g, 0.499 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield of two diastereomers (dr=61:39) 0.054 g (26%). Isolated as a mixture of diastereomers.

Major Diastereomer: R_f (CH_3Cl) 0.15; δ_H (500 MHz, $CDCl_3$) 0.81 (9H, s), 2.76 (1H, dd, *J* 6.0, 20.8 Hz), 4.06 (3H, s), 4.58 (1H, d, *J* 19.2 Hz), 5.73 (1H, dd, *J* 6.3, 10.1 Hz), 6.23 (1H, d, *J* 9.8 Hz), 6.50–6.53 (1H, m), 6.76–6.81 (1H, m), 6.89–8.10 (11H, m); δ_C (126 MHz, $CDCl_3$) 26.9, 36.6 (d, *J* 15.4 Hz), 40.6 (d, *J* 63.6 Hz), 42.0 (d, *J* 2.7 Hz), 55.6, 111.0 (d, *J* 7.3 Hz), 121.0 (d, *J* 10.9 Hz), 126.1 (d, *J* 4.5 Hz), 126.5 (d, *J* 3.6 Hz), 127.0 (d, *J* 3.6 Hz), 127.1 (d, *J* 11.8 Hz), 127.6 (d, *J* 2.7 Hz), 128.4 (d, *J* 1.8 Hz), 131.1 (d, *J* 2.7 Hz), 132.6 (d, *J* 8.2 Hz), 133.8 (d, *J* 1.8 Hz), 135.5 (d, *J* 6.4 Hz), 160.5 (d, *J* 3.6 Hz); δ_P (202 MHz, $CDCl_3$) 35.35; GC t_R=28.55 min; GC–MS (EI, 70 eV) *m*/*z*=359 (9, M^+), 358 (44), 357 (100), 342 (5), 341 (15), 328 (17), 327 (71), 250 (9), 249 (46), 233 (7), 220 (5), 218 (6), 217 (21), 215 (5), 203 (7), 202 (22), 201 (5), 200 (5), 199 (17), 189 (6), 173 (10), 152 (11), 142 (6), 141 (21), 128 (6), 127 (12), 126 (7), 115 (6), 101 (8), 91 (13), 77 (18), 51 (9%).

Minor Diastereomer: R_f (CH_3Cl) 0.15; δ_H (500 MHz, $CDCl_3$) 0.80 (9H, s), 2.43 (1H, dd, *J* 6.0, 21.1 Hz), 4.02 (3H, s), 4.44 (1H, d, *J* 12.9 Hz), 5.87 (1H, dd, *J* 6.3, 9.8 Hz), 6.56–6.58 (1H, m), 6.59 (1H, d, *J* 9.5 Hz), 6.70–6.75 (1H, m), 6.89–8.10 (11H, m); δ_C (126 MHz, $CDCl_3$) 27.1, 36.8 (d, *J* 17.3 Hz), 38.1 (d, *J* 63.6 Hz), 42.5 (d, *J* 2.7 Hz), 55.0, 110.1 (d, *J* 7.3 Hz), 121.3 (d, *J* 10.9 Hz), 126.1 (d, *J* 3.6 Hz), 126.4 (d, *J* 3.6 Hz), 126.9 (d, *J* 3.6 Hz), 127.9 (d, *J* 11.8 Hz), 127.8 (d, *J* 1.8 Hz), 128.5 (d, *J* 1.8 Hz), 131.3 (d, *J* 2.7 Hz), 132.1 (d, *J* 10.0 Hz), 133.4 (d, *J* 1.8 Hz), 135.3 (d, *J* 4.5 Hz), 158.7 (d, *J* 4.5 Hz); δ_P (202 MHz, $CDCl_3$) 34.35; GC t_R=28.55 min; GC–MS (EI, 70 eV) *m*/*z*=359 (9, M^+), 358 (44), 357 (100), 342 (5), 341 (15), 328 (17), 327 (71), 250 (9), 249 (46), 233 (7), 220 (5), 218 (6), 217 (21), 215 (5), 203 (7), 202 (22), 201 (5), 200 (5), 199 (17), 189 (6), 173 (10), 152 (11), 142 (6), 141 (21), 128 (6), 127 (12), 126 (7), 115 (6), 101 (8), 91 (13), 77 (18), 51 (9%).

*4.1.39. m-Anisylphenyl(2-tert-butyl-1,2-dihydronaphth-1-yl)phosphine oxide (**15i**).* This compound was prepared according to general procedure (*Method A*) from *m*-anisyl-1-naphthylphenylphosphine oxide (**14g**) (0.179 g, 0.499 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield of two diastereomers (dr=50:50) 0.119 g (57%). Isolated as a mixture of diastereomers. R_f (CH_3Cl) 0.21; δ_H (500 MHz, $CDCl_3$) 0.85 (9H, s) and 0.85 (9H, s), 2.87 (1H, t, *J* 6.31 Hz) and 2.91 (1H, t, *J* 6.3 Hz), 3.66 (3H, s) and 3.82 (3H, s), 3.93 (1H, d, *J* 3.2 Hz) and 3.97 (1H, d, *J* 3.8 Hz), 5.71 (1H, t, *J* 6.0 Hz) and 5.73 (1H, t, *J* 6.0 Hz), 6.19 (1H, d, *J* 11.0 Hz) and 6.21 (1H, d, *J* 10.7 Hz), 6.38–6.42 (1H, m) and 6.41–6.44 (1H, m), 6.80–7.86 (13H, m) and 6.80–7.86 (13H, m); δ_C (126 MHz, $CDCl_3$) 26.96 and 26.98, 36.7 (d, *J* 16.4 Hz), 41.7 (d, *J* 2.7 Hz) and 41.8 (d, *J* 1.8 Hz), 42.4 (d, *J* 62.7 Hz) and 42.5 (d, *J* 62.7 Hz), 55.3 and 55.4, 116.6 (d, *J* 9.1 Hz) and 117.1 (d, *J* 10.0 Hz), 117.7 (d, *J* 1.8 Hz) and 118.3 (d, *J* 2.7 Hz), 124.0 (d, *J*

9.1 Hz) and 124.5 (d, *J* 8.2 Hz), 126.20 (d, *J* 2.7 Hz) and 126.23 (d, *J* 2.7 Hz), 126.6 (d, *J* 3.6 Hz) and 127.2 (d, *J* 3.6 Hz), 127.5 (d, *J* 10.9 Hz) and 128.4 (d, *J* 11.8 Hz), 127.8 (d, *J* 2.7 Hz) and 127.9 (d, *J* 2.7 Hz), 128.0 (d, *J* 1.8 Hz) and 128.1 (d, *J* 1.8 Hz), 128.6 (d, *J* 13.6 Hz) and 129.5 (d, *J* 13.6 Hz), 129.27 (d, *J* 3.6 Hz) and 129.31 (d, *J* 3.6 Hz), 131.4 (d, *J* 2.7 Hz) and 131.7 (d, *J* 1.8 Hz), 131.9 (d, *J* 8.2 Hz) and 132.3 (d, *J* 8.2 Hz), 134.9 (d, *J* 5.5 Hz) and 135.0 (d, *J* 5.5 Hz), 158.7 (d, *J* 13.6 Hz) and 159.4 (d, *J* 13.6 Hz); δ_P (202 MHz, $CDCl_3$) 32.69; GC t_R=29.08 min; GC–MS (EI, 70 eV) *m*/*z*=359 (6, M^+), 358 (35), 357 (100), 343 (5), 279 (5), 265 (5), 250 (5), 202 (8), 189 (5), 173 (9), 127 (8), 77 (11%).

*4.1.40. 1-(4-Methoxyphenyl)-4,7-methoxydibenzophospholane oxide (**16f**).* This compound was prepared according to general procedure (*Method A*) from tri-*p*-anisylphosphine oxide (**14h**) (0.184 g, 0.500 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield 0.027 g (15%). Isolated as a mixture with starting material. R_f (CH_3Cl) 0.15; δ_H (500 MHz, $CDCl_3$) 3.80 (3H, s), 3.92 (6H, s), 6.86–6.91 (4H, m), 7.25–7.28 (2H, m), 7.55–7.63 (4H, m); δ_C (126 MHz, $CDCl_3$) 55.3, 55.6, 107.2 (d, *J* 10.9 Hz), 114.2 (d, *J* 13.6 Hz), 114.6 (d, *J* 11.8 Hz), 122.4 (d, *J* 110.8 Hz), 125.7 (d, *J* 112.6 Hz), 131.1 (d, *J* 10.9 Hz), 132.9 (d, *J* 12.7 Hz), 143.6 (d, *J* 22.7 Hz), 162.6 (d, *J* 2.7 Hz), 163.9 (d, *J* 2.7 Hz); δ_P (202 MHz, $CDCl_3$) 31.53; GC t_R=27.25 min; GC–MS (EI, 70 eV) *m*/*z*=351 (23), 350 (M-16), 349 (8), 335 (28), 319 (15), 243 (25), 228 (8), 200 (20), 175 (12), 157 (22), 121 (8%).

*4.1.41. Di(p-anisyl)(2-hydroxy-4-methoxyphenyl)phosphine oxide (**15j**).* This compound was prepared according to general procedure (*Method A*) from tri-*p*-anisylphosphine oxide (**14h**) (0.184 g, 0.500 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield 0.013 g (7%); pale yellow sticky oil; [Found: C, 65.46; H, 5.30. $C_{21}H_{21}O_5P$ requires C, 65.62; H, 5.51%]; R_f (CH_3Cl) 0.23; δ_H (500 MHz, $CDCl_3$) 3.80 (3H, s), 3.86 (6H, s), 6.38–6.42 (1H, m), 6.47–6.50 (1H, m), 6.82–6.88 (1H, m), 6.95–7.00 (4H, m), 7.56–7.63 (4H, m), 11.38 (1H, br s); δ_C (126 MHz, $CDCl_3$) 55.3, 55.4, 102.1 (d, *J* 8.2 Hz), 103.4 (d, *J* 111.7 Hz), 107.3 (d, *J* 12.7 Hz), 114.2 (d, *J* 13.6 Hz), 123.7 (d, *J* 112.6 Hz), 133.0 (d, *J* 10.9 Hz), 133.9 (d, *J* 11.8 Hz), 162.8 (d, *J* 2.7 Hz), 164.4 (d, *J* 1.8 Hz), 165.7 (d, *J* 4.5 Hz); δ_P (202 MHz, $CDCl_3$) 39.14; GC t_R=31.45 min; GC–MS (EI, 70 eV) *m*/*z*=385 (19), 384 (100, M^+), 383 (80), 277 (13), 276 (64), 275 (23), 261 (26), 259 (21), 245 (12), 230 (9), 229 (11), 216 (9), 171 (8), 169 (7), 155 (9), 153 (9), 138 (8), 128 (9), 115 (11), 108 (24), 79 (10), 78 (11), 77 (33), 65 (8), 63 (8), 51 (10%).

*4.1.42. Diphenyl(1-hydroxyethyl)phosphine oxide (**21**).* This compound was prepared according to general procedure (*Method A*) from diphenylphosphine oxide (**20**) (0.101 g, 0.500 mmol) and *sec*-butyllithium (1.070 mL, 1.499 mmol, 1.4 M solution in cyclohexane): yield 0.101 g (82%); white thick oil; [Found: C, 68.51; H, 6.38. $C_{14}H_{15}O_2P$ requires C, 68.29; H, 6.14%]; R_f (CH_3Cl/MeOH=15:1) 0.36; δ_H (500 MHz, $CDCl_3$) 1.42 (3H, dd, *J* 6.9, 15.5 Hz), 4.52 (1H, br s), 4.52–4.62 (1H, m), 7.40–7.49 (4H, m), 7.49–7.57 (2H, m), 7.73–7.82 (2H, m), 7.84–7.91 (2H, m); δ_C (126 MHz, $CDCl_3$) 16.9 (d, *J* 2.7 Hz), 66.6 (d, *J* 84.5 Hz), 128.4 (d, *J* 11.8 Hz), 128.5 (d, *J* 10.9 Hz), 130.1 (d, *J* 98.1 Hz), 130.8 (d, *J* 95.4 Hz), 131.4 (d, *J* 9.1 Hz), 131.90 (d, *J* 9.1 Hz), 131.91 (d, *J* 3.6 Hz), 131.93 (d, *J* 2.7 Hz); δ_P (202 MHz, $CDCl_3$) 32.93. Analytical data are in accordance with those reported in the literature.[39]

*4.1.43. n-Butyl(t-butyl)phenylphosphine oxide (**22a**).* This compound was prepared according to general procedure (*Method A*) from *tert*-butyldiphenylphosphine oxide (**10a**) (0.129 g, 0.499 mmol) and *n*-butyllithium (0.625 mL, 0.999 mmol, 1.6 M solution in hexanes): yield 0.052 g (44%); white solid; mp 89.9–91.7 °C; [Found: C, 70.34; H, 9.65. $C_{14}H_{23}OP$ requires C, 70.56; H, 9.73%]; R_f (CH_3Cl/MeOH=15:1) 0.63; δ_H (500 MHz, $CDCl_3$) 0.87 (3H, t, *J* 7.3 Hz), 1.12 (9H, d, *J* 14.5 Hz), 1.23–1.33 (1H, m), 1.34–1.45 (2H, m), 1.63–1.74 (1H, m), 1.97–2.06 (2H, m), 7.44–7.54 (3H, m), 7.66–7.72 (2H, m); δ_C (126 MHz, $CDCl_3$) 13.6, 22.5 (d, *J* 65.4 Hz), 23.5 (d, *J* 4.5 Hz), 24.3 (d, *J* 13.6 Hz), 24.5, 32.6 (d, *J* 68.1 Hz), 128.1 (d, *J* 10.9 Hz), 130.1 (d, *J* 86.3 Hz), 131.3 (d, *J* 1.8 Hz), 131.8 (d, *J* 8.2 Hz); δ_P (202 MHz, $CDCl_3$) 49.91; GC t_R=9.59 min; GC–MS (EI, 70 eV) *m*/*z*=238 (0.6, M^+), 182 (11), 140 (100), 125 (29), 57 (11), 47 (27%). Analytical data are in accordance with those reported in the literature.[40]

*4.1.44. t-Butylmethylphenylphosphine oxide (**22b**).* This compound was prepared according to general procedure (*Method A*) from *tert*-butyldiphenylphosphine oxide (**10a**) (0.129 g, 0.499 mmol) and methyllithium (0.625 mL, 0.999 mmol, 1.6 M solution in diethyl ether): yield 0.007 g (7%); white solid; mp 59.3–60.4 °C; [Found: C, 67.24; H, 8.65. $C_{11}H_{17}OP$ requires C, 67.33; H, 8.73%]; R_f (CH_3Cl/MeOH=15:1) 0.57; δ_H (500 MHz, $CDCl_3$) 1.13 (9H, d, *J* 14.8 Hz), 1.72 (3H, d, *J* 12.0 Hz), 7.44–7.55 (3H, m), 7.67–7.74 (2H, m); δ_C (126 MHz, $CDCl_3$) 10.2 (d, *J* 66.3 Hz), 24.2, 32.5 (d, *J* 70.8 Hz), 128.1 (d, *J* 10.9 Hz), 131.46 (d, *J* 8.2 Hz), 131.52 (d, *J* 80.9 Hz); δ_P (202 MHz, $CDCl_3$) 47.44; GC t_R=8.62 min; GC–MS (EI, 70 eV) *m*/*z*=196 (0.83, M^+), 140 (100), 125 (60), 77 (14), 47 (23%). Analytical data are in accordance with those reported in the literature.[41]

*4.1.45. n-Butylphenylmethylphosphine oxide (**22c**).* This compound was prepared according to general procedure (*Method A*) from diphenylmethylphosphine oxide (**10d**) (0.108 g, 0.499 mmol) and *n*-butyllithium (0.624 mL, 0.999 mmol, 1.6 M solution in hexanes) except that reaction performed in diethyl ether: yield 0.025 g (25%); yellow oil; [Found: C, 67.41; H, 8.80. $C_{11}H_{17}OP$ requires C, 67.33; H, 8.73%]; R_f (CH_3Cl/MeOH=20:1) 0.57; δ_H (500 MHz, $CDCl_3$) 0.86 (3H, t, *J* 7.3 Hz), 1.29–1.51 (3H, m), 1.52–1.62 (1H, m), 1.70 (3H, d, *J* 12.9 Hz), 1.82–2.00 (2H, m), 7.42–7.55 (3H, m), 7.65–7.74 (2H, m); δ_C (126 MHz, $CDCl_3$) 13.5, 15.9 (d, *J* 69.9 Hz), 23.6 (d, *J* 3.6 Hz), 23.9 (d, *J* 14.5 Hz), 31.4 (d, *J* 70.8 Hz), 128.6 (d, *J* 10.9 Hz), 130.0 (d, *J* 9.1 Hz), 131.5 (d, *J* 2.7 Hz), 133.6 (d, *J* 96.3 Hz); δ_P (202 MHz, $CDCl_3$) 37.82; GC t_R=9.10 min; GC–MS (EI, 70 eV) *m*/*z*=196 (1, M^+), 154 (100), 140 (28), 139 (59), 125 (29), 92 (20), 91 (65), 77 (27), 51 (13), 47 (23%). Analytical data are in accordance with those reported in the literature.[42]

*4.1.46. s-Butylphenylmethylphosphine oxide (**22d**).* This compound was prepared according to general procedure (*Method A*) from diphenylmethylphosphine oxide (**10d**) (0.108 g, 0.499 mmol) and *s*-butyllithium (0.714 mL, 0.999 mmol, 1.4 M solution in cyclohexane) except that reaction performed in diethyl ether: yield of two diastereomers (dr=52:48) 0.008 g (8%); Isolated as a mixture of diastereomers.

Major Diastereomer: R_f (CH_3Cl/MeOH=20:1) 0.51; δ_H (500 MHz, $CDCl_3$) 1.01 (3H, t, *J* 7.3 Hz), 1.20 (3H, dd, *J* 7.3, 17.0 Hz), 1.72 (3H, d, *J* 12.3 Hz), 1.74–1.92 (3H, m), 7.46–7.56 (3H, m), 7.67–7.73 (2H, m); δ_C (126 MHz, $CDCl_3$) 11.7 (d, *J* 12.7 Hz), 12.2 (d, *J* 12.7 Hz), 13.1 (d, *J* 67.2 Hz), 22.1 (d, *J* 1.8 Hz), 36.4 (d, *J* 70.9 Hz), 128.5 (d, *J* 10.9 Hz), 130.4 (d, *J* 7.3 Hz), 131.5 (d, *J* 2.7 Hz); δ_P (202 MHz, $CDCl_3$) 43.19; GC t_R=8.98 min; GC–MS (EI, 70 eV) *m*/*z*=196 (2, M^+), 168 (35), 141 (11), 140 (100), 139 (47), 125 (64), 92 (11), 91 (10), 77 (28), 51 (14), 47 (31%).

Minor Diastereomer: R_f (CH_3Cl/MeOH=20:1) 0.45; δ_H (500 MHz, $CDCl_3$) 0.93 (3H, t, *J* 7.3 Hz), 1.07 (3H, dd, *J* 7.3, 17.0 Hz), 1.25–1.38 (3H, m), 1.70 (3H, d, *J* 12.3 Hz), 7.46–7.56 (3H, m), 7.67–7.73 (2H, m); δ_C (126 MHz, $CDCl_3$) 11.7 (d, *J* 12.7 Hz), 12.2 (d, *J* 13.6 Hz), 13.2 (d, *J* 68.1 Hz), 22.3 (d, *J* 1.8 Hz), 36.4 (d, *J* 70.8 Hz), 128.5 (d, *J* 10.9 Hz), 130.5 (d, *J* 6.4 Hz), 131.5 (d, *J* 2.7 Hz); δ_P (202 MHz, $CDCl_3$) 43.24; GC t_R=8.95 min; GC–MS (EI, 70 eV) *m*/*z*=196 (2, M^+), 168 (35), 141 (11), 140 (100), 139 (45), 125 (63), 92 (12), 91 (10), 77 (28), 51 (14), 47

(32%). Analytical data are in accordance with those reported in the literature.[43]

*4.1.47. [(Trimethylsilyl)methyl]methylphenylphosphine oxide (**22e**).* This compound was prepared according to general procedure (*Method A*) from diphenylmethylphosphine oxide (**10d**) (0.108 g, 0.499 mmol) and (trimethylsilyl)methyllithium (0.999 mL, 0.999 mmol, 1 M solution in pentane): yield 0.006 g (5%); pale yellow oil; [Found: C, 58.48; H, 8.63. $C_{11}H_{19}OPSi$ requires C, 58.37; H, 8.46%]; R_f (CH_3Cl/MeOH=20:1) 0.45; δ_H (500 MHz, $CDCl_3$) 0.07 (9H, s), 1.32–1.47 (2H, m), 1.70 (3H, d, *J* 12.9 Hz), 7.44–7.51 (3H, m), 7.69–7.74 (2H, m); δ_C (126 MHz, $CDCl_3$) 0.15 (d, *J* 2.7 Hz), 20.2 (d, *J* 69.9 Hz), 21.1 (d, *J* 60.9 Hz), 128.5 (d, *J* 10.9 Hz), 129.7 (d, *J* 10.0 Hz), 131.2 (d, *J* 2.7 Hz), 136.5 (d, *J* 97.2 Hz); δ_P (202 MHz, $CDCl_3$) 36.12; GC t_R=7.70 min; GC–MS (EI, 70 eV) *m*/*z*=154 (63), 139 (100), 92 (10), 91 (43), 77 (32), 51 (21), 47 (10%). Analytical data are in accordance with those reported in the literature.[44]

*4.1.48. (But-3-enyl)dimethylphosphine oxide (**24**).* This compound was prepared according to general procedure (*Method A*) from 1-phenylphosphol-2-ene oxide (**22**) (0.089 g, 0.500 mmol) and methyllithium (0.624 mL, 0.999 mmol, 1.6 M solution in diethyl ether): yield 0.015 g (22%); colorless oil; [Found: C, 54.36; H, 9.70. $C_6H_{13}OP$ requires C, 54.54; H, 9.92%]; R_f (CH_3Cl/MeOH=15:1) 0.25; δ_H (500 MHz, $CDCl_3$) 1.50 (6H, d, *J* 12.6 Hz), 1.76–1.88 (2H, m), 2.34–2.44 (2H, m), 5.02–5.15 (2H, m), 5.81–5.93 (1H, m); δ_C (126 MHz, $CDCl_3$) 16.3 (d, *J* 68.1 Hz), 25.9 (d, *J* 2.7 Hz), 30.9 (d, *J* 68.1 Hz), 115.5, 137.2 (d, *J* 14.5 Hz); δ_P (202 MHz, $CDCl_3$) 42.28; GC t_R=6.68 min; GC–MS (EI, 70 eV) *m*/*z*=132 (2, M^+), 131 (3), 117 (5), 104 (7), 92 (9), 78 (100), 77 (34), 76 (9), 63 (53), 55 (11), 49 (14), 47 (25), 46 (8), 45 (13%).

*4.1.49. (But-2-enyl)phenylmethylphosphine oxide (**26**).* This compound was prepared according to general procedure (*Method A*) from 1-phenylphosphol-3-ene oxide (**25**) (0.089 g, 0.500 mmol) and methyllithium (0.624 mL, 0.999 mmol, 1.6 M solution in diethyl ether): yield of two isomers 0.011 g (11%). Isolated as a mixture of isomers *cis* and *trans*.

trans isomer: R_f (CH_3Cl/MeOH=15:1) 0.24; δ_H (500 MHz, $CDCl_3$) 1.47–1.53 (3H, m), 1.71 (3H, d, *J* 12.9 Hz), 2.66–2.88 (2H, m), 5.35–5.46 (1H, m), 5.64–5.74 (1H, m), 7.43–7.57 (3H, m), 7.65–7.78 (2H, m); δ_C (126 MHz, $CDCl_3$) 12.9 (d, *J* 1.8 Hz), 14.8 (d, *J* 70.8 Hz), 31.8 (d, *J* 68.1 Hz), 119.0 (d, *J* 8.2 Hz), 128.5 (d, *J* 11.8 Hz), 129.2 (d, *J* 11.8 Hz), 130.1 (d, *J* 9.1 Hz), 131.6 (d, *J* 2.7 Hz), 133.4 (d, *J* 96.3 Hz); δ_P (202 MHz, $CDCl_3$) 36.16; GC t_R=11.02 min; GC–MS (EI, 70 eV) *m*/*z*=194 (6, M^+), 140 (80), 139 (100), 125 (47), 109 (8), 95 (8), 91 (21), 78 (11), 77 (67), 70 (13), 69 (10), 65 (9), 63 (8), 55 (21), 53 (11), 51 (45), 50 (12), 47 (52), 45 (9%).

cis isomer: R_f (CH_3Cl/MeOH=15:1) 0.24; δ_H (500 MHz, $CDCl_3$) 1.47–1.53 (3H, m), 1.69 (3H, d, *J* 12.9 Hz), 2.66–2.88 (2H, m), 5.35–5.46 (1H, m), 5.51–5.59 (1H, m), 7.43–7.57 (3H, m), 7.65–7.78 (2H, m); δ_C (126 MHz, $CDCl_3$) 18.1 (d, *J* 1.8 Hz), 14.8 (d, *J* 70.8 Hz), 34.1 (d, *J* 68.1 Hz), 119.6 (d, *J* 9.1 Hz), 127.9 (d, *J* 11.8 Hz), 129.5 (d, *J* 10.0 Hz), 131.6 (d, *J* 2.7 Hz), 133.8 (d, *J* 92.6 Hz); δ_P (202 MHz, $CDCl_3$) 35.64; GC t_R=10.90 min; GC–MS (EI, 70 eV) *m*/*z*=194 (9, M^+), 169 (7), 140 (52), 139 (100), 125 (24), 109 (12), 95 (9), 92 (9), 91 (21), 78 (12), 77 (60), 70 (20), 69 (12), 63 (9), 57 (9), 55 (34), 53 (15), 51 (49), 50 (15), 47 (39), 45 (8%).

*4.1.50. 1-t-Butylphospholane oxide (**28**).* This compound was prepared according to general procedure (*Method A*) from 1-phenylphospholane oxide (**27**) (0.090 g, 0.500 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield 0.004 g (5.4%). Isolated as a mixture with **29**. R_f (CH_3Cl/MeOH=15:1) 0.47; δ_H (500 MHz, $CDCl_3$) 1.18 (9H, d, *J* 14.5 Hz), 1.62–1.78 (4H, m), 1.78–1.88 (2H, m), 1.98–2.16 (2H, m); δ_C (126 MHz, $CDCl_3$) 23.4 (d, *J* 60.9 Hz), 24.3, 25.2 (d, *J* 6.4 Hz), 31.7 (d, *J* 62.7 Hz); δ_P (202 MHz, $CDCl_3$) 82.74; GC t_R=8.50 min; GC–MS (EI, 70 eV) *m*/*z*=160 (3, M^+), 104 (100), 103 (27), 78 (11), 76 (28), 57 (20), 47 (11%).

*4.1.51. trans-1-Phenyl(2-hydroxy)phospholane oxide (**29**).* This compound was prepared according to general procedure (*Method A*) from 1-phenylphospholane oxide (**27**) (0.090 g, 0.500 mmol) and *tert*-butyllithium (0.588 mL, 0.999 mmol, 1.7 M solution in pentane): yield 0.005 g (4.6%). Isolated as a mixture with **28**. R_f (CH_3Cl/MeOH=15:1) 0.47; δ_H (500 MHz, $CDCl_3$) 1.77–1.88 (1H, m), 1.97–2.19 (3H, m), 2.19–2.35 (2H, m), 4.08–4.16 (1H, m), 4.19 (1H, br s), 7.47–7.52 (2H, m), 7.52–7.58 (1H, m), 7.66–7.74 (2H, m); δ_C (126 MHz, $CDCl_3$) 20.3 (d, *J* 7.3 Hz), 26.7 (d, *J* 65.4 Hz), 33.9 (d, *J* 15.4 Hz), 68.9 (d, *J* 71.8 Hz), 128.8 (d, *J* 11.8 Hz), 130.1 (d, *J* 10.0 Hz), 131.7 (d, *J* 87.2 Hz), 132.1 (d, *J* 2.7 Hz); δ_P (202 MHz, $CDCl_3$) 55.32; GC t_R=12.14 min; GC–MS (EI, 70 eV) *m*/*z*=196 (6, M^+), 195 (14), 168 (27), 167 (26), 150 (10), 142 (40), 141 (10), 139 (49), 126 (13), 125 (83), 124 (7), 122 (9), 121 (10), 105 (13), 104 (12), 91 (27), 79 (20), 78 (26), 77 (58), 69 (6), 65 (7), 51 (39), 50 (11), 47 (100%).

*4.1.52. 1-s-Butylphospholane oxide (**30**).* This compound was prepared according to general procedure (*Method A*) from 1-phenylphospholane oxide (**27**) (0.090 g, 0.500 mmol) and *sec*-butyllithium (0.714 mL, 0.999 mmol, 1.4 M solution in cyclohexane): yield 0.010 g (12%). Isolated as a mixture with **29**. R_f (CH_3Cl/MeOH=15:1) 0.27; δ_H (500 MHz, $CDCl_3$) 1.04 (3H, t, *J* 7.6 Hz), 1.20 (3H, dd, *J* 6.9, 16.4 Hz), 1.61–1.80 (5H, m), 1.81–1.92 (2H, m), 1.96–2.21 (3H, m); δ_C (126 MHz, $CDCl_3$) 12.2 (d, *J* 10.0 Hz), 12.3, 22.8 (d, *J* 1.8 Hz), 24.77 (d, *J* 7.3 Hz), 24.84 (d, *J* 6.4 Hz), 25.3 (d, *J* 62.7 Hz), 25.7 (d, *J* 62.7 Hz), 35.5 (d, *J* 62.7 Hz); δ_P (202 MHz, $CDCl_3$) 77.16; GC t_R=9.14 min; GC–MS (EI, 70 eV) *m*/*z*=160 (2, M^+), 145 (2), 132 (24), 131 (13), 104 (9), 104 (100), 103 (22), 85 (6), 78 (80), 76 (23), 75 (7), 57 (7), 55 (9), 47 (15%).

*4.1.53. Tri(n-butyl)phosphine oxide (**31**).* This compound was prepared according to general procedure (*Method A*) from 1-phenylphospholane oxide (**27**) (0.090 g, 0.500 mmol) and *n*-butyllithium (0.624 mL, 0.999 mmol, 1.6 M solution in hexanes): yield 0.044 g (40%). Isolated as a mixture with starting material. δ_H (500 MHz, $CDCl_3$) 0.92 (9H, t, *J* 7.3 Hz), 1.37–1.45 (6H, m), 1.49–1.57 (6H, m), 1.63–1.70 (6H, m); δ_C (126 MHz, $CDCl_3$) 13.6, 23.7 (d, *J* 3.6 Hz), 24.2 (d, *J* 14.5 Hz), 27.6 (d, *J* 65.4 Hz); δ_P (202 MHz, $CDCl_3$) 48.99; GC t_R=10.22 min; GC–MS (EI, 70 eV) *m*/*z*=189 (22, M^+), 176 (5), 162 (14), 161 (10), 147 (20), 134 (14), 120 (30), 105 (8), 92 (100), 78 (63), 63 (29), 55 (22%). Analytical data are in accordance with those reported in the literature.[45]

*4.1.54. 1-Methylphospholane oxide (**32**).* This compound was prepared according to general procedure (*Method A*) from 1-phenylphospholane oxide (**27**) (0.090 g, 0.500 mmol) and *n*-butyllithium (0.624 mL, 0.999 mmol, 1.6 M solution in hexanes): conversion (95%); pale yellow liquid. Isolated as a mixture with starting material. δ_H (500 MHz, $CDCl_3$) 1.61 (3H, d, *J* 12.6 Hz), 1.69–1.81 (4H, m), 1.81–1.92 (2H, m), 1.92–2.08 (2H, m); δ_C (126 MHz, $CDCl_3$) 17.1 (d, *J* 61.8 Hz), 24.4 (d, *J* 8.2 Hz), 28.3 (d, *J* 67.2 Hz); δ_P (202 MHz, $CDCl_3$) 67.14; GC t_R=9.71 min; GC–MS (EI, 70 eV) *m*/*z*=118 (53, M^+), 117 (70), 103 (18), 90 (100), 85 (15), 77 (12), 75 (27), 72 (14), 64 (13), 63 (19), 62 (36), 55 (12), 47 (35%). Analytical data are in accordance with those reported in the literature.[46]

4.2. The synthesis of *p*-tolyl(*t*-butyl)phosphine oxide 19

In the flame-dried two-neck round-bottom flask (250 mL), equipped with magnetic stirrer and inert gas inlet PCl_3 (1.220 mL, 0.014 mol) was dissolved in Et_2O (40 mL) and the mixture was

cooled to −78 °C. A solution of *t*-BuMgCl (7 mL, 2 M solution in THF) was slowly added via syringe. After the addition was finished the reaction mixture was allowed to warm slowly with stirring for 15 h. Then, the mixture was cooled again to −78 °C and *p*-TolMgBr (14 mL, 1 M solution in THF) was added dropwise. The mixture was allowed to warm slowly to room temperature for 7 h. Then, the mixture was cooled to 0 °C and 20% H_2SO_4 was slowly added until all solids were dissolved. The mixture was extracted with EtOAc (4×50 mL), combined organic phases were dried over $MgSO_4$ and evaporated. The residue was purified using flash chromatography with $CHCl_3$:MeOH 50:1 as eluent. Yield 1.346 g (49%); colorless oil; [Found: C, 67.52; H, 8.85. $C_{11}H_{17}OP$ requires C, 67.33; H, 8.73%]; R_f (CH_3Cl/MeOH=15:1) 0.43; δ_H (500 MHz, $CDCl_3$) 1.14 (9H, d, *J* 16.7 Hz), 2.42 (3H, s), 7.02 (1H, d, *J* 455.2 Hz), 7.29–7.33 (2H, m), 7.55–7.60 (2H, m); δ_C (126 MHz, $CDCl_3$) 20.8, 23.4 (d, *J* 2.7 Hz), 32.0 (d, *J* 69.0 Hz), 125.1 (d, *J* 92.6 Hz), 129.3 (d, *J* 2.7 Hz), 130.9 (d, *J* 10.0 Hz), 143.1 (d, *J* 2.7 Hz); δ_P (202 MHz, $CDCl_3$) 48.08; GC t_R=10.52 min; GC–MS (EI, 70 eV) *m*/*z*=196 (M) (3), 140 (39), 94 (8), 93 (100), 91 (27), 65 (8), 57 (11), 47 (12).

4.3. The synthesis of 15b and 15e through copper-catalyzed coupling with aryl iodides

In the flame-dried Schlenk flask (50 mL), equipped with magnetic stirrer and inert gas inlet secondary phosphine oxide **18** (0.546 g, 0.003 mol) was dissolved in toluene (5 mL). Then, aryl iodide (3,4-dimethyliodobenzene (0.696 g, 0.426 mL, 0.003 mol) or 4-iodotoluene (0.655 g, 0.003 mol)) was added, followed by CuI (0.057 g, 0.300 mmol), α-phenylethylamine (0.073 g, 0.077 mL, 0.600 mmol) and K_2CO_3 (0.829 g, 0.006 mmol). The mixture was heated at reflux for 24 h, then cooled to room temperature. Saturated NH_4Cl solution (15 mL) was then added and the mixture was extracted with $CHCl_3$ (3×40 mL). The organic phase was dried over $MgSO_4$ and evaporated and the residue was purified by flash chromatography using $CHCl_3$:MeOH 50:1 as eluent yielding **15b** (0.808 g, 94%) as white solid or **15e** (0.727 g, 89%) as pale yellow solid.

4.4. The synthesis of 15f and 15g through palladium-catalyzed coupling with 3-bromoanizole

In the flame-dried Schlenk flask (50 mL), equipped with magnetic stirrer and inert gas inlet secondary phosphine oxide **18** (0.546 g, 0.003 mol) or **19** (0.589 g, 0.003 mol) was dissolved in toluene (5 mL). Then, 3-bromoanizole (0.561 g, 0.380 mL, 0.003 mol) was added, followed by $(Ph_3P)_2PdCl_2$ (0.105 g, 0.150 mmol) and Cs_2CO_3 (1.955 g, 0.006 mmol). The mixture was heated at reflux for 24 h, then cooled to room temperature. Saturated NH_4Cl solution (15 mL) was then added and the mixture was extracted with $CHCl_3$ (3×40 mL). The organic phase was dried over $MgSO_4$ and evaporated and the residue was purified by flash chromatography using $CHCl_3$:MeOH 50:1 as eluent yielding **15f** (0.856 g, 99%) as yellow oil or **15g** (0.535 g, 59%) as yellow oil.

4.5. The synthesis of 16b–e from 15b, 15f and 15g

In the flame-dried Schlenk flask (25 mL), equipped with magnetic stirrer and inert gas inlet phosphine oxide **15b** (0.143 g, 0.500 mmol), **15f** (0.144 g, 0.500 mmol) or **15g** (0.151 g, 0.500 mmol) was dissolved in THF (5 mL). The mixture was cooled to −78 °C and organolithium compound (PhLi (0.556 mL, 2 M solution in *n*-Bu_2O) for **15b** or *t*-BuLi (0.59 mL, 1.7 M in pentane) for **15f** and **15g**) was slowly added. The reaction mixture was then warmed to room temperature and stirred for 24 h (for **15f** and **15g**) or was heated at 55 °C for 24 h (for **15b**). The reaction was finished by addition of saturated NH_4Cl solution (10 mL) and then extracted with $CHCl_3$ (3×15 mL). The organic phase was dried over $MgSO_4$ and evaporated. The residue was purified using flash chromatography with EtOAc:MeOH 40:1 as eluent affording an inseparable mixture of **16b** and **16c** (0.020 g, 14% overall yield, 2.5:1 ratio), **16d** (0.093 g, 65%) as yellow pasty solid or **16e** (0.042 g, 28%) colorless sticky oil.

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Supplementary data

Supplementary data (^1H, ^{13}C and ^{31}P NMR spectras of the products.) associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.12.043.

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