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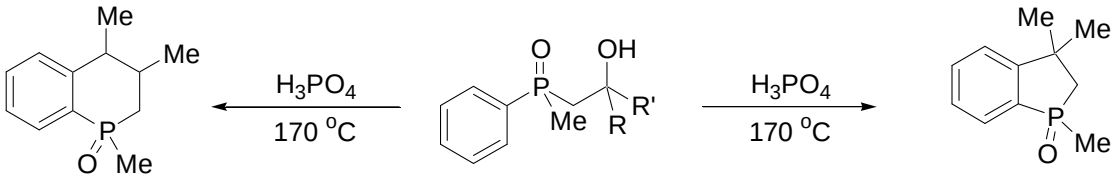

54% R = Et, R' = Me R, R' = Me 74%

Intramolecular cationic cyclization of β-hydroxyalkylphosphine oxides – a route towards the benzophosphorinane core

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ABSTRACT

Intramolecular cationic cyclization of β-hydroxyalkylphosphine oxides in the presence of an acid lead to the formation of fused bicyclic compounds with an incorporated phosphorus atom. Depending on the structure of the starting compound the formation of either phosphaindane or benzophosphorinane oxides has been observed. The key difference in the reactivity arises from the substitution pattern at the carbinolic carbon atom of β-hydroxyalkylphosphine oxide.

KEYWORDS

β-Hydroxyalkylphosphine oxide, intramolecular, cationic cyclization, phosphaindane, benzophosphorinane

1. Introduction

The synthesis of organophosphorus compounds with a phosphorus atom incorporated into the cyclic structure is always a synthetic challenge[1] but, at the same time, these compounds have been found to exhibit high selectivities as ligands in transition metal catalysis (Figure 1).[2]

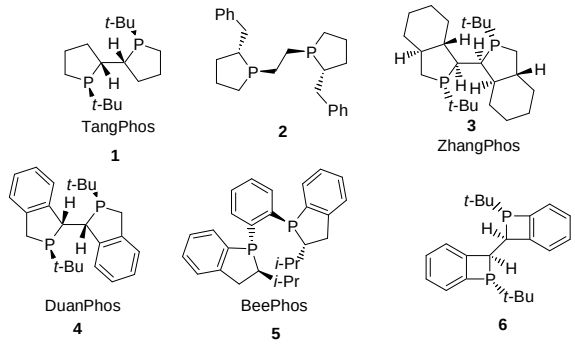
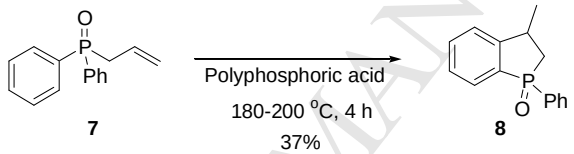


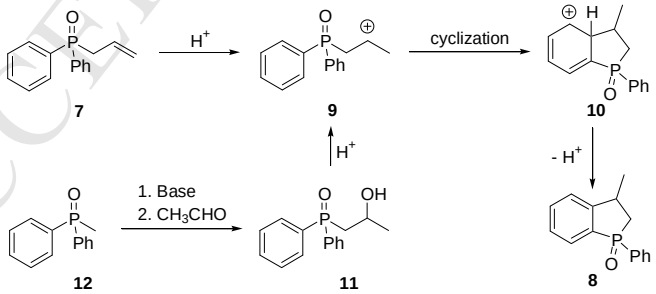
Figure 1. Examples of cyclic phosphine ligands

The synthetic methods leading to cyclic phosphine precursors are mostly based on double nucleophilic substitution of the phosphine dianion with the appropriate dielectrophile,[2c-d,3] double nucleophilic substitution with $RPHal_2$-type compounds and bis-Grignard reagents,[2a,4] McCormack cyclization,[5] ring-closing metathesis[6] or intramolecular hydrophosphination.[7] The synthesis of cyclic organophosphorus compounds possessing a fused aromatic ring is much less is developed. Both DuanPhos **4** and BeePhos **5** ligands were synthesized through double nucleophilic substitution methodology of phosphine dianion PhP_2- with the appropriate electrophile[2d,e] whereas ligand **6** was prepared through double nucleophilic substitution at phosphorus using bis-Grignard reagent and $RPHal_2$-type compound.[2f] Other methods for the synthesis of these compounds include intramolecular coupling reaction,[8] ring-closing metathesis[9] or electrophilic substitution at phosphorus.[10] From a synthetic point of view, the most useful approach is based on intramolecular electrophilic cyclization of alkenylphosphine derivatives (Scheme 1)[11] where the arylphosphine derivatives possessing an alkenyl substituent undergo protonation upon treatment with a strong acid followed by an intramolecular reaction of the formed cation with adjacent aryl substituent.



Scheme 1. Intramolecular cationic cyclization of **7**.

This method is operationally simple and could potentially be used in the synthesis of a wide range of fused organophosphorus ligand systems for use in catalysis. The above reaction must proceed through the formation of a carbocation which undergoes a cyclization reaction (Scheme 2).



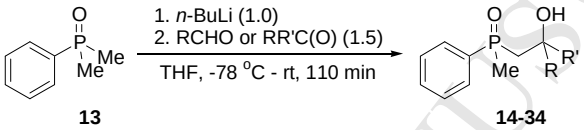
Scheme 2. Probable cyclization mechanism of **7** and **11**.

If this mechanism is true, the carbocation **9** could be more conveniently obtained from the β-hydroxyalkylphosphine oxide **11** (Scheme 2). A treatment of this molecule with a strong acid should similarly lead to the cation **9**. The oxide **11** is easily available from methylphosphine oxide **12** and acetaldehyde. Regarding the availability of both carbonyl compounds and methylphosphine oxides it

is easy to conclude that β-hydroxyalkylphosphine oxides could be regarded as very convenient substrates for the synthesis of fused systems with incorporated phosphorus atoms. Herein, our results concerning the use of β-hydroxyalkylphosphine oxides in the cationic cyclization are presented.

2. Results and discussion

The problem of acidic cyclization of β-hydroxyalkylphosphine oxides has never been a subject of a detailed investigation although some precedent can be found in the literature.[12] For test reactions, β-hydroxyalkylphosphine oxides derived from dimethylphenylphosphine oxide **13** have been chosen (Scheme 3, Table 1). The choice of **13** has been rationalized by the relatively easy access to the non-racemic P-stereogenic adduct using sparteine chemistry[13] although it should be pointed out that this approach is effective only with phosphine-boranes and phosphine sulfides.



13 **14-34**

Scheme 3. Synthesis of substrates for cyclization

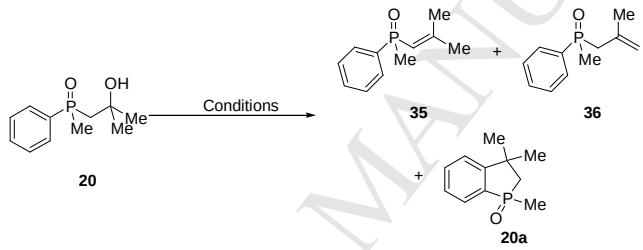
Table 1. Synthesis of substrates for cyclization

Entry	Substituents		Product	Yields (%) (dr)
	R	R'		
1	Me	H	**14**	86 (53:47)
2	Ph	H	**15**	86 (54.4:45.5)
3	*i*-Pr	H	**16**	83 (52.5:47.5)
4	*t*-Bu	H	**17**	85 (58:42)
5	Et	H	**18**	75 (54:46)
6	*c*-Hex	H	**19**	97 (53:47)
7	Me	Me	**20**	89
8	*n*-Bu	Me	**21**	76 (56:44)
9	*n*-Pr	Me	**22**	85 (52:48)
10	Ph	Me	**23**	92 (66.5:33.5)
11	*i*-Pr	Me	**24**	87 (55.5:44.5)
12	Et	Me	**25**	77 (53.5:46.5)
13	*t*-Bu	Me	**26**	80 (60:40)
14	*t*-BuCH_2	Me	**27**	83 (91:9)
15	Ph	Ph	**28**	84
16	*n*-Bu	*n*-Bu	**29**	82

17	*i*-Pr	*i*-Pr	**30**	60
18	Et	Et	**31**	75
19	-$(CH_2)_4$-		**32**	71
20	-$(CH_2)_5$-		**33**	76
21	-$(CH_2)_6$-		**34**	90

A reaction of phosphine oxide **13** with carbonyl compounds in the presence of base afforded the corresponding products **14**-**34** with high yields. In the case of aldehydes and unsymmetrical ketones a mixtures of diastereomers have been obtained (Table 1, Entries 1-6, 8-14) but, generally, the diastereoselectivity of the addition was low. At this point, the relative configuration of the major diastereomers was not established.

In order to develop the mildest conditions for the cyclization reaction, an optimization of the reaction conditions has been undertaken with **20** as the model compound (Scheme 4, Table 2).



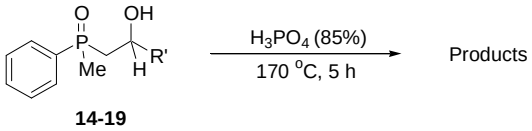
Scheme 4. Optimization of the reaction conditions

Table 2. Optimization of the reaction conditions

Entry	Conditions	Products
1	BF_3-OEt_2 (1.5), DCE, reflux, 4 h	**35** (20%), **36** (55%)
2	AcOH, rt, 4 h	No reaction
3	AcOH, reflux, 4 h	No reaction
4	HBF_4 (1.0), DCM, -78-0 oC, 4.5 h	No reaction
5	HBF_4 (1.0), DCM, rt, 4 h	No reaction
6	HBF_4 (3.0), DCE, reflux, 4 h	**35** (63%), **36** (23%)
7	TFA, 45 ^oC, 4 h	**36** (47%)
8	H_3PO_4 (85%), 120 ^oC, 4 h	**35** (65%), **36** (24%), **20a** (5%)
9	**H_3PO_4 (85%), 170 ^oC, 5 h**	**20a (72%)**

It appeared that conditions similar to those reported previously[12] are optimal for cyclization of β-hydroxyalkylphosphine oxides (Table 2, Entry 9). The use of other Brønstedt acids was either inefficient (AcOH) or led to dehydration of substrate (HBF_4, TFA).

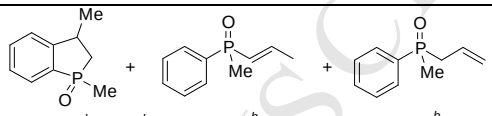
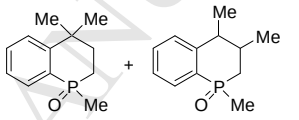
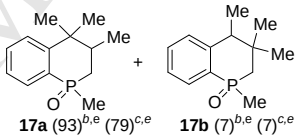
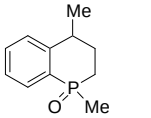
At first, β-hydroxyalkylphosphine oxides obtained from aldehydes have been subjected to cationic cyclization (Scheme 5, Table 3).



14-19

Scheme 5. Cyclization of **14-19**.

Table 3. Cyclization of **14-19**.

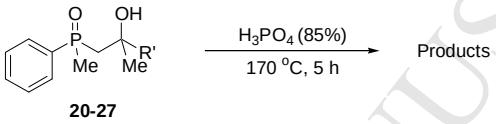
Entry	Substrate	Products
1[a]	**14** (R= Me, R'= H)	 **14a** (81)[b,e] (34)[d,e] **14b** (8)[b] **14c** (5)[b]
2	**15** (R= Ph, R'= H)	Complex micture
3	**16** (R= *i*-Pr, R'= H)	 **16a** (88)[b] (86)[c] **16b** (12)[b,e] (12)[c,e]
4	**17** (R= *t*-Bu, R'= H)	 **17a** (93)[b,e] (79)[c,e] **17b** (7)[b,e] (7)[c,e]
5	**18** (R= Et, R'= H)	 **18a** (100)[b,e] (40)[d,e]
6	**19** (R= *c*-Hex, R'= H)	Traces of the product

[a] The reaction took 72 h. After 5 h the product ratio was: **14a** (15%), **14b** (77%), **14c** (8%). [b] Conversion based on ^{31}P NMR spectrum of the crude mixture. [c] Yields of the products isolated as mixtures with other compounds. [d] Yields of pure compounds. [e] Isolated as a mixture of diastereomers.

Attempted cationic cyclization of compounds **14-19** revealed that the reaction pathway observed for **20** is followed only in the case of adduct **14**. Phosphine oxide derived from acetaldehyde underwent cyclization to a very limited extent under the developed reaction conditions and the main products were **14b** and **14c** after heating the mixture for 5 h (Table 3, Entry 1). Prolonged heating of **14** in phosphoric acid was needed to achieve the desired cyclization product as a mixture of two diastereomers. This result might be the consequence of the lower stability of secondary carbocation generated by removal of the water molecule.

On the other hand, compounds **16**-**18** derived from isobutyraldehyde, pivalaldehyde or propionaldehyde readily underwent cyclization reaction but the main or even only products were not phosphaindane oxides but benzophosphorinane oxides **16b**, **17a** and **18b**, all formed as mixtures of diastereomers (Table 3, Entries 3-5). The formation of these products must therefore involve the rearrangement of the initial carbocation. As it could be judged from the data presented in the Table 3, the rearrangement might involve the transfer of either hydride (**16b**, **18a**) or alkyl group (**16c**, **17a**, **17b**).

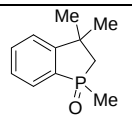
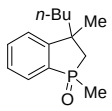
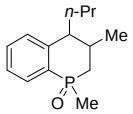
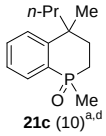
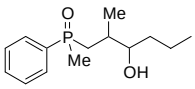
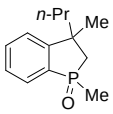
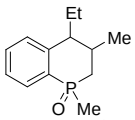
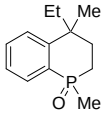
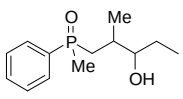
Following the research course, adducts **20**-**27** derived from methyl ketones have been subjected to the cyclization reaction (Scheme 6, Table 4).

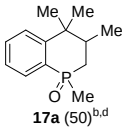
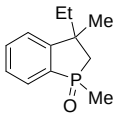
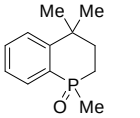
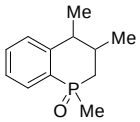
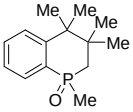
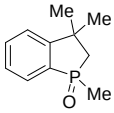
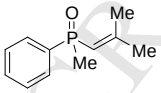


20-27

Scheme 6. Cyclization of compounds **20**-**27**.

Table 4. Cyclization of compounds **20**-**27**.

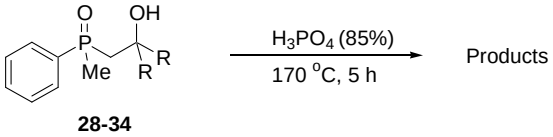
Entry	Substrate	Products
1	**20** (R= Me, R‘= Me)	 **20a** (100)[a] (74)[c]
2	**21** (R= *n*-Bu, R‘= Me)	 **21a** (13)[a,d]  **21b** (45)[a,d]  **21c** (10)[a,d]  **21d** (32)[a,d]
3	**22** (R= *n*-Pr, R‘= Me)	 **22a** (3)[a,d]  **22b** (36)[a,d]  **22c** (3)[a,d]  **22d** (58)[a,d]
4	**23** (R= Ph, R‘= Me)	Complex reaction mixture

5	**24** (R= *i*-Pr, R'= Me)	 **17a** (50)[b,d]
6	**25** (R= Et, R'= Me)	 **25a** (6)[a] (3)[b]  **16a** (10)[a,d] (6)[b,d]  **16b** (84)[a,d] (54)[b,d]
7	**26** (R= *t*-Bu, R'= Me)	 **26a** (45)[c]
8	**27** (R= *t*-BuCH$_2$, R'= Me)	 **20a** (31)[c]  **35** (11)[c]

[a] Conversion based on ^{31}P NMR of the crude mixture. [b] Yields of the products isolated as mixtures with other compounds. [c] Yields of pure compounds. [d] A mixture of diastereomers.

A screen of the products derived from methyl ketones revealed that only **20** undergoes cyclization towards phosphaindane. The outcome in the case of compounds **21**-**27** depended on the structure of the substrates around the carbinolic carbon atom. Compounds with long alkyl substituents at this atom (**21** and **22**) afforded complex mixtures consisting of isomeric alcohols **21d** and **22d** as major products along with some diastereomeric benzophosphorinane oxides (**21b**, **21c**, **22b** and **22c**) and trace amounts of phosphaindane oxides **21a** and **22a**. Adducts with shorter or branched alkyl groups at the carbinolic carbon atom underwent preferentially or exclusively cyclization to benzophosphorinane oxides (Table 4, Entries 5-7). Attempted cyclization of adduct **23** with a phenyl group at the carbinolic atom afforded a complex reaction mixture (Table 4, Entry 4) whereas adduct **27** with a neopentyl group at the same carbon atom underwent isobutene elimination prior to cyclization into the phosphaindane core (Table 4, Entry 8).

Finally, a set of adducts **28**-**34** derived from symmetrical ketones other than acetone has been subjected to cyclization reaction (Scheme 7, Table 5).

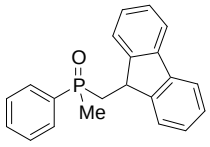
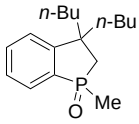
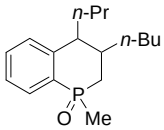
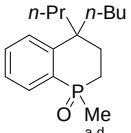
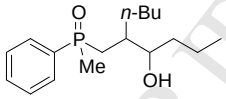
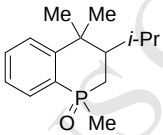
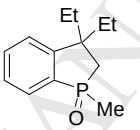
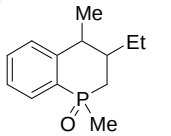
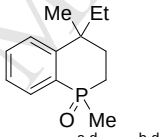
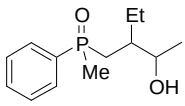
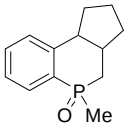
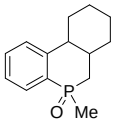


28-34

Scheme 7. Cyclization of compounds **28**-**34**.

Table 5. Cyclization of compounds **28**-**34**.

Entry	Substrate	Products

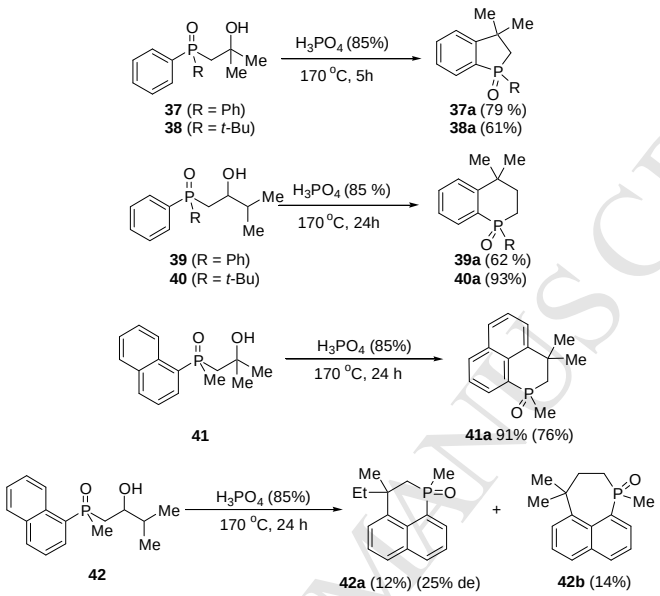
1	**28** (R= Ph, R‘= Ph)	 **28a** (22)[c]
2	**29** (R= *n*-Bu, R‘= *n*-Bu)	 **29a** (9)[a,d]  **29b** (22)[a,d]  **29c** (4)[a,d]  **29d** (65)[a,d]
3	**30** (R= *i*-Pr, R‘= *i*-Pr)	 **30a** (18)[c,d]
4	**31** (R= Et, R‘= Et)	 **31a** (1)[a] (1)[b]  **31b** (65)[a,d] (47)[b,d]  **22c** (24)[a,d] (22)[b,d]  **31d** (11)[a,d] (4)[b,d]
5	**32** (R=R‘= -$(CH_2)_4$-)	 **32a** (38)[c,d]
6	**33** (R=R‘= -$(CH_2)_5$-)	 **33a** (27)[c,d]
7	**34** (R=R‘= -$(CH_2)_6$-)	Traces of the product

[a] Conversion based on ^{31}P NMR spectrum of the crude mixture. [b] Yields of the products isolated as mixtures with other compounds. [c] Yields of pure compounds. [d] A mixture of diastereomers.

Under the standard reaction conditions compound **28** underwent intramolecular cyclization to the corresponding fluorene **28a** albeit with low yield (Table 5, Entry 1). The adduct derived from dibutyl ketone afforded mainly the isomeric alcohol **29d** but the one derived from 3-pentanone afforded preferentially a mixture of two benzophosphorinanes **31b** and **31c** where the latter is formed through ethyl group migration (Table 5, Entry 4). The adduct derived from diisopropyl ketone afforded benzophosphorinane oxide **30a** albeit in low yield (Table 4, Entry 3). Interestingly, adducts derived

from cyclic ketones like cyclopentanone or cyclohexanone (but not cycloheptanone) afforded tricyclic products as mixtures of isomers (Table 5, Entries 5 and 6).

The results presented so far show the general reactivity pathway for the transformation of β-hydroxyalkyl(phenyl)phosphine oxides in acidic media. It was therefore interesting to find the behaviour of other phosphine oxides possessing different substituents at phosphorus (Scheme 8).

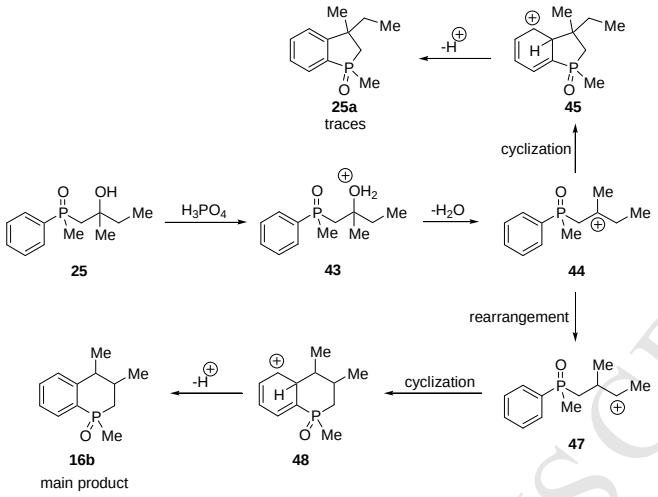


Scheme 8. Cyclization of phosphine oxides **37**-**42**.

It appeared that the developed method could be extended to other tertiary phosphine oxides possessing at least one aryl substituent at phosphorus. Compounds **37** and **39** with two phenyl substituents at phosphorus afforded either phosphaindane oxide **37a** or benzophosphorinane oxide **39a** with good yields. Similarly, phosphine oxides **38** and **40** possessing a bulky *t*-butyl group underwent clean formation of fused bicyclic systems **38a** and **40a**, respectively. An interesting issue was the reaction of compounds **41** and **42** possessing a 1-naphthyl moiety. In the case of **41**, the formation of tricyclic phosphadihydrophenalene **41a** as the sole product has been observed. This suggests, that the carbocation tends to undergo cyclization with the distant naphthalene fragment instead of the adjacent ortho carbon atom. Phosphine oxide **42**, on the other hand, underwent competitive formation of tricyclic **42a** and **42b**. Here, the competition between 6-*endo*-*trig* (processing through alkyl group migration) and 7-*endo*-*trig* processes (processing through proton migration) is evidently seen.

Regarding the results presented above, the formation of phosphaindane core could be attributed to a 5-*endo*-*trig* process and the formation of benzophosphorinane to a 6-*endo*-*trig* process. Unfortunately, Baldwin's rules[14] cannot be applied to cationic cyclization reaction where no such generalization could be made.[15] Nevertheless, phosphaindane is the main product only in cases where the intermediary

carbocation cannot undergo any rearrangement. In other cases the main or even the only product will be benzophospholane. This is extremely well seen in the case of compound **25** (Scheme 9).



Scheme 8. Rearrangement-cyclization of **25**.

Protonation of this substrate should afford cation **43** which loses water molecule yielding the cation **44**. The most obvious step here would be cyclization to cation **45** followed by rearomatization which should lead to phosphaindane **25a**. This proces, however, is marginal and the main reaction pathway leads through a rearrangement of tertiary cation **44** into secondary (!) cation **47** which then undergoes cyclization into **48** which upon rearomatization provides benzophospholane **16b**. There must undoubtedly be an energy increase due to the formation of the less stable secondary carbocation but this reaction pathway still prevails over the formation of **25a**. A detailed mechanism of the cationic cyclization is currently underway in our laboratory.

3. Conclusions

In conclusion, we have described the intramolecular cationic cyclization of a series of β-hydroxyalkylphosphine oxides. Depending on the structure, the formation of either the phosphaindane or the benzophosphorinane skeleton has been observed. The formation of the latter proceeds with rearrangement of the initial tertiary carbocation prior to the cyclization step. The crucial element of the selectivity of this transformation is the substitution pattern at the carbinolic carbon atom. The formation of the benzophospholane core proceeds through a 6-*endo-trig* process, compared to a 5-*endo-trig* cyclization observed for the phosphaindane framework. The parent carbocation would preferentially undergo a rearrangement-cyclization sequence for compounds with branched or moderately long (2-3 carbon atom chain) alkyl substituents at carbinolic carbon atom.

4. Experimental section

4.1. General informations

All reactions were performed under an argon atmosphere 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. *n*-BuLi was commercially available and used as received.

Analytics and Instruments. The NMR spectra was recorded with Bruker Ascend (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 with Shimadzu GC-MS QP2010S spectrometer working in electron ionization (EI) mode with Phenomenex Zebron ZB-20HT INFERNO column using following parameters: pressure 65 kPa, total flow 33.9 mL/min, column flow 1.0 mL/min, linear velocity 36.8 cm/s, split 30, temperature program (80 °C hold 0.5 min, 80−340 °C/19 °C/min hold 2 min, 300−340 °C/15 °C/min hold 3.26 min total 20 min). Thin layer chromatography (TLC) was performed with precoated silica gel plates and visualized by UV light or $KMnO_4$ solution or iodide on silica gel. The reaction mixtures were purified by column chromatography over silica gel (60−240 mesh). Melting points were determined in a capillary tube and were uncorrected.

The starting compound dimethylphenylphosphine oxide (**13**),[16] methyldiphenylphosphine oxide[17] and tert-butylmethylphenylphosphine oxide[18] were prepared according to the literature procedures.

4.2. General Procedure A for the synthesis of β-hydroxyalkylphosphine oxides 14-34, 37-42.

In a flame-dried Schlenk tube (50 mL) equipped with magnetic stirrer and inert gas inlet was placed methylphosphine oxide (1.0 mmol) in THF (5 mL). The mixture was cooled to −78 °C (dry ice-acetone) and n-BuLi (1.0 mmol, 1.6 M in hexane) was added. After the orange mixture was stirred for 50 min at −78 °C, aldehyde or ketone (1.5 mmol) was added until no colour remained. Reaction was allowed to warm to room temperature and was stirred for 1 hour. The reaction was quenched by addition of saturated NH_4Cl solution (10 mL) and extracted with DCM (3×20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by flash column chromatography using AcOEt/MeOH (v/v = 9:1) or Hexane/$CHCl_3$/*i*-PrOH (v/v = 10:1:1) as eluent.

4.2.1. (2-Hydroxypropyl)methylphenylphosphine oxide ***(14).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide 13 (0.300 g, 1.9 mmol) and acetaldehyde (0.129 g, 2.9 mmol) as a pale yellow oil; yield 0.335 g (86%). Isolated as a mixture of diastereomers (dr = 53:47).

Major diastereomer: R_f (AcOEt/MeOH 9:1) 0.29; δ_H (500 MHz, $CDCl_3$) 1.20 (3H, dd, *J* 6.1 Hz, *J* 1.7 Hz), 1.77 (3H, d, *J* 13.2 Hz), 1.94−1.99 (1H, m), 2.15−2.20 (1H, m), 3.42 (1H, bs), 4.24−4.35 (1H, m), 7.44−7.56 (3H, m), 7.65−7.74 (2H, m); δ_C (126 MHz, $CDCl_3$) 17.5 (d, *J* 69.9 Hz), 25.1 (d, *J* 9.1 Hz),

40.3 (d, *J* 8.2 Hz), 62.8 (d, *J* 5.4 Hz), 128.7 (d, *J* 11.8 Hz), 129.8 (d, *J* 9.1 Hz), 131.8 (d, *J* 2.7 Hz), 133.1 (d, *J* 96.3 Hz); δ_P (202 MHz, $CDCl_3$) 39.34; GC t_R = 8.05 min; GC−MS (EI, 70 eV) m/z=183 (22), 180 (M−H_2O) (3), 154 (66), 141 (14), 140 (32), 139 (100), 125 (23), 92 (20), 91 (80%).

Minor diastereomer: R_f (AcOEt/MeOH 9:1) 0.29; δ_H (500 MHz, $CDCl_3$) 1.28 (3H, dd, *J* 6.0 Hz, *J* 1.6 Hz), 1.77 (3H, d, *J* 13.2 Hz), 2.01−2.08 (1H, m), 2.11−2.15 (1H, m), 4.13−4.24 (1H, m), 4.73 (1H, bs), 7.45−7.55 (3H, m), 7.66−7.73 (3H, m); δ_C (126 MHz, $CDCl_3$) 16.5 (d, *J* 69.9 Hz), 24.9 (d, *J* 9.1 Hz), 39.9 (d, *J* 69.0 Hz), 63.3 (d, *J* 4.5 Hz), 128.7 (d, *J* 11.8 Hz), 129.6 (d, *J* 10.0 Hz), 131.8 (d, *J* 2.7 Hz), 133.6 (d, *J* 97.2 Hz); δ_C (202 MHz, $CDCl_3$) 38.92; GC t_R = 7.97 min; GC−MS (EI, 70 eV) m/z=183 (23), 180 (M−H_2O) (3), 154 (66), 141 (15), 140 (36), 139 (100), 125 (26), 92 (20), 91 (80%);
v max (ATR) for a mixture of diastereomers: 3296, 3050, 2964, 2897, 1652, 1436, 1294, 1148, 1109,1068, 1024, 936, 894, 809, 740, 693, 506, 486, 422.

4.2.2. (2-Hydroxy-2-phenylethyl)methylphenylphosphine oxide ***(15).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.464 g, 3.0 mmol) and benzaldehyde (0.479 g, 4.52 mmol) as a white solid; yield 0.672 g (86%). Isolated as a mixture of diastereomers (dr = 54.5:45.5).

Major diastereomer: R_f (AcOEt/MeOH 9:1) 0.53; (500 MHz, $CDCl_3$) 1.82 (3H, d, *J* 12.9 Hz), 2.19−2.31 (2H, m), 4.63 (1H, bs), 5.25−5.35 (1H, m), 7.22−7.27 (1H, m), 7.29−7.36 (3H, m), 7.37−7.41 (1H, m), 7.44−7.61 (3H, m), 7.66−7.79 (2H, m); δ_C (126 MHz, $CDCl_3$) 16.4 (d, *J* 70.0 Hz), 41.1 (d, *J* 10.9 Hz), 69.5 (d, *J* 4.5 Hz), 125.5, 127.7, 128.5, 128.7 (d, *J* 11.8 Hz), 129.6 (d, *J* 9.1 Hz), 131.9 (d, *J* 2.7 Hz), 133.6 (d, *J* 98.1 Hz), 143.8 (d, *J* 11.8 Hz); δ_P (202 MHz, $CDCl_3$) 38.42; GC t_R = 12.99 min; GC−MS (EI, 70 eV) m/z=260 (M^+) (1), 242 (M^+−H_2O) (14), 241 (13), 164 (12), 154 (100), 140 (57), 139 (64), 125 (36), 121 (12), 105 (19), 92 (21), 91 (80), 78 (20), 77 (66), 51 (33), 50 (11), 47 (21%).

Minor diastereomer: R_f (AcOEt/MeOH 9:1) 0.53; δ_H (500 MHz, $CDCl_3$) 1.79 (3H, d, *J* 13.2 Hz), 2.42−2.52 (2H, m), 4.63 (1H, bs), 5.06−5.19 (1H, m), 7.22−7.27 (1H, m), 7.29−7.36 (3H, m), 7.37−7.41 (1H, m), 7.44−7.61 (3H, m), 7.66−7.79 (2H, m); δ_H (126 MHz, $CDCl_3$) 17.7 (d, *J* 70.0 Hz), 40.6 (d, *J* 10.9 Hz), 69.0 (d, *J* 4.5 Hz), 125.4, 127.6, 128.5, 128.9 (d, *J* 11.8 Hz), 129.9 (d, *J* 10.0 Hz), 131.9 (d, *J* 2.7 Hz), 133.1 (d, *J* 96.3 Hz), 144.1 (d, *J* 13.6 Hz); δ_P (202 MHz, $CDCl_3$) 39.02; GC t_R = 12.88 min; GC−MS (EI, 70 eV) m/z=260 (M^+) (1), 242 (M^+−H_2O) (7), 241 (11), 165 (11), 154 (100), 140 (55), 139 (54), 125 (34), 121 (10), 92 (21), 91 (81), 78 (16), 77 (47), 51 (22), 47 (21%);
v max (ATR) for a mixture of diastereomers: 3241, 3055, 2903, 2854, 1588, 1487, 1435, 1347, 1294, 1228, 1160, 1114, 1080, 1059, 1025, 986, 882, 877, 825, 739, 694, 513, 481, 443.

*4.2.3. (2-Hydroxy-3-methylbutyl)methylphenylphosphine oxide **(16).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide **(13)** (0.326 g, 2.1 mmol) and isobutyraldehyde (0.228 g, 3.17 mmol); yield of two diastereomers 0.395 g, (83%), (dr = 52.5:47.5).

Major diastereomer: Yield 45% (0.182 g, 38% isolated as a pure compound); white solid; mp 90.3–92.1 °C; [Found C, 63.68; H, 8.50. $C_{12}H_{19}O_2P$ requires C, 63.70; H, 8.46%]; R_f (Hexane/$CHCl_3$/*i*-PrOH 5:1:1) 0.52; *v* max (ATR) 3236, 2948, 2910, 2866, 1436, 1382, 1326, 1286, 1221, 1169, 1114, 1093, 1036, 887, 694, 689, 553, 507, 477, 418; δ_H (500 MHz, $CDCl_3$) 0.86 (3H, d, *J* 6.6 Hz), 0.87 (6H, d, *J* 3.8 Hz), 1.59−1.70 (1H, m), 1.78 (3H, d, *J* 13.6 Hz), 1.88−1.97 (1H, m), 2.00−2.11 (1H, m), 3.75−3.83 (1H, m), 4.52 (1H, bs), 7.43−7.53 (3H, m), 7.66−7.73 (2H, m); δ_C (126 MHz, $CDCl_3$) 17.3, 17.6 (d, *J* 69.9 Hz), 17.8, 34.6 (d, *J* 11.8 Hz), 34.9 (d, *J* 70.8 Hz), 70.8 (d, *J* 5.4 Hz), 128.6 (d, *J* 11.8 Hz), 129.7 (d, *J* 9.1 Hz), 131.6 (d, *J* 2.7 Hz), 133.5 (d, *J* 96.3 Hz); δ_P (202 MHz, $CDCl_3$) 40.27; GC t_R = 9.89 min; GC−MS (EI, 70 eV) *m/z*=208 (M^+-H_2O) (3), 183 (72), 154 (12), 140 (37), 139 (100), 125 (18), 91 (29), 77 (26), 47 (16%).

Minor diastereomer: Yield 37% (0.140 g, 29% isolated as a pure compound); colorless oil; R_f (Hexane/$CHCl_3$/*i*-PrOH 5:1:1) 0.42; [Found C, 63.92; H, 8.71. $C_{12}H_{19}O_2P$ requires C, 63.70; H, 8.46%]; *v* max (ATR) 3308, 2969, 2902, 2859,1437, 1359, 1291, 1237, 1158, 1118, 1071, 1019, 965, 890, 740, 693, 668, 519, 490, 460, 437; δ_H (500 MHz, $CDCl_3$) 0.90 (3H, d, *J* 6.9 Hz), 0.94 (6H, d, *J* 6.9 Hz), 1.69−1.76 (1H, m), 1.78 (3H, d, *J* 12.9 Hz), 1.94−2.12 (2H, m), 3.87−3.96 (1H, m), 4.06 (1H, bs), 7.46−7.56 (3H, m), 7.67−7.75 (2H, m); δ_C (126 MHz, $CDCl_3$) 16.1 (d, *J* 69.9 Hz), 17.5, 17.9, 34.6 (d, *J* 11.8 Hz), 34.9 (d, *J* 69.9 Hz), 71.6 (d, *J* 5.4 Hz), 128.7 (d, *J* 11.8 Hz), 129.6 (d, *J* 10.0 Hz), 131.8 (d, *J* 2.7 Hz), 133.8 (d, *J* 97.2 Hz); δ_P (202 MHz, $CDCl_3$) 40.14; GC t_R = 10.04 min; GC−MS (EI, 70 eV) *m/z*=208 (M^+-H_2O) (4), 183 (75), 154 (12), 140 (32), 139 (100), 125 (14), 91 (28), 77 (23), 47 (14%). Analytical data are in accordance with those reported in the literature.[19]

*4.2.4. (2-Hydroxy-3,3-dimethylbutyl)methylphenylphosphine oxide **(17).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.295 g, 1.92 mmol) and pivalaldehyde (0.247 g, 2.87 mmol); yield of two diastereomers 0.388 g (84%), (dr = 58:42).

Major diastereomer: Yield 53% (0.215 g, 47% isolated as a pure compound); white solid; mp 137–138.1 °C; R_f (Hexane/$CHCl_3$/*i*-PrOH 5:1:1) 0.58; [Found C, 65.01; H, 8.84. $C_{13}H_{21}O_2P$ requires C, 64.98; H, 8.81%]; *v* max (ATR) 3277, 2952, 2867, 1476, 1438, 1361, 1323, 1286, 1229, 1168, 1114, 1069, 1013, 884, 823, 743, 695, 654, 493, 431; δ_H (500 MHz, $CDCl_3$) 0.83 (9H, s), 1.78 (3H, d, *J* 13.2 Hz), 1.95−2.07 (2H, m), 3.58−3.64 (1H, m), 4.30 (1H, bs), 7.46−7.55 (3H, m), 7.68−7.73 (2H, m); δ_C (126 MHz, $CDCl_3$) 17.9 (d, *J* 69.9 Hz), 25.3, 32.9 (d, *J* 70.8 Hz), 35.1 (d *J* 11.8 Hz), 73.9 (d, *J* 5.5 Hz), 128.7 (d, *J* 10.9 Hz), 129.9 (d, *J* 9.1 Hz), 131.7 (d, *J* 2.7 Hz), 133.4 (d, *J* 95.4 Hz); δ_P (202 MHz, $CDCl_3$) 40.67; GC t_R = 9.92 min; GC−MS (EI, 70 eV) m/z=183 (93), 140 (32), 139 (100), 125 (13), 91 (23), 77 (20), 47 (14%).

Minor diastereomer: Yield 32% (0.077 g, 17% isolated as a pure compound); white solid; mp 123.4–124.4 °C; R_f (Hexane/$CHCl_3$/*i*-PrOH 5:1:1) 0.50; [Found C, 64.95; H, 8.77. $C_{13}H_{21}O_2P$ requires C, 64.98; H, 8.81%]; *v* max (ATR) 3244, 2953, 2866, 1477, 1434, 1361, 1297, 1238, 1149, 1139, 1108, 1066, 1013, 906, 873, 827, 740, 691, 554, 493, 427; δ_H (500 MHz, $CDCl_3$) 0.91 (9H, s), 1.79 (3H, d, *J* 12.6 Hz), 1.97−2.03 (2H, m), 3.79−3.85 (1H, m), 4.01 (1H, bs), 7.47−7.56 (3H, m), 7.69−7.75 (2H, m); δ_C (126 MHz, $CDCl_3$) 15.8 (d, *J* 70.8 Hz), 25.34, 33.2 (d, *J* 70.8 Hz), 35.2 (d, *J* 11.8 Hz), 74.5 (d, *J* 5.4 Hz), 128.7 (d, *J* 11.8 Hz), 129.6 (d, *J* 10.0 Hz), 131.8 (d, *J* 2.7 Hz), 133.9 (d, *J* 97.2 Hz); δ_P (202 MHz, $CDCl_3$) 40.42; GC t_R = 10.11 min; GC−MS (EI, 70 eV) m/z=183 (95), 140 (32), 139 (100), 125 (13), 91 (22), 77 (20), 47 (13%).

4.2.5. (2-Hydroxybutyl)methylphenylphosphine oxide ***(18).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.335 g, 2.17 mmol) and propionaldehyde (0.189 g, 3.26 mmol); yield of two diastereomers 0.346 g (75%), (dr = 54:46).

Major diastereomer: Yield 46% (0.187 g, 41% isolated as a pure compound); colorless oil; R_f (AcOEt/MeOH 9:1) 0.32; [Found C, 62.48; H, 8.31. $C_{11}H_{17}O_2P$ requires C, 62.25; H, 8.31%]; δ_H (500 MHz, $CDCl_3$) 0.87 (3H, t, *J* 7.4 Hz), 1.37−1.50 (1H, m), 1.50-1.61 (1H, m), 1.79 (3H, d, *J* 12.3 Hz), 1.92−2.03 (1H, m), 2.05−2.17 (1H, m), 3.86−3.98 (1H, m), 4.54 (1H, bs), 7.42−7.58 (3H, m), 7.64−7.77 (2H, m); δ_C (126 MHz, $CDCl_3$) 9.5, 17.7 (d, *J* 69.0 Hz), 31.6 (d, *J* 13.6 Hz), 37.8 (d, *J* 67.2 Hz), 67.7 (d, *J* 5.4 Hz), 128.7 (d, *J* 10.9 Hz), 129.9 (d, *J* 9.1 Hz), 131.7 (d, *J* 2.7 Hz), 133.4 (d, *J* 96.3 Hz); δ_P (202 MHz, $CDCl_3$) 39.53; GC t_R = 9.70 min; GC−MS (EI, 70 eV) m/z=194 (M^+-H_2O) (4), 183 (58), 154 (23), 140 (36), 139 (100), 125 (18), 92 (10), 91 (45%).

Minor diastereomer: Yield 30% (0.109 g, 24% isolated as a pure compound); white solid; mp 106.4–108.2 °C; R_f (AcOEt/MeOH 9:1) 0.26; [Found C, 62.28; H, 9.01. $C_{11}H_{17}O_2P$ requires C, 62.25; H, 8.31%]; *v* max (ATR) 3307, 2968, 2923, 1437, 1358, 1291, 1237, 1158, 1117, 1071, 1025, 1018, 965, 890, 739, 693, 667, 518, 491, 460, 436; δ_H (500 MHz, $CDCl_3$) 0.90 (3H, t, *J* 7.6 Hz), 1.43−1.65 (2H, m), 1.76 (3H, d, *J* 12.9 Hz), 1.95−2.16 (2H, m), 3.96−4.09 (1H, m), 4.21 (1H, bs), 7.42−7.56 (3H, m), 7.62−7.76 (2H, m); δ_C (126 MHz, $CDCl_3$) 9.6, 16.4 (d, *J* 69.9 Hz), 31.5 (d, *J* 12.7 Hz), 37.8 (d, *J* 69.9 Hz), 68.4 (d, *J* 5.4 Hz), 128.7 (d, *J* 11.8 Hz), 129.6 (d, *J* 10.0 Hz), 131.8 (d, *J* 2.7 Hz), 133.8 (d, *J* 97.2 Hz); δ_P (202 MHz, $CDCl_3$) 39.16; GC t_R = 9.84 min; GC−MS (EI, 70 eV) m/z=194 (M^+-H_2O) (7), 183 (54), 154 (26), 140 (35), 139 (100), 125 (16), 92 (11), 91 (46) 77 (29), 51 (12), 47 (17%).

4.2.6. (2-Cyclohexyl-2-hydroxyethyl)methylphenylphosphine oxide ***(19).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.317 g, 2.1 mmol) and cyclohexanal (0.346 g, 3.09 mmol); yield of two diastereomers 0.530 g (97%), (dr = 53:47).

Major diastereomer: Yield 50% (0.105 g, 19% isolated as a pure compound); white solid; mp 102.8–104.2 °C; R_f (Hexane/$CHCl_3$/*i*-PrOH 5:1:1) 0.62; [Found C, 67.78; H, 8.81. $C_{15}H_{23}O_2P$ requires C,

67.65; H, 8.70%]; *v* max (ATR) 3266, 2912, 2850, 1436, 1286, 1165, 1111, 1061, 989, 882, 742, 689, 580, 487, 430; δ_H (500 MHz, $CDCl_3$) 0.87−1.01 (2H, m), 1.02−1.16 (3H, m), 1.27−1.36 (1H, m), 1.56−1.65 (2H, m), 1.66−1.76 (3H, m), 1.78 (3H, d, *J* 13.2 Hz), 1.94−2.01 (1H, m), 2.05−2.15 (1H, m), 3.72−3.81 (1H, m), 4.35 (1H, bs), 7.43−7.55 (3H, m), 7.66−7.73 (2H, m); δ_C (126 MHz, $CDCl_3$) 17.8 (d, *J* 69.9 Hz), 25.6 (d, *J* 89.0 Hz), 26.2 (d, *J* 39.1 Hz), 28.1 (d, *J* 70.8 Hz), 35.2 (d, *J* 70.8 Hz), 44.6 (d, *J* 11.8 Hz), 70.3 (d, *J* 5.5 Hz), 128.7 (d, *J* 11.8 Hz), 129.8 (d, *J* 9.1 Hz), 131.7 (d, *J* 1.8 Hz), 133.4 (d, *J* 96.3 Hz); δ_P (202 MHz, $CDCl_3$) 40.32; GC t_R = 12.47 min; GC−MS (EI, 70 eV) m/z=248 (M^+-H_2O) (1), 183 (100), 154 (13), 140 (33), 139 (68), 125 (13), 91 (22), 77 (40), 51 (12), 47 (11%).

Minor diastereomer: Yield 47% (0.051 g, 9% isolated as a pure compound); white solid; mp 113.8–115.1 °C; R_f (Hexane/$CHCl_3$/*i*-PrOH 5:1:1) 0.51; [Found C, 67.82; H, 8.79. $C_{15}H_{23}O_2P$ requires C, 67.65; H, 8.70%]; *v* max (ATR) 3233, 2916, 2847, 1434, 1297, 1136, 1102, 989, 908, 823, 744, 691, 502, 424; δ_H (500 MHz, $CDCl_3$) 0.86−1.04 (2H, m), 1.05−1.17 (3H, m), 1.19−1.25 (1H, m), 1.32−1.45 (1H, m), 1.58−1.68 (2H, m), 1.68−1.74 (1H, m), 1.77 (3H, d, *J* 12.9 Hz), 1.80−1.87 (1H, m), 1.95−2.14 (2H, m), 3.87−3.96 (1H, m), 4.05 (1H, bs), 7.43−7.56 (3H, m), 7.65−7.74 (2H, m); δ_C (126 MHz, $CDCl_3$) 16.2 (d, *J* 69.9 Hz), 25.6 (d, *J* 87.2 Hz), 26.2 (d, *J* 41.8 Hz), 28.3 (d, *J* 62.7 Hz), 35.2 (d, *J* 70.8 Hz), 44.5 (d, *J* 11.8 Hz), 71.2 (d, *J* 6.4 Hz), 128.7 (d, *J* 10.9 Hz), 129.6 (d, *J* 10.0 Hz), 131.8 (d, *J* 2.7 Hz), 133.9 (d, *J* 97.2 Hz); δ_P (202 MHz, $CDCl_3$) 40.05; GC t_R = 12.59 min; GC−MS (EI, 70 eV) m/z=248 (M^+-H_2O) (2), 184 (10), 183 (100), 154 (17), 140 (40), 139 (73), 125 (15), 91 (24), 77 (18), 55 (11), 47 (12%).

4.2.7. (2-Hydroxy-2-methylpropyl)methylphenylphosphine oxide ***(20).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.077 g, 0.5 mmol) acetone (0.043 g, 0.75 mmol) as a white solid; yield 0.094 g (89%); mp 92.4–93.1 °C; R_f (AcOEt/MeOH 9:1) 0.34; [Found C, 62.33; H, 8.13. $C_{11}H_{17}O_2P$ requires C, 62.25; H, 8.07%]; *v* max (ATR) 3312, 3063, 2966, 2963, 2920, 2885, 1443, 1376, 1273, 1227, 1158, 1111, 971, 892, 875, 823, 743, 695, 547, 495, 437; δ_H (500 MHz, $CDCl_3$) 1.22 (3H, s), 1.38 (3H, s), 1.76 (3H, d, *J* 12.9 Hz), 2.17−2.35 (2H, m), 4.31 (1H, bs), 7.41−7.59 (3H, m), 7.63−7.78 (2H, m); δ_C (126 MHz, $CDCl_3$) 19.3 (d, *J* 69.9 Hz), 30.9 (d, *J* 6.4 Hz), 31.9 (d, *J* 9.1 Hz), 43.0 (d, *J* 69.0 Hz), 70.6 (d, *J* 5.5 Hz), 128.7 (d, *J* 11.8 Hz), 129.6 (d, *J* 10.0 Hz), 131.7 (d, *J* 2.7 Hz), 134.8 (d, *J* 96.3 Hz); δ_P (202 MHz, $CDCl_3$) 38.10; GC t_R = 9.16 min; GC−MS (EI, 70 eV) m/z=194 (M^+-H_2O) (13), 197 (46), 194 (14), 154 (56), 139 (100), 92 (18), 91 (73), 77 (30), 51 (12), 47 (16%). Analytical data are in accordance with those reported in the literature.[20]

4.2.8. (2-Hydroxy-2-methylhexyl)methylphenylphosphine oxide ***(21)***. This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.201 g, 1.30 mmol) and 2-hexanone (0.196 g, 1.95 mmol) as a white solid; yield 0.251 g (75%). Isolated as a mixture of diastereomers (dr = 56:44).

Major diastereomer: R_f (AcOEt/MeOH 9:1) 0.54; δ_H (500 MHz, $CDCl_3$) 0.71 (3H, t, *J* 7.3 Hz), 0.86−0.99 (1H, m), 1.01−1.13 (1H, m), 1.17 (3H, s), 1.29−1.33 (2H, m), 1.55−1.63 (2H, m), 1.76 (3H, d, *J* 12.9 Hz), 2.12−2.35 (2H, m), 4.56 (1H, bs), 7.47−7.60 (3H, m), 7.68−7.79 (2H, m); δ_C (126 MHz, $CDCl_3$) 14.0, 19.4 (d, *J* 69.9 Hz), 23.0, 26.2, 28.7 (d, *J* 79.0 Hz), 41.3 (d, *J* 69.0 Hz), 44.5 (d, *J* 10.0 Hz), 72.7 (d, *J* 5.4 Hz), 128.8 (d, *J* 11.8 Hz), 129.7 (d, *J* 10.0 Hz), 131.6 (d, *J* 2.7 Hz), 134.9 (d, *J* 95.4 Hz); δ_P (202 MHz, $CDCl_3$) 38.58; GC t_R = 10.66 min; GC−MS (EI, 70 eV) m/z=236 (M^+-H_2O) (6), 197 (80), 157 (12), 154 (38), 140 (49), 139 (100), 125 (13), 92 (11), 91 (48), 77 (29), 47 (17%).

Minor diastereomer: R_f (AcOEt/MeOH 9:1) 0.54; δ_H (500 MHz, $CDCl_3$) 0.87−0.97 (m, 1H), 0.91 (3H, t, *J* 6.9 Hz), 1.18−1.22 (1H, m), 1.29−1.34 (2H, m), 1.34 (3H, d, *J* 1.6 Hz), 1.42−1.56 (2H, m), 1.78 (3H, d, *J* 12.9 Hz), 2.13−2.34 (2H, m), 4.72 (1H, bs), 7.48−7.58 (3H, m), 7.68−7.77 (2H, m); δ_C (126 MHz, $CDCl_3$) 13.9, 19.3 (d, *J* 69.9 Hz), 22.8, 26.6, 28.6 (d, *J* 75.4 Hz), 41.3 (d, *J* 69.0 Hz), 43.3 (d, *J* 6.4 Hz), 72.9 (d, *J* 6.4 Hz), 128.7 (d, *J* 11.8 Hz), 129.7 (d, *J* 10.0 Hz), 131.7 (d, *J* 2.7 Hz), 135.0 (d, *J* 95.4 Hz); δ_P (202 MHz, $CDCl_3$) 38.42; GC t_R = 10.57 min; GC−MS (EI, 70 eV) m/z=236 (M^+-H_2O) (7), 197 (74), 154 (33), 140 (55), 139 (100), 125 (15), 92 (11), 91 (48), 77 (29), 58 (11), 47 (17%);
v max (ATR) for a mixture of diastereomers: 3723, 3623, 3358, 3291, 3058, 2932, 2858, 1440, 1373, 1291, 1237, 1150, 1105, 1028, 941, 879, 822, 738, 693, 538, 499, 434.

4.2.9. (2-Hydroxy-2-methylpentyl)methylphenylphosphine oxide ***(22).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.373 g, 2.42 mmol) and 2-pentanone (0.312 g, 3.63 mmol) as a colorless oil; yield 0.495 g (85%). Isolated as a mixture of diastereomers (dr = 52:48).

Major diastereomer: R_f (AcOEt/MeOH 9:1) 0.50; δ_H (500 MHz, $CDCl_3$) 0.94 (3H, t, *J* 7.3 Hz), 1.19 (3H, s), 1.37−1.45 (2H, m), 1.55−1.62 (2H, m), 1.78 (3H, d, *J* 13.2 Hz), 2.12−2.37 (2H, m), 4.59 (1H, bs), 7.48−7.59 (3H, m), 7.69−7.80 (2H, m); δ_C (126 MHz, $CDCl_3$) 14.4, 17.2, 19.4 (d, *J* 69.9 Hz), 28.6 (d, *J* 71.8 Hz), 41.7 (d, *J* 2.7 Hz), 47.1 (d, *J* 9.1 Hz), 72.7 (d, *J* 6.4 Hz), 128.8 (d, *J* 11.8 Hz), 129.7 (d, *J* 2.7 Hz), 131.7 (d, *J* 5.4 Hz), 135.0 (d, *J* 96.3 Hz); δ_C (202 MHz, $CDCl_3$) 38.63; GC t_R = 10.16 min; GC−MS (EI, 70 eV) m/z=225 (M^+-CH_3) (11), 223 (M^+-H_2O) (2), 197 (84), 157 (14), 154 (37), 140 (40), 139 (100), 125 (10), 92 (12), 91 (55), 77 (29), 47 (16%).

Minor diastereomer: R_f (AcOEt/MeOH 9:1) 0.50; δ_H (500 MHz, $CDCl_3$) 0.66 (3H, t, *J* 7.3 Hz), 0.97−1.06 (1H, m), 1.22−1.27 (1H, m), 1.36 (3H, d, *J* 1.3 Hz), 1.45−1.54 (2H, m), 1.80 (3H, d, *J* 12.9 Hz), 2.13−2.36 (2H, m), 4.59 (1H, bs), 7.49−7.59 (3H, m), 7.70−7.78 (2H, m); δ_C (126 MHz, $CDCl_3$) 14.1, 17.7, 19.3 (d, *J* 69.9 Hz), 28.7 (d, *J* 75.4 Hz), 41.1 (d, *J* 2.7 Hz), 45.8 (d, *J* 6.4 Hz), 72.9 (d, *J* 5.4 Hz), 128.8 (d, *J* 10.9 Hz), 129.6 (d, *J* 2.7 Hz), 131.7 (d, *J* 5.4 Hz), 134.9 (d, *J* 96.3 Hz); δ_P (202 MHz, $CDCl_3$) 38.44; GC t_R = 10.11 min; GC−MS (EI, 70 eV) m/z=225 (M^+-CH_3) (9), 222 (M^+-H_2O) (9), 197 (86), 157 (13), 154 (34), 140 (45), 139 (100), 125 (11), 92 (12), 91 (55), 77 (29), 47 (17%);

v max (ATR) for a mixture of diastereomers: 3329, 2957, 2869, 1436, 1372, 1294, 1151, 1112, 1015, 892, 822, 738, 694, 489, 437;

4.2.10. (2-Hydroxy-2-phenylpropyl)methylphenylphosphine oxide ***(23).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.211 g, 1.37 mmol) and acetophenone (0.247 g, 2.05 mmol) as a white solid; yield 0.345 g (93%). Isolated as a mixture of diastereomers (dr = 66.5:33.5).

Major diastereomer: R_f (AcOEt/MeOH 9:1) 0.68; δ_H (500 MHz, $CDCl_3$) 1.68 (3H, d, *J* 1.9 Hz), 1.78 (3H, d, *J* 12.9 Hz), 2.68 (2H, d, *J* 8.5 Hz), 5.90 (1H, bs), 6.98-7.08 (3H, m), 7.23−7.27 (2H, m), 7.34−7.42 (2H, m), 7.53−7.66 (3H, m); δ_C (126 MHz, $CDCl_3$) 18.7 (d, *J* 70.8 Hz), 33.4 (d, *J* 10.9 Hz), 43.8 (d, *J* 68.1 Hz), 74.0 (d, *J* 5.4 Hz), 124.8, 126.5, 127.6, 128.2 (d, *J* 12.7 Hz), 129.4 (d, *J* 9.1 Hz), 129.6 (d, *J* 10.0 Hz), 131.0 (d, *J* 2.7 Hz), 133.1 (d, *J* 98.1 Hz), 146.0 (d, *J* 4.5 Hz); δ_C (202 MHz, $CDCl_3$) 38.91; GC t_R = 12.20 min; GC−MS (EI, 70 eV) m/z=259 (M^+-CH_3) (49), 241 (M^+-H_2O) (1), 157 (29), 154 (100), 139 (80), 121 (10), 105 (17), 103 (12), 92 (20), 91 (83), 78 (10), 77 (50), 51 (20), 47 (14%).

Minor diastereomer: R_f (AcOEt/MeOH 9:1) 0.74; δ_H (500 MHz, $CDCl_3$) 1.67 (3H, d, *J* 1.9 Hz), 1.81 (3H, d, *J* 12.9 Hz), 2.57 (2H, d, *J* 10.1 Hz), 6.05 (1H, bs), 7.21−7.27 (1H, m), 7.28−7.32 (1H, m), 7.34−7.42 (3H, m), 7.43−7.49 (1H, m), 7.52−7.67 (3H, m), 7.69−7.76 (1H, m); δ_C (126 MHz, $CDCl_3$) 16.9 (d, *J* 68.1 Hz), 32.9 (d, *J* 10.9 Hz), 44.2 (d, *J* 67.2 Hz), 74.1 (d, *J* 6.4 Hz), 125.0, 127.0, 128.4, 128.7 (d, *J* 11.8 Hz), 128.8 (d, *J* 11.8 Hz), 129.3 (d, *J* 9.1 Hz), 131.9 (d, *J* 2.7 Hz), 134.8 (d, *J* 96.3 Hz), 147.3 (d, *J* 4.5 Hz); δ_P (202 MHz, $CDCl_3$) 39.96; GC t_R = 12.48 min; GC−MS (EI, 70 eV) m/z=259 (M^+-CH_3) (50), 241 (M^+-H_2O) (1), 157 (29), 154 (100), 140 (10), 139 (68), 103 (13), 92 (20), 91 (83), 78 (10), 77 (35), 51 (12), 47 (11%);
v max (ATR) for a mixture of diastereomers: 3231, 3054, 3023, 2965, 1591, 1490, 1436, 1369, 1292, 1256, 1142, 1114, 1068, 1024, 919, 893, 824, 737, 685, 501, 425.

4.2.11. (2-Hydroxy-2,3-dimethylbutyl)methylphenylphosphine oxide ***(24).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.204 g, 1.32 mmol) and 3-methyl-2-butanone (0.171 g, 1.99 mmol) as a white sticky solid; yield 0.275 g (87%). Isolated as a mixture of diastereomers (dr = 55.5:45.5).

Major diastereomer: R_f (AcOEt/MeOH 9:1) 0.55; δ_H (500 MHz, $CDCl_3$) 0.91 (6H, d, *J* 6.3 Hz), 1.10 (3H, d, *J* 6.6 Hz), 1.81 (3H, d, *J* 12.9 Hz), 1.83−1.88 (1H, m), 2.06−2.18 (1H, m), 2.23−2.34 (1H, m), 4.61 (1H, bs), 7.46−7.58 (3H, m), 7.68−7.78 (2H, m); δ_C (126 MHz, $CDCl_3$) 16.9, 17.5, 19.5 (d, *J* 70.8 Hz), 25.1 (d, *J* 4.5 Hz), 38.2 (d, *J* 69.9 Hz), 39.6 (d, *J* 10.0 Hz), 75.0 (d, *J* 6.4 Hz), 128.8 (d, *J* 11.8 Hz), 129.6 (d, *J* 11.8 Hz), 131.6 (d, *J* 2.7 Hz), 135.1 (d, *J* 95.4 Hz); δ_P (202 MHz, $CDCl_3$) 39.40; GC t_R

= 10.06 min; GC−MS (EI, 70 eV) m/z=225 (M^+−CH_3) (7), 198 (11), 197 (98), 157 (15), 154 (20), 140 (24), 139 (100), 91 (38), 77 (25), 47 (15%).

Minor diastereomer: R_f (AcOEt/MeOH 9:1) 0.55; δ_H (500 MHz, $CDCl_3$) 0.66 (3H, d, *J* 6.6 Hz), 0.94 (3H, d, *J* 6.6 Hz), 1.33 (3H, s), 1.76 (3H, d, *J* 12.9 Hz), 1.80−1.82 (1H, m), 2.06−2.18 (1H, m), 2.22−2.33 (1H, m), 4.55 (1H, bs), 7.46−7.60 (3H, m), 7.68−7.78 (2H, m); δ_C (126 MHz, $CDCl_3$) 16.8, 17.7, 19.3 (d, *J* 69.0 Hz), 24.6 (d, *J* 7.3 Hz), 38.5 (d, *J* 8.2 Hz), 38.8 (d, *J* 70.8 Hz), 75.3 (d, *J* 6.4 Hz), 128.7 (d, *J* 11.8 Hz), 129.7 (d, *J* 12.7 Hz), 131.7 (d, *J* 2.7 Hz), 135.1 (d, *J* 96.3 Hz); δ_P (202 MHz, $CDCl_3$) 39.03; GC t_R = 10.09 min; GC−MS (EI, 70 eV) m/z=225 (M^+−CH_3) (5), 198 (10), 197 (97), 157 (14), 154 (20), 140 (28), 139 (100), 125 (11), 91 (40), 77 (26), 47 (16%);
v max (ATR) for a mixture of diastereomers: 3344, 3051, 2959, 2874, 1466, 1437, 1409, 1383, 1294, 1155, 1110, 1011, 923,894, 817, 737, 693, 576, 530, 493, 436.

4.2.12. (2-Hydroxy-2-methylbutyl)methylphenylphosphine oxide ***(25).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.223 g, 1.45 mmol) and 2-butanone (0.157 g, 2.17 mmol) as a colorless oil; yield 0.253 g (77%). Isolated as a mixture of diastereomers (dr = 53.5:46.5).

Major diastereomer: R_f (AcOEt/MeOH 9:1) 0.42; δ_H (500 MHz, $CDCl_3$) 0.86 (3H, t, *J* 7.6 Hz), 1.14 (3H, s), 1.42−1.51 (1H, m), 1.51−1.58 (1H, m), 1.73 (3H, d, *J* 12.9 Hz), 2.06−2.14 (1H, m), 2.15-2.27 (1H, m), 5.25 (1H, bs), 7.40−7.51 (3H, m), 7.62−7.73 (2H, m); δ_C (126 MHz, $CDCl_3$) 8.1, 18.9 (d, *J* 69.9 Hz), 27.4 (d, *J* 4.5 Hz), 37.1 (d, *J* 9.1 Hz), 41.0 (d, *J* 69.9 Hz), 72.6 (d, *J* 6.4 Hz), 128.6 (d, *J* 11.8 Hz), 129.5 (d, *J* 10.0 Hz), 131.5 (d, *J* 2.7 Hz), 134.5 (d, *J* 96.3 Hz); δ_P (202 MHz, $CDCl_3$) 39.35; GC t_R = 9.74 min; GC−MS (EI, 70 eV) m/z=208 (M^+−H_2O) (11), 197 (67), 157 (13), 154 (32), 140 (34), 139 (100), 92 (13), 91 (55), 77 (28), 47 (16%).

Minor diastereomer: R_f (AcOEt/MeOH 9:1) 0.42; δ_H (500 MHz, $CDCl_3$) 0.68 (3H, t, *J* 7.4 Hz), 1.27 (3H, s), 1.52−1.59 (2H, m), 1.74 (3H, d, *J* 12.9 Hz), 2.15−2.26 (2H, m), 5.17 (1H, bs), 7.39−7.52 (3H, m), 7.62−7.72 (2H, m); δ_C (126 MHz, $CDCl_3$) 8.2, 18.6 (d, *J* 7.3 Hz), 28.1 (d, *J* 8.2 Hz), 35.9 (d, *J* 6.4 Hz), 41.2 (d, *J* 69.0 Hz), 72.9 (d, *J* 5.4 Hz), 128.6 (d, *J* 11.8 Hz), 129.4 (d, *J* 10.0 Hz), 131.6 (d, *J* 2.7 Hz), 134.6 (d, *J* 96.3 Hz); δ_P (202 MHz, $CDCl_3$) 39.08; GC t_R = 9.74 min; GC−MS (EI, 70 eV) m/z=208 (M^+−H_2O) (11), 197 (67), 157 (13), 154 (32), 140 (34), 139 (100), 92 (13), 91 (55), 77 (28), 47 (16%);
v max (ATR) for a mixture of diastereomers: 3324, 3053, 2966, 2927, 2879, 1442, 1436, 1408, 1372, 1294, 1151, 1112, 995, 904, 892, 823, 737, 694, 536, 492, 436.

4.2.13. (2-Hydroxy-2,3,3-trimethylbutyl)methylphenylphosphine oxide ***(26).*** This was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.354 g, 2.29 mmol)

and 3,3-dimethyl-2-butanone (0.345 g, 3.35 mmol) as a white solid; yield 0.469 g (80%). Isolated as a mixture of diastereomers (dr = 60:40).

Major diastereomer: R_f (AcOEt/MeOH 9:1) 0.62; δ_H (500 MHz, $CDCl_3$) 0.95 (9H, s), 1.17 (3H, d, *J* 0.9 Hz), 1.75 (3H, d, *J* 12.9 Hz), 1.99−2.14 (1H, m), 2.37−2.47 (1H, m), 4.27 (1H, bs), 7.46−7.57 (3H m), 7.66−7.79 (2H, m); δ_C (126 MHz, $CDCl_3$) 19.3, 24.0 (d, *J* 3.6 Hz), 24.9, 36.8 (d, *J* 70.8 Hz), 38.6 (d, *J* 10.0 Hz), 76.5 (d, *J* 6.4 Hz), 128.8 (d, *J* 10.9 Hz), 129.7 (d, *J* 10.0 Hz), 131.5 (d, *J* 2.7 Hz), 135.2 (d, *J* 94.5 Hz); δ_P (202 MHz, $CDCl_3$) 39.77; GC t_R = 10.27 min; GC−MS (EI, 70 eV) m/z= 198 (11), 197 (100), 157 (14), 154 (12), 140 (11), 139 (87), 91 (24), 77 (19), 47 (11%).

Minor diastereomer: R_f (AcOEt/MeOH 9:1) 0.62; δ_H (500 MHz, $CDCl_3$) 0.93 (9H, s), 1.55 (3H, d, *J* 0.6 Hz), 1.85 (3H, d, *J* 12.9 Hz), 1.97−2.14 (1H, m), 2.36−2.49 (1H, m), 4.25 (1H, bs), 7.46−7.58 (3H, m), 7.65−7.80 (2H, m); δ_C (126 MHz, $CDCl_3$) 19.8, 24.4 (d, *J* 2.7 Hz), 24.9, 37.4 (d, *J* 69.9 Hz), 38.7 (d, *J* 9.1 Hz), 76.4 (d, *J* 6.4 Hz), 128.7 (d, *J* 11.8 Hz), 129.4 (d, *J* 9.1 Hz), 131.6 (d, *J* 2.7 Hz), 135.6 (d, *J* 98.1 Hz); δ_P (202 MHz, $CDCl_3$) 39.62; GC t_R = 10.37 min; GC−MS (EI, 70 eV) m/z=198 (11), 197 (100), 157 (12), 154 (11), 140 (13), 139 (84), 91 (24), 77 (19), 47 (11%);
v max (ATR) for a mixture of diastereomers: 3421, 3271, 2957, 2909, 2871, 1477, 1438, 1370, 1298, 1142, 1112, 1001, 895, 831, 743, 697, 493, 447.

4.2.14. (2-Hydroxy-2,4,4-trimethylpentyl)methylphenylphosphine oxide ***(27).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.226 g, 1.47 mmol) and 4,4-dimethyl-2-pentanone (0.251 g, 2.20 mmol) as a white solid; yield 0.325 g (83%). Isolated as a mixture of diastereomers (dr = 91:9).

Major diastereomer: R_f (AcOEt/MeOH 9:1) 0.73; δ_H (500 MHz, $CDCl_3$) 0.92 (9H, s), 1.24−1.35 (2H, m), 1.49 (3H, d, *J* 1.6 Hz), 1.77 (3H, d, *J* 12.9 Hz), 2.17−2.24 (1H, m), 2.26−2.35 (1H, m), 4.54 (1H, bs), 7.46−7.57 (3H, m), 7.66−7.76 (2H, m); δ_C (126 MHz, $CDCl_3$) 19.4 (d, *J* 69.0 Hz), 30.6 (d, *J* 8.2 Hz), 31.3, 31.4, 44.8 (d, *J* 68.1 Hz), 55.2 (d, *J* 7.3 Hz), 74.3 (d, *J* 6.4 Hz), 128.7 (d, *J* 11.8 Hz), 129.6 (d, *J* 10.0 Hz), 131.6 (d, *J* 2.7 Hz), 135.2 (d, *J* 96.3 Hz); δ_P (202 MHz, $CDCl_3$) 38.17; GC t_R = 10.57 min; GC−MS (EI, 70 eV) m/z=253 (M^+−CH_3) (6), 198 (11), 197 (100), 154 (39), 140 (12), 139 (90), 92 (11), 91 (43), 77 (22), 57 (14), 47 (12%).

Minor diastereomer: R_f (AcOEt/MeOH 9:1) 0.73; δ_H (500 MHz, $CDCl_3$) 1.03 (9H, s), 1.25 (3H, s), 1.32−1.33 (2H, m), 1.75 (3H, d, *J* 12.8 Hz), 2.17−2.22 (1H, m), 2.36−2.44 (1H, m), 4.47 (1H, bs), 7.47−7.57 (3H, m), 7.67−7.76 (2H, m); δ_C (126 MHz, $CDCl_3$) 19.7 (d, *J* 69.9 Hz), 30.0 (d, *J* 5.4 Hz), 31.4, 31.6, 43.9 (d, *J* 68.1 Hz), 56.6 (d, *J* 10.0 Hz), 74.2 (d, *J* 6.4 Hz), 128.8 (d, *J* 11.8 Hz), 129.6 (d, *J* 9.3 Hz), 131.6 (d, *J* 2.7 Hz), 136.6 (d, *J* 95.4 Hz); δ_P (202 MHz, $CDCl_3$) 38.17; GC t_R = 10.37 min; GC−MS (EI, 70 eV) m/z=253 (M^+−CH_3) (8), 198 (11), 197 (95), 193 (11), 157 (10), 154 (45), 140 (13), 139 (100), 92 (11), 91 (48), 77 (27), 57 (21), 47 (14%);

v max (ATR) for a mixture of diastereomers: 3296, 2953, 2904, 2866, 1448, 1435, 1375, 1361, 1296, 1239, 1154, 1098, 918, 899, 894, 857, 795, 741, 733, 691, 597, 512, 441.

4.2.15. (2-Hydroxy-2,2-diphenylethyl)methylphenylphosphine oxide ***(28).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.105 g, 0.68 mmol) and benzophenone (0.185 g, 1.0 mmol) as a white solid; yield 0.191 g (84%); mp 144.8–146.2 °C; R_f (AcOEt/MeOH 9:1) 0.77; [Found C, 75.15; H, 6.46. $C_{21}H_{21}O_2P$ requires C, 74.99; H, 6.29%]; *v* max (ATR) 3207, 3054, 2914, 1591, 1440, 1438, 1296, 1223, 1146, 1112, 982, 930, 874, 826, 741, 689, 599, 531, 485, 464; δ_H (500 MHz, $CDCl_3$) 1.36 (3H, d, *J* 12.9 Hz), 1.65 (1H, bs), 2.90−3.09 (2H, m), 7.02−7.15 (3H, mH), 7.21−7.27 (1H, m), 7.29−7.37 (4H, m), 7.36−7.42 (2H, m), 7.44−7.52 (3H, m), 7.52−7.58 (2H, m); δ_C (126 MHz, $CDCl_3$) 17.5 (d, *J* 69.0 Hz), 42.4 (d, *J* 68.1 Hz), 125.7, 125.9, 126.9, 127.1, 127.9, 128.3, 128.6 (d, *J* 11.8 Hz), 129.4 (d, *J* 9.1 Hz), 131.6 (d, *J* 2.7 Hz), 134.0 (d, *J* 99.0 Hz), 146.0 (d, *J* 8.2 Hz), 146.7 (d, *J* 6.4 Hz); δ_P (202 MHz, $CDCl_3$) 40.40; GC t_R = 19.71 min; GC−MS (EI, 70 eV) m/z=182 (33), 154 (34), 139 (50), 105 (100%).

4.2.16. (2-Butyl-2-hydroxyhexyl)methylphenylphosphine oxide ***(29).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.366 g, 2.4 mmol)) and 5-nonanone (0.506g, 3.56 mmol) as a white solid; yield 0.557 g (82%); mp 106.3–108 °C; R_f (AcOEt/MeOH 9:1) 0.73; [Found C, 68.94; H, 9.93. $C_{17}H_{29}O_2P$ requires C, 68.89; H, 9.86%]; *v* max (ATR) 3311, 3061, 2951, 2917, 2867, 1462, 1436, 1375, 1290, 1267, 1143, 1107, 996, 897, 879, 831, 744, 694, 606, 495, 488, 432, 428; δ_H (500 MHz, $CDCl_3$) 0.62 (3H, t, *J* 7.9 Hz), 0.70−0.83 (2H, m), 0.86 (3H, t, *J* 6.9 Hz), 0.91−1.01 (1H, m), 1.03−1.14 (1H, m), 1.19−1.31 (4H, m), 1.31−1.42 (1H, m), 1.43−1.55 (3H, m), 1.70 (3H, d, *J* 12.9 Hz), 2.09−2.25 (2H, m), 4.66 (1H, s), 7.41−7.52 (3H, m), 7.65−7.73 (2H, m); δ_C (126 MHz, $CDCl_3$) 13.8, 14.0, 19.4 (d, *J* 69.0 Hz), 22.7, 23.1, 25.5, 26.3, 39.5 (d, *J* 68.1 Hz), 40.1 (d, *J* 5.4 Hz), 40.7 (d, *J* 9.1 Hz), 74.8 (d, *J* 5.4 Hz), 128.7 (d, *J* 10.9 Hz), 129.7 (d, *J* 9.1 Hz), 131.6 (d, *J* 2.7 Hz), 135.0 (d, *J* 95.4 Hz); δ_P (202 MHz, CDCl3) 38.70; GC t_R = 11.58 min; GC−MS (EI, 70 eV) m/z=278 (M^+-H_2O) (5), 240 (14), 239 (100), 157 (21), 154 (32), 140 (41), 139 (68), 125 (11), 91 (35), 77 (21), 57 (15), 55 (10), 47 (11%).

4.2.17. (2-Hydroxy-2-i-propyl-3-methylbutyl)methylphenylphosphine oxide ***(30)***. This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.198 g, 1.3 mmol)) and 2,4-dimethyl-3-pentanone (0.220g, 1.93 mmol) as a colorless oil; yield 0.204 g (60%); R_f (AcOEt/MeOH 9:1) 0.71; [Found C, 67.28; H, 9.57. $C_{15}H_{25}O_2P$ requires C, 67.14; H, 9.39%]; *v* max (ATR) 3361, 2960, 2914, 2876, 1467, 1436, 1411, 1384, 1292, 1145, 1110, 990, 894, 741, 694, 530, 488, 434; δ_H (500 MHz, $CDCl_3$) 0.72 (3H, d, *J* 6.9 Hz), 0.88 (3H, d, *J* 6.9 Hz), 0.92 (3H, d, *J* 6.9 Hz), 1.01 (3H, d, *J* 6.6 Hz), 1.81 (3H, d, *J* 12.9 Hz), 1.82−1.87 (1H, m), 1.90−1.98 (1H, m), 2.03−2.20 (2H, m), 4.32 (1H, bs), 7.43−7.54 (3H, m), 7.64−7.75 (2H, m); δ_C (126 MHz, $CDCl_3$) 17.1, 17.3, 17.4, 17.5, 18.8 (d, *J* 70.8 Hz), 34.1 (d, *J* 69.0 Hz), 35.4 (d, *J* 4.5 Hz), 36.3 (d, *J* 2.7 Hz), 78.7 (d, *J* 6.4 Hz), 128.6

(d, *J* 10.9 Hz), 129.7 (d, *J* 9.1 Hz), 131.5 (d, *J* 2.7 Hz), 135.2 (d, *J* 96.3 Hz); δ_P (202 MHz, $CDCl_3$) 39.03; GC t_R = 10.79 min; GC−MS (EI, 70 eV) m/z=250 (M^+-H_2O) (2), 226 (14), 225 (100), 157 (28), 154 (22), 140 (30), 139 (78), 125 (12), 91 (36), 77 (24), 71 (12), 69 (14), 47 (16%).

4.2.18. (2-Ethyl-2-hydroxybutyl)methylphenylphosphine oxide ***(31).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.205 g, 1.3 mmol)) and pentan-3-one (0.172g, 1.99 mmol) as a colorless oil; yield 0.240 g (75%); R_f (AcOEt/MeOH 9:1) 0.56; [Found C, 65.15; H, 9.08. $C_{13}H_{21}O_2P$ requires C, 64.98; H, 8.81%]; *v* max (ATR) 3302, 2967, 2960, 2934, 2873, 1440, 1296, 1254, 1210, 1152, 1111, 1023, 978, 961, 899, 890, 825, 745, 693, 582, 500, 430; δ_H (500 MHz, $CDCl_3$) 0.66 (3H, t, *J* 7.6 Hz), 0.88 (3H, t, *J* 7.6 Hz), 1.39−1.52 (1H, m), 1.53−1.70 (3H, m), 1.78 (3H, d, *J* 12.9 Hz), 2.12−2.27 (2H, m), 4.40 (1H, bs), 7.46−7.56 (3H, m), 7.67−7.75 (2H, m); δ_C (126 MHz, $CDCl_3$) 7.8, 7.9, 19.3 (d, *J* 69.9 Hz), 32.1 (d, *J* 5.4 Hz), 32.6 (d, *J* 9.1 Hz), 38.9 (d, *J* 69.0 Hz), 75.2 (d, *J* 5.5 Hz), 128.7 (d, *J* 11.8 Hz), 129.5 (d, *J* 10.0 Hz), 131.6 (d, *J* 2.7 Hz), 135.0 (d, *J* 96.3 Hz); δ_P (202 MHz, $CDCl_3$) 38.95; GC t_R = 10.20 min; GC−MS (EI, 70 eV) m/z=222 (M^+-H_2O) (12), 212 (10), 211 (89), 157 (25), 154 (35), 140 (48), 139 (100), 125 (15), 92 (13), 91 (57), 77 (33), 57 (16), 55 (13), 51 (11), 47 (21%).

4.2.19. [(1-Hydroxy)cyclopentylmethyl)]methylphenylphosphine oxide ***(32).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.118 g, 0.7 mmol)) and pentanone (0.097g, 1.15 mmol) as a white solid; yield 0.129 g (71%); mp 80.7–81.4 °C; R_f (AcOEt/MeOH 9:1) 0.43; [Found C, 65.59; H, 8.14. $C_{13}H_{21}O_2P$ requires C, 65.53; H, 8.04%]; *v* max (ATR) 3301, 3057, 2957, 2885, 2841, 1424, 1402, 1378, 1299, 1296, 1262, 1224, 1162, 1144, 1110, 1002, 892, 873, 829, 746, 697, 499, 447; δ_H (500 MHz, $CDCl_3$) 1.16−1.30 (1H, m), 1.42−1.60 (3H, m), 1.67−1.77 (2H, m), 1.74 (3H, d, *J* 12.9 Hz), 1.78−1.85 (1H, m), 1.87−1.96 (1H, m), 2.20−2.30 (1H, m), 2.37−2.47 (1H, m), 4.29 (1H, bs), 7.41−7.54 (3H, m), 7.64−7.76 (2H, m); δ_C (126 MHz, $CDCl_3$) 19.0 (d, *J* 69.0 Hz), 23.1, 23.5, 40.7 (d, *J* 6.4 Hz), 41.2 (d, *J* 69.0 Hz), 41.8 (d, *J* 8.2 Hz), 80.4 (d, *J* 6.4 Hz), 128.7 (d, *J* 11.8 Hz), 129.7 (d, *J* 9.1 Hz), 131.7 (d, *J* 2.7 Hz), 134.6 (d, *J* 96.3 Hz); δ_P (202 MHz, $CDCl_3$) 38.53; GC t_R = 9.30 min; GC−MS (EI, 70 eV) m/z=238 (M^+) (1), 220 (M^+-H_2O) (17), 219 (12), 209 (36), 196 (50), 181 (36), 157 (11), 154 (60), 140 (56), 139 (100), 125 (29), 99 (10), 92 (19), 91 (86%).

4.2.20. [(1-Hydroxy)cyclohexylmethyl)]methylphenylphosphine oxide ***(33).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.101 g, 0.65 mmol) and hexanone (0.097g, 0.98 mmol) as a white solid; yield 0.126 g (76%); mp 108.8–110.4 °C; R_f (AcOEt/MeOH 9:1) 0.55; [Found C, 66.48; H, 8.23. $C_{14}H_{21}O_2P$ requires C, 66.65; H, 8.39%]; *v* max (ATR) 3306, 2929, 2888, 2844, 1438, 1261, 1175, 1153, 1109, 981, 892, 819, 747, 695, 511, 487, 446; δ_H (500 MHz, $CDCl_3$) 1.10−1.25 (2H, m), 1.26−1.35 (1H, m), 1.35−1.47 (2H, m), 1.48−1.58 (2H, m), 1.60−1.71 (2H, m), 1.75 (3H, d, *J* 12.9 Hz), 1.76−1.80 (1H, m), 2.14−2.28 (2H, m), 4.53 (1H, bs),

7.43−7.55 (3H, m), 7.65−7.74 (2H, m); δ_C (126 MHz, $CDCl_3$) 19.5 (d, *J* 69.9 Hz), 22.0, 22.2, 25.4, 39.0 (d, *J* 6.4 Hz), 40.1 (d, *J* 10.0 Hz), 41.8 (d, *J* 70.8 Hz), 71.9 (d, *J* 6.4 Hz), 128.7 (d, *J* 11.8 Hz), 129.6 (d, *J* 10.0 Hz), 131.6 (d, *J* 2.7 Hz), 135.1 (d, *J* 95.4 Hz); δ_P (202 MHz, $CDCl_3$) 38.65; GC t_R = 11.64 min; GC−MS (EI, 70 eV) m/z=252 (M^+) (3), 234 (M^+-H_2O) (26), 233 (11), 210 (16), 209 (68), 196 (30), 181 (17), 157 (15), 154 (70), 141 (18), 140 (75), 139 (100), 125 (30), 121 (10), 95 (10), 92 (22), 91 (97), 77 (41), 65 (10), 55 (19), 51 (14), 47 (30%).

4.2.21. [(1-Hydroxy)cycloheptylmethyl)]methylphenylphosphine oxide ***(34).*** This compound was prepared according to General Procedure A from dimethylphenylphosphine oxide (**13**) (0.204 g, 1.33 mmol) and heptanone (0.233g, 1.99 mmol) as a white solid; yield 0.319 g (90%); mp 80.6–82.6 °C; R_f (AcOEt/MeOH 9:1) 0.50; [Found C, 67.49; H, 8.61. $C_{15}H_{23}O_2P$ requires C, 67.65; H, 8.70%]; *v* max (ATR) 3350, 2923, 2858, 1436, 1290, 1246, 1155, 1146, 1103, 1033, 901, 879, 801, 745, 736, 690, 571, 494, 445; δ_H (500 MHz, $CDCl_3$) 1.04−1.17 (1H, m), 1.24−1.37 (2H, m), 1.38−1.46 (2H, m), 1.46−1.56 (3H, m), 1.59−1.63 (2H, m), 1.72 (3H, d, *J* 12.9 Hz), 1.75−1.82 (1H, m), 1.87−1.95 (1H, m), 2.16−2.28 (2H, m), 4.54 (1H, bs), 7.41−7.53 (3H, m), 7.64−7.71 (2H, m); δ_C (126 MHz, $CDCl_3$) 19.3 (d, *J* 69.9 Hz), 21.8, 21.8, 24.2, 29.4 (d, *J* 16.3 Hz), 42.2 (d, *J* 6.4 Hz), 42.9 (d, *J* 69.0 Hz), 43.7 (d, *J* 9.1 Hz), 75.8 (d, *J* 6.4 Hz), 128.6 (d, *J* 10.9 Hz), 129.5 (d, *J* 10.0 Hz), 131.5 (d, *J* 3.6 Hz), 135.0 (d, *J* 95.4 Hz); δ_P (202 MHz, $CDCl_3$) 38.54; GC t_R = 12.38 min; GC−MS (EI, 70 eV) m/z=266 (M^+) (2), 248 (M^+-H_2O) (17), 209 (50), 196 (32), 181 (23), 157 (15), 155 (11), 154 (92), 141 (20), 140 (100), 139 (98), 125 (35), 109 (12), 95 (10), 92 (22), 91 (96), 79 (11), 77 (43), 68 (14), 67 (14), 55 (24), 51 (14), 47 (31%).

4.2.22. (2-Hydroxy-2-methylpropyl)diphenylphosphine oxide ***(37).*** This compound was prepared according to General Procedure A from diphenylmethylphosphine oxide (0.302 g, 1.4 mmol) and acetone (0.122 g, 2.1 mmol) as a white solid; yield 0.278 g (73%); mp 103.8–105.7 °C; R_f (AcOEt/MeOH 9:1) 0.64; [Found C, 69.96; H, 6.85. $C_{16}H_{19}O_2P$ requires C, 70.06; H, 6.98%]; *v* max (ATR) 3321, 3055, 2977, 2924, 2878, 1477, 1435, 1376, 1232, 1163, 1098, 972, 902, 804, 748, 711, 667, 567, 511, 487; δ_H (500 MHz, $CDCl_3$) 1.28 (6H, s), 2.60 (2H, d, *J* 9.5 Hz), 4.41 (1H, bs), 7.45−7.54 (6H, m), 7.72−7.78 (4H, m); δ_C (126 MHz, $CDCl_3$) 31.5, 31.6, 41.2 (d, *J* 69.9 Hz), 70.8 (d, *J* 6.4 Hz), 128.7 (d, *J* 11.8 Hz), 130.4 (d, *J* 9.1 Hz), 131.8 (d, *J* 2.7 Hz), 133.9 (d, *J* 99.0 Hz); δ_C (202 MHz, $CDCl_3$) 32.45; GC t_R = 12.18 min; GC−MS (EI, 70 eV) m/z=256 (M^+-H_2O) (21), 255 (31), 216 (27), 215 (87), 202 (14), 201 (100), 152 (12), 131 (14), 125 (17), 91 (24), 78 (13), 77 (71), 51 (41), 47 (45%). Analytical data are in accordance with those reported in the literature.[21]

4.2.23. (2-Hydroxy-2-methylpropyl)-t-butylphenylphosphine oxide ***(38).*** This compound was prepared according to General Procedure A from tert-butylmethylphenylphosphine oxide (0.142 g, 0.7 mmol) and acetone (0.063 g, 1.1 mmol) as a white solid; yield 0.116 g (63%); mp 114.8–115.9 °C; R_f (AcOEt/MeOH 9:1) 0.60; [Found C, 66.01; H, 9.08. $C_{14}H_{23}O_2P$ requires C, 66.12; H, 9.12%]; *v* max

(ATR) 3258, 3063, 2970, 2903, 2868, 1461, 1435, 1364, 1246, 1208, 1147, 1104, 903, 813, 745, 695, 627, 527, 491, 461; δ_H (500 MHz, $CDCl_3$) 1.06 (3H, s), 1.10 (9H, d, *J* 14.8 Hz), 1.33 (3H, d, *J* 2.5 Hz), 2.15−2.21 (1H, m), 2.35−2.44 (1H, m), 4.48 (1H, bs), 7.45−7.58 (3H, m), 7.68−7.82 (2H, m); δ_C (126 MHz, $CDCl_3$) 23.7, 30.1 (d, *J* 3.6 Hz), 32.91 (d, *J* 69.0 Hz), 32.92 (d, *J* 11.8 Hz), 34.1 (d, *J* 62.7 Hz), 70.4 (d, *J* 5.4 Hz), 128.3 (d, *J* 10.9 Hz), 131.3 (d, *J* 86.3 Hz), 131.4 (d, *J* 7.3 Hz), 131.6 (d, *J* 2.7 Hz); δ_P (202 MHz, $CDCl_3$) 50.17; GC t_R = 9.63 min; GC−MS (EI, 70 eV) m/z=236 (M^+-H_2O) (3), 239 (16), 197 (25), 180 (16), 179 (10), 142 (27), 141 (33), 140 (46), 125 (100), 91 (15), 78 (13), 78 (16), 77 (26), 57 (67) 47 (49%).

4.2.24. (2-Hydroxy-3-methylbutyl)diphenylphosphine oxide ***(39).*** This compound was prepared according to General Procedure A from diphenylmethylphosphine oxide (0.282 g, 1.3 mmol) and isobutyraldehyde (0.141 g, 2.0 mmol) as a colorless oil; yield 0.295 g (78%); R_f (AcOEt/MeOH 9:1) 0.72; [Found C, 70.98; H, 7.52. $C_{17}H_{21}O_2P$ requires C, 70.82; H, 7.34%]; *v* max (ATR) 3333, 3053, 2957, 2870, 1436, 1154, 1118, 994, 742, 699, 692, 539; δ_H (500 MHz, $CDCl_3$) 0.90 (3H, d, *J* 2.2 Hz), 0.91 (3H, d, *J* 2.2 Hz), 1.72−1.81 (1H, m), 2.32−2.44 (2H, m), 3.78−3.89 (1H, m), 4.43 (1H, bs), 7.42−7.55 (6H, m), 7.69−7.80 (4H, m); δ_C (126 MHz, $CDCl_3$) 17.5, 17.8, 32.9 (d, *J* 72.7 Hz), 34.4 (d, *J* 12.7 Hz), 71.3 (d, *J* 5.4 Hz), 128.7 (d, *J* 6.4 Hz), 128.8 (d, *J* 6.4 Hz), 130.4 (d, *J* 10.0 Hz), 130.9 (d, *J* 10.0 Hz), 131.7 (d, *J* 98.1 Hz), 131.98 (d, *J* 2.7 Hz), 132.0 (d, *J* 2.7 Hz), 133.5 (d, *J* 99.9 Hz); δ_P (202 MHz, $CDCl_3$) 35.29; GC t_R = 11.12 min; GC−MS (EI, 70 eV) m/z=270 (M^+-H_2O) (5), 246 (13), 245 (86), 215 (26), 202 (44), 201 (100), 77 (41); 51 (16), 47 (27%). Analytical data are in accordance with those reported in the literature.[22]

4.2.25. (2-Hydroxy-3-methylbutyl)-t-butylphenylphosphine oxide ***(40).*** This compound was prepared according to General Procedure A from tert-butylmethylphenylphosphine oxide (0.142 g, 0.7 mmol) and isobutyraldehyde (0.078 g, 1.1 mmol) as a white solid; yield 0.126 g (65%). Isolated as a mixture of diastereomers (dr = 52:48).

Major diastereomer: R_f (AcOEt/MeOH 9:1) 0.65; *v* max (ATR) 3284, 2955, 2871, 1477, 1434, 1364, 1138, 1105, 997, 844, 816, 779, 695, 632, 599, 476; δ_H (500 MHz, $CDCl_3$) 0.88 (3H, d, *J* 6.6 Hz), 0.92 (3H, d, *J* 6.6 Hz), 1.10 (9H, d, *J* 14.8 Hz), 1.62−1.77 (1H, m), 2.06−2.14 (2H, m), 3.47−3.59 (1H, m), 4.82 (1H, bs), 7.37−7.55 (3H, m), 7.59−7.72 (2H, m); δ_C (126 MHz, $CDCl_3$) 17.60, 17.62, 23.8, 25.5 (d, *J* 64.5 Hz), 32.6 (d, *J* 68.1 Hz), 34.3 (d, *J* 11.8 Hz), 71.3 (d, *J* 5.5 Hz), 128.0 (d, *J* 10.9 Hz), 129.0 (d, *J* 86.3 Hz), 131.68 (d, *J* 8.2 Hz), 131.70 (d, *J* 2.7 Hz); δ_P (202 MHz, $CDCl_3$) 54.46; GC t_R = 10.26 min; GC−MS (EI, 70 eV) m/z=250 (M^+-H_2O) (2), 225 (74), 211 (25), 193 (13), 142 (20), 141 (29); 140 (32), 126 (24) 125 (100) 91 (12%).

Minor diastereomer: R_f (AcOEt/MeOH 9:1) 0.65; *v* max (ATR) 3276, 2955, 2869, 1463, 1436, 1364, 1139, 1106, 998, 844, 817, 778, 696, 633, 508, 473; δ_H (500 MHz, $CDCl_3$) 0.86 (6H, d, *J* 6.6 Hz), 1.09

(9H, d, *J* 15.1 Hz), 1.64−1.77 (1H, m), 2.09−2.13 (1H, m), 2.30−2.37 (1H, m), 3.92−4.04 (1H, m), 4.31 (1H, bs), 7.39−7.55 (3H, m), 7.62−7.69 (2H, m); δ_C (126 MHz, $CDCl_3$) 17.7, 18.1, 24.2, 27.8 (d, *J* 64.5 Hz), 33.2 (d, *J* 68.1 Hz), 34.5 (d, *J* 10.0 Hz), 72.5 (d, *J* 6.4 Hz), 128.3 (d, *J* 10.0 Hz), 131.1 (d, *J* 8.2 Hz), 131.6 (d, *J* 88.1 Hz), 131.4 (d, *J* 2.7 Hz); δ_P (202 MHz, $CDCl_3$) 49.99; GC t_R = 10.53 min; GC−MS (EI, 70 eV) m/z=250 (M^+-H_2O) (3), 225 (56), 211 (31), 193 (16), 142 (27), 141 (35); 140 (34), 126 (31) 125 (100) 91 (13%).

4.2.26. (2-Hydroxy-2-methylpropyl)methyl-1-naphthylphosphine oxide ***(41).*** This compound was prepared according to General Procedure A from dimethyl-1-naphthylphosphine oxide (0.123 g, 0.6 mmol) and acetone (0.052 g, 0.9 mmol) as a white solid; yield 0.154 g (98%); mp 95.8–97.4 °C; R_f (AcOEt/MeOH 9:1) 0.43; [Found C, 68.75; H, 7.38. $C_{15}H_{19}O_2P$ requires C, 68.69; H, 7.30%]; *v* max (ATR) 3364, 3298, 2966, 2919, 1505, 1459, 1377, 1296, 1270, 1204, 1132, 1096, 1024, 984, 961, 907, 889, 834, 802, 774, 741, 550, 440; δ_H (500 MHz, $CDCl_3$) 1.26 (3H, s), 1.46 (3H, s), 2.00 (3H, d, *J* 12.9 Hz), 2.35−2.42 (1H, m), 2.49−2.58 (1H, m), 5.09 (1H, bs), 7.55 (2H, ddd, *J* 8.4 Hz, 7.3 Hz, 1.7 Hz), 7.58−7.64 (1H, m), 7.92 (1H, d, *J* 8.2 Hz), 8.01 (1H, d, *J* 8.2 Hz), 8.06 (1H, ddd, *J* 14.6 Hz, 7.0 Hz, 1.1 Hz), 8.38 (1H, d, *J* 8.5 Hz); δ_C (126 MHz, $CDCl_3$) 19.9 (d, *J* 69.9 Hz), 31.1 (d, *J* 7.3 Hz), 31.7 (d, *J* 8.2 Hz), 43.3 (d, *J* 68.1 Hz), 70.8 (d, *J* 6.4 Hz), 124.7 (d, *J* 12.7 Hz), 125.1 (d, *J* 4.5 Hz), 126.2, 127.4, 129.5, 130.6 (d, *J* 93.6 Hz), 131.5 (d, *J* 8.2 Hz), 132.0 (d, *J* 10.0 Hz), 132.9 (d, *J* 2.7 Hz), 133.7 (d, *J* 9.1 Hz); δ_P (202 MHz, $CDCl_3$) 39.38; GC t_R = 12.31 min; GC−MS (EI, 70 eV) m/z=262 (M^+) (10), 247 (50), 245 (14), 244 (25), 243 (23), 229 (57) 204 (26), 203 (98), 190 (13), 189 (100), 181 (11), 180 (15); 174 (13), 173 (36) 171 (19), 170 (12), 165 (12), 142 (17), 141 (75), 128 (47); 127 (48), 126 (18) (100), 119 (31); 115 (35), 101 (11), 77 (23); 63 (11%).

4.2.27. (2-Hydroxy-3-methylpropyl)methyl-1-naphthylphosphine oxide ***(42).*** This compound was prepared according to General Procedure A from dimethyl-1-naphthylphosphine oxide (0.216 g, 1.1 mmol) and isobutyraldehyde (0.114 g, 1.6 mmol); yield of two diastereomers 0.273 g (94%), (dr = 50.5:49.5).

Major diastereomer: Yield 0.127 g (44% isolated as a pure compound); white solid; mp 97.7–99.7 °C; R_f (Hexane/$CHCl_3$/*i*-PrOH 5:1:1) 0.38; [Found C, 69.63; H, 7.69. $C_{16}H_{21}O_2P$ requires C, 69.55; H, 7.66%]; *v* max (ATR) 3249, 2958, 2906, 2874, 1505, 1460, 1299, 1111, 1024, 1000, 904, 823, 795, 769, 715, 509, 439; δ_H (500 MHz, $CDCl_3$) 0.93 (3H, d, *J* 6.9 Hz), 0.97 (3H, d, *J* 6.3 Hz), 1.74−1.85 (1H, m), 2.02 (3H, d, *J* 12.6 Hz), 2.09−2.20 (1H, m), 2.28−2.44 (1H, m), 4.00-4.15 (1H, m), 4.52 (1H, bs), 7.49−7.62 (2H, m), 7.62−7.67 (1H, m), 7.88−7.98 (2H, m), 8.04 (1H, d, *J* 8.2 Hz), 8.60 (1H, d, *J* 8.5 Hz); δ_C (126 MHz, $CDCl_3$) 16.7 (d, *J* 70.8 Hz), 17.7, 18.1, 34.6 (d, *J* 6.4 Hz), 34.9 (d, *J* 63.6 Hz), 72.1 (d, *J* 5.4 Hz), 124.6 (d, *J* 12.7 Hz), 125.6 (d, *J* 4.5 Hz), 126.5, 127.6, 129.4, 129.9 (d, *J* 94.5 Hz), 130.8 (d, *J* 9.1 Hz), 132.6 (d, *J* 8.2 Hz), 133.2 (d, *J* 2.7 Hz), 133.8 (d, *J* 9.1 Hz); δ_P (202 MHz, $CDCl_3$) 42.11; GC t_R = 12.89 min; GC−MS (EI, 70 eV) m/z=276 (M^+) (14), 234 (11), 233 (80), 214 (30), 203

(32), 190 (52) 189 (100), 175 (30), 173 (27), 171 (14), 141 (36), 128 (47); 127 (34), 126 (10) 115 (18), 77 (16%).

Minor diastereomer: Yield 0.146 g (50% isolated as a pure compound); white sticky solid; R_f (Hexane/$CHCl_3$/*i*-PrOH 5:1:1) 0.56; [Found C, 69.68; H, 7.66. $C_{16}H_{21}O_2P$ requires C, 69.55; H, 7.66%]; *v* max (ATR) 3236, 2957, 2922, 2871, 1507, 1461, 1294, 1142, 1135, 1025, 987, 890, 801, 773, 451, 428; δ_H (500 MHz, $CDCl_3$) 0.88 (3H, d, *J* 6.6 Hz), 0.88 (3H, d, *J* 6.9 Hz), 1.62−1.78 (1H, m), 2.04 (3H, d, *J* 12.9 Hz), 2.20−2.41 (2H, m), 3.84−3.97 (1H, m), 4.23 (1H, bs), 7.52−7.67 (3H, m), 7.96 (1H, d, *J* 7.9 Hz), 8.00−8.16 (2H, m), 8.42 (1H, d, *J* 8.5 Hz); δ_C (126 MHz, $CDCl_3$) 17.4, 18.0, 19.1 (d, *J* 69.9 Hz), 34.6 (d, *J* 12.7 Hz), 35.3 (d, *J* 69.9 Hz), 71.6 (d, *J* 5.4 Hz), 124.8 (d, *J* 12.7 Hz), 125.2 (d, *J* 3.6 Hz), 126.3, 127.4, 129.4 (d, *J* 91.7 Hz), 129.5, 132.1 (d, *J* 8.2 Hz), 132.5 (d, *J* 9.1 Hz), 133.1 (d, *J* 2.7 Hz), 133.8 (d, *J* 9.1 Hz); δ_P (202 MHz, $CDCl_3$) 40.79; GC t_R = 12.88 min; GC−MS (EI, 70 eV) m/z= 276 (M^+) (14), 234 (11), 233 (77), 214 (18), 203 (37), 190 (49) 189 (100), 175 (26), 174 (10), 171 (12), 141 (40), 128 (48); 127 (36), 126 (12) 115 (19), 77 (20%).

4.3. General Procedure B. Attempted synthesis of Cyclic Phosphine Oxides.

Method 1. In a flame-dried Schlenk tube (20 mL) equipped with magnetic stirrer and inert gas inlet was placed (2-hydroxy-2-methylpropyl)methylphenylphosphine oxide (**20**) (0.076g, 0.36 mmol) in DCE (3 mL) and BF_3-OEt_2 (0.132 g 0.54 mmol) was added. Reaction was stirred of reflux for 4 hours. After that time the reaction was cooled to room temperature and quenched by addition of H_2O (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 column chromatography using AcOEt/MeOH (v/v = 9:1) as eluent.

Method 2. In a flame-dried Schlenk tube (20 mL) equipped with magnetic stirrer and inert gas inlet was placed (2-hydroxy-2-methylpropyl)methylphenylphosphine oxide (**20**) (0.053g, 0.25 mmol) and AcOH (1 mL) was added. Reaction was stirred of room temperature or reflux for 4 hours. The reaction was quenched by addition of H_2O (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 column chromatography using AcOEt/MeOH (v/v = 9:1) as eluent.

Method 3. In a flame-dried Schlenk tube (20 mL) equipped with magnetic stirrer and inert gas inlet was placed (2-hydroxy-2-methylpropyl)methylphenylphosphine oxide (**20**) (0.072g, 0.33 mmol) and HBF_4-OEt_2 (0.164 g 1.0 mmol) was added. Reaction was stirred of reflux for 4 hours. The reaction was quenched by addition of H_2O (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 column chromatography using AcOEt/MeOH (v/v = 9:1) as eluent.

Method 4. In a flame-dried Schlenk tube (20 mL) equipped with magnetic stirrer and inert gas inlet was placed (2-hydroxy-2-methylpropyl)methylphenylphosphine oxide ([20]) (0.072g, 0.34 mmol) and TFA (1 mL) was added. Reaction was warmed to 45 °C and stirred for 4 hours. The reaction was quenched by addition of H_2O (10 mL) with $NaHCO_3$ and extracted with $CHCl_3$ (3×20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography using AcOEt/MeOH (v/v = 9:1) as eluent.

4.3.1. (2-Methylprop-1-enyl)(methylphenyl)phosphine oxide ***(35).*** This compound was prepared according to General Procedure B, Method 3 from (2-hydroxy-2-methylpropyl)methylphenylphosphine oxide (**20**) (0.072 g, 0.33 mmol) as a white sticky solid; yield 0.041 g (63%); R_f (AcOEt/MeOH 9:1) 0.36; [Found C, 68.09; H, 7.86. $C_{11}H_{15}OP$ requires C, 68.03; H, 7.78%]; δ_H (500 MHz, $CDCl_3$) 1.69 (3H, d, *J* 13.2 Hz), 1.91 (3H, s), 1.98 (3H, dd, *J* 2.5 Hz, *J* 0.9 Hz), 5.67 (1H, d, *J* 26.2 Hz), 7.41−7.51 (3H, m), 7.68−7.76 (2H, m); δ_C (126 MHz, $CDCl_3$) 18.8 (d, *J* 74.5 Hz), 21.3 (d, *J* 8.2 Hz), 28.4 (d, *J* 17.3 Hz), 117.9 (d, *J* 102.6 Hz), 128.4 (d *J* 11.8 Hz), 129.9 (d, *J* 10.0 Hz), 131.1 (d, *J* 2.7 Hz), 135.6 (d, *J* 101.7 Hz), 158.7; δ_P (202 MHz, $CDCl_3$) 24.52; GC t_R = 10.19 min; GC−MS (EI, 70 eV) m/z=194 (M^+) (32), 193 (100), 179 (19), 139 (59), 131 (16), 130 (18), 129 (26), 125 (15), 121 (12), 117 (13), 115 (26), 91 (41), 78 (17), 77 (62), 69 (11), 65 (17), 63 (28), 55 (10), 53 (19), 51 (60), 50 (19), 47 (66%).

4.3.2. (2-Methylprop-2-enyl)(methylphenyl)phosphine oxide ***(36).*** This compound was prepared according to General Procedure B, Method 3 from (2-hydroxy-2-methylpropyl)methylphenylphosphine oxide (**20**) (0.072 g, 0.33 mmol) as a white solid; yield 0.015 g (23%); mp 56.3–58.4 °C; R_f (AcOEt/MeOH 9:1) 0.45; [Found C, 68.11; H, 7.84. $C_{11}H_{15}OP$ requires C, 68.03; H, 7.78%]; *v* max (ATR) 3409, 3061, 3054, 2939, 2912, 1712, 1642, 1437, 1293, 1169, 1111, 894, 740, 695, 530, 485, 435; δ_H (500 MHz, $CDCl_3$) 1.75 (3H, d, *J* 12.6 Hz), 1.78−1.82 (3H, m), 2.76 (2H, d, *J* 14.8 Hz), 4.70−4.75 (1H, m), 4.90−4.95 (1H, m), 7.45−7.57 (3H, m), 7.69−7.77 (2H, m); δ_C (126 MHz, $CDCl_3$) 15.3 (d, *J* 71.8 Hz), 24.3, 41.9 (d, *J* 65.4 Hz), 115.5 (d, *J* 10.0 Hz), 128.5 (d, *J* 10.9 Hz), 130.2 (d, *J* 9.1 Hz), 131.6 (d, *J* 2.7 Hz), 133.6 (d, *J* 95.4 Hz), 137.0 (d, *J* 10.0 Hz); δ_P (202 MHz, $CDCl_3$) 35.03; GC t_R = 10.00 min; GC−MS (EI, 70 eV) m/z=194 (M^+) (16), 193 (37), 139 (100), 131 (13), 91 (37), 78 (11), 77 (53), 63 (11), 51 (38), 50 (11), 47 (30%).

4.4. General Procedure C for the Synthesis of Cyclic Phosphine Oxides from β-hydroxyalkylphosphine oxides 14-34, 37-42.

The alcohol **14-34**, **37-42** (0.1mmol) was stirred at 170 °C with 85% H_3PO_4 (6.3mmol) for 5 h. The mixture was cooled below 100 °C and poured on to ice-water (10 mL). The solution was extracted with dichloromethane or chloroform (4x10 ml). The aqueous solution was washed with sodium hydrogen carbonate solution (10 mL) and water (10 mL). The extracts were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography

using $CHCl_3$/MeOH (v/v = 15:1), AcOEt/MeOH (v/v = 9:1) or hexane/$CHCl_3$/*i*-PrOH (v/v = 5:1:1) as eluent.

4.4.1. 1,3-Dimethylphosphindoline-1-oxide ***(14a).*** This compound was prepared according to General Procedure C from (2-hydroxypropyl)methylphenylphosphine oxide (**14**) (0.083 g, 0.42 mmol) as a colorless oil; yield 81% (0.03 g, 34% isolated as a pure compound). Isolated as a mixture of diastereomers (dr = 56:44).

Major diastereomer: R_f (EtOAc/MeOH 9:1) 0.34; δ_H (500 MHz, $CDCl_3$) 1.47 (3H, d, *J* 6.9 Hz), 1.67 (3H, d, *J* 12.9 Hz), 1.75−1.82 (2H, m), 3.16−3.29 (1H, m), 7.32−7.41 (2H, m), 7.48−7.55 (1H, m), 7.67−7.78 (1H, m); δ_C (126 MHz, $CDCl_3$) 16.7 (d, *J* 67.2 Hz), 21.8 (d, *J* 9.1 Hz), 34.5 (d, *J* 4.5 Hz), 36.5 (d, *J* 69.0 Hz), 124.8 (d, *J* 11.8 Hz), 127.5 (d, *J* 3.6 Hz), 127.8 (d, *J* 9.1 Hz), 132.5 (d, *J* 2.7 Hz), 133.6 (d, *J* 99.9 Hz), 150.1 (d, *J* 28.2 Hz); δ_P (202 MHz, $CDCl_3$) 53.50; GC t_R = 9.72 min; GC−MS (EI, 70 eV) m/z=181 (M^++1) (7), 180 (M^+) (55), 179 (39), 166 (10), 165 (100), 147 (39), 117 (16), 116 (12), 115 (29) 91 (12%).

Minor diastereomer: R_f (EtOAc/MeOH 9:1) 0.34; δ_H (500 MHz, $CDCl_3$) 1.38 (3H, d, *J* 6.9 Hz), 1.82 (3H, d, *J* 13.6 Hz), 2.44−2.59 (2H, m), 3.59−3.73 (1H, m), 7.32−7.40 (2H, m), 7.47−7.55 (1H, m), 7.67−7.78 (1H, m); δ_C (126 MHz, $CDCl_3$) 18.8 (d, *J* 67.2 Hz), 22.5 (d, *J* 7.3 Hz), 35.5 (d, *J* 69.0 Hz), 35.3 (d, *J* 4.5 Hz), 125.3 (d, *J* 11.8 Hz), 127.6 (d, *J* 4.5 Hz), 127.7 (d, *J* 10.9 Hz), 132.7 (d, *J* 1.8 Hz), 133.4 (d, *J* 99.0 Hz), 151.3 (d, *J* 28.2 Hz); δ_P (202 MHz, $CDCl_3$) 55.60; GC t_R = 9.50 min; GC−MS (EI, 70 eV) m/z=181 (M^++1) (14), 180 (M^+) (94), 179 (99), 166 (11), 165 (100), 149 (13), 147 (53), 145 (10), 117 (27), 116 (16), 115 (39) 91 (19%);
v max (ATR) for a mixture of diastereomers: 3238, 2972, 2910, 2835, 1445, 1400, 1369, 1174, 1118, 1059, 884, 823, 764, 482, 442.

4.4.2. (Methylprop-1-enyl)(methylphenyl)phosphine oxide ***(14b).*** This compound was prepared according to General Procedure C from (2-hydroxypropyl)methylphenylphosphine oxide (**14**) (0.083 g, 0.42 mmol) afforded the product **14b**; conversion 8% (based on ^{31}P NMR spectra of the mixture); R_f (EtOAc/MeOH 9:1) 0.34; δ_P (202 MHz, $CDCl_3$) 26.12; GC t_R = 8.39 min; GC−MS (EI, 70 eV) m/z=180 (M^+) (67), 179 (100), 165 (29), 147 (24), 139 (24), 125 (26), 117 (40), 116 (25), 115 (31), 91 (22), 77 (41), 65 (10), 63 (11), 51 (31), 47 (49%).

4.4.3. (Methylprop-2-enyl)(methylphenyl)phosphine oxide ***(14c).*** This compound was prepared according to General Procedure C from (2-hydroxypropyl)methylphenylphosphine oxide (**14**) (0.083 g, 0.42 mmol) afforded the product **14c**; conversion 5% (based on ^{31}P NMR spectra of the mixture); R_f (EtOAc/MeOH 9:1) 0.34; δ_P (202 MHz, $CDCl_3$) 34.11; GC t_R = 8.57 min; GC−MS (EI, 70 eV) m/z=180 (M^+) (6), 179 (14), 139 (100), 77 (23), 51 (13%).

4.4.4. 1,4,4-Trimethyl-1,2,3,4-tetrahydrophosphinoline-1-oxide ***(16a).*** This compound was prepared according to General Procedure C from (2-hydroxy-3-methylbutyl)methylphenylphosphine oxide (**16**) (0.432 g, 1.91 mmol) as a pale yellow oil; yield 0.430 g (86%) of title compound containing 12% of **16b**; R_f (AcOEt/MeOH 9:1) 0.26; δ_H (500 MHz, $CDCl_3$) 1.36 (3H, s), 1.37 (3H, s), 1.70 (3H, d, *J* 12.0 Hz), 1.91−2.04 (1H, m), 2.07−2.21 (2H, m), 2.26−2.39 (1H, m), 7.31−7.37 (1H, m), 7.40−7.50 (2H, m), 7.79−7.89 (1H, m); δ_C (126 MHz, $CDCl_3$) 17.4 (d, *J* 71.8 Hz), 23.5 (d, *J* 67.2 Hz), 30.9, 31.0, 34.9 (d, *J* 3.6 Hz), 35.5 (d, *J* 4.5 Hz), 126.6 (d, *J* 10.9 Hz), 126.6 (d, *J* 9.1 Hz), 129.1 (d, *J* 93.5 Hz), 130.5 (d, *J* 6.4 Hz), 131.9 (d, *J* 2.7 Hz), 150.7 (d, *J* 7.3 Hz); δ_P (202 MHz, $CDCl_3$) 29.52; GC t_R = 10.63 min; GC−MS (EI, 70 eV) m/z=208 (M^+) (29), 207 (14), 194 (12), 193 (100), 179 (13), 178 (20), 165 (23), 131 (15), 130 (24), 129 (21), 128 (13), 116 (12), 115 (22), 91 (16), 78 (30), 77 (13), 63 (11%). Analytical data are in accordance with those reported in the literature.[18]

4.4.5. 1,4,4-Trimethyl-1,2,3,4-tetrahydrophosphinoline-1-oxide ***(16b).*** This compound was prepared according to General Procedure C from (2-hydroxy-2-methylbutyl)methylphenylphosphine oxide (**25**); yield 54%, (isolated as a mixture of diastereomers contaminated with **16a**). R_f (AcOEt/MeOH 9:1) 0.26; δ_H (500 MHz, $CDCl_3$) (due to overlapping only selected peaks of epimers are described) 1.08 (3H, d, *J* 7.6 Hz) and 1.14 (3H, d, *J* 6.9 Hz) and 1.17 (3H, d, *J* 6.8 Hz) and 1.17 (3H, d, *J* 6.8 Hz) and 1.20 (3H, d, *J* 7.3 Hz) and 1.22 (3H, d, *J* 6.9 Hz) and 1.28 (3H, d, *J* 7.3 Hz) and 1.41 (3H, d, *J* 7.3 Hz), 1.65 (3H, d, *J* 12.4 Hz) and 1.65 (3H, d, *J* 12.0 Hz) and 1.69 (3H, d, *J* 12.8 Hz) and 1.71 (3H, d, *J* 12.6 Hz), 2.12−2.25 (7H, m), 2.25−2.38 (3H, m), 2.38−2.50 (1H, m), 2.56−2.66 (1H, m), 2.66−2.73 (1H, m), 2.79−2.89 (2H, m), 2.89−2.99 (1H, m), 7.13−7.18 (1H, m), 7.19−7.23 (1H, m), 7.23−7.30 (2H, m), 7.31−7.38 (4H, m), 7.39−7.48 (4H, m), 7.74−7.91 (4H, m); δ_P (202 MHz, $CDCl_3$) 24.82 and 26.00 and 27.86 and 31.53; GC peak 1; t_R = 10.45 min; GC−MS (EI, 70 eV) m/z=208 (M^+) (21), 194 (12), 193 (100), 165 (22), 151 (11), 133 (23), 129 (14), 115 (14), 91 (10); GC peak 2; t_R = 10.64 min; GC−MS (EI, 70 eV) m/z=208 (M^+) (42), 207 (12), 194 (12), 193 (100), 179 (27), 178 (15), 166 (25); 165 (72), 151 (17), 147 (15); 133 (35), 131 (17), 130 (20), 129 (25), 128 (17), 116 (14), 115 (28), 91 (21); GC peak 3; t_R = 10.69 min; GC−MS (EI, 70 eV) m/z=208 (M^+) (38), 194 (12), 193 (100), 179 (26), 178 (10), 166 (35); 165 (90), 151 (20), 147 (13); 133 (41), 131 (14), 130 (20), 129 (25), 128 (16), 116 (10), 115 (23), 91 (18); GC peak 4; t_R = 10.77 min; GC−MS (EI, 70 eV) m/z=208 (M^+) (19), 194 (12), 193 (100), 165 (18), 133 (19), 129 (14), 115 (12%).

4.4.6. 1,3,4,4-Tetramethyl-1,2,3,4-tetrahydrophosphinoline-1-oxide ***(17a).*** This compound was prepared according to General Procedure C from (2-hydroxy-3,3-dimethylbutyl)methylphenylphosphine oxide (**17**) (0.099 g, 0.41 mmol) as a colorless oil; yield 79% (isolated as a mixture containing 7% of **17b**). Isolated as a mixture of diastereomers (dr = 56:44).

Major diastereomer: R_f (AcOEt/MeOH 9:1) 0.21; δ_H (500 MHz, $CDCl_3$) 1.10 (3H, dd, *J* 6.9 Hz, *J* 1.3 Hz), 1.20 (3H, s), 1.41 (3H, s), 1.68 (3H, d, *J* 12.6 Hz), 1.91−2.00 (1H, m), 2.02−2.14 (1H, m),

2.36−2.46 (1H, m), 7.28−7.35 (1H, m), 7.42−7.50 (2H, m), 7.71−7.79 (1H, m); δ_C (126 MHz, $CDCl_3$) 18.7 (d, *J* 71.8 Hz), 18.6 (d, *J* 10.9 Hz), 24.9, 30.0, 31.7 (d, *J* 67.2 Hz), 36.0 (d, *J* 4.5 Hz), 39.1 (d, *J* 4.5 Hz), 126.3 (d, *J* 10.9 Hz), 126.8 (d, *J* 10.0 Hz), 128.9 (d, *J* 94.5 Hz), 130.3 (d, *J* 8.2 Hz), 131.9 (d, *J* 2.7 Hz), 151.0 (d, *J* 8.2 Hz); δ_P (202 MHz, $CDCl_3$) 26.18; GC t_R = 11.22 min; GC−MS (EI, 70 eV) m/z=222 (M^+) (22), 208 (13), 207 (100), 193 (27), 192 (19), 180 (14), 179 (45), 165 (78), 147 (17), 145 (22), 144 (37), 143 (11), 133 (10), 129 (26), 128 (19), 117 (10), 115 (29), 91 (17) 79 (19), 78 (45), 77 (17), 63 (11) 47 (10%).

Minor diastereomer: R_f (AcOEt/MeOH 9:1) 0.21; δ_H (500 MHz, $CDCl_3$) 1.15 (3H, dd, *J* 6.6 Hz, *J* 1.6 Hz), 1.26 (3H, s), 1.33 (3H, s), 1.67 (3H, d, *J* 12.9 Hz), 2.14−2.21 (2H, m), 2.23−2.32 (1H, m), 7.29−7.35 (1H, m), 7.41−7.51 (2H, m), 7.82−7.88 (1H, m); δ_C (126 MHz, $CDCl_3$) 18.3 (d, *J* 61.8 Hz), 18.5 (d, *J* 10.9 Hz), 25.6, 29.6, 31.5 (d, *J* 66.3 Hz), 37.6 (d, *J* 3.6 Hz), 39.0 (d, *J* 4.5 Hz), 126.5 (d, *J* 10.9 Hz), 126.6 (d, *J* 10.0 Hz), 129.5 (d, *J* 91.7 Hz), 130.0 (d, *J* 6.4 Hz), 131.9 (d, *J* 2.7 Hz), 150.7 (d, *J* 8.2 Hz); δ_P (202 MHz, $CDCl_3$) 27.43; GC t_R = 11.00 min; GC−MS (EI, 70 eV) m/z=222 (M^+) (59), 221 (12), 207 (62), 193 (28), 192 (17), 180 (18), 179 (85), 166 (18), 165 (100), 154 (21), 147 (22), 145 (22), 144 (29), 143 (12), 133 (14), 130 (11), 129 (29), 128 (22), 117 (17), 116 (11), 115 (38), 103 (10), 91 (23) 79 (20), 78 (77), 77 (22), 63 (14) 47 (12%).

4.4.7. 1,3,3,4-Tetramethyl-1,2,3,4-tetrahydrophosphinoline-1-oxide ***(17b).*** This compound was prepared according to General Procedure C from (2-hydroxy-3,3-dimethylbutyl)methylphenylphosphine oxide (**17**) (0.099 g, 0.41 mmol) afforded the product **17b**; yield 7% (isolated as a mixture with **17a**); R_f (AcOEt/MeOH 9:1) 0.21; δ_H (500 MHz, $CDCl_3$) (due to overlapping only selected peaks are described) 1.12 (3H, s) and 1.33 (3H, s) and 1.29 (3H, s) and 1,31 (3H, s), 1.66 (3H, d, *J* 12.9 Hz) and 1.70 (3H, d, *J* 12.3 Hz); δ_P (202 MHz, $CDCl_3$) 24.89 (*Major diastereomer*) and 27.15 ppm (*Minor diastereomer*). GC (*Major diastereomer*) t_R = 10.49 min; GC−MS (EI, 70 eV) m/z=222 (M^+) (26), 208 (10), 207 (100), 193 (41), 192 (16), 180 (18), 179 (20), 166 (16), 165 (62), 151 (28), 149 (11), 145 (14), 144 (33), 143 (10), 133 (50), 130 (11), 129 (30), 128 (21), 117 (11), 115 (22), 103 (11), 91 (17), 79 (29), 78 (95), 77 (25), 63 (17), 51 (10), 47 (11); GC (*Minor diastereomer*) t_R = 10.79 min; GC−MS (EI, 70 eV) m/z=222 (M^+) (23), 207 (44), 193 (20), 180 (12), 179 (12), 166 (42), 165 (100), 151 (35), 149 (10), 144 (15), 143 (10), 133 (43), 129 (14), 128 (10), 115 (14), 91 (12), 79 (13), 78 (40), 77 (17%).

4.4.8. 1,4-Dimethyl-1,2,3,4-tetrahydrophosphinoline-1-oxide ***(18a).*** This compound was prepared according to General Procedure C from (2-hydroxybutyl)methylphenylphosphine oxide (**18**) (0.149 g, 0.70 mmol) as a colorless oil; yield 0.054 g (40%). Isolated as a mixture of diastereomers (dr = 51:49).

Major diastereomer: R_f (AcOEt/MeOH 9:1) 0.15; δ_H (500 MHz, $CDCl_3$) 1.35 (3H, d, *J* 7.3 Hz), 1.64 (3H, dd, *J* 12.6 Hz, *J* 0.6 Hz), 1.99−2.13 (2H, m), 2.29−2.42 (2H, m), 2.96−3.04 (1H, m), 7.25−7.29 (1H, m), 7.29−7.35 (1H, m), 7.37−7.45 (1H, m), 7.77−7.85 (1H, m); δ_C (126 MHz, CDCl3) 17.7 (d, *J*

69.9 Hz), 22.4, 24.6 (d, *J* 68.1 Hz), 27.6 (d, *J* 4.5 Hz), 34.2 (d, *J* 4.5 Hz), 126.7 (d, *J* 10.9 Hz), 128.4 (d, *J* 9.1 Hz), 129.8 (d, *J* 92.6 Hz), 130.4 (d, *J* 7.3 Hz), 131.6 (d, *J* 2.3 Hz), 147.5 (d, *J* 7.3 Hz); δ_P NMR (202 MHz, $CDCl_3$) 29.30; GC t_R = 11.51 min; GC−MS (EI, 70 eV) m/z=194 (M^+) (27), 183 (10), 182 (100), 181 (34), 168 (11), 167 (99), 149 (33), 133 (12), 130 (12), 125 (10), 115 (22), 103 (12), 91 (21), 77 (25), 51 (12), 47 (17%).

Minor diastereomer: R_f (AcOEt/MeOH 9:1) 0.15; δ_H (500 MHz, $CDCl_3$) 1.29 (3H, d, *J* 6.9 Hz), 1.69 (3H, d, *J* 12.9 Hz), 1.79−1.94 (1H, m), 2.12−2.24 (3H, m), 3.03−3.13 (1H, m), 7.19−7.24 (1H, m), 7.29−7.35 (1H, m), 7.38−7.45 (1H, m), 7.75−7.86 (1H, m); δ_C (126 MHz, $CDCl_3$) 17.7 (d, *J* 70.8 Hz), 21.7, 23.3 (d, *J* 68.1 Hz), 27.3 (d, *J* 5.4 Hz), 34.2 (d, *J* 5.4 Hz), 126.8 (d, *J* 10.9 Hz), 128.1 (d, *J* 9.1 Hz), 129.7 (d, *J* 92.6 Hz), 130.4 (d, *J* 8.2 Hz), 131.6 (d, *J* 2.3 Hz), 147.1 (d, *J* 7.3 Hz); δ_P (202 MHz, $CDCl_3$) 28.05; GC t_R = 11.47 min; GC−MS (EI, 70 eV) m/z=194 (M^+) (73), 193 (28), 192 (45), 182 (81), 183 (10), 181 (41), 177 (18), 168 (34), 167 (100), 149 (47), 133 (21), 131 (11), 130 (20), 129 (24), 128 (13), 116 (12), 115 (35), 103 (17), 91 (32), 78 (12), 77 (37), 65 (11), 63 (13), 51 (17), 47 (23%);

v max (ATR) for a mixture of diastereomers: 3254, 2962, 2917, 2849, 1683, 1407, 1295, 1258, 1124, 1060, 953, 872, 797, 761, 691, 489.

4.4.9. 1,3,3-Trimethylphosphindoline-1-oxide ***(20a).*** This compound was prepared according to General Procedure C from (2-hydroxy-2-methylpropyl)methylphenylphosphine oxide (**20**) (0.074 g, 0.35 mmol) as a white oil, except when the product was purified by distillation, b.p. 115-120 ^oC at 0.1 mmHg, which crystallised in the receiver but could not be isolated in the crystalline form due to the high hygroscopicity; yield 0.05 g (74%); R_f (AcOEt/MeOH 9:1) 0.30; [Found C, 68.09; H, 7.82. $C_{11}H_{15}OP$ requires C, 68.03; H, 7.78%]; *v* max (ATR) 3410, 2960, 2910, 2864, 16341592, 1445, 1443, 1406, 1294, 1269, 1185, 1151, 1135, 1068, 892, 818, 765, 481, 439; δ_H (500 MHz, $CDCl_3$) 1.37 (3H, s), 1.49 (3H, s), 1.78 (3H, d, *J* 13.2 Hz), 2.04−2.15 (1H, m), 2.17−2.30 (1H, m), 7.30−7.44 (2H, m), 7.47−7.57 (1H, m), 7.65−7.74 (1H, m); δ_C (126 MHz, $CDCl_3$) 18.6 (d, *J* 67.2 Hz), 31.4 (d, *J* 5.4 Hz), 32.6 (d, *J* 4.5 Hz), 41.6 (d, *J* 4.5 Hz), 42.6 (d, *J* 69.0 Hz), 123.9 (d, *J* 12.7 Hz), 127.7 (d, *J* 6.4 Hz), 127.8 (d, *J* 5.4 Hz), 132.6 (d, *J* 98.1 Hz), 133.0 (d, *J* 1.8 Hz), 155.3 (d, *J* 27.2 Hz); δ_P (202 MHz, $CDCl_3$) 52.60; GC t_R = 8.16 min; GC−MS (EI, 70 eV) m/z=194 (M^+) (49), 193 (42), 180 (11), 179 (100), 133 (17), 116 (12), 115 (33), 91 (15%). Analytical data are in accordance with those reported in the literature.[19]

4.4.10. 3-Butyl-1,3-dimethylphosphindoline-1-oxide ***(21a).*** This compound was prepared according to General Procedure C from (2-hydroxy-2-methylhexyl)methylphenylphosphine oxide (**21**); conversion 13% (based on ^{31}P NMR spectra) as a mixture with **21b**, **21c** and **21d**; δ_P (202 MHz, $CDCl_3$) 56.20 and 55.52; GC-MS analyses are included in the supporting material.

4.4.11. 1,3-Dimethyl-4-propyl-1,2,3,4-tetrahydrophosphinoline-1-oxide ***(21b).*** This compound was prepared according to General Procedure C from (2-hydroxy-2-methylhexyl)methylphenylphosphine oxide (**21**); conversion 45% (based on ^{31}P NMR spectra) as a mixture with **21a**, **21c** and **21d**; δ_P (202 MHz, $CDCl_3$) 22.90 and 25.58 and 27.72 and 31.43; GC-MS analyses are included in the supporting material.

4.4.12. 1,4-Dimethyl-4-propyl-1,2,3,4-tetrahydrophosphinoline-1-oxide ***(21c).*** This compound was prepared according to General Procedure C from (2-hydroxy-2-methylhexyl)methylphenylphosphine oxide (**21**); conversion 10% (based on ^{31}P NMR spectra) as a mixture with **21a**, **21b** and **21d**; ^{31}P NMR (202 MHz, $CDCl_3$): δ = 26.55 and 26.89; GC-MS analyses are included in the supporting material.

4.4.13. (3-Hydroxy-2-methylhexyl)methylphenylphosphine oxide ***(21d).*** This compound was prepared according to General Procedure C from (2-hydroxy-2-methylhexyl)methylphenylphosphine oxide (**21**); conversion 32% (based on ^{31}P NMR spectra) as a mixture with **21a**, **21b** and **21c**; δ_P (202 MHz, $CDCl_3$) 36.17 and 37.30 and 37.66 and 38.74; GC-MS analyses are included in the supporting material.

4.4.14. 1,3-Dimethyl-3-n-propylphosphindoline-1-oxide ***(22a).*** This compound was prepared according to General Procedure C from (2-hydroxy-2-methylpentyl)methylphenylphosphine oxide (**22**); conversion 3% (based on ^{31}P NMR spectra) as a mixture with **22b**, **22c** and **22d**; δ_P (202 MHz, $CDCl_3$) 53.35 and 53.67; GC-MS analyses are included in the supporting material.

4.4.15. 4-Ethyl-1,3-dimethyl-1,2,3,4-tetrahydrophosphinoline-1-oxide ***(22b).*** This compound was prepared according to General Procedure C from (2-hydroxy-2-methylpentyl)methylphenylphosphine oxide (**22**); conversion 36% (based on ^{31}P NMR spectra) as a mixture with **22a**, **22c** and **22d**; δ_P (202 MHz, $CDCl_3$) 22.56 and 25.12 and 27.14 and 30.8; GC-MS analyses are included in the supporting material.

4.4.16. 4-Ethyl-1,4-dimethyl-1,2,3,4-tetrahydrophosphinoline-1-oxide ***(22c).*** This compound was prepared according to General Procedure C from (2-hydroxy-2-methylpentyl)methylphenylphosphine oxide (**22**); conversion 3% (based on ^{31}P NMR spectra) as a mixture with **22a**, **22b** and **22d**; (202 MHz, $CDCl_3$) 28.97 and 29.26; GC-MS analyses are included in the supporting material.

4.4.17. (3-Hydroxy-2-methylpentyl)methylphenylphosphine-1-oxide ***(22d).*** This compound was prepared according to General Procedure C from (2-hydroxy-2-methylpentyl)methylphenylphosphine oxide (**22**); conversion 58% (based on ^{31}P NMR spectra) as a mixture with **21a**, **21b** and **21c**; δ_P (202 MHz, $CDCl_3$) 35.41 and 37.23 and 38.44 and 41.41; GC-MS analyses are included in the supporting material.

*4.4.18. 3-Ethyl-1,3-dimethylphosphindoline-1-oxide **(25a.)*** This compound was prepared according to General Procedure C from (2-hydroxy-2-methylbutyl)methylphenylphosphine oxide (**25**); yield 3% (isolated as a mixture of diastereomers contaminated by **16b**). R_f (EtOAc/MeOH 9:1) 0.26; δ_H (500 MHz, $CDCl_3$) (due to overlapping only selected peaks are described) 0.82 (3H, t, *J* 7.6 Hz) and 0.83 (3H, t, *J* 7.6 Hz), 1.34 (3H, s) and 1.45 (3H, s), 1.78 (3H, d, *J* 12.9 Hz) and 1.79 (3H, d, *J* 12.9 Hz), 2.08−2.14 (2H, m), 2.14−2.17 (2H, m), 7.50−7.57 (2H, m), 7.66−7.73 (2H, m); δ_P (202 MHz, $CDCl_3$) 53.84 and 54.20.

Major diastereomer: GC t_R = 10.15 min; GC−MS (EI, 70 eV) m/z=208 (M^+) (10), 193 (70), 180 (13), 179 (100), 133 (11), 128 (10), 116 (11), 115 (27), 91 (13%).

Minor diastereomer: GC t_R = 10.03 min; GC−MS (EI, 70 eV) m/z=208 (M^+) (16), 193 (64), 180 (43), 179 (100), 165 (18), 133 (18), 128 (10), 116 (12), 115 (33), 91 (14%).

*4.4.19. 1,3,3,4,4-Pentamethyl-1,2,3,4-tetrahydrophosphinoline-1-oxide **(26a).*** This compound was prepared according to General Procedure C from (2-hydroxy-2,3,3-trimethylbutyl)methylphenylphosphine oxide (**26**) (0.174 g, 0.68 mmol) as a colorless oil; yield 0.072 g (45%); R_f (AcOEt/MeOH 9:1) 0.19; [Found C, 71.28; H, 9.17. $C_{14}H_{21}OP$ requires C, 71.16; H, 8.96%]; δ_H (500 MHz, $CDCl_3$) 1.04 (3H, d, *J* 1.3 Hz), 1.13 (3H, d, *J* 1.6 Hz), 1.23 (3H, s), 1.38 (3H, s), 1.64 (3H, d, *J* 12.6 Hz), 2.05−2.36 (2H, m), 7.27−7.35 (1H, m), 7.38−7.50 (2H, m), 7.75−7.87 (1H, m); δ_C (126 MHz, DMSO-d6) 19.1 (d, *J* 71.8 Hz), 24.7, 24.9, 25.5 (d, *J* 8.2 Hz), 25.9 (d, *J* 8.2 Hz), 37.0 (d, *J* 3.6 Hz), 39.9 (d, *J* 64.8 Hz), 41.4 (d, *J* 5.4 Hz), 125.0 (d, *J* 10.0 Hz), 125.5 (d, *J* 10.9 Hz), 129.9 (d, *J* 6.4 Hz), 130.4 (d, *J* 89.9 Hz), 131.1 (d, *J* 2.7 Hz), 150.2 (d, *J* 8.2 Hz); δ_P (202 MHz, $CDCl_3$) 23.51; GC t_R = 11.41 min; GC−MS (EI, 70 eV) m/z=236 (M^+) (19), 221 (32), 193 (47), 180 (25), 179 (57), 166 (11), 165 (100), 158 (11), 154 (14), 147 (17), 128 (11), 115 (23) 91 (13%).

*4.4.20. Methylphenyl((9H-fluoren-9-yl)methyl)phosphine oxide **(28a).*** This compound was prepared according to General Procedure C from (2-hydroxy-2,2-diphenylethyl)methylphenylphosphine oxide (**28**) (0.055 g, 0.16 mmol) as a brown sticky solid; yield 0.012 g (22%); R_f ($CHCl_3$/MeOH 15:1) 0.62; [Found C, 79.32; H, 6.14. $C_{21}H_{19}OP$ requires C, 79.23; H, 6.02%]; *v* max (ATR) 3730, 3052, 2920, 2851, 1708, 1589, 1436, 1294, 1255, 1149, 1109, 881, 752, 733, 691, 491; δ_H (500 MHz, $CDCl_3$) 1.75 (3H, d, *J* 12.9 Hz), 2.51−2.65 (2H, m), 4.21 (1H, dt, *J* 17.9 Hz, *J* 5.7 Hz), 7.12−7.20 (1H, m), 7.20−7.27 (1H, m), 7.28−7.33 (1H, m), 7.33−7.42 (2H, m), 7.46−7.60 (3H, m), 7.66−7.74 (2H, m), 7.75−7.82 (2H, m), 7.88−7.98 (1H, m); δ_C (126 MHz, $CDCl_3$) 17.2 (d, *J* 70.8 Hz), 36.3 (d, *J* 68.1 Hz), 41.4 (d, *J* 3.6 Hz), 119.7 (d, *J* 5.4 Hz), 124.6, 125.6, 127.1, 127.4 (d, *J* 12.7 Hz), 128.8 (d, *J* 11.8 Hz), 130.2 (d, *J* 9.1 Hz), 131.8 (d, *J* 2.7 Hz), 133.9 (d, *J* 96.3 Hz), 140.5 (d, *J* 13.6 Hz), 146.8 (d, *J* 11.8 Hz), 146.8 (d, *J* 10.0 Hz); δ_P (202 MHz, $CDCl_3$) 36.02; GC t_R = 9.47 min; GC−MS (EI, 70 eV) m/z=181 (14), 180 (100), 152 (58), 151 (27), 150 (18), 76 (29), 75 (11), 63 (16%).

4.4.21. 3-Dibutyl-1-methylphosphindoline-1-oxide ***(29a).*** This compound was prepared according to General Procedure C from (2-butyl-2-hydroxyhexyl)methylphenylphosphine oxide (**29**); conversion 9% (based on ^{31}P NMR spectra) as a mixture with **29b**, **29c** and **29d**; δ_P (202 MHz, $CDCl_3$) 56.78; GC-MS analyses are included in the supporting material.

4.4.22. 3-n-Butyl-4-n-propyl-1-methyl-1,2,3,4-tetrahydrophosphinoline-1-oxide ***(29b).*** This compound was prepared according to General Procedure C from (2-butyl-2-hydroxyhexyl)methylphenylphosphine oxide (**29**); conversion 22% (based on ^{31}P NMR) spectra as a mixture with **29a**, **29c** and **29d**; δ_P (202 MHz, $CDCl_3$) 22.57 and 25.68 and 27.72 and 31.81; GC-MS analyses are included in the supporting material.

4.4.23. 4-n-Butyl-4-n-propyl-1-methyl-1,2,3,4-tetrahydrophosphinoline-1-oxide ***(29c).*** This compound was prepared according to General Procedure C from (2-butyl-2-hydroxyhexyl)methylphenylphosphine oxide (**29**); conversion 4% (based on ^{31}P NMR) spectra as a mixture with **29a**, **29b** and **29d**; δ_P (202 MHz, $CDCl_3$) 29.39 and 29.68; GC-MS analyses are included in the supporting material.

4.4.24. (2-Butyl-3-hydroxyhexyl)methylphenylphosphine-1-oxide ***(29d).*** This compound was prepared according to General Procedure C from (2-butyl-2-hydroxyhexyl)methylphenylphosphine oxide (**29**); conversion 65% (based on ^{31}P NMR spectra) as a mixture with **29a**, **29b** and **29c**; δ_P (202 MHz, $CDCl_3$) 36.99 and 37.69 and 38.17 and 41.81; GC-MS analyses are included in the supporting material.

4.4.25. 3-i-Propyl-1,4,4-trimethyl-1,2,3,4-tetrahydrophosphinoline-1-oxide ***(30a).*** This compound was prepared according to General Procedure C from (2-hydroxy-2-*i*-propyl-3-methylbutyl)methylphenylphosphine oxide (**30**) (0.112 g, 0.42 mmol) as a colorless oil; yield of two diastereomers 0.018 g (18%), (dr = 51:49).

Major diastereomer: Yield 0.010 g (10% isolated as a pure compound); colorless oil; R_f (EtOAc/MeOH 9:1) 0.21; [Found C, 72.09; H, 9.33. $C_{15}H_{23}OP$ requires C, 71.97; H, 9.26%]; δ_H (500 MHz, $CDCl_3$) 0.90 (3H, d, *J* 6.6 Hz), 1.05 (3H, d, *J* 6.9 Hz), 1.22 (3H, s), 1.27−1.37 (1H, m), 1.49 (3H, s), 1.67−1.72 (1H, m), 1.74 (3H, d, *J* 12.9 Hz), 2.06−2.14 (1H, m), 2.23−2.30 (1H, m), 7.29−7.35 (1H, m), 7.45−7.50 (1H, m), 7.51−7.56 (1H, m), 7.72−7.79 (1H, m); δ_C (126 MHz, $CDCl_3$) 17.5 (d, *J* 72.7 Hz), 18.4, 23.3 (d, *J* 69.0 Hz), 24.1, 25.6, 27.2 (d, *J* 10.9 Hz), 29.0, 40.8 (d, *J* 3.6 Hz), 43.9 (d, *J* 3.6 Hz), 126.2 (d, *J* 10.9 Hz), 127.4 (d, *J* 10.0 Hz), 129.6 (d, *J* 97.2 Hz), 130.1 (d, *J* 7.3 Hz), 131.9 (d, *J* 2.7 Hz), 152.3 (d, *J* 8.2 Hz); δ_P (202 MHz, $CDCl_3$) 28.72; GC t_R = 11.88 min; GC−MS (EI, 70 eV) m/z=250 (M^+) (6), 235 (35), 208 (14), 207 (100), 193 (18), 192 (15), 180 (15), 179 (37), 168 (11), 165 (65), 147 (12), 129 (16), 128 (13), 115 (20), 91 (12%).

Minor diastereomer: Yield 0.008 g (8% isolated as a pure compound); colorless oil R_f (EtOAc/MeOH 9:1) 0.26; [Found C, 72.11; H, 9.39. $C_{15}H_{23}OP$ requires C, 71.97; H, 9.26%]; δ_H (500 MHz, $CDCl_3$) 0.91 (3H, d, *J* 6.6 Hz), 1.00 (3H, d, *J* 6.6 Hz), 1.24−1.29 (1H, m), 1.31 (3H, s), 1.45 (3H, s), 1.71 (3H, d, *J* 12.3 Hz), 1.73−1.82 (1H, m), 2.05−2.13 (1H, m), 2.23−2.35 (1H, m), 7.30−7.39 (1H, m), 7.45−7.49 (2H, m), 7.81−7.90 (1H, m); δ_C (126 MHz, $CDCl_3$) 17.1 (d, *J* 72.7 Hz), 18.2, 23.3 (d, *J* 69.0 Hz), 24.1, 26.6, 27.4 (d, *J* 12.7 Hz), 29.2, 40.6 (d, *J* 3.6 Hz), 47.8 (d, *J* 2.7 Hz), 126.5 (d, *J* 10.9 Hz), 126.8 (d, *J* 10.0 Hz), 129.7 (d, *J* 97.2 Hz), 130.3 (d, *J* 6.4 Hz), 132.0 (d, *J* 1.8 Hz), 152.4 (d, *J* 9.1 Hz); δ_P (202 MHz, $CDCl_3$) 32.40; GC t_R = 11.76 min; GC−MS (EI, 70 eV): m/z=250 (M^+) (15), 235 (16), 208 (15), 207 (100), 194 (12), 193 (47), 192 (17), 182 (18), 180 (18), 179 (49), 168 (48), 166 (11), 165 (89), 154 (20), 147 (18), 133 (12), 130 (11), 129 (22), 128 (18), 117 (11), 116 (10), 115 (29), 91 (18%).

4.4.26. 3-Diethyl-1-methylphosphindoline-1-oxide ***(31a).*** This compound was prepared according to General Procedure C from 1-[(methyl)phenylphosphinoyl]-2-ethylbutan-2-ol (**31**); conversion 1% (based on ^{31}P NMR spectra); Isolated as a mixture with **31b**, **22c** and **31d**; δ_P (202 MHz, $CDCl_3$) 54.74.

4.4.27. 3-Ethyl-1,4-dimethyl-1,2,3,4-tetrahydrophosphinoline-1-oxide ***(31b).*** This compound was prepared according to General Procedure C using (2-ethyl-2-hydroxybutyl)methylphenylphosphine oxide (**31**); conversion 65% (based on ^{31}P NMR spectra); Yield 47%, isolated as a mixture with **31a**, **22c** and **31d**.

Major diastereomer (isolated as a mixture with other compounds): colorless oil; R_f (EtOAc/MeOH 9:1) 0.37; δ_H (500 MHz, $CDCl_3$) 1.00 (3H, t, *J* 7.4 Hz), 1.19 (3H, d, *J* 8.5 Hz), 1.39−1.50 (1H, m), 1.50−1.59 (1H, m), 1.67 (3H, d, *J* 12.3 Hz), 1.93−2.04 (1H, m), 2.06−2.16 (2H, m), 2.94−3.04 (1H, m), 7.16−7.22 (1H, m), 7.33−7.38 (1H, m), 7.40−7.47 (1H, m), 7.80−7.88 (1H, m); δ_C (126 MHz, $CDCl_3$) 11.6, 17.0, 18.1 (d, *J* 71.8 Hz), 27.9 (d, *J* 67.2 Hz), 28.4 (d, *J* 15.4 Hz), 38.5 (d, *J* 3.6 Hz), 39.0 (d, *J* 2.7 Hz), 127.0 (d, *J* 10.9 Hz), 129.4 (d, *J* 93.6 Hz), 129.1 (d, *J* 10.0 Hz), 130.5 (d, *J* 7.3 Hz), 131.8 (d, *J* 1.8 Hz), 148.9 (d, *J* 8.2 Hz); δ_P (202 MHz, $CDCl_3$) 31.75; GC t_R = 11.08 min; GC−MS (EI, 70 eV) m/z=222 (M^+) (15), 207 (33), 194 (14), 193 (88), 180 (12), 179 (31), 167 (11), 166 (32), 165 (100), 151 (24), 147 (13), 145 (22), 144 (11), 133 (45), 129 (30), 128 (18), 116 (15), 115 (28), 91 (20), 79 (35), 78 (31), 77 (25), 63 (13), 47 (11%).

Mixture of minor diastereomers: colorless oil; R_f (EtOAc/MeOH 9:1) 0.37; δ_H (500 MHz, $CDCl_3$): (due to overlapping only selected peaks are described) 0.95 (3H, t, *J* 7.4 Hz) and 0.97 (3H, t, *J* 7.4 Hz), 1.06 (3H, d, *J* 7.3 Hz) and 1.26 (3H, d, *J* 7.3 Hz) and 1.41 (3H, d, *J* 7.3 Hz), 1.65 (3H, d, *J* 12.3 Hz) and 1.69 (3H, d, *J* 12.3 Hz) and 1.71 (3H, d, *J* 12.3 Hz), 2.45−2.53 (1H, m) and 2.86−2.90 (1H, m), 3.02−3.07 (1H, m); δ_P (202 MHz, $CDCl_3$) 27.75 and 25.75 and 23.59; (compound 1) GC t_R = 10.94 min; GC−MS (EI, 70 eV) m/z=222 (M^+) (7), 207 (20), 194 (28), 193 (26), 180 (17), 179 (33),

167 (12), 166 (12), 165 (100), 147 (12), 133 17), 129 (16), 115 (19), 91 (16), 78 (28), 77 (24), 63 (10), 51 (10), 47 (11); (compound 2) GC t_R = 11.20 min; GC−MS (EI, 70 eV) m/z=222 (M^+) (14), 207 (43), 194 (14), 165 (100), 151 (11), 133 (23), 129 (16), 128 (12), 115 (16), 91 (13), 78 (16), 77 (15); (compound 3) GC t_R = 11.27 min; GC−MS (EI, 70 eV) m/z=222 (M^+) (9), 207 (34), 194 (16), 165 (100), 151 (13), 133 (25), 129 (12), 128 (18), 115 (21), 91 (13), 78 (14), 77 (11%).

4.4.28. 5-Methyl-2,3,3a,4,5,9b-hexahydro-1H-cyclopenta[c]phosphinoline-5-oxide ***(32a).*** This compound was prepared according to General Procedure C from [(1-hydroxy)cyclopentylmethyl)]methylphenylphosphine oxide (**32**) (0.062 g, 0.26 mmol) afforded the product **32a** (0.22 g, 0.1 mmol); yield 38% (52:48 dr).

Major diastereomer: colorless oil; R_f (EtOAc/MeOH 9:1) 0.28; δ_H (500 MHz, $CDCl_3$) 1.50−1.64 (2H, m), 1.74 (3H, d, *J* 12.9 Hz), 1.77−1.86 (2H, m), 2.01−2.09 (2H, m), 2.09−2.16 (1H, m), 2.17−2.25 (1H, m), 2.93−3.04 (1H, m), 3.19−3.28 (1H, m), 7.24−7.27 (1H, m), 7.29−7.35 (1H, m), 7.40−7.46 (1H, m), 7.68−7.74 (1H, m); δ_C (126 MHz, $CDCl_3$) 16.4 (d, *J* 72.6 Hz), 22.5, 28.8 (d, *J* 69.0 Hz), 32.8, 32.9 (d, *J* 4.5 Hz), 34.1 (d, *J* 13.6 Hz), 44.8 (d, *J* 6.4 Hz), 126.4 (d, *J* 10.9 Hz), 128.4 (d, *J* 96.3 Hz), 129.4 (d, *J* 9.1 Hz), 130.1 (d, *J* 9.1 Hz), 131.7 (d, *J* 1.8 Hz), 144.5 (d, *J* 8.2 Hz); δ_P (202 MHz, $CDCl_3$) 27.30; GC t_R = 12.34 min; GC−MS (EI, 70 eV) m/z=221 (M^++1) (12), 220 (M^+) (91), 219 (79), 205 (11), 193 (12), 192 (100), 191 (33), 179 (11), 165 (15), 141 (14), 133 (16), 130 (14), 129 (35), 128 (28), 116 (18), 115 (40), 91 (14%).

Minor diastereomer: colorless oil; R_f (EtOAc/MeOH 9:1) 0.42; [Found C, 71.12; H, 8.16. $C_{13}H_{17}OP$ requires C, 70.89; H, 7.78%]; δ_H (500 MHz, $CDCl_3$) 1.66 (3H, d, *J* 12.6 Hz), 1.73−1.84 (3H, m), 1.86−1.95 (1H, m), 2.00−2.12 (3H, m), 2.14−2.24 (1H, m), 2.51−2.65 (1H, m), 3.06−3.22 (1H, m), 7.19−7.24 (1H, m), 7.29−7.38 (1H, m), 7.39−7.46 (1H, m), 7.85−7.95 (1H, m); δ_C (126 MHz, $CDCl_3$) 17.3 (d, *J* 69.9 Hz), 22.4, 28.8 (d, *J* 67.2 Hz), 33.4, 34.4 (d, *J* 14.5 Hz), 36.7 (d, *J* 2.7 Hz), 44.6 (d, *J* 5.4 Hz), 126.6 (d, *J* 10.0 Hz), 129.2 (d, *J* 96.4 Hz), 129.5 (d, *J* 10.0 Hz), 130.0 (d, *J* 6.4 Hz), 131.7 (d, *J* 1.8 Hz), 144.5 (d, *J* 9.1 Hz); δ_P (202 MHz, $CDCl_3$) 30.78; GC tR = 12.03 min; GC−MS (EI, 70 eV) m/z=221 (M^++1) (12), 220 (M^+) (91), 219 (74), 217 (10), 205 (24), 192 (62), 191 (58), 180 (11), 179 (100), 178 (11), 166 (42), 165 (75), 155 (11), 154 (18), 149 (12), 143 (11), 141 (26), 139 (16), 133 (26), 130 (11), 129 (37), 128 (39), 127 (10), 117 (13), 116 (32), 115 (65), 92 (11), 91 (43) 89 (12%).

4.4.29. 5-Methyl-5,6,6a,7,8,9,10,10a-octahydrophosphanthridine-5-oxide ***(33a).*** This compound was prepared according to General Procedure C from [(1-hydroxy)cyclohexylmethyl)]methylphenylphosphine oxide (**33**) (0.054 g, 0.21 mmol) as a pale yellow oil; yield 0.013 g (27%). Isolated as a mixture of diastereomers (dr = 17:11:50:22); R_f (EtOAc/MeOH 9:1) 0.42.

δ_H (500 MHz, $CDCl_3$) (due to overlapping only selected peaks are described) 1.67 (3H, d, *J* 12.6 Hz) and 1.69 (3H, d, *J* 12.6 Hz) and 1.72 (3H, d, *J* 12.6 Hz) and 1.74 (3H, d, *J* 12.6 Hz); 2.41−2.46 (1H, m) and 2.51−2.59 (1H, m) and 2.76−2.86 (1H, m) and 2.88−2.94 (1H, m), 7.15−7.20 (1H, m), 7.21−7.25 (1H, m), 7.30−7.38 (2H, m), 7.39−7.46 (1H, m), 7.47−7.51 (1H, m), 7.75−7.82 (1H, m), 7.82−7.93 (1H, m); δ_P (202 MHz, $CDCl_3$) 26.73 and 28.50 and 30.62 and 32.71; GC t_R = 12.72 min; GC−MS (EI, 70 eV) m/z=234 (M^+) (83), 233 (38), 219 (20), 205 (39), 193 (21), 192 (38), 191 (98), 180 (23), 179 (100), 178 (14), 166 (17), 165 (47), 154 (11), 141 (16), 133 (21), 129 (26), 128 (32), 117 (12), 116 (28), 115 (52), 91 (30) 89 (10); and GC t_R = 12.84 min; GC−MS (EI, 70 eV) m/z= 234 (M^+) (65), 233 (21), 219 (17), 206 (11), 205 (34), 193 (15), 192 (100), 191 (19), 165 (12), 141 (11), 133 (13), 129 (21), 128 (20), 116 (13), 115 (27), 91 (14); and GC t_R = 12.88 min; GC−MS (EI, 70 eV) m/z=234 (M^+) (87), 233 (38), 219 (22), 206 (12), 205 (53), 193 (20), 192 (100), 191 (39), 180 (12), 165 (16), 143 (11), 141 (16), 133 (13), 129 (30), 128 (28), 116 (19), 115 (38), 91 (19); and GC t_R = 12.91 min; GC−MS (EI, 70 eV) m/z=234 (M^+) (89), 233 (42), 219 (17), 206 (15), 205 (61), 193 (24), 192 (100), 191 (48), 179 (14), 165 (15), 143 (11), 141 (18), 133 (16), 129 (30), 128 (26), 116 (17), 115 (33), 91 (21%).

Isolated single diastereomer: δ_H (500 MHz, $CDCl_3$) 1.27−1.56 (4H, m), 1.69 (3H, d, *J* 12.6 Hz), 1.72−1.77 (1H, m), 1.81−1.88 (1H, m), 1.88−2.01 (2H, m), 2.03−2.16 (1H, m), 2.16−2.27 (1H, m), 2.31−2.43 (1H, m), 2.45−2.63 (1H, m), 7.30−7.39 (1H, m), 7.40−7.53 (2H, m), 7.75−7.94 (1H, m); δ_C (126 MHz, $CDCl_3$) 17.7 (d, *J* 71.8 Hz), 25.8 (d, *J* 2.7 Hz), 26.6, 31.8, 34.8 (d, *J* 67.2 Hz), 34.9 (d, *J* 3.6 Hz), 36.6 (d, *J* 14.5 Hz), 44.8 (d, *J* 4.5 Hz), 126.5 (d, *J* 10.9 Hz), 126.6 (d, *J* 11.8 Hz), 130.4 (d, *J* 7.3 Hz), 131.1 (d, *J* 69.9 Hz), 131.7 (d, *J* 1.8 Hz), 145.6 (d, *J* 8.2 Hz); δ_P (202 MHz, $CDCl_3$) 26.70; GC t_R = 12.84 min; GC−MS (EI, 70 eV) m/z=234 (M^+) (65), 233 (21), 219 (17), 206 (11), 205 (34), 193 (15), 192 (100), 191 (19), 165 (12), 141 (11), 133 (13), 129 (21), 128 (20), 116 (13), 115 (27), 91 (14%).

4.4.30. 3,3-Dimethyl-1-phenylphosphindoline-1-oxide ***(37a).*** This compound was prepared according to General Procedure C from (2-hydroxy-2-methylpropyl)diphenylphosphine oxide (**37**) (0.116 g, 0.42 mmol) as a pale yellow solid; yield 0.09 g (79%); mp 104.8−106.1 °C; R_f (EtOAc/MeOH 9:1) 0.66; [Found C, 74.84; H, 6.52. $C_{16}H_{17}OP$ requires C, 74.99; H, 6.69%]; *v* max (ATR) 3054, 2964, 2909, 2862, 1589, 1445, 1439, 1264, 1195, 1138, 1109, 1066, 817, 771, 742, 698, 538, 499, 480; δ_H (500 MHz, $CDCl_3$) 1.44 (3H, s), 1.57 (3H, s), 2.19−2.32 (1H, m), 2.33−2.46 (1H, m), 7.34−7.41 (1H, m), 7.41−7.49 (3H, m), 7.49−7.54 (1H, m), 7.54−7.66 (4H, m); δ_C (126 MHz, $CDCl_3$) 30.9 (d, *J* 8.2 Hz), 33.2 (d, *J* 2.7 Hz), 42.0 (d, *J* 4.5 Hz), 43.7 (d, *J* 70.8 Hz), 123.8 (d, *J* 13.6 Hz), 127.8 (d, *J* 10.0 Hz), 128.5 (d, *J* 12.7 Hz), 128.9 (d, *J* 9.1 Hz), 131.0 (d, *J* 10.9 Hz), 131.7 (d, *J* 100.8 Hz), 131.7 (d, *J* 2.7 Hz), 133.2 (d, *J* 2.7 Hz), 133.7 (d, *J* 99.0 Hz), 157.3 (d, *J* 27.2 Hz); δ_P (202 MHz, $CDCl_3$) 48.53; GC t_R = 12.54 min; GC−MS (EI, 70 eV) m/z=257 (M^+) (16), 256 (95), 255 (70), 242 (16), 241 (100), 179

(11), 165 (16), 163 (49), 133 (24), 116 (24), 115 (38), 91 (23%). Analytical data are in accordance with those reported in the literature.[19,22]

4.4.31. 3,3-Dimethyl-1-tert-butylphosphindoline-1-oxide ***(38a).*** This compound was prepared according to General Procedure C from (2-hydroxy-2-methylpropyl)-*t*-butylphenylphosphine oxide (**38**) (0.102 g, 0.41 mmol) as a white solid; yield 0.06 g (61%); mp 101.6−103.4 °C; R_f (AcOEt/MeOH 9:1) 0.40; [Found C, 71.08; H, 8.81. $C_{14}H_{21}OP$ requires C, 71.16; H, 8.96%]; *v* max (ATR) 2951, 2900, 2864, 1593, 1469, 1440, 1363, 1269, 1186, 1155, 1137, 1064, 825, 763, 742, 625, 484; δ_H (500 MHz, $CDCl_3$) 1.19 (9H, d, *J* 14.8 Hz), 1.42 (3H, s), 1.44 (3H, s), 1.93−2.04 (1H, m), 2.04−2.13 (1H, m), 7.26−7.37 (2H, m), 7.46−7.52 (1H, m), 7.62−7.69 (1H, m); δ_C (126 MHz, $CDCl_3$) 24.6, 30.4 (d, *J* 8.2 Hz), 32.7 (d, *J* 69.0 Hz), 34.4 (d, *J* 1.8 Hz), 36.6 (d, *J* 62.7 Hz), 41.5 (d, *J* 2.7 Hz), 124.1 (d, *J* 11.8 Hz), 127.3 (d, *J* 10.0 Hz), 128.8 (d, *J* 8.2 Hz), 130.2 (d, *J* 90.8 Hz), 132.9 (d, *J* 1.8 Hz), 157.2 (d, *J* 25.4 Hz); δ_P (202 MHz, $CDCl_3$) 68.92; GC t_R = 10.17 min; GC−MS (EI, 70 eV) m/z=236 (M^+) (5), 181 (12), 180 (100), 179 (30), 165 (66), 147 (44), 133 (12), 115 (19%).

*4.4.32. 4,4-Dimethyl-1-phenyl-1,2,3,4-tetrahydrophosphinoline-1-oxide (****39a****).* This compound was prepared according to General Procedure C from (2-hydroxy-3-methylbutyl)diphenylphosphine oxide (**39**) (0.120 g, 0.42 mmol) as a pale yellow solid; yield 0.070 g (62%); mp 96.2−97.7 °C; R_f (AcOEt/MeOH 9:1) 0.60; [Found C, 75.73; H, 7.27. $C_{17}H_{19}OP$ requires C, 75.54; H, 7.08%]; *v* max (ATR) 3422, 3056, 2924, 2869, 1592, 1478, 1433, 1309, 1176, 1113, 1067, 881, 878, 746, 743, 697, 491; δ_H (500 MHz, $CDCl_3$) 1.41 (3H, s), 1.45 (3H, s), 1.89−2.04 (1H, m), 2.12−2.33 (2H, m), 2.36−2.49 (1H, m), 7.27−7.31 (1H, m), 7.40−7.46 (2H, m), 7.48−7.53 (3H, m), 7.56−7.65 (3H, m); δ_C (126 MHz, $CDCl_3$) 24.4 (d, *J* 69.0 Hz), 31.1, 31.1, 34.3 (d, *J* 4.5 Hz), 35.6 (d, *J* 5.4 Hz), 126.5 (d, *J* 10.9 Hz), 126.6 (d, *J* 9.1 Hz), 127.5 (d, *J* 96.3 Hz), 128.4 (d, *J* 11.8 Hz), 131.1 (d, *J* 10.0 Hz), 131.5 (d, *J* 2.7 Hz), 132.18 (d, *J* 2.7 Hz), 132.21 (d, *J* 7.3 Hz), 134.2 (d, *J* 100.8 Hz), 152.2 (d, *J* 8.2 Hz); δ_P (202 MHz, $CDCl_3$) 26.02; GC t_R = 13.64 min; GC−MS (EI, 70 eV) m/z=270 (M^+) (41), 269 (22), 256 (18), 255 (100), 227 (13), 179 (48), 149 (13), 140 (40), 133 (12), 131 (11), 130 (18), 129 (20), 128 (14), 125 (13), 116 (12), 115 (25), 91 (22), 77 (19), 51 (12), 47 (30%). Analytical data are in accordance with those reported in the literature.[11b]

4.4.33. 1-t-Butyl-4,4-dimethyl-1,2,3,4-tetrahydrophosphinoline-1-oxide ***(40a).*** This compound was prepared according to General Procedure C from (2-hydroxy-3-methylbutyl)-*t*-butylphenylphosphine oxide (**40**) (0.118 g, 0.44 mmol) as a pale yellow sticky solid; yield 0.103 g (93%); R_f (AcOEt/MeOH 9:1) 0.38; [Found C, 71.83; H, 9.14. $C_{15}H_{23}OP$ requires C, 71.97; H, 9.26%]; *v* max (ATR) 3409, 2958, 2865, 1475, 1363, 1148, 1105, 901, 872, 817, 764, 741, 669, 626, 478; δ_H (500 MHz, $CDCl_3$) 1.21 (9H, d, *J* 14.2 Hz), 1.31 (3H, s), 1.37 (3H, s), 1.88−2.05 (2H, m), 2.15−2.33 (2H, m), 7.27−7.34 (1H, m), 7.41−7.51 (2H, m), 7.79−7.91 (1H, m); δ_C (126 MHz, $CDCl_3$) 19.2 (d, *J* 61.8 Hz), 25.2, 29.7, 31.8, 33.4 (d, *J* 69.9 Hz), 34.2 (d, *J* 4.5 Hz), 35.4 (d, *J* 4.5 Hz), 125.7 (d, *J* 10.0 Hz), 126.8 (d, *J* 86.3

Hz), 126.7 (d, *J* 9.1 Hz), 131.6 (d, *J* 2.7 Hz), 131.9 (d, *J* 6.4 Hz), 152.2 (d, *J* 6.4 Hz); δ_P (202 MHz, $CDCl_3$) 38.94; GC t_R = 11.55 min; GC−MS (EI, 70 eV) m/z=250 (M^+) (3), 195 (13), 194 (100), 193 (51), 179 (93), 166 (19), 165 (15), 161 (11), 152 (11), 151 (22), 147 (15), 133 (19), 131 (10), 129 (16), 128 (14), 116 (11), 115 (24), 91 (16%).

4.4.34. 1,3,3-Trimethyl-1-oxa-1-phospha-2,3-dihydrophenalene ***(41a).*** This compound was prepared according to General Procedure C from (2-hydroxy-2-methylpropyl)methyl-1-naphthylphosphine oxide (**41**) (0.152 g, 0.58 mmol) as a pale yellow solid; yield 0.107 g (76%); mp 164.1−165.7 °C ; R_f (AcOEt/MeOH 9:1) 0.23; [Found C, 73.82; H, 7.08. $C_{15}H_{17}OP$ requires C, 73.76; H, 7.01%]; *v* max (ATR) 3382, 3042, 2959, 2918, 1496, 1464, 1334, 1295, 1181, 1149, 1065, 892, 834, 783, 762, 510, 435; δ_H (500 MHz, $CDCl_3$) 1.61 (3H, s), 1.65 (3H, s), 1.75 (3H, d, *J* 12.6 Hz), 2.24 (1H, dd, *J* 14.8 Hz, *J* 5.0 Hz), 2.47 (1H, dd, *J* 8.0 Hz, *J* 15.1 Hz), 7.44−7.54 (1H, m), 7.56−7.62 (1H, m), 7.64 (1H, d, *J* 7.3 Hz), 7.77 (1H, d, *J* 7.9 Hz), 8.02 (1H, d, *J* 8.2 Hz), 8.09 (1H, dd, *J* 14.0 Hz, *J* 7.1 Hz); δ_C (126 MHz, $CDCl_3$) 18.8 (d, *J* 72.7 Hz), 32.4 (d, *J* 6.4 Hz), 32.9 (d, *J* 12.7 Hz), 36.2 (d, *J* 4.5 Hz), 40.3 (d, *J* 66.3 Hz), 123.9, 124.9 (d, *J* 12.7 Hz), 126.1, 127.6, 128.1 (d, *J* 93.5 Hz), 129.6, 129.7 (d, *J* 6.4 Hz), 133.2 (d, *J* 2.7 Hz), 133.7 (d, *J* 9.1 Hz), 142.9 (d, *J* 6.4 Hz); δ_P (202 MHz, $CDCl_3$) 24.37; GC t_R = 13.24 min; GC−MS (EI, 70 eV) m/z=244 (M^+) (22), 229 (53), 181 (20), 180 (54), 173 (16), 167 (41), 166 (17), 165 (59), 153 (10), 152 (34), 115 (12), 78 (100).

4.4.35. 3-Ethyl-1,3-dimethyl-1-oxa-1-phospha-2,3-dihydrophenalene ***(42a).*** This compound was prepared according to General Procedure C from (2-hydroxy-3-methylpropyl)methyl-1-naphthylphosphine oxide (**42**) (0.094 g, 0.34 mmol) as a yellow sticky solid; yield 0.010 g (12%). Isolated as a mixture of diastereomers (dr = 62.5:37.5).

Major diastereomer: R_f (AcOEt/MeOH 9:1) 0.30; δ_H (500 MHz, $CDCl_3$) 0.76 (3H, t, *J* 7.3 Hz), 1.61 (3H, s), 1.74 (3H, d, *J* 12.9 Hz), 1.89−2.04 (2H, m), 2.16−2.23 (1H, m), 2.53−2.66 (1H, m), 7.49−7.55 (1H, m), 7.57−7.60 (1H, m), 7.60−7.65 (1H, m), 7.77−7.83 (1H, m), 8.03−8.07 (1H, m), 8.07−8.16 (1H, m); δ_C (126 MHz, $CDCl_3$) 9.1, 19.3 (d, *J* 74.5 Hz), 28.8 (d, *J* 12.7 Hz), 35.6 (d, *J* 5.4 Hz), 38.6 (d, *J* 66.3 Hz), 39.6, 125.0, 125.2, 125.8, 127.7, 128.2 (d, *J* 92.6 Hz), 129.9 (d, *J* 6.4 Hz), 133.3 (d, *J* 2.7 Hz), 133.8 (d, *J* 9.1 Hz), 141.6 (d, *J* 6.4 Hz); δ_P (202 MHz, $CDCl_3$) 24.52; GC t_R = 11.63 min; GC−MS (EI, 70 eV) m/z=258 (M^+) (38), 243 (27), 230 (15), 229 (100), 215 (13), 194 (18), 181 (30), 180 (23), 179 (10), 167 (33), 166 (19), 165 (70), 153 (16), 152 (43), 121 (11%).

Minor diastereomer: R_f (AcOEt/MeOH 9:1) 0.30; δ_H (500 MHz, $CDCl_3$) 0.95 (3H, t, *J* 7.4 Hz), 1.62 (3H, s), 1.75−1.82 (3H, m), 1.85 (3H, d, *J* 12.9 Hz), 2.15−2.22 (1H, m), 7.48−7.55 (1H, m), 7.56−7.60 (1H, m), 7.60−7.66 (1H, m), 7.77−7.84 (1H, m), 8.02−8.07 (1H, m), 8.07−8.16 (1H, m); δ_C (126 MHz, CDCl*3*) 8.8, 18.7 (d, *J* 70.8 Hz), 31.3 (d, *J* 6.4 Hz), 36.0 (d, *J* 50.9 Hz), 36.3 (d, *J* 5.4 Hz), 39.6, 124.9, 125.1, 126.1, 128.0 (d, *J* 92.6 Hz), 127.7, 129.7 (d, *J* 6.4 Hz), 133.5 (d, *J* 2.7 Hz), 134.0 (d, *J* 9.1 Hz), 141.3 (d, *J* 6.4 Hz); δ_P (202 MHz, $CDCl_3$) 25.18ppm. GC t_R = 11.88 min; GC−MS (EI, 70 eV)

m/z=258 (M^+) (20), 243 (13), 230 (19), 229 (100), 194 (32), 181 (11), 167 (21), 166 (13), 165 (48), 153 (10), 152 (27), 115 (12%);

v max (ATR) for a mixture of diastereomers: 3396, 2963, 2920, 2873, 1635, 1497, 1457, 1295, 1172, 1141, 995, 893, 826, 775, 431.

4.4.36. 7,10,10-Trimethyl-7-oxa-7-phospha-7,8,9,10-tetrahydrocyclohepta[de]naphthalene ***(42b).*** This compound was prepared according to General Procedure C from (2-hydroxy-3-methylpropyl)methyl-1-naphthylphosphine oxide (**42**) (0.094 g, 0.34 mmol) as a yellow sticky solid; yield 0.012 g (14%); R_f (AcOEt/MeOH 9:1) 0.21; [Found C, 74.59; H, 7.62. $C_{16}H_{19}OP$ requires C, 74.40; H, 7.41%]; δ_H (500 MHz, $CDCl_3$) 1.72 (3H, s), 1.76 (3H, d, *J* 12.9 Hz), 1.77 (3H, s), 2.02-2.22 (2H, m), 2.22-2.40 (2H, m), 7.50-7.56 (2H, m), 7.79-7.89 (3H, m), 8.46-8.52 (1H, m); δ_C (126 MHz, $CDCl_3$) 17.1 (d, *J* 70.8 Hz), 22.0 (d, *J* 71.8 Hz), 29.3, 30.2, 37.1 (d, *J* 5.4 Hz), 38.8 (d, *J* 3.6 Hz), 125.45, 125.50 (d, *J* 6.6 Hz), 126.7, 127.8 (d, *J* 94.5 Hz), 127.6, 128.3 (d, *J* 10.0 Hz), 129.7, 131.0 (d, *J* 10.0 Hz), 132.4 (d, *J* 5.4 Hz), 147.9 (d, *J* 6.4 Hz); δ_P (202 MHz, $CDCl_3$) 31.44; GC t_R = 14.70 min; GC−MS (EI, 70 eV) m/z=258 (M^+) (41), 257 (30), 244 (17), 243 (100), 215 (11), 181 (22), 180 (34), 179 (31), 178 (16), 166 (29), 165 (62), 153 (21), 152 (35), 141 (11), 128 (19), 121 (11), 115 (15), 78 (19), 63 (21%).

4.5. 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/....

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4.7. References and notes

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