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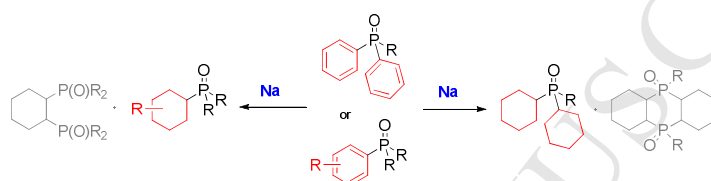
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## Graphical Abstract

**The reactivity of arylphosphine oxides under  
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 Ewelina Korzeniowska<sup>a</sup>, Anna E. Koziol<sup>b</sup>, Elżbieta Łastawiecka<sup>a</sup>, Anna Flis<sup>a</sup>, Marek Stankevič<sup>a,\*</sup>
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- 24 examples, up to 78% yield
- inexpensive Na as a reducing agent
- transition metal-free, convenient procedure under mild reaction conditions
- inexpensive, readily available reactants, broad substrate scope



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# The reactivity of arylphosphine oxides under Bouveault-Blanc reaction conditions

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## ABSTRACT

Treatment of tertiary arylphosphine oxides with alkali metal/alcohol reagent system lead to the corresponding cyclohexyl-substituted phosphine oxides. This transformation makes use of the inexpensive sodium as the electron donor and an alcohol as the proton source, and provides an attractive alternative to reactions mediated by expensive transition metals. Under optimized conditions numerous mono- and diaryl substituted phosphine oxides were transformed into the corresponding mono- and dicyclohexyl-substituted phosphine oxides in good yields. Furthermore, the formation of 1,2-bis(phosphinoyl)cyclohexanes or unknown 5,10-dialkyltetradecahydrophosphanthrene 5,10-dioxides as side products was observed, which are hardly accessible by other procedures.

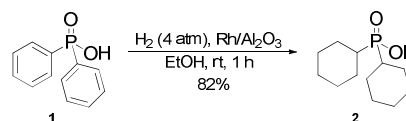
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## 1. Introduction

Molecules with incorporated cyclohexane frameworks are very popular in organic chemistry and can be found in many useful substances such as natural products, pharmaceuticals or fuel.<sup>1</sup> One of the possible substrates of these compounds could be the corresponding aromatic compounds which upon treatment with a hydrogen source should undergo saturation of the aromatic ring. Transformation of arenes into the corresponding cycloalkanes could be achieved by three different pathways: reduction with metal hydrides,<sup>2</sup> Birch reduction<sup>3</sup> or catalytic heterogeneous hydrogenation.<sup>4</sup> The use of metal hydrides is usually associated with the formation of large amount of metal salts, while Birch reduction of arenes lead to 1,4-cyclohexadienes which should be further hydrogenated using classic catalysts. From synthetic point of view, catalytic hydrogenation is up to now the most convenient way for the transformation of arenes into cycloalkanes.<sup>4</sup> However, the catalysts used in these reactions are usually active only under high pressures and temperatures, although some progress has been made when using nanoparticle catalysts<sup>5</sup> or water as a solvent.<sup>6</sup>

In the case of functionalized arenes, catalytic hydrogenation might be a good choice if the corresponding cycloalkanes are the target molecules. The examples include hydrogenation of phenols,<sup>4d,6b</sup> simple alkyl-substituted arenes,<sup>6a</sup> phenylalanine and phenylglycine derivatives<sup>7</sup> or monosubstituted benzenes.<sup>5b</sup> Contrary to this, hydrogenation

of the aryl fragment in arylphosphorus compounds is relatively underexplored. The first attempted hydrogenation of arylphosphinic and arylphosphonic acids was performed by Freedman and coworkers who used Rh/Al<sub>2</sub>O<sub>3</sub> as a catalyst (Scheme 1).<sup>8</sup> Other catalysts used in hydrogenation of aryl substituents in organophosphorus compounds, such as Ru/C, Raney-Ni or Nb(p-TolCH<sub>2</sub>)<sub>3</sub>(2,6-Ph<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>O)<sub>2</sub>, appeared to exhibit good activity and selectivity towards complete hydrogenation of aromatic groups.<sup>9</sup>

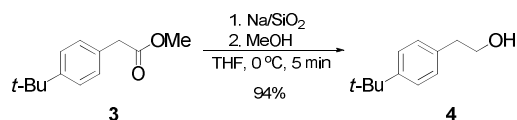


Scheme 2. Hydrogenation of phenyl substituents in 1.

Reductive dearomatization of arylphosphorus compounds using alkali metals in liquid ammonia could also be regarded as a method for transformation of aryl substituents into their cycloalkyl analogues.<sup>10</sup> Two isolated double bonds in the formed 1,4-cyclohexadiene unit are far more reactive towards hydrogenation than the parent aryl substituent. Despite the obvious advantages of this reaction the main drawback is the use of ammonia due to its irritant odor. Therefore, it would be desirable to develop alternative reaction conditions for Birch reduction where ammonia is replaced by a more friendly solvent. It seems that a good alternative here would be Bouveault-Blanc reduction, a reaction based on the reduction of carboxylic acid

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esters to the corresponding primary alcohols with an alkali metal in alcohol (Scheme 2).<sup>11</sup>



Scheme 2. Bouveault-Blanc reduction of **3**.

To the best of our knowledge, no examples of the reduction of other classes of organic compounds under these conditions have been reported.

## 2. Results and discussion

An obvious advantage of Bouveault-Blanc reduction over Birch reduction is the use of readily available and more manipulation-friendly alcohols compared to ammonia. Regarding this, we decided to check the reactivity of a simple tertiary phosphine oxide under Bouveault-Blanc reduction. For initial screening, *t*-butylmethylphenylphosphine oxide (**5**) was used as a model compound (Table 1).

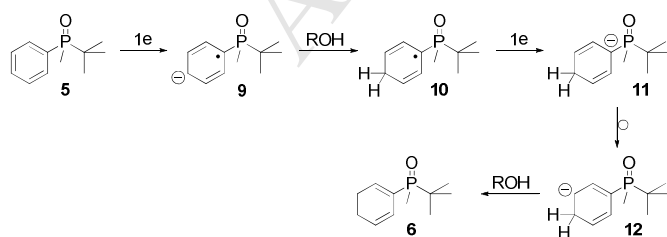
Table 1

The reactivity of **5** under Bouveault-Blanc reduction.

Entry	Conditions	Products <sup>a</sup>		
		6	7	8
1	EtOH, rt, 1 h	22%	-	-
2	<i>n</i> -BuOH, rt, 0.5 h	30%	11%	4%
3	<i>i</i> -PrOH, rt, 1 h	23%	-	-
4	<i>i</i> -PrOH, rt, 2 h	16%	-	-
5	<i>i</i> -PrOH, rt, 3 h	26%	-	-
6	<i>i</i> -PrOH, rt, 4 h	22%	-	-
7	<i>i</i> -PrOH, rt, 22 h	12%	-	-

[a] Yields based on NMR analysis of the reaction mixtures.

Addition of sodium into a solution of **5** in ethanol led to a vigorous evolution of gas which ceased in ca. 5 min (Table 1, Entry 1). The analysis of the reaction mixture revealed the presence of phosphine oxide **6** as the only reaction product but the overall conversion was moderate. This compound is most probably formed by *in situ* reduction of phenyl substituent by metallic sodium followed by double bond migration and protonation of the carbanion (Scheme 3).



Scheme 3. Plausible mechanism for the formation of **6**.

Further efforts were put towards the optimization of the reaction conditions. Replacement of ethanol with *n*-BuOH led to a quite striking change in the product composition (Table 1, Entry 2). Apart from **6**, the presence of *t*-butyl(cyclohex-3-

enyl)methylphosphine oxide **7** has been observed which suggests that compound **6** undergoes saturation of conjugated double bond in the presence of an excess of an alkali metal. However, the most intriguing was the presence of trialkylphosphine oxide **8** where the phenyl group underwent complete saturation under the reaction conditions. This reaction could be regarded as the first example of transition metal and hydrogen-free arene hydrogenation. Here, an alkali metal serves as the electron source and the alcohol is the proton source.

Contrary to *n*-BuOH, the use of *i*-PrOH led to a complete shift of the selectivity towards monohydrogenation product **6**, although the conversions were usually low. One of the reasons for the incomplete conversion of **5** might be the loss of an alkali metal due to its reaction with an excess of an alcohol present in the reaction. Therefore, a slight modification of the reaction conditions was proposed. In this case, the reaction was undertaken in THF as a solvent and 6-fold excess of both alkali metal and *i*-PrOH was used (Table 2).

Table 2

Optimization of reduction conditions for **5**.

Entry	Na (equiv.)	ROH (equiv.)	Time (h)	Products	
				7	8
1	6.0	<i>i</i> -PrOH (6.0)	48	37%	57%
2	10.0	<i>i</i> -PrOH (6.0)	48	40%	60%
3	6.0	<i>i</i> -PrOH (6.0)	1	34%	66%
4	6.0	<i>i</i> -PrOH (6.0)	2	33%	67%
5	6.0	<i>i</i> -PrOH (6.0)	3	30%	70%
6	6.0	<i>i</i> -PrOH (6.0)	4	30%	70%
7	6.0	<i>s</i> -BuOH (6.0)	4	28%	72%
8	6.0	<i>t</i> -BuOH (6.0)	4	30%	70%
9	6.0	<i>t</i> -BuOH (6.0)	24	28%	72%

[a] Conversions based on NMR analysis.

Under these conditions the main product was fully saturated phosphine oxide **8** along with a remarkable amount of cyclohexenylphosphine oxide **7** which suggests the crucial influence of the amount of used alcohol on the selectivity of the reaction.

It appeared also that the reaction selectivity can be modified slightly by modification of the reaction conditions. The highest conversion of **5** into **8** was observed after 4 h at 50 °C; the reaction temperature was raised in order to shorten the reaction time. The use of different alcohols had some influence on the selectivity of the reaction; the use of *s*-BuOH or *t*-BuOH led to the formation of minor amounts of unidentified by-products. On the other hand, an increase of the amount of alkali metal had no influence on the selectivity of the reaction.

To test the utility of the optimized reaction conditions a set of tertiary phosphine oxides was submitted to the modified Bouveault-Blanc reduction. First, dialkylphenylphosphine oxides were used as substrates (Table 3).

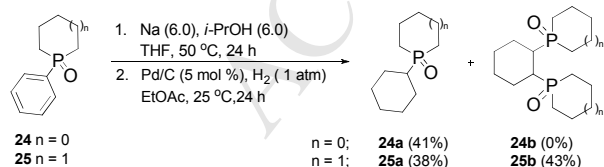
**Table 3**  
Reduction of dialkylphenylphosphine oxides.

Entry	Substrate	R <sup>1</sup>	R <sup>2</sup>	Products	
1	<b>13</b>	Me	Me	<b>13a</b> (45%)	<b>13b</b> (26%)
2	<b>14</b>	Et	Et	<b>14a</b> (38%)	-
3	<b>15</b>	<i>n</i> -Bu	<i>n</i> -Bu	<b>15a</b> (39%)	<b>15b</b> (22%)
4	<b>16</b>	<i>n</i> -Pr	<i>n</i> -Pr	<b>16a</b> (23%)	<b>16b</b> (11%)
5	<b>17</b>	<i>i</i> -Pr	<i>i</i> -Pr	<b>17a</b> (78%)	-
6	<b>18</b>	<i>c</i> -Pen	<i>c</i> -Pen	<b>18a</b> (62%)	-
7	<b>19</b>	Bn	Bn	<b>19a</b> (21%)	-
8	<b>20</b>	Bn	Me	<b>20a</b> (23%)	-
9	<b>21</b>	Bn	<i>n</i> -Bu	<b>21a</b> (31%)	-
10	<b>22</b>	Bn	<i>i</i> -Pr	<b>22a</b> (28%)	-
11	<b>23</b>	Bn	<i>t</i> -Bu	<b>23a</b> (49%)	-
12	<b>5</b>	Me	<i>t</i> -Bu	<b>8</b> (71%)	<b>5b</b> (4%) <sup>b</sup>

[a] Yield of isolated products. [b] A mixture of two isomers.

It was a pleasure to conclude that all reductions took place smoothly and afforded complete conversion of substrates within 4 h. Unfortunately, small amounts of unsaturated by-products were observed even after 24 h. To simplify the products isolation the crude reaction mixtures were submitted to hydrogenation in the presence of Pd/C. For the symmetrically substituted substrates **13-19** the reaction afforded the corresponding saturated products with moderate to good yields (Table 3, entries 1-7). Surprisingly, the reduction of phosphine oxides possessing Me, *n*-Bu and *n*-Pr substituents at phosphorus gave substantial amounts of 1,2-bis(phosphinoyl)cyclohexanes as byproducts (Table 3, entries 1, 3 and 4). When unsymmetrically substituted phosphine oxides were used, the formation of trialkylphosphine oxides was observed with moderate yields (Table 3, entries 8-11).

For a comparison, two cyclic phosphine oxides have been submitted to the reaction with the Na/*i*-PrOH system (Scheme 4).



**Scheme 4.** The reactivity of cyclic phosphine oxides **24** and **25**.

Upon treatment with the reagent mixture, phenylphospholane oxide (**24**) cleanly yielded the reduction product **24a**. On the other hand, the reduction of 1-phenylphosphorinane-1-oxide (**25**) took place smoothly affording a mixture of the expected 1-cyclohexylphosphorinane-1-oxide (**25a**) and the corresponding diphosphine dioxide **25b** with comparable yields.

Next, alkylidiphenylphosphine oxides were submitted to the reaction under modified Bouveault-Blanc reaction conditions (Table 4).

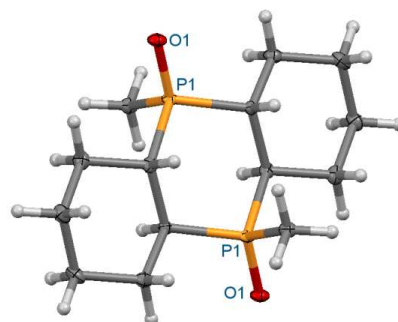
**Table 4**  
Reduction of alkylidiphenylphosphine oxides.

Entry	Substrate	R	Products		
1	<b>26</b>	Me	<b>26a</b> (17%)	<b>26b</b> (42%) <sup>b</sup>	(4:3:3:13%) <sup>c</sup>
2	<b>27</b>	<i>n</i> -Bu	<b>27a</b> (24%)	<b>27b</b> (40%; 4 isomers) <sup>b</sup>	
3	<b>28</b>	<i>i</i> -Pr	<b>28a</b> (45%)	<b>28b</b> (30%; 4 isomers) <sup>b</sup>	
4	<b>29</b>	<i>c</i> -Pen	<b>29a</b> (23%)	<b>29b</b> (33%; 4 isomers) <sup>b</sup>	(5%) <sup>c</sup>

[a] Yield of isolated product; [b] Yields based on NMR analysis of the reaction mixtures; [c] Yield of isolated isomers

For these substrates, the 12-fold excess of both sodium and *i*-PrOH was used. As can be seen from Table 4, phosphine oxides **26-29** can be directly transformed into dicyclohexylphosphine oxides **26a-29a** but with low to moderate yield. Surprisingly, the formation of different products as a mixture of four isomers has been observed under the reaction conditions. NMR and HRMS analysis of these compounds allowed to ascribe their structure as 5,10-dialkyltetradecahydrophosphanthrene 5,10-dioxides **26b-29b**.

One isomer of **26b**, which could be obtained in a crystalline form, has been subjected to an X-ray structural analysis. The molecular structure of this isomer is given in Fig. 1.



**Fig. 1.** X-ray structure of one of the isomers of **26b-F3** (CCDC No. 1537702).

The X-ray analysis of **26b-F3** confirmed the predicted 5,10-dialkyltetradecahydrophosphanthrene 5,10-dioxide structure of the molecule. As it can be seen from the Figure 1, the tricyclic structure possess *trans* arrangement of the bridgehead carbon atoms and also both methyl groups at phosphorus atoms. It could be assumed that the remaining three isomers should also possess *trans* arrangement of bridgehead carbon atoms and methyl groups could be either in *cis* or *trans* mutual correlation.

Next, a set of reactions has been performed with dialkylarylphosphine oxides possessing different substitution pattern in aryl fragment (Table 5).

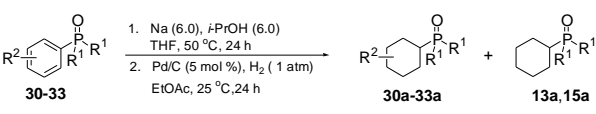
In this case, the applied reduction protocol for (methylphenyl)-substituted phosphine oxides afforded the



corresponding methyl-substituted cyclohexylphosphine oxides with good yield as mixtures of isomers (Table 5, entries 3 and 4). Substrates possessing anisyl substituents at phosphorus (**30** and **33**) underwent additional C-OMe bond cleavage leading to overall low yields of desired isomeric products and predominant formation of **13a** and **15a** (Table 5, entries 1 and 2).

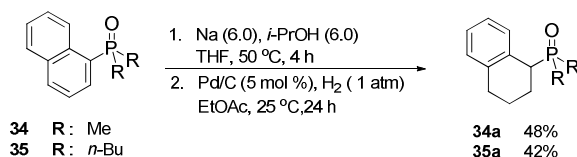
**Table 5**

The reactivity of dialkylarylphosphine oxides **30-33**.

				
Entry	Substrate	Aryl	R <sup>1</sup>	Yield <sup>a</sup>
1	<b>30</b>	<i>m</i> -OMe-C <sub>6</sub> H <sub>4</sub>	Me	<b>30a</b> (30%) (1:6.2) <sup>b</sup> <b>13a</b> (33%)
2	<b>31</b>	<i>p</i> -OMe-C <sub>6</sub> H <sub>4</sub>	<i>n</i> -Bu	<b>31a</b> (10%) (1:3.2) <sup>b</sup> <b>15a</b> (56%)
3	<b>32</b>	<i>p</i> -Me-C <sub>6</sub> H <sub>4</sub>	<i>n</i> -Bu	<b>32a</b> (74%) (1:1.7) <sup>b</sup>
4	<b>33</b>	3,5-Me <sub>2</sub> -C <sub>6</sub> H <sub>3</sub>	<i>n</i> -Bu	<b>33a</b> (77%) (1:1.7:2) <sup>b</sup>

[a] Yield of isolated products; [b] isomers ratio was determined by <sup>31</sup>P NMR analysis of crude reaction mixture.

Finally, it was decided to submit phosphine oxides with naphthyl substituent at phosphorus to the modified Bouveault-Blanc reduction (Scheme 5).



**Scheme 5.** The reduction of naphthylphosphine oxides **34** and **35**.

Here, the formation of partially saturated compounds **34a** and **35a** has been observed. The aryl fragment bonded directly to the phosphorus group underwent reduction whereas the non-conjugated arene ring remained unchanged under the reaction conditions.

### 3. Conclusions

In conclusion, an alternative method for arene saturation in phosphorus-substituted arenes has been presented. The modified Bouveault-Blanc reduction of arylphosphine oxides led to the formation of the corresponding cyclohexylphosphine oxides as the main products. The developed method practically excludes the use of expensive transition metals as catalysts and H<sub>2</sub> gas as hydrogen source.

## 4. Experimental section

### 4.1. General remarks

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 and extraction were commercially available and used as received without further purification. Tetrahydrofuran was dried over sodium/benzophenone ketyl. Sodium (ingot) was commercially available and used as received.

The NMR spectra was recorded with 500 MHz spectrometer in CDCl<sub>3</sub> as a solvent at room temperature unless otherwise

noted. Chemical shifts (δ) are given in ppm relative to residual CHCl<sub>3</sub>. The following abbreviations are used in reporting NMR data: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Coupling constants (*J*) are in Hz. High-resolution mass spectrometry analyses were obtained using LCMS IT-TOF spectrometer. Mass spectra were recorded with GC-MS spectrometer working in electron ionization (EI) mode. Thin layer chromatography (TLC) was performed with precoated silica gel plates and visualized by potassium permanganate (KMnO<sub>4</sub>) stain. The reaction mixtures were purified by column chromatography over silica gel (60–240 mesh). Melting points were determined in a capillary tube.

### 4.2. Synthesis of Substrates

#### 4.2.1. Tertiary Dialkylarylphosphine Oxides

*t*-Butylmethylphenylphosphine oxide (**5**) was prepared according to literature procedure.<sup>12</sup> The symmetrically substituted substrates **13-18** were prepared according to general procedure described below.

Into a flame-dried two-necked flask equipped with magnetic stirrer and argon inlet was placed Grignard or organolithium reagent (15 mmol) in dry and degassed THF (30 mL). The mixture was cooled to 0 °C or -78 °C and phenylphosphonic dichloride (6 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for overnight under argon atmosphere. The mixture was cooled to 0 °C and hydrogen peroxide (30% in H<sub>2</sub>O<sub>2</sub>; 2.5 equiv.) was added slowly via syringe, allowed to warm to room temperature and stirred for 2 h. The reaction was quenched by addition of saturated NH<sub>4</sub>Cl solution (20 mL), the mixture was extracted with DCM (3×50 mL), the organic layers were collected, dried over MgSO<sub>4</sub>, filtered, and evaporated. The residue was purified by flash chromatography using chloroform/methanol 15:1 as eluent.

Analytical data for dimethylphenylphosphine oxide (**13**),<sup>10b</sup> di-*n*-propylphenylphosphine oxide (**16**),<sup>13</sup> dicyclopentylphenylphosphine oxide (**18**),<sup>14</sup> diethylphenylphosphine oxide (**14**), di-*n*-butylphenylphosphine oxide (**15**) and di-*i*-propylphenylphosphine oxide (**17**)<sup>15</sup> are in accordance with previously reported.

Dibenzylphenylphosphine oxide (**19**), benzylmethylphenylphosphine oxide (**20**), benzyl(*t*-butyl)phenylphosphine oxide (**23**) were prepared according to the literature procedure.<sup>10b</sup>

Benzyl(*n*-butyl)phenylphosphine oxide (**21**) and benzyl(*i*-propyl)phenylphosphine oxide (**22**) were prepared as follows:

Into a flame-dried two-necked flask equipped with magnetic stirrer and argon inlet was placed benzylphenylphosphine oxide (1.080 g, 5 mmol) in dry and degassed THF (15 mL). The mixture was cooled to 0 °C and sodium hydride (0.22 g, 5.5 mmol, 60% dispersion in mineral oil) was added in one portion. After the evolution of hydrogen ceased, the appropriate alkyl halide (*n*-bromobutane or *i*-propyl bromide) (5.5 mmol) was added in one portion and the reaction was allowed to reach room temperature and stirred for overnight under argon. The reaction was quenched by addition of saturated NH<sub>4</sub>Cl solution (10 mL), the mixture was extracted with DCM (3 × 30 mL), the organic layers were collected, dried over MgSO<sub>4</sub>, filtered and evaporated. The residue was purified by flash chromatography using chloroform:methanol 15:1 as eluent. Analytical data for benzyl(*n*-butyl)phenylphosphine oxide (**21**) are in accordance with those reported earlier.<sup>16</sup>

#### 4.2.1.1. Benzyl(*i*-propyl)phenylphosphine oxide (**22**)

Yield: 0.337 g (26%). White solid, mp = 121-122 °C,  $R_f$  = 0.70 (CHCl<sub>3</sub>/MeOH = 15:1) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.06 (dd,  $J_{H-H}$  = 6.9 Hz,  $J_{P-H}$  = 16.4 Hz, 3H), 1.29 (dd,  $J_{H-H}$  = 7.3 Hz,  $J_{P-H}$  = 15.8 Hz, 3H), 2.09-2.21 (m, 1H), 3.30-3.48 (m, 2H), 7.09-7.15 (m, 2H), 7.15-7.25 (m, 3H), 7.39-7.45 (m, 2H), 7.47-7.53 (m, 1H), 7.54-7.61 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 15.0 (d,  $J_{P-C}$  = 3.6 Hz), 15.8 (d,  $J_{P-C}$  = 2.7 Hz), 26.9 (d,  $J_{P-C}$  = 69.0 Hz), 35.4 (d,  $J_{P-C}$  = 59.0 Hz), 126.7, 128.2 (d,  $J_{P-C}$  = 10.9 Hz), 128.4 (d,  $J_{P-C}$  = 2.7 Hz), 129.8 (d,  $J_{P-C}$  = 5.5 Hz), 131.2 (d,  $J_{P-C}$  = 8.2 Hz), 131.5. <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 43.78. GC  $t_R$  = 13.78 min; GCMS (EI, 70 eV),  $m/z$  258 (M) (24), 257 (39), 167 (53), 125 (100), 109 (10), 105 (13), 92 (10), 91 (85), 77 (13), 65 (24), 47 (49). HRMS (ESI):  $m/z$  = 259.1236 [C<sub>16</sub>H<sub>19</sub>OP+H]<sup>+</sup>,  $m/z$  (calc'd) = 259.1246, diff. = -3.86 ppm.

Cyclic 1-phenylphospholane oxide (**24**)<sup>17</sup> and 1-phenylphosphorinane-1-oxide (**25**)<sup>18</sup> were synthesized according to reported procedures. Analytical data match previously reported values.

#### 4.2.2. Tertiary Alkyldiarylphosphine Oxides

The diphenylphosphine oxides **26-29** were prepared according to general procedure described below.

Into a flame-dried two-necked flask equipped with magnetic stirrer and argon inlet was placed chlorodiphenylphosphine (6 mmol) in dry and degassed THF (30 mL). The mixture was cooled to 0 °C and Grignard or organolithium reagent (7.5 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for overnight under argon atmosphere. The mixture was cooled to 0 °C and hydrogen peroxide (30% in H<sub>2</sub>O<sub>2</sub>; 2.5 equivalents) was added slowly via syringe and allowed to warm to room temperature and stirred for 2 h. The reaction was quenched by addition of saturated NH<sub>4</sub>Cl solution (20 mL), the mixture was extracted with DCM (3×50 mL), the organic layers were collected, dried over MgSO<sub>4</sub>, filtered, and evaporated. Analytical data for methyldiphenylphosphine oxide (**26**)<sup>19</sup>, *n*-butyldiphenylphosphine oxide (**27**), *i*-propyldiphenylphosphine oxide (**28**)<sup>20</sup> and cyclopentyldiphenylphosphine oxide (**29**)<sup>21</sup> are in accordance with previously reported.

The dialkylarylphosphine oxides possessing different substitution pattern in aryl fragment such as di-*n*-butyl(3-methoxyphenyl)phosphine oxide (**30**), di-*n*-butyl(4-methoxyphenyl)phosphine oxide (**31**), di-*n*-butyl(4-methylphenyl)phosphine oxide (**32**), di-*n*-butyl(3,5-dimethylphenyl)phosphine oxide (**33**), dimethyl(naphthalen-1-yl)phosphine oxide (**34**) and di-*n*-butyl(naphthalen-1-yl)phosphine oxide (**35**) were prepared following the synthetic procedure developed in our laboratory.

#### 4.3. General experimental procedure for the reduction of phosphine oxides with Na/*i*-PrOH system

In a flame-dried Schlenk tube (20 mL) equipped with magnetic stirrer and an inert gas inlet a substrate (0.3-1 mmol) was dissolved in 3-10 mL of dry THF. To this solution was added (6 or 12 equiv) of *i*-PrOH followed by (6 or 12 equiv) of sodium and the reaction mixture was heated at 50 °C for 24 h. The reaction was then quenched with sat. NaCl (5 mL) and extracted with DCM (3×20 mL). The combined organic phases were dried over MgSO<sub>4</sub>, filtered, and evaporated under the reduced pressure. The obtained residue and Pd/C (5 mol%) were placed in a flame-dried Schlenk tube (20 mL) under argon. Dry EtOAc was added (5 mL, the reaction vessel was evacuated three times and filled with hydrogen, and the reaction mixture was

stirred under hydrogen (1 atm), at room temperature for 24 h.

After this time, the reaction mixture was then filtered through Celite, which was washed with DCM (2×20 mL) and solvent was evaporated under reduced pressure. The product was purified by silica-gel column chromatography (CHCl<sub>3</sub>/MeOH 15/1).

#### 4.3.1. *t*-Butyl(cyclohex-2-en-1-yl)methylphosphine oxide (**7**)

This compound was formed during the first step of general procedure from *t*-butylmethylphenylphosphine oxide (**5**). The two diastereoisomers in a 1:1 ratio were isolated as an inseparable mixture with **8**, yield: 16%.  $R_f$  = 0.26 (CHCl<sub>3</sub>/MeOH = 15:1) <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 56.1 and 56.2. GC  $t_R$  = 7.86 min; GCMS (EI, 70 eV),  $m/z$  57 (100) 120 (59) 121 (39) 65 (35) 79 (31) 78 (28) 116 (28) 64 (28) 81 (14) 80 (14) 91 (13) 77 (12) 115 (11) 146 (11) 63 (11) 55 (11) 129 (11). GC  $t_R$  = 7.89 min; GCMS (EI, 70 eV),  $m/z$  57(100) 120 (49) 121 (37) 65 (28) 79 (26) 64 (26) 78 (24) 116 (18) 80 (11) 77 (11). HRMS (ESI):  $m/z$  = 201.1393 [C<sub>11</sub>H<sub>21</sub>OP+H]<sup>+</sup>,  $m/z$  (calc'd) = 201.1403, diff. = -4.97 ppm.

#### 4.3.2. *t*-Butylcyclohexylmethylphosphine oxide (**8**)

The compound **8** was prepared according to the general procedure from *t*-butylmethylphenylphosphine oxide (**5**) (0.13 g, 0.66 mmol), sodium (0.09g, 3.97 mmol, 6 equiv) and *i*-PrOH (0.29 mL, 3.97 mmol, 6 equiv). Yield: 0.095 g (71%). Colorless oil.  $R_f$  = 0.26 (CHCl<sub>3</sub>/MeOH = 15:1) <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.18 (d,  $J_{P-H}$  = 13.9 Hz, 9H), 1.21-1.30 (m, 3H), 1.30 (d,  $J_{P-H}$  = 11.4 Hz, 3H), 1.34-1.49 (m, 2H), 1.69-1.72 (m, 1H), 1.77-1.91 (m, 4H), 2.05-2.15 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 7.9 (d,  $J_{P-C}$  = 60.0 Hz), 25.2, 25.9, 26.5 (d,  $J_{P-C}$  = 3.6 Hz), 26.6 (d,  $J_{P-C}$  = 11.8 Hz), 26.8 (d,  $J_{P-C}$  = 12.7 Hz), 27.7 (d,  $J_{P-C}$  = 2.7 Hz), 32.8 (d,  $J_{P-C}$  = 65.4 Hz), 35.9 (d,  $J_{P-C}$  = 64.6 Hz). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 56.0. GC  $t_R$  = 7.8 min; GCMS (EI, 70 eV),  $m/z$  65 (100) 91 (88) 146 (85) 57 (81) 120 (59) 55 (56) 64 (36) 147 (29) 83 (27) 78 (25) 105 (21) 104 (20) 121 (20) 81 (18) 63 (18) 92 (16) 131 (15) 117 (12) 67 (11) 79 (10) 118 (10). HRMS (ESI):  $m/z$  = 203.1549 [C<sub>11</sub>H<sub>23</sub>OP+H]<sup>+</sup>,  $m/z$  (calc'd) = 203.1559, diff. = -4.92 ppm.

#### 4.3.3. Cyclohexyldimethylphosphine oxide (**13a**)

The compound **13a** was prepared according to the general procedure from dimethylphenylphosphine oxide (**13**) (0.15 g, 1 mmol), sodium (0.14 g, 6 mmol, 6 equiv) and *i*-PrOH (0.45 mL, 6 mmol, 6 equiv). Yield: 0.072 g (45%). Colorless crystals, mp = 127-128 °C  $R_f$  = 0.31 (CHCl<sub>3</sub>/MeOH = 15:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.19-1.34 (m, 5H), 1.41 (d,  $J_{P-H}$  = 12.0 Hz, 6H), 1.55-1.65 (m, 1H), 1.74 (d,  $J_{P-H}$  = 9.8 Hz, 1H), 1.82-1.89 (m, 2H), 1.92-1.98 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 13.6 (d,  $J_{P-C}$  = 66.3 Hz), 25.4 (d,  $J_{P-C}$  = 2.7 Hz), 25.8 (d,  $J_{P-C}$  = 1.2 Hz), 26.3 (d,  $J_{P-C}$  = 13.6 Hz), 39.5 (d,  $J_{P-C}$  = 70.8 Hz). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 45.95. GC  $t_R$  = 7.1 min; GCMS (EI, 70 eV),  $m/z$  78 (100) 79 (42) 105 (31) 63 (16) 55 (15) 77 (10) 81 (6) 92 (5). HRMS (ESI):  $m/z$  = 161.1087 [C<sub>8</sub>H<sub>17</sub>OP+H]<sup>+</sup>,  $m/z$  (calc'd) = 161.1090, diff. = -1.86 ppm.

#### 4.3.4. 1,2-Bis(dimethylphosphinoyl)cyclohexane (**13b**)

The compound **13b** was prepared according to the general procedure from dimethylphenylphosphine oxide (**13**) (0.15 g, 1 mmol), sodium (0.14 g, 6 mmol, 6 equiv) and *i*-PrOH (0.45 mL, 6 mmol, 6 equiv). Yield: 0.031 g (26%). White crystal, mp = 223-226 °C,  $R_f$  = 0.05 (CHCl<sub>3</sub>/MeOH = 15:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.57 (d,  $J_{P-H}$  = 12.0 Hz, 6H), 1.62 (d,  $J_{P-H}$  = 11.7 Hz, 6H), 1.65-1.79 (m, 4H), 1.82-1.93 (m, 2H), 2.18 (m, 2H), 2.27-2.36 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 15.5-16.6 (m, CH<sub>3</sub>), 22.6, 23.4, 34.18-35.17 (m, CH). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 48.5. GC  $t_R$  = 10.3 min; GCMS (EI, 70 eV),  $m/z$  159 (100) 81 (37) 79 (34) 77 (25) 78 (13) 139 (12) 63 (10) 160 (10)

221 (8) 47 (6). HRMS (ESI):  $m/z$  = 495.2077  $[C_{20}H_{44}O_2P_2+Na]^+$ ,  $m/z$  (calc'd) = 495.2082, diff. = -1.01 ppm.

#### 4.3.5. Cyclohexyldiethylphosphine oxide (**14a**)

The compound **14a** was prepared according to the general procedure from diethylphenylphosphine oxide (**14**) (0.11 g, 0.6 mmol), sodium (83 mg, 6 equiv) and *i*-PrOH (0.274 mL, 6 equiv). Yield: 0.043 g (38%). Colorless oil.  $R_f$  = 0.35 ( $CH_2Cl_2$ /MeOH = 15:1).  $^1H$  NMR (500 MHz,  $CHCl_3$ )  $\delta$  1.10-1.18 (m, 6H), 1.21-1.40 (m, 5H), 1.58-1.75 (m, 6H), 1.79-1.93 (m, 4H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  5.7 (d,  $J_{P-C}$  = 5.5 Hz), 17.7 (d,  $J_{P-C}$  = 64.5 Hz), 25.3 (d,  $J_{P-C}$  = 2.7 Hz), 25.9 (d,  $J_{P-C}$  = 1.8 Hz), 26.5 (d,  $J_{P-C}$  = 11.8 Hz), 36.1 (d,  $J_{P-C}$  = 66.3 Hz).  $^{31}P$  NMR (202 MHz,  $CDCl_3$ )  $\delta$  52.9. GC  $t_R$  = 8.8 min; GCMS (EI, 70 eV),  $m/z$  106 (100) 78 (51) 133 (33) 107 (32) 77 (23) 55 (20) 79 (14) 81 (12) 49 (11) 105 (9). HRMS (ESI):  $m/z$  = 377.2717  $[C_{20}H_{42}O_2P_2+H]^+$ ,  $m/z$  (calc'd) = 377.2733, diff. = -4.24 ppm.

#### 4.3.6. Di-*n*-butylcyclohexylphosphine oxide (**15a**)

The compound **15a** was prepared according to the general procedure from di-*n*-butylphenylphosphine oxide (**15**) (0.08 g, 0.33 mmol), sodium (46 mg, 6 equiv) and *i*-PrOH (0.15 mL, 6 equiv). Yield: 0.031 g (39%). Colorless oil.  $R_f$  = 0.43 ( $CH_2Cl_2$ /MeOH = 15:1).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  0.94 (t,  $J_{H-H}$  = 7.3 Hz, 6H), 1.21-1.37 (m, 5H), 1.43 (dq,  $J_{P-H}$  = 14.5 Hz,  $J_{H-H}$  = 7.3 Hz, 4H), 1.51-1.77 (m, 10H), 1.81-1.96 (m, 4H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  13.7, 23.7 (d,  $J_{P-C}$  = 4.5 Hz), 24.5 (d,  $J_{P-C}$  = 14.5 Hz), 25.2 (d,  $J_{P-C}$  = 63.4 Hz), 25.4 (d,  $J_{P-C}$  = 2.7 Hz), 26.0 (d,  $J_{P-C}$  = 1.2 Hz), 26.5 (d,  $J_{P-C}$  = 12.7 Hz), 36.9 (d,  $J_{P-C}$  = 66.3 Hz).  $^{31}P$  NMR (202 MHz,  $CDCl_3$ )  $\delta$  50.6. GC  $t_R$  = 8.9 min; GCMS (EI, 70 eV),  $m/z$  78 (100) 55 (65) 120 (55) 63 (41) 146 (38) 79 (35) 162 (25) 105 (19) 81 (19) 215 (19) 173 (17) 65 (17) 92 (15) 188 (15) 121 (14) 91 (14) 64 (14) 147 (13) 107 (13) 160 (13) 133 (11) 83 (11) 106 (10). HRMS (ESI):  $m/z$  = 511.3798  $[C_{28}H_{58}O_2P_2+Na]^+$ ,  $m/z$  (calc'd) = 511.3804, diff. = -1.17 ppm.

#### 4.3.7. 1,2-Bis(di(*n*-butyl)phosphinoyl)cyclohexane (**15b**)

The compound **15b** was prepared according to the general procedure from di-*n*-butylphenylphosphine oxide (**15**) (0.08 g, 0.33 mmol), sodium (46 mg, 6 equiv) and *i*-PrOH (0.15 mL, 6 equiv). Yield: 0.015 g (22%). Colorless oil.  $R_f$  = 0.35 ( $CH_2Cl_2$ /MeOH = 15:1).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  0.95 (q,  $J_{H-H}$  = 6.9 Hz, 12H), 1.38-1.49 (m, 9H), 1.50-1.59 (m, 5H), 1.60-1.95 (m, 16H), 2.14-2.28 (m, 2H), 2.34 (bs, 2H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  13.7 (d,  $J_{P-C}$  = 1.8 Hz), 23.0 (d,  $J_{P-C}$  = 74.5 Hz), 24.1 (d,  $J_{P-C}$  = 24.5 Hz), 24.4 (d,  $J_{P-C}$  = 20.0 Hz), 24.4 (d,  $J_{P-C}$  = 7.3 Hz), 26.2-27.5 (m,  $CH_2$ ), 30.71-31.69 (m,  $CH$ ).  $^{31}P$  NMR (202 MHz,  $CDCl_3$ )  $\delta$  54.1. GC  $t_R$  = 12.9 min; GCMS (EI, 70 eV),  $m/z$  243 (100) 244 (17) 161 (14) 63 (13) 291 (11) 55 (11) 81 (9) 78 (8) 347 (6). HRMS (ESI):  $m/z$  = 405.3053  $[C_{22}H_{46}O_2P_2+H]^+$ ,  $m/z$  (calc'd) = 405.3046, diff. = 1.73 ppm.

#### 4.3.8. Cyclohexyldi(*n*-propyl)phosphine oxide (**16a**)

The compound **16a** was prepared according to the general procedure from di-*n*-propylphenylphosphine oxide (**16**) (0.063 g, 0.3 mmol), sodium (41 mg, 6 equiv) and *i*-PrOH (0.14 mL, 6 equiv). Yield: 0.015 g (23%). Colorless oil.  $R_f$  = 0.45 ( $CH_2Cl_2$ /MeOH = 15:1).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  0.99-1.07 (m, 6H), 1.19-1.38 (m, 5H), 1.55-1.76 (m, 10H), 1.81-1.87 (m, 2H), 1.90 (m, 2H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  15.3 (d,  $J_{P-C}$  = 3.6 Hz), 16.0 (d,  $J_{P-C}$  = 14.5 Hz), 25.4 (d,  $J_{P-C}$  = 2.7 Hz), 25.9, 26.5 (d,  $J_{P-C}$  = 12.7 Hz), 27.7 (d,  $J_{P-C}$  = 62.7 Hz), 36.9 (d,  $J_{P-C}$  = 66.3 Hz).  $^{31}P$  NMR (202 MHz,  $CDCl_3$ )  $\delta$  50.5. GC  $t_R$  = 9.3 min; GCMS (EI, 70 eV),  $m/z$  134 (100) 92 (79) 106 (72) 78 (57) 93 (53) 174 (50) 55 (49) 63 (37) 119 (36) 132 (31) 133 (29) 135 (27) 161 (27) 64 (27) 81 (24) 73 (23) 91 (19) 146 (18) 83 (14) 201 (14) 173 (13) 159 (13) 107 (12) 79 (11) 65 (11) 47 (10). HRMS

(ESI):  $m/z$  = 217.1709  $[C_{12}H_{25}OP+H]^+$ ,  $m/z$  (calc'd) = 217.1716, diff. = -3.22 ppm.

#### 4.3.9. 1,2-Bis(di(*n*-propyl)phosphinoyl)cyclohexane (**16b**)

The compound **16b** was prepared according to the general procedure from di-*n*-propylphenylphosphine oxide (**16**) (0.063 g, 0.3 mmol), sodium (41 mg, 6 equiv) and *i*-PrOH (0.14 mL, 6 equiv). Yield: 0.006 g (11%). Colorless oil.  $R_f$  = 0.35 ( $CH_2Cl_2$ /MeOH = 15:1).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  1.01-1.10 (m, 12H), 1.51-1.77 (m, 18H), 1.77-1.92 (m, 4H), 2.13-2.26 (m, 2H), 2.28-2.36 (m, 2H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  15.8 (d,  $J_{P-C}$  = 20.0 Hz), 15.9-16.1 (m,  $CH_3$ ) 22.7, 23.3, 28.7-30.0 (m), 30.8-31.9 (m).  $^{31}P$  NMR (202 MHz,  $CDCl_3$ )  $\delta$  53.6. GC  $t_R$  = 20.0 min; GCMS (EI, 70 eV),  $m/z$  215 (100) 133 (22) 2162 (20) 263 (13) 63 (10) 81 (10) 73 (8) 181 (8) 135 (7) 305 (6) 79 (5). HRMS (ESI):  $m/z$  = 349.2409  $[C_{18}H_{38}O_2P_2+H]^+$ ,  $m/z$  (calc'd) = 349.2420, diff. = -3.15 ppm.

#### 4.3.10. Cyclohexyldi(*i*-propyl)phosphine oxide (**17a**)

The compound **17a** was prepared according to the general procedure from di-*i*-propylphenylphosphine oxide (**17**) (0.14 g, 0.66 mmol), sodium (0.092 g, 6 equiv) and *i*-PrOH (0.299 mL, 6 equiv). Yield: 0.123 g (78%). Colorless oil.  $R_f$  = 0.48 ( $CHCl_3$ /MeOH = 15:1).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  1.16 (dd,  $J_{P-H}$  = 14.2 Hz,  $J_{P-H}$  = 7.3 Hz, 12 H), 1.18-1.24 (m, 3H), 1.37 (d,  $J_{P-H}$  = 12.0 Hz, 2H), 1.64-1.69 (m, 1H), 1.78 (dd,  $J_{P-H}$  = 10.3 Hz,  $J_{H-H}$  = 3.0 Hz, 2H), 1.83 (dt,  $J_{P-H}$  = 12.0 Hz,  $J_{H-H}$  = 3.0 Hz, 1H), 1.88 (d,  $J_{P-H}$  = 12.3 Hz, 2H), 2.01-2.12 (m, 2H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  16.42 (d,  $J_{P-C}$  = 4.5 Hz), 16.45 (d,  $J_{P-C}$  = 2.7 Hz), 24.4 (d,  $J_{P-C}$  = 61.0 Hz), 26.0 (d,  $J_{P-C}$  = 1.8 Hz), 26.3 (d,  $J_{P-C}$  = 2.7 Hz), 26.8 (d,  $J_{P-C}$  = 11.8 Hz), 35.53 (d,  $J_{P-C}$  = 61.0 Hz).  $^{31}P$  NMR (202 MHz,  $CDCl_3$ )  $\delta$  56.6. GC  $t_R$  = 8.18 min; GCMS (EI, 70 eV),  $m/z$  (%) 134 (100), 92 (62), 93 (35), 55 (33), 81 (30), 173 (27), 91 (24), 63 (19), 135 (19), 74 (19), 161 (19), 73 (18), 83 (12), 119 (11), 132 (10). HRMS (ESI):  $m/z$  = 239.1524  $[C_{12}H_{25}OP+Na]^+$ ,  $m/z$  (calc'd) = 239.1535, diff. = -4.60 ppm.

#### 4.3.11. Cyclohexyldicyclopentylphosphine oxide (**18a**)

The compound **18a** was prepared according to the general procedure from dicyclopentylphenylphosphine oxide (**18**) (0.087 g, 0.33 mmol), sodium (0.046 g, 6 equiv) and *i*-PrOH (0.151 mL, 6 equiv). Yield: 0.055 g (62%). Colorless oil.  $R_f$  = 0.38 ( $CH_2Cl_2$ /MeOH = 15:1).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  1.21-1.37 (m, 5H), 1.54-1.64 (m, 4H), 1.70-1.78 (m, 5H), 1.81-1.94 (m, 11H), 1.98-2.09 (m, 4H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  26.0 (d,  $J_{P-C}$  = 10.0 Hz), 26.3 (d,  $J_{P-C}$  = 1.2 Hz), 26.4 (d,  $J_{P-C}$  = 9.1 Hz), 26.6 (d,  $J_{P-C}$  = 2.7 Hz), 27.0 (d,  $J_{P-C}$  = 13.5 Hz), 27.1, 27.2 (d,  $J_{P-C}$  = 1.8 Hz), 36.0 (d,  $J_{P-C}$  = 65.4 Hz), 38.4 (d,  $J_{P-C}$  = 64.5 Hz).  $^{31}P$  NMR (202 MHz,  $CDCl_3$ )  $\delta$  53.3. GC  $t_R$  = 12.6 min; GCMS (EI, 70 eV),  $m/z$  119 (100) 118 (72) 55 (51) 145 (44) 99 (44) 67 (43) 200 (42) 186 (42) 132 (32) 69 (29) 133 (25) 227 (19) 81 (19) 83 (17) 51 (14) 159 (14) 185 (13) 199 (10) 201 (10). HRMS (ESI):  $m/z$  = 291.1835  $[C_{16}H_{29}OP+Na]^+$ ,  $m/z$  (calc'd) = 291.1848, diff. = -4.46 ppm.

#### 4.3.12. Dibenzylcyclohexylphosphine oxide (**19a**)

The compound **19a** was prepared according to the general procedure from dibenzylphenylphosphine oxide (**19**) (0.092 g, 0.3 mmol), sodium (0.041 g, 6 equiv) and *i*-PrOH (0.137 mL, 6 equiv). Yield: 0.020 g (21%). White crystal, mp = 151-153 °C;  $R_f$  = 0.4 ( $CH_2Cl_2$ /MeOH = 15:1).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  1.10-1.23 (m, 3H), 1.23-1.35 (m, 2H), 1.62-1.73 (m, 2H), 1.82 (s, 2H), 1.95 (s, 2H), 2.97-3.15 (m, 4H), 7.24-7.38 (m, 10H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  25.7 (d,  $J_{P-C}$  = 2.7 Hz), 25.9 (d,  $J_{P-C}$  = 1.8 Hz), 26.4 (d,  $J_{P-C}$  = 12.7 Hz), 33.5 (d,  $J_{P-C}$  = 58.1 Hz), 36.5 (d,  $J_{P-C}$  = 66.3 Hz), 126.8 (d,  $J_{P-C}$  = 2.9 Hz), 128.7 (d,  $J_{P-C}$  = 2.7 Hz), 129.8 (d,  $J_{P-C}$  = 4.5 Hz), 132.2 (d,  $J_{P-C}$  = 7.3 Hz).  $^{31}P$  NMR (202 MHz,  $CDCl_3$ )  $\delta$  45.4. GC  $t_R$  = 15.2 min; GCMS (EI, 70 eV),  $m/z$



91 (100) 139 (62) 230 (24) 55 (23) 312 (18) 65 (14) 121 (13) 81 (12) 221 (10). HRMS (ESI):  $m/z = 625.3370$  [ $C_{40}H_{50}O_2P_2+H$ ] $^+$ ,  $m/z$  (calc'd) = 625.3359, diff. = 1.76 ppm.

#### 4.3.13. Benzylcyclohexylmethylphosphine oxide (20a)

The compound **20a** was prepared according to the general procedure from benzylmethylphenylphosphine oxide (**20**) (0.076 g, 0.33 mmol), sodium (0.046 g, 6 equiv) and *i*-PrOH (0.153 mL, 6 equiv). Yield: 0.018 g (23%). White crystal, mp = 107-109 °C;  $R_f = 0.43$  ( $CH_2Cl_2/MeOH = 15:1$ ).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  1.22-1.28 (m, 2H), 1.28-1.31 (m, 3H), 1.32-1.49 (m, 3H), 1.61-1.71 (m, 1H), 1.72-1.96 (m, 4H), 2.05 (d,  $J_{P-H} = 12.3$  Hz, 1H), 3.03-3.25 (m, 2H), 7.26-7.31 (m, 3H), 7.32-7.37 (m, 2H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  11.1 (d,  $J_{P-C} = 66.3$  Hz), 25.8 (d,  $J_{P-C} = 2.7$  Hz), 25.6 (d,  $J_{P-C} = 2.7$  Hz), 25.9 (d,  $J_{P-C} = 1.9$  Hz), 26.2 (d,  $J_{P-C} = 6.4$  Hz), 26.3 (d,  $J_{P-C} = 6.4$  Hz), 35.6 (d,  $J_{P-C} = 60.0$  Hz), 37.5 (d,  $J_{P-C} = 69.0$  Hz), 126.8 (d,  $J_{P-C} = 2.7$  Hz), 128.8 (d,  $J_{P-C} = 1.8$  Hz), 129.6 (d,  $J_{P-C} = 4.5$  Hz), 132.4 (d,  $J_{P-C} = 7.3$  Hz).  $^{31}P$  NMR (202 MHz,  $CDCl_3$ )  $\delta$  46.8. GC  $t_R = 11.6$  min; GCMS (EI, 70 eV),  $m/z$  91 (100) 154 (89) 81 (32) 181 (26) 155 (24) 236 (23) 92 (21) 83 (11). HRMS (ESI):  $m/z = 473.2754$  [ $C_{28}H_{42}O_2P_2+H$ ] $^+$ ,  $m/z$  (calc'd) = 473.2733, diff. = 4.44 ppm.

#### 4.3.14. Benzyl(*n*-butyl)cyclohexylphosphine oxide (21a)

The compound **21a** was prepared according to the general procedure from benzyl(*n*-butyl)phenylphosphine oxide (**21**) (0.082 g, 0.3 mmol), sodium (0.41 g, 6 equiv) and *i*-PrOH (0.137 mL, 6 equiv). Yield: 0.026 g (31%). White crystal, mp = 95-97 °C;  $R_f = 0.45$  ( $CH_2Cl_2/MeOH = 15:1$ ).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  0.87-0.92 (m, 3H), 1.22-1.28 (m, 3H), 1.33-1.40 (m, 3H), 1.44-1.66 (m, 5H), 1.70 (dt,  $J_{P-H} = 12.0$  Hz,  $J_{H-H} = 3.0$  Hz, 1H), 1.74 (dd,  $J_{H-H} = 5.4$  Hz,  $J_{P-H} = 5.42$  Hz, 1H), 1.83-2.01 (m, 4H), 3.02-3.21 (m, 2H), 7.22-7.40 (m, 5H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  13.6, 23.6 (d,  $J_{P-C} = 4.5$  Hz), 24.3, 24.4 (d,  $J_{P-C} = 5.5$  Hz), 25.0, 25.5 (d,  $J_{P-C} = 2.7$  Hz), 25.5 (d,  $J_{P-C} = 2.7$  Hz), 25.9, 26.4 (d,  $J_{P-C} = 13.6$  Hz), 33.8 (d,  $J_{P-C} = 57.2$  Hz), 36.6 (d,  $J_{P-C} = 66.3$  Hz), 126.7 (d,  $J_{P-C} = 2.7$  Hz), 128.8 (d,  $J_{P-C} = 1.8$  Hz), 129.6 (d,  $J_{P-C} = 5.5$  Hz), 132.5 (d,  $J_{P-C} = 7.3$  Hz).  $^{31}P$  NMR (202 MHz,  $CDCl_3$ )  $\delta$  48.4. GC  $t_R = 12.3$  min; GCMS (EI, 70 eV),  $m/z$  91 (100) 154 (86) 81 (31) 196 (30) 187 (21) 222 (17) 155 (16) 92 (16) 249 (16) 278 (15) 223 (10) 83 (10). HRMS (ESI):  $m/z = 557.3663$  [ $C_{34}H_{54}O_2P_2+H$ ] $^+$ ,  $m/z$  (calc'd) = 557.3672, diff. = -1.61 ppm.

#### 4.3.15. Benzylcyclohexyl(*i*-propyl)phosphine oxide (22a)

The compound **22a** was prepared according to the general procedure from benzyl(*i*-propyl)phenylphosphine oxide (**22**) (0.039 g, 0.15 mmol), sodium (0.021 g, 6 equiv) and *i*-PrOH (0.069 mL, 6 equiv). Yield: 0.011 g (28%). White crystal, mp = 71-73 °C;  $R_f = 0.46$  ( $CH_2Cl_2/MeOH = 15:1$ ).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  1.10-1.23 (m, 6H), 1.20-1.28 (m, 3H), 1.29-1.38 (m, 1H), 1.38-1.47 (m, 1H), 1.65-1.77 (m, 1H), 1.80-1.97 (m, 5H), 1.97-2.04 (m, 1H), 3.12 (dd,  $J_{P-H} = 12.6$ ,  $J_{H-H} = 4.1$  Hz, 2H), 7.23-7.28 (m, 1H), 7.30-7.37 (m, 4H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  16.0 (d,  $J_{P-C} = 2.7$  Hz), 16.1 (d,  $J_{P-C} = 2.7$  Hz), 25.6 (d,  $J_{P-C} = 63.3$  Hz), 25.7 (d,  $J_{P-C} = 3.6$  Hz), 25.8 (d,  $J_{P-C} = 2.7$  Hz), 26.0, 26.6 (d,  $J_{P-C} = 5.5$  Hz), 26.7 (d,  $J_{P-C} = 6.4$  Hz), 32.1 (d,  $J_{P-C} = 56.3$  Hz), 36.2 (d,  $J_{P-C} = 63.6$  Hz), 126.7 (d,  $J_{P-C} = 2.7$  Hz), 128.7 (d,  $J_{P-C} = 1.8$  Hz), 129.8 (d,  $J_{P-C} = 4.5$  Hz), 132.8 (d,  $J_{P-C} = 7.3$  Hz).  $^{31}P$  NMR (202 MHz,  $CDCl_3$ )  $\delta$  51.4. GC  $t_R = 12.0$  min; GCMS (EI, 70 eV),  $m/z$  91 (100) 182 (51) 140 (36) 81 (31) 173 (27) 264 (20) 139 (17) 92 (14) 183 (12) 222 (11) 93 (11) 209 (11) 83 (10). HRMS (ESI):  $m/z = 529.3342$  [ $C_{32}H_{50}O_2P_2+H$ ] $^+$ ,  $m/z$  (calc'd) = 529.3359, diff. = -3.21 ppm.

#### 4.3.16. Benzyl(*t*-butyl)cyclohexylphosphine oxide (23a)

The compound **23a** was prepared according to the general procedure from benzyl(*t*-butyl)phenylphosphine oxide (**23**)

(0.082 g, 0.3 mmol), sodium (0.41 g, 6 equiv) and *i*-PrOH (0.137 mL, 6 equiv). Yield: 0.041 g (49%). White crystal, mp = 113 °C;  $R_f = 0.35$  ( $CH_2Cl_2/MeOH = 15:1$ ).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  1.10-1.29 (m, 4H), 1.19 (d,  $J_{P-H} = 13.60$  Hz, 9H), 1.37-1.48 (m, 1H), 1.65-1.71 (m, 1H), 1.75-1.83 (m, 2H), 1.83-1.93 (m, 1H), 1.99-2.10 (m, 1H), 3.06-3.19 (m, 1H), 7.22-7.26 (m, 1H), 7.31 (t,  $J_{H-H} = 7.6$  Hz, 2H), 7.42 (d,  $J_{H-H} = 7.6$  Hz, 2H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  25.8, 26.1 (d,  $J_{P-C} = 1.2$  Hz), 27.0 (d,  $J_{P-C} = 1.8$  Hz), 27.1 (d,  $J_{P-C} = 1.8$  Hz), 27.3 (d,  $J_{P-C} = 2.7$  Hz), 27.5 (d,  $J_{P-C} = 2.7$  Hz), 30.0 (d,  $J_{P-C} = 53.6$  Hz), 34.1 (d,  $J_{P-C} = 61.8$  Hz), 37.2 (d,  $J_{P-C} = 60.0$  Hz), 126.5 (d,  $J_{P-C} = 1.8$  Hz), 128.5, 130.2 (d,  $J_{P-C} = 4.5$  Hz), 133.2 (d,  $J = 6.4$  Hz).  $^{31}P$  NMR (202 MHz,  $CDCl_3$ )  $\delta$  53.1. GC  $t_R = 12.0$  min; GCMS (EI, 70 eV),  $m/z$  91 (100) 140 (59) 129 (52) 196 (41) 222 (39) 122 (37) 141 (37) 113 (33) 278 (23) 81 (23) 167 (22) 131 (20) 139 (18) 83 (14) 121 (13) 92 (12) 187 (11) 223 (10). HRMS (ESI):  $m/z = 557.3680$  [ $C_{34}H_{54}O_2P+H$ ] $^+$ ,  $m/z$  (calc'd) = 557.3672, diff. = 1.44 ppm.

#### 4.3.17. 1-Cyclohexylphosphinane 1-oxide (24a)

The compound **24a** was prepared according to the general procedure from 1-phenylphospholane oxide (**24**) (0.108 g, 0.6 mmol), sodium (0.083 g, 6 equiv) and *i*-PrOH (0.276 mL, 6 equiv). Yield: 0.040 g (36%). Colorless oil.  $R_f = 0.40$  ( $CH_2Cl_2/MeOH = 15:1$ ).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  1.21-1.33 (m, 3H), 1.33-1.44 (m, 2H), 1.60-1.83 (m, 8H), 1.83-1.90 (m, 2H), 1.92-1.98 (m, 2H), 1.99-2.07 (m, 2H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  24.9 (d,  $J_{P-C} = 62.7$  Hz), 24.8 (d,  $J_{P-C} = 7.3$  Hz), 25.5 (d,  $J_{P-C} = 2.7$  Hz), 25.8 (d,  $J_{P-C} = 1.8$  Hz), 26.2 (d,  $J_{P-C} = 12.7$  Hz), 38.8 (d,  $J_{P-C} = 64.5$  Hz).  $^{31}P$  NMR (202 MHz,  $CDCl_3$ )  $\delta$  75.4. GC  $t_R = 9.9$  min; GCMS (EI, 70 eV),  $m/z$  (%) 104 (100) 105 (51) 131 (43) 55 (19) 103 (19) 76 (17) 47 (11). HRMS (ESI):  $m/z = 187.1250$  [ $C_{10}H_{19}OP+H$ ] $^+$ ,  $m/z$  (calc'd) = 187.1246, diff. = 2.14 ppm.

#### 4.3.18. 1-Cyclohexylphosphinane 1-oxide (25a)

The compound **25a** was prepared according to the general procedure from 1-phenylphosphorinane-1-oxide (**25**) (0.194 g, 1 mmol), sodium (0.138 g, 6 equiv) and *i*-PrOH (0.449 mL, 6 equiv). Yield: 0.076 g (38%). White crystal, mp = 164 °C.  $R_f = 0.30$  ( $CHCl_3/MeOH = 15:1$ ).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  1.24-1.34 (m, 3H), 1.40-1.54 (m, 3H), 1.60-1.84 (m, 9H), 1.85-1.92 (m, 4H), 1.96-2.08 (m, 2H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  22.0 (d,  $J_{P-C} = 5.5$  Hz), 24.4 (d,  $J_{P-C} = 2.7$  Hz), 24.8 (d,  $J_{P-C} = 60.9$  Hz), 25.8 (d,  $J_{P-C} = 1.2$  Hz), 26.3 (d,  $J_{P-C} = 12.7$  Hz), 26.8 (d,  $J_{P-C} = 5.5$  Hz), 35.9 (d,  $J_{P-C} = 68.1$  Hz).  $^{31}P$  NMR (202 MHz,  $CDCl_3$ )  $\delta$  43.7. GC  $t_R = 9.2$  min; GCMS (EI, 70 eV),  $m/z$  (%) 118 (100) 119 (33) 145 (30) 55.05 (16) 90 (16) 117 (14) 78 (10). HRMS (ESI):  $m/z = 201.1398$  [ $C_{11}H_{21}OP+H$ ] $^+$ ,  $m/z$  (calc'd) = 201.1403, diff. = -2.49 ppm.

#### 4.3.19. 1,2-Bis(phosphorinane 1-oxide)cyclohexane (25b)

The compound **25b** was prepared according to the general procedure from 1-phenylphosphorinane-1-oxide (**25**) (0.194 g, 1 mmol), sodium (0.138 g, 6 equiv) and *i*-PrOH (0.449 mL, 6 equiv). Yield: 0.068 g (43%). Colorless oil.  $R_f = 0.22$  ( $CHCl_3/MeOH = 15:1$ ).  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  1.41-1.51 (m, 2H), 1.60-2.08 (m, 24H), 2.14-2.28 (m, 2H), 2.34 (bs, 2H).  $^{13}C$  NMR (126 MHz,  $CDCl_3$ )  $\delta$  22.3 (dd,  $J_{P-C} = 30.8$  Hz,  $J_{P-C} = 2.70$  Hz), 22.6 (d,  $J_{P-C} = 2.7$  Hz), 26.6 (dd,  $J_{P-C} = 2.7$  Hz,  $J_{P-C} = 2.7$  Hz), 26.9 (dd,  $J_{P-C} = 60.8$  Hz,  $J_{P-C} = 3.6$  Hz), 26.9-27.0 (m), 30.2-31.5 (m).  $^{31}P$  NMR (202 MHz,  $CDCl_3$ )  $\delta$  46.3. GC  $t_R = 15.3$  min; GCMS (EI, 70 eV),  $m/z$  199 (100) 119 (15) 117 (14) 81 (13) 200 (13). HRMS (ESI):  $m/z = 339.1623$  [ $C_{16}H_{30}O_2P_2+Na$ ] $^+$ ,  $m/z$  (calc'd) = 339.1613, diff. = 2.95 ppm.

#### 4.3.20. Dicyclohexylmethylphosphine oxide (26a)

The compound **26a** was prepared according to the general procedure from methyldiphenylphosphine oxide (**26**) (0.1 g, 0.46

mmol), sodium (0.128 g, 12 equiv) and *i*-PrOH (0.415 mL, 12 equiv). Yield: 0.018 g (17%). White crystal, mp = 82–83 °C (lit. 79–81 °C)<sup>22</sup>; Rf = 0.36 (CHCl<sub>3</sub>/MeOH = 15:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.22–1.34 (m, 9H), 1.34–1.47 (m, 4H), 1.66–1.77 (m, 4H), 1.77–1.83 (m, 2H), 1.86 (d, *J*<sub>P-H</sub> = 7.6 Hz, 4H), 1.96–2.04 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 8.6 (d, *J*<sub>P-C</sub> = 61.8 Hz), 24.8 (d, *J*<sub>P-C</sub> = 3.1 Hz), 25.7 (d, *J*<sub>P-C</sub> = 2.5 Hz), 25.9 (d, *J*<sub>P-C</sub> = 1.2 Hz), 26.4 (d, *J*<sub>P-C</sub> = 11.8 Hz), 26.5 (d, *J*<sub>P-C</sub> = 12.7 Hz), 35.8 (d, *J*<sub>P-C</sub> = 66.3 Hz). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 50.8. GC t<sub>R</sub> = 9.6 min; GCMS (EI, 70 eV), m/z 146 (100) 65 (58) 55 (45) 91 (42) 147 (29) 173 (25.63) 81 (18) 83 (17) 92 (12) 105 (11) 104 (11) 63 (10) 64 (10). HRMS (ESI): m/z = 457.3378 [C<sub>26</sub>H<sub>50</sub>O<sub>2</sub>P<sub>2</sub>+H]<sup>+</sup>, m/z (calc'd) = 457.3359, diff. = 4.15 ppm.

#### 4.3.21. 5,10-Dimethyltetradecahydrophosphanthrene 5,10-dioxide (26b)

The four isomers of compounds **26b** were formed according to the general procedure from methylphenylphosphine oxide (**26**) (0.1 g, 0.46 mmol), sodium (0.128 g, 12 equiv) and *i*-PrOH (0.415 mL, 12 equiv). According to <sup>31</sup>P NMR spectrum, the total yield of four isomers is 42%. The isomers of 26b(F1-F4) were separated by column chromatography in 4%+3%+3%+13% yield, respectively.

**Isomer 26b-F1**; Yield: 0.005 g (4%); White solid. Rf = 0.13 (CHCl<sub>3</sub>/MeOH = 15:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.20–1.32 (m, 1H), 1.37–1.40 (m, 2H), 1.47 (d, *J*<sub>P-H</sub> = 12.3 Hz, 3H), 1.50 (d, *J*<sub>P-H</sub> = 11.7 Hz, 3H), 1.61 (m, 1H), 1.64 (m, 1H), 1.70 (bs, 4H), 1.78 (m, 2H), 1.91 (m, 3H), 2.07–2.18 (m, 3H), 2.20–2.26 (m, 1H), 2.29 (dt, *J*<sub>P-H</sub> = 13.6, *J*<sub>P-H</sub> = 3.8 Hz, 1H), 2.38 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 10.8 (d, *J*<sub>P-C</sub> = 65.4 Hz), 12.1 (d, *J*<sub>P-C</sub> = 66.3 Hz), 21.9, 23.1–23.2 (m), 23.7, 24.9 (d, *J*<sub>P-C</sub> = 12.7 Hz), 26.4 (d, *J*<sub>P-C</sub> = 13.6 Hz), 27.1–27.3 (m), 32.0 (dd, *J*<sub>P-C</sub> = 64.5 Hz, *J*<sub>P-C</sub> = 2.7 Hz), 32.8 (dd, *J*<sub>P-C</sub> = 62.7 Hz, *J*<sub>P-C</sub> = 2.7 Hz), 36.3 (dd, *J*<sub>P-C</sub> = 63.6 Hz, *J*<sub>P-C</sub> = 3.6 Hz), 40.7 (d, *J*<sub>P-C</sub> = 64.5 Hz). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 44.9 (dd, *J*<sub>P-P</sub> = 266.2, 14.9 Hz). GC t<sub>R</sub> = 13.1 min; GCMS (EI, 70 eV), m/z 191 (100) 273 (85) 81 (52) 206 (30) 127 (26) 145 (18) 126 (15) 288 (15) 80 (14) 207 (13) 144 (12) 274 (11). HRMS (ESI): m/z = 289.1479 [C<sub>14</sub>H<sub>26</sub>O<sub>2</sub>P<sub>2</sub>+H]<sup>+</sup>, m/z (calc'd) = 289.1481, diff. = -0.69 ppm.

**Isomer 26b-F2**; Yield: 0.004 g (3%); White solid. Rf = 0.12 (CHCl<sub>3</sub>/MeOH = 15:1). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 42.4. GC t<sub>R</sub> = 13.5 min; GCMS (EI, 70 eV), m/z 191 (100) (78) 81 (37) 206 (28) 144 (22) 207 (15) 288 (12) 274 (12) 145 (11) 127 (10). HRMS (ESI): m/z = 289.1473 [C<sub>14</sub>H<sub>26</sub>O<sub>2</sub>P<sub>2</sub>+H]<sup>+</sup>, m/z (calc'd) = 289.1481, diff. = -2.77 ppm.

**Isomer 26b-F3**; White crystal, mp > 400 °C; Yield: 0.004 g (3%). Rf = 0.11 (CHCl<sub>3</sub>/MeOH = 15:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.21–1.37 (m, 8H), 1.47 (d, *J*<sub>P-H</sub> = 11.4 Hz, 6H), 1.79–1.86 (m, 4H), 1.92–1.99 (m, 4H), 2.36–2.42 (m, 4H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 5.3 (d, *J*<sub>P-C</sub> = 65.4 Hz), 24.38–24.67 (m), 25.29–25.58 (m), 39.1 (dd, *J*<sub>P-C</sub> = 66.3 Hz, *J*<sub>P-C</sub> = 2.7 Hz). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 43.0. GC t<sub>R</sub> = 14.6 min; GCMS (EI, 70 eV), m/z 191 (100) 81 (57) 79 (56) 273 (52) 206 (44) 207 (43) 145 (34) 127 (26) 63 (20) 67 (20) 126 (18) 53 (17) 65 (17) 144 (16) 77 (16) 288 (15) 80 (13) 54 (11). HRMS (ESI): m/z = 599.2695 [C<sub>28</sub>H<sub>52</sub>O<sub>4</sub>P<sub>4</sub>+Na]<sup>+</sup>, m/z (calc'd) = 599.2708, diff. = -2.17 ppm.

**Isomer 26b-F4**; White solid, mp = 257–258 °C; Yield: 0.017 g (13%). Rf = 0.10 (CHCl<sub>3</sub>/MeOH = 15:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.18–1.35 (m, 5H), 1.35–1.42 (m, 2H), 1.38 (d, *J*<sub>P-H</sub> = 11.0 Hz, 3H), 1.4 (d, *J*<sub>P-H</sub> = 11.7 Hz, 3H), 1.42–1.52 (m, 2H), 1.78–1.86 (m, 2H), 1.86–1.98 (m, 6H), 2.35–2.46 (m, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 4.9 (d, *J*<sub>P-C</sub> = 62.7 Hz), 10.6 (d, *J*<sub>P-C</sub> = 65.4 Hz), 23.7–24.0 (m), 25.0 (d, *J*<sub>P-C</sub> = 11.8 Hz), 25.3 (d, *J*<sub>P-C</sub> = 11.8 Hz), 36.4 (dd, *J*<sub>P-C</sub> = 64.5 Hz, *J*<sub>P-C</sub> = 3.6 Hz), 39.1 (d, *J*<sub>P-C</sub> =

66.3 Hz). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 41.3 (dd, *J* = 604.6, 10.0 Hz). GC t<sub>R</sub> = 14.2 min; GCMS (EI, 70 eV), m/z 200 (100) 273 (83) 79 (36) 81 (34) 206 (27) 144 (23) 145 (15) 63 (14) 127 (12) 274 (12) 67 (12) 53 (11) 129 (10) 65 (10). HRMS (ESI): m/z = 599.2695 [C<sub>28</sub>H<sub>52</sub>O<sub>4</sub>P<sub>4</sub>+Na]<sup>+</sup>, m/z (calc'd) = 599.2708, diff. = -2.17 ppm.

#### 4.3.22. *n*-Butyldicyclohexylphosphine oxide (27a)

The compound **27a** was prepared according to the general procedure from *n*-butyldiphenylphosphine oxide (**27**) (0.086 g, 0.33 mmol), sodium (0.092 g, 12 equiv) and *i*-PrOH (0.299 mL, 12 equiv). Yield: 0.021 g (24%). Colorless oil. Rf = 0.39 (CHCl<sub>3</sub>/MeOH = 15:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.95 (t, *J*<sub>H-H</sub> = 7.4 Hz, 3H), 1.22–1.33 (m, 7H), 1.36–1.47 (m, 5H), 1.56–1.69 (m, 4H), 1.73–1.78 (m, 3H), 1.78–1.82 (m, 1H), 1.83–1.90 (m, 5H), 1.91–2.05 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 13.7 (d, *J*<sub>P-C</sub> = 64.5 Hz), 23.3, 23.7, 24.1 (d, *J*<sub>P-C</sub> = 4.5 Hz), 24.7 (d, *J*<sub>P-C</sub> = 13.6 Hz), 25.6 (d, *J*<sub>P-C</sub> = 2.7 Hz), 25.9 (d, *J*<sub>P-C</sub> = 2.7 Hz), 26.0 (d, *J*<sub>P-C</sub> = 1.2 Hz), 26.6 (d, *J*<sub>P-C</sub> = 3.6 Hz), 26.7 (d, *J*<sub>P-C</sub> = 4.5 Hz), 36.2 (d, *J*<sub>P-C</sub> = 64.5 Hz). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 51.6. GC t<sub>R</sub> = 9.6 min; GCMS (EI, 70 eV), m/z 146 (100) 65 (60) 55.10 (47.96) 91 (45) 147 (30) 173 (24) 83 (18) 81 (17) 92 (12) 105 (11) 104 (11) 63 (10) 64 (10). HRMS (ESI): m/z = 541.4312 [C<sub>32</sub>H<sub>62</sub>O<sub>2</sub>P<sub>2</sub>+H]<sup>+</sup>, m/z (calc'd) = 541.4298, diff. = 2.59 ppm.

#### 4.3.23. Dicyclohexyl(*i*-propyl)phosphine oxide (28a)

The compound **28a** was prepared according to the general procedure from *i*-propyldiphenylphosphine oxide (**28**) (0.081 g, 0.33 mmol), sodium (0.092 g, 12 equiv) and *i*-PrOH (0.298 mL, 12 equiv). Yield: 0.038 g (45%). White crystal, mp = 79–81 °C; Rf = 0.40 (CHCl<sub>3</sub>/MeOH = 15:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.23 (dd, *J*<sub>P-H</sub> = 14.2, *J*<sub>H-H</sub> = 7.3 Hz, 6H), 1.22–1.32 (m, 6H), 1.39–1.50 (m, 4H), 1.75 (dt, *J*<sub>H-H</sub> = 2.9, *J*<sub>H-H</sub> = 1.5 Hz, 2H), 1.82–1.91 (m, 5H), 1.92–1.99 (m, 4H), 2.07–2.16 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 16.5 (d, *J*<sub>P-C</sub> = 2.7 Hz), 24.4 (d, *J*<sub>P-C</sub> = 60.9 Hz), 26.1 (d, *J*<sub>P-C</sub> = 1.2 Hz), 26.4 (d, *J*<sub>P-C</sub> = 2.7 Hz), 26.9 (d, *J*<sub>P-C</sub> = 10.9 Hz), 35.5 (d, *J*<sub>P-C</sub> = 60.9 Hz). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 52.9. GC t<sub>R</sub> = 9.9 min; GCMS (EI, 70 eV), m/z 174 (100) 93 (92) 55 (74) 132 (52) 81 (43) 119 (32) 92 (32) 133 (32) 83 (27) 175 (20) 201 (16) 113 (15) 63 (15) 213 (14) 79 (14) 67 (12) 73 (11) 91 (11) 173 (10). HRMS (ESI): m/z = 513.4004 [C<sub>30</sub>H<sub>58</sub>O<sub>2</sub>P<sub>2</sub>+H]<sup>+</sup>, m/z (calc'd) = 513.3985, diff. = 3.70 ppm.

#### 4.3.24. Dicyclohexylcyclopentylphosphine oxide (29a)

The compound **29a** was prepared according to the general procedure from cyclopentylphenylphosphine oxide (**29**) (0.27 g, 1 mmol), sodium (0.276 g, 12 equiv) and *i*-PrOH (0.896 mL, 12 equiv). Yield: 0.065 g (23%). Colorless oil. Rf = 0.33 (CHCl<sub>3</sub>/MeOH = 15:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.20–1.25 (m, 6H), 1.29–1.40 (m, 4H), 1.51–1.60 (m, 3H), 1.72 (bs, 5H), 1.78–1.88 (m, 9H), 1.94 (m, 4H), 2.02–2.08 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 26.1, 26.3 (d, *J*<sub>P-C</sub> = 8.2 Hz), 26.6 (d, *J*<sub>P-C</sub> = 2.7 Hz), 26.7, 26.9 (d, *J*<sub>P-C</sub> = 11.8 Hz), 33.9 (d, *J*<sub>P-C</sub> = 64.5 Hz), 37.1 (d, *J*<sub>P-C</sub> = 62.7 Hz). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 53.9. GC t<sub>R</sub> = 11.3 min; GCMS (EI, 70 eV), m/z 55 (100) 200 (90) 132 (90) 133 (89) 119 (86) 118 (49) 81 (46) 83 (39) 99 (39) 67 (31) 159 (28) 214 (25) 145 (21) 201 (19) 199 (18) 69 (18) 79 (18) 82 (16) 113 (13) 51 (12) 227 (11) 241 (11) 117 (10). HRMS (ESI): m/z = 565.4307 [C<sub>34</sub>H<sub>62</sub>O<sub>2</sub>P<sub>2</sub>+H]<sup>+</sup>, m/z (calc'd) = 565.4298, diff. = 1.59 ppm.

#### 4.3.25. 5,10-Dicyclopentyltetradecahydrophosphanthrene 5,10-dioxide (29b)

The four isomers of compound **29b** was formed according to the general procedure from cyclopentylphenylphosphine oxide (**29**) (0.27 g, 1 mmol), sodium (0.276 g, 12 equiv) and *i*-PrOH (0.896 mL, 12 equiv). According to <sup>31</sup>P NMR spectrum, the total yield of four isomers is 33%. The only one isomer **29b** was

isolated in a yield of 5% and characterized. White crystal, mp = 353–355 °C; Yield: 0.020 g (5%). Rf = 0.33 (CHCl<sub>3</sub>/MeOH = 15:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 1.17–1.27 (m, 4H), 1.47–1.55 (m, 4H), 1.59–1.68 (m, 5H), 1.75–1.84 (m, 5H), 1.87–1.84 (m, 4H), 1.96–2.10 (m, 9H), 2.12–2.24 (m, 5H), 2.33–2.40 (m, 5H), 2.41–2.49 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 25.3–25.6 (m), 25.7–26.0 (m), 28.6, 34.5 (d, J<sub>P-C</sub> = 63.6 Hz), 40.5 (d, J<sub>P-C</sub> = 58.1 Hz). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 45.5. GC t<sub>R</sub> = 16.0 min; GCMS (EI, 70 eV), m/z 327.10 (100.00) 246.05 (36.55) 81.10 (30.46) 67.05 (26.22) 79.05 (22.98) 328.10 (20.52) 245.10 (17.81) 69.05 (16.31) 247.00 (10.48) 113.05 (10.07) 178.05 (10.07) 85.05 (9.88). HRMS (ESI): m/z = 419.2237 [C<sub>22</sub>H<sub>38</sub>O<sub>2</sub>P<sub>2</sub>+Na]<sup>+</sup>, m/z (calc'd) = 419.2239, diff. = -0.48 ppm.

#### 4.3.26. Di-*n*-butyl(3-methoxycyclohexyl)phosphine oxide (30a)

The compound **30a** was prepared according to the following general procedure from di-*n*-butyl(3-methoxyphenyl)phosphine oxide (**30**) (0.081 g, 0.3 mmol), sodium (0.041 g, 6 equiv) and *i*-PrOH (0.137 mL, 6 equiv). Yield: 0.025 g (30%, as a mixture of two isomers in a ratio of 6.16:1). Colorless oil. Rf = 0.27 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 15:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (*major isomer*) 0.95 (t, J<sub>H-H</sub> = 7.25 Hz, 6H), 1.12–1.38 (m, 4H), 1.39–1.47 (m, 4H), 1.54–1.73 (m, 8H), 1.79 (d, J<sub>P-H</sub> = 13.2 Hz, 1H), 1.88 (d, J<sub>P-H</sub> = 12.0 Hz, 1H), 1.89–1.97 (m, 1H), 2.10–2.17 (m, 1H), 2.26–2.33 (m, 1H), 3.16 (s, 1H), 3.38 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 13.7, 23.6 (d, J<sub>P-C</sub> = 3.6 Hz), 23.6 (d, J<sub>P-C</sub> = 3.6 Hz), 24.4 (d, J<sub>P-C</sub> = 1.8 Hz), 24.5 (d, J<sub>P-C</sub> = 1.8 Hz), 24.8 (d, J<sub>P-C</sub> = 14.5 Hz), 24.9 (d, J<sub>P-C</sub> = 2.7 Hz), 25.2 (d, J<sub>P-C</sub> = 4.5 Hz), 25.7 (d, J<sub>P-C</sub> = 5.5 Hz), 30.9 (d, J<sub>P-C</sub> = 1.8 Hz), 31.8, 35.6 (d, J<sub>P-C</sub> = 66.3 Hz), 55.8, 79.2 (d, J<sub>P-C</sub> = 14.5 Hz), signals for the minor isomer are omitted for clarity. <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 49.8 (*major isomer*) and 51.3 (*minor isomer*) (signals ratio 6.16: 1). GC (*major isomer*) t<sub>R</sub> = 11.2 min; GCMS (EI, 70 eV), m/z 78 (100) 79 (88) 120 (64) 81 (51) 55 (41) 63 (40) 121 (36) 163 (34) 147 (30) 162 (27) 146 (25) 243 (25) 161 (24) 105 (24) 45 (23) 159 (22) 201 (20) 218 (19) 133 (18) 144 (18) 71 (16) 135 (15) 189 (15) 245 (14) 187 (14) 57 (14) 160 (13) 107 (13) 213 (11) 188 (11) 83 (11) 53 (11) 145 (10) 203 (10) 64 (10) 111 (10) 176 (10) 77 (10). (*minor isomer*) t<sub>R</sub> = 11.9 min; GCMS (EI, 70 eV), m/z 78 (100) 147 (99) 111 (86) 163 (73) 79 (70) 189 (69) 121 (63) 133 (63) 81 (62) 55 (57) 120 (56) 63 (52) 105 (45) 97 (44) 45 (43) 259 (40) 217 (33) 71 (26) 162 (25) 161 (24) 243 (24) 218 (22) 107 (22) 175 (17) 203 (16) 245 (16) 201 (15) 77 (15) 91 (15) 92 (15) 53 (15) 159 (14) 64 (14) 187 (12) 86 (11) 146 (10) 213 (10) 112 (10) 57 (10) 49 (10). HRMS (ESI): m/z = 275.2137 [C<sub>15</sub>H<sub>31</sub>O<sub>2</sub>P+H]<sup>+</sup>, m/z (calc'd) = 275.2134, diff. = 1.09 ppm.

#### 4.3.27. Di-*n*-butyl(4-methoxycyclohexyl)phosphine oxide (31a)

The compound **31a** was prepared according to the following general procedure from di-*n*-butyl(4-methoxyphenyl)phosphine oxide (**31**) (0.08 g, 0.3 mmol), sodium (0.041 g, 6 equiv) and *i*-PrOH (0.137 mL, 6 equiv). Yield: 0.08 g (10%, as a mixture of two isomers in a ratio of 1:3.24). Colorless oil. Rf = 0.39 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 15:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ (*major isomer*) 0.94 (t, J<sub>H-H</sub> = 7.3 Hz, 6H), 1.37–1.48 (m, 6H), 1.54–1.72 (m, 12H), 2.04–2.13 (m, 3H) 3.31 (s, 3H), 3.49–3.54 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ (*major isomer*) 13.7, 19.6 (d, J<sub>P-C</sub> = 1.8 Hz), 23.5 (d, J<sub>P-C</sub> = 3.6 Hz), 24.5 (d, J<sub>P-C</sub> = 13.5 Hz), 25.2 (d, J<sub>P-C</sub> = 63.4 Hz), 29.5 (d, J<sub>P-C</sub> = 11.8 Hz), 36.7 (d, J<sub>P-C</sub> = 66.5 Hz), 55.7 73.8. <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 50.5 (*minor isomer*) and 50.6 (*major isomer*) (signals ratio 1:3.24). GC (*major isomer*) t<sub>R</sub> = 11.2 min; GCMS (EI, 70 eV), m/z 78 (100) 79 (69) 120 (54) 121 (36) 81 (34) 243 (34) 55 (33) 159 (32) 63 (31) 163 (31) 162 (22) 201 (21) 161 (15) 218 (12) 144 (11) 133 (11) 57 (10) 45 (10) 158 (10). (*minor isomer*) t<sub>R</sub> = 11.3 min; GCMS (EI, 70 eV), m/z 78 (100) 120 (56) 79 (46) 217 (44) 55 (42) 243 (41) 81 (41) 63 (37) 203 (31) 163 (30) 259 (29) 121 (27) 161 (27) 201

(25) 159 (24) 162 (23) 133 (22) 175 (21) 111 (20) 45 (20) 218 (18) 245 (17) 58 (12) 71 (11) 64 (10) 77 (10) 53 (10). HRMS (ESI): m/z = 275.2123 [C<sub>15</sub>H<sub>31</sub>O<sub>2</sub>P+H]<sup>+</sup>, m/z (calc'd) = 275.2134, diff. = -4.00 ppm.

#### 4.3.28. Di-*n*-butyl(4-methylcyclohexyl)phosphine oxide (32a)

The compound **32a** was prepared according to the following general procedure from di-*n*-butyl(4-methylphenyl)phosphine oxide (**32**) (0.076 g, 0.3 mmol), sodium (0.041 g, 6 equiv) and *i*-PrOH (0.137 mL, 6 equiv). Yield: 0.057 g (74%, as a mixture of two isomers in a ratio of 1.7:1). Colorless oil. Rf = 0.37 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH = 15:1). <sup>1</sup>H NMR (500 MHz, CHLOROFORM-*d*) δ ppm 0.85–1.02 (m, 10H), 1.32–1.48 (m, 6H), 1.50–1.77 (m, 12H), 1.79–1.99 (m, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ (*major isomer*) 13.7, 20.0 (d, J<sub>P-C</sub> = 2.7 Hz), 22.6 (d, J<sub>P-C</sub> = 1.8 Hz), 23.7 (d, J<sub>P-C</sub> = 4.5 Hz), 24.4 (d, J<sub>P-C</sub> = 13.6 Hz), 25.3 (d, J<sub>P-C</sub> = 63.7 Hz), 32.3 (d, J<sub>P-C</sub> = 1.2 Hz), 35.0 (d, J<sub>P-C</sub> = 12.7 Hz), 36.4 (d, J<sub>P-C</sub> = 66.3 Hz). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 51.6 (*major isomer*) and 51.7 (*minor isomer*) (signals ratio 1.7:1). GC (*major isomer*) t<sub>R</sub> = 10.4 min; GCMS (EI, 70 eV), m/z 78 (100) 120 (71) 55 (61) 160 (34) 162 (31) 63 (29) 95 (24) 229 (23) 187 (21) 79 (20) 202 (19) 174 (17) 121 (17) 92 (16) 133 (16) 105 (15) 91 (14) 107 (14) 163 (12) 161 (12) 147 (12) 67 (11) 64 (10) 106 (10); (*minor isomer*) t<sub>R</sub> = 10.3 min; GCMS (EI, 70 eV), m/z 78 (100) 55 (74) 120 (72) 160 (35) 63 (35) 162 (33) 229 (31) 92 (24) 202 (22) 79 (20) 133 (19) 187 (18) 95 (17) 105 (16) 107 (16) 91 (16) 121 (15) 147 (15) 189 (14) 163 (13) 161 (12) 174 (12) 106 (12) 64 (11) 67 (11) 145 (11) 97 (10). HRMS (ESI): m/z = 517.4304 [C<sub>30</sub>H<sub>62</sub>O<sub>2</sub>P<sub>2</sub>+H]<sup>+</sup>, m/z (calc'd) = 517.4298, diff. = 1.16 ppm.

#### 4.3.29. Di-*n*-butyl(3,5-dimethylcyclohexyl)phosphine oxide (33a)

The compound **33a** was prepared according to the following general procedure from di-*n*-butyl(3,5-dimethylphenyl)phosphine oxide (**33**) (0.08 g, 0.3 mmol), sodium (0.041 g, 6 equiv) and *i*-PrOH (0.137 mL, 6 equiv). Yield: 0.063 g (77%, as a mixture of three isomers in a ratio of A:B:C = 1:1.7:2.0). Colorless oil.

*Isomer A.* Colorless oil; Rf<sub>A</sub> = 0.4 (CHCl<sub>3</sub>/MeOH = 15:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.89 (d, J<sub>H-H</sub> = 6.31 Hz, 6H), 0.96 (t, J<sub>H-H</sub> = 7.10 Hz, 6H), 1.14–1.26 (m, 2H), 1.39–1.50 (m, 6H), 1.51–1.62 (m, 2H), 1.64–1.76 (m, 4H), 1.77–1.90 (m, 3H), 1.97–2.09 (m, 4H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 13.7, 18.4, 22.9, 24.33 (d, J<sub>P-C</sub> = 6.4 Hz), 24.4 (d, J<sub>P-C</sub> = 16.4 Hz), 26.7 (d, J<sub>P-C</sub> = 62.7 Hz), 28.7, 33.0 (d, J<sub>P-C</sub> = 65.4 Hz), 33.8 (d, J<sub>P-C</sub> = 2.7 Hz), 43.7. <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 54.2. GC t<sub>R</sub> = 8.7 min; GCMS (EI, 70 eV), m/z 189 (100) 120 (64) 92 (45) 109 (40) 162 (39) 216 (36) 174 (36) 243 (34) 147 (26) 163 (22) 134 (21) 133 (19) 107 (17) 201 (13) 121 (12) 106 (11) 161 (11) 190 (10) 217 (10) 160 (10) 81 (10) 132 (10). HRMS (ESI): m/z = 545.4619 [C<sub>32</sub>H<sub>66</sub>O<sub>2</sub>P<sub>2</sub>+H]<sup>+</sup>, m/z (calc'd) = 545.4611, diff. = 1.47 ppm.

*Isomer B.* Colorless oil; Rf<sub>B</sub> = 0.36 (CHCl<sub>3</sub>/MeOH = 15:1). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.91 (d, J<sub>H-H</sub> = 6.31 Hz, 3H), 0.95 (t, J<sub>H-H</sub> = 7.30 Hz, 6H), 1.02 (d, J<sub>P-H</sub> = 7.25 Hz, 3H), 1.16 (td, J<sub>P-H</sub> = 12.77, 4.73 Hz, 1H), 1.39–1.48 (m, 4H), 1.50–1.74 (m, 13H), 1.80–1.91 (m, 1H), 2.01 (qt, J<sub>P-H</sub> = 12.85, 3.11 Hz, 1H), 2.14–2.21 (m, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 13.7 17.7–18.4 (m) 22.8, 23.6 (d, J<sub>P-C</sub> = 3.6 Hz), 23.7 (d, J<sub>P-C</sub> = 4.5 Hz), 24.4 (d, J<sub>P-C</sub> = 2.2 Hz), 24.5 (d, J<sub>P-C</sub> = 1.8 Hz), 25.0 (d, J<sub>P-C</sub> = 6.4 Hz), 25.5 (d, J<sub>P-C</sub> = 6.4 Hz), 26.4 (d, J<sub>P-C</sub> = 12.7 Hz), 27.6 (d, J<sub>P-C</sub> = 12.7 Hz), 30.3 (d, J<sub>P-C</sub> = 2.7 Hz), 30.8 (d, J<sub>P-C</sub> = 67.2 Hz), 33.8 (d, J<sub>P-C</sub> = 3.6 Hz), 40.1. <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>) δ 51.5. GC t<sub>R</sub> = 9.1 min; GCMS (EI, 70 eV), m/z 120 (100) 92 (50) 109 (47) 162 (46) 174 (41) 147 (34) 243 (27) 133 (27) 121 (26) 216 (25) 163 (21) 201 (20) 189 (20) 105 (20) 188.05 (18) 107 (17) 91 (14) 106 (13) 134 (12) 161 (11) 132 (11) 118 (10). HRMS (ESI): m/z = 273.2334 [C<sub>16</sub>H<sub>33</sub>OP+H]<sup>+</sup>, m/z (calc'd) = 273.2342, diff. = -2.93 ppm.



*Isomer C*. Colorless oil;  $R_f = 0.37$  ( $\text{CHCl}_3/\text{MeOH} = 15:1$ ).  $^{31}\text{P}$  NMR (202 MHz,  $\text{CDCl}_3$ )  $\delta$  50.0. GC  $t_R = 9.0$  min; GCMS (EI, 70 eV),  $m/z$  120 (100) 174 (48) 162 (42) 243 (38) 216 (30) 109 (29) 121 (29) 188 (23) 163 (21) 92 (19) 133 (17) 107 (16) 201 (15) 159 (13) 105 (13) 106 (12) 111 (10) 161 (10). HRMS (ESI):  $m/z = 273.2335$  [ $\text{C}_{16}\text{H}_{33}\text{OP}+\text{H}$ ] $^+$ ,  $m/z$  (calc'd) = 273.2342, diff. = -2.56 ppm.

#### 4.3.30. Dimethyl(1,2,3,4-tetrahydronaphthalen-1-yl)phosphine oxide (34a)

The compound **34a** was prepared according to the following general procedure from dimethyl(naphthalen-1-yl)phosphine oxide (**34**) (0.082 g, 0.4 mmol), sodium (0.041 g, 4 equiv) and *i*-PrOH (0.122 mL, 4 equiv). Yield: 0.040 g (48%). White crystal, mp = 51–52 °C;  $R_f = 0.33$  ( $\text{CH}_2\text{Cl}_2/\text{MeOH} = 15:1$ ).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  1.54 (d,  $J_{\text{P-H}} = 12.0$  Hz, 6H), 1.69–1.81 (m, 1H), 2.08 (m, 1H), 2.23–2.31 (m, 1H), 2.82–3.11 (m, 4H), 7.10–7.18 (m, 4H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5 (d,  $J_{\text{P-C}} = 7.3$  Hz), 14.1 (d,  $J_{\text{P-C}} = 7.3$  Hz), 22.5 (d,  $J_{\text{P-C}} = 2.7$  Hz), 28.4, 29.1 (d,  $J_{\text{P-C}} = 12.7$  Hz), 36.2 (d,  $J_{\text{P-C}} = 71.8$  Hz), 126.1, 126.2, 129.0, 134.5 (d,  $J_{\text{P-C}} = 12.7$  Hz,  $C^{IV}$ ) 135.8.  $^{31}\text{P}$  NMR (202 MHz,  $\text{CDCl}_3$ )  $\delta$  46.2. GC  $t_R = 11.3$  min; GCMS (EI, 70 eV),  $m/z$  130 (100) 129 (57) 115 (31) 128 (28) 131 (17) 91 (14) 127 (12) 208 (10). HRMS (ESI):  $m/z = 417.2118$  [ $\text{C}_{24}\text{H}_{34}\text{O}_2\text{P}_2+\text{H}$ ] $^+$ ,  $m/z$  (calc'd) = 417.2107, diff. = 2.64 ppm.

#### 4.3.31. Di-*n*-butyl(1,2,3,4-tetrahydronaphthalen-1-yl)phosphine oxide (35a)

The compound **35a** was prepared according to the following general procedure from di-*n*-butyl(naphthalen-1-yl)phosphine oxide (**35**) (0.086 g, 0.3 mmol), sodium (0.028 g, 4 equiv) and *i*-PrOH (0.092 mL, 4 equiv). Yield: 0.037 g (42%). Colorless oil;  $R_f = 0.45$  ( $\text{CH}_2\text{Cl}_2/\text{MeOH} = 15:1$ ).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (dt,  $J_{\text{P-H}} = 14.5$ , 7.3 Hz, 6H), 1.30–1.42 (m, 4H), 1.46–1.73 (m, 9H), 1.96–2.11 (m, 3H), 2.79 (t,  $J_{\text{P-H}} = 5.4$  Hz, 2H), 3.40–3.48 (m, 1H), 7.10–7.13 (m, 1H), 7.14–7.17 (m, 2H), 7.49–7.53 (m, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  13.6 (d,  $J_{\text{P-C}} = 1.8$  Hz), 21.5 (d,  $J_{\text{P-C}} = 5.5$  Hz), 23.6 (d,  $J_{\text{P-C}} = 4.5$  Hz), 23.7 (d,  $J_{\text{P-C}} = 4.5$  Hz), 23.9 (d,  $J_{\text{P-C}} = 1.9$  Hz), 24.3 (d,  $J_{\text{P-C}} = 2.7$  Hz), 24.4 (d,  $J_{\text{P-C}} = 2.7$  Hz), 26.0 (d,  $J_{\text{P-C}} = 62.7$  Hz), 26.7 (d,  $J_{\text{P-C}} = 63.6$  Hz), 29.5 (d,  $J_{\text{P-C}} = 1.2$  Hz), 38.4 (d,  $J_{\text{P-C}} = 60.0$  Hz), 125.9 (d,  $J_{\text{P-C}} = 2.7$  Hz), 126.5 (d,  $J_{\text{P-C}} = 2.7$  Hz), 129.5 (d,  $J_{\text{P-C}} = 1.8$  Hz), 129.8 (d,  $J_{\text{P-C}} = 3.6$  Hz), 131.9 (d,  $J_{\text{P-C}} = 5.5$  Hz,  $C^{IV}$ ) 138.1 (d,  $J_{\text{P-C}} = 5.5$  Hz,  $C^{IV}$ ).  $^{31}\text{P}$  NMR (202 MHz,  $\text{CDCl}_3$ )  $\delta$  52.4. GC  $t_R = 12.2$  min; GCMS (EI, 70 eV),  $m/z$  131 (100) 130 (55) 78 (41) 91 (25) 120 (23) 163 (20) 129 (20) 115 (13) 236 (13) 292 (13) 63 (11) 132 (11) 116 (10). HRMS (ESI):  $m/z = 315.1840$  [ $\text{C}_{18}\text{H}_{29}\text{OP}+\text{Na}$ ] $^+$ ,  $m/z$  (calc'd) = 315.1848, diff. = -2.54 ppm.

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## Supplementary Material

Supplementary data include the copies of  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR spectra for all products and a copy of CIF file for **26b-F3** (Cambridge Crystallographic Data Centre No. 1537702) described in this article can be found at...

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