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Sodium in liquid ammonia—a versatile tool in modifications of arylphosphine oxides

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ABSTRACT

A simple and practical method for modifications of tertiary arylphosphine oxides based on their reaction with sodium in liquid ammonia is presented. Depending on the structure of the starting compounds, either dearomatisation of the phenyl substituent or cleavage of a *P*-aryl bond from phosphorus atom can be selectively performed and the corresponding (1,4-cyclohexadien-3-yl)phosphine oxides or secondary phosphine oxides were obtained in good to excellent yields.

1. Introduction

A glance at current mono- and diphosphines reveals that they generally possess at least one aromatic substituent at the phosphorus atom.[1] This is at least partially because of the greater resistance to oxidation of arylphosphines than trialkylphosphines, which means that arylphosphines can often be handled without special precautions. However, the better σ-donor ability of alkylphosphines constitutes a fundamental advantage when designing ligands, in that it enhances the stability of complexes with transition metals and thus influences the binding of the reactants to the metal center; trialkyl mono- and diphosphines, such as bisP*,[2] TangPhos,[3] Et-bpe[4] or MiniPhos[5] have been shown to be excellent ligands in many catalytic asymmetric transformations. Their superior performance underlines why developing new, efficient methodologies for the synthesis of alkylphosphines is still an area of major importance.

One interesting approach to trialkylphosphines might involve taking advantage of the wide range of readily available arylphosphines and transforming them into alkylphosphines. Aryl groups introduced at phosphorus are normally left unchanged as the phosphine is elaborated, and the minority of papers that deal with the modification of aryl moieties in mono- and diphosphine derivatives tend to involve FGI at preexisting functional groups attached to the arene,[6] rather than any profound modification of the aryl groups themselves.[7] In cases where phosphine aryl substituents are transformed into alkyl groups, the protocol almost always involves reductive cleavage of *P*-aryl bond using an alkali metal and subsequent alkylation of the phospide[8] although there are precedents for the substitution of an aryl fragment by alkyl anions.[9] Both of these processes will generally cause a significant change in the shape of the molecule as the aryl fragment is replaced by a (differently sized) alkyl group, and this will not necessarily be beneficial if the starting arylphosphine provides good organization of molecular space. A process allowing the direct transformation of an aromatic fragment into an aliphatic analogue without breaking the phosphorus–carbon bond, and which also allows 'broad-brush' retention of the shape of parent compound, is therefore highly desirable. This kind of transformation is potentially accessible through Birch reduction. Surprisingly, this very useful dearomatization of arenes in the presence of strong reducing agents like alkali metals[10] is almost unexplored in organophosphorus chemistry, with the only contribution prior to our work being due to van Doorn and Meijboom who observed Birch reduction products in the reaction between some electron-rich arylphosphines and sodium in liquid ammonia.[11,12] Given that the Birch reduction generates a phosphorus-bound 1,4-cyclohexadiene group, it should also open up a very broad spectrum of post-modification protocols for organophosphorus compounds, through the reactivity at the isolated or conjugated double bonds, or through allyl anions.

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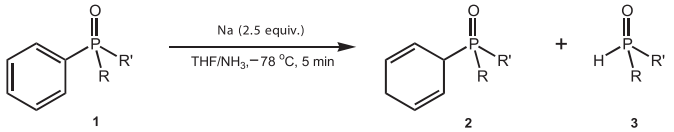
2. Results and discussion

An ongoing interest in using simple transformations to effect structural modifications of organophosphorus compounds recently led us to present results concerning the reactivity of aryldialkylphosphine–boranes toward solutions of alkali metals in liquid ammonia.[13] These phosphine-boranes generally undergo phenyl ring dearomatisation in the presence of alkali metals, to furnish the corresponding (1,4-cyclohexadien-3-yl)phosphine-boranes in good yields. However, the scope of the organophosphorus Birch reduction is not yet clear, so we have attempted to define its potential in more detail. Here, we present some outlined rules concerning its compatibility with representative members of a much wider and more easily accessible range of compounds: phosphine oxides.

An initial set of experiments tested the reactivity of various tertiary phosphine oxides toward sodium dissolved in liquid ammonia. A summary of this initial screening process is presented in the Table 1.

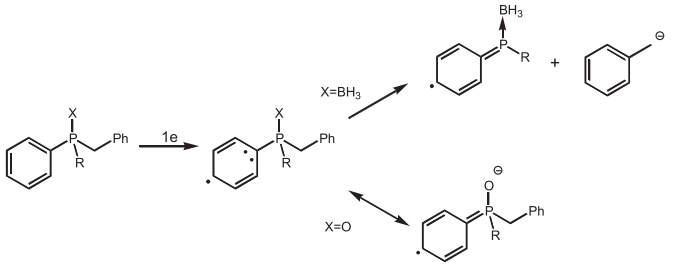
Table 1
The reactivity of acyclic tertiary phosphine oxides toward sodium in liquid ammonia



Entry	Compd	Substituents		Isolated yields (%)	
		R	R′	**2**	**3**
1	**1a**	*t*-Bu	Me	59	—
2	**1b**	*t*-Bu	Bn	59	—
3	**1c**	Bn	Me	—	47
4	**1d**	Bn	Bn	—	81
5	**1e**	Bn	2-PyCH$_2$	—	29
6	**1f**	Bn	MOM	24	36[a,c] 14[b,c]
7	**1g**	Me	Me	98	—
8	**1h**	Ph	Me	9[d]	34 (87)[e]
9	**1i**	*o*-An	Me	10[d]	87
10	**1j**	*o*-An	Bn	—	29 (73)[e]
11	**1k**	1-Np	Me	—	66
12	**1l**	Ph	Ph	—	32 (89)[e]
13	**1m**	*o*-An$_3$P(O)		—	61
14	**1n**	*o*-An	*m*-Xylyl	Complex mixture	
15	**1o**	(*p*-Cl–C$_6$H$_4$)$_3$P(O)		No reaction	

[a] The yield of phenyl(methoxymethyl)phosphine oxide, Ph(MeOCH$_2$)P(O)H, **3c**.
[b] The yield of benzyl(methoxymethyl)-phosphine oxide, Bn(MeOCH$_2$)P(O)H, **3d**.
[c] Yields calculated from ^{1}H NMR spectra of the fraction isolated by flash chromatography.
[d] Yields calculated from ^{1}H NMR spectra of crude reaction mixture.
[e] The yields in parentheses correspond to the reaction with 5 equiv of sodium.

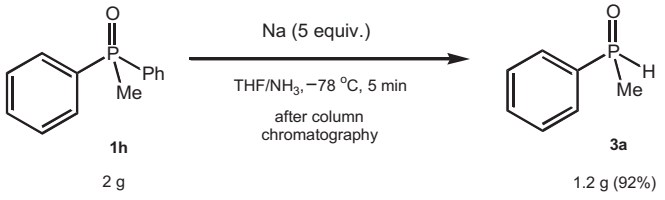
The results indicate that the behavior of different phosphine oxides toward sodium in liquid ammonia depends strongly on the nature of the starting material. Simple aryldialkylphosphine oxides possessing non-functionalized substituents undergo selective Birch reduction to the corresponding (1,4-cyclohexadien-3-yl)phosphine oxides **2a**,**b**, and **g** in good yields. The case of phosphine oxide **1b** is noteworthy: the reaction of this compound with sodium gives a clean Birch reduction of the phenyl moiety even in the presence of a chemically labile benzyl group, and this result contrasts sharply with our previous findings with benzyl(*t*-butyl)phenylphosphine-borane, which predominantly underwent *P*-benzyl bond cleavage under the same reaction conditions.[12] This quite striking difference in the behavior of phosphine–boranes and phosphine oxides toward alkali metals can be attributed to the ability of the P=O group to stabilize the intermediate anion radical, which favors the Birch reduction (Scheme 1).



Scheme 1. The possible explanation of the difference in reactivity of benzylphosphine-boranes and oxides.

Further experiments performed with different benzylphosphine oxides **1c**–**f** and **j** revealed a clear influence of the phosphorus substituents upon the lability of benzyl group (Table 1, entries 3–6 and 10). The presence of *tert*-butyl group at phosphorus atom drives the reaction with sodium toward the Birch reduction product (Table 1, entry 2) whereas methoxymethyl group yields a mixture of the Birch product (24%) and two secondary phosphine oxides formed upon *P*-benzyl (**3c**) or *P*-phenyl (**3d**) bond cleavage (Table 1, entry 6). Compounds having methyl or benzyl groups, such as **1c** and **1d**, reacted with sodium in liquid ammonia to give the corresponding secondary phosphine oxides as the sole reaction products (Table 1, entries 3 and 4). When the starting phosphine oxide has two labile groups, the reaction proceeds through the cleavage of the more stabilized carbanion, as is illustrated in the case of benzylphenyl(2-pyridylmethyl)phosphine oxide **1e** (Table 1, entry 5) and *o*-anisylbenzylphenylphosphine oxide **1j** (Table 1, entry 10). Here, both 2-pyridylmethyl carbanion and *o*-anisyl carbanions are more stabilized than the benzyl anion, so no cleavage of the benzyl group is seen upon treatment with sodium.

Unlike the aryldialkylphosphine oxides **1a**,**b**, and **g**, representative diarylalkylphosphine oxides **1h**–**k** reacted with sodium in liquid ammonia with preferential *P*-aryl bond cleavage, to give the corresponding secondary phosphine oxides. Small amounts of Birch reduction product were observed for phosphine oxide **1i** (Table 1, entry 9), and **1h** provided a small amount of bis-reduction product **2h** (Table 1, entry 8). In the case of **1h** and **1j**, the yields of the corresponding secondary phosphine oxides could be raised to 87% and 73%, respectively, by the use of 5 equiv of sodium. Clearly, these results suggest that sodium in liquid ammonia can be a good synthetic tool for preparation of secondary phosphine oxides by cleavage of one aryl moiety from diarylalkylphosphine oxides, and this was examined using phosphine oxide **1h**, which was subjected to reaction with sodium in liquid ammonia on a 2 gram-scale (Scheme 2).



Scheme 2. Gram-scale synthesis of methylphenylphosphine oxide **3a**.

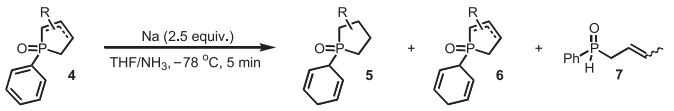
The reaction of **1h** with excess of sodium afforded **3a** cleanly in 92% yield after purification by column chromatography.

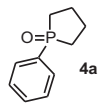
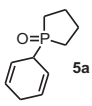
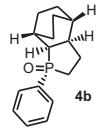
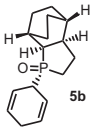
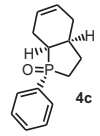
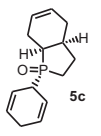
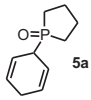
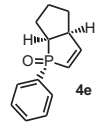
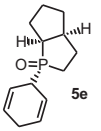
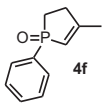
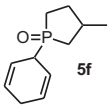
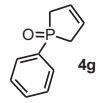
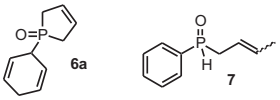
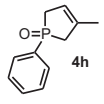
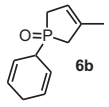
Triphenylphosphine oxide **1l** and tris(*o*-anisyl)phosphine oxide **1m** when treated with a solution of sodium in liquid ammonia yielded the corresponding secondary phosphine oxides **3e** and **3f** in 32% and 61% yields, respectively (Table 1, entries 12 and 13). As with **1h** and **1j**, reaction of triphenylphosphine oxide **1l** with excess sodium raised the yield of **3e** to 89%. It therefore appears that the

sodium–liquid ammonia system may constitute a simple and efficient way for recycling triphenylphosphine oxide, which is formed in very large amounts as a side-product in Wittig and Mitsunobu reactions, into organic synthesis. Unlike **1l**, *o*-anisylphenyl(*m*-xylyl) phosphine oxide **1n** yielded a mixture of four compounds three of them being secondary phosphine oxides, which suggests that for compounds, which do not possess preferential leaving group the reaction follow the non-selective mode. On the other hand tris(*p*-chlorophenyl)phosphine oxide **1o** failed to react with sodium under our standard reaction conditions (Table 1, entry 15), probably because the enhanced stability of the intermediate radical anion hampers further transformation.

The importance of cyclic phosphine ligands in asymmetric catalysis is very well documented[14] so it was important to check the dearomatisation of cyclic phosphine oxides possessing a *P*-phenyl under Birch reduction conditions (Table 2).

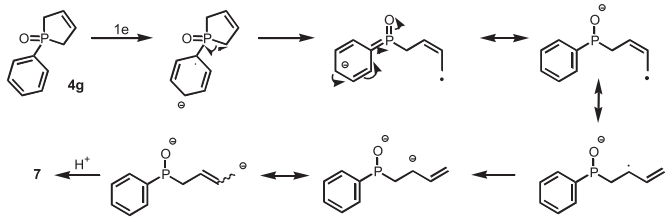
Table 2
The reactivity of cyclic tertiary phosphine oxides toward sodium in liquid ammonia



Entry	Substrate	Products	Isolated yields (%)
1			95
2			75
3			15 (73)[a]
4			52
5			62
6			44
7			56[b] 22[c]
8			70

[a] Yields in parentheses correspond to the reaction with **5** equiv of sodium.
[b] The yield of **6a**.
[c] The yield of **7**.

Upon treatment with sodium in liquid ammonia, phospholane oxides **4a–c** cleanly and exclusively yielded the corresponding Birch reduction products (Table 2, entries 1–3), with the double bond in **4c** proving stable under the reaction conditions (Table 2, entry 3). For phospholenes, the outcome of the reaction with sodium in liquid ammonia reflects the site of the double bond in the starting material. The *P*-conjugated phosphol-2-ene oxides **4d–f** reacted with sodium to give the corresponding saturated Birch reduction products. This suggests an initial reduction of the phospholene double bond by sodium metal followed by Birch reduction of the in situ formed arylphospholane oxide.[15] However, all attempts to trap the intermediate phospholane oxide failed, indicating that the putative arylphospholane is a better partner for the reaction with sodium than the starting material. Conversely, the phosphol-3-ene oxides **4g** and **4h** reacted with sodium to yield the Birch reduction products **6a** and **6b** without affecting the phospholene double bonds (Table 2, entries 7 and 8). Interestingly, treatment of phospholene oxide **4g** with sodium also gave the phospholene ring opening product **7** in 22% yield. The formation of the latter product can be explained by fragmentation of the intermediate radical anion, with a possible mechanism for the transformation of **4g** into **7** being presented in Scheme 3.



Scheme 3. Proposed mechanism of the formation of secondary phosphine oxide **7**.

One-electron reduction of phospholene oxide **4g** generates the expected radical anion which then rearranges under phospholene ring opening to give a new species having stabilized secondary phosphine oxide and stabilized allyl radical fragments. A further one-electron reduction leads to a dianion, which yields **7** upon protonation.

3. Conclusions

In summary, we have presented results concerning the reactivity of tertiary arylphosphine oxides toward sodium in liquid ammonia and shown that the structure of the starting material seems to govern the outcome of the reaction in a way, which is quite predictable. Simple aryldialkylphosphine oxides give the corresponding Birch reduction products, whereas benzylphosphine oxides, diarylalkylphosphine oxides, and triarylphosphine oxides react under the same conditions to give the corresponding secondary phosphine oxides through cleavage of a benzyl or aryl group from phosphorus. The reactivity of cyclic phosphine oxides toward sodium also reflects the structure of the starting material: phospholane oxides react with sodium yielding the corresponding dearomatisation products, whereas phosphol-2-ene oxides afford products showing both reduction of the double bond and dearomatization of phenyl ring. Phosphol-3-ene oxides yield the corresponding Birch reduction products without affecting the double bond.

4. Experimental section

4.1. General

All reactions were performed in vacuum- and flame-dried glass reaction flasks under argon atmosphere. All reagents were purchased from commercial sources and used as received. Ammonia

was passed through a column filled with a solid potassium hydroxide before condensation. Oxygen and moisture-free tetrahydrofuran was prepared by heating at reflux with sodium and benzophenone. The course of the reaction was followed by TLC (Merck) and the visualization of the TLC plates was afforded with UV light (254 nm), $KMnO_4$ solution or iodine adsorbed on silica. Separations of the reaction mixtures were performed on Merck silica gel 60 (0.015–0.040 mm).

Compounds were characterized by ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, GC–MS, and HPLC-MS. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker Avance 300 MHz or Varian Mercury 400BB. All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals for $CHCl_3$ (7.26 ppm). All ^{13}C NMR spectra were reported in parts per million relative to residual $CHCl_3$ (77.00 ppm) and were obtained with 1H decoupling. GC–MS analyses were performed on Shimadzu GC–MS QP2010S equipped with FID detector for gas chromatograph and EI ionization source for mass spectroscopy. The samples were run on Phenomenex Zebron ZB-35HT INFERNO column (presssure—53.5 kPa, total flow—24 mL/min, column flow—1 mL/min, linear velocity—36.3 cm/s, split—20), temperature program (50 °C—hold 2 min, 50–250 °C–10 °C/min—hold 2 min, 250–280 °C–10 °C/min—hold 3.34 min—total 35 min) or Phenomenex Zebron ZB-5MSi column (pressure—65 kPa, total flow—23.9 mL/min, column flow—1.2 mL/min, linear velocity—36.8 cm/s, split—20), temperature program (80–250 °C—20 °C/min—hold 5 min, 250–300 °C—10 °C/min—hold 30.5 min—total 50 min). RP-HPLC-HRMS analysis was performed on Shimadzu LC-MS IT-TOF equipped with IT-TOF detector and ESI ionization. The samples were run on Phenomenex Kinetex 2.6u C18 100A column using H_2O/MeOH isocratic flow. Melting points were obtained on HMK VEB Analytik apparatus and were uncorrected.

tert-Butylmethylphenylphosphine oxide **1a**,[16] methyldiphenylphosphine oxide **1h**,[17] tris(*o*-anisyl)phosphine oxide **1m**[18], and tris(*p*-chlorophenyl)phosphine oxide **1o**[19] were prepared according to literature procedures. Secondary phosphine oxides used for the synthesis of starting material were prepared according to procedure of Emmick and Letsinger.[20] Phospholane oxide **4a**,[21] phosphol-2-ene oxides **4d**,[22] **e**,[23] **f**,[21] and phosphol-3-ene oxides **4g**,[24] **h**[25] were prepared according to literature procedures. Phospholane oxides **4b**,**c** were prepared as a part of another project running in our laboratory[26] and the procedures will be published soon. All data are in according with previously reported.

4.2. General procedure for the synthesis of phosphine oxides 1b–f,i–k

Into a flame-dried two-necked flask equipped with magnetic stirrer and argon inlet was placed secondary phosphine oxide (3 mmol) in dry and degassed THF (15 mL). The mixture was cooled to 0 °C and sodium hydride (3.3 mmol, 60% dispersion in mineral oil) was added in one portion. After the evolution of hydrogen ceased, the appropriate alkyl halide (3.3 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_4Cl solution (10 mL), the mixture was extracted with DCM (3×30 mL), the organic layers were collected, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by flash chromatography using chloroform/methanol 15:1 as eluent.

*4.2.1. Benzyl-tert-butylphenylphosphine oxide (**1b**).* Prepared from *tert*-butylphenylphosphine oxide (0.546 g, 3 mmol) and benzyl chloride (0.380 mL, 3.3 mmol) using general procedure. Yield 0.726 g (89%). White solid. Mp=186.0–188.0 °C (lit.[27] 190–191 °C); [Found: C, 74.86; H, 7.92%. $C_{17}H_{21}OP$ requires C, 74.98; H, 7.77%]; R_f (EtOAc) 0.50; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.08 (d, J_{P-H}=14.8 Hz, 9H), 3.33–3.45 (m, 2H), 7.10–7.25 (m, 6H), 7.28–7.40 (m, 2H), 7.60–7.69 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 24.6, 31.2 (d, J_{P-C}=58.3 Hz), 33.3 (d, J_{P-C}=67.8 Hz), 126.5 (d, J_{C-P}=2.3 Hz), 128.0 (d, J_{C-P}=10.9 Hz), 128.25 (d, J_{C-P}=1.7 Hz), 129.29 (d, J_{C-P}=109.2 Hz), 130.1 (d, J_{C-P}=4.9 Hz), 131.5 (d, J_{C-P}=2.6 Hz), 131.7 (d, J_{C-P}=9.8 Hz), 131.9 (d, J_{C-P}=8.1 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ: 46.66 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=21.03 min; GC–MS (EI, 70 eV) *m*/*z*: 272 ($M^{\bullet+}$) (8%), 271 (15%), 216 (16%), 125 (100%), 92 (16%), 91 (50%). NMR data are consistent with previously reported.[27]

*4.2.2. Benzylmethylphenylphosphine oxide (**1c**).* Prepared from benzylphenylphosphine oxide (0.648 g, 3 mmol) and methyl iodide (0.206 mL, 3.3 mmol) using general procedure. Yield 0.566 g (82%). White solid. Mp=139.7–142.0 °C (lit.[28] 142–144 °C); [Found: C, 73.24; H, 6.70%. $C_{14}H_{15}OP$ requires C, 73.03; H, 6.57%]; R_f ($CHCl_3$/MeOH 15:1) 0.27; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.68 (d, J_{P-H}=12.9 Hz, 3H), 3.23–3.39 (m, 2H), 7.07–7.11 (m, 2H), 7.21–7.28 (m, 3H), 7.42–7.47 (m, 2H), 7.50–7.55 (m, 1H), 7.58–7.64 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.6 (d, J_{P-C}=71.0 Hz), 40.4 (d, J_{P-C}=65.2 Hz), 126.9 (d, J_{P-C}=3.4 Hz), 128.5 (d, J_{P-C}=15.8 Hz), 128.5 (d, J_{P-C}=1.4 Hz), 129.7 (d, J_{P-C}=5.2 Hz), 130.3 (d, J_{P-C}=9.2 Hz), 131.7 (d, J_{P-C}=2.9 Hz), 131.8 (d, J_{P-C}=7.5 Hz), 133.0 (d, J_{P-C}=96.8 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 35.55 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=14.26 min; GC–MS (EI, 70 eV) *m*/*z*: 230 ($M^{\bullet+}$) (13%), 229 (53%), 140 (8%), 139 (100%), 91 (34%).

*4.2.3. Dibenzylphenylphosphine oxide (**1d**).* Prepared from benzylphenylphosphine oxide (0.648 g, 3 mmol) and benzyl chloride (0.380 mL, 3.3 mmol) using general procedure. Yield 0.698 g (76%). White solid. Mp=178.0–181.0 °C; [Found: C, 78.20; H, 6.00%. $C_{20}H_{19}OP$ requires C, 78.41; H, 6.25%]; R_f ($CHCl_3$/MeOH 20:1) 0.36; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.26 (d, J_{P-H}=13.9 Hz, 4H), 7.00–7.07 (m, 4H), 7.09–7.18 (m, 6H), 7.25–7.33 (m, 2H), 7.35–7.47 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 37.4 (d, J_{P-C}=63.2 Hz), 126.75 (d, J_{P-C}=2.9 Hz), 128.16 (d, J_{P-C}=11.5 Hz), 128.4 (d, J_{P-C}=2.6 Hz), 129.9 (d, J_{P-C}=5.2 Hz), 130.9 (d, J_{P-C}=94.8 Hz), 131.0 (d, J_{P-C}=8.3 Hz), 131.4 (d, J_{P-C}=7.5 Hz), 131.6 (d, J_{P-C}=2.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 35.19 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=18.51 min; GC–MS (EI, 70 eV) *m*/*z*: 306 ($M^{\bullet+}$) (11%), 305 (12%), 215 (8%), 91 (100%). NMR data are consistent with previously reported.[29]

*4.2.4. Benzylphenyl(2-pyridylmethyl)phosphine oxide (**1e**).* Prepared from benzylphenylphosphine oxide (0.648 g, 3 mmol) and 2-(chloromethyl)pyridine (0.421 g, 3.3 mmol) using general procedure. Yield 0.645 g (70%). White solid. Mp=141.0–141.5 °C; [Found: C, 74.50; H, 6.00%. $C_{19}H_{18}NOP$ requires C, 74.25; H, 5.90%]; R_f ($CHCl_3$/MeOH 20:1) 0.25; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.40–3.46 (m, 2H), 3.57–3.62 (m, 2H), 7.11–7.23 (m, 6H), 7.27–7.31 (m, 1H), 7.32–7.39 (m, 2H), 7.43–7.48 (m, 1H), 7.48–7.60 (m, 3H), 8.49–8.53 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 37.7 (d, J_{P-C}=63.8 Hz), 39.9 (d, J_{P-C}=61.5 Hz), 121.9 (d, J_{P-C}=2.3 Hz), 125.0 (d, J_{P-C}=4.6 Hz), 126.7 (d, J_{P-C}=2.9 Hz), 128.2 (d, J_{P-C}=11.2 Hz), 128.4 (d, J_{P-C}=3.2 Hz), 130.1 (d, J_{P-C}=6.0 Hz), 130.9 (d, J_{P-C}=8.6 Hz), 131.1 (d, J_{P-C}=94.8 Hz), 131.4 (d, J_{P-C}=8.3 Hz), 131.7 (d, J_{P-C}=3.4 Hz), 136.6 (d, J_{P-C}=1.7 Hz), 149.3 (d, J_{P-C}=1.7 Hz), 152.9 (d, J_{P-C}=7.8 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 34.86 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=22.73 min; GC–MS (EI, 70 eV) *m*/*z*: 307 ($M^{\bullet+}$) (21%), 216 (100%), 199 (5%), 169 (26%), 168 (24%), 93 (68%), 92 (36%), 91 (57%); HPLC (Phenomenex Kinetex 2.6u C18 100A) t_R=0.89 min; HPLC-MS: *m*/*z* 308 ($M+H^+$).

*4.2.5. Benzyl(methoxymethyl)phenylphosphine oxide (**1f**).* Prepared from benzylphenylphosphine oxide (0.648 g, 3 mmol) and

chloromethyl methyl ether (0.251 mL, 3.3 mmol) using general procedure. Yield 0.601 g (77%). White solid. Mp=89.0–90.0 °C; [Found: C, 69.10; H, 6.40%. $C_{15}H_{17}O_2P$ requires C, 69.22; H, 6.58%]; R_f ($CHCl_3$/MeOH 20:1) 0.40; ^1H NMR ($CDCl_3$, 400 MHz) δ: 3.33–3.57 (m, 2H), 3.43 (m, 2H), 3.80 (d, J_{P-H}=7.9 Hz, 2H), 7.20–7.31 (m, 5H), 7.43–7.49 (m, 2H), 7.51–7.57 (m, 1H), 7.75–7.82 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 35.6 (d, J_{P-C}=63.2 Hz), 61.5 (d, J_{P-C}=13.5 Hz), 69.1 (d, J_{P-C}=85.9 Hz), 126.8 (d, J_{P-C}=2.9 Hz), 128.4 (d, J_{P-C}=12.1 Hz), 128.5 (d, J_{P-C}=3.2 Hz), 130.0 (d, J_{P-C}=5.5 Hz), 131.0 (d, J_{P-C}=93.7 Hz), 131.0 (d, J_{P-C}=8.3 Hz), 131.2 (d, J_{P-C}=8.6 Hz), 132.0 (d, J_{P-C}=2.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 33.08 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=14.84 min; GC–MS (EI, 70 eV) m/z: 260 ($M^{\bullet+}$) (2%), 230 (19%), 229 (55%), 139 (25%), 92 (8%), 91 (100%).

*4.2.6. o-Anisylmethylphenylphosphine oxide (**1i**).* Prepared from *o*-anisylphenylphosphine oxide (0.696 g, 3 mmol) and iodomethane (0.206 mL, 3.3 mmol) using general procedure. Yield 0.738 g (100%). White solid. Mp=131.0–134.0 °C (lit.[30] 130 °C); [Found: C, 68.30; H, 6.32%. $C_{14}H_{15}O_2P$ requires C, 68.29; H, 6.14%]; R_f ($CHCl_3$/MeOH 20:1) 0.33; ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.04 (d, J_{P-H}=13.3 Hz, 3H), 3.74 (s, 3H), 6.89–6.99 (m, 1H), 7.09–7.19 (m, 1H), 7.40–7.61 (m, 4H), 7.70–7.84 (m, 2H), 7.93–8.06 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 16.0 (d, J_{P-C}=75.4 Hz), 55.8, 111.5 (d, J_{P-C}=6.15 Hz), 121.2 (d, J_{P-C}=11.1 Hz), 128.5 (d, J_{P-C}=12.5 Hz), 130.1 (d, J_{P-C}=10.5 Hz), 131.8 (d, J_{P-C}=2.9 Hz), 133.3 (d, J_{P-C}=6.4 Hz), 134.6 (d, J_{P-C}=2.3 Hz); ^{31}P NMR ($CDCl_3$, 202 MHz) δ: 34.86 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=21.52 min; GC–MS (EI, 70 eV) m/z: 246 ($M^{\bullet+}$) (55%), 245 (51%), 229 (24%), 228 (37%), 217 (28%), 216 (15%), 215 (100%), 213 (18%), 199 (33%), 167 (17%), 155 (69%), 153 (12%), 152 (33%), 140 (15%), 139 (37%), 137 (12%), 125 (19%), 121 (10%), 115 (12%), 109 (11%), 107 (12%), 95 (11%), 92 (20%), 91 (85%). NMR data are consistent with previously reported.[31]

*4.2.7. o-Anisylbenzylphenylphosphine oxide (**1j**).* Prepared from *o*-anisylphenylphosphine oxide (0.696 g, 3 mmol) and benzyl chloride (0.380 mL, 3.3 mmol) using general procedure. Yield 0.908 g (94%). White solid. Mp=144.0–146.0 °C; [Found: C, 74.70; H, 6.02%. $C_{20}H_{19}O_2P$ requires C, 74.52; H, 5.94%]; R_f ($CHCl_3$/MeOH 20:1) 0.77; ^1H NMR ($CDCl_3$, 300 MHz) δ: 3.19–3.54 (m, 2H), 3.82 (s, 3H), 6.91–7.32 (m, 5H), 7.34–7.60 (m, 3H), 7.62–7.80 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 37.1 (d, J_{P-C}=68.1 Hz), 55.7, 111.0 (d, J_{P-C}=6.9 Hz), 120.1 (d, J_{P-C}=98.0 Hz), 121.7 (d, J_{P-C}=10.9 Hz), 127.0 (d, J_{P-C}=3.2 Hz), 128.6 (d, J_{P-C}=12.1 Hz), 128.7 (d, J_{P-C}=2.6 Hz), 130.4 (d, J_{P-C}=5.5 Hz), 131.3 (d, J_{P-C}=9.5 Hz), 131.8 (d, J_{P-C}=2.9 Hz), 132.4 (d, J_{P-C}=8.3 Hz), 134.2 (d, J_{P-C}=100.9 Hz), 134.4 (d, J_{P-C}=2.0 Hz), 135.4 (d, J_{P-C}=5.2 Hz), 159.9 (d, J_{P-C}=4.6 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ: 29.97 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=30.04 min; GC–MS (EI, 70 eV) m/z: 322 ($M^{\bullet+}$) (36%), 321 (12%), 291 (10%), 231 (75%), 201 (10%), 200 (100%), 199 (77%), 152 (26%), 91 (100%), 77 (31%).

*4.2.8. Methyl(1-naphthyl)phenylphosphine oxide (**1k**).* Prepared from 1-naphthylphenylphosphine oxide (0.756 g, 3 mmol) and methyl iodide (0.206 mL, 3.3 mmol) using general procedure. Yield 0.638 g (80%). Pale yellow solid. Mp=147.0–148.0 °C (lit.[32] 151–152 °C); [Found: C, 76.90; H, 5.81%. $C_{17}H_{15}OP$ requires C, 76.68; H, 5.68%]; R_f ($CHCl_3$/MeOH 20:1) 0.50; ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.16 (d, J_{P-H}=13.0 Hz, 3H), 7.38–7.56 (m, 6H), 7.67–7.77 (m, 2H), 7.84–7.90 (m, 2H), 7.99–8.04 (m, 1H), 8.40–8.46 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 17.6 (d, J_{P-C}=73.3 Hz), 124.4 (d, J_{P-C}=13.5 Hz), 126.3, 126.6 (d, J_{P-C}=5.5 Hz), 127.2, 128.6 (d, J_{P-C}=11.8 Hz), 129.5 (d, J_{P-C}=102.0 Hz), 130.2 (d, J_{P-C}=1.4 Hz), 130.4 (d, J_{P-C}=10.4 Hz), 131.6 (d, J_{P-C}=6.0 Hz), 131.7 (d, J_{P-C}=1.7 Hz), 132.9 (d, J_{P-C}=8.6 Hz), 133.2 (d, J_{P-C}=2.9 Hz), 133.8 (d, J_{P-C}=8.9 Hz), 134.6 (d, J_{P-C}=100.9 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ: 32.27 ppm. GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=27.60 min; GC–MS (EI, 70 eV) m/z: 266 ($M^{\bullet+}$) (25%), 265 (100%), 202 (8%), 173 (9%), 127 (9%), 77 (12%). NMR data are consistent with previously reported.[31]

*4.2.9. The synthesis of dimethylphenylphosphine oxide (**1g**).* In a flame-dried three-necked round-bottom flask (250 mL) equipped with magnetic stirrer, reflux condenser, argon inlet and a septum was placed magnesium (2.4 g, 100 mmol) and one piece of iodine in 100 mL of dry degassed diethyl ether. Then methyl iodide (6.23 mL, 100 mmol) was added dropwise through syringe. First, 10% of MeI was added to initiate the reaction and after the reaction started the rest of alkyl halide was added at a rate allowing gentle refluxing of the solvent. After addition of the halide the mixture was heated to 35 °C and stirred until all magnesium dissolved. Then, the Grignard solution was cooled to 0 °C and dichlorophenylphosphine (5.43 mL, 40 mmol) was added dropwise by syringe. The reaction mixture was allowed to warm to room temperature and stirred for overnight under argon atmosphere. The reaction was quenched by addition of aqueous NH_4Cl solution, the mixture was extracted with chloroform (5×30 mL), the organic fraction was dried over $MgSO_4$, then filtered, and evaporated. The residue was redissolved in chloroform and the solution was cooled to 0 °C. Then, 15% H_2O_2 (50 mL) was added and the mixture was stirred for 2 h at this temperature. The mixture was diluted with water, organic layer was removed and the aqueous layer was washed with chloroform (3×30 mL). The organic fractions were collected, dried over $MgSO_4$, filtered, and evaporated. The residue was purified by flash chromatography using chloroform/methanol 15:1 as eluent yielding 4.25 g (69%) of title compound. White solid. Mp=118.0–120.0 °C (lit.[33] 115–116 °C); [Found: C, 62.29; H, 7.09%. $C_8H_{11}OP$ requires C, 62.33; H, 7.19%]; R_f ($CHCl_3$/MeOH 20:1) 0.58; ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.67 (d, J_{P-H}=12.8 Hz, 6H), 7.39–7.51 (m, 3H), 7.62–7.72 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 17.8 (d, J_{P-C}=71.9 Hz), 128.5 (d, J_{P-C}=11.6 Hz), 129.4 (d, J_{P-C}=9.8 Hz), 131.5 (d, J_{P-C}=3.1 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ: 34.44 ppm; GC (Phenomenex Zebron ZB-5MSi): t_R=10.33 min; GC–MS (EI, 70 eV) m/z: 139 (4%), 79 (22%), 78 (100%), 77 (31%), 63 (36%).

*4.2.10. The synthesis of o-anisylphenyl(m-xylyl)phosphine oxide (**1n**).* In a flame-dried Schlenk flask (100 mL) under argon atmosphere were placed *m*-xylyl iodide (0.162 g, 0.7 mmol), copper(I) iodide (0.013 g, 0.07 mmol), 1,2-diaminocyclohexane (0.016 g, 0.14 mmol), *o*-anisyphenylphosphine oxide (0.162 g, 0.7 mmol), and potassium carbonate (0.193 g, 1.4 mmol). The flask was sealed, placed in preheated oil bath (110 °C) and heated for 24 h. Then, the mixture was allowed to cool to room temperature, water (30 mL) was added and the mixture was extracted with DCM (3×30 mL). The organic layer was dried over $MgSO_4$, filtered, and evaporated. The residue was purified by flash chromatography using ethyl acetate as eluent yielding 0.221 g (94%) of **1m**. Pale brown solid. Mp=208.0–209.0 °C; [Found: C, 75.12; H, 6.39%. $C_{21}H_{21}O_2P$ requires C, 74.99; H, 6.29%]; R_f ($CHCl_3$/MeOH 20:1) 0.35; ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.66 (s, 6H, Me), 3.53 (s, 3H, OMe), 6.84–6.92 (m, 1H), 6.97–7.07 (m, 1H), 7.09 (s, 1H), 7.18 (s, 2H), 7.36–7.50 (m, 3H), 7.60–7.79 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 21.3, 55.3, 111.4 (d, J_{P-C}=5.9 Hz), 120.8 (d, J_{P-C}=8.8 Hz), 128.0 (d, J_{P-C}=12.2 Hz), 129.3 (d, J_{P-C}=9.8 Hz), 129.4 (d, J_{P-C}=9.8 Hz), 129.4 (d, J_{P-C}=9.8 Hz), 131.3, 131.7 (d, J_{P-C}=10.7 Hz), 133.2, 134.1, 134.9 (d, J_{P-C}=7.3 Hz), 137.7 (d, J_{P-C}=13.2 Hz), 160.9 (d, J_{P-C}=3.4 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ: 28.26 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=25.63 min; GC–MS (EI, 70 eV) m/z: 336 ($M^{\bullet+}$) (100%), 335 (40%), 319 (19%), 318 (47%), 317 (18%), 307 (13%), 305 (38%), 246 (13%), 245 (76%), 229 (37%), 228 (10%), 227 (61%), 218 (12%), 217 (86%), 215 (10%), 213 (16%), 212 (26%), 201 (19%), 200 (14%), 199 (88%), 183 (22%), 180 (12%), 179 (13%), 178 (10%), 167 (11%), 166

(17%), 165 (42%), 153 (16%), 152 (41%), 139 (23%), 120 (12%), 119 (46%), 115 (13%), 109 (10%), 105 (36%), 103 (15%), 92 (13%), 91 (52%).

4.3. The general procedure of the reaction between tertiary phosphine oxides and sodium in liquid ammonia

A flame-dried two-necked flask (100 mL) equipped with magnetic stirrer, cold trap with acetone-dry ice and argon inlet was placed in the acetone-dry ice bath. The argon inlet was then replaced with an argon balloon and gaseous ammonia was passed through cold trap. After 15 mL of ammonia was condensed, the cold trap was replaced by stopcock and pieces of sodium (0.029–0.058 g, 1.25–2.5 mmol) were added to the reaction flask. After dissolution of sodium (usually 10–15 min) a solution of phosphine oxide (0.5 mmol) in 5 mL of THF was added at once via syringe. In most of cases, the immediate change of color from deep blue to colorless or yellow was observed. After 5 min the reaction was quenched by addition of solid NH_4Cl (0.5 g). The ammonia was evaporated under water pump, the residue was diluted with chloroform (20 mL), filtered and evaporated. The obtained mixture was purified with column chromatography using chloroform/methanol 15:1 as eluent.

*4.3.1. tert-Butyl-(1,4-cyclohexadien-3-yl)methylphosphine oxide (**2a**).* Yield 0.058 g (59%). Colorless pasty solid. [Found: C, 66.80; H, 9.59%. $C_{11}H_{19}OP$ requires C, 66.64; H, 9.66%]; R_f (EtOAc) 0.18; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.16 (d, J_{P-H}=14.2 Hz, 9H), 1.29 (d, J_{P-H}=11.1 Hz, 3H), 2.60–2.76 (m, 2H), 3.38–3.56 (m, 1H), 5.66–5.96 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 7.2 (d, J_{P-C}=63.8 Hz), 25.1, 26.2 (d, J_{P-C}=4.9 Hz), 39.0 (d, J_{P-C}=59.5 Hz), 130.0 (d, J_{P-C}=4.3 Hz), 127.0 (d, J_{P-C}=8.9 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ: 58.50 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=11.10 min; GC–MS (EI, 70 eV) *m/z*: 140 (3%), 121 (7%), 120 (M−78$^{\bullet+}$) (100%), 119 (7%).

*4.3.2. Benzyl-tert-butyl-(1,4-cyclohexadien-3-yl)phosphine oxide (**2b**).* Yield 0.081 g (59%). Colorless waxy solid. [Found: C, 74.29; H, 8.39%. $C_{17}H_{23}OP$ requires C, 74.43; H, 8.45%]; R_f (EtOAc) 0.50; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.13 (d, J_{P-H}=14.1 Hz, 9H), 2.55–2.72 (m, 2H), 3.11 (d, J_{P-H}=11.2 Hz, 2H), 3.28–3.49 (m, 1H), 5.69–5.86 (m, 4H), 7.03–7.25 (m, 3H), 7.28–7.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 25.7, 26.1 (d, J_{P-C}=5.2 Hz), 29.6 (d, J_{P-C}=54.3 Hz), 34.9 (d, J_{P-C}=59.2 Hz), 38.0 (d, J_{P-C}=58.1 Hz), 121.8 (d, J_{P-C}=5.6 Hz), 121.8 (d, J_{P-C}=5.6 Hz), 126.6 (d, J_{P-C}=6.9 Hz), 128.2 (d, J_{P-C}=2.3 Hz), 128.4 (d, J_{P-C}=1.7 Hz), 130.0 (d, J_{P-C}=4.6 Hz), 131.9 (d, J_{P-C}=7.8 Hz), 132.4 (d, J_{P-C}=7.8 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ: 52.83 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=17.78 min; GC–MS (EI, 70 eV) *m/z*: 196 (39%), 140 (57%), 139 (19%), 122 (64%), 121 (15%), 92 (11%), 91 (100%).

*4.3.3. Methylphenylphosphine oxide (**3a**).* Yield 0.061 g (87%). Colorless oil. [Found: C, 60.09; H, 6.38%. C_7H_9OP requires C, 60.00; H, 6.47%]; R_f ($CHCl_3$/MeOH 20:1) 0.08; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.75 (dd, J_{H-H}=3.88 Hz, J_{P-H}=13.8 Hz), 7.25–7.61 (m, 3H), 7.62–7.81 (m, 2H), 7.59 (dm, J_{P-H}=472.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 16.2 (d, J_{P-C}=69.0 Hz), 128.8 (d, J_{P-C}=12.6 Hz), 129.4 (d, J_{P-C}=11.5 Hz), 131. 9 (d, J_{P-C}=99.7 Hz), 132.3 (d, J_{P-C}=2.9 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ: 19.77 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=12.87 min; GC–MS (EI, 70 eV) *m/z*: 140 (M$^{\bullet+}$) (100%), 139 (20%), 125 (84%), 91 (19%), 78 (55%), 77 (41%). NMR data are consistent with previously reported.[34]

*4.3.4. Benzylphenylphosphine oxide (**3b**).* Yield 0.031 g (29%). White solid, mp=152.0–154.0 °C (lit.[18] 121.5–123 °C); [Found: C, 72.35; H, 6.19%. $C_{13}H_{13}OP$ requires C, 72.21; H, 6.06%]; R_f ($CHCl_3$/MeOH 20:1) 0.41; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.29–3.60 (m, 2H), 7.50 (dt, J_{P-H}=476.0 Hz, 1H), 7.03–7.15 (m, 2H), 7.23–7.33 (m, 3H), 7.40–7.64 (m, 5H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 38.77 (d, J_{P-C}=62.1 Hz), 127.07 (d, J_{P-C}=3.6 Hz), 128,51 (d, J_{P-C}=12.4 Hz), 128.66 (d, J_{P-C}=3.1 Hz), 129.6 (d, J_{P-C}=5.6 Hz), 129.9 (d, J_{P-C}=10.8 Hz), 132.43 (d, J_{P-C}=2.8 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 29.60 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=19.89 min; GC–MS (EI, 70 eV) *m/z*: 216 (M$^{\bullet+}$) (16%), 215 (15%), 125 (49%), 91 (100%), 92 (28%), 77 (11%); HRMS (ESI) for $C_{13}H_{13}ONaP$ (M+Na$^+$): calcd 239.0596. Found: 239.0608. NMR data are consistent with previously reported.[35]

*4.3.5. Benzyl-(1,4-cyclohexadien-3-yl)(methoxymethyl)phosphine oxide (**2f**).* Yield 0.032 g (24%). Colorless oil. [Found: C, 68.58; H, 7.40%. $C_{15}H_{19}O_2P$ requires C, 68.69; H, 7.30%]; R_f ($CHCl_3$/MeOH 20:1) 0.40; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.70–2.81 (m, 2H), 3.16–3.21 (m, 2H), 3.36 (s, 3H), 3.44–3.55 (m, 1H), 3.54–3.60 (m, 1H), 3.62–3.68 (m, 1H), 5.71–5.81 (m, 2H), 5.90–5.97 (m, 2H), 7.19–7.34 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 26.3 (d, J_{P-C}=5.7 Hz), 31.3 (d, J_{P-C}=57.5 Hz), 38.3 (d, J_{P-C}=62.9 Hz), 61.4 (d, J_{P-C}=4.6 Hz), 67.0 (d, J_{P-C}=80.7 Hz), 119.6 (d, J_{P-C}=7.5 Hz), 119.9 (d, J_{P-C}=6.9 Hz), 126.8 (d, J_{P-C}=1.7 Hz), 128.1 (d, J_{P-C}=9.5 Hz), 128.7 (d, J_{P-C}=2.3 Hz), 129.8 (d, J_{P-C}=5.5 Hz), 131.1 (d, J_{P-C}=8.0 Hz), 131.4 (d, J_{P-C}=8.6 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 43.99 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=21.69 min; GC–MS (EI, 70 eV) *m/z*: 262 (M$^{\bullet+}$) (4%), 229 (7%), 184 (15%), 154 (40%), 139 (32%), 121 (15%), 105 (11%), 93 (23%), 91 (100%), 79 (33%), 78 (85%), 77 (48%).

*4.3.6. (Methoxymethyl)phenylphosphine oxide (**3c**).* Yield 36% (isolated as a mixture with **3d**—the yield is calculated from ^{1}H NMR spectra). R_f ($CHCl_3$/MeOH 20:1) 0.39; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.41 (s, 3H), 3.95–3.92 (m, 1H), 4.02–4.08 (m, 1H), 7.48 (ddd, J_{H-H}=2.2 Hz, J_{H-H}=4.8 Hz, J_{P-H}=478.2 Hz, 1H), 7.47–7.53 (m, 2H), 7.55–7.61 (m, 1H), 7.72–7.79 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 61.6 (d, J_{P-C}=12.1 Hz), 70.2 (d, J_{P-C}=84.5 Hz), 128.7 (d, J_{P-C}=13.2 Hz), 128.8 (d, J_{P-C}=97.1 Hz), 130.3 (d, J_{P-C}=11.2 Hz), 132.8 (d, J_{P-C}=3.7 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 22.45 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=10.40 min; GC–MS (EI, 70 eV) *m/z*: 169 (3%), 140 (100%), 125 (36%), 124 (14%), 91 (17%), 78 (13%), 77 (36%).

*4.3.7. Benzyl(methoxymethyl)phosphine oxide (**3d**).* Yield 14% (isolated as a mixture with **3c**—the yield is calculated from ^{1}H NMR spectra). R_f ($CHCl_3$/MeOH 20:1) 0.39; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.24–3.30 (m, 1H), 3.33–3.38 (m, 1H), 3.43 (s, 3H), 3.65–3.71 (m, 1H), 3.74–3.79 (m, 1H), 6.93 (dm, J_{P-H}=470.4 Hz, 1H), 7.18–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 33.6 (d, J_{P-C}=60.9 Hz), 61.5 (d, J_{P-C}=12.6 Hz), 66.7 (d, J_{P-C}=82.5 Hz), 127.2 (d, J_{P-C}=3.7 Hz), 128.2 (d, J_{P-C}=12.6 Hz), 128.9 (d, J_{P-C}=3.2 Hz), 129.5 (d, J_{P-C}=5.5 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 30.39 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=15.27 min; GC–MS (EI, 70 eV) *m/z*: 184 (M$^{\bullet+}$) (4%), 154 (35%), 121 (4%), 92 (15%), 91 (100%), 65 (22%).

*4.3.8. (1,4-Cyclohexadien-3-yl)dimethylphosphine oxide (**2g**).* Yield 0.076 g (98%). Colorless solid. Mp=80–82 °C; [Found: C, 61.55; H, 8.50%. $C_8H_{13}OP$ requires C, 61.53; H, 8.39%]; R_f (EtOAc/MeOH 20:1) 0.10; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.39 (d, J_{P-H}=12.2 Hz, 6H), 2.52–2.79 (m, 2H), 3.18–3.37 (m, 1H), 5.67–5.77 (m, 2H), 5.82–5.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 12.8 (d, J_{P-C}=67.0 Hz), 26.2 (d, J_{P-C}=5.5 Hz), 41.2 (d, J_{P-C}=66.4 Hz), 120.4 (d, J_{P-C}=6.7 Hz), 127.6 (d, J_{P-C}=10.4 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ: 47.15 ppm; GC (Phenomenex Zebron ZB-5MSi): t_R=10.74 min; GC–MS (EI, 70 eV) *m/z*: 170 (M$^{\bullet+}$) (21%), 143 (20%), 142 (56%), 141 (47%), 125 (28%), 105 (17%), 79 (70%), 78 (100%), 77 (81%).

*4.3.9. Bis(1,4-cyclohexadien-3-yl)methylphosphine oxide (**2h**).* Yield 9% (calculated from the ^{1}H NMR spectra of crude reaction mixture). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.70 (d, J_{P-H}=13.4 Hz, 3H), 2.69–2.80

(m, 4H), 3.37–3.51 (m, 2H), 5.70–5.81 (m, 4H), 5.84–5.96 (m, 4H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 38.55 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=16.72 min; GC–MS (EI, 70 eV) *m*/*z*: 142 (M−78$^{\bullet+}$) (15%), 141 (12%), 140 (57%), 139 (11%), 125 (60%), 124 (55%), 80 (100%).

*4.3.10. o-Anisyl-(1,4-cyclohexadien-3-yl)methylphosphine oxide (**2i**).* Yield 10% (calculated from the ^{1}H NMR spectra of crude reaction mixture). ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 2.03 (d, J_{P-H}=14.23 Hz, 3H), 2.64–2.78 (m, 2H), 3.32–3.41 (m, 1H), 3.68 (s, 3H, OMe), 5.68–5.75 (m, 2H), 5.82–5.90 (m, 2H), 6.87–6.92 (m, 1H), 7.03–7.10 (m, 1H), 7.74–7.81 (m, 1H), 7.88–7.95 (m, 1H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 49.96 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=16.85 min; GC–MS (EI, 70 eV) *m*/*z*: 141 (12%), 140 (100%), 125 (80%), 109 (19%), 94 (19%).

*4.3.11. Diphenylphosphine oxide (**3e**).* Yield 0.090 g (89%). Pasty white solid. [Found: C, 71.42; H, 5.50%. $C_{12}H_{11}OP$ requires C, 71.28; H, 5.48%]; R_f ($CHCl_3$/MeOH 20:1) 0.44; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.44–7.64 (m, 6H), 7.65–7.80 (m, 6H), 8.08 (d, *J*=480.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 128.8 (d, J_{P-C}=12.7 Hz), 130.6 (d, J_{P-C}=11.2 Hz), 131.3 (d, J_{P-C}=100.8 Hz), 132.4 (d, J_{P-C}=2.7 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 21.93 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=19.77 min; GC–MS (EI, 70 eV) *m*/*z*: 202 (M$^{\bullet+}$) (32%), 201 (100%), 183 (22%), 125 (11%), 124 (41%), 96 (9%); HRMS (ESI) for $C_{12}H_{11}ONaP$ (M+Na$^+$): calcd: 225.0440. Found: 225.0449. NMR data are consistent with previously reported.[36]

*4.3.12. Di-o-anisylphosphine oxide (**3f**).* Yield 0.080 g (61%). Colorless solid. Mp=128–130 °C (lit.[36] 130–132 °C); [Found: C, 64.30; H, 5.75%. $C_{14}H_{15}O_3P$ requires C, 64.12; H, 5.77%]; R_f ($CHCl_3$/MeOH 20:1) 0.62; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 3.69 (s, 6H), 6.84–7.05 (m, 4H), 7.35–7.52 (m, 4H), 8.20 (d, J_{P-H}=514.9 Hz, 1H); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ: 8.82 ppm. Data are in according with previously reported.[37]

*4.3.13. 1-(1,4-Cyclohexadien-3-yl)phospholane oxide (**5a**).* Yield 0.086 g (95%). Colorless solid. Mp=52–54 °C; [Found: C, 65.99; H, 8.25%. $C_{10}H_{15}OP$ requires C, 65.92; H, 8.30%]; R_f (EtOAc/MeOH 20:1) 0.59; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.48–2.05 (m, 8H), 2.56–2.76 (m, 2H), 3.31–3.52 (m, 1H), 5.64–5.73 (m, 2H), 5.78–5.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 24.5 (d, J_{P-C}=63.2 Hz), 24.7 (d, J_{P-C}=6.6 Hz), 26.2 (d, J_{P-C}=6.0 Hz), 40.2 (d, J_{P-C}=58.9 Hz), 120.3 (d, J_{P-C}=6.6 Hz), 127.7 (d, J_{P-C}=9.8 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ: 74.87 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=12.43 min. GC–MS (EI, 70 eV) *m*/*z*: 181 (0.6%), 104 (100%), 103 (40%).

*4.3.14. 3-(1,4-Cyclohexadien-3-yl)-3-oxa-3-phosphatricyclo-[5.2.2.0^{2,6}]undecane (**5b**).* Yield 0.098 g (75%). Colorless oil. [Found: C, 73.41; H, 8.60%. $C_{16}H_{23}OP$ requires C, 73.26; H, 8.84%]; R_f (EtOAc/MeOH 20:1) 0.21; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.27–1.36 (m, 2H), 1.36–1.46 (m, 2H), 1.50–1.73 (m, 4H), 1.82–2.08 (m, 6H), 2.61–2.77 (m, 2H), 3.30–3.48 (m, 1H), 5.67–5.78 (m, 2H), 5.79–5.89 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 20.1, 22.1, 25.0, 25.7 (d, J_{P-C}=11.0 Hz), 26.2 (d, J_{P-C}=4.9 Hz), 26.6, 27.1 (d, J_{P-C}=12.8 Hz), 28.1, 35.5 (d, J_{P-C}=65.2 Hz), 40.3 (d, J_{P-C}=46.9 Hz), 40.8, 41.0 (d, J_{P-C}=5.5 Hz), 120.5 (d, J_{P-C}=4.9 Hz), 127.3 (d, J_{P-C}=9.1 Hz), 127.5 (d, J_{P-C}=9.7 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz) δ: 76.61 ppm.

4.3.15. (1R,3aS*,7aS*)-1-(1,4-Cyclohexadien-3-yl)-1-phospha-1-oxa-bicyclo[4.3.0]non-5-ene (**5c**).* Yield 0.090 g (77%). Colorless oil. [Found: C, 71.59; H, 8.01%. $C_{14}H_{19}OP$ requires C, 71.77; H, 8.17%]; R_f ($CHCl_3$/EtOAc/MeOH 5:5:1) 0.56; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.75–2.56 (m, 10H), 2.72–2.84 (m, 2H), 3.44–3.59 (m, 1H), 5.63–5.86 (m, 4H), 5.89–5.97 (m, 2H); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 73.16 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=21.89 min; GC–MS (EI, 70 eV) *m*/*z*: 234 (M$^{\bullet+}$) (3%), 233 (3%), 232 (3%), 156 (60%), 155 (11%), 128 (25%), 114 (18%), 102 (26%), 91 (14%), 79 (100%), 78 (86%), 77 (67%).

4.3.16. (1R,3aS*,6aS*)-1-(1,4-Cyclohexadien-3-yl)-1-oxa-1-phosphabicyclo[3.3.0]octane (**5e**).* Yield 0.069 g (62%). Colorless oil. [Found: C, 70.50; H, 8.75%. $C_{13}H_{19}OP$ requires C, 70.25; H, 8.62%]; R_f (EtOAc/MeOH 20:1) 0.32; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.34–1.45 (m, 1H), 1.56–1.87 (m, 8H), 2.02.-2.15 (m, 1H), 2.19–2.28 (m, 1H), 2.43–2.54 (m, 1H), 2.67–2.79 (m, 2H), 3.35–3.49 (m, 1H), 5.70–5.79 (m, 2H), 5.84–5.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 24.6 (d, J_{P-C}=61.5 Hz), 25.2 (d, J_{P-C}=2.4 Hz), 25.8 (d, J_{P-C}=2.4 Hz), 26.3 (d, J_{P-C}=5.5 Hz), 26.8, 27.2 (d, J_{P-C}=8.5 Hz), 32.7 (d, J_{P-C}=3.7 Hz), 36.6 (d, J_{P-C}=64.6 Hz), 40.2 (d, J_{P-C}=57.3 Hz), 120.6 (d, J_{P-C}=7.3 Hz), 127.5 (d, J_{P-C}=7.3 Hz), 127.6 (d, J_{P-C}=7.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz) δ: 75.05 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=20.13 min; GC–MS (EI, 70 eV) *m*/*z*: 221 (7%), 220 (35%), 219 (14%), 192 (25%), 180 (13%), 179 (100%), 154 (18%), 144 (16%), 140 (28%), 126 (25%), 125 (50%), 116 (13%), 103 (14%), 91 (28%), 84 (17%), 79 (38%), 78 (61%), 77 (57%), 67 (63%).

*4.3.17. 1-(1,4-Cyclohexadien-3-yl)-3-methylphospholane oxide (**5f**).* Yield 0.041 g (42%) (mixture of diastereoisomers dr=71:29). Colorless oil. [Found: C, 67.49; H, 8.81%. $C_{11}H_{17}OP$ requires C, 67.33; H, 8.73%]; R_f (EtOAc/MeOH 20:1) 0.35; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 0.99 (dd, J_{H-H}=6.50 Hz, J_{P-H}=0.9 Hz, 3H) and 1.04 (dd, J_{H-H}=6.3 Hz, J_{P-H}=0.7 Hz, 3H, minor), 1.19–1.34 (m, 1H), 1.98–2.13 (m, 2H), 2.14–2.30 (m, 2H), 2.33–2.50 (m, 2H), 2.61–2.79 (m, 2H), 3.31–3.51 (m, 1H), 5.62–5.91 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: (major) 20.9 (d, J_{P-C}=13.2 Hz), 26.8 (d, J_{P-C}=61.2 Hz), 26.3 (d, J_{P-C}=6.0 Hz), 31.8 (d, J_{P-C}=64.1 Hz), 33.7 (d, J_{P-C}=5.4 Hz), 33.0 (d, J_{P-C}=8.3 Hz), 40.5 (d, J_{P-C}=58.6 Hz), 120.5 (d, J_{P-C}=6.9 Hz), 120.6 (d, J_{P-C}=6.3 Hz), 127.6 (d, J_{P-C}=9.5 Hz), 127.9 (d, J_{P-C}=9.8 Hz); (minor) 20.9 (d, J_{P-C}=12.1 Hz), 24.3 (d, J_{P-C}=62.6 Hz), 26.3 (d, J_{P-C}=6.0 Hz), 33.9 (d, J_{P-C}=61.8 Hz), 32.5 (d, J_{P-C}=6.0 Hz), 34.2 (d, J_{P-C}=8.3 Hz), 40.5 (d, J_{P-C}=58.6 Hz), 120.4 (d, J_{P-C}=6.9 Hz), 120.6 (d, J_{P-C}=6.3 Hz), 127.7 (d, J_{P-C}=9.5 Hz), 127.9 (d, J_{P-C}=9.8 Hz); ^{31}P NMR ($CDCl_3$, 121 MHz) δ: 75.11 ppm (minor) and 74.82 ppm (major); GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=17.04 min; GC–MS (EI, 70 eV) *m*/*z*: 194 (5%), 193 (6%), 118 (91%), 117 (28%), 90 (28%), 79 (33%), 78 (100%), 77 (50%).

*4.3.18. 1-(1,4-Cyclohexadien-3-yl)-3-phospholene oxide (**6a**).* Yield 0.050 g (56%). Colorless oil. [Found: C, 66.89; H, 7.10%. $C_{10}H_{13}OP$ requires C, 66.66; H, 7.27%]; R_f (EtOAc/MeOH 20:1) 0.21; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.25–2.52 (m, 4H), 2.58–2.74 (m, 2H), 3.33–3.52 (m, 1H), 5.57–5.67 (m, 2H), 5.69 (s, 1H), 5.78 (s, 1H), 5.76–5.85 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 26.3 (d, J_{P-C}=6.1 Hz), 29.1 (d, J_{P-C}=63.7 Hz), 40.0 (d, J_{P-C}=60.7 Hz), 119.7 (d, J_{P-C}=6.9 Hz), 127.4 (d, J_{P-C}=11.1 Hz), 128.0 (d, J_{P-C}=9.9 Hz); ^{31}P NMR ($CDCl_3$, 121 MHz) δ: 70.21 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=14.83 min; GC–MS (EI, 70 eV) *m*/*z*: 179 (M−1$^{\bullet+}$) (9%), 178 (55%), 150 (21%), 129 (11%), 124 (36%), 102 (100%), 101 (11%).

*4.3.19. (4-But-1-enyl)phenylphosphine oxide (**7**).* Yield 0.02 g (22%). Colorless oil. [Found: C, 66.03; H, 8.32%. $C_{10}H_{15}OP$ requires C, 65.92; H, 8.30%]; R_f (EtOAc/MeOH 20:1) 0.45; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.44–1.48 (m, 2H), 5.23–5.33 (m, 1H), 7.27 (dm, J_{P-H}=476.7 Hz, 1H), 7.27–7.51 (m, 3H), 7.54–7.77 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 12.9 (d, J_{P-C}=3.4 Hz), 30.0 (d, J_{P-C}=64.9 Hz), 117.0 (d, J_{P-C}=8.4 Hz), 128.7 (d, J_{P-C}=12.2 Hz), 130.0 (d, J_{P-C}=10.3 Hz), 130.5 (d, J_{P-C}=13.0 Hz), 132.5 (d, J_{P-C}=2.7 Hz); ^{31}P NMR ($CDCl_3$, 121 MHz) δ: 26.80 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=14.83 min. GC–MS (EI, 70 eV) *m*/*z*: 179 (M−1$^{\bullet+}$) (12%), 126 (23%), 125 (51%), 79 (100%).

*4.3.20. 1-(1,4-Cyclohexadien-3-yl)-3-methyl-3-phospholene oxide (**6b**).* Yield 0.068 g (70%). Colorless oil. [Found: C, 68.22; H, 7.90%.

$C_{11}H_{15}OP$ requires C, 68.03; H, 7.78%]; R_f (EtOAc/MeOH 20:1) 0.49; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 1.63–1.69 (m, 3H, Me), 2.28–2.51 (m, 4H), 2.61–2.78 (m, 2H), 3.34–3.53 (m, 1H), 5.29–5.44 (m, 1H), 5.58–5.69 (m, 2H), 5.77–5.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 20.6 (d, J_{P-C}=68.1 Hz), 20.8 (d, J_{P-C}=12.9 Hz), 31.3 (d J_{P-C}=62.3 Hz), 34.4 (d, J_{P-C}=65.8 Hz), 35.5 (d, J_{P-C}=65.5 Hz), 35.5 (d, J_{P-C}=3.2 Hz), 119.8 (d, J_{P-C}=9.5 Hz), 127.9 (d, J_{P-C}=9.8 Hz), 128.7 (d, J_{P-C}=11.8 Hz), 129.5 (d, J_{P-C}=9.8 Hz); ^{31}P NMR ($CDCl_3$, 121 MHz) δ: 72.34 ppm; GC (Phenomenex Zebron ZB-35HT INFERNO): t_R=14.45 min; GC–MS (EI, 70 eV) m/z: 194 (1%), 118 (100%), 117 (30%), 103 (15%), 90 (32%).

Supplementary data

^{1}H, ^{13}C, ^{31}P NMR spectra and GC–MS of compounds. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2011.09.045.

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