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# Efficient synthesis of heterophosphole-2-sulfides by solvent-free microwave reaction

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ABSTRACT

Microwave irradiation of a stoichiometric amount of Lawesson's reagent in the presence of *o*-aminophenols, *o*-aminothiophenols, *o*-phenylenediamines, or catechols leads to benzoxazaphosphole-, benzothiazaphosphole-, benzodiazaphosphole-, and benzodioxaphosphole-2-sulfides, respectively, in good yields in a fast and direct way under solventless conditions. The procedure requires short reaction times and is similar for all reagents; thus it may be used in parallel synthesis.



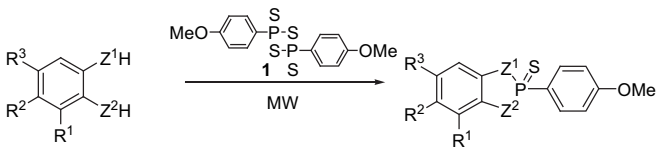
## 1. Introduction

Organophosphorus compounds are ubiquitous in nature and have applications in the field of agriculture, medicine, and industry.[1,2] Some of them are important pesticides,[3] bactericides,[4–6] and antibiotics.[4] Phosphorus analogues of α-pyrones act as HIV protease inhibitors.[7] There exists growing interest in organophosphorus heterocyclic compounds since extensive use as pesticides in agriculture, as stabilizers in polymers and as lubricant oil additives has been found. Among them, many heterocyclic phosphole derivatives are interesting due to their properties.[8–14] Lawesson's reagent (**1**), commonly utilized as a thionating agent,[15] has been used to build anisyl derivatives of phosphole-2-sulfides with heteroatoms in positions 1 and 3,[16–19] by reaction with catechols, 1, 2-phenylenediamines or *o*-aminophenols. However, these procedures require the use of refluxing conditions in different solvents (acetonitrile, toluene, etc.) and long reaction times, but only low yields are obtained.

## 2. Results

Recently, we have reported the formation of 2-(4-methoxyphenyl)-4,4-dimethyl-1,3,2-thiazaphospholidine-2-sulfide as an intermediate in the preparation of thiazolidines under microwave irradiation from 2-aminoalcohols, carboxylic acids, and Lawesson's reagent in very short reaction times.[20] This led us to study the use of a microwave protocol to prepare phosphole-2-sulfides under neat conditions, since this reaction involves a nucleophilic addition to Lawesson's reagent followed by the elimination of $H_2S$ through polar mechanisms and, consequently, should be a good candidate to be promoted by microwaves.[21]

Therefore, in order to prepare benzoxazaphosphole-2-sulfides **6**, the reaction of *o*-aminophenol with Lawesson's reagent was used as a model. Both compounds were irradiated with microwaves under different conditions, and it was found that the reaction of *o*-aminophenol (**2a**) with a stoichiometric amount (50 mol %) of Lawesson's reagent (**1**) for 1 min at 190 °C, in an open vessel, led to pure (by $^1$H NMR) 2-(4-methoxyphenyl)-2,3-dihydro-1,3,2-benzoxazaphosphole-2-sulfide (**6a**). Further purification by flash chromatography of the crude reaction yielded 73% of **6a** (Scheme 1, Table 1, entry 1). Higher ratio of Lawesson's reagent




**2a-c**, $Z^1$=O, $Z^2$=NH
**3a-b**, $Z^1$=S, $Z^2$=NH
**4a-d**, $Z^1$=NH, $Z^2$=NH
**5a-c**, $Z^1$=O, $Z^2$=O

**6a-c**, $Z^1$=O, $Z^2$=NH
**7a-b**, $Z^1$=S, $Z^2$=NH
**8a-d**, $Z^1$=NH, $Z^2$=NH
**9a-c**, $Z^1$=O, $Z^2$=O

**Scheme 1.**

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**Table 1**
Synthesis of benzoxazaphosphole-, benzothiazaphosphole-, benzodiazaphosphole-, and benzodioxaphosphole-2-sulfides by microwave irradiation

| Entry | Reactant | $Z^1$ | $Z^2$ | $R^1$ | $R^2$ | $R^3$ | Product | Yield MW (%) | Yield reflux (%)[a] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **2a** | O | NH | H | H | H | **6a** | 73 | 6[22] |
| 2 | **2b** | O | NH | H | H | Me | **6b** | 100 | |
| 3 | **2c** | O | NH | H | Cl | H | **6c** | 93 | 32[18] |
| 4 | **3a** | S | NH | H | H | H | **7a** | 100 | |
| 5 | **3b** | S | NH | H | Cl | H | **7b** | 86 | |
| 6 | **4a** | NH | NH | H | H | H | **8a** | 68 | 24[22] |
| 7 | **4b** | NH | NH | H | Me | H | **8b** | 64 | 8[22] |
| 8 | **4c** | NH | NH | H | Cl | H | **8c** | 80 | 72[22] |
| 9 | **4d** | NH | NH | H | Cl | Cl | **8d** | 73 | |
| 10 | **5a** | O | O | H | H | H | **9a** | 77 | 32[19] |
| 11 | **5b** | O | O | H | $^t$Bu | H | **9b** | 74 | 48[19] |
| 12 | **5c** | O | O | $^t$Bu | H | $^t$Bu | **9c** | 64 | |
| 13 | **10** | O | O | $^t$Bu | H | $^t$Bu | **9c** | 74 | |

[a] Yields reported in the literature under conventional conditions (refluxing in toluene or xylene and 50 or 100 mol % of Lawesson's reagent).

produced by-products, while with lower Lawesson's reagent ratio the yield decreased, as expected. Moreover, shorter reaction times gave lower yields; while longer ones did not lead to yield improvement.

The reaction was also studied under conventional heating in the same conditions (open tube at 190 °C for 1 min), providing after chromatography a slightly lower yield of **6a** (68% vs 73%). As several commercial setups for monomode microwave ovens only allow carrying out reactions in sealed vessels, the above microwave reaction was checked in a sealed vessel. Analysis of the $^1$H NMR spectrum of the raw reaction showed unreacted starting materials and some signals that were not present in the NMR of the crude for reaction in open vessel, obtaining only a 53% yield after purification. Analogous results were obtained when the reaction was carried out under conventional conditions in a sealed tube (58% yield). This indicated the lack of a specific microwave effect, since in conventional and microwave reactions yields and times are comparable. Despite this similarity, we consider that the best method for the synthesis of heterophosphole-2-sulfides is by means of microwave irradiation in an open vessel since the yields are high and the reaction conditions are easier to control. Finally, a mixture of **1** and **2a** was refluxed in toluene for 30 min by irradiation with microwaves, after purification a 46% yield of **6a** was obtained; meanwhile **6a** was previously prepared by conventional refluxing for 3 h in the same solvent in only 6% yield.[22] The use of solvent is expendable affording even lower yields than solventless conditions.

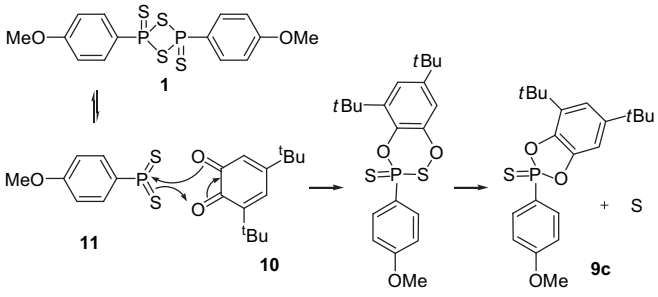
The scope of the reaction was examined by using substituted *o*-aminophenols. The reaction of 2-amino-5-methylphenol and 2-amino-4-chlorophenol led to even higher yields, 100% and 93%, of benzoxazaphosphole-2-sulfides **6b** and **6c**, respectively (Table 1, entries 2 and 3). Azaphosphole **6c** had been previously reported in a 32% yield by refluxing the corresponding aminophenol with Lawesson's reagent in toluene.[18]

These results prompted us to explore the reactivity of 2-aminothiophenols. So, under the same reaction conditions, 2-aminobenzenethiol (**3a**) led to the corresponding 1,3,2-benzothiazaphosphole-2-sulfide **7a** quantitatively (Table 1, entry 4). Similarly, the reaction of 2-amino-4-chlorobenzenethiol (**3b**) with Lawesson's reagent led to the corresponding phosphorus heterocycle **7b** in an 86% yield (Table 1, entry 5).

Analogously, 1,2-phenylenediamines reacted with Lawesson's reagent in the same conditions described above, yielding the corresponding 1,3,2-benzodiazaphosphole-2-sulfides in good yields (Table 1, entries 6–9). The improvement over previously reported yields for compounds **8a** and **8b** under conventional conditions is remarkable (24 and 8%,[22] respectively, Table 1, entries 6 and 7).

In the light of these results, the reaction of Lawesson's reagent with catechols under irradiation with microwaves was also studied. The corresponding 1,3,2-benzodioxaphosphole-2-sulfides **9a**–**c** were obtained (Table 1, entries 10–12), with an astounding reduction in reaction times as well as an increase in previously reported yields[19] for compounds **9a**,**b** (Table 1, entries 10 and 11).

In order to explore the reactivity of *o*-quinones with Lawesson's reagent, 2,4-di-*tert*-butyl-1,6-benzoquinone **10** was tested in the conditions previously described, giving 1,3,2-benzodioxaphosphole-2-sulfide **9c**, the same as that obtained from reaction of the catechol **5c**, in 74% yield. No thionation[23] of the carbonyl groups of the quinone was observed (Table 1, entry 13). The formation of compound **9c** may be envisaged to take place through a [4+2] cycloaddition followed by sulfur extrusion (Scheme 2), instead of a nucleophilic attack from the oxygen atom on the dithiophosphine ylide **11**, as it is the case for catechols.




**Scheme 2.**

## 3. Conclusion

In summary, a new, fast, and direct method for the preparation of heterophosphole-2-sulfides was developed by reacting a stoichiometric amount of Lawesson's reagent with different 2-aminophenols, 2-aminothiophenols, 1,2-phenylenediamines, and catechols. The method was successfully applied for the preparation, under microwave irradiation in an open vessel and neat reaction conditions, of a wide variety of compounds, which might be valuable as potential antibacterials.[24] An alternative mechanism is proposed for the obtention of 4,6-di-*tert*-butyl-2-(4-methoxyphenyl)-1,3,2-benzodioxaphosphole-2-sulfide (**9c**), when an *o*-quinone is used instead of the corresponding catechol. Among the compounds described here, only one (**6c**) had been reported as fully characterized in the literature. An advantage of this procedure is the very short reaction times, which are similar for all reagents, and, thus, may be used in parallel synthesis.

## 4. Experimental section

### 4.1. General

Melting points were measured in open capillaries and are uncorrected. $^1$H NMR spectra were recorded at 300 MHz ($^1$H) and 75 MHz ($^{13}$C) in the solvent specified (Varian Mercury 300). Mass spectra were recorded in a low-resolution spectrometer (Hewlett–Packard 1100 MSD) or high resolution when stated (Micromass Autospec). Infrared spectra were measured on FT-IR instrument (ABB BOMEN MB102). Irradiation was carried out in a monomode oven Discover, CEM Corp. Elemental analysis was performed on a LECO CHNS-932.

## 4.2. General procedure

*4.2.1. Synthesis of 2,3-dihydro-2-(4-methoxyphenyl)-1,3,2-benzoxazaphosphole-2-sulfide (**6a**).* A mixture of 2-aminophenol (**2a**) (109 mg, 1 mmol) and Lawesson's reagent (**1**) (206 mg, 0.51 mmol) was irradiated in an open vessel with microwaves in a monomode oven (300 W and temperature control set at 190 °C measured with an IR sensor) for 1 min.[25] The crude was dissolved in dichloromethane (1 mL) and purified by short column chromatography (silica gel, AcOEt–hexane, 2:8) giving **6a** (202 mg, 73%), as a solid. Mp 125–126 °C. IR (*Golden-Gate*): 3314, 1595, 1484, 1236, 1115, 821, 747, 704 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 3.85 (s, 3H, $OCH_3$), 5.25 (d, 1H, NH, $J_{PH}$=17.7 Hz), 6.84–7.03 (m, 6H, ArH), 7.87 (dd, 2H, Ar*H*, $J_{PH}$=15.1; $J$=8.9 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 50.9 ($OCH_3$), 106.8 (d, $J_{PC}$=11.1 Hz, $C_{Ar}$), 107.8 (d, $J_{PC}$=9.0 Hz, $C_{Ar}$), 109.4 (d, $J_{PC}$=17.0 Hz, $C_{Ar}$), 116.5 ($C_{Ar}$), 118.7 ($C_{Ar}$), 121.1 (d, $J_{PC}$=145 Hz, $C_{Ar}$), 129.0 (d, $J_{PC}$=15.1 Hz, $C_{Ar}$), 129.3 (d, $J_{PC}$=1.5 Hz, $C_{Ar}N$), 141.5 (d, $J_{PC}$=2.0 Hz, $C_{Ar}O$), 159.1 (d, $J_{PC}$=3.1 Hz, *C*$OCH_3$). MS *m*/*z* (%): 279 ($M^+$+2, 18), 277 ($M^+$, 100), 244 (31), 140 (47), 138 (89), 108 (56), 63 (32). Anal. Calcd for $C_{13}H_{12}NO_2PS$: C, 56.31; H, 4.36; N, 5.05; S, 11.56. Found: C, 55.99; H, 4.45; N, 4.82; S, 11.27.

*4.2.2. 2-(4-Methoxyphenyl)-6-methyl-2,3-dihydro-1,3,2-benzoxazaphosphole 2-sulfide (**6b**).* Mp 178–179 °C ($CH_2Cl_2$). IR (*Golden-Gate*): 3328, 1589, 1500, 1251, 1117, 821, 792, 704 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.30 (s, 3H, $CH_3$), 3.85 (s, 3H, $OCH_3$), 5.10 (d, 1H, NH $J_{PH}$=16.8 Hz), 6.71–6.78 (m, 2H, ArH), 6.85 (br s, 1H, ArH), 6.93 (dd, 2H, $J$=8.8 Hz; $J_{PH}$=3.4 Hz, ArH), 7.87 (dd, 2H, ArH, $J_{PH}$=15.0 Hz; $J$=8.8 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 21.4 ($CH_3$), 55.7 ($OCH_3$), 111.2 (d, $J_{PC}$=11.0 Hz, $C_{Ar}$), 113.4 (d, $J_{PC}$=9.0 Hz, $C_{Ar}$), 114.1 (d, $J_{PC}$=17.1 Hz, $C_{Ar}$), 123.5 ($C_{Ar}$), 125.9 (d, $J_{PC}$=145.4 Hz, $C_{Ar}$), 131.3 ($C_{Ar}$), 131.5 (d, $J_{PC}$=7.5 Hz, $C_{Ar}$), 133.8 (d, $J_{PC}$=15.1 Hz, $C_{Ar}$), 146.2 (d, $J_{PC}$=2.3 Hz, $C_{Ar}O$), 163.8 (d, $J_{PC}$=3.3 Hz, *C*$OCH_3$). MS *m*/*z* (%): 293 ($M^+$+2, 6), 292 ($M^+$+1, 16), 291 ($M^+$, 85), 258 (52), 183 (60), 152 (100), 108 (42), 63 (41). HRMS Anal. Calcd for $C_{14}H_{14}NO_2PS$, 291.048289. Found: 291.049123. Anal. Calcd for $C_{14}H_{14}NO_2PS$: C, 57.72; H, 4.84; N, 4.81; S, 11.01. Found: C, 57.37; H, 4.92; N, 4.84; S, 10.80.

*4.2.3. 5-Chloro-2-(4-methoxyphenyl)-2,3-dihydro-1,3,2-benzoxazaphosphole 2-sulfide (**6c**).* Mp 136–139 °C ($CH_2Cl_2$). Lit.[18] 194–196 °C. IR (*Golden-Gate*): 3319, 1594, 1482, 1171, 1114, 886, 823, 803, 707 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 3.83 (s, 3H, $OCH_3$), 5.88 (d, 1H, NH, $J_{PH}$=18.6 Hz), 6.76–6.79 (m, 2H, ArH), 6.88 (d, 1H, ArH, $J$=8.1 Hz), 6.92 (dd, 2H, ArH, $J$=8.9 Hz, $J_{PH}$=3.5 Hz), 7.81 (dd, 2H, ArH, $J_{PH}$=15.1, $J$=8.9 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 55.7 ($OCH_3$), 111.8 (d, $J_{PC}$=11.0 Hz, $C_{Ar}$), 113.1 (d, $J_{PC}$=8.7 Hz, $C_{Ar}$), 114.2 (d, $J_{PC}$=17.2 Hz, $C_{Ar}$), 120.8 ($C_{Ar}$), 125.1 (d, $J_{PC}$=145.2 Hz, $C_{Ar}$), 128.4 ($C_{Ar}Cl$), 133.9 (d, $J_{PC}$=15.3 Hz, $C_{Ar}$), 135.0 (d, $J_{PC}$=7.6 Hz, $C_{Ar}N$), 144.7 (d, $J_{PC}$=2.5 Hz, $C_{Ar}O$), 164.1 (d, $J_{PC}$=3.2 Hz, *C*$OCH_3$). MS *m*/*z* (%): 313 ($M^+$+2, 22), 312 ($M^+$+1, 12), 311 ($M^+$, 71), 172 (83), 140 (85), 108 (100), 63 (62). Anal. Calcd for $C_{13}H_{11}ClNO_2PS$: C, 50.09; H, 3.56; N, 4.49; S, 10.29. Found: C, 49.88; H, 4.01; N, 4.45; S, 10.66.

*4.2.4. 2-(4-Methoxyphenyl)-2,3-dihydro-1,3,2-benzothiazaphosphole 2-sulfide (**7a**).* Mp 137–139 °C (MeOH). IR (*Golden-Gate*): 3213, 1589, 1453, 1257, 1102, 1023, 892, 750, 678 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 3.85 (s, 3H, $OCH_3$), 5.63 (d, 1H, NH, $J_{PH}$=12.2 Hz), 6.84 (ddd, 1H, $J$=7.9, 1.2, 0.6 Hz, ArH), 6.90 (dd, 1H, $J$=7.7, 1.3 Hz, ArH), 6.94 (dd, 2H, ArH $J$=9.0 Hz, $J_{PH}$=3.4 Hz), 7.07 (tdd, 1H, ArH, $J$=7.7, 1.3, 0.9 Hz), 7.20 (ddd, 1H, ArH, $J$=7.9, 1.2, 0.6 Hz), 7.98 (dd, 2H, ArH, $J_{PH}$=15.4 Hz, $J$=9.0 Hz,). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 55.7 ($OCH_3$), 112.7 (d, $J_{PC}$=12.1 Hz, $C_{Ar}$), 114.0 (d, $J_{PC}$=16.8 Hz, $C_{Ar}$), 121.7 ($C_{Ar}$), 123.1 ($C_{Ar}$), 124.7 (d, $J_{PC}$=7.1 Hz, $C_{Ar}$), 126.7 ($C_{Ar}$), 128.9 (d, $J_{PC}$=117.2 Hz, $C_{Ar}$), 134.0 (d, $J_{PC}$=15.2 Hz, $C_{Ar}$), 140.0 (d, $J_{PC}$=5.8 Hz, $C_{Ar}S$), 163.5 (d, $J_{PC}$=3.4 Hz, *C*$OCH_3$). MS *m*/*z* (%): 295 ($M^+$+2, 21), 294 ($M^+$+1, 33), 293 ($M^+$, 100), 260 (73), 245 (31), 154 (89), 125 (31). Anal. Calcd for $C_{13}H_{12}NOPS_2$: C, 53.23; H, 4.12; N, 4.77; S, 21.86. Found: C, 52.85; H, 3.87; N, 4.84; S, 21.65.

*4.2.5. 5-Chloro-2-(4-methoxyphenyl)-2,3-dihydro-1,3,2-benzothiazaphosphole 2-sulfide (**7b**).* Mp 159–161 °C (MeOH). IR (*Golden-Gate*): 3323, 1589, 1581, 1427, 1250, 1105, 918, 800, 702 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 3.85 (s, 3H, $OCH_3$), 6.30 (d, 1H, NH, $J_{PH}$=12.3 Hz,), 6.80 (dd, 1H, ArH, $J$=8.3, 2.0 Hz), 6.85 (d, 1H, ArH, $J$=2.0 Hz), 6.93 (dd, 2H, ArH, $J$=8.9, $J_{PH}$=3.5 Hz), 7.08 (d, 1H, ArH, $J$=8.3 Hz), 7.94 (dd, 2H, ArH, $J_{PH}$=15.5, $J$=8.9 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 55.8 ($OCH_3$), 112.9 (d, $J_{PC}$=12.2 Hz, $C_{Ar}$), 114.1 (d, $J_{PC}$=16.9 Hz, $C_{Ar}$), 121.3 (d, $J_{PC}$=1.2 Hz, $C_{Ar}$), 121.6 ($C_{Ar}$), 125.1 (d, $J_{PC}$=6.7 Hz, $C_{Ar}$), 128.1 (d, $J_{PC}$=117.5 Hz, $C_{Ar}$), 132.2 (d, $J_{PC}$=1.2 Hz, $C_{Ar}N$), 134.1 (d, $J_{PC}$=15.4 Hz, $C_{Ar}$), 140.9 (d, $J_{PC}$=6.3 Hz, $C_{Ar}S$), 163.6 (d, $J_{PC}$=3.3 Hz, *C*$OCH_3$). MS *m*/*z* (%): 329 ($M^+$+2, 41), 328 ($M^+$+1, 16), 327 ($M^+$, 96), 294 (56), 245 (31), 188 (100), 140 (29), 63 (36). Anal. Calcd for $C_{13}H_{11}ClNOPS_2$: C, 47.63; H, 3.38; N, 4.27; S, 19.56. Found: C, 47.69; H, 3.44; N, 4.65; S, 19.17.

*4.2.6. 2-(4-Methoxyphenyl)-2,3-dihydro-1H-1,3,2-benzodiazaphosphole 2-sulfide (**8a**).* Mp 200–202 °C ($CHCl_3$). IR (*Golden-Gate*): 3401, 3293, 1593, 1488, 1381, 1246, 1108, 1012, 882, 744, 688 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 3.85 (s, 3H, $OCH_3$), 5.05 (d, 2H, 2×NH, $J_{PH}$=17.9 Hz), 6.74–6.82 (m, 4H, ArH), 6.92 (dd, 2H, ArH, $J$=8.8 Hz, $J_{PH}$=3.2 Hz,), 7.92 (dd, 2H, ArH, $J_{PH}$=14.9 Hz, $J$=8.8 Hz,). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 55.6 ($OCH_3$), 110.9 (d, $J_{PC}$=9.6 Hz, $C_{Ar}$), 113.8 (d, $J_{PC}$=16.5 Hz, $C_{Ar}$), 120.8 ($C_{Ar}$), 130.0 (d, $J_{PC}$=151.0 Hz, $C_{Ar}$), 133.2 (d, $J_{PC}$=5.6 Hz, $C_{Ar}N$), 133.9 (d, $J_{PC}$=14.9 Hz, $C_{Ar}$), 163.3 (d, $J_{PC}$=3.1 Hz, *C*$OCH_3$). MS *m*/*z* (%): 278 ($M^+$+2, 7), 277 ($M^+$+1, 17), 276 ($M^+$, 84), 243 (100), 228 (37), 200 (33), 137 (99), 63 (29). Anal. Calcd for $C_{13}H_{13}N_2OPS$: C, 56.51; H, 4.74; N, 10.14; S, 11.61. Found: C, 56.44; H, 5.08; N, 10.09; S, 11.36.

*4.2.7. 2-(4-Methoxyphenyl)-5-methyl-2,3-dihydro-1H-1,3,2-benzodiazaphosphole 2-sulfide (**8b**).* Mp 193–194 °C (AcOEt–hexane). IR (*Golden-Gate*): 3400, 3284, 1593, 1499, 1372, 1253, 1108, 885, 799, 688 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 2.25 (s, 3H, $CH_3$), 3.83 (s, 3H, $OCH_3$), 5.12 (d, 1H, NH, $J_{PH}$=17.6 Hz,), 5.21 (d, 1H, NH, $J_{PH}$=18.0 Hz,), 6.56–6.64 (m, 3H, ArH), 6.89 (dd, 2H, ArH, $J$=8.9 Hz, $J_{PH}$=3.2 Hz), 7.88 (dd, 2H, ArH, $J_{PH}$=14.9 Hz, $J$=8.9 Hz,). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 21.3 ($CH_3$), 55.6 ($OCH_3$), 110.6 (d, $J_{PC}$=9.5 Hz, $C_{Ar}$), 111.7 (d, $J_{PC}$=9.5 Hz, $C_{Ar}$), 113.8 (d, $J_{PC}$=16.4 Hz, $C_{Ar}$), 120.9 ($C_{Ar}$), 128.5 (d, $J_{PC}$=137.2 Hz, $C_{Ar}$), 130.3 ($C_{Ar}$), 130.9 (d, $J_{PC}$=5.6 Hz, $C_{Ar}N$), 133.3 (d, $J_{PC}$=5.7 Hz, $C_{Ar}N$), 133.9 (d, $J_{PC}$=14.9 Hz, $C_{Ar}$), 163.2 (d, $J_{PC}$=3.2 Hz, *C*$OCH_3$). MS *m*/*z* (%): 291 ($M^+$+1, 31), 290 ($M^+$, 100), 257 (82), 242 (34), 122 (45). Anal. Calcd for $C_{14}H_{15}N_2OPS$: C, 57.92; H, 5.21; N, 9.65; S, 11.04. Found: C, 57.70; H, 5.41; N, 9.74; S, 10.60.

*4.2.8. 5-Chloro-2-(4-methoxyphenyl)-2,3-dihydro-1H-1,3,2-benzodiazaphosphole 2-sulfide (**8c**).* Mp 171–173 ($CHCl_3$). IR (*Golden-Gate*): 3252, 1592, 1485, 1260, 1105, 840, 796, 678 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 3.83 (s, 3H, $OCH_3$), 5.39 (d, 1H, NH, $J_{PH}$=17.9 Hz), 5.53 (d, 1H, NH, $J_{PH}$=18.2 Hz), 6.60 (d, 1H, ArH, $J$=8.8 Hz), 6.67–6.70 (m, 2H, ArH), 6.89 (dd, 2H, ArH, $J$=8.9 Hz, $J_{PH}$=3.2 Hz), 7.84 (dd, 2H, ArH, $J_{PH}$=15.0 Hz, $J$=8.9 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 55.7 ($OCH_3$), 111.1 (d, $J_{PC}$=9.7 Hz, $C_{Ar}$), 111.3 (d, $J_{PC}$=9.4 Hz, $C_{Ar}$), 114.0 (d, $J_{PC}$=16.6 Hz, $C_{Ar}$), 120.3 ($C_{Ar}$), 125.5 ($C_{Ar}$), 127.7 (d, $J_{PC}$=137.6 Hz, $C_{Ar}$), 131.8 (d, $J_{PC}$=5.5 Hz, $C_{Ar}N$), 134.0 (d, $J_{PC}$=15.2 Hz, $C_{Ar}$), 134.2 ($C_{Ar}N$), 163.4 (d, $J_{PC}$=3.2 Hz, *C*$OCH_3$). MS *m*/*z* (%): 312 ($M^+$+2; 51), 311 ($M^+$+1; 21), 310 ($M^+$, 100), 279 (40), 278 (19), 277 (82), 171 (38), 142 (73). Anal. Calcd for $C_{13}H_{12}ClN_2OPS$: C, 50.25; H, 3.89; N, 9.02; S, 10.32. Found: C, 50.45; H, 4.01; N, 8.88; S, 10.10.

*4.2.9. 5,6-Dichloro-2-(4-methoxyphenyl)-2,3-dihydro-1H-1,3,2-benzodiazaphosphole 2-sulfide (**8d**).* Mp 208–210 °C. IR (*Golden-Gate*): 3259, 3244, 1589, 1483, 1258, 1179, 1103, 884, 840, 682 $cm^{-1}$. $^1H$ NMR

(300 MHz, $CDCl_3$) $\delta$ 3.85 (s, 3H, $OCH_3$), 5.44 (d, 2H, NH, $J_{PH}$=18.0 Hz), 6.79 (br s, 2H, ArH), 6.92 (dd, 2H, ArH, $J$=8.9 Hz, $J_{PH}$=3.3 Hz), 7.84 (dd, 2H, ArH, $J_{PH}$=15.0 Hz, $J$=8.9 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 55.7 ($OCH_3$), 112.0 (d, $J_{PC}$=9.3 Hz, $C_{Ar}$), 114.0 (d, $J_{PC}$=16.7 Hz, $C_{Ar}$), 123.4 ($C_{Ar}$), 127.3 (d, $J_{PC}$=133.4 Hz, $C_{Ar}$), 132.8 (d, $J_{PC}$=5.8 Hz, $C_{Ar}N$), 134.0 (d, $J_{PC}$=15.2 Hz, $C_{Ar}$), 163.6 (d, $J_{PC}$=3.2 Hz, $COCH_3$). MS $m/z$ (%): 346 ($M^+$+2, 75), 346 ($M^+$+1, 2), 344 ($M^+$, 100), 313 (65), 311 (85), 205 (44), 176 (35). Anal. Calcd for $C_{13}H_{11}Cl_2N_2OPS$: C, 45.23; H, 3.21; N, 8.12; S, 9.29. Found: C, 44.87; H, 3.50; N, 7.69; S, 9.66.

*4.2.10. 2-(4-Methoxyphenyl)-1,3,2-benzodioxaphosphole 2-sulfide (**9a**).* Mp 86–88 °C (hexane). IR (*Golden-Gate*): 1597, 1479, 1263, 1230, 1122, 868, 777, 742, 719 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 3.85 (s, 3H, $OCH_3$), 6.95 (dd, 2H, ArH, $J$=8.9 Hz, $J_{PH}$=3.7 Hz), 7.01–7.07 (m, 2H, ArH), 7.07–7.16 (m, 2H, ArH), 7.82 (dd, 2H, ArH, $J_{PH}$=15.0 Hz, $J$=8.9 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 55.8 ($OCH_3$), 112.8 (d, $J_{PC}$=10.3 Hz, $C_{Ar}$), 114.4 (d, $J_{PC}$=17.5 Hz, $C_{Ar}$), 122.8 (d, $J_{PC}$=149.6 Hz, $C_{Ar}$), 123.8 ($C_{Ar}$), 133.9 (d, $J_{PC}$=15.2 Hz, $C_{Ar}$), 146.0 (s, $C_{Ar}$–O) 164.5 (d, $J_{PC}$=3.5 Hz, $COCH_3$). MS $m/z$ (%): 279 ($M^+$+1, 6), 278 ($M^+$, 42), 155 (32), 139 ($C_6H_4O_2P^+$, 100), 92 (26), 63 (33), 52 (20). Anal. Calcd for $C_{13}H_{11}O_3PS$: C, 56.11; H, 3.98; S, 11.52. Found: C, 55.86; H, 4.11; S, 11.82.

*4.2.11. 5-tert-Butyl-2-(4-methoxyphenyl)-1,3,2-benzodioxaphosphole 2-sulfide (**9b**).* Oil. IR (*Golden-Gate*): 2964, 1597, 1502, 1491, 1261, 1227, 1121, 920, 864, 806 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 1.32 (s, 9H, $C(CH_3)_3$), 3.85 (s, 3H, $OCH_3$), 6.96 (dd, 2H, ArH, $J$=9.0 Hz, $J_{PH}$=3.7 Hz), 7.00–7.07 (m, 2H, ArH), 7.16 (br s, 1H, ArH), 7.84 (dd, 2H, ArH, $J_{PH}$=15.0 Hz, $J$=9.0 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 31.7 ($C(CH_3)_3$), 35.1 ($C(CH_3)_3$), 55.8 ($OCH_3$), 110.3 (d, $J_{PC}$=10.0 Hz, $C_{Ar}$), 111.9 (d, $J_{PC}$=9.9 Hz, $C_{Ar}$), 114.4 (d, $J_{PC}$=17.4 Hz, $C_{Ar}$), 120.2 ($C_{Ar}$), 122.9 (d, $J_{PC}$=148.0 Hz, $C_{Ar}$), 134.0 (d, $J_{PC}$=15.2 Hz, $C_{Ar}$), 143.6 ($C_{Ar}O$), 145.7 ($C_{Ar}O$), 147.7 ($C_{Ar}C(CH_3)_3$), 164.4 (d, $J_{PC}$=3.3 Hz, $COCH_3$). MS $m/z$ (%): 335 ($M^+$+1, 9), 334 ($M^+$, 47), 319 ($M^+$, 100), 211 (12), 139 (9), 58 (13). Anal. Calcd for $C_{17}H_{19}O_3PS$: C, 61.06; H, 5.73; S, 9.59. Found: C, 61.01; H, 6.04; S, 9.10.

*4.2.12. 4,6-Di-tert-butyl-2-(4-methoxyphenyl)-1,3,2-benzodioxaphosphole 2-sulfide (**9c**).* Mp 134–135 °C ($CH_2Cl_2$). IR (*Golden-Gate*): 2962, 1593, 1410, 1261, 1121, 972, 864 $cm^{-1}$. $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 1.33 (s, 9H, $C(CH_3)_3$), 1.42 (s, 9H, $C(CH_3)_3$), 3.85 (s, 3H, $OCH_3$), 6.97 (dd, 2H, ArH, $J$=8.8 Hz, $J_{PH}$=3.6 Hz), 7.03 (s, 2H, ArH), 7.86 (dd, 2H, ArH, $J_{PH}$=15.0 Hz, $J$=8.8 Hz). $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 29.8 ($C(CH_3)_3$), 31.8 ($C(CH_3)_3$), 34.8 ($C(CH_3)_3$), 35.2 ($C(CH_3)_3$), 55.7 ($OCH_3$), 108.1 (d, $J_{PC}$=10.2 Hz, $C_{Ar}$), 114.3 (d, $J_{PC}$=17.3 Hz, $C_{Ar}$), 117.5 ($C_{Ar}$), 123.4 (d, $J_{PC}$=148.0 Hz, $C_{Ar}$), 133.9 (d, $J_{PC}$=15.1 Hz, $C_{Ar}$), 135.3 (d, $J_{PC}$=8.1 Hz, $C_{Ar}$), 141.6; 145.9; 146.7 ($C_{Ar}$), 164.3 (d, $J_{PC}$=3.3 Hz, $COCH_3$). MS $m/z$ (%): 391 ($M^+$+1; 12), 390 ($M^+$, 49), 375 ($M^+$–$CH_3$; 100), 319 (6), 211 (9), 108 (5), 91 (5), 77 (5), 58 (10), 57 (12). Anal. Calcd for $C_{21}H_{27}O_3PS$: C, 64.59; H, 6.97; S, 8.21. Found: C, 64.32; H, 7.04; S, 8.05.

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## Supplementary data

Spectra ($^1H$ NMR and $^{13}C$ NMR) of all products are provided. Supplementary data for this article can be found in the online version, at doi:10.1016/j.tet.2010.08.011. These data include MOL files and InChIKeys of the most important compounds described in this article.

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