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A DIRECT AND NEW CONVENIENT OXIDATION : SYNTHESIS OF SUBSTITUTED ARYLPHOSPHONATES FROM AROMATICS.

Fabrice Siméon, Paul-Alain Jaffrès and Didier Villemin*

Ecole Nationale Supérieure d'Ingénieurs de Caen (ISMRA) Université de Caen,

UMR CNRS 6507, 6 Boulevard du Maréchal Juin F-14050 Caen Cedex, France

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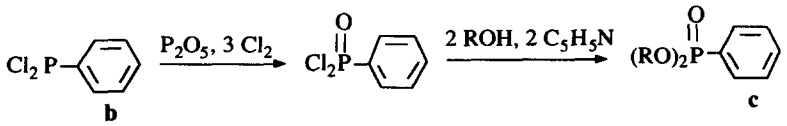
Abstract : An easy synthesis of aryl phosphonates by oxidation from aryldichlorophosphines with iodine in good yields is described. Aryldichlorophosphines are obtained by reaction of phosphorous trichloride with some aromatics in presence of various Lewis acids. $BiCl_3$ and $Bi(OTf)_3$ are used for the first time and bismuth trichloride is, for the first time in the case of anisole or thioanisole phosphonylation, used as a true regenerable Lewis acid catalyst in a reaction of direct phosphonylation of aromatics.

INTRODUCTION

We are interested in the direct phosphonation of aromatics in order to prepare hybrid organic-inorganic[1] materials via phosphonic acids. Arylphosphonates, precursors of arylphosphonic acids are well known[2,3] and of industrial interest[4] but only few methods described are cheap and efficient[5-7] to obtain these compounds from parent aromatic hydrocarbons. Various aryldichlorophosphines have been synthesized by Friedel-Crafts reaction of phosphorous trichloride with aromatic hydrocarbons using the method first described by Michaelis[8] and improved by Büchner and Lockhart[9]. Then these dichlorophosphines were oxidized directly into dialkoxyphosphonates by action of iodine in presence of sodium alkoxide. Surprisingly, it seems that it is the first fast and direct example of synthesis of arylphosphonates from aryldichlorophosphines. Previous authors have described the direct oxidation of dichlorophosphines into arylphosphonic acids[10] $ArP(O)(OH)_2$, aryldialkylphosphonites[11] $ArP(OR)_2$, aryldichlorophosphine oxides[12] $ArP(O)Cl_2$ or arylphosphinic acids[13] $ArP(OH)_2$ but no authors had described any way for the one-pot preparation of aryldialkylphosphonates from the dichlorophosphines. Nevertheless a two-step procedure, that we remind hereunder has been earlier described by Toy [12] and widely used.



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*Fax : 33 (0)2 31452877 E-mail : villemin@ismra.fr

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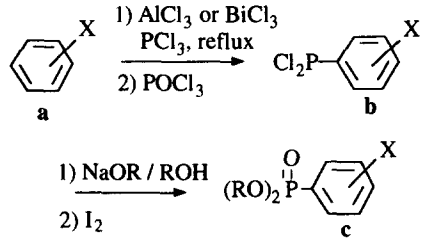
These observations allowed us to propose a one-pot oxidation reaction and an improvement in the preparation of aryldichlorophosphines. The results obtained are presented in tables I and II and the reactions are presented in scheme 1.

Scheme 1



X = $(-CH_3)_n$, $(-OCH_3)_n$, $(-SCH_3)$ and n=0, 1, 2 or 3

RESULTS AND DISCUSSION

In order to study this oxidation reaction, we decided to prepare some various aryldichlorophosphines. When using $AlCl_3$ as a Lewis acid promoter, method A, according to the literature[14] we observed that the Michaelis phosphonation is often highly regioselective, and gives almost only the isomer in para position. Nevertheless, in the case of toluene **2a** and amylbenzene **6a**, traces of ortho isomers have been observed[15] (3-5%) whereas ortho-xylene **3a** and pseudocumene **5a** give no isomers. It is also important to note a high steric effect in this reaction. This observation allows us to understand the reason of the ortho isomers low rate in the substitution by a phosphoryl group.

In cases where the aromatic ring is substituted by a heteroatom like oxygen or sulfur, Michaelis[16] and Kunz[17] described conflicting results upon the treatment of anisole **7a** and PCl_3 with $AlCl_3$. Miles and Beeny[18] have shown that the use of Lewis acid catalysts such as $FeCl_3$, $ZnCl_2$ or $SnCl_4$ increased the yield and the selectivity of the synthesis. But the reaction times were longer (15 to 75 hours) and the Lewis acids were not used as true catalysts (about 40 % of Lewis acids per mole of reactant, lost after reaction, are used).

We have been very interested in the recent improvement of the Friedel-Crafts acylation of anisole described by Dubac *et al.*[19] who use bismuth (III) chloride as a regenerable catalyst. This work and the most recent[20] concerning bismuth (III) trifluoromethanesulfonate (triflate)[20, 21] opened a wide path to the catalytic used of bismuth complexes. In our case, bismuth (III) chloride has been revealed as a very selective and powerful catalyst that allowed us to produce, in short reaction time (3 to 6 hours), the phosphonation of anisole **7a**, 1,2-dimethoxybenzene **9a** and p-thioanisole **8a**. In method B, best results were reached for 10 % of catalyst that can be used three times giving more than 50 % yield. Whilst bismuth chloride (III) is an efficient catalyst for the aromatic ether phosphonylations, it is not efficient enough to carry out the phosphonylation of non activated aromatics. To circumvent this problem, some experiments have been led using other bismuth derivatives. If $BiCl_3$ reacts preferably with hydrocarbone aromatics, $Bi(OTf)_3$[21] seems to react as good with hetero as with

homosubstituted aromatics. Used in method C (10 % of $Bi(OTf)_3$) it looks like the best recyclable catalyst for the phosphonation of aromatics. Attempts are being made in our laboratory to define the limits of this new method. The results obtained are reported in tables I and II.

Table I: Synthesis of aryldichlorophosphines (ADCP)

Products R-PCl_2	N°	Method[1]	Bp °C* (mm Hg)[lit]	Yield of ADCP (%)
C_6H_5-	**1b**	A	37 (0.03)[a]	96
4-CH_3-C_6H_4-	**2b**	A	51 (0.05)[b]	96
3,4-$(CH_3)_2$-C_6H_3-	**3b**	A, C	97 (0.04)	95-90
2,4,6-$(CH_3)_3$-C_6H_2-	**4b**	A	80 (0.03)	36
2,4,5-$(CH_3)_3$-C_6H_2-	**5b**	A	83 (0.02)	47
4-(n-C_5H_{11})-C_6H_4-	**6b**	A	78 (0.02)[c]	96
4-CH_3O-C_6H_4-	**7b**	A	76 (0.05)[d]	36
3,4-$(CH_3O)_2$-C_6H_3-	**9b**	A	93 (0.04)[e]	22
4-CH_3O-C_6H_4-	**7b**	B, C	76 (0.05)[d]	80-70
4-CH_3S-C_6H_4-	**8b**	B	101 (0.02)[f]	82
3,4-$(CH_3O)_2$-C_6H_3-	**9b**	B	93 (0.04)[e]	78

1 - method A : $AlCl_3$, method B : $BiCl_3$, method C : $Bi(OTf)_3$.

* for all compounds : bp ± 2°C are given, [a]Lit.[9] bp.68-70 / 1.0, [b]Lit.[22] bp.103-104 / 0.4, [c]Lit.[9] bp.118-121 / 1.0, [d]Lit.[18] bp.74-78 / 0.05, [e]Lit.[18] bp.112-115 / 0.4, [f]Lit.[18] bp.98-103 / 0.02.

Table II: Synthesis of aryldiethylphosphonates (ADEP)*

N°	**1c**	**2c**	**3c**	**4c**	**5c**	**6c**	**7c**	**8c**	**9c**
Bp °C*	88	89	102	112	110	120	92	105	91
(mm Hg)[lit]	(0.02)[a]	(0.03)[b]	(0.02)	(0.05)[c]	(0.05)	(0.03)	(0.05)[d]	(0.04)	(0.04)
Yield of ADEP (%)	97	98	96	85	95	98	98	97	95

*Satisfactory elemental analysis obtained for the new compounds **5c-6c** (C ± 0,25%, H ± 0,25 %).

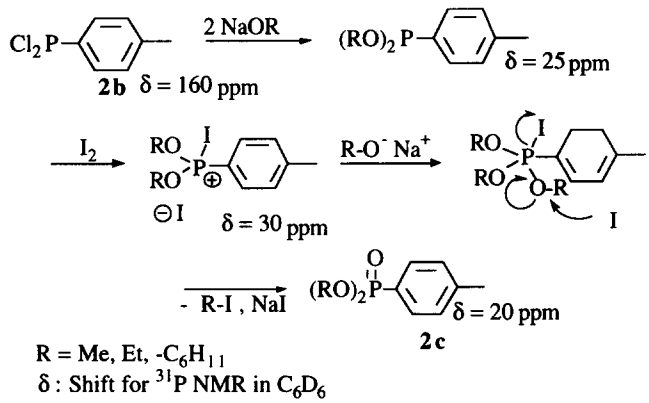
[a]Lit.[23] bp.96-98 / 0.2, [b]Lit.[23] bp.118-119 / 0.05, [c]Lit.[23] bp.111-112 / 0.05, [d]Lit.[3] bp.105-107 / 0.3 .

Aryldichlorophosphines are stable but react rapidly with the moisture of air to give the corresponding aryldihydroxyphosphines. Both react, aryldichlorophosphines more than aryldihydroxyphosphines, with a sodium alkoxide to give aryldialkoxyphosphonites. These compounds have not been fully characterized and undergoes the oxidation of iodine in presence of a sodium alkoxide to give the corresponding aryldialkoxyphosphonate.

In order to understand how the oxidation by iodine takes place, the transformation has been studied using ^{31}P NMR Spectroscopy. The complete reaction was conducted in a NMR tube, and signals were recorded regularly when adding each reactant. These measurements

were made within a 20 % (by volume) of the tolyldichlorophosphine **2b** in C_6D_6. The corresponding initial peak is at about 162 ppm from the external reference in H_3PO_4. Slow additions of sodium ethoxide powder, let appear a singlet at 25 ppm corresponding to the diethoxy- arylphosphonite. When the reaction is done in a solution of sodium ethoxide in ethanol, NMR scans may indicate one peak at 175 ppm. We suppose that this by-product may be the mono-ethoxy substituted compound for which isolation has not been possible. Oxidation with iodine of the diethoxyarylphosphonite into arylphosphonate leads to the formation of a phosphonium cation (30 ppm) which reacts vigorously with an alkoxide to liberate an iodide ion. This reaction mechanism is presented in scheme 2. It is of interest to notice that no oxidation of the sulfur group by iodine has been observed during the transformation of the thioanisyldichlorophosphine into the corresponding phosphonate.

Scheme 2 : Suggested mechanism for tolyldichlorophosphine oxidation by iodine



Aryldichlorophosphines (ADCP) and aryldiethylphosphonates (ADEP) have been synthesised. But if previous authors have described either IR or some NMR spectra for aryldichlorophosphines[24] or the corresponding phosphonic acids, to our knowledge, no complete spectroscopic analyses of these arylphosphonates have been published. Then we propose some spectroscopic data for these compounds and the first description for compounds **5c** and **6c**.

CONCLUSION

We describe in this paper a direct path for the preparation of arylphosphonates from aryldichlorophosphines. This simple reaction has been analysed and a reaction mechanism, based upon phosphorus NMR is proposed. At least the use of bismuth salts as catalysts in the Michaelis modification of the Friedel-Crafts reaction has been studied. However more efforts should be done to prove the nature of each catalyst used, to improve this easy process and to determine the limits of the catalysts.

EXPERIMENTAL

General method. ^{1}H NMR spectra were recorded with a "Bruker AC 250" spectrometer at 250.13 MHz in $CDCl_3$ using TMS as internal standard, δ are given in ppm and J in Hz. The ^{13}C NMR spectra were recorded with a "Bruker AC 250" spectrometer at 62.89 MHz, in $CDCl_3$ using TMS as internal standard (proton decoupled, J_{CP} given in Hz). With a "Bruker WP 80 SY" spectrometer were recorded the ^{31}P NMR spectra at 32.44 MHz with H_3PO_4 as external standard. Chemical shifts are given in δ ppm and coupling constants in Hz. Conventional abbreviations are used. The infra-red spectra FT-IR were recorded with a "Perkin Elmer 16 PC" spectrometer on the liquid film and ν are given in cm^{-1}. Bismuth tris(triflate) was prepared according to the literature [20] by a slow addition of triflic acid on triphenylbismuth at -78°C in the dichloromethane.

Synthesis of aryldichorophosphines (ADCP)

The apparatus consists in a flask equipped with a refrigerant and a hydrogen chloride trap bent to a solution of sodium hydroxide.

Method A : with $AlCl_3$.

To 5.33 g of aluminium trichloride (0.04 mol), 0.036 mole of an aromatic compound and 11.05 ml (0.11 mol) of phosphorus trichloride are added. The resulting mixture is vigorously stirred and refluxed during three hours. When no evolution of hydrogen chloride is seen the electrical heater is removed and 3.72 ml (0.04 mol) of phosphorous oxychloride is added to the hot mixture. The organic compound is separated from the granular compound precipitated in 40 ml petroleum ether. After distillation of the solvent and the excess of PCl_3 under vacuum, distillation under reduced pressure gives the aryldichlorophosphines as colourless liquids.

Method B, C : with bismuth complexes $BiCl_3$ or $Bi(OTf)_3$.

Example with $BiCl_3$: 2.75 g (20 mmol) of phosphorus trichloride and 60 mmol of an aromatic compound (widely in excess) are added in a dry flask containing 0.315 g (1 mmol) of bismuth trichloride. The resulting mixture is vigorously stirred and refluxed during two or three hours. Then 0.315 g more of bismuth trichloride are added for two hours reflux. When no evolution of hydrogen chloride can be observed, heating is stopped and the organic compound is separated from the residue precipitated in 2 times 40 ml petroleum ether. After distillation of the solvent under vacuum and the excess of the aromatic compound when possible, distillation under reduced pressure gives the aryldichlorophosphines as colourless liquids.

Reuse of the catalyst : The precipitated complexes of bismuth salts are vigorously washed 3 times with petroleum ether (3X40ml) under dry nitrogen and then the complexes can be reused to an other phosphonation.

Synthesis of aryldiethylphosphonates (ADEP)

Aryldichlorophosphine (0.018 mol) is added slowly to a fresh solution of sodium ethylate in ethyl alcohol. The white milky solution obtained is stirred during one hour and then 4.23 g (0.018 mol) of iodine is added in three portions. The mixture is stirred for two hours and then 10 ml of acidic water (HCl 5%) and 50 ml of diethyl ether are added for the extraction. The organic phase is decanted, washed with 10 ml water, twice with 15 ml of a solution of sodium bisulfite, and dried over magnesium sulphate. Evaporation of the solvent yields a yellow oil, which is purified by column chromatography on silica gel (EP/AcOEt : 95/5 then 80/20) or

distilled under reduced pressure. The phosphonates, are colourless or slightly yellow liquids and have been obtained in good yields from the ADCP.

Phenyl diethylphosphonate **1c** ^{1}H NMR ($CDCl_3$) : δ 1.33 (t, J=7.07, 6H, $(\mathbf{CH_3}CH_2O)_2P$) 4.11 & 4.12 (2dqd, 4H, J_{HP}=7.26, J_{HH}=7.07, $(CH_3\mathbf{CH_2}O)_2P$) 7.51 (m, 3H, H_4 & 2 H_O) 7,81 (ddd, 2H, $^2J_{HH}$=8.3, $^2J_{HP}$=13.2, $^3J_{HH}$=1.6, H_o) ^{13}C NMR ($CDCl_3$) : 16.43 (d, $^3J_{CP}$=6.79, $(CH_3CH_2O)_2P$), 62.18 (d, $^2J_{CP}$=7.8, $(CH_3CH_2O)_2P$) 126.46 (d, $^2J_{CP}$=187.6, C_1) 128.55 (d, $^3J_{CP}$=15.16, C_3) 131.87 (d, $^2J_{CP}$=9.87, C_2) 132.47 (d, $^4J_{CP}$=2.89, C_4) ^{31}P NMR ($CDCl_3/H_3PO_4$) : 19.42, s IR (NaCl) : 3460 (L, s), 3060, 2984 (w), 2932 (w), 2342 (w), 2234 (w), 1654 (w), 1594, 1560, 1440 (vs), 1392, 1246 (vs), 1164 (vs), 1132 (vs), 1054, 1026 (vs), 966, 748, 732 (w),696.

p-Tolyldiethylphosphonate **2c** ^{1}H NMR($CDCl_3$) : δ 1.31 (t, 6H, J=7.02) 2.40 (s, 3H, $\mathbf{CH_3}$-Ph) 4.12 (dqd, 4H, J_{HH}=7.02, J_{HP}=7.32, $(CH_3\mathbf{CH_2}O)_2$)) 7.27 (dd, 2H, $^4J_{CP}$=4.0. J_{HH}=8.2, H_3) 7.70 (dd, 2H, $^3J_{CP}$=13.1, J_{HH}=8.2, H_2) ^{13}C NMR ($CDCl_3$) : 16.4 (d, $^3J_{CP}$=6.48, $(CH_3CH_2O)_2$), 21.72 (s, CH3-Ph) 62.03 (d, $^2J_{CP}$=5.03, $(CH_3\mathbf{CH_2}O)_2$) 125.89 (d, $^2J_{CP}$=189.6, C_1) 129.27 (d, $^3J_{CP}$=15.6, C_3) 131.89 (d, $^2J_{CP}$=9.9, C_2) 142.99 (d, $^4J_{CP}$=3.5, C_4) ^{31}P NMR ($CDCl_3/H_3PO_4$) : 19.42, s. IR (NaCl) : 3472 (w), 2980 (vs), 2980, 2938 (w), 2906 (w), 1448 (w), 1386 (s), 1250 (vs), 1195, 1164 (w), 1110, 1098, 1054 (s), 1026 (vs), 964, 758 (w), 662.

(3,4-dimethyl)phenyldiethylphosphonate **3c** ^{1}H NMR($CDCl_3$) : δ 1.31 (t, 6H, J=7.1,$(\mathbf{CH_3}CH_2O)_2P$) 2.3 (s, 6H, $2(CH_3)_{3+4}$) 4.08 & 4.1 (2dqd, 4H, J_{HP}=7.4, J_{HH}=4.5, $(CH_3\mathbf{CH_2}O)_2P$) 7.21 (dd, 1H, J_{HH}=4.5, J_{HH}=7.8, H_3) 7.53 (dd, 2H, $^3J_{CP}$=13.1, J_{HH}=7.8, H_2) ^{13}C NMR ($CDCl_3$) : 16.33 (d, $^3J^{CP}$=6.41, $(CH_3CH_2O)_2$), 19.28 & 19.54 (2s, $(CH3\text{-}Ph)_{3+4}$) 61.90 (d, $^2J_{CP}$=5.41, $(CH_3\mathbf{CH_2}O)_2$) 125.69 (d, J_{CP}=189.38, C_1) 129.35 (d, J_{CP}=9.31, C_2) 128.77 (d, J_{CP}=15.33, C_5) 132.93 (d, J_{CP}=10.44, C_6) 136.90 (d, J_{CP}=15.35, C_3) 141.53 (d, J_{CP}=3.65, C_4) ^{31}P NMR ($CDCl_3/H_3PO_4$) : 20.41, s. IR (NaCl) : 3524 (w), 2980 (vs), 2938, 2906, 2360 (w), 2234 (f), 1606(w), 1496(w), 1448, 1386, 1250 (s), 1228, 1194, 1110 (s), 1098 (s), 1054 (s), 1026 (vs), 962 (w), 794, 662.

(2,4,6-trimethylphenyl)diethylphosphonate **4c** ^{1}H NMR($CDCl_3$) : δ 1.23 (t, 6H, J=7.05 $(\mathbf{CH_3}CH_2O)_2P$) 2.21 (s, 3H, $(CH_3)_4$) 2.52 (2s, 6H, $(CH_3)_{2+6}$) 3.97 & 4.05 (2 dqd, 4H, J_{HP}=7.18, J_{HH}=6.96, $(CH_3\mathbf{CH_2}O)_2P$) 6.8 (d, 2H, J= 4.34, H_{3+5}) ^{13}C NMR ($CDCl_3$) : 19.1 (d, $^3J_{CP}$=7.18, $(CH_3CH_2O)_2P$), 21.16 (s, $(CH_3)_4$), 23.20 & 23.25 (s, $(CH_3)_{5+6}$), 122.16 (d, J=182.2), 130.45 (d, J=16.20), 141.96 (d, J=2.7), 143.85 (d, J=12.56), ^{31}P NMR ($CDCl_3/H_3PO_4$) : 20.5, s IR (NaCl) : 3480 (w, L), 2980, 2934, 2358 (w), 1732 (w), 1606, 1558, 1446, 1412 (w), 1390 (w), 1256, 1164 (w), 1086, 1050 (s), 1024 (vs), 962 (s), 796, 758 (f), 648.

(1,3,4-trimethyl)phenyldiethylphosphonate **5c** ^{1}H NMR($CDCl_3$) : δ 1.31 (t, 6H, J=7.07 $(\mathbf{CH_3}CH_2O)_2P$) 2.25 (s, 6H, $(CH_3)_{4+5}$) 2.48 (s, 3H, $(CH_3)_2$) 4.09 & 4.10 (2dqd, 4H, J_{HP}=7.18, J_{HH}=6.96, $(CH_3\mathbf{CH_2}O)_2P$) 7.03 (d, 1H, J=5.8, H_2) 7,69 (d, 1 H, $^3J_{HP}$=13.2, H_5) ^{13}C NMR ($CDCl_3$) : 16.43 (d, $^3J_{CP}$=7.18, $(CH_3CH_2O)_2P$), 19.1 (s, $(CH_3)_4$) 19.8 (s, $(CH_3)_5$) 20.6 (s, $(CH_3)_2$) 61.7 (d, $^2J_{CP}$=5.38, $(CH_3CH_2O)_2P$) 123.61 (d, $^2J_{CP}$=187.6, C_1) 132.8 (d, $^3J_{CP}$=15.26, C_3) 133.7 (d, J_{CP}=14.36, C_5) 135.3 (d, J_{CP}=11.67, C_6) 139.0 (d, J_{CP}=9.88, C_2) 141.6 (d, J_{CP}=3.59, C_4) ^{31}P NMR ($CDCl_3/H_3PO_4$) : 20.42, s IR (NaCl) : 3528 (w), 2980, 2928, 2868 (w),2360 (w), 2342 (w), 1652 (w), 1610 (w), 1490 w, 1456, 1388 (w), 1248 (s), 1198 (s), 1168, 1136, 1098, 1054 (s), 1026 (vs), 962 (s), 872 (w), 792, 754, 724 (w), 668 (w), 636.

4-pentylphenyldiethylphosphonate **6c** ^{1}H NMR($CDCl_3$) : δ 0.89 (t, 3H, J=6.7, $(CH_3)_e$) 1.32 (m, 10H, $(CH_2)_{d+c}$ + $(\mathbf{CH_3}CH_2O)_2P$) 1.62 (m, 2H, $(CH_2)_b$) 2.64 (t, 2H, J=7.73, $(CH_2)_a$) 4.11 & 4.12 (2dqd, 4H, J_{HP}=7.2, J_{HH}=7.8, $(CH_3\mathbf{CH_2}O)_2P$) 7.27 (dd, 2H, J_{HP}=4.1, J_{HH}=8.1, H_{3+5}) 7.71 (dd, 2H, J_{HP}=13.1, J_{HH}=8.1, H_{2+6}) ^{13}C NMR ($CDCl_3$) : 14.04 (s, $(CH_3)_e$) 16.38 (d, $^3J_{CP}$=6.6, $(CH_3CH_2O)_2P$) 22.53 (s, $(CH_2)_d$) 28.85 (s, $(CH_2)_b$) 31.48 (s, $(CH_2)_c$) 36.04 (s, $(CH_2)_a$) 62.0 (d, $^2J_{CP}$=5.15, $(CH_3CH_2O)_2P$) 125.26 (d, $^2J_{CP}$=188.87, C_1) 128.61 (d, $^3J_{CP}$=15.28, C_{3+5}) 131.8 (d, $^2J_{CP}$=9.87, C_{2+6}) 131.91

(d, $^4J_{CP}$=4.46, C_4) ^{31}P NMR ($CDCl_3/H_3PO_4$) : 19.43, s IR (NaCl) : 3476 (L,w), 2980, 2958 (s), 2930 (s), 2858, 1606 (w), 1458 (w), 1444 (w), 1392, 1252 (s), 1164, 1130,1098, 1054 (vs), 1026 (vs), 964, 792, 672.

4-methoxyphenyldiethylphosphonate **7c** ^1H NMR($CDCl_3$) : δ 1.33 (t, 6H, J=7.10, ($\mathbf{CH_3}CH_2O)_2P$) 3.85 (s, 3H, $\mathbf{CH_3}$-O) 4.11 (dqd, 4H, J_{HH}=7.09, J_{HP}=7.42, ($CH_3\mathbf{CH_2}O)_2$)) 6.96 (dd, 2H, $^4J_{CP}$=4.6, J_{HH}=8.1, H_3) 7.74 (dd, 2H, $^3J_{CP}$=13.1, J_{HH}=8.1, H_2) ^{13}C NMR ($CDCl_3$) : 16.4 (d, $^3J_{CP}$=6.48, ($CH_3CH_2O)_2$), 21.98 (s, CH3-O) 62.09 (d, $^2J_{CP}$=5.25, ($CH_3CH_2O)_2$) 114.10 (d, $^2J_{CP}$=16.19, C_3) 119.60 (d, $^3J_{CP}$=195.72, C_1) 133.85 (d, $^2J_{CP}$=11.59, C_2) 162.95 (d, $^4J_{CP}$=5.28, C_4) ^{31}P NMR ($CDCl_3/H_3PO_4$) : 19.91, s. IR (NaCl) : 3470 (w), 2980 (vs), 2938 (w), 2904 (w), 1450 (w), 1385 (s), 1252 (vs), 1195, 1130 (w), 1098, 1055 (s), 1026 (vs), 960, 806, 757 (w).

4-thiophenyldiethylphosphonate **8c** ^1H NMR($CDCl_3$) : δ 1.33 (t, 6H, J=7.10, ($\mathbf{CH_3}CH_2O)_2P$) 2.51 (s, 3H, $\mathbf{CH_3}$-S) 4.10 (dqd, 4H, J_{HH}=7.05, J_{HP}=7.41, ($CH_3\mathbf{CH_2}O)_2$)) 7.28 (dd, 2H, $^4J_{CP}$=3.6, J_{HH}=8.2, H_3) 7.70 (dd, 2H, $^3J_{CP}$=12.9, J_{HH}=8.2, H_2) ^{13}C NMR ($CDCl_3$) : 16.4 (d, $^3J_{CP}$=6.48, ($CH_3CH_2O)_2$), 14.81 (s, CH3-S) 62.11 (d, $^2J_{CP}$=5.21, ($CH_3CH_2O)_2$) 123.84 (d, $^3J_{CP}$=191.21, C_1) 125.21 (d, $^2J_{CP}$=15.6, C_3) 132.13 (d, $^2J_{CP}$=10.69, C_2) 144.96 (d, $^4J_{CP}$=3.58, C_4) ^{31}P NMR ($CDCl_3/H_3PO_4$) : 18.81, s. IR (NaCl) : 3470 (w), 2980 (vs), 2938 (w), 2904 (w), 1450 (w), 1385 (s), 1252 (vs), 1195, 1130 (w), 1098, 1055 (s), 1026 (vs), 960, 806, 757 (w).

(3,4-dimethoxy)phenyldiethylphosphonate **9c** ^1H NMR($CDCl_3$) : δ 1.35 (t, 6H, J=7.10, ($\mathbf{CH_3}CH_2O)_2P$) 3.93 (s, 6H, $\mathbf{CH_3}$-O) 4.13 (dqd, 4H, J_{HH}=7.09, J_{HP}=7.42, ($CH_3\mathbf{CH_2}O)_2$)) 6.94 (dd, 2H, $^4J_{CP}$=4.51, J_{HH}=8.19, H_2) 7.27 (d, 1H, $^3J_{CP}$=14.0, H_5) 7.41 (dd, 1H, $^3J_{CP}$=13.41, J_{HH}=4.5, H_6) ^{13}C NMR ($CDCl_3$) : 16.4 (d, $^3J_{CP}$=6.48, ($CH_3CH_2O)_2$), 19.28 & 19.54 (2s, CH3-O) 62.10 (d, $^2J_{CP}$=5.25, ($CH_3CH_2O)_2$) 125.69 (d, $^3J_{CP}$=189.42, C_1) 129.35 (d, $^3J_{CP}$=9.29, C_3) 128.77 (d, $^2J_{CP}$=15.29, C_2) 132.93 (d, $^4J_{CP}$=10.4, C_4) 136.93 (d, $^4J_{CP}$=15.3, C_4) 141.53 (d, $^4J_{CP}$=3.62, C_4) ^{31}P NMR ($CDCl_3/H_3PO_4$) : 19.72, s. IR (NaCl) : 3468 (w), 2982 (vs), 2936 (w), 2905 (w), 1448 (w), 1385 (s), 1262 (vs), 1250, 1138 (w), 1098, 1054 (s), 1024 (vs), 964, 792, 755 (w).

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