Effective Catalysisof Knoevenagel-phospha-Michael Addition Reaction by ZnCl$_2$Doped Natural Phosphate

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Abstract

This paper studied the catalysis of the Knoevenagel-phospha-Michael addition reaction for the synthesis of β-phosphonomalonates, known for their very interesting biological properties. The β-phosphonomalonate compounds as enzyme inhibitors and metabolic probes, as well as intermediates in organic synthesis, exhibit a wide variety of biological, anticancer, anti-inflammatory, antimalarial, and antimicrobial activities.Thecatalyst based on natural phosphate doped with zinc chloride was prepared and characterized by different analysis methods. Thus, various aldehydes with malononitrile and diethylphosphite were used to test the prepared catalyst. In order to investigate the best catalysts and operating conditions, natural phosphate, fluorapatite, and hydroxyapatite were tested as catalysts for this reaction. The findings, with a slight advantage for natural phosphate doped byzinc chloride, showed the existence of a synergy between zinc chloride and natural phosphate.

Keywords: Heterogeneous catalysis, Natural phosphate, β-phosphonomalonate, Knoevenagel-phospha Addition of Michael.

1. Introduction

The development of a simple and environmentally friendly chemicalprocess is one of the main goals of the synthesis of organic compounds with important biological activity and one ofthe fundamental objectives of chemical industry. From an economic and ecological point of view,Multi-Component Reactions (MCR) are very important, as they offer the possibility to condense three or more components in one step[1]. Although the main advantages of Multi-Component Reactions are their ability to create two or more Carbon-Carbon and Carbon-Phosphorus bonds in a one put one step, they still present a typical challenge to overcome in order to obtain the desired product only and when selectivity plays a determining role in the reaction outcome.

The natural phosphate is the first mining wealth of Morocco.Its valorization is a continual objective sought by researchers. The application of phosphates in heterogeneous catalysis has been successfully developed in the nineties in acidic and basic reactions. Indeed, natural phosphate (NP), fluorapatite (Fap), and hydroxyapatite (Hap) alone or doped have been used mainly in reactions as heterogeneous catalysts[2][3],such as the reaction of Friedel-Crafts [4], Nitrile hydration [5], Michael [6], Knoevenagel[7], Suzuki Miyaura[8], and the synthesis of α-hydroxyphosphonates[9],Chalcones[10],and Spiropyrimidine[11].

However, phosphonates are an important intermediate in organic synthesis, and their uses in associated reactions are widely researched[12].Currently, they have also been intensively studied for their activities as enzyme inhibitors, metabolic probes, peptidic mimetics [13], antibiotics, and pharmacological agents [14, 15].

Many natural products containing the (C- P) bond are also known for their important biological activities [16]. Due to such a wide range of applications, the development of efficient protocols for the synthesis of phosphonates, phosphoric acid and related compounds via C - P bond formation has been of increasing interest.Themain objectivesare to prepare and characterize the natural phosphate doped with zinc chloride ZnCl$_2$/NP as acatalyst and its application in the multi-component addition of Knoevenagel-phospha Michael.

2. Experimental section

2.1. Catalyst Preparation and Characterization of catalysts

Before its use, natural phosphate (NP) is treated by different techniques, such as attrition, sieving, calcination (800 - 900°C), washing and recalcination. These treatments lead to a rich phosphate fraction between 100 and 400 μm. Table Ishows the chemical composition of the natural phosphate after treatment. Other metals are present in the chemical composition of the phosphate treated in ppm, such as Cd, Zn, Cu, U, Cr, V. The specific surface of NP is 1.4 m^2/g and its total pore volume is VT = 0.0055 cm^3/g.

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Table.IChemical composition of natural phosphate

Chemical element	Ca	P	F	Si	S	C	Na	Mg	Al	Fe	K
Percentage (%)	54.2	34.24	3.37	2.25	2.25	1.16	0.92	0.70	0.54	0.26	0.08

Natural phosphate was doped in order to improve its activity. The preparation of zinc chloridedoped natural phosphate ($ZnCl_2$/NP) was carried out according to the procedure used in various reactions, such as Dithio-acetalization [17]and Friedel-Crafts alkylation [4].This doping is achieved by the addition of 9.4 g of NP and 0.6 g of $ZnCl_2$ salt in 25 mL of water. The mixture is stirred for two hours and then evaporated under vacuum. The obtained solid is dried at 120°C for 24 hours, thus obtaining the catalyst dopedat 6% ($ZnCl_2$/NP).

2.2. Structural characterization

The X-ray diffraction peaks were detected to be finer and more intense for natural phosphate, following the enrichment treatment of the phosphate phase, particularly by washing and calcination. The corresponding peaks are characteristic of

### 2.3. Morphological characterization

The morphological appearance of undoped natural phosphate (NP) and zinc chloride-doped natural phosphate ($ZnCl_2$/NP) was observed by scanning electron microscope (SEM) and shown in Fig. 2. The SEM images show a change in the

fluorapatite, with a hexagonal structure of the space group $P6_3/m$ [18].

However, the comparison of the XRD spectra of NP and $ZnCl_2$-doped NP, shows a slight positive shift of some peaks (Fig. 1), assigned to the diffraction planes (0 0 2), (2 1 0), (3 0 0), (2 0 2),and (3 2 2), which could be due to the low percentage of $ZnCl_2$ in the prepared sample, or the Zn particles are highly dispersed or embedded in the natural phosphate matrix and too small to be detected by XRD[19].

Fig. 1 X-ray diffraction patterns of NP undoped and dopedZnCl$_2$/NP

surface of $ZnCl_2$-doped phosphate grains. The NP image shows porous and heterogeneous grains. On the other hand, the $ZnCl_2$/NP grains appear as agglomerations of different sizes.
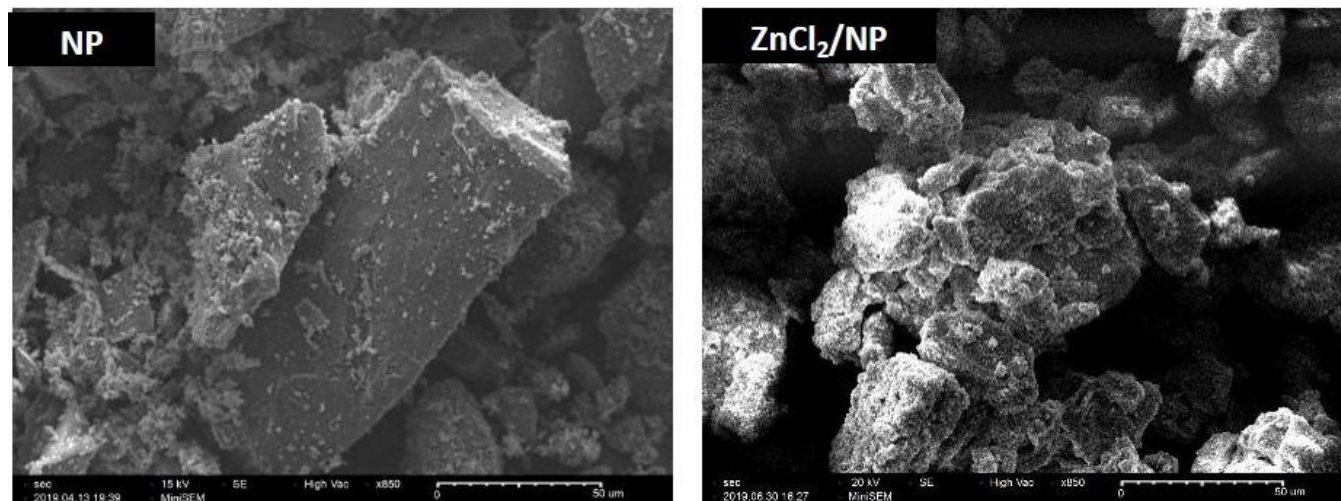

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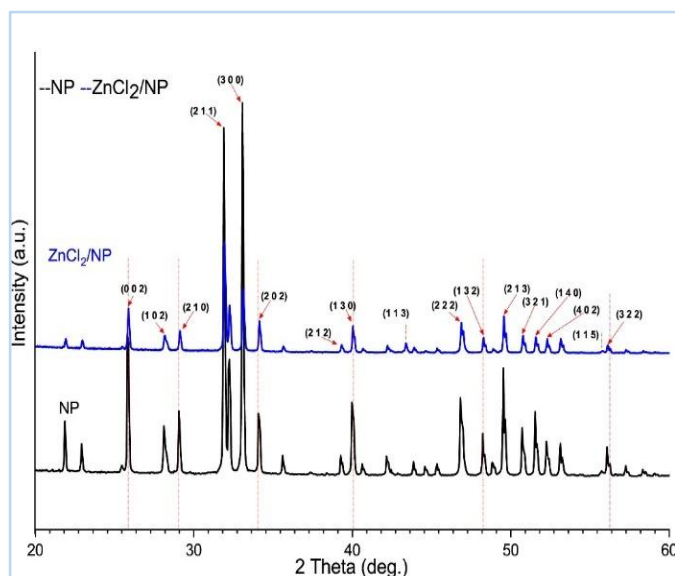
Fig.2 SEM of NP and NP doped with $ZnCl_2$/NP

2.4. Infrared spectroscopy characterization

The infrared spectra of the naturel phosphate (NP) and $ZnCl_2$/NP-doped naturel phosphate showed no change due to the addition of $ZnCl_2$ (Fig. 3), indicating that the impregnation of NP with $ZnCl_2$ did not alter the apatitic structure of the natural phosphate [20].
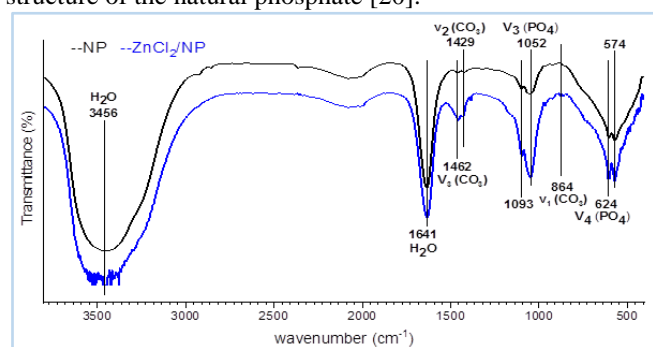

Fig. 3 FTIR spectra of NP and $ZnCl_2$/NP

The observed peaks at 605 - 574 cm^{-1} correspondto (PO_4^{3-})[21] and the bonds included between 1043 - 1093 cm^{-1} correspond to the asymmetric stretching mode of (PO_4^{3-}) [22]. Different absorption peaks are located at 1462, 1429,and 864 cm^{-1}corresponding to (CO_3^{2-})[23]. As for the bands observed at 1641,and 3459 cm^{-1}, are attributed to adsorbed water molecules [24],which could be due to the presence of zinc chloride, given its hygroscopic aspect, to form hydrates of zinc chloride[25].

3. Procedure of the Knoevenagel-phospha-addition reaction

In a 50 ml flask, the three reagents, 1 mmol of benzaldehyde, 1 mmol of malononitrile, and 2 mmol of diethylphosphite are mixed and stirred with a catalyst at a temperature of 25°C for the required reaction time (Fig. 4).

Fig.4 Synthesis of Diethyl(2,2-dicyano-1-phenylethyl)phosphonate**4a**

At the end of the reaction, the catalyst is separated from the reaction medium by simple filtration with ethyl acetate, which is then removed by evaporation under vacuum and purified by column chromatography. The outcome of the synthesis was determined by the ratio between the mass of the product recovered at the end of the reaction and that of the product that should theoretically be obtained, taking into account the stoichiometric coefficients of all reagents.The obtained product, thus, was characterized by ^{1}H-NMR,^{13}C-NMR, and ^{31}P-NMR(the data concerning this characterization are presented in the supplementary materials section).

3.1. Catalytic tests with phosphate-based catalysts

The choice of an efficient catalyst for a reaction is based on its catalytic activity and its capacity to increase the outcome of the reaction. In this sense, a series of catalysts were tested in order to choose the most efficient one.Each catalyst was used with an amount of 100 mg, except for $ZnCl_2$,where a mass of 6 mg corresponding to the quantity of the salt present in 100 mg of $ZnCl_2$/NP was used.The catalysts were tested with a reaction time of 12 hours and without solvent.

Table II.Comparison of the activity of different catalysts in the synthesis of β-phosphonomalonate4a

Catalyst	Quantity (mg)	Yields (%)
Without catalyst	--	0
$ZnCl_2$	6	12
NP	100	40
Fap	100	35

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| Hap | 100 | 23 |
| ZnCl$_2$/NP | 100 | 75 |

From the results presented in Table II, it is observed that the use of NP, Fap, and Hap leads to results of 40%, 35%, and 23%, respectively, after 12 hours of reaction and without solvent. The NP appears more reactive and allowed to obtain a higher outcome than that obtained by Fap or Hap. However, the outcomewent up to 75% with the use of the ZnCl$_2$/NP doped catalyst, while NP alone or zinc chloride alone could only achieve a rate of 40% and 12%, respectively.

3.2. Optimization of the reaction conditions

In this part, the influence of the various parameters of the reaction was studied on the outcome of the synthesis of β-phosphonomalonate**4a**,such asthe mass of the catalyst, the nature of the solvent, and the speed of the reaction.

– *Catalyst mass Effect*

To evaluate the catalytic power of the catalyst, masses ranging from 25 to 125 mg were used sequentiallyunder the same operating conditions indicated previously. The obtained results are shown in Fig 5.
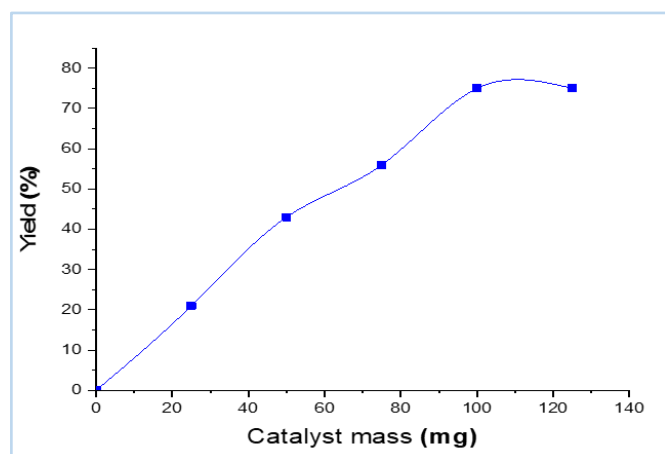

Fig 5. Effect of ZnCl$_2$/NP catalyst mass on β-phosphonomalonate**4a**synthesis

The mass of the catalyst was increased from 25 to 125 mg to explore the effect of mass on the outcome, which had improved from 21% to 75% and remained stable.An amount of 100 mg of catalyst was sufficient to obtain a good outcome under the operating conditions used.

– *Kinetics of the Reaction*

The kinetic of the reaction is essential to determining the optimal time corresponding to the highoutcome. The tests were carried out with the same operating conditions as before, varying the reaction time from 3 to 18 hours. Fig.6 shows that the yield increases from 3 hours to reach the maximum outcome of 75% at 9 hours of reaction.And beyond 12hours, the outcome decreases to 70% at 18hours.By extending the time frame, the reduction in the reaction yieldcould bedue to the degradation of the Nitrile

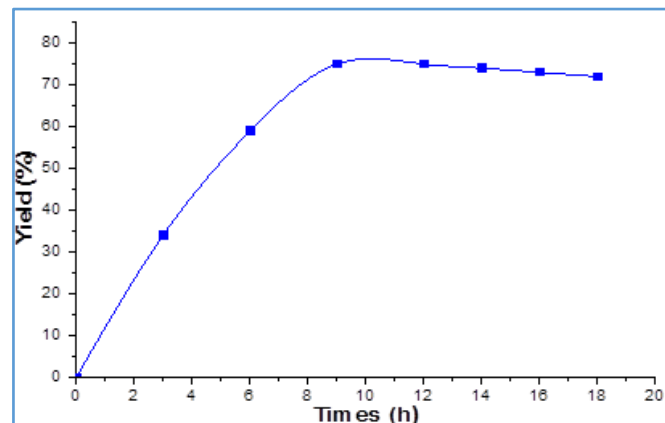group by hydration in the presence of the phosphate catalyst and of the water in the reaction medium [26, 27].

Fig 6. Kinetics of β-phosphonomalonate**4a**synthesis by ZnCl$_2$/NP catalysis

– *Temperature effect*

The temperature is a significant parameter for the progress of the reaction; for that reason, the synthesis of β-phosphonomalonate**4a**was carried out under the same conditionsas previously, by varying the temperature of the reaction medium (25°C, 40°C, 60°C, and 80°C), the results are shown in Fig 7.
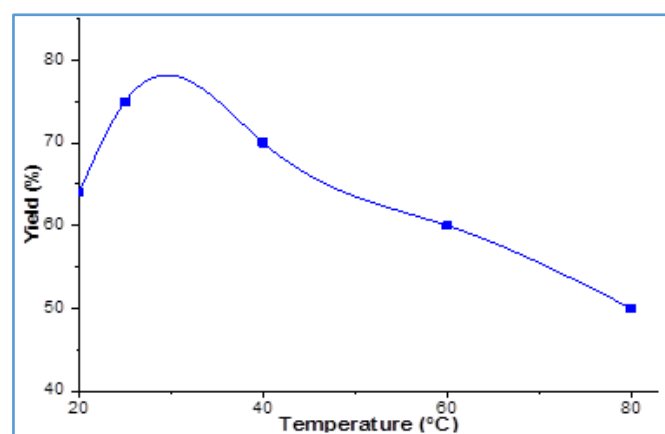

Fig 7. Effect of temperature on β-phosphonomalonate**4a** synthesis in the presence of ZnCl$_2$/NP

According to the time and catalyst mass study, the reaction yield reaches its maximum at 9 hours with 100 mg of catalyst and a temperature of 25°C and then decreases to 50% when the temperature rises to 80°C, which increases the rate of oxidation of the aldehyde, which is highly dependent on the temperature, especially in the presence of a small amount of catalyst, and consequently reduces the reaction outcomes[28, 29].The pore size and volume play an important role in evaluating the activity of the catalyst[30].Doping the natural phosphate with zinc chloride (ZnCl$_2$) with a uniform distribution on the surface of the support, increases the catalytic activity to provide a synergistic effect of the catalyst [31].

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– *Solvent effect*

The solvent can have an important influence on the speed of the reaction. Indeed, it can interact with the reactants, mainly through its polarization, to activate the reaction or, on the contrary, inhibit it. Several solvents were tested in this reaction under the same operating conditions, and the obtained results are grouped in Fig 8.
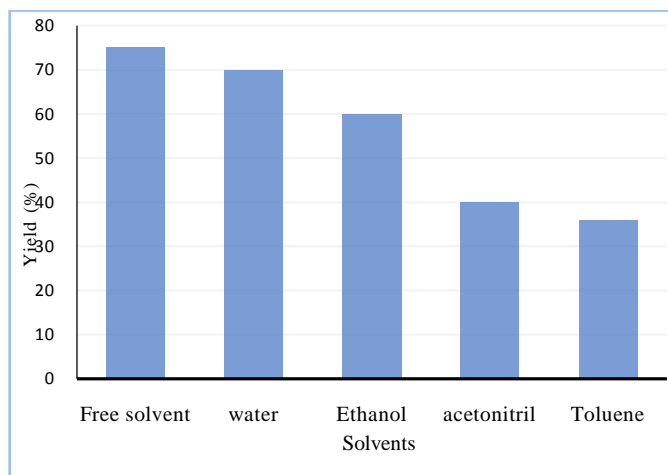
Fig. 8 Effect of solvent in the synthesis of β-phosphonomalonate**4a**in the presence of ZnCl$_2$/NP

From the obtained results, the Knoevenagel-phospha-Michael Addition Reaction gives relatively good results in polar and protic solvents, such as water and ethanol. When the reaction is carried out in acetonitrile and toluene, polar aprotic solvents, the obtained outcomesare lower. The best outcome is obtained without solvent. It can be concluded that the solventshave a relatively inhibitory effect.

3.3. Generalization

Fig. 9 shows the yields obtained with different aldehydes in the Knoevenagel-phospha-Michael addition reactionunder the optimal conditions of the synthesis.Therefore, the same optimization conditions were applied for the generalization of the synthesis of β-phosphonomalonate in the presence of the phosphate catalyst ZnCl$_2$/NP, with different aldehydes and the same amount of malononitrileand diethylphosphite at room temperature and without solvent for 12 hours.

Fig. 9. Knoevenagel-phospha-Michael addition reaction
Table III.Comparison of the activity of ZnCl$_2$/NP in the synthesis of different β-phosphonomalonate4

N Aldehydes	Products	ields %
1		75
2		69
3		74
4		73
5		70

The yields of the reaction of the synthesis of β-phosphonomalonate by the aromatic aldehydes, grouped together in table III, depend on the nature of the substitution (group donating or attracting electrons). The benzaldehyde gave a good yield of 75% of diethyl(2,2-dicyano-1-phenylethyl)phosphonate**4a** due to the absence of groups that could disturb the electronic density of the molecule. The aldehyde bearing the electron-withdrawing group (NO$_2$) gave a 73% yield of diethyl(2,2-dicyano-1-(4-nitrophenyl)ethyl)phosphonate **d4**, whereas the alkyl-substituted aldehyde (Me) gave a 70% yield of diethyl(2,2-dicyano-1-(p-tolyl)ethyl)phosphonate **4e**. It seems that the nature of the substituent does not have a great effect on the catalysis of the reaction by our phosphate support.

4. Conclusion

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The catalyst based on NP doped with zinc chloride $ZnCl_2$/NP was prepared and characterized by different analysis methods (XRD, SEM,and IR). The catalysis of the Knoevenagel-phospha-Michael Addition Reaction for the synthesis of β-phosphonomalonates, known for their very interesting biological properties, was studied.Thus, various aldehydes with malononitrile and diethylphosphitewere used to test the prepared catalyst. In order to investigate the best operating conditions,natural phosphate, fluorapatite, and hydroxyapatite were tested as catalysts for this reaction. The obtained outcomes are average, with a slight advantage for natural phosphate. Using $ZnCl_2$/NP, the yield reached got up to 75%, which shows the existence of a synergy between $ZnCl_2$ and NP, while the findings with fluorapatite and hydroxyapatite went only to 35% and 23% respectively. This result is very interesting and shows that natural phosphate is better than other synthetic phosphate varieties.Subsequently, the influence of the mass of the catalyst, the nature of the solvent,and the kinetics of the reaction were studied, which allowed for the determination of the optimal conditions for this synthesis. Theobtained productwas thuscharacterized by ^{1}H-NMR, ^{13}C NMR and^{31}P NMR. The $ZnCl_2$doped natural phosphate, this study opens the way for further catalytic studies with metals or metal salts supported on natural phosphate catalysts.

According to the obtained results, it seems that this study opens the way to new applications of catalysis by natural phosphate or natural phosphate doping by other metals or metal salts in the Knoevenagel-phospha-Michael Addition reaction.

Appendix A. Supplementary material

Diethyl (2,2-dicyano-1-phenylethyl)phosphonate (4a) : ^{1}*H NMR (400 MHz, CDCl₃) δ: 7.47-7.42 (m, 5H), 4.57-4.53 (m, 1H), 4.23-*

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4.11 (m, 2H), 4.03-3.71 (m, 2H), 3.60 (dd, J = 21.2, 8.0 Hz, 1H), 1.34 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H); ^{13}*C NMR (100 MHz, CDCl₃) δ: 130.40 (d), 129.71, 129.59, 129.45, 129.39, 111.40 (d), 111.20 (d), 64.54 (d), 63.53 (d), 44.10 (d), 25.66, 16.30 (d), 16.16 (d);* ^{31}*P NMR (162 MHz, CDCl₃) δ: 19.62.*

Diethyl (1-(4-chlorophenyl)-2,2-dicyanoethyl)phosphonate (4b) : ^{1}*H NMR (400 MHz, CDCl₃) δ: 7.47-7.38 (m, 4H), 4.56-4.52 (m, 1H), 4.23-4.12 (m, 2H), 4.08-3.81 (m, 2H), 3.63-3.54 (m, 1H), 1.35 (t, J = 7.1 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H);* ^{13}*C NMR (100 MHz, CDCl₃) δ: 135.89 (d), 130.83, 130.77, 129.77, 128.89, 111.23 (d), 111.03 (d), 64.53 (d), 63.63 (d), 43.35 (d), 25.59, 16.29 (d), 16.22 (d);*^{31}*P NMR (162 MHz, CDCl₃) δ: 18.90.*

Diethyl(2,2-dicyano-1-(4methoxyphenyl)ethyl)phosphonate (4c) : ^{1}*H NMR (400 MHz, CDCl₃) δ: 7.39 (dd, J = 8.7, 1.9 Hz, 2H), 6.93 (d, J = 8.7 Hz, 2H), 4.52-4.48 (m, 1H), 4.21-4.09 (m, 2H), 4.04-3.95 (m, 1H), 3.80 (s, 3H), 3.79-3.72 (m, 1H), 3.54 (dd, J = 21.3, 7.7 Hz, 1H), 1.33 (t, J = 7.1 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H);* ^{13}*C NMR (100 MHz, CDCl₃) δ: 160.47 (d), 130.71, 130.65, 122.02, 114.88, 114.86, 111.51 (d), 111.29 (d), 64.34 (d), 63.32 (d), 55.37, 43.19 (d), 25.91, 16.27 (d), 16.19 (d);* ^{31}*P NMR (162 MHz, CDCl₃) δ 19.54.*

Diethyl (2,2-dicyano-1-(4-nitrophenyl)ethyl)phosphonate (4d):^{1}*H NMR (400 MHz, CDCl₃) δ: 8.18 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 7.8 Hz, 2H), 4.83-4.77 (m, 1H), 4.13-3.97 (m, 4H), 3.89-3.81 (m, 1H), 1.24 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H);* ^{13}*C NMR (100 MHz, CDCl₃) δ: 148.18 (d), 137.83, 130.58, 130.52, 124.16, 124.15, 111.13 (d), 111.02 (d), 64.43 (d), 63.84 (d), 42.85 (d), 24.91, 16.10 (d), 15.99 (d);*^{31}*P NMR (162 MHz, CDCl₃) δ: 17.87.*

Diethyl (2,2-dicyano-1-(p-tolyl)ethyl)phosphonate (4e) : ^{1}*H NMR (400 MHz, CDCl₃) δ: 7.35 (d, J = 8.2, 2H), 7.21 (d, J = 8.2 Hz, 2H), 4.57-4.53 (m, 1H), 4.20-4.09 (m, 2H), 4.03-3.72 (m, 2H), 3.57 (dd, J = 21.2, 7.9 Hz, 1H), 2.35 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H), 1.12 (t, J = 7.1 Hz, 3H);* ^{13}*C NMR (100 MHz, CDCl₃) δ: 139.54 (d), 130.12, 129.22, 129.16, 127.25, 127.19, 111.51 (d), 111.32 (d), 64.29 (d), 63.29 (d), 43.53 (d), 25.69, 21.22, 16.22 (d), 16.10 (d);* ^{31}*P NMR (162 MHz, CDCl₃) δ: 19.58.*

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