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The Kabachnik–Fields Reaction Accelerated in External Magnetic Field

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ABSTRACT: *The significant acceleration in the Kabachnik–Fields reaction in an external magnetic field has been observed. The phenomenon is explained by the proper orientation of substrate molecules forced by external magnetic field. Diamagnetic dipoles are repulsed to the center by both electromagnet poles, being simultaneously arranged. This phenomenon may then promote the acceleration of the reaction.* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 00:1–8, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21149

INTRODUCTION

The constant magnetic field found its important application in polymer, material, or fuel industry to improve, e.g., properties of water and fuels by maintaining appropriate magnetic dipoles of liquids so that it change flow properties [1].

Some examples of the influence of external constant magnetic field on organic reactions were also reported, and the photoisomerization of isoquinoline *N*-oxide in an external magnetic field [2–5] seems to be very interesting. It was demonstrated that the reaction leading to 2*H*-isoquinolin-1-one underwent the external magnetic field effect, whereas the one leading to 8,9-dihydro-5-oxa-7-aza-benzocycloheptene did not. Different results were obtained for the photoisomerization of 1–cyano-isoquinoline *N*-oxide [5].

It was also demonstrated that high magnetic field ($B = 8$ T) influences the growth of benzophenone crystals [6]. The X-ray structure of crystals demonstrated the orthorhombic needles, which, in the absence of magnetic field, were oriented in random directions, whereas in the presence of high magnetic field needles' long axes tended to stay perpendicular to the direction of magnetic field. The degree of orientation depends on the magnetic flux density of the field.

Magnetic field also influences the structure of surface of an electrode modified by organic polymers; for example, electropolymerization of diamagnetic *o*–phenylenediamine on platinum occurred more efficiently in a magnetic field of $B = 6$ T [7].

All above-mentioned examples concerned with either a physical process of solidification [6] or typical radical reactions [2–5, 7], whereas intermediates were paramagnetic and applied external magnetic field acted in rather predictable way. Our team contributed to this topic too while studying the action of constant magnetic field on properties of alloys and other materials [8, 9].

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In memoriam of Professor Romuald Skowroński.

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It seemed interesting that what would be the effect of moderate magnetic field of $B = 1$ T on the reaction of the typical nonradical, ionic mechanism. Therefore, we have investigated the influence of external magnetic field on the Kabachnik–Fields reaction.

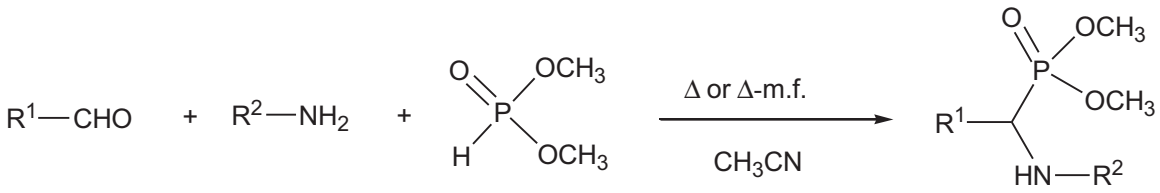
RESULTS AND DISCUSSION

For the first investigation, we have chosen the Kabachnik–Fields reaction because of two reasons. First, the products of the Kabachnik–Fields reaction, i.e., aminophosphonic derivatives, despite their old history are still en vogue, which is recently concluded by Kafarski [10]; it is much of interest to find a more efficient method for their synthesis. The second reason is a highly pragmatic one, the Kabachnik–Field reaction is very easy to monitor by the ^{31}P NMR spectroscopy, which is an easy tool, so that we chose it for its simplicity.

That is why we performed the Kabachnik–Fields reaction for six representative aldehydes **1a–f** with two representative amines **2A–B** and dimethyl phosphite (Scheme 1). Reactions were carried out in refluxing acetonitrile in a magnetic field of $B = 1$ T and, to compare, reactions in classical thermal conditions were launched simultaneously (see Figs. S1–S3 in the Supporting Information). Both reactions were simultaneously monitored by the ^{31}P NMR spectroscopy at certain intervals of time. Samples were taken at the same time, and ^{31}P NMR spectra were recorded simultaneously (±5 min), so that the conversion rates could be estimated by comparing integrations of peaks assigned to formed aminophosphonates (between 20 and 26 ppm) to signal of dimethyl phosphite (a doublet around 11.5 ppm).

The results were really astonishing because, in all studied cases, reactions carried out in a magnetic field allowed us to isolate aminophosphonates **3Aa–3Bf** at much more higher yields than reactions carried out in classical thermal conditions (Table 1).

Moreover, the ^{31}P NMR monitoring revealed that reactions in magnetic field occurred much faster, i.e., achieving higher conversion rates in a short time. The reaction of thiophene (**1d**) with benzylamine (**2A**) as well as the reaction of furfural (**1c**) with *p*–toluidine (**2B**) and dimethyl phosphite gave the best results and demonstrated the most distinctive difference in conversion rates between a reaction under constant magnetic field and classical thermal reaction. In the first case, dimethyl *N*-benzylamino(2-thienyl)-methylphosphonate (**3Ad**) was formed in 50% after 73 h of heating accompanied by the magnetic field and only in 16% under classical conditions. After 79 h, aminophosphonate **3Ad** was formed in 70% under the magnetic field and 28% under classical conditions (Fig. 1). The case of the reaction with furfural (**1c**) with *p*–toluidine (**2B**) and dimethyl phosphite gave similarly impressive results. Dimethyl *N*-(*p*-methyl-phenyl)amino(2-furyl)methylphosphonate (**3Bc**) was formed in 50% after 28 h of heating with magnetic field and only in 29% under classical conditions. After 55 h, aminophosphonate **3Bc** was formed in 70% under the magnetic field and in 40% under classical conditions and after 100 h, 80% and 48%, under magnetic field and classical conditions, respectively (Fig. 2).



1a-f **2A-B** **3Aa-Bf**

R^1 = **a**: Ph, **b**: ferrocenyl, **c**: 2-furyl, **d**: 2-thienyl, **e**: 2-phenylethenyl, **f**: *c*-Hex

R^2 = **A**: CH_2Ph, **B**: 4-methylphenyl

SCHEME 1 Kabachnik–Fields reaction with dimethyl phosphite, amines **2A–B**, and aldehydes **1a–f** with or without constant magnetic field.

TABLE 1 Results of the Kabachnik–Fields Reaction in External Magnetic Field ($B = 1$ T) and Classical Thermal Conditions ($B = 0$ T)

R^1	R^2	*Time of Reaction (h)*	*B = 1 T Yield (%) (Mass [g])*	*B = 0 T Yield (%) (Mass [g])*
Ph (**a**)	CH_2Ph (**A**)	52	70 (1.07)	30 (0.46)
Fc (**b**)	CH_2Ph (**A**)	28	75 (1.55)	64 (1.32)
2-Furyl (**c**)	CH_2Ph (**A**)	55	71 (1.05)	55 (0.81)
2-Thien (**d**)	CH_2Ph (**A**)	79	59 (0.92)	22 (0.34)
PhCH=CH (**e**)	CH_2Ph (**A**)	73	68 (1.13)	53 (0.88)
c-Hex (**f**)	CH_2Ph (**A**)	28	73 (1.14)	58 (0.91)
Ph (**a**)	*p*-CH_3-C_6H_4 (**B**)	52	74 (1.13)	68 (1.04)
Fc (**b**)	*p*-CH_3-C_6H_4 (**B**)	28	69 (1.42)	64 (1.32)
2-Furyl (**c**)	*p*-CH_3-C_6H_4 (**B**)	105	64 (0.95)	39 (0.58)
2-Thien (**d**)	*p*-CH_3-C_6H_4 (**B**)	76	73 (1.14)	63 (0.98)
PhCH=CH (**e**)	*p*-CH_3-C_6H_4 (**B**)	100	69 (1.15)	56 (0.93)
c-Hex (**f**)	*p*-CH_3-C_6H_4 (**B**)	25	71 (1.10)	63 (0.95)

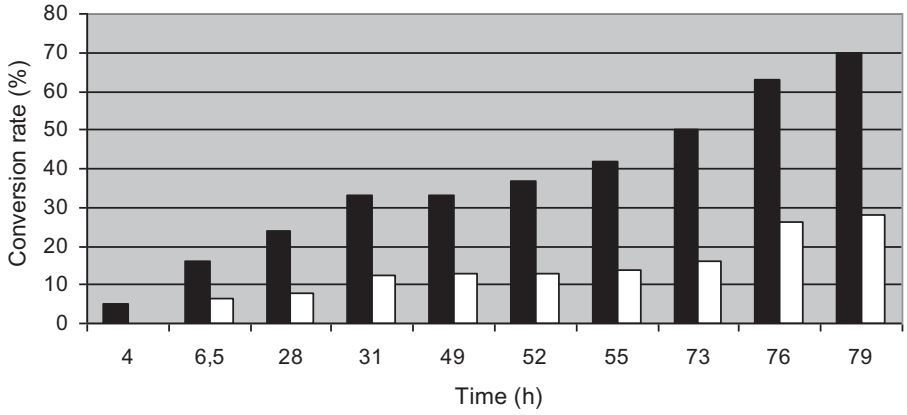


FIGURE 1 Conversion rates estimated at given intervals of time for a reaction of benzylamine **2A** with 2-thiophenecarboxaldehyde **1d** and dimethyl phosphite at $B = 1$ T (■) and 0 T (□).

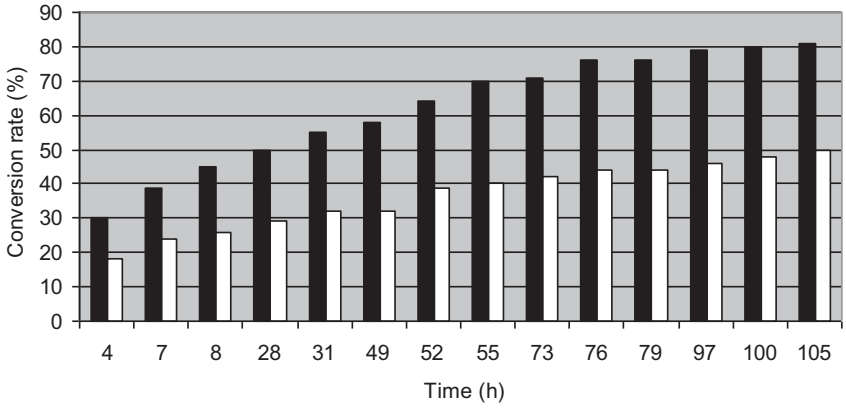


FIGURE 2 Conversion rates estimated at given intervals of time for a reaction of *p*-toluidine **2B** with 2-furfural **1c** and dimethyl phosphite at $B = 1$ T (■) and 0 T (□).

The formation of dimethyl *N*-benzylamino (phenyl)-methylphosphonate (**3Aa**) is also highly promoted by the presence of magnetic field as compared to a classical thermal reaction. After 8 h of heating under constant magnetic field, the conversion reached 60%, whereas classical heating allowed the system to produce 19% aminophosphonate **3Aa** only. When a magnetic field forced system to form **3Aa** in 90% during 52 h, a classical thermal reaction occurred at 39% conversion rate only (Fig. 3). Similar results were also obtained for other reactions, but a distinctive difference was

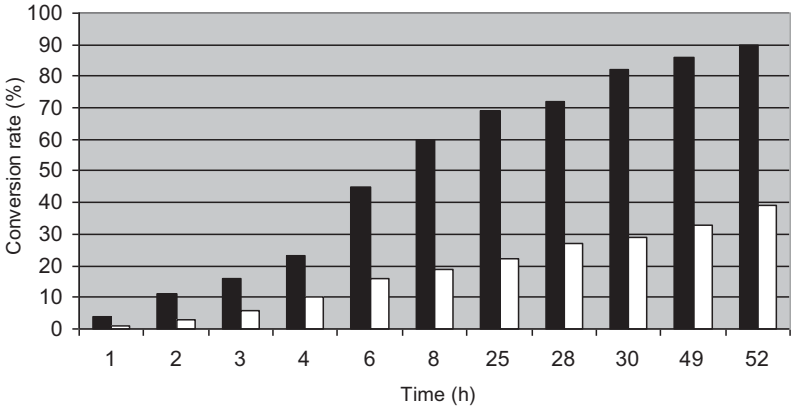


FIGURE 3 Conversion rates estimated at given intervals of time for a reaction of benzylamine **2A** with benzaldehyde **1a** and dimethyl phosphite at $B = 1$ T (■) and 0 T (□).

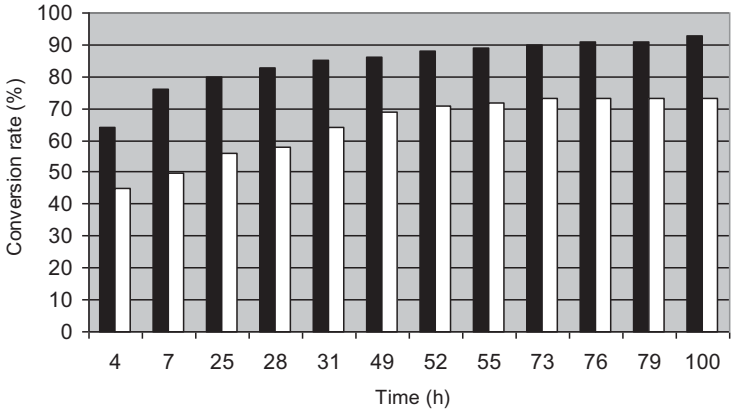


FIGURE 4 Conversion rates estimated at given intervals of time for a reaction of *p*-toluidine **2B** with cinnamaldehyde **1e** and dimethyl phosphite at $B = 1$ T (■) and 0 T (□).

also observed for the reaction with *p*-toluidine **2B** with cinnamaldehyde **1e** and dimethyl phosphite (Fig. 4).

All these results tend to state that the Kabachnik–Fields reaction of a known ionic mechanism [11] occurs much better when apart from heating, a constant magnetic field is applied. Therefore, the constant magnetic field has an accelerating effect on this reaction. Why?

It is known that the thermal energy is necessary to accelerate the velocity of substrate molecules to increase the reaction rate for slow reactions, whereas the magnetic field did not change the velocity of various chemical species [1]. However, the magnetic field changes the direction of atoms' or molecules' movement and causes orientation of their magnetic moments in a given direction, i.e., a certain orientation of their magnetic dipoles [1]. But there is no comprehensive theoretical model that accounts for the magnetic field effects on chemical processes, despite the observation that the external magnetic field actually has a significant effect on the chemical and biochemical systems [12]. Of course, some attempts were made to construct models explaining how an applied weak magnetic field might influence the steady state of a nonequilibrium chemical system. It was assumed that external magnetic field can have an effect on the rates of radical reactions occurring in a system leading to drastic changes in the properties of chemical systems such as temperature and reagent concentration [10]. It is concluded that though the energy of magnetic interactions is small, under certain conditions relatively weak magnetic fields can significantly affect the rates of chemical reactions with the participation of paramagnetic particles [12, 13].

We did not find any study in the literature describing the action of magnetic field on diamagnetic systems. However, Li et al. [14] suggested that effects of an applied magnetic field on chemical reactions are due to the fact that applied magnetic field can have an orientational effect on some

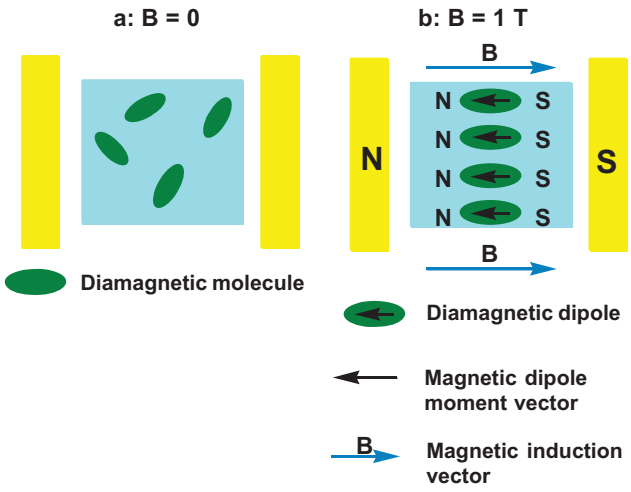


FIGURE 5 Arrangement of a diamagnetics molecule, when (a) no external magnetic field was applied and (b) external magnetic field of $B = 1$ T was applied.

organic polymers and biological molecules, which enhance mass transfer and morphological changes in organic films [14], and we took this suggestion as a basis for our consideration.

In diamagnetic substances, the resultant magnetic moments are zero, so, when external magnetic field is not applied, no magnetic organization occurs [15, 16]. However, external constant magnetic field is able to induce certain magnetic dipole moments in diamagnetic organic molecules, and their value is proportional to magnetic field induction [1]. These dipoles are arranged in such a way that their magnetic dipole moment vector is oriented in the opposite direction to the vector *B*. If a magnetic dipole of a diamagnetic substance is considered as an elemental magnet of poles N i S, it arranges in such a way that its pole N will be facing to the electromagnet pole S and the dipole pole S is facing to the electromagnet pole N (Fig. 5). Diamagnetic dipoles are repulsed to the center by both poles of an electromagnet, being simultaneously arranged. This phenomenon may then promote the acceleration of the reaction.

CONCLUSIONS

We have demonstrated the significant accelerating effect of the constant magnetic field on the Kabachnik–Fields reaction. As far as can be ascertained, this is the first example of a nonradical reaction, which was accelerated when external magnetic field was applied. The described phenomena is described in the patent application [17]. We tried to find a reasonable explanation for this phenomenon, and it seems that the proper orientation of substrate molecules, which is forced by external magnetic field, plays a key role, as it forces a shorter distance between molecules. Further investigations will focus on the influence of external magnetic field on other Mannich-type reactions.

EXPERIMENTAL

General

Acetonitrile (Aldrich, Poznań, Poland) was routinely distilled and dried prior to use. Aldehydes, amines, and dimethyl phosphite (Aldrich) were used as received. ^{1}H and ^{31}P NMR spectra were recorded on a Bruker Avance III 600 MHz apparatus operating at 600 MHz (^{1}H NMR), 150 MHz (^{13}C NMR), and 243 MHz (^{31}P NMR). In two cases (**3Ab** and **3Ad**), ^{13}C NMR spectra were recorded on a Varian Gemini 2000BB 200 MHz apparatus operating at 50 MHz. Elemental analyses were performed in the Microanalysis Lab, the Centre of Molecular and Macromolecular Studies Polish Academy of Science (PAS), in Łódź, Poland. Melting points were measured in a MelTemp II apparatus and were uncorrected.

Reactions in magnetic field were carried out with the use of the apparatus constructed in the Division of Radio Equipment (RADIOPAN) of PAS (Poznań, Poland) consisting of following components: a laboratory electromagnet with N and S pole shoes (ER-2505 type), a electrochemical cell with a three-electrode system, a PZP-80 control device for the electromagnet, a stable current source for the electromagnet, a Hall sensor for a constant magnetic field, and a Hall teslameter (TH-26 type) (Figs. S1–S4 in the Supporting Information).

General Procedure for the Synthesis of Aminophosphonates **3Aa–3Bf**

An appropriate aldehyde **1a–f** (5 mmol), amine **2A–B** (5 mmol), and dimethyl phosphite (5 mmol, 0.55 g) were dissolved in 30 mL of acetonitrile in two independent reaction vessels equipped with reflux condensers. One of the vessels was placed between poles of an electromagnet and was heated with a heat gun (see Figs. S1–S4 in the Supporting Information), and the other was heated with a magnetic stirrer. Both solutions were then refluxed during the day and stirred at room temperature overnight. At certain intervals, both reactions were monitored by ^{31}P NMR, i.e., 0.5 mL samples were taken simultaneously from each reaction; to each sample, 0.5 mL of $CDCl_3$ was added, ^{31}P NMR

nondecoupled spectra were recorded at nearly the same time (± 5 min), and conversion rates were estimated by comparing of integrations. Results are presented in Tables S1 and S2 in the Supporting Information. After the reaction was considered to be accomplished, a solvent was evaporated, the residue dissolved in dichloromethane washed with saturated, aqueous $NaHCO_3$, an organic layer was dried and evaporated to obtain residues containing almost pure aminophosphonate **3Aa–Bf**, which were chromatographed on silica gel and eluted with ethyl an acetate–hexane (4:1) solvent system. All new aminophosphonates **3Ab**, **3Ad**, and **3Af** as well as **3Bb**, **3Bd**, and **3Bf** were characterized by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy, and their purity was confirmed by elemental analyses. Data of known synthesized aminophsophonates are described in the literature, and their identity was confirmed by ^{1}H and ^{31}P NMR spectroscopy, and melting point measurements, which were compared with the literature data [18–22]. Yields of reactions carried out under influence of magnetic field are also given.

*Dimethyl N-Benzylamino(phenyl)methylphosphonate (***3Aa***)*

Y = 70% (1.07 g). Yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.43–7.42 (m, PhH, 2H); 7.39–7.36 (m, PhH, 2H); 7.33–7.29 (m, PhH, 4H); 7.25–7.23 (m, PhH, 2H); 4.05 (d, $^2J_{PH}$ = –19.8 Hz, CHP, 1H); 3.80 (d, $^2J_{HH}$ = –13.2 Hz, CH_2Ph, 1H); 3.73 (d, $^3J_{PH}$ = 10.8 Hz, $POCH_3$, 3H); 3.55 (d, $^2J_{HH}$ = –13.2 Hz, CH_2Ph, 1H); 3.54 (d, $^3J_{PH}$ = 10.8 Hz, $POCH_3$, 3H). ^{31}P NMR ($CDCl_3$, 243 MHz): δ (ppm) 25.75 [18].

*Dimethyl N-Benzylamino(ferrocenyl)methylphosphonate (***3Ab***)*

Y = 75% (1.55 g). Brown oil. ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.45–7.43 (m, PhH, 2H); 7.38–7.36 (m, PhH, 2H); 7.30–7.28 (m, PhH, 1H); 4.29–4.28 (m, 1H, C_5H_4); 4.27–4.25 (m, 1H, C_5H_4); 4.22 (d, $^2J_{HH}$ = –13.2 Hz, CH_2Ph, 1H); 4.18–4.17 (m, 1H, C_5H_4); 4.15–4.14 (m, 1H, C_5H_4); 4.07 (s, 5H, C_5H_5); 4.06 (d, $^2J_{HH}$ = –13.2 Hz, CH_2Ph, 1H); 3.76 (d, $^2J_{PH}$ = –11.0 Hz, 1H, CHP); 3.71 and 3.67 (2d, $^3J_{PH}$ = 10.8 Hz, 2×3H, $POCH_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) 138.68 (C_{phen}-CH_2); 127.30 (C_{phen}-H); 127.21 (C_{phen}-H); 126.01 (C_{phen}-H); 84.46 (C_{ferr}-CH); 67.50 (d, $^3J_{PC}$ = 2.5 Hz, C_{ferr}); 67.36 (C_5H_5); 66.59 (C_{ferr}); 66.54 (C_{ferr}); 64.87 (d, $^3J_{PC}$ = 2.5 Hz, C_{ferr}); 53.52 (d, $^1J_{PC}$ = 157.5 Hz, C–P); 52.37 (d, $^2J_{PC}$ = 8.5 Hz, P–O–C); 52.21 (CH_2); 52.25 (d, $^2J_{PC}$ = 7.5 Hz, P–O–C). ^{31}P NMR ($CDCl_3$, 243 MHz): δ (ppm) 24.85. Anal. calcd for $C_{20}H_{24}FeNO_3P$: C, 58.13; H, 5.85; N, 3.39. Found: C, 58.06; H, 5.90; N, 3.43.

*Dimethyl N-Benzylamino(2-furyl)methylphosphonate (***3Ac***)*

Y = 71% (1.05 g). Yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.69–7.68 (m, $^5H_{fur}$, 1H); 7.57.43–7.42 (m, PhH, 2H); 7.39–7.36 (m, PhH, 2H); 7.33–7.29 (m, PhH, 4H); 6.50–6.49 (m, $^3H_{fur}$, 1H); 6.42–6.41 (m, $^4H_{fur}$, 1H); 4.23 (d, $^2J_{PH}$ = –19.8 Hz, CHP, 1H); 3.88 (d, $^2J_{HH}$ = –13.2 Hz, CH_2Ph, 1H); 3.83 (d, $^3J_{PH}$ = 10.8 Hz, $POCH_3$, 3H); 3.65 (d, $^2J_{HH}$ = –13.2 Hz, CH_2Ph, 1H); 3.59 (d, $^3J_{PH}$ = 10.8 Hz, $POCH_3$, 3H). ^{31}P NMR ($CDCl_3$, 243 MHz): δ (ppm) 25.75 [19].

*Dimethyl N-Benzylamino(2-thienyl)methylphosphonate (***3Ad***)*

Y = 59% (0.92 g). Yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.39–7.38 (m, PhH, 2H); 7.34–7.32 (m, PhH, $^5H_{thioph}$, 3H); 7.28–7.25 (m, PhH, $^3H_{thioph}$, 2H); 7.09 (dd, J = 5.4 and 3.6 Hz, $^4H_{thioph}$, 1H); 4.36 (d, $^2J_{PH}$ = –24.0 Hz, 1H, CHP); 3.88 (d, $^2J_{HH}$ = −13.2 Hz, CH_2Ph, 1H); 3.87 (d, $^3J_{PH}$ = 10.8 Hz, 3H, $POCH_3$); 3.56 (d, $^3J_{PH}$ = 10.8 Hz, 3H, $POCH_3$); 3.48 (d, $^2J_{HH}$ = –13.2 Hz, CH_2Ph, 1H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) 137.31 (C_{phen}-CH_2); 131.40 (d, $^2J_{PC}$ = 8.5 Hz, $C^2{}_{thioph}$-C-P); 127.92 ($C^4{}_{thioph}$); 127.81 (C_{phen}-H); 127.09 (C_{phen}-H); 126.01 (C_{phen}-H); 125.69 ($C^5{}_{thioph}$); 124.62 ($C^4{}_{thioph}$); 58.47 (d, $^3J_{PC}$ = 12.0 Hz, CH_2); 57.17 (d, $^1J_{PC}$ = 165.0 Hz, C–P); 52.55 (d, $^2J_{PC}$ = 7.0 Hz, P–O–C); 51.60 (d, $^2J_{PC}$ = 7.0 Hz, P–O–C). ^{31}P NMR ($CDCl_3$, 243 MHz): δ (ppm) 23.96. Anal. calcd for $C_{14}H_{18}NO_3PS$: C, 54.01; H, 5.83; N, 4.50. Found: C, 54.08; H, 5.95; N, 4.55.

*Dimethyl N-Benzylamino(2-phenylethenyl) methyl-phosphonate (***3Ae***)*

Y = 68% (1.13 g). Yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.43–7.39 (m, PhH, 2H); 7.36–7.34 (m, PhH, 2H); 7.33–7.31 (m, PhH, 4H); 7.28–7.24 (m, PhH, 2H); 6.62 (ddd, $^4J_{HH}$ = 1.2 Hz, $^4J_{PH}$ = 4.8 Hz, $^3J_{HH}$ = 15.6 Hz, C$\underline{H}$ = CH, 1H); 6.15 (ddd, $^3J_{PH}$ = 5.4 Hz, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 15.6 Hz, CH = C$\underline{H}$, 1H); 4.07 (ddd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 6.6 Hz, $^2J_{PH}$ = –25.8 Hz, CHP, 1H); 3.80 (d, $^3J_{PH}$ = 10.8 Hz, $POCH_3$, 3H); 3.79 (d, $^2J_{HH}$ = –13.2 Hz, CH_2Ph, 1H); 3.77 (d, $^3J_{PH}$ = 10.8 Hz, $POCH_3$, 3H); 3.76 (d, $^2J_{HH}$ = −13.2 Hz, CH_2Ph, 1H). ^{31}P NMR ($CDCl_3$, 243 MHz): δ (ppm) 25.86 [20].

*Dimethyl N-Benzylamino(cyclohexyl)methylphosphonate (***3Af***)*

Y = 73% (1.14 g). Yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.36–7.35 (m, PhH, 2H); 7.32–7.30 (m, PhH, 2H); 7.26–7.23 (m, PhH, 1H); 4.02 (d, $^2J_{HH}$ = –13.2 Hz, CH_2Ph, 1H); 3.87 (dd, $^2J_{HH}$ = −13.2 and $^4J_{PH}$ = 1.8 Hz, CH_2Ph, 1H); 3.78 and 3.75 (2d, $^3J_{PH}$ = 10.8 Hz, 2 × 3H, $POCH_3$); 2.77 (dd, $^3J_{PH}$ = 14.4 and $^3J_{HH}$ = 4.2 Hz, 1H, NH); 1.88–1.76 (m, cHex, 4H); 1.69–1.61 (m, cHex, 2H); 1.49–1.42 (m, cHex, 1H); 1.32–1.16 (m, cHex, 4H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 140.06 (C_{phen}-CH_2); 128.36 (C_{phen}-H); 128.23 (C_{phen}-H); 127.02 (C_{phen}-H); 59.35 (d, $^1J_{PC}$ = 140.9 Hz, C–P); 53.39 (d, $^3J_{PC}$ = 4.4 Hz, CH_2); 52.41 (d, $^2J_{PC}$ = 7.1 Hz, P–O–C); 52.30 (d, $^2J_{PC}$ = 7.5 Hz, P–O–C); 39.23 (d, $^2J_{PC}$ = 4.5 Hz, $C^1{}_{c\text{-}hex}$-P); 30.82 (d, $^3J_{PC}$ = 11.7 Hz, $C^2{}_{c\text{-}hex}$-P); 28.29 (d, $^4J_{PC}$ = 4.1 Hz, $C^3{}_{c\text{-}hex}$-P); 26.55 ($C_{c\text{-}hex}$); 26.36 ($C_{c\text{-}hex}$); 26.14 ($C_{c\text{-}hex}$). ^{31}P NMR ($CDCl_3$, 243 MHz): δ (ppm) 30.88. Anal. calcd for $C_{16}H_{26}NO_3P$: C, 61.72; H, 8.42; N, 4.50. Found: C, 61.77; H, 8.43; N, 4.66.

*Dimethyl N-(p-Methylphenyl)amino(phenyl)methylphosphonate (***3Ba***)*

Y = 74% (1.13 g). Mp: 68–71°C. Lit [21]: 69–70°C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.47–7.45 (m, PhH, 2H); 7.34–7.32 (m, PhH, 2H); 7.28–7.25 (m, PhH, 1H); 6.91 and 6.52 (AA′XX′ system, $^3J_{HH}$ = 8.4 and $^4J_{HH}$ = 1.8 Hz and $^4J_{HH}$ = 1.8 Hz, p-C_6H_4, 2 × 2H); 4.77 (d, $^2J_{PH}$ = –24.0 Hz, CHP, 1H); 3.75 and 3.48 (2d, $^3J_{PH}$ = 10.8 Hz, $POCH_3$, 2 × 3H); 2.18 (s, CH_3, 3H). ^{31}P NMR ($CDCl_3$, 243 MHz): δ (ppm) 25.12.

*Dimethyl N-(p-Methylphenyl)amino(ferrocenyl)methylphosphonate (***3Bb***)*

Y = 69% (1.42 g). Mp: 167–169°C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.05 and 6.72 (AA′XX′ system, $^3J_{HH}$ = 8.4 Hz, 2 × 2H, p-C_6H_4); 4.46 (d, $^2J_{PH}$ = –16.2 Hz, 1H, CHP); 4.32–4.30 (m, 2H, C_5H_4); 4.21–4.19 (m, 2H, C_5H_4); 4.09 (s, 5H, C_5H_5); 4.01–3.99 (m, 1H, NH); 3.67 and 3.62 (2d, $^3J_{PH}$ = 10.2 Hz, 2 × 3H, $POCH_3$); 2.26 (s, CH_3, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 144.84 (d, $^3J_{PC}$ = 6.0 Hz, C_{phen}-NH); 129.97 (C_{phen}-H); 127.82 (C_{phen}-CH_3); 113.75 (C_{phen}-H); 85.51 (d, $^2J_{PC}$ = 6.6 Hz, C_{ferr}-CH); 68.79 (C_5H_5); 68.64 (d, $^3J_{PC}$ = 4.1 Hz, C_{ferr}); 68.18 (C_{ferr}); 67.86 (C_{ferr}); 65.99 (d, $^3J_{PC}$ = 1.7 Hz, C_{ferr}); 53.91 (d, $^2J_{PC}$ = 6.8 Hz, P–O–C); 53.25 (d, $^2J_{PC}$ = 7.1 Hz, P–O–C); 52.19 (d, $^1J_{PC}$ = 161.0 Hz, C–P); 20.42 (CH_3). ^{31}P NMR ($CDCl_3$, 243 MHz): δ (ppm) 23.94. Anal. calcd for $C_{20}H_{24}FeNO_3P$: C, 58.13; H, 5.85; N, 3.39. Found: C, 57.85; H, 5.67; N, 3.59.

*Dimethyl N-(p-Methylphenyl)amino(2-furyl)methylphosphonate (***3Bc***)*

Y = 64% (0.95 g). Mp: 79–81°C. Lit [21]: 83–85°C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.39–7.38 (m, $^5H_{fur}$, 1H); 6.96 and 6.59 (AA′XX′ system, $^3J_{HH}$ = 8.4 and $^4J_{HH}$ = 1.8 and $^4J_{HH}$ = 1.2 Hz, p-C_6H_4, 2 × 2H); 7.38–7.37 (m, $^3H_{fur}$, 1H); 7.33–7.32 (m, $^4H_{fur}$, 1H); 4.88 (d, $^2J_{PH}$ = −24.0 Hz, CHP, 1H); 3.81 and 3.63 (2d, $^3J_{PH}$ = 10.8 Hz, $POCH_3$, 2 × 3H); 2.12 (s, CH_3, 3H). ^{31}P NMR ($CDCl_3$, 243 MHz): δ (ppm) 22.69.

*Dimethyl N-(p-Methylphenyl)amino(2-thienyl)methylphosphonate (***3Bd***)*

Y = 73% (1.14 g). Mp: 104–106°C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.22 (dd, $^3J_{HH}$ = 4.8 and $^4J_{HH}$ = 1.5 Hz, 1H, $^5H_{thioph}$); 7.15 (dd, $^3J_{HH}$ = 3.3 and $^4J_{HH}$ = 1.1 Hz, 1H, $^3H_{thioph}$); 6.98–6.95 (m, 3H, part of AA′XX′ system p-C_6H_4 and $^4H_{thioph}$); 6.59 (part of AA′XX′ system, $^3J_{HH}$ = 8.4 and $^4J_{HH}$ = 1.8 Hz and $^4J_{HH}$ = 1.8 Hz, 2 × 2H, p-C_6H_4); 5.03 (d, $^2J_{PH}$ = −24.0 Hz, 1H, CHP); 3.78 and 3.62 (2d, $^3J_{PH}$ = 10.8 Hz, 2 × 3H, $POCH_3$); 2.20 (s, CH_3, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 143.59 (d, $^2J_{PC}$ = 13.6 Hz, $C^2{}_{thioph}$-C-P); 139.74 (C_{phen}-NH); 129.78 (C_{phen}-H); 128.43 (C_{phen}-CH_3); 127.14 (d, $^5J_{PC}$ = 3.2 Hz, $C^5{}_{thioph}$); 126.23 (d, $^3J_{PC}$ = 7.2 Hz, $C^3{}_{thioph}$); 125.40 (d, $^4J_{PC}$ = 3.4 Hz, $C^4{}_{thioph}$); 114.25 (C_{phen}-H); 52.12 (d, $^1J_{PC}$ = 158.0 Hz, C–P); 54.13 (d, $^2J_{PC}$ = 7.4 Hz, P–O–C); 53.80 (d, $^2J_{PC}$ = 6.8 Hz, P–O–C); 20.38 (CH_3). ^{31}P NMR ($CDCl_3$, 243 MHz): δ (ppm) 23.25. Anal. calcd for $C_{14}H_{18}NO_3PS$: C, 54.01; H, 5.83; N, 4.50. Found: C, 53.92; H, 5.86; N, 4.66.

*Dimethyl N-(p-Methylphenyl)amino(2-phenylethenyl)methylphosphonate (***3Be***)*

Y = 69% (1.15 g). Yellow oil. ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 7.40–7.36 (m, PhH, 2H); 7.33–7.32 (m, PhH, 2H); 7.26–7.24 (m, PhH, 1H); 6.94 and 6.65 (AA′XX′ system, $^3J_{HH}$ = 8.4 and $^4J_{HH}$ = 1.8 Hz and $^4J_{HH}$ = 1.8 Hz, p-C_6H_4, 2 × 2H); 6.74 (ddd, $^4J_{HH}$ = 1.2 Hz, $^4J_{PH}$ = 4.8 Hz, $^3J_{HH}$ = 15.6 Hz, C$\underline{H}$ = CH, 1H); 6.28 (ddd, $^3J_{PH}$ = 5.4 Hz, $^3J_{HH}$ = 6.6 Hz, $^3J_{HH}$ = 15.6 Hz, CH = C$\underline{H}$, 1H); 4.77 (ddd, $^4J_{HH}$ = 1.2 Hz, $^3J_{HH}$ = 6.6 Hz, $^2J_{PH}$ = –25.8 Hz, CHP, 1H); 3.84 and 3.82 (2d, $^3J_{PH}$ = 10.8 Hz, $POCH_3$, 2 × 3H); 2.26 (s, CH_3, 3H). ^{31}P NMR ($CDCl_3$, 243 MHz): δ (ppm) 24.81 [22].

*Dimethyl N-(p-Methylphenyl)amino(cyclohexyl)-methylphosphonate (**3Bf**)*

Y = 71% (1.10 g). Mp: 118–120°C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ (ppm) 6.97 and 6.56 (AA′XX′ system, $^{3}J_{HH}$ = 8.4 Hz, 2 × 2H, p-C_6H_4); 3.71 and 3.67 (2d, $^{3}J_{PH}$ = 10.8 Hz, 2 × 3H, $POCH_3$); 3.61 (dd, $^{2}J_{PH}$ = –18.6 and $^{3}J_{HH}$ = 4.2 Hz, 1H, CHP); 2.23 (s, CH_3, 3H); 1.96–1.94 (m, cHex, 1H); 1.88–1.85 (m, cHex, 1H); 1.76–1.71 (m, cHex, 3H); 1.63–1.61 (m, cHex, 1H); 1.31–1.09 (m, cHex, 5H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ (ppm) 145.27 (d, $^{3}J_{PC}$ = 5.7 Hz, C_{phen}-NH); 129.83 (C_{phen}-H); 127.15 (C_{phen}-CH_3); 113.29 (C_{phen}-H); 56.39 (d, $^{1}J_{PC}$ = 150.5 Hz, C–P); 53.34 (d, $^{2}J_{PC}$ = 6.8 Hz, P–O–C); 52.33 (d, $^{2}J_{PC}$ = 7.2 Hz, P–O–C); 39.97 (d, $^{2}J_{PC}$ = 5.6 Hz, $C^{1}_{c\text{-}hex}$-P); 30.90 (d, $^{3}J_{PC}$ = 11.3 Hz, $C^{2}_{c\text{-}hex}$-P); 28.39 (d, $^{4}J_{PC}$ = 4.7 Hz, $C^{3}_{c\text{-}hex}$-P); 26.29 ($C_{c\text{-}hex}$); 26.17 ($C_{c\text{-}hex}$); 26.01 ($C_{c\text{-}hex}$); 20.33 (CH_3). ^{31}P NMR ($CDCl_3$, 243 MHz): δ (ppm) 27.91. Anal. calcd for $C_{16}H_{26}NO_3P$: C, 61.72; H, 8.42; N, 4.50. Found: C, 61.42; H, 8.30; N, 4.65.

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