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An Efficient Green Synthesis of a New Class of α-Aminophosphonates under Microwave Irradiation Conditions in the Presence of PS/*P*TSA

Chandra Sekhar Reddy Gangireddy,[1–3] Radha Rani Chinthaparthi,[2,3] Veeranarayana Reddy Mudumala,[2] Madhav Mamilla,[3] and Uma Ravi Sankar Arigala[2]

[1]*Department of Chemistry, Sri Venkateswara College of Engineering, Tirupati 517 507, India*

[2]*Department of Chemistry, Sri Venkateswara University, Tirupati 517 502, India*

[3]*Department of Chemistry, Sri Venkateswara Degree & PG College, Kadapa 16 003, India*

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ABSTRACT: *The present work focuses on the study of catalytic activity of polystyrene-supported p-toluenesulfonic acid (PS/PTSA) and the synthesis of α-aminophosphonates from the Kabachnik–Fields (KF) reaction under microwave irradiation in solvent-free conditions. Recently, the catalytic activity of PS/PTSA was tested with good yields. This procedure is the simplest, most straightforward, environment friendly method for the synthesis of α-aminophosphonates from simple to different substituted aldehyde substrates. Furthermore, this catalyst can be recovered and reused without loss of its catalytic activity.* © 2014 Wiley Periodicals, Inc. Heteroatom Chem. 00:1–10, 2014; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.21147

Correspondence to: Chandra Sekhar Reddy Gangireddy; e-mail: drcsreddyg@gmail.com.

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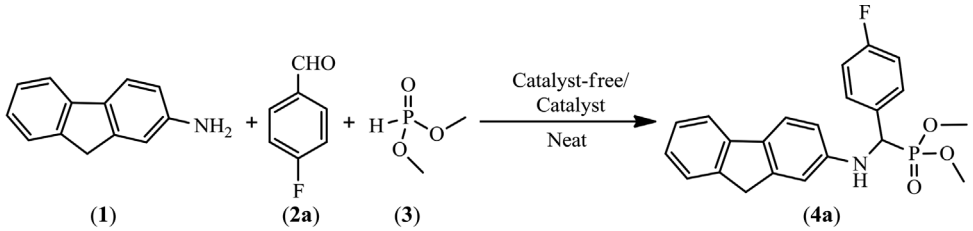
INTRODUCTION

The formation of the phosphorus–carbon bond has attracted much attention because phosphonates have wide applications in organic synthesis and bioorganic chemistry. α-Functionalized phosphonic acid esters serve as valuable intermediates for the preparation of synthetic intermediates [1–4] and antibacterial/viral/inflammatory and cancer drugs [5–7]. The synthesis of α-aminophosphonates using Brönsted and Lewis acids, heteropoly acids, heterogeneous catalysts, microwave irradiation (MWI), ultrasound irradiation, catalyst free, ionic liquid, and nanocatalysts has been reported [8–17] by using the Kabachnik–Fields (KF) reaction [18–20].

Several green chemical synthetic approaches using the KF reaction are reported in solvent- and catalyst-free conditions [21–24], solvent-free under MWI using [25–32] heterocyclic amines, oxo-component, and >P(O)H species [33–35]. All of these reports are based on few model reactions [22, 36, 37]. Later phospha-Mannich condensation [36–38] was further improvised in microwave-heated solvent- and catalyst-free conditions. Recently, all the microwave-assisted KF reactions in a simple, straightforward, and most environmentally friendly way were revised elaborately under solvent- and



Reaction conditions: a) Conventional method, 70-120 °C, 55-140 min; b) μw method, 70-120 °C, 5-10 min

SCHEME 1 Model synthetic reaction of dimethyl (((9H-fluoren-2-yl)amino)(4-fluorophenyl)methyl)phosphonate (**4a**).

catalyst-free reaction conditions [39, 40]. Our study group has already reported a simple, convenient, mild and fast procedure for the KF reaction [23] in solvent-free MWI conditions using alumina and montmorillonite K-10 as a solid-supported catalyst. We achieved good results in all these reactions.

Although significant advances have been made in the reported syntheses, still there are several limitations such as the use of expensive and toxic solvents and catalysts, a longer reaction time, high temperature, and low yields. Therefore, a better synthetic procedure for their synthesis is warranted.

A solid-supported catalyst polystyrene *p*-toluenesulfonic acid (PS/*P*TSA) complex with a number of advantages such as improving the availability of active sites, stability, hygroscopic properties, handling, reusability, and good product yields [21, 41–44] was selected and used as a catalyst in this reaction. This catalyst despite of its great advantages has not been exploited fully in organic synthesis [45–47].

Eventually, a better one-pot synthetic procedure for α-aminophosphonates in terms of operational simplicity, economic viability, and greater selectivity by the KF reaction of 2-aminofluorene, an aldehyde, and a dimethyl phosphite in the presence of a catalytic amount (5 mol%) of PS/*P*TSA under solvent-free MWI conditions is accomplished.

RESULTS AND DISCUSSION

The reaction conditions are optimized for the model reaction between 2-aminofluorene (**1**), 4-fluorobenzaldehyde (**2a**), and dimethyl phosphite (**3**) to afford α-aminophosphonate (**4a**) under solvent-free conditions (Scheme 1), employing different catalysts under both conventional heating and MWI conditions (Table 1).

TABLE 1 Optimization of Required Catalyst and Reaction Conditions[a] of **4a**

		Conventional Heating			*MWI*	
Entry	*Catalyst (mol%)*	*Temperature (°C)*	*Time (min)*	*Yield[b] (%)*	*Temperature (°C)*	*Yield[b] (%)*
1	Catalyst free	r.t.	24 h	12	70	19
2	Catalyst free	100	180	22	150	34
3	Catalyst free	120	180	26	180	40
4	InF_3 (10)	90	120	25	90	40
5	CAN-SiO_2 (10)	90	120	30	90	45
6	$ZnCl_2$-SiO_2 (10)	90	130	25	90	35
7	$MnCl_2 \cdot 4H_2O$ (10)	90	110	55	90	60
8	$Yb(OAc)_3 \cdot H_2O$ (10)	90	140	40	90	40
9	CuBr (10)	90	120	29	90	35
10	$NbCl_5$ (10)	90	100	50	90	60
11	$FePO_4$ (10)	90	100	55	90	65
12	Al_2O_3 (10)	90	120	50	90	60
13	*P*TSA (10)	90	100	55	90	70
14	PS/$GaCl_3$ (10)	90	80	75	90	80
15	PS/$AlCl_3$ (10)	90	75	80	90	82
16	PS/*P*TSA (10)	90	55	82	90	97
17	PS/*P*TSA (10)	70	55	76	70	96
18[c]	PS/*P*TSA (5)	90	55	81	70	96,95,93, 90
19	PS/*P*TSA (3)	90	55	75	90	85

[a]Reaction conditions: 2-Aminofluorene (**1**), 4-methylbenzaldehyde (**2a**), and dimethyl phosphite (**3**) at equimolar ratio, and 20 min (for entries 1 and 3), 10 min (for entries 4–16) and 5 min (for entries 17–19) reaction time in solvent-free and MWI conditions (at 210 W).
[b]Isolated yield.
[c]Catalyst recovery.

TABLE 2 Optimization of MW Power[a] for the Synthesis of **4a**

Entry	*MW Power (W)*	*Temperature (°C)*	*Time (min)*	*Yield[b] (%)*
1	140	90	30	20
2	245	140	20	38
3	140	90	10	88
4	210	120	10	97
5	210	70	5	96
6	245	140	5	90
7	280	170	5	84
8	350	210	5	81
9	490	245	5	64
10	700	340	5	10

[a]Reaction conditions: An equimolar ratios of 2-aminofluorene (**1**), 4-methylbenzaldehyde (**2a**), and dimethyl phosphite (**3**) in catalyst-free conditions (entries 1 and 2) and 5 mol% of PS/*P*TSA catalyst (entries 3–10).
[b]Isolated yield.

Initially, the model reaction was carried without any catalyst, resulting in poor yields (Table 1, entries 1–3). This reaction, when conducted using InF_3, CAN-SiO_2, and $ZnCl_2$-SiO_2, produced very low yields (Table 1, entries 4–6). Although catalysts such as $MnCl_2 \cdot 4H_2O$, $Yb(OAc)_3$, CuBr, $NbCl_5$, $FePO_4$, Al_2O_3, and *P*TSA promoted the reaction to a considerable extent, the yield of compounds was not satisfactory (Table 1, entries 7–13). But polymer-supported Lewis acid catalysts such as PS/$GaCl_3$, PS/$AlCl_3$, and PS/*P*TSA (Table 1, entries 14–16) worked efficiently. Among them, PS/*P*TSA showed excellent catalytic activity under MWI conditions even at lower temperature (Table 1, entries 17). All these catalytic reactions were carried out with 10 mol% of the catalyst. To assert the minimum optimum concentration of the PS/*P*TSA catalyst, the same reaction was carried out with 5 and 3 mol% concentrations. It was found that the yield of the products was 81% under conventional conditions and 96% under MWI with 5 mol% of the PS/*P*TSA catalyst in 55 and 5 min, respectively (Table 1, entry 18). Therefore, 5 mol% of PS/*P*TSA was found necessary and sufficient for the total completion of the model reaction in both conditions. The reaction remains incomplete with 3 mol% of the catalyst (Table 1, entry 19).

To check the reusability of the catalyst, the same reaction was run with fresh and isolated PS/*P*TSA for three consecutive cycles in the preparation of α-aminophosphonate (**4a**) and in all the three consecutive reactions the yield of α-aminophosphonates was 95%, 93%, and 90% (Table 1, entry 18). The PS/*P*TSA was recovered from the reaction mixture by dissolving it in hot EtOH and filtration. These data demonstrate high stability and reusability of the catalyst under these reaction conditions.

The model reaction was also studied at various MW conditions to choose the best irradiation condition with and without 5 mol% of the PS/*P*TSA catalyst. Even in the absence of the catalyst, a significant yield of the product was recorded (Table 2, entries 1 and 2); it is not a sufficient reaction condition because of the requirement of higher reaction temperature for a prolonged period. While using the PS/PTSA catalyst, excellent product yield was possible in a short reaction time at lower reaction temperature (**4a**; Table 2, entry 5). It was found that at 210 W MWI 70°C for 5 min with 5 mol% of catalyst is ideal to accomplish maximum conversion of reactants to products. Increasing the MWI power decreases the product yield due to overheating and formation of char residue (Table 2, entry 10).

To ascertain the effect of solvent and temperature in catalyst-free and 5 mol% of PS/*P*TSA catalyst conditions, the model reaction was run under both

TABLE 3 Optimization of Solvent and Temperature[a] for the Synthesis **4a**

		Conventional Heating			*MWI*		
			Yield[b] (%)			*Yield[b] (%)*	
Entry	*Solvent*	*Temperature (°C)*	*Catalyst-Free*	*PS/PTSA*	*Temperature (°C)*	*Catalyst-Free*	*PS/PTSA*
1	Toluene	110	38.4	64.6	110	61.9	90.3
2	Chlorobenzene	130	37.2	65.7	130	62.8	91.1
3	Ethanol	75	42.1	64.4	75	65.6	78.5
4	Acetonitrile	80	43.6	66.8	80	66.2	82.6
5	THF	65	42.8	67.4	65	65.7	85.4
6	CCl_4	75	41.4	65.2	75	60.7	73.4
7	Solvent-free 1	90	18.1	66.2	70	60.3	96.4
8	Solvent-free 2	150	25.3	69.5	110	63.8	97.6

[a]Reaction conditions: 2-Aminofluorene (**1**), 4-methylbenzaldehyde (**2a**), and dimethyl phosphite (**3**) in a 1:1:1 molar ratio using 5 mol% PS/*P*TSA catalyst. All the reactions are carried out by 55 and 5 min, respectively, in conventional heating and MWI (at 210 W) conditions.
[b]Isolated yield.

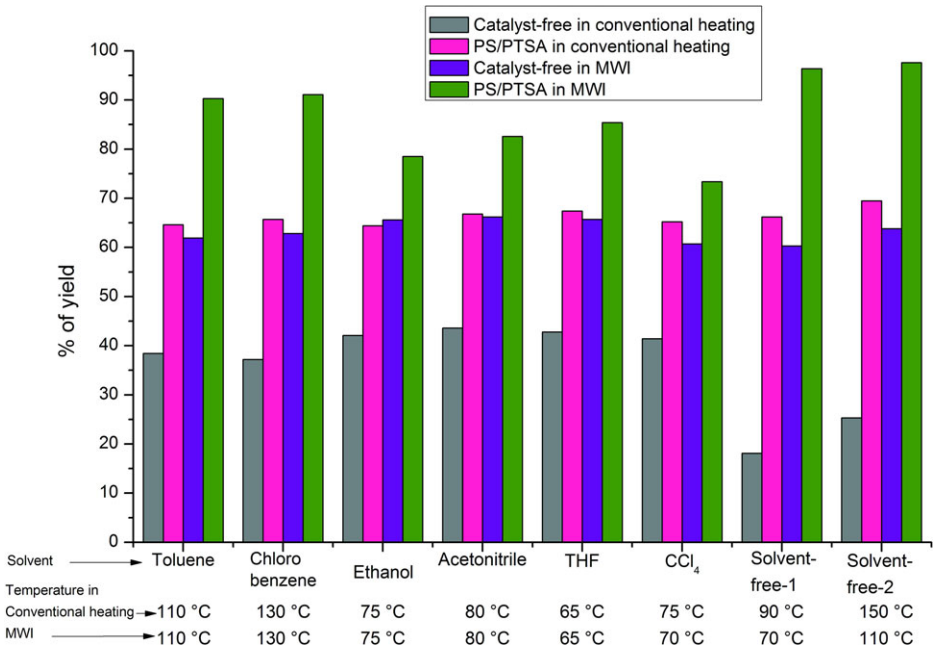
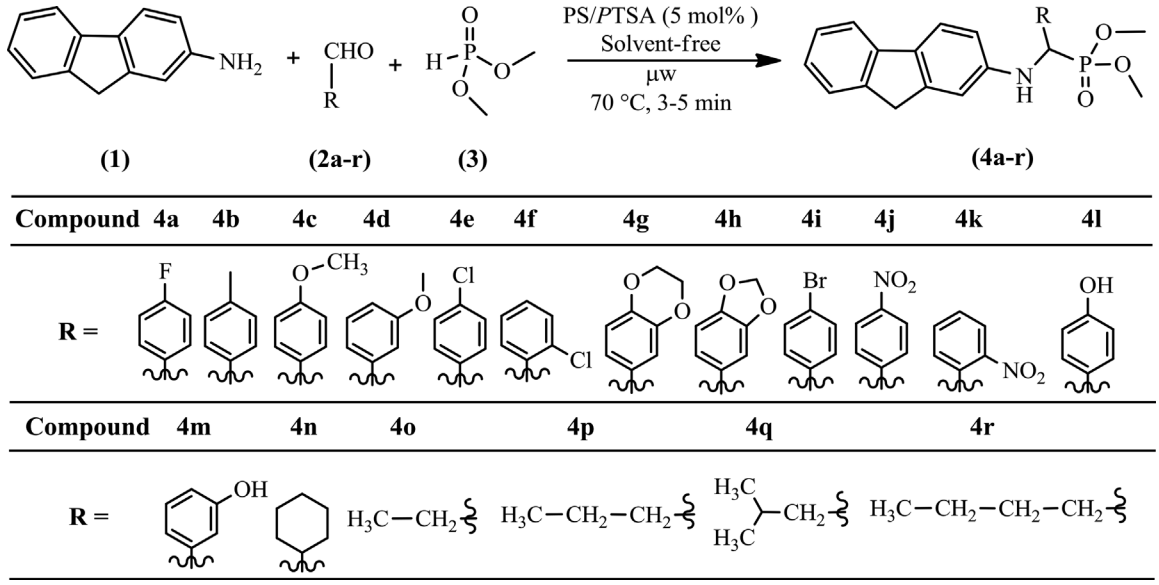


FIGURE 1 Optimization of solvent and temperature for the synthesis of **4a–r** in both conventional heating and MWI.



SCHEME 2 PS/*P*TSA-MWI synthesis of **4a–r**.

conventional and MW (210 W) heating in different solvents for 55 and 5 min, respectively. Irrespective of the nature of the solvent, the yield of the products was low (Table 3, entries 1–6). But under solvent-free conditions, better yield of product resulted (Table 3, entries 7 and 8). The poor yields in the solvent medium may be attributed to solvation of the substrates in the reaction medium. Therefore, it is established that MWI at 70°C without the solvent is the best condition for this reaction (Fig. 1).

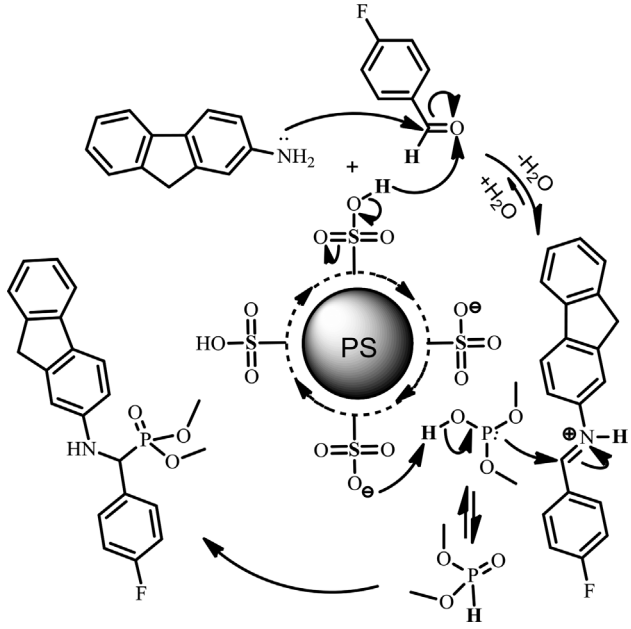
Under the optimized experimental reaction conditions, 5 mol% of PS/*P*TSA, MW heating at 210 W, 70°C, 5–7 min in solvent-free conditions, a number of aldehydes (**2b–r**) successfully reacted with 2-aminofluorene (**1**) and dimethyl phosphite (**3**) and produced corresponding α-aminophosphonates (**4b–r**; Scheme 2) in excellent yields (Table 4).

Interestingly, aromatic aldehydes with electron-withdrawing substituents gave products with comparable yields when compared to those having

TABLE 4 MWI Synthesis of **4a–r** with PS/*P*TSA as a Catalyst[a]

Compound	*Time (min)*	*Yield[b] (%)*	*Reference*
4a	5	95	
4b	5	98	
4c	5	98	
4d	5	95	
4e	6	94	
4f	6	92	
4g	5	95	
4h	5	93	
4i	5	93	
4j	4	96	[6]
4k	6	94	
4l	5	95	
4m	6	92	
4n	6	88	
4o	7	88	[6]
4p	7	86	
4q	6	86	
4r	7	84	

[a]Reaction conditions: 2-Aminofluorene (**1**), various aldehydes (**2a–r**), and dimethyl phosphite (**3**) using 5 mol% a PS/*P*TSA catalyst at 210 W in neat conditions.
[b]Isolated yields.



SCHEME 3 Mechanistic pathway for one-pot KF synthesis of **4a–r** with PS/*P*TSA as a catalyst.

electron-donating groups. The negative inductive effect resulted in a stronger electrophilic center at the carbonyl carbon, which facilitates the addition of amines to the carbonyl carbon to form imines that subsequently unites with the nucleophilic phosphonate phosphorus (Scheme 3). The reaction with aliphatic aldehydes (**2n–r**; Table 4, entries 14–18) also occurred smoothly, but the yield of products, though good, is lower than those with aromatic aldehydes (**2a–m**; Table 4, entries 1–13). Various other aldehydes with different functional groups were also found to react under these conditions. In general, the reaction with different substituents in the aldehydes was almost quantitative, and no side products are formed.

CONCLUSIONS

We have successfully developed a simple, green, and efficient MW-assisted one-pot multicomponent KF synthesis of α-aminophosphonates from easily available starting materials using PS/*P*TSA as a solid-supported catalyst under solvent-free conditions. Even though catalyst-free KF reactions are reported, here we report the use of solid-supported PS/*P*TSA as an effective catalyst. The reactivity of 2-aminofluorene, dimethyl phosphite, and various aldehydes not only accelerated under MWI conditions in the presence of PS/*P*TSA but also afforded excellent yields. Therefore, this method serves as an attractive one for industries for the synthesis of various functionalized α-aminophosphonates.

EXPERIMENTAL

Materials and Methods

All the chemicals procured from Sigma–Aldrich (Hyderabad, India), Merck (Mumbai, India), and Lancaster Chemical (Mumbai, India) were used as such without further purification. All solvents used for spectroscopic and other physical studies were of reagent grade and were further purified by employing the reported methods. Melting points were determined using a calibrated thermometer by a Guna Digital melting point apparatus. IR spectra were recorded on a Sumhazud IR Prestige-21, Fourier transform infrared spectrometer with a scanning range of 400–4000 cm^{-1} for 32 scans at a spectral resolution of 4 cm^{-1} using KBr optical disks. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in $CDCl_3$ on a Varian 400 MHz NMR spectrometer operating at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR, and 161.89 MHz for ^{31}P NMR at Pusan National University, Pusan, Republic of Korea, and referenced to TMS (^{1}H and ^{13}C) and 85% H_3PO_4 (^{31}P). Mass spectra were recorded on a Jeol JMS-700 mass spectrometer at Pukyong National University, Busan, Republic of Korea. Elemental analyses were performed on a Thermo Finnigan instrument at the University of Hyderabad, Hyderabad, India.

*General Method for the Synthesis of Dimethyl (((9H-fluoren-2-yl)amino)(4-fluorophenyl) methyl)phosphonate (**4a**) by MWI*

2-Aminofluorene (**1**, 0.90 g, 0.005 mol), 4-fluorobenzaldehyde (**2a**, 0.62 g, 0.005 mol), dimethyl phosphite (**3**, 0.46 mL, 0.005 mol), and various catalysts in 3, 5, and 10 mol% were mixed thoroughly in a two-necked 25-mL round-bottomed (RB) flask, which was fitted with an air condenser in one neck and a thermo probe at the other neck and was exposed to 140–700 W MWI using a synthetic microwave oven CATA-4R-Scientific MW oven (Catalyst Systems) at 70–340°C at ambient pressure. The reaction mixture was stirred continually while irradiating with MW radiation to maintain uniform temperature. By monitoring with TLC, the reaction was stopped after 5–7 min. Then chloroform (3 × 5 mL) was added to the RB flask, and PS/*P*TSA was separated by filtration to recover the catalyst. The crude reaction products obtained by evaporation of filtrate were purified by column chromatography on 60–120 mesh silica gel using ethyl acetate:hexane (1:3) as an eluent, and the solvent was evaporated in a rotary evaporator. The residue was recrystallized from ethyl acetate to afford pure **4a** (Table 1).

All the other compounds (**4b–r**) were prepared by following the procedure with 5 mol% PS/*P*TSA at 70°C of 210 W of MWI at ambient pressure (Scheme 2). The reaction was successfully completed in 3–5 min and afforded **4b–r** in high yields (Table 2). The structures of all the newly synthesized compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR, ^{31}P NMR, mass spectral, and elemental analysis.

Conventional Heating Method for the Synthesis of **4a**. On the other hand, in conventional heating method, all the above reactants were heated in an oil bath at 65–130°C for 55–140 min, and the workup and purification of products were carried out in a similar way by following the MWI procedure.

Physical and Spectral Characteristics of **4a–*r***.

*Dimethyl (((9H-fluoren-2-yl)amino)(4-fluorophenyl) methyl)phosphonate (**4a**)*. Brown solid, mp: 155–157°C. ^{31}P NMR (161.89, MHz, $CDCl_3$) δ: 21.07; ^{13}C NMR (100.56 MHz, $CDCl_3$) δ: 114.7 (C-1), 150.4 (C-2), 108.3 (C-3), 121.4 (C-4), 122.3 (C-5), 127.5 (C-6), 128.4 (C-7), 126.8 (C-8), 37.5 (C-9), 145.6 (C-10), 129.2 (C-11), 138.1 (C-12), 140.4 (C-13), 56.4 (C-15), 131.9 (C-16), 130.4 (C-17 and C-21), 116.4 (C-18 and C-20), 163.2 (C-19), 52.5 (P—OCH_3), 53.4 (P—OCH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.55 (3H, d, $^{3}J_{H\text{-}P}$ = 10.4 Hz, P—OCH_3), 3.77 (3H, d, $^{3}J_{H\text{-}P}$ = 10.4 Hz, P—OCH_3), 3.73 (2H, s, Ar—CH_2—Ar), 6.57–6.59 (1H, dd, $^{2}J_{H\text{-}P}$ = 8.4 Hz, P-CH and $^{3}J_{H\text{-}H}$ = 2.0 Hz, NH—CH), 6.74 (1H, m, NH), 7.13–7.58 (11H, m, Ar—H). IR (KBr) (ν_{max} cm^{-1}): 3305 (N—H), 2956 and 2867 (C—$H_{aromatic}$), 1259 (P=O), 763 (P—$C_{aliphatic}$). EI-MS *m/z* (%): 397 (12) $M^{+\bullet}$. Anal. Calcd for $C_{22}H_{21}FNO_3P$: C, 66.49; H, 5.33; N, 3.52; Found: C, 66.37; H, 5.26; N, 3.45.

*Dimethyl (((9H-fluoren-2-yl)amino)(p-tolyl)methyl) phosphonate (**4b**)*. White solid, mp: 178–120°C. ^{31}P NMR (161.89, MHz, $CDCl_3$) δ: 21.27; ^{13}C NMR (100.56 MHz, $CDCl_3$) δ: 114.3 (C-1), 150.7 (C-2), 108.6 (C-3), 121.5 (C-4), 122.5 (C-5), 127.7 (C-6), 128.2 (C-7), 126.7 (C-8), 37.3 (C-9), 145.7 (C-10), 129.6 (C-11), 138.4 (C-12), 140.2 (C-13), 56.3 (C-15), 131.4 (C-16), 128.2 (C-17 and C-21), 126.6 (C-18 and C-20), 138.6 (C-19), 22.4 (Ar—CH_3), 52.2 (P—OCH_3), 53.3 (P—OCH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.15 (3H, s, Ar—$\underline{CH_3}$), 3.51 (3H, d, $^{3}J_{H\text{-}P}$ = 10.4 Hz, P—$O\underline{CH_3}$), 3.73 (3H, d, $^{3}J_{H\text{-}P}$ = 10.4 Hz, P—$O\underline{CH_3}$), 3.70 (2H, s, Ar—$\underline{CH_2}$—Ar), 6.53–6.56 (1H, dd, $^{2}J_{H\text{-}P}$ = 8.4 Hz, P—$\underline{CH}$ and $^{3}J_{H\text{-}H}$ = 2.0 Hz, NH—$\underline{CH}$), 6.74 (1H, m, $\underline{NH}$), 7.12–7.56 (11H, m, $\underline{Ar}$—$\underline{H}$). IR (KBr) (ν_{max} cm^{-1}): 3311 (N—H), 2960 and 2859 (C—$H_{aromatic}$), 1229 (P=O), 763 (P—$C_{aliphatic}$). EI-MS *m/z* (%): 393 (10) $M^{+\bullet}$. Anal. Calcd. for $C_{23}H_{24}NO_3P$: C, 70.22; H, 6.15; N, 3.56; Found: C, 70.15; H, 6.08; N, 3.49.

*Dimethyl (((9H-fluoren-2-yl)amino)(4-methoxyphenyl) methyl)phosphonate (**4c**)*. Brown solid, mp: 187–189°C. ^{31}P NMR (161.89, MHz, $CDCl_3$) δ: 21.37; ^{13}C NMR (100.56 MHz, $CDCl_3$) δ: 115.1 (C-1), 151.3 (C-2), 108.2 (C-3), 122.1 (C-4), 121.9 (C-5), 127.8 (C-6), 128.3 (C-7), 126.5 (C-8), 37.7 (C-9), 145.2 (C-10), 129.1 (C-11), 138.7 (C-12), 140.8 (C-13), 56.5 (C-15), 130.8 (C-16), 127.1 (C-17 and C-21), 114.1 (C-18 and C-20), 158.3 (C-19), 55.7 (OCH_3), 52.6 (P—OCH_3), 53.7 (P—OCH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.79 (3H, s, Ar—$O\underline{CH_3}$), 3.57 (3H, d, $^{3}J_{H\text{-}P}$ = 10.4 Hz, P—$O\underline{CH_3}$), 3.87 (3H, d, $^{3}J_{H\text{-}P}$ = 10.4 Hz, P—$O\underline{CH_3}$), 3.73 (2H, s, Ar—$\underline{CH_2}$—Ar), 6.57–6.61 (1H, dd, $^{2}J_{H\text{-}P}$ = 8.4 Hz, P—$\underline{CH}$ and $^{3}J_{H\text{-}H}$ = 2.0 Hz, NH—$\underline{CH}$), 6.61 (1H, m, $\underline{NH}$), 7.25–7.69 (11H, m, $\underline{Ar}$—$\underline{H}$). IR (KBr) (ν_{max} cm^{-1}): 3314 (N—H), 2967 and 2866 (C—$H_{aromatic}$), 1258 (P=O), 756 (P—$C_{aliphatic}$). EI-MS *m/z* (%): 409 (16) $M^{+\bullet}$. Anal. Calcd. for $C_{23}H_{24}NO_4P$: C, 67.47; H, 5.91; N, 3.42; Found: C, 67.35; H, 5.85; N, 3.46.

*Dimethyl (((9H-fluoren-2-yl)amino)(3-methoxyphenyl) methyl)phosphonate (**4d**)*. Brown solid, mp: 192–194°C. ^{31}P NMR (161.89, MHz, $CDCl_3$) δ:

21.32; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.82 (3H, s, Ar—O$\underline{CH_3}$), 3.59 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—O$\underline{CH_3}$), 3.84 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—O$\underline{CH_3}$), 3.75 (2H, s, Ar—$\underline{CH_2}$—Ar), 6.55–6.60 (1H, dd, $^2J_{H\text{-}P}$ = 8.4 Hz, P-$\underline{CH}$ and $^3J_{H\text{-}H}$ = 2.0 Hz, NH—$\underline{CH}$), 6.62 (1H, m, $\underline{NH}$), 7.21–7.65 (11H, m, $\underline{Ar}$—$\underline{H}$). IR (KBr) (ν_{max} cm^{-1}): 3314 (N—H), 2967 and 2867 (C—$H_{aromatic}$), 1258 (P=O), 757 (P—$C_{aliphatic}$). Anal. Calcd. for $C_{23}H_{24}NO_4P$: C, 67.47; H, 5.91; N, 3.42; Found: C, 67.34; H, 5.82; N, 3.47.

*Dimethyl (((9H-fluoren-2-yl)amino)(4-chlorophenyl) methyl)phosphonate (***4e***)*. Pale yellow solid, mp: 170–172°C. ^{31}P NMR (161.89, MHz, $CDCl_3$) δ: 20.51; ^{13}C NMR (100.56 MHz, $CDCl_3$) δ: 114.2 (C-1), 150.5 (C-2), 108.4 (C-3), 121.1 (C-4), 122.7 (C-5), 127.5 (C-6), 128.6 (C-7), 126.9 (C-8), 37.3 (C-9), 145.5 (C-10), 129.3 (C-11), 138.5 (C-12), 140.7 (C-13), 56.5 (C-15), 131.7 (C-16), 129.7 (C-17 and C-21), 115.6 (C-18 and C-20), 161.3 (C-19), 52.4 (P—OCH_3), 53.1 (P—OCH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.53 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—O$\underline{CH_3}$), 3.77 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—O$\underline{CH_3}$), 3.65 (2H, s, Ar—$\underline{CH_2}$—Ar), 6.55–6.56 (1H, dd, $^2J_{H\text{-}P}$ = 8.4 Hz, P-$\underline{CH}$ and $^3J_{H\text{-}H}$ = 2.0 Hz, NH—$\underline{CH}$), 6.70 (1H, m, $\underline{NH}$), 7.12–7.55 (11H, m, $\underline{Ar}$—$\underline{H}$). IR (KBr) (ν_{max} cm^{-1}): 3313 (N—H), 2963 and 2864 (C—$H_{aromatic}$), 1236 (P=O), 752 (P—$C_{aliphatic}$). EI-MS *m/z* (%): 413 (10) $M^{+\bullet}$. Anal. Calcd. for $C_{22}H_{21}ClNO_3P$: C, 63.85; H, 5.11; N, 3.38; Found: C, 63.78; H, 5.05; N, 3.26.

*Dimethyl (((9H-fluoren-2-yl)amino)(2-chlorophenyl) methyl)phosphonate (***4f***)*. Pale yellow solid, mp: 168–170°C. ^{31}P NMR (161.89, MHz, $CDCl_3$) δ: 20.72; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.57 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—O$\underline{CH_3}$), 3.78 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—O$\underline{CH_3}$), 3.67 (2H, s, Ar—$\underline{CH_2}$—Ar), 6.55–6.56 (1H, dd, $^2J_{H\text{-}P}$ = 8.4 Hz, P—$\underline{CH}$ and $^3J_{H\text{-}H}$ = 2.0 Hz, NH—$\underline{CH}$), 6.70 (1H, m, $\underline{NH}$), 7.12–7.55 (11H, m, $\underline{Ar}$—$\underline{H}$). IR (KBr) (ν_{max} cm^{-1}): 3314 (N—H), 2961 and 2865 (C—$H_{aromatic}$), 1231 (P=O), 752 (P—$C_{aliphatic}$). Anal. Calcd. for $C_{22}H_{21}ClNO_3P$: C, 63.85; H, 5.11; N, 3.38; Found: C, 63.79; H, 5.08; N, 3.25.

*Dimethyl (((9H-fluoren-2-yl)amino)(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)methyl) phosphonate (***4g***)*. Brown solid, mp: 196–198°C. ^{31}P NMR (161.7, MHz, $CDCl_3$) δ: 20.36; ^{13}C NMR (100.56 MHz, $CDCl_3$) δ: 114.1 (C-1), 150.6 (C-2), 109.2 (C-3), 121.5 (C-4), 122.2 (C-5), 128.2 (C-6), 129.4 (C-7), 126.3 (C-8), 36.8 (C-9), 145.1 (C-10), 129.7 (C-11), 138.8 (C-12), 141.5 (C-13), 56.2 (C-15), 129.5 (C-16), 116.4 (C-17), 112.8 (C-18), 65.8 (C-20 and C-21), 110.3 (C-23), 151.2 (C-24), 150.8 (C-25), 52.9 (P—OCH_3), 53.6 (P—OCH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.52 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—O$\underline{CH_3}$), 3.64 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—O$\underline{CH_3}$), 4.32 (4H, s, O($\underline{CH_2}$)$_2$O), 6.48–6.13 (1H, dd, $^2J_{H\text{-}P}$ = 8.4 Hz, P—$\underline{CH}$ and $^3J_{H\text{-}H}$ = 2.0 Hz, NH—$\underline{CH}$), 6.63 (1H, m, $\underline{NH}$), 7.16–7.52 (10H, m, $\underline{Ar}$—$\underline{H}$). IR (KBr) (ν_{max} cm^{-1}): 3318 (N—H), 2964 and 2863 (C—$H_{aromatic}$), 1230 (P=O), 757 (P—$C_{aliphatic}$). EI-MS *m/z* (%): 437 (8) $M^{+\bullet}$. Anal. Calcd. for $C_{24}H_{24}NO_5P$: C, 65.90; H, 5.53; N, 3.20; Found: C, 65.85; H, 5.48; N, 3.15.

*Dimethyl (((9H-fluoren-2-yl)amino) (benzo[d]-[1,3]dioxol-5-yl)methyl)phosphonate (***4h***)*. Brown solid, mp: 196–198°C. ^{31}P NMR (161.7, MHz, $CDCl_3$) δ: 20.65; ^{13}C NMR (100.56 MHz, $CDCl_3$) δ: 113.7 (C-1), 150.7 (C-2), 109.8 (C-3), 121.1 (C-4), 122.6 (C-5), 127.7 (C-6), 129.1 (C-7), 126.7 (C-8), 36.5 (C-9), 145.3 (C-10), 129.4 (C-11), 138.2 (C-12), 141.1 (C-13), 57.4 (C-15), 128.7 (C-16), 119.6 (C-17), 111.7 (C-18), 96.9 (C-20), 111.7 (C-22), 149.2 (C-23), 145.7 (C-24), 52.5 (P—OCH_3), 53.7 (P—OCH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.50 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—O$\underline{CH_3}$), 3.62 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—O$\underline{CH_3}$), 5.83 (4H, s, O$\underline{CH_2}$O), 6.52–6.18 (1H, dd, $^2J_{H\text{-}P}$ = 8.4 Hz, P—$\underline{CH}$ and $^3J_{H\text{-}H}$ = 2.0 Hz, NH—$\underline{CH}$), 6.41 (1H, m, $\underline{NH}$), 7.18–7.54 (10H, m, $\underline{Ar}$—$\underline{H}$). IR (KBr) (ν_{max} cm^{-1}): 3320 (N—H), 2969 and 2865 (C—$H_{aromatic}$), 1240 (P=O), 1536 and 1347 (N—O), 757 (P—$C_{aliphatic}$). Anal. Calcd. for $C_{23}H_{22}NO_5P$: C, 65.24; H, 5.24; N, 3.31; Found: C, 65.19; H, 5.18; N, 3.17.

*Dimethyl (((9H-fluoren-2-yl)amino)(4-bromophenyl) methyl)phosphonate (***4i***)*. Brown solid, mp: 159–161°C. ^{31}P NMR (161.7, MHz, $CDCl_3$) δ: 20.84; ^{13}C NMR (100.56 MHz, $CDCl_3$) δ: 114.4 (C-1), 150.5 (C-2), 108.2 (C-3), 121.7 (C-4), 122.6 (C-5), 127.4 (C-6), 128.5 (C-7), 126.5 (C-8), 37.2 (C-9), 145.4 (C-10), 129.5 (C-11), 138.1 (C-12), 140.4 (C-13), 56.7 (C-15), 135.8 (C-16), 130.8 (C-17 and C-21), 135.1 (C-18 and C-20), 127.2 (C-19), 53.3 (P—OCH_3), 53.5 (P—OCH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.51 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—O$\underline{CH_3}$), 3.74 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—O$\underline{CH_3}$), 3.66 (2H, s, Ar—$\underline{CH_2}$-Ar), 6.54–6.59 (1H, dd, $^2J_{H\text{-}P}$ = 8.4 Hz, P—$\underline{CH}$ and $^3J_{H\text{-}H}$ = 2.0 Hz, NH—$\underline{CH}$), 6.67 (1H, m, $\underline{NH}$), 7.01–7.45 (11H, m, $\underline{Ar}$—$\underline{H}$). IR (KBr) (ν_{max} cm^{-1}): 3315 (N—H), 2958 and 2860 (C—$H_{aromatic}$), 1238 (P=O), 756 (P—$C_{aliphatic}$). Anal. Calcd. for $C_{22}H_{21}BrNO_3P$: C, 57.66; H, 4.62; N, 3.06; Found: C, 57.59; H, 4.58; N, 3.01.

*Dimethyl (((9H-fluoren-2-yl)amino)(4-nitrophenyl) methyl)phosphonate (***4j***)* [6]. Yellow solid, mp: 186–188°C. ^{31}P NMR (161.7, MHz, $CDCl_3$) δ: 21.26;

^{13}C NMR (100.56 MHz, $CDCl_3$) δ: 114.5 (C-1), 150.6 (C-2), 108.1 (C-3), 121.8 (C-4), 122.4 (C-5), 127.6 (C-6), 128.7 (C-7), 126.3 (C-8), 37.6 (C-9), 145.2 (C-10), 129.6 (C-11), 138.4 (C-12), 140.6 (C-13), 56.9 (C-15), 138.8 (C-16), 128.8 (C-17 and C-21), 126.2 (C-18 and C-20), 151.2 (C-19), 52.3 (P—OCH_3), 53.2 (P—OCH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.56 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—OCH_3), 3.76 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—OCH_3), 3.76 (2H, s, Ar—CH_2—Ar), 6.66–6.71 (1H, dd, $^2J_{H\text{-}P}$ = 8.4 Hz, P—CH and $^3J_{H\text{-}H}$ = 2.0 Hz, NH—CH), 6.69 (1H, m, NH), 7.23–7.75 (11H, m, Ar—H). IR (KBr) (ν_{max} cm^{-1}): 3331 (N—H), 2965 and 2862 (C—$H_{aromatic}$), 1261 (P=O), 753 (P—$C_{aliphatic}$). Anal. Calcd. for $C_{22}H_{21}N_2O_5P$: C, 62.26; H, 4.99; N, 6.60; Found: C, 62.20; H, 4.93; N, 6.56.

*Dimethyl (((9H-fluoren-2-yl)amino)(2-nitrophenyl) methyl)phosphonate (***4k***)*. Yellow solid, mp: 182–184°C. ^{31}P NMR (161.7, MHz, $CDCl_3$) δ: 21.67; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.55 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—OCH_3), 3.78 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—OCH_3), 3.71 (2H, s, Ar—CH_2—Ar), 6.65–6.70 (1H, dd, $^2J_{H\text{-}P}$ = 8.4 Hz, P—CH and $^3J_{H\text{-}H}$ = 2.0 Hz, NH—CH), 6.53 (1H, m, NH), 7.30–7.78 (11H, m, Ar—H). IR (KBr) (ν_{max} cm^{-1}): 3329 (N—H), 2965 and 2861 (C—$H_{aromatic}$), 1262 (P=O), 755 (P—$C_{aliphatic}$). EI-MS *m/z* (%): 424 (5) $M^{+\bullet}$. Anal. Calcd. for $C_{22}H_{21}N_2O_5P$: C, 62.26; H, 4.99; N, 6.60; Found: C, 62.21; H, 4.93; N, 6.52.

*Dimethyl (((9H-fluoren-2-yl)amino)(4-hydroxyphenyl) methyl)phosphonate (***4l***)*. Brown solid, mp: 192–194°C. ^{31}P NMR (161.7, MHz, $CDCl_3$) δ: 22.01; ^{13}C NMR (100.56 MHz, $CDCl_3$) δ: 114.8 (C-1), 150.9 (C-2), 108.6 (C-3), 121.5 (C-4), 122.4 (C-5), 127.9 (C-6), 128.8 (C-7), 126.8 (C-8), 37.6 (C-9), 145.2 (C-10), 129.8 (C-11), 138.8 (C-12), 140.3 (C-13), 56.9 (C-15), 130.9 (C-16), 129.9 (C-17 and C-21), 115.2 (C-18 and C-20), 161.7 (C-19), 52.8 (P—OCH_3), 53.5 (P—OCH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.58 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—OCH_3), 3.78 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—OCH_3), 3.69 (2H, s, Ar—CH_2—Ar), 6.54–6.59 (1H, dd, $^2J_{H\text{-}P}$ = 8.4 Hz, P—CH and $^3J_{H\text{-}H}$ = 2.0 Hz, NH—CH), 6.77 (1H, m, NH), 7.11–7.53 (11H, m, Ar—H). IR (KBr) (ν_{max} cm^{-1}): 3329 (N—H), 2960 and 2858 (C—$H_{aromatic}$), 1260 (P=O), 751 (P—$C_{aliphatic}$). EI-MS *m/z* (%): 395 (9) $M^{+\bullet}$. Anal. Calcd. for $C_{22}H_{22}NO_4P$: C, 66.83; H, 5.61; N, 3.54; Found: C, 66.79; H, 5.58; N, 3.48.

*Dimethyl (((9H-fluoren-2-yl)amino)(3-hydroxyphenyl) methyl)phosphonate (***4m***)*. Brown solid, mp: 191–193°C. ^{31}P NMR (161.7, MHz, $CDCl_3$) δ: 21.79; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.58 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—OCH_3), 3.76 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—OCH_3), 3.68 (2H, s, Ar—CH_2—Ar), 6.53–6.58 (1H, dd, $^2J_{H\text{-}P}$ = 8.4 Hz, P—CH and $^3J_{H\text{-}H}$ = 2.0 Hz, NH—CH), 6.79 (1H, m, NH), 7.10–7.54 (11H, m, Ar—H). IR (KBr) (ν_{max} cm^{-1}): 3340 (N—H), 2965 and 2862 (C—$H_{aromatic}$), 1248 (P=O), 759 (P—$C_{aliphatic}$). Anal. Calcd. for $C_{22}H_{22}NO_4P$: C, 66.83; H, 5.61; N, 3.54; Found: C, 66.77; H, 5.56; N, 3.47.

*Dimethyl (((9H-fluoren-2-yl)amino) (cyclohexyl) methyl)phosphonate (***4n***)*. Pale yellow solid, mp: 167–169°C. ^{31}P NMR (161.7, MHz, $CDCl_3$) δ: 20.61; ^{13}C NMR (100.56 MHz, $CDCl_3$) δ: 113.8 (C-1), 149.8 (C-2), 109.6 (C-3), 121.6 (C-4), 122.8 (C-5), 127.8 (C-6), 128.3 (C-7), 126.5 (C-8), 36.9 (C-9), 145.9 (C-10), 129.8 (C-11), 138.2 (C-12), 140.5 (C-13), 53.8 (C-15), 23.4 (C-16), 29.7 (C-17 and 21), 25.9 (C-18 and 20), 26.8 (C-19), 52.7 (P—OCH_3), 53.5 (P—OCH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.50 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—OCH_3), 3.69 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—OCH_3), 3.51 (2H, s, Ar—CH_2—Ar), 6.65–6.67 (1H, dd, $^2J_{H\text{-}P}$ = 8.4 Hz, P—CH and $^3J_{H\text{-}H}$ = 2.0 Hz, NH—CH), 6.74 (1H, m, NH), 7.08–7.75 (7H, m, Ar—H), 1.35–1.53 (12H, m, C—$H_{cyclohexane}$). IR (KBr) (ν_{max} cm^{-1}): 3339 (N-H), 2966 and 2865 (C—$H_{aromatic}$), 1230 (P=O), 759 (P—$C_{aliphatic}$). EI-MS *m/z* (%): 385 (11) $M^{+\bullet}$. Anal. Calcd. for $C_{22}H_{28}NO_3P$: C, 68.55; H, 7.32; N, 3.63; Found: C, 68.47; H, 7.28; N, 3.58.

*Dimethyl (1-((9H-fluoren-2-yl)amino) propyl)-phosphonate (***4o***)* [6]. Brown solid, mp: 128–130°C. ^{31}P NMR (161.7, MHz, $CDCl_3$) δ: 20.59; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.55 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—OCH_3), 3.71 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—OCH_3), 3.58 (2H, s, Ar—CH_2—Ar), 6.63–6.65 (1H, dd, $^2J_{H\text{-}P}$ = 8.4 Hz, P-CH and $^3J_{H\text{-}H}$ = 2.0 Hz, NH—CH), 5.87 (1H, m, NH), 7.07–7.63 (7H, m, Ar—H), 1.35–1.43 (2H, m, CH_2), 1.08 (3H, t, CH_3). IR (KBr) (ν_{max} cm^{-1}): 3309 (N—H), 2960 and 2857 (C—$H_{aromatic}$), 1242 (P=O), 759 (P—$C_{aliphatic}$). EI-MS *m/z* (%): 331 (10) $M^{+\bullet}$. Anal. Calcd. for $C_{18}H_{22}NO_3P$: C, 65.25; H, 6.69; N, 4.23; Found: C, 65.19; H, 6.62; N, 4.18.

*Dimethyl (1-((9H-fluoren-2-yl)amino) butyl)-phosphonate (***4p***)*. Brown solid, mp: 134–136°C. ^{31}P NMR (161.7, MHz, $CDCl_3$) δ: 21.11; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.52 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—OCH_3), 3.73 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—OCH_3), 3.56 (2H, s, Ar—CH_2—Ar), 6.61–6.65 (1H, dd, $^2J_{H\text{-}P}$ = 8.4 Hz, P—CH and $^3J_{H\text{-}H}$ = 2.0 Hz, NH—CH), 5.85 (1H, m, NH), 7.11–7.62 (7H, m, Ar—H), 1.31–1.45 (4H, m, 2 × CH_2), 1.08 (3H, t, CH_3). IR (KBr) (ν_{max} cm^{-1}): 3311 (N—H), 2968 and 2866 (C—$H_{aromatic}$),

1254 (P═O), 762 (P—$C_{aliphatic}$). EI-MS *m/z* (%): 345 (5) $M^{+\bullet}$. Anal. Calcd. for $C_{19}H_{24}NO_3P$: C, 66.07; H, 7.00; N, 4.06; Found: C, 66.01; H, 6.96; N, 4.02.

*Dimethyl (1-((9H-fluoren-2-yl)amino)-3-methylbutyl) phosphonate (***4q***)*. Pale yellow solid, mp: 137–139°C. ^{31}P NMR (161.7, MHz, $CDCl_3$) δ: 21.59; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.52 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—O$\underline{CH_3}$), 3.70 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—O$\underline{CH_3}$), 3.54 (2H, s, Ar—$\underline{CH_2}$—Ar), 6.66–6.69 (1H, dd, $^2J_{H\text{-}P}$ = 8.4 Hz, P-$\underline{CH}$ and $^3J_{H\text{-}H}$ = 2.0 Hz, NH-$\underline{CH}$), 5.85 (1H, m, $\underline{NH}$), 7.13–7.63 (7H, m, $\underline{Ar}$—$\underline{H}$), 1.36–1.48 (2H, m, $\underline{CH_2}$), 1.59 (1H, m, $\underline{CH}$), 1.04 (6H, d, $(\underline{CH_3})_2$). IR (KBr) (ν_{max} cm^{-1}): 3314 (N—H), 2964 and 2862 (C—$H_{aromatic}$), 1248 (P═O), 760 (P-$C_{aliphatic}$). EI-MS *m/z* (%): 359 (8) $M^{+\bullet}$. Anal. Calcd. for $C_{20}H_{26}NO_3P$: C, 66.84; H, 7.29; N, 3.90; Found: C, 66.78; H, 7.23; N, 3.84.

*Dimethyl (1-((9H-fluoren-2-yl)amino) pentyl)-phosphonate (***4r***)*. Pale yellow solid, mp: 141–143°C. ^{31}P NMR (161.7, MHz, $CDCl_3$) δ: 21.10; ^{13}C NMR (100.56 MHz, $CDCl_3$) δ: 113.6 (C-1), 149.5 (C-2), 109.4 (C-3), 121.5 (C-4), 122.7 (C-5), 127.6 (C-6), 128.4 (C-7), 126.5 (C-8), 36.7 (C-9), 145.6 (C-10), 129.4 (C-11), 138.1 (C-12), 140.4 (C-13), 53.7 (C-15), 22.3 (C-16), 29.1 (C-17), 23.2 (C-18), 15.8 (C-19), 52.2 (P—OCH_3), 53.1 (P—OCH_3); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.54 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—O$\underline{CH_3}$), 3.76 (3H, d, $^3J_{H\text{-}P}$ = 10.4 Hz, P—O$\underline{CH_3}$), 3.58 (2H, s, Ar—$\underline{CH_2}$—Ar), 6.63–6.66 (1H, dd, $^2J_{H\text{-}P}$ = 8.4 Hz, P-$\underline{CH}$ and $^3J_{H\text{-}H}$ = 2.0 Hz, NH—$\underline{CH}$), 5.89 (1H, m, $\underline{NH}$), 7.13–7.61 (7H, m, $\underline{Ar}$—$\underline{H}$), 1.23–1.52 (6H, m, 3 × $\underline{CH_2}$), 1.01 (3H, t, $\underline{CH_3}$). IR (KBr) (ν_{max} cm^{-1}): 3319 (N—H), 2963 and 2862 (C—$H_{aromatic}$), 1252 (P═O), 764 (P—$C_{aliphatic}$). Anal. Calcd. for $C_{20}H_{26}NO_3P$: C, 66.84; H, 7.29; N, 3.90; Found: C, 66.76; H, 7.21; N, 3.83.

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