

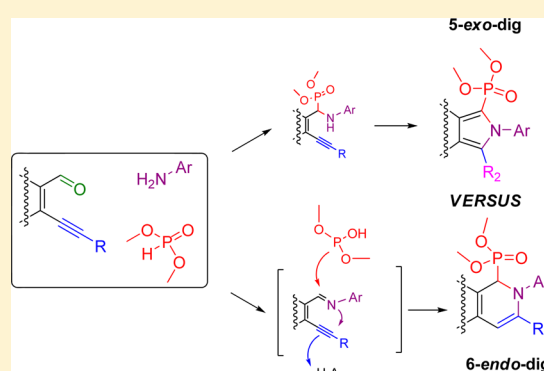
Formation of Condensed 1*H*-Pyrrol-2-ylphosphonates and 1,2-Dihydropyridin-2-ylphosphonates via Kabachnik–Fields Reaction of Acetylenic Aldehydes and Subsequent 5-*exo-dig* or 6-*endo-dig* Cyclizations

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S Supporting Information

ABSTRACT: Kabachnik–Fields reactions of various carbocyclic or heterocyclic acetylenic aldehydes together with subsequent Lewis acid catalyzed cyclizations have been studied. It was found that 5-*exo-dig* versus 6-*endo-dig* cyclization mode strongly depends on the structure of starting materials. Thus, nonaromatic acetylenic α -anilinomethylphosphonates underwent gold(III)-catalyzed or iodine-mediated 5-*exo-dig* cyclization to 1*H*-pyrrol-2-ylphosphonates. In contrast, electron-withdrawing heteroaromatic substrates formed 1,2-dihydropyridin-2-ylphosphonate ring containing materials via an exclusive 6-*endo-dig* ring-closure process. The dual mode of cyclization is possible only for α -amino (2-alkynylphenyl)methylphosphonates containing a benzene ring.



INTRODUCTION

Both heterocyclic pyrrole¹ and 1,2-dihydropyridine² ring systems are important skeletons in natural and synthetic bioactive products. Also, it is well-known that α -amino-phosphonates attract attention as analogues of α -amino acids possessing a variety of important biological activities.³ Combination of pyrrole and dihydropyridine rings together with the phosphonate functionality would represent a class of cyclic α -aminophosphonates with promising biological applications.⁴

In 2007 several manuscripts about the formation of dialkyl 1*H*-pyrrol-2-ylphosphonates and 1,2-dihydropyridin-2-ylphosphonates (Figure 1) via Lewis acid catalyzed cyclizations

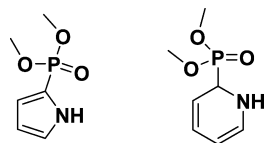
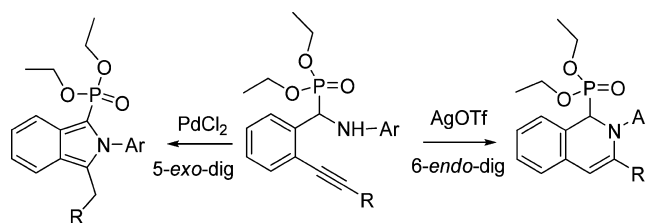


Figure 1. Structures of 1*H*-pyrrol-2-ylphosphonate and 1,2-dihydropyridin-2-ylphosphonate.

of α -amino (2-alkynylphenyl)methylphosphonates were published by Ding et al.⁵ The authors proved that, in principle, both cyclization modes are possible and showed that 5-*exo-dig* versus 6-*endo-dig* cyclization regioselectivity could be simply switched by changing the catalyst (Scheme 1).^{5a}

However, we envisioned that the cyclization regioselectivity of acetylenic α -anilinomethylphosphonates could also depend

Scheme 1. Results of Ding et al. Published in 2007^{5a}



on the structure of starting material, due to different electronic densities on triple bond carbons. For the evaluation of this idea we chose a variety of carbocyclic and heterocyclic acetylenic α -anilinomethylphosphonates and tested their cyclization reactions.

In this work we present the results of our investigations.

RESULTS AND DISCUSSION

The corresponding 2-alkynylcyclopent-1-enecarbaldehydes **1**, 2-alkynylcyclohex-1-enecarbaldehydes **2**, 2-alkynylbenzaldehydes **3**, 2-alkynylindole-3-carbaldehydes **4**, 2-alkynylpyridine-3-carbaldehydes **5**, and 2-alkynylquinoline-3-carbaldehydes **6** (Figure 2) were reacted by the classical Sonogashira coupling⁶ between 2-bromocyclopent-1-enecarbaldehyde,⁷ 2-bromocyclohex-1-enecarbaldehyde,⁸ and commercially available 2-bromobenzaldehyde, 2-bromo-1*H*-indole-3-carbaldehyde, 2-bromo-

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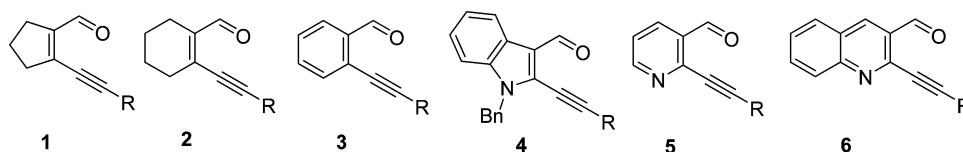
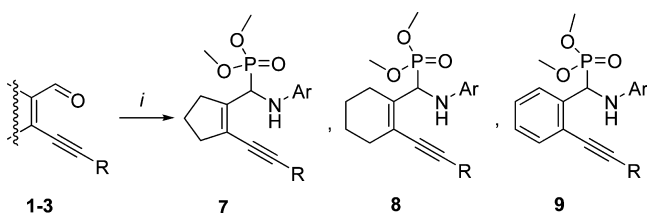


Figure 2. Starting acetylenic aldehydes. **1a:** R = Ph; **1b:** R = 4-MeC₆H₄; **1c:** R = 4-EtC₆H₄; **1d:** R = Bu; **1e:** R = C₅H₁₁; **1f:** R = *c*-Pr; **1g:** R = TMS. **2a:** R = Ph; **2b:** R = 4-MeC₆H₄; **2c:** R = Pr; **2d:** R = Bu; **2e:** R = C₅H₁₁; **2f:** R = *c*-Pr. **3a:** R = Ph; **3b:** R = TMS. **4a:** R = Ph; **4b:** R = Bu; **4c:** R = *c*-Pr. **5a:** R = Ph; **5b:** R = Pr; **5c:** R = *c*-Pr; **5d:** R = H; **5e:** R = CH₂OTHP. **6a:** R = Ph; **6b:** R = Bu; **6c:** R = Pr; **6d:** *c*-Pr.

pyridine-5-carbaldehyde, 2-chloroquinoline-3-carbaldehyde, and terminal acetylenes. The reactions proceeded smoothly in THF at room temperature under argon atmosphere in the presence of 4 mol % PdCl₂(PPh₃)₂ and 2 mol % CuI and 2 equiv of triethylamine. Then with the synthesized acetylenic aldehydes in hand, we utilized the Kabachnik–Fields reaction⁹ between starting materials, anilines, and dimethylphosphite and screened synthetic approaches for the preparation of various phosphonated pyrrole or dihydropyridine core contacting compounds.

Synthetic Utility of Carbocyclic Acetylenic Aldehydes for the Preparation of Materials Having Pyrrole-1-phosphonate Functionalities. The Kabachnik–Fields reaction is a three-component process forming α -amino-phosphonates from carbonyl compounds, amines, and dialkyl phosphonates. Despite a variety of method variations,¹⁰ the presence of a Lewis acid in solution or in solvent-free conditions is usually required. After a brief search of optimal reaction conditions, we found that 1 equiv of BF₃·OEt₂ in dichloromethane at room temperature gave the best results and did not cause polymerization of chemically unstable aldehydes **1** and **2**. Thus, when carbocyclic aldehydes **1–3** were stirred with anilines and dimethylphosphite in dichloromethane in the presence of 1 equiv of BF₃·OEt₂ at room temperature, the corresponding acetylenic α -anilinomethylphosphonates **7–9** were formed in moderate or good yields (Scheme 2).

Scheme 2. Kabachnik–Fields Reaction of Carbocyclic Acetylenic Aldehydes **1–3**^a



^aReagents and conditions: (i) ArNH₂ (1 equiv), dimethylphosphite (1.1 equiv), BF₃·OEt₂ (1 equiv), DCM, rt, 12–24 h. Structures of **7–9** are depicted in Tables 4 and 5.

Next, the cyclization reaction of dimethyl (phenylamino)[2-(phenylethynyl)cyclopent-1-enyl]methylphosphonate **7a** was chosen for optimization of conditions. The aromatic substrate dimethyl (phenylamino)[2-(phenylethynyl)phenyl]-methylphosphonate **9a** was used as a model substrate for comparison. The data obtained are depicted in Tables 1 and 2.

First of all, it should be noted that in all successful cases the starting material **7a** underwent regioselective 5-*exo-dig* cyclization followed by aromatization and formation of the tetrahydrocyclopenta[*c*]pyrrole core. No 6-*endo-dig* cyclization product was observed by TLC and NMR monitoring of crude mixtures. Screening of Lewis acids revealed that copper(I)

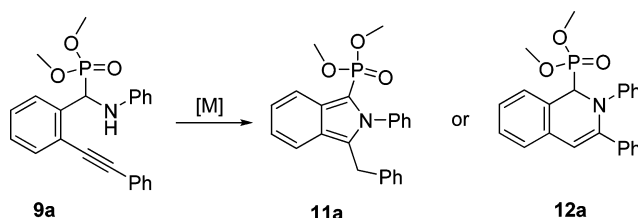
iodide was totally ineffective for the cyclization and the starting material **7a** was isolated after the workup of reaction mixture (Table 1, entry 1). When PdCl₂ was utilized as a catalyst in

Table 1. Screening of the Cyclization Reaction of Dimethyl (Phenylamino)[2-(phenylethynyl)cyclopent-1-enyl]methylphosphonate **7a**

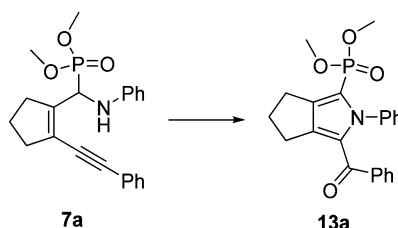
entry	reaction conditions	time, h	yield	recovered
			10a , %	7a , %
1	CuI (10 mol %), CHCl ₃ , rt	48		95
2	PdCl ₂ (10 mol %), CHCl ₃ , rt	48	10	79
3	PdCl ₂ (10 mol %), CH ₃ CN, rt	48	11	78
4	PdCl ₂ (PPh ₃) ₂ (10 mol %), CHCl ₃ , rt	48	30	42
5	AgNO ₃ (10 mol %), CHCl ₃ , rt	48	20	36
6	CF ₃ CO ₂ Ag (10 mol %), CHCl ₃ , rt	48	8	74
7	CF ₃ SO ₃ Ag (10 mol %), CHCl ₃ , rt	48	13	68
8	AuBr ₃ (5 mol %), CHCl ₃ , rt	48	45	45
9	AuBr ₃ (10 mol %), CHCl ₃ , rt	48	70	
10	AuBr ₃ (10 mol %), KOtBu (1 equiv), CHCl ₃ , rt	0.5	99	

chloroform or acetonitrile solutions, poor conversion of **7a** was reached and compound **10a** was isolated in 10% and 11% yields (Table 1, entries 2, 3). PdCl₂(PPh₃)₂ as well as various silver salts (AgNO₃, CF₃CO₂Ag, and CF₃SO₃Ag) also were not very effective, and after insufficient conversion of the starting material, pyrrole derivative **10a** was isolated in 20%, 8%, and 13% yields, respectively (Table 1, entries 4–7). After treatment of the starting alkyne by 5 mol % gold(III) bromide in chloroform at room temperature, 50% conversion of **7a** was reached in 48 h, affording 45% of final **10a** (Table 1, entry 8). Increasing the amount of AuBr₃ to 10 mol % resulted in full conversion of the starting material in 48 h, and **10a** was obtained in 70% yield (Table 1, entry 9). To our delight, addition of 1 equiv of potassium *tert*-butoxide speeded up the reaction, and high-yielding formation of **10a** was achieved after 30 min of stirring at room temperature (Table 1, entry 10).¹¹

In contrast, aromatic dimethyl (phenylamino)(2-phenylethynylphenyl)methylphosphonate **9a** is able to undergo either 5-*exo-dig* or 6-*endo-dig* cyclizations. This dual reactivity of dialkyl (arylamino)(2-alkynylphenyl)methylphosphonates was described by Ding et al. in 2007.^{5a} The authors showed that on one hand, palladium chloride in acetonitrile initiated regioselective 5-*exo-dig* cyclization followed by [1,5]-H shift

Table 2. Data of 5-*exo-dig* or 6-*endo-dig* Cyclization Reactions of Dimethyl (phenylamino)(2-phenylethynylphenyl)methylphosphonate **9a**

entry	reaction conditions	time, h	product	yield, %
1	AuBr ₃ (10 mol %), KO ^t Bu (1 equiv), CHCl ₃ , rt	24	11a	53
2	PdCl ₂ (5 mol %), CH ₃ CN, 60–70 °C	32	11a	72
3	CF ₃ SO ₃ Ag (5 mol %), CH ₃ CN, 60–70 °C	72	12a	86

Table 3. Screening of the Iodine-Mediated Cyclization Reaction of Dimethyl (Phenylamino)[2-(phenylethynyl)cyclopent-1-enyl]methylphosphonate **7a**

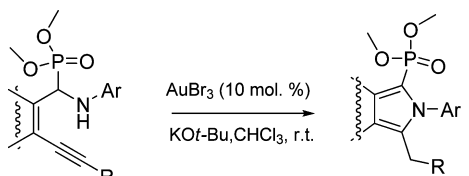
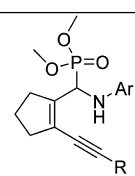
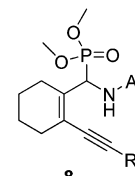
entry	reaction conditions	time, h	yield 13a , %	recovered 7a , %
1	I ₂ (4 equiv), CHCl ₃ , rt	12	12	
2	I ₂ (1 equiv), KO ^t Bu (1 equiv), CHCl ₃ , 0 °C → rt	12	11	
3	I ₂ (1 equiv), K ₂ CO ₃ (1 equiv), CHCl ₃ , 0 °C → rt	12	48	
4	I ₂ (1 equiv), K ₂ CO ₃ (1 equiv), acetone, rt	12	24	24
5	I ₂ (1 equiv), K ₂ CO ₃ (1 equiv), CH ₃ CN, rt	12	30	32
6	I ₂ (1 equiv), K ₂ CO ₃ (1 equiv), CH ₃ NO ₂ , rt	12	28	43
7	I ₂ (1 equiv), K ₂ CO ₃ (1 equiv), CH ₃ OH, rt	12		85
8	I ₂ (1 equiv), K ₂ CO ₃ (1 equiv), C ₆ H ₅ CH ₃ , rt	12		
9	I ₂ (1 equiv), NaHCO ₃ (1 equiv), CHCl ₃ , 0 °C → rt	12	65	
10	I ₂ (1 equiv), K ₃ PO ₄ (1 equiv), CHCl ₃ , 0 °C → rt	12	67	
11	Py ₂ IBF ₄ (1 equiv), CHCl ₃ , rt	12		49
12	I ₂ (1 equiv), PhI(OAc) ₂ (2 equiv), CHCl ₃ , 0 °C → rt	1	89	

to the corresponding 2,3-disubstituted-2*H*-isindol-1-ylphosphonates. On the other hand, silver triflate catalyzed 6-*endo-dig* cyclization reaction to 2,3-disubstituted-1,2-dihydroisquinolin-1-ylphosphonates. Indeed benzene derivative **9a** was able to undergo both cyclization processes as it was reported by Ding et al. (Table 2, entries 2 and 3).^{5a} These methods required prolonged heating in acetonitrile. It should be noted that gold(III) bromide together with 1 equiv of potassium *tert*-butanoate in chloroform also initiated 5-*exo-dig* cyclization process at room temperature and final **11a** was formed in 53% yield (Table 2, entry 1).

Thus, gold(III) bromide was able to initiate exclusive 5-*exo-dig* cyclization reactions of carbocyclic acetylenic α -anilino-methylphosphonates. With these promising results in hands and having in mind literature facts that various intramolecular transformations of functionally substituted alkynes can be carried out with either gold catalysts or iodine electrophiles to access the same core unit,¹² we decided to evaluate the usefulness of iodine electrophiles in this cyclization. Indeed, we found, that molecular iodine was able to mediate the cyclization process of (phenylamino)[2-(phenylethynyl)cyclopent-1-enyl]-methylphosphonate **7a**. In all cases dimethyl 3-benzoyl-2-phenyl-2,4,5,6-tetrahydrocyclopenta[*c*]pyrrol-1-ylphosphonate

13a bearing a carbonyl functionality instead of a methylene group was formed. Full conversion of the starting material **7a** was reached in 12 h. However, use of an excess of molecular iodine (Table 3, entry 1), as well as 1 equiv of molecular iodine together with 1 equiv of potassium *tert*-butanoate at 0 °C temperature (Table 3, entry 2) facilitated the formation of tars, and only minor quantities of **13a** were isolated. While use of potassium carbonate (Table 3, entry 3), sodium bicarbonate (Table 3, entry 9), and potassium phosphate (Table 3, entry 10) in chloroform at 0 °C temperature improved yield of the cyclization product, potassium carbonate in acetone (Table 3, entry 4), acetonitrile (Table 3, entry 5), and nitromethane (Table 3, entry 6) led to insufficient conversion of the starting alkyne. It also should be noted that combination of equivalent amounts of the starting material, molecular iodine, and potassium carbonate in methanol (Table 3, entry 7) or toluene (Table 3, entry 8) did not give the desired product, and 85% of starting alkyne was recovered or full decomposition of it was observed, respectively. The Barluenga reagent¹³ was not able to mediate the cyclization process, and 49% of the starting material was recovered (Table 3, entry 11). Then, the electrophilicity of iodine was improved by adding hypervalent iodine oxidant.¹⁴ To our delight, the combination of 1 equiv of

Table 4. Data on the Synthesis of Polysubstituted Pyrrol-1-ylphosphonates via Gold(III) Bromide Mediated Cyclization

			
7-8 10, 14			
Entry	Starting material	Product	Yield, %
1	 7 7a: R = Ph, Ar = Ph	10a	98
2	7b: R = Ph, Ar = 4-MeOC ₆ H ₄	10b	73
3	7c: R = Ph, Ar = 4-EtOC ₆ H ₄	10c	74
4	7d: R = Ph, Ar = 4-FC ₆ H ₄	10d	86
5	7e: R = Ph, Ar = 4-ClC ₆ H ₄	10e	73
6	7f: R = 4-MeC ₆ H ₄ , Ar = Ph	10f	58
7	7g: R = 4-MeC ₆ H ₄ , Ar = 4-MeOC ₆ H ₄	10g	76
8	7h: R = 4-EtC ₆ H ₄ , Ar = 4-MeOC ₆ H ₄	10h	96
9	7i: R = C ₄ H ₉ , Ar = Ph	10i	96
10	7j: R = C ₄ H ₉ , Ar = 4-MeOC ₆ H ₄	10j	78
11	7k: R = C ₄ H ₉ , Ar = 4-FC ₆ H ₄	10k	80
12	7l: R = C ₄ H ₉ , Ar = 4-ClC ₆ H ₄	10l	76
13	7m: R = C ₅ H ₁₁ , Ar = Ph	10m	90
14	7n: R = C ₅ H ₁₁ , Ar = 4-MeOC ₆ H ₄	10n	63
15	7o: R = <i>cyclo</i> Pr, Ar = Ph	10o	77
16	7p: R = <i>cyclo</i> Pr, Ar = 4-MeOC ₆ H ₄	10p	73
17	7r: R = <i>cyclo</i> Pr, Ar = 4-EtOC ₆ H ₄	10r	90
18	7s: R = H, Ar = Ph	10s	66
19	 8 8a: R = Ph, Ar = Ph	14a	82
20	8b: R = Ph, Ar = 4-MeOC ₆ H ₄	14b	95
21	8c: R = Ph, Ar = 4-FC ₆ H ₄	14c	56
22	8d: R = Ph, Ar = 4-ClC ₆ H ₄	14d	68
23	8e: R = 4-MeC ₆ H ₄ , Ar = Ph	14e	92
24	8f: R = 4-MeC ₆ H ₄ , Ar = 4-MeOC ₆ H ₄	14f	79
25	8g: R = C ₃ H ₇ , Ar = Ph	14g	89
26	8h: R = C ₃ H ₇ , Ar = 4-MeOC ₆ H ₄	14h	99
27	8i: R = C ₃ H ₇ , Ar = 4-FC ₆ H ₄	14i	81
28	8j: R = C ₄ H ₉ , Ar = Ph	14j	88
29	8k: R = C ₄ H ₉ , Ar = 4-MeOC ₆ H ₄	14k	82
30	8l: R = <i>cyclo</i> Pr, Ar = Ph	14l	83
31	8m: R = <i>cyclo</i> Pr, Ar = 4-MeOC ₆ H ₄	14m	92
32	8n: R = <i>cyclo</i> Pr, Ar = 4-ClC ₆ H ₄	14n	92

molecular iodine together with 2 equiv of phenyliodine diacetate in chloroform at 0 °C temperature resulted in full conversion of the starting alkyne and smooth formation of **13a** in 89% yield (Table 3, entry 12).

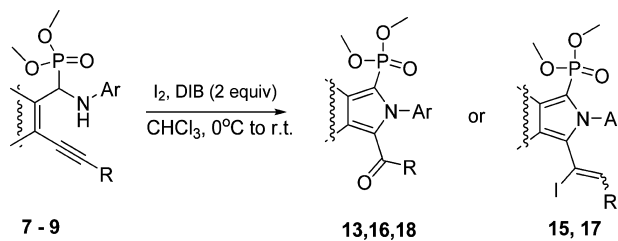
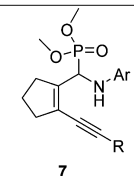
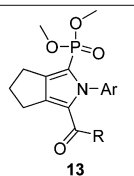
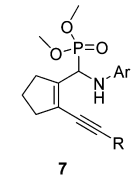
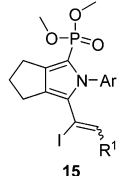
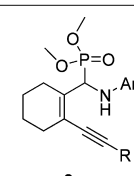
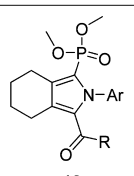
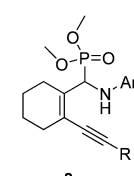
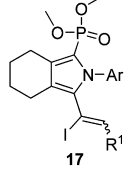
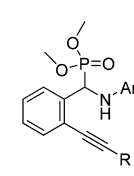
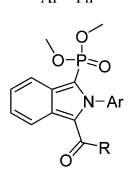
Optimized reaction conditions (Table 1, entry 10 and Table 3, entry 12) were applied for the synthesis of polysubstituted pyrrol-1-ylphosphonates **10** and **13–18**. The results are summarized in Tables 4 and 5. As is seen from Table 4, both starting substrates **7** and **8** having cyclopentene and cyclohexene rings underwent smooth and high-yielding formation of pyrrol-1-ylphosphonates **10** and **14** via gold(III) bromide catalyzed process (entries 1–32).

Molecular iodine mediated cyclizations proceeded smoothly for substrates **7a–h,j,s** (Table 5, entries 1–10), **8a,b,o,p** (Table 5, entries 13–15), and **9b,c** (Table 5, entries 18, 19) having arylethynyl or ethynyl functionality. The corresponding ketones **13a–g,h,j**, **16a,b,o**, **18b** and aldehydes **13s** and **18c** were

isolated in moderate or good yields. However, derivatives **7i**, **7o** (Table 5, entries 11, 12) and **8k**, **8l** (Table 5, entries 16, 17) bearing an alkylethynyl substituent cyclized into pyrrol-1-ylphosphonates bearing 1-iodoalkenyl substituents. The latter four compounds were isolated as mixtures of *E* and *Z* isomers.

The plausible mechanism of the iodine-mediated cyclization is depicted in Scheme 3. We believe that at the first step, molecular iodine is converted to 2 equiv of acetyl hypoiodite during oxidation by phenyliodine diacetate.¹⁴ Thus, an electrophilic I⁺ is generated in an efficient and atom-economic way. The formation of byproduct iodobenzene was proved by NMR and MS methods. Next, after direct iodonium activation (intermediate I) of the triple bond of the starting substrate, the intramolecular 5-*exo-dig* nucleophilic attack of the neighboring arylamino group takes place, leading to intermediate II, and loss of a proton gives neutral intermediate III. Next, the second electrophilic iodine attack of the exocyclic double bond occurs,

Table 5. Data on the Synthesis of Polysubstituted Pyrrol-1-ylphosphonates 13 and 15–18 via Iodine-Mediated Cyclization

			
Entry	Starting material	Product	Yield, %
1	 7a: R = Ph, Ar = Ph	 13a	89
2	7b: R = Ph, Ar = 4-MeOC ₆ H ₄	13b	67
3	7c: R = Ph, Ar = 4-EtOC ₆ H ₄	13c	70
4	7d: R = Ph, Ar = 4-FC ₆ H ₄	13d	58
5	7e: R = Ph, Ar = 4-ClC ₆ H ₄	13e	51
6	7g: R = 4-MeC ₆ H ₄ , Ar = 4-MeOC ₆ H ₄	13g	56
7	7h: R = 4-EtC ₆ H ₄ , Ar = 4-MeOC ₆ H ₄	13h	54
9	7j: R = 4-EtC ₆ H ₄ , Ar = 4-ClC ₆ H ₄	13j	44
10	7s: R = H, Ar = Ph	13s	42
11	 7i: R = C ₄ H ₉ , Ar = Ph	 15i: R ¹ = C ₃ H ₇ , Ar = Ph	58
12	7o: R = cycloPr, Ar = Ph	15o: R ¹ = (CH ₂) ₂ I, Ar = Ph	49
13	 8a: R = Ph, Ar = Ph	 16a	61
14	8b: R = Ph, Ar = 4-MeOC ₆ H ₄	16b	60
15	8o: R = 4-MeC ₆ H ₄ , Ar = 4-ClC ₆ H ₄	16o	69
16	 8k: R = C ₄ H ₉ , Ar = 4-MeOC ₆ H ₄	 17k: R ¹ = C ₃ H ₇ , Ar = 4-MeOC ₆ H ₄	25
17	8l: R = cycloPr, Ar = Ph	17l: R ¹ = (CH ₂) ₂ I, Ar = Ph	83
18	 9b: R = Ph, Ar = 4-ClC ₆ H ₄	 18b	44
19	9c: R = H, Ar = 4-MeOC ₆ H ₄	18c	56

thus affording intermediate IV. Abstraction of a proton leads to aromatization of the pyrrole ring and formation of di-iodo intermediates VI and VII. However, when starting compound has a cyclopropyl functionality next to the triple bond, during the iodination-aromatization processes cleavage of the cyclopropane ring occurs, giving di-iodo derivatives 15 and 17. Intermediate VI can undergo nucleophilic displacement reaction with water, forming carbonyl group bearing products 13, 16, 18. In contrast, intermediate VII, bearing a CH₂R¹ group, undergoes base-mediated elimination reaction to compounds 15 and 17.

The role of water in formation of products 13, 16, and 18 was proved by addition of ¹⁸O-labeled water to the reaction mixture. Stirring of 7a with 1 equiv of molecular iodine and 2 equiv of phenyliodine diacetate in chloroform in the presence of 3 equiv of ¹⁸O-labeled water resulted in smooth formation of 13a-¹⁸O in 86% yield. The HRMS spectrum of 13a-¹⁸O confirmed absolute incorporation of ¹⁸O in final ketone. Moreover, an observed δ 0.04 ppm (4 Hz) upfield chemical

shift was found for ketone carbonyl carbon in ¹³C NMR spectrum of 13a-¹⁸O, thus confirming position of ¹⁸O.¹⁵

Kabachnik–Fields Reactions of Heterocyclic Aldehydes and Cyclization Reaction of Obtained Adducts. After exploring the reactivity of carbocyclic acetylenic aldehydes and their Kabachnik–Fields adducts, we turned our attention to heterocyclic substrates. Electron-rich 2-(alkynyl)-1-benzyl-1H-indole-3-carbaldehydes (4) reacted under the Kabachnik–Fields reaction condition and formed the corresponding adducts 19 in moderate yields (Scheme 4).

Unfortunately, the presence of an electron-rich indole ring deactivated isolated compounds 19 toward the cyclization reaction. No changes of the starting materials 19 were observed by TLC or NMR monitoring during prolonged stirring or refluxing of compounds 19 in dichloroethane, in the presence of gold(III) bromide, palladium(II) chloride, silver(I) triflate, or I₂/DIB.

However, when we tried to perform the Kabachnik–Fields reaction of electron-deficient pyridine or quinoline substrates 5 and 6, we surprisingly found that these reactions were not so

Table 6. Data on the Synthesis of Dimethyl 6-Aryl-5,6-dihydro-1,6-naphthyridin-5-ylphosphonates **20** and Dimethyl 2-Aryl-1,2-dihydrobenzo[*b*][1,6]naphthyridin-1-ylphosphonates **21**^a

Entry	Starting material	ArNH ₂	Product	Yield, %
1				58
	5a: R = Ph		20a	
2	5a: R = Ph		20b	61
3	5b: R = C ₃ H ₇		20c	52
4	5c: R = cycloPr		20d	63
5	5c: R = cycloPr		20e	59
6	5d: R = H		20f	50
7	5e: R = CH ₂ OTHP		20g	51
8	5e: R = CH ₂ OTHP		20h	48
9				48
	6a R = Ph		21a	
10	6b: C ₆ H ₉		21b	48
11	6b: C ₆ H ₉		21c	45
12	6b: C ₆ H ₉		21d	52
13	6c: C ₃ H ₇		21e	69
14	6d: R = cycloPr		21f	67
15	6d: R = cycloPr		21g	67
16	6d: R = cycloPr		21h	48

^aReactions between starting materials, the corresponding aniline (1 equiv), and dimethylphosphite (1.1 equiv) were carried out in DCM at rt in the presence of CuI (10 mol %) for 2–4 h.

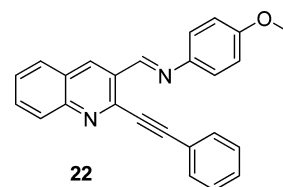


Figure 3. (*E*)-4-Methoxy-*N*-{[2-(phenylethynyl)quinolin-3-yl]-methylene}aniline **22**.

bromide (Scheme 6). Together with compound **23**, the corresponding cyclized 1,2-dihydrobenzo[*b*][1,6]naphthyridin-1-ylphosphonate **21e** was formed. After isolation and purification of **23**, we tested its reactivity toward various Lewis acids (AuBr₃, AgOTf, CuI, I₂ in neutral and basic media) and found that in all cases slow formation of 6-*endo-dig* cyclization product **21e** with incomplete conversion of compound **23** took place. Thus, it was showed that reaction of electron-withdrawing heterocyclic acetylenic aldehydes with anilines and dimethylphosphite likely does not proceed via the Kabachnik–Fields reaction adducts, but mainly via imines **VIII**. The triple bond of intermediates **VIII** is activated by neighboring electron-withdrawing pyridine and quinoline rings, and therefore smooth tandem dimethylphosphite attack–6-*endo-dig* cyclization reactions take place.

CONCLUSION

Kabachnik–Fields reactions between 2-alkynylcyclopent-1-enecarbaldehydes, 2-alkynylcyclohex-1-enecarbaldehydes, 2-alkynylbenzaldehydes, 2-alkynylindole-3-carbaldehydes, 2-alkynylpyridine-3-carbaldehydes, and 2-alkynylquinoline-3-carbaldehydes have been studied. It has been found that substrates having carbocyclic and electron-rich indole ring successfully undergo BF₃·OEt₂-mediated reactions with anilines and dimethylphosphite, yielding the corresponding Kabachnik–Fields adducts. In contrast, electron-deficient 2-alkynylpyridine-3-carbaldehydes and 2-alkynylquinoline-3-carbaldehydes undergo smooth tandem imine formation–6-*endo-dig* cyclization processes forming the corresponding dimethyl 6-aryl-5,6-dihydro-1,6-naphthyridin-5-ylphosphonates and dimethyl 2-aryl-1,2-dihydrobenzo[*b*][1,6]naphthyridin-1-ylphosphonates.

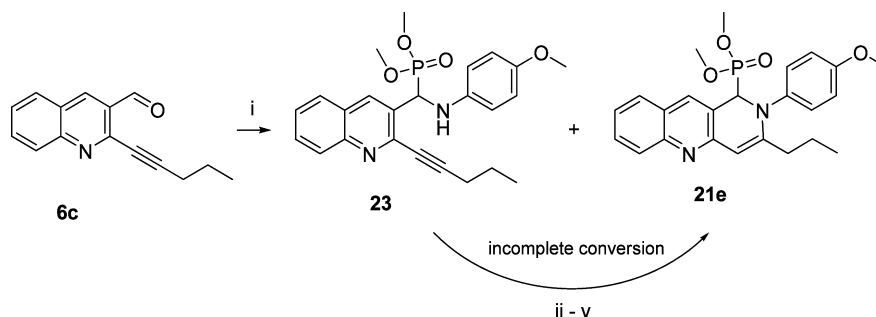
A variety of Lewis acids have been investigated for the cyclization processes of all isolated acetylenic α -anilinomethylphosphonates (Scheme 7).

An important conclusion of this study is that 5-*exo-dig* and 6-*endo-dig* cyclization processes can be switched by using a different catalyst only in the case of starting benzene derivatives. However, while on one hand substrates having nonaromatic cyclopentene or cyclohexene rings undergo exclusive 5-*exo-dig* cyclization processes to form polysubstituted pyrrole derivatives, on the other hand, substrates having electron-deficient pyridine or quinoline rings always undergo 6-*endo-dig* cyclization processes. Finally, substrates bearing an electron-donating indole ring are totally unreactive toward Lewis acid catalyzed cyclization processes.

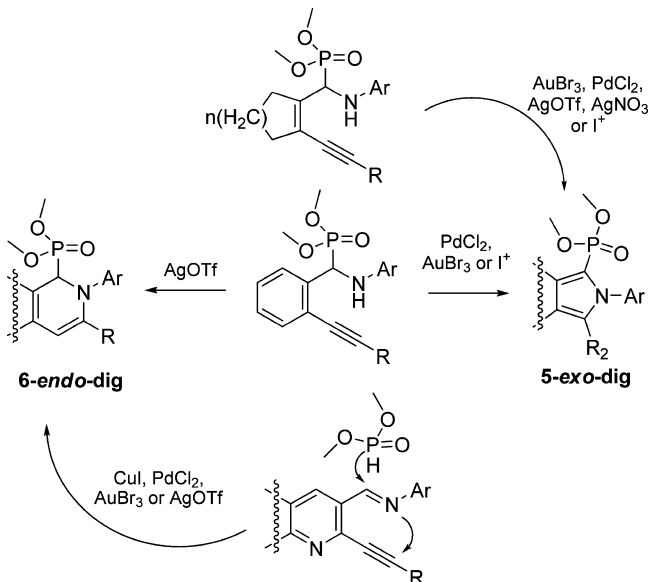
Additionally, during this study, a new iodine-mediated synthetic method of aroyl- or formyl-substituted pyrrole-1-phosphonates has been developed.

EXPERIMENTAL SECTION

General Information. IR spectra were run in KBr discs. ¹H and ¹³C NMR spectra were recorded at either 300 or 400 MHz in chloroform-*d* or dimethylsulfoxide-*d*₆, using the residual solvent signal

Scheme 6^a

^aReagents and conditions: (i) 4-methoxyaniline (1 equiv), dimethylphosphite (1.1 equiv), AuBr₃ (10 mol %), DCM, rt, 3 h. (ii) AuBr₃ (10 mol %), DCM, rt, 24 h. (iii) AgOTf (10 mol %), DCM, rt, 24 h. (iv) CuI (10 mol %), DCM, rt, 24 h. (v) I₂ (1 equiv), K₃PO₄ (1 equiv), CHCl₃, 0 °C → rt, 10 h.

Scheme 7. Dependence of the Cyclization Mode on the Structures of the Starting Acetylenic α -Anilinomethylphosphonates

as internal standard. Signal multiplicity is denoted as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet). Unambiguous assignment of signals was made using a combination of NMR experiments, including COSY, HSQC, and HMBC. High resolution mass spectra were recorded on a Dual-ESI Q-TOF 6520 mass spectrometer by electrospray ionization. All reactions and purity of the synthesized compounds were monitored by TLC using silica gel 60 F254 aluminum plates. Visualization was accomplished by UV light and by treating the plates with vanillin stain followed by heating.

Synthesis of 2-alkynylcyclopent-1-enecarbaldehydes **1**,¹⁶ 2-alkynylcyclohex-1-enecarbaldehydes **2**,¹⁵ 2-alkynylbenzaldehydes **3**,¹⁷ 2-alkynylindole-3-carbaldehydes **4**,¹⁸ 2-alkynylpyridine-3-carbaldehydes **5**,¹⁹ 2-alkynylquinoline-3-carbaldehydes **6**,²⁰ dimethyl 3-benzyl-2-phenyl-2H-isoindol-1-ylphosphonate (**11a**),^{5a} and dimethyl 2,3-diphenyl-1,2-dihydroisoquinolin-1-ylphosphonate (**12a**)^{5a} were performed by methods reported in the literature.

General Procedure for the Preparation of Compounds 7–9 and 19. To a solution of starting corresponding acetylenic aldehyde **1–4** (2 mmol) was added the corresponding aniline (2 mmol) and dimethylphosphite (0.242 g, 2.2 mmol) in dry dichloromethane (5 mL) boron trifluoride etherate (0.284 g, 2 mmol). The resulting solution was stirred at room temperature. When the completion of the reaction was observed by TLC (after 12–24 h), the solution was

quenched with aqueous sodium bicarbonate. The organic layer was separated, washed with water (2 × 20 mL), and dried over anhydrous Na₂SO₄. After the evaporation of solvent under reduced pressure, the residue was purified by flash column chromatography eluting with hexane–ethyl acetate mixtures.

Dimethyl (Phenylamino)(2-(phenylethynyl)cyclopent-1-enyl)methylphosphonate (7a). Yellow solid, mp 114–115 °C. Yield 0.48 g, 63%. IR (KBr): ν_{max} 3488 (NH), 2200 (C≡C) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 1.77–1.99 (2H, m, CH₂CH₂CH₂), 2.37–2.50 (1H, m, CH₂CH₂CH₂), 2.56–2.68 (3H, m, CH₂CH₂CH₂), 3.80 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 3.85 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 5.02 (1H, d, ³J_{H,P} = 24.9 Hz, CH), 6.70–6.78 (3H, m, ArH), 7.15–7.20 (2H, m, ArH), 7.33–7.37 (3H, m, ArH), 7.48–7.51 (2H, m, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 22.2 (CH₂), 32.6 (CH₂), 36.7 (d, ⁵J_{C,P} = 2.1 Hz, CH₂), 51.3 (d, ¹J_{C,P} = 153.6 Hz, CH), 53.6 (d, ²J_{C,P} = 7.2 Hz, OCH₃), 53.8 (d, ²J_{C,P} = 6.6 Hz, OCH₃), 84.9 (d, ⁴J_{C,P} = 5.1 Hz, C-sp), 96.0 (d, ⁵J_{C,P} = 2.4 Hz, C-sp), 113.9 (ArC), 118.9 (ArC), 123.1 (ArC), 124.2 (d, ³J_{C,P} = 12.9 Hz, C-sp²), 128.3 (ArC), 128.4 (ArC), 129.2 (ArC), 131.3 (ArC), 144.9 (d, ³J_{C,P} = 4.7 Hz, C-sp²), 145.9 (d, ³J_{C,P} = 15.3 Hz, ArC) ppm. HRMS (ESI): MNa⁺, found 404.1830. C₂₂H₂₄NNaO₃P requires 404.1836.

Dimethyl (4-Methoxyphenylamino)(2-(phenylethynyl)cyclopent-1-enyl)methylphosphonate (7b). Yellow solid, mp 121–122 °C. Yield 0.44 g, 54%. IR (KBr): ν_{max} 3436 (NH), 2200 (C≡C) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 1.76–1.98 (2H, m, CH₂CH₂CH₂), 2.38–2.49 (1H, m, CH₂CH₂CH₂), 2.56–2.68 (3H, m, CH₂CH₂CH₂), 3.80 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 3.85 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 4.94 (1H, d, ³J_{H,P} = 24.6 Hz, CH), 6.67–6.77 (4H, m, ArH), 7.32–7.36 (3H, m, ArH), 7.45–7.50 (2H, m, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 22.2 (CH₂), 32.6 (CH₂), 36.7 (d, ⁵J_{C,P} = 2.0 Hz, CH₂), 52.2 (d, ¹J_{C,P} = 153.8 Hz, CH), 53.5 (d, ²J_{C,P} = 7.0 Hz, OCH₃), 53.8 (d, ²J_{C,P} = 6.6 Hz, OCH₃), 55.5 (OCH₃), 85.0 (d, ⁴J_{C,P} = 6.9 Hz, C-sp), 95.9 (d, ⁵J_{C,P} = 2.7 Hz, C-sp), 114.7 (ArC), 115.3 (ArC), 123.1 (ArC), 124.1 (d, ³J_{C,P} = 11.9 Hz, C-sp²), 128.3 (ArC), 128.4 (ArC), 131.3 (ArC), 139.9 (d, ³J_{C,P} = 13.8 Hz, ArC), 145.1 (d, ²J_{C,P} = 6.7 Hz, C-sp²), 152.9 (ArC) ppm. HRMS (ESI): MNa⁺, found 434.1497. C₂₃H₂₆NNaO₄P requires 434.1492.

Dimethyl (4-Ethoxyphenylamino)(2-(phenylethynyl)cyclopent-1-enyl)methylphosphonate (7c). Yellow solid, mp 139–141 °C. Yield 0.49 g, 57%. IR (KBr): ν_{max} 3443 (NH), 2198 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.35 (3H, t, ³J = 6.8 Hz, CH₃), 1.78–1.96 (2H, m, CH₂CH₂CH₂), 2.38–2.47 (1H, m, CH₂CH₂CH₂), 2.56–2.65 (3H, m, CH₂CH₂CH₂), 3.80 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 3.84 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 3.93 (2H, q, ³J = 6.8 Hz, CH₂CH₃), 4.93 (1H, d, ³J_{H,P} = 24.4 Hz, CH), 6.66–6.69 (2H, m, ArH), 6.73–6.77 (2H, m, ArH), 7.32–7.37 (3H, m, ArH), 7.47–7.49 (2H, m, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 15.0 (CH₃), 22.3 (CH₂), 32.7 (d, ³J_{C,P} = 1.2 Hz, CH₂), 36.8 (d, ⁵J_{C,P} = 2.2 Hz, CH₂), 52.2 (d, ¹J_{C,P} = 153.8 Hz, CH), 53.6 (d, ²J_{C,P} = 7.1 Hz, OCH₃), 53.9 (d, ²J_{C,P} = 6.8 Hz, OCH₃), 63.9 (OCH₂CH₃), 85.1 (d, ⁴J_{C,P} = 5.3 Hz, C-sp), 96.0 (d, ⁵J_{C,P} = 2.6 Hz, C-sp), 115.3 (ArC), 115.5

(ArC), 123.2 (d, $^6J_{\text{C,P}} = 1.1$ Hz, ArC), 124.1 (d, $^3J_{\text{C,P}} = 12.8$ Hz, C-sp²), 128.3 (ArC), 128.4 (ArC), 131.4 (ArC), 140.0 (d, $^3J_{\text{C,P}} = 16.0$ Hz, ArC), 145.3 (d, $^2J_{\text{C,P}} = 4.7$ Hz, C-sp²), 152.3 (ArC) ppm. HRMS (ESI): MNa⁺, found 448.1669. C₂₄H₂₈NNaO₄P requires 448.1648.

Dimethyl (4-Fluorophenylamino)(2-(phenylethynyl)-cyclopent-1-enyl)methylphosphonate (7d). Yellow solid, mp 102–104 °C. Yield 0.56 g, 70%. IR (KBr): ν_{max} 3453 (NH), 2220(C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.79–1.97 (2H, m, CH₂CH₂CH₂), 2.34–2.44 (1H, m, CH₂CH₂CH₂), 2.57–2.63 (3H, m, CH₂CH₂CH₂), 3.80 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH₃), 3.85 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH₃), 4.93 (1H, d, $^3J_{\text{H,P}} = 24.8$ Hz, CH), 6.62–6.65 (2H, m, ArH), 6.84–6.90 (2H, m, ArH), 7.33–7.36 (3H, m, ArH), 7.46–7.49 (2H, m, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 22.3 (CH₂), 32.6 (d, $^3J_{\text{C,P}} = 1.2$ Hz, CH₂), 36.8 (d, $^5J_{\text{C,P}} = 2.3$ Hz, CH₂), 51.9 (d, $^1J_{\text{C,P}} = 154.0$ Hz, CH), 53.7 (d, $^2J_{\text{C,P}} = 7.2$ Hz, OCH₃), 53.9 (d, $^2J_{\text{C,P}} = 6.8$ Hz, OCH₃), 84.9 (d, $^4J_{\text{C,P}} = 5.3$ Hz, C-sp), 96.2 (d, $^5J_{\text{C,P}} = 2.6$ Hz, C-sp), 114.8 (d, $^3J_{\text{C,F}} = 7.4$ Hz, ArC), 115.7 (d, $^2J_{\text{C,F}} = 22.3$ Hz, ArC), 123.0 (d, $^6J_{\text{C,P}} = 0.9$ Hz, ArC), 124.4 (d, $^3J_{\text{C,P}} = 12.7$ Hz, C-sp²), 128.5 (ArC), 131.4 (ArC), 142.5 (dd, $^3J_{\text{C,P}} = 16.3$ Hz, $^4J_{\text{C,F}} = 2.0$ Hz, ArC), 144.9 (d, $^2J_{\text{C,P}} = 4.9$ Hz, C-sp²), 156.5 (d, $^1J_{\text{C,F}} = 234.9$ Hz, ArC) ppm. HRMS (ESI): MNa⁺, found 422.1283. C₂₂H₂₃FNNaO₃P requires 422.1292.

Dimethyl (4-Chlorophenylamino)(2-(phenylethynyl)-cyclopent-1-enyl)methylphosphonate (7e). Yellow solid, mp 129–131 °C. Yield 0.49 g, 59%. IR (KBr): ν_{max} 3418 (NH), 2215 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.79–1.97 (2H, m, CH₂CH₂CH₂), 2.34–2.43 (1H, m, CH₂CH₂CH₂), 2.58–2.63 (3H, m, CH₂CH₂CH₂), 3.80 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH₃), 3.84 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH₃), 4.94 (1H, d, $^3J_{\text{H,P}} = 24.8$ Hz, CH), 6.13–6.65 (2H, m, ArH), 7.09–7.13 (2H, m, ArH), 7.33–7.37 (3H, m, ArH), 7.46–7.49 (2H, m, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 22.2 (CH₂), 32.6 (d, $^3J_{\text{C,P}} = 1.1$ Hz, CH₂), 36.7 (d, $^5J_{\text{C,P}} = 2.4$ Hz, CH₂), 51.3 (d, $^1J_{\text{C,P}} = 153.9$ Hz, CH), 53.6 (d, $^2J_{\text{C,P}} = 7.2$ Hz, OCH₃), 53.8 (d, $^2J_{\text{C,P}} = 6.8$ Hz, OCH₃), 84.8 (d, $^4J_{\text{C,P}} = 5.3$ Hz, C-sp), 96.3 (d, $^5J_{\text{C,P}} = 2.6$ Hz, C-sp), 114.9 (ArC), 123.0 (d, $^6J_{\text{C,P}} = 0.9$ Hz, ArC), 124.4 (d, $^3J_{\text{C,P}} = 12.7$ Hz, C-sp²), 128.4 (ArC), 128.4 (ArC), 129.0 (ArC), 131.3 (ArC), 144.5 (d, $^2J_{\text{C,P}} = 5.0$ Hz, C-sp²), 144.8 (d, $^3J_{\text{C,P}} = 15.8$ Hz, ArC) ppm. HRMS (ESI): MNa⁺, found 438.0999. C₂₂H₂₃ClNNaO₃P requires 438.0996.

Dimethyl (Phenylamino)(2-(*p*-tolylethynyl)cyclopent-1-enyl)methylphosphonate (7f). Yellow solid, mp 143–145 °C. Yield 0.65 g, 82%. IR (KBr): ν_{max} 3402 (NH), 2179 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.78–1.96 (2H, m, CH₂CH₂CH₂), 2.37 (3H, s, CH₃), 2.40–2.47 (1H, m, CH₂CH₂CH₂), 2.57–2.67 (3H, m, CH₂CH₂CH₂), 3.80 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH₃), 3.84 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH₃), 5.01 (1H, d, $^3J_{\text{H,P}} = 24.8$ Hz, CH), 6.70–6.77 (3H, m, ArH), 7.15–7.19 (4H, m, ArH), 7.37–7.39 (2H, m, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 21.5 (CH₃), 22.2 (CH₂), 32.6 (d, $^3J_{\text{C,P}} = 1.5$ Hz, CH₂), 36.7 (d, $^5J_{\text{C,P}} = 2.3$ Hz, CH₂), 51.1 (d, $^1J_{\text{C,P}} = 153.6$ Hz, CH), 53.6 (d, $^2J_{\text{C,P}} = 7.1$ Hz, OCH₃), 53.8 (d, $^2J_{\text{C,P}} = 6.7$ Hz, OCH₃), 84.4 (d, $^4J_{\text{C,P}} = 5.3$ Hz, C-sp), 96.2 (d, $^5J_{\text{C,P}} = 2.8$ Hz, C-sp), 113.7 (ArC), 118.6 (ArC), 120.0 (d, $^6J_{\text{C,P}} = 1.1$ Hz, ArC), 124.1 (d, $^3J_{\text{C,P}} = 12.6$ Hz, C-sp²), 129.1 (ArC), 129.2 (ArC), 131.2 (ArC), 131.3 (ArC), 138.5 (ArC), 144.6 (d, $^2J_{\text{C,P}} = 4.7$ Hz, C-sp²), 146.2 (d, $^3J_{\text{C,P}} = 14.0$ Hz, ArC) ppm. HRMS (ESI): MNa⁺, found 418.1542. C₂₃H₂₆NNaO₃P requires 418.1543.

Dimethyl (4-Methoxyphenylamino)(2-(*p*-tolylethynyl)-cyclopent-1-enyl)methylphosphonate (7g). Yellow solid, mp 110–112 °C. Yield 0.63 g, 74%. IR (KBr): ν_{max} 3488 (NH), 2197 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.77–1.95 (2H, m, CH₂CH₂CH₂), 2.36 (3H, s, CH₃), 2.39–2.45 (1H, m, CH₂CH₂CH₂), 2.55–2.66 (3H, m, CH₂CH₂CH₂), 3.72 (3H, s, OCH₃), 3.79 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH₃), 3.84 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH₃), 4.80 (1H, d, $^3J_{\text{H,P}} = 24.4$ Hz, CH), 6.68 (2H, d, $^3J = 8.8$ Hz, ArH), 7.15 (2H, d, $^3J = 8.8$ Hz, ArH), 7.15 (2H, d, $^3J = 7.6$ Hz, ArH), 7.37 (2H, d, $^3J = 8.0$ Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 21.5 (CH₃), 22.3 (CH₂), 32.6 (d, $^3J_{\text{C,P}} = 1.1$ Hz, CH₂), 36.8 (d, $^5J_{\text{C,P}} = 2.2$ Hz, CH₂), 52.1 (d, $^1J_{\text{C,P}} = 153.6$ Hz, CH), 53.6 (d, $^2J_{\text{C,P}} = 7.1$ Hz, OCH₃), 53.9 (d, $^2J_{\text{C,P}} = 6.7$ Hz, OCH₃), 55.6 (OCH₃), 84.5 (d, $^4J_{\text{C,P}} = 5.4$ Hz, C-sp), 96.2 (d, $^5J_{\text{C,P}} = 2.7$ Hz, C-sp), 114.7 (ArC), 115.3, (ArC), 120.1

(d, $^6J_{\text{C,P}} = 0.1$ Hz, ArC), 124.3 (d, $^3J_{\text{C,P}} = 12.8$ Hz, C-sp²), 129.2 (ArC), 131.3 (ArC), 138.6 (ArC), 140.1 ($^3J_{\text{C,P}} = 16.4$ Hz, ArC), 144.8 (d, $^2J_{\text{C,P}} = 4.8$ Hz, C-sp²) ppm. HRMS (ESI): MNa⁺, found 448.1642. C₂₄H₂₈NNaO₄P requires 448.1648.

Dimethyl (2-((4-Ethylphenyl)ethynyl)cyclopent-1-enyl)(4-methoxyphenylamino)methylphosphonate (7h). Yellow solid, mp 93–95 °C. Yield 0.35 g, 40%. IR (KBr): ν_{max} 3448 (NH), 2202 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.24 (3H, t, $^3J = 7.6$ Hz, CH₂CH₃), 1.77–1.95 (2H, m, CH₂CH₂CH₂), 2.37–2.46 (1H, m, CH₂CH₂CH₂), 2.55–2.62 (3H, m, CH₂CH₂CH₂), 2.66 (2H, q, $^3J = 7.6$ Hz, CH₂CH₃), 3.72 (3H, s, OCH₃), 3.79 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH₃), 3.84 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH₃), 4.94 (1H, d, $^3J_{\text{H,P}} = 24.8$ Hz, CH), 6.68 (2H, d, $^3J = 9.2$ Hz, ArH), 6.75 (2H, d, $^3J = 8.8$ Hz, ArH), 7.18 (2H, d, $^3J = 8.4$ Hz, ArH), 7.40 (2H, d, $^3J = 8.4$ Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 15.3 (CH₃), 22.2 (CH₂), 28.8 (CH₂), 32.6 (d, $^3J_{\text{C,P}} = 1.1$ Hz, CH₂), 36.7 (d, $^5J_{\text{C,P}} = 2.2$ Hz, CH₂), 52.1 (d, $^1J_{\text{C,P}} = 153.6$ Hz, CH), 53.5 (d, $^2J_{\text{C,P}} = 7.1$ Hz, OCH₃), 53.8 (d, $^2J_{\text{C,P}} = 6.7$ Hz, OCH₃), 84.4 (d, $^4J_{\text{C,P}} = 5.4$ Hz, C-sp), 96.2 (d, $^5J_{\text{C,P}} = 2.6$ Hz, C-sp), 114.7 (ArC), 115.2, (ArC), 120.3 (d, $^6J_{\text{C,P}} = 1.1$ Hz, ArC), 124.3 (d, $^3J_{\text{C,P}} = 12.9$ Hz, C-sp²), 127.9 (ArC), 131.3 (ArC), 140.0 (d, $^3J_{\text{C,P}} = 16.8$ Hz, ArC), 144.7 (d, $^2J_{\text{C,P}} = 4.6$ Hz, C-sp²), 144.8 (ArC), 152.9 (ArC) ppm. HRMS (ESI): MNa⁺, found 462.1808. C₂₅H₃₀NNaO₄P requires 462.1805.

Dimethyl (2-(Hex-1-ynyl)cyclopent-1-enyl)(phenylamino)-methylphosphonate (7i). Yellowish oil. Yield 0.36 g, 50%. IR (KBr): ν_{max} 3440 (NH), 2214 (C≡C) cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 0.94 (3H, t, $^3J = 7.2$ Hz, CH₂(CH₂)₂CH₃), 1.42–1.63 (4H, m, CH₂(CH₂)₂CH₃), 1.69–1.91 (2H, m, CH₂CH₂CH₂), 2.29–2.55 (6H, m, CH₂CH₂CH₂ and CH₂(CH₂)₂CH₃), 3.77 (3H, d, $^3J_{\text{H,P}} = 10.5$ Hz, OCH₃), 3.82 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH₃), 4.78 (1H, d, $^3J_{\text{H,P}} = 24.6$ Hz, CH), 6.66–6.69 (2H, m, ArH), 6.71–6.76 (1H, m, ArH), 7.13–7.18 (2H, m, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 13.5 (CH₃), 19.3 (CH₂), 21.9 (CH₂), 22.0 (CH₂), 32.0 (CH₂), 36.9 (d, $^5J_{\text{C,P}} = 2.1$ Hz, CH₂), 50.9 (d, $^1J_{\text{C,P}} = 154.2$ Hz, CH), 53.5 (d, $^2J_{\text{C,P}} = 7.3$ Hz, OCH₃), 53.6 (d, $^2J_{\text{C,P}} = 6.9$ Hz, OCH₃), 76.2 (d, $^4J_{\text{C,P}} = 5.4$ Hz, C-sp), 97.3 (d, $^5J_{\text{C,P}} = 2.2$ Hz, C-sp), 113.7 (ArC), 118.5 (ArC), 124.9 (d, $^3J_{\text{C,P}} = 13.0$ Hz, C-sp²), 129.1 (ArC), 142.3 (d, $^2J_{\text{C,P}} = 4.4$ Hz, C-sp²), 146.2 (d, $^3J_{\text{C,P}} = 15.5$ Hz, ArC) ppm. HRMS (ESI): MNa⁺, found 384.1698. C₂₀H₂₈NNaO₃P requires 384.1704.

Dimethyl (2-(Hex-1-ynyl)cyclopent-1-enyl)(4-methoxyphenylamino)methylphosphonate (7j). Yellowish oil. Yield 0.46 g, 59%. IR (KBr): ν_{max} 3418 (NH), 2211 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.94 (3H, t, $^3J = 7.6$ Hz, CH₂(CH₂)₂CH₃), 1.43–1.61 (4H, m, CH₂(CH₂)₂CH₃), 1.69–1.88 (2H, m, CH₂CH₂CH₂), 2.26–2.56 (6H, m, CH₂CH₂CH₂ and CH₂(CH₂)₂CH₃), 3.72 (3H, s, OCH₃), 3.76 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH₃), 3.81 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH₃), 4.83 (1H, d, $^3J_{\text{H,P}} = 24.4$ Hz, CH), 6.62 (2H, d, $^3J = 9.2$ Hz, ArH), 6.74 (2H, d, $^3J = 9.2$ Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 13.5 (CH₃), 19.3 (CH₂), 21.9 (CH₂), 22.0 (CH₂), 32.0 (d, $^3J_{\text{C,P}} = 1.0$ Hz, CH₂), 36.9 (d, $^5J_{\text{C,P}} = 2.3$ Hz, CH₂), 51.7 (d, $^1J_{\text{C,P}} = 154.2$ Hz, CH), 53.4 (d, $^2J_{\text{C,P}} = 7.1$ Hz, OCH₃), 53.6 (d, $^2J_{\text{C,P}} = 6.7$ Hz, OCH₃), 55.5 (OCH₃), 76.3 (d, $^4J_{\text{C,P}} = 5.2$ Hz, C-sp), 97.1 (d, $^5J_{\text{C,P}} = 2.5$ Hz, C-sp), 114.6 (ArC), 115.0 (ArC), 124.9 (d, $^3J_{\text{C,P}} = 13.0$ Hz, C-sp²), 140.2 (d, $^2J_{\text{C,P}} = 16.6$ Hz, ArC), 142.6 (d, $^2J_{\text{C,P}} = 4.5$ Hz, C-sp²), 152.7 (ArC) ppm. HRMS (ESI): MNa⁺, found 414.1785. C₂₁H₃₀NNaO₄P requires 414.1810.

Dimethyl (4-Fluorophenylamino)(2-(hex-1-ynyl)cyclopent-1-enyl)methylphosphonate (7k). Yellow solid, mp 68–70 °C. Yield 0.42 g, 55%. IR (KBr): ν_{max} 3469 (NH), 2216 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.94 (3H, t, $^3J = 7.6$ Hz, CH₂(CH₂)₂CH₃), 1.43–1.52 (2H, m, CH₂CH₂CH₂CH₃), 1.54–1.61 (2H, m, CH₂CH₂CH₂CH₃), 1.70–1.89 (2H, m, CH₂CH₂CH₂), 2.25–2.34 (1H, m, CH₂CH₂CH₂), 2.41–2.57 (5H, m, CH₂CH₂CH₂ and CH₂(CH₂)₂CH₃), 3.77 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH₃), 3.82 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH₃), 4.83 (1H, d, $^3J_{\text{H,P}} = 24.4$ Hz, CH), 6.58–6.61 (2H, m, ArH), 6.83–6.88 (2H, m, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 13.5 (CH₃), 19.3 (CH₂), 21.9 (CH₂), 22.1 (CH₂), 30.9 (CH₂), 32.0 (d, $^3J_{\text{C,P}} = 1.0$ Hz, CH₂), 36.9 (d, $^5J_{\text{C,P}} = 2.3$ Hz, CH₂), 51.5 (d, $^1J_{\text{C,P}} = 154.3$ Hz, CH), 53.5 (d, $^2J_{\text{C,P}} = 7.1$ Hz, OCH₃), 53.6 (d, $^2J_{\text{C,P}} = 6.8$ Hz, OCH₃), 76.2 (d, $^4J_{\text{C,P}} = 5.2$ Hz, C-sp), 97.4 (d, $^5J_{\text{C,P}}$

= 2.5 Hz, C-sp), 114.7 (d, $^3J_{\text{C,F}} = 7.4$ Hz, ArC), 115.5, (d, $^2J_{\text{C,F}} = 22.2$ Hz, ArC), 125.3 (d, $^3J_{\text{C,P}} = 12.9$ Hz, C-sp 2), 142.1 (d, $^2J_{\text{C,P}} = 4.6$ Hz, C-sp 2), 142.5 (dd, $^3J_{\text{C,P}} = 16.2$ Hz, $^4J_{\text{C,F}} = 1.8$ Hz, ArC), 156.3 (d, $^1J_{\text{C,F}} = 234.7$ Hz, ArC) ppm. HRMS (ESI): MNa^+ , found 402.1603. $\text{C}_{20}\text{H}_{27}\text{FNNaO}_3\text{P}$ requires 402.1605.

Dimethyl (4-Chlorophenylamino)(2-(hex-1-ynyl)cyclopent-1-enyl)methylphosphonate (7l). Yellow solid, mp 73–75 °C. Yield 0.36 g, 45%. IR (KBr): ν_{max} 3433 (NH), 2213 ($\text{C}\equiv\text{C}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 0.94 (3H, t, $^3J = 7.2$ Hz, $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.42–1.51 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.53–1.61 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.70–1.89 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.26–2.31 (1H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.41–2.55 (5H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 3.76 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH_3), 3.81 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH_3), 4.84 (1H, d, $^3J_{\text{H,P}} = 24.8$ Hz, CH), 6.58 (2H, d, $^3J = 9.2$ Hz, ArH), 7.09 (2H, d, $^3J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.5 (CH_3), 19.2 (CH_2), 21.9 (CH_2), 22.0 (CH_2), 30.9 (CH_2), 32.0 (d, $^3J_{\text{C,P}} = 1.1$ Hz, CH_2), 36.8 (d, $^5J_{\text{C,P}} = 2.2$ Hz, CH_2), 51.0 (d, $^1J_{\text{C,P}} = 154.3$ Hz, CH), 53.5 (d, $^2J_{\text{C,P}} = 4.3$ Hz, OCH_3), 53.6 (d, $^2J_{\text{C,P}} = 3.9$ Hz, OCH_3), 76.1 (d, $^4J_{\text{C,P}} = 5.3$ Hz, C-sp), 97.5 (d, $^5J_{\text{C,P}} = 2.4$ Hz, C-sp), 114.9 (ArC), 123.1 (ArC), 125.4 (d, $^3J_{\text{C,P}} = 12.9$ Hz, C-sp 2), 128.9 (ArC), 141.8 (d, $^2J_{\text{C,P}} = 4.6$ Hz, C-sp 2), 144.8 (d, $^3J_{\text{C,P}} = 16.6$ Hz, ArC) ppm. HRMS (ESI): MNa^+ , found 418.1301. $\text{C}_{20}\text{H}_{27}\text{ClNNaO}_3\text{P}$ requires 418.1309.

Dimethyl (2-(Hept-1-ynyl)cyclopent-1-enyl)(phenylamino)methylphosphonate (7m). Yellowish oil. Yield 0.31 g, 41%. IR (KBr): ν_{max} 3409 (NH), 2216 ($\text{C}\equiv\text{C}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 0.91 (3H, t, $^3J = 7.6$ Hz, $\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.30–1.39 (2H, m, $\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.40–1.48 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.60 (2H, quint, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.71–1.89 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.31–2.59 (6H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 3.77 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH_3), 3.82 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH_3), 4.92 (1H, d, $^3J_{\text{H,P}} = 24.8$ Hz, CH), 6.67 (2H, d, $^3J = 7.6$ Hz, ArH), 6.74 (1H, t, $^3J = 7.6$ Hz, ArH), 7.16 (2H, t, $^3J = 7.6$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.9 (CH_3), 19.6 (CH_2), 22.0 (CH_2), 22.2 (CH_2), 28.5 (CH_2), 31.0 (CH_2), 32.0 (d, $^3J_{\text{C,P}} = 1.0$ Hz, CH_2), 36.9 (d, $^5J_{\text{C,P}} = 2.3$ Hz, CH_2), 50.9 (d, $^1J_{\text{C,P}} = 154.0$ Hz, CH), 53.5 (d, $^2J_{\text{C,P}} = 7.0$ Hz, OCH_3), 53.7 (d, $^2J_{\text{C,P}} = 6.8$ Hz, OCH_3), 76.2 (d, $^4J_{\text{C,P}} = 5.3$ Hz, C-sp), 97.3 (d, $^5J_{\text{C,P}} = 2.5$ Hz, C-sp), 113.7 (ArC), 118.5 (ArC), 124.9 (d, $^3J_{\text{C,P}} = 13.0$ Hz, C-sp 2), 129.1 (ArC), 142.3 (d, $^2J_{\text{C,P}} = 4.5$ Hz, C-sp 2), 146.2 (d, $^3J_{\text{C,P}} = 15.4$ Hz, ArC) ppm. HRMS (ESI): MNa^+ , found 398.1851. $\text{C}_{21}\text{H}_{30}\text{NNaO}_3\text{P}$ requires 398.1856.

Dimethyl (2-(Hept-1-ynyl)cyclopent-1-enyl)(4-methoxyphenylamino)methylphosphonate (7n). Yellowish oil. Yield 0.41 g, 50%. IR (KBr): ν_{max} 3450 (NH), 2221 ($\text{C}\equiv\text{C}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 0.91 (3H, t, $^3J = 7.2$ Hz, $\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.30–1.37 (2H, m, $\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.39–1.47 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.59 (2H, quint, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.70–1.88 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 2.30–2.56 (6H, m, $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 3.73 (3H, s, OCH_3), 3.77 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH_3), 3.82 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH_3), 4.84 (1H, d, $^3J_{\text{H,P}} = 24.4$ Hz, CH), 6.65 (2H, d, $^3J = 9.2$ Hz, ArH), 6.75 (2H, d, $^3J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.9 (CH_3), 19.6 (CH_2), 22.1 (CH_2), 22.2 (CH_2), 28.5 (CH_2), 31.0 (CH_2), 32.0 (CH_2), 36.9 (d, $^5J_{\text{C,P}} = 2.2$ Hz, CH_2), 51.9 (d, $^1J_{\text{C,P}} = 154.3$ Hz, CH), 53.5 (d, $^2J_{\text{C,P}} = 7.0$ Hz, OCH_3), 53.7 (d, $^2J_{\text{C,P}} = 6.7$ Hz, OCH_3), 55.6 (OCH_3), 76.2 (d, $^4J_{\text{C,P}} = 5.3$ Hz, C-sp), 97.3 (d, $^5J_{\text{C,P}} = 2.5$ Hz, C-sp), 114.6 (ArC), 115.4 (ArC), 125.1 (d, $^3J_{\text{C,P}} = 13.1$ Hz, C-sp 2), 139.8 (d, $^3J_{\text{C,P}} = 16.2$ Hz, ArC), 142.3 (d, $^2J_{\text{C,P}} = 4.6$ Hz, C-sp 2), 152.9 (ArC) ppm. HRMS (ESI): MNa^+ , found 428.1958. $\text{C}_{22}\text{H}_{32}\text{NNaO}_4\text{P}$ requires 428.1961.

Dimethyl (2-(Cyclopropylethynyl)cyclopent-1-enyl)(phenylamino)methylphosphonate (7o). Yellow solid, mp 143–145 °C. Yield 0.37 g, 53%. IR (KBr): ν_{max} 3407 (NH), 2211 ($\text{C}\equiv\text{C}$) cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 0.73–0.78 (2H, m, $\text{CH}(\text{CH}_2)_2$), 0.85–0.92 (2H, m, $\text{CH}(\text{CH}_2)_2$), 1.41–1.50 (1H, m, $\text{CH}(\text{CH}_2)_2$), 1.67–1.89 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.27–2.58 (4H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.77 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH_3), 3.82 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH_3), 4.86 (1H, d, $^3J_{\text{H,P}} = 24.9$ Hz, CH), 6.63–6.67 (2H, m, ArH), 6.71–6.76 (1H, m, ArH), 7.12–7.19 (2H, m, ArH) ppm. ^{13}C

NMR (75 MHz, CDCl_3): δ 0.3 ($\text{CH}(\text{CH}_2)_2$), 8.9 ($\text{CH}(\text{CH}_2)_2$), 9.0 ($\text{CH}(\text{CH}_2)_2$), 22.0 (CH_2), 32.1 (CH_2), 36.8 (d, $^3J_{\text{C,P}} = 2.2$ Hz, CH_2), 50.9 (d, $^1J_{\text{C,P}} = 154.2$ Hz, CH), 53.5 (d, $^2J_{\text{C,P}} = 7.1$ Hz, OCH_3), 53.7 (d, $^2J_{\text{C,P}} = 6.7$ Hz, OCH_3), 71.3 (d, $^4J_{\text{C,P}} = 5.1$ Hz, C-sp), 100.4 (d, $^5J_{\text{C,P}} = 2.5$ Hz, C-sp), 113.6 (ArC), 118.4 (ArC), 124.6 (d, $^3J_{\text{C,P}} = 13.2$ Hz, C-sp 2), 129.1 (ArC), 142.8 (d, $^2J_{\text{C,P}} = 4.5$ Hz, C-sp 2), 146.3 (d, $^3J_{\text{C,P}} = 16.6$ Hz, ArC) ppm. HRMS (ESI): MH^+ , found 346.1569. $\text{C}_{19}\text{H}_{25}\text{NO}_3\text{P}$ requires 346.1567.

Dimethyl (2-(Cyclopropylethynyl)cyclopent-1-enyl)(4-methoxyphenylamino)methylphosphonate (7p). Yellowish oil. Yield 0.41 g, 55%. IR (KBr): ν_{max} 3451 (NH), 2211 ($\text{C}\equiv\text{C}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 0.73–0.77 (2H, m, $\text{CH}(\text{CH}_2)_2$), 0.86–0.90 (2H, m, $\text{CH}(\text{CH}_2)_2$), 1.42–1.48 (1H, m, $\text{CH}(\text{CH}_2)_2$), 1.69–1.87 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.27–2.56 (4H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.73 (3H, s, OCH_3), 3.76 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH_3), 3.82 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH_3), 4.79 (1H, d, $^3J_{\text{H,P}} = 24.4$ Hz, CH), 6.61 (2H, d, $^3J = 9.2$ Hz, ArH), 6.75 (1H, d, $^3J = 9.2$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 0.42 ($\text{CH}(\text{CH}_2)_2$), 8.9 ($\text{CH}(\text{CH}_2)_2$), 9.0 ($\text{CH}(\text{CH}_2)_2$), 22.1 (CH_2), 32.2 (d, $^3J_{\text{C,P}} = 1.2$ Hz, CH_2), 36.9 (d, $^5J_{\text{C,P}} = 2.1$ Hz, CH_2), 51.8 (d, $^1J_{\text{C,P}} = 154.0$ Hz, CH), 53.4 (d, $^2J_{\text{C,P}} = 7.1$ Hz, OCH_3), 53.7 (d, $^2J_{\text{C,P}} = 6.7$ Hz, OCH_3), 55.6 (OCH_3), 71.4 (d, $^4J_{\text{C,P}} = 5.3$ Hz, C-sp), 100.4 (d, $^5J_{\text{C,P}} = 2.3$ Hz, C-sp), 114.6 (ArC), 115.1 (ArC), 124.6 (d, $^3J_{\text{C,P}} = 13.0$ Hz, C-sp 2), 140.2 (d, $^3J_{\text{C,P}} = 16.4$ Hz, ArC), 143.0 (d, $^2J_{\text{C,P}} = 4.5$ Hz, C-sp 2), 152.7 (ArC) ppm. HRMS (ESI): MNa^+ , found 398.1487. $\text{C}_{20}\text{H}_{26}\text{NNaO}_4\text{P}$ requires 398.1492.

Dimethyl (2-(Cyclopropylethynyl)cyclopent-1-enyl)(4-ethoxyphenylamino)methylphosphonate (7r). Yellow solid, mp 139–141 °C. Yield 0.44 g, 57%. IR (KBr): ν_{max} 3460 (NH), 2212 ($\text{C}\equiv\text{C}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 0.73–0.77 (2H, m, $\text{CH}(\text{CH}_2)_2$), 0.85–0.90 (2H, m, $\text{CH}(\text{CH}_2)_2$), 1.35 (3H, t, $^3J = 7.2$ Hz, OCH_2CH_3), 1.41–1.48 (1H, m, $\text{CH}(\text{CH}_2)_2$), 1.68–1.87 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.26–2.54 (4H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.76 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH_3), 3.82 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH_3), 3.94 (2H, q, $^3J = 7.2$ Hz, OCH_2CH_3), 4.79 (1H, d, $^3J_{\text{H,P}} = 24.4$ Hz, CH), 6.59 (2H, d, $^3J = 8.8$ Hz, ArH), 6.74 (1H, d, $^3J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 0.38 ($\text{CH}(\text{CH}_2)_2$), 8.9 ($\text{CH}(\text{CH}_2)_2$), 9.0 ($\text{CH}(\text{CH}_2)_2$), 14.9 (OCH_2CH_3), 22.1 (CH_2), 32.2 (d, $^3J_{\text{C,P}} = 1.0$ Hz, CH_2), 36.9 (d, $^5J_{\text{C,P}} = 2.3$ Hz, CH_2), 51.7 (d, $^1J_{\text{C,P}} = 154.1$ Hz, CH), 53.4 (d, $^2J_{\text{C,P}} = 7.1$ Hz, OCH_3), 53.7 (d, $^2J_{\text{C,P}} = 6.7$ Hz, OCH_3), 63.8 (OCH_2CH_3), 71.4 (d, $^4J_{\text{C,P}} = 5.4$ Hz, C-sp), 100.3 (d, $^5J_{\text{C,P}} = 2.4$ Hz, C-sp), 115.0 (ArC), 115.4 (ArC), 124.5 (d, $^3J_{\text{C,P}} = 12.9$ Hz, C-sp 2), 140.2 (d, $^3J_{\text{C,P}} = 16.4$ Hz, ArC), 143.1 (d, $^2J_{\text{C,P}} = 4.5$ Hz, C-sp 2), 152.0 (ArC) ppm. HRMS (ESI): MH^+ , found 390.1844. $\text{C}_{21}\text{H}_{29}\text{NO}_4\text{P}$ requires 390.1829.

Dimethyl (Phenylamino)(2-((trimethylsilyl)ethynyl)cyclopent-1-enyl)methylphosphonate (7s-TMS). Yellow solid, mp 141–143 °C. Yield 0.41 g, 54%. IR (KBr): ν_{max} 3437 (NH), 2134 ($\text{C}\equiv\text{C}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 0.24 (9H, s, $\text{Si}(\text{CH}_3)_3$), 1.73–1.91 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.35–2.60 (4H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.78 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH_3), 3.83 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH_3), 4.93 (1H, d, $^3J_{\text{H,P}} = 24.8$ Hz, CH), 6.68 (2H, d, $^3J = 7.6$ Hz, ArH), 6.76 (1H, t, $^3J = 7.6$ Hz, ArH), 7.15–7.19 (2H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 0.0 ($\text{Si}(\text{CH}_3)_3$), 22.2 (CH_2), 32.5 (d, $^3J_{\text{C,P}} = 1.2$ Hz, CH_2), 36.5 (d, $^5J_{\text{C,P}} = 2.1$ Hz, CH_2), 50.9 (d, $^1J_{\text{C,P}} = 153.3$ Hz, CH), 53.5 (d, $^2J_{\text{C,P}} = 7.1$ Hz, OCH_3), 53.8 (d, $^2J_{\text{C,P}} = 6.8$ Hz, OCH_3), 101.0 (d, $^4J_{\text{C,P}} = 5.0$ Hz, C-sp), 101.3 (d, $^5J_{\text{C,P}} = 2.1$ Hz, C-sp), 113.7 (ArC), 118.6 (ArC), 124.2 (d, $^3J_{\text{C,P}} = 12.6$ Hz, C-sp 2), 129.2 (ArC), 146.1 (d, $^3J_{\text{C,P}} = 15.2$ Hz, ArC), 146.5 (d, $^2J_{\text{C,P}} = 4.2$ Hz, C-sp 2) ppm. HRMS (ES): MNa^+ , found 400.1464. $\text{C}_{19}\text{H}_{28}\text{NNaO}_3\text{PSi}$ requires 400.1468.

Dimethyl (2-Ethynylcyclopent-1-enyl)(phenylamino)methylphosphonate (7s). This compound was synthesized from 7s-TMS by treating by 2 equiv of $\text{KF}_2\cdot\text{H}_2\text{O}$ in methanol at room temperature for 2 h. After evaporation of solvent, the residue was purified by column chromatography. Yellow solid, mp 118–119 °C. Yield 0.27 g, 83%. IR (KBr): ν_{max} 3452 (NH), 2088 ($\text{C}\equiv\text{C}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.74–1.92 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.34–2.40 (1H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.49–2.61 (3H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.38 (1H, br. s, $\text{C}\equiv\text{CH}$), 3.78 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH_3), 3.83 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH_3), 4.93 (1H, d, $^3J_{\text{H,P}} = 24.8$ Hz, CH), 6.64–6.67

(2H, m, ArH), 6.73–6.77 (1H, m, ArH), 7.14–7.19 (2H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 22.0 (CH_2), 32.4 (d, $^3J_{\text{C,P}} = 1.1$ Hz, CH_2), 36.6 (d, $^5J_{\text{C,P}} = 2.3$ Hz, CH_2), 50.9 (d, $^1J_{\text{C,P}} = 153.5$ Hz, CH), 53.5 (d, $^2J_{\text{C,P}} = 7.2$ Hz, OCH_3), 53.8 (d, $^2J_{\text{C,P}} = 6.7$ Hz, OCH_3), 79.4 (d, $^4J_{\text{C,P}} = 5.2$ Hz, C-sp), 83.9 (d, $^5J_{\text{C,P}} = 2.6$ Hz, C-sp), 113.6 (ArC), 118.6 (ArC), 123.1 (d, $^3J_{\text{C,P}} = 12.7$ Hz, C-sp 2), 129.2 (ArC), 146.1 (d, $^3J_{\text{C,P}} = 15.4$ Hz, ArC), 146.9 (d, $^2J_{\text{C,P}} = 4.6$ Hz, C-sp 2) ppm. HRMS (ESI): MH^+ , found 306.1261. $\text{C}_{16}\text{H}_{21}\text{NO}_3\text{P}$ requires 306.1254.

Dimethyl (Phenylamino)(2-(phenylethynyl)cyclohex-1-enyl)methylphosphonate (8a). Light Orange solid, mp 139–140 °C. Yield 0.39 g, 49%. IR (KBr): ν_{max} 2200 ($\text{C}\equiv\text{C}$) 3405 (NH), cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.54–1.62 (4H, m, $2 \times \text{CH}_2$), 2.04–2.17 (1H, m, CHH), 2.32–2.34 (3H, m, CHH , CH_2), 3.80 (3H, d, $^3J_{\text{H,P}} = 6.8$ Hz, OCH_3), 3.83 (3H, d, $^3J_{\text{H,P}} = 6.8$ Hz, OCH_3), 5.29 (1H, d, $^2J_{\text{H,P}} = 25.6$ Hz, CHNH), 6.70–6.76 (3H, m, ArH), 7.16–7.20 (2H, m, ArH), 7.33–7.35 (3H, m, ArH), 7.47–7.49 (2H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 21.9 (CH_2), 22.0 (CH_2), 24.8 (d, $^3J_{\text{C,P}} = 1.5$ Hz, CH_2), 30.4 (d, $^4J_{\text{C,P}} = 1.9$ Hz, CH_2), 53.7 (d, $^2J_{\text{C,P}} = 6.9$ Hz, OCH_3), 53.8 (d, $^2J_{\text{C,P}} = 7.1$ Hz, OCH_3), 54.8 (d, $^1J_{\text{C,P}} = 150.5$ Hz, CH), 88.5 (d, $^4J_{\text{C,P}} = 5.2$ Hz, C_{sp}), 94.6 (d, $^3J_{\text{C,P}} = 2.2$ Hz, C_{sp}), 113.5 (ArC), 118.3 (ArC), 120.8 (d, $^3J_{\text{C,P}} = 12.4$ Hz, C_{sp}), 123.3 (ArC), 128.2 (ArC), 128.4 (ArC), 129.3 (ArC), 131.3 (ArC), 139.5 (d, $^2J_{\text{C,P}} = 3.7$ Hz, C_{sp}), 146.3 (d, $^3J_{\text{C,P}} = 16.0$ Hz, ArC) ppm. HRMS (ESI): MNa^+ , found 418.1547. $\text{C}_{23}\text{H}_{26}\text{NNaO}_3\text{P}$ requires 418.1543.

Dimethyl (4-Methoxyphenylamino)(2-(phenylethynyl)cyclohex-1-enyl)methylphosphonate (8b). Brownish solid, mp 142–141 °C. Yield 0.43 g, 51%. IR (KBr): ν_{max} 3343 (NH), 2202 ($\text{C}\equiv\text{C}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.52–1.65 (4H, m, $2 \times \text{CH}_2$), 2.02–2.08 (1H, m, CHH), 2.31–2.39 (3H, m, CHH , CH_2), 3.73 (3H, s, OCH_3), 3.79 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH_3), 3.83 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH_3), 5.22 (1H, d, $^2J_{\text{H,P}} = 25.6$ Hz, CHNH), 6.67 (2H, d, $J = 8.8$ Hz, ArH), 6.76 (2H, d, $J = 9.2$ Hz, ArH), 7.31–7.35 (3H, m, ArH), 7.46–7.49 (2H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 21.9 (CH_2), 22.0 (CH_2), 24.8 (d, $^3J_{\text{C,P}} = 1.2$ Hz, CH_2), 30.4 (d, $^4J_{\text{C,P}} = 1.8$ Hz, CH_2), 53.6 (d, $^2J_{\text{C,P}} = 2.6$ Hz, OCH_3), 53.7 (d, $^2J_{\text{C,P}} = 2.9$ Hz, OCH_3), 55.6 (d, $^1J_{\text{C,P}} = 150.8$ Hz, CH), 55.6 (OCH_3), 88.6 (d, $^4J_{\text{C,P}} = 5.0$ Hz, C_{sp}), 94.5 (d, $^3J_{\text{C,P}} = 2.2$ Hz, C_{sp}), 114.8 (ArC), 114.9 (ArC), 120.9 (d, $^3J_{\text{C,P}} = 12.4$ Hz, C_{sp}), 123.3 (ArC), 128.2 (ArC), 128.4 (ArC), 131.3 (ArC), 139.6 (d, $^2J_{\text{C,P}} = 3.6$ Hz, C_{sp}), 140.1 (d, $^3J_{\text{C,P}} = 16.9$ Hz, ArC), 152.7 (ArC) ppm. HRMS (ESI): MNa^+ , found 448.1641. $\text{C}_{24}\text{H}_{28}\text{NNaO}_4\text{P}$ requires 448.1648.

Dimethyl (4-Fluorophenylamino)(2-(phenylethynyl)cyclohex-1-enyl)methylphosphonate (8c). Brownish solid, mp 158–159 °C. Yield 0.46 g, 56%. IR (KBr): ν_{max} 3295 (NH), 2158 ($\text{C}\equiv\text{C}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.51–1.67 (4H, m, $2 \times \text{CH}_2$), 1.98–2.01 (1H, m, CHH), 2.32–2.35 (3H, m, CHH , CH_2), 3.80 (3H, d, $^3J_{\text{H,P}} = 8.4$ Hz, OCH_3), 3.83 (3H, d, $^3J_{\text{H,P}} = 8.8$ Hz, OCH_3), 5.21 (1H, d, $^2J_{\text{H,P}} = 25.6$ Hz, CHNH), 6.63 (2H, dd, $J = 13.2$; 4.4 Hz, ArH), 6.88 (2H, t, $J = 8.8$ Hz, ArH), 7.33–7.36 (3H, m, ArH), 7.46–7.48 (2H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 21.9 (CH_2), 22.0 (CH_2), 24.8 (d, $^3J_{\text{C,P}} = 1.5$ Hz, CH_2), 30.4 (d, $^4J_{\text{C,P}} = 1.8$ Hz, CH_2), 53.6 (d, $^2J_{\text{C,P}} = 6.8$ Hz, OCH_3), 53.7 (d, $^2J_{\text{C,P}} = 7.1$ Hz, OCH_3), 55.3 (d, $^1J_{\text{C,P}} = 150.9$ Hz, CH), 88.4 (d, $^4J_{\text{C,P}} = 5.0$ Hz, C_{sp}), 94.7 (d, $^3J_{\text{C,P}} = 2.2$ Hz, C_{sp}), 114.5 (d, $^3J_{\text{C,F}} = 7.4$ Hz, ArC), 115.7 (d, $^2J_{\text{C,F}} = 22.3$ Hz, ArC), 121.2 (d, $^3J_{\text{C,P}} = 12.4$ Hz, C_{sp}), 123.2 (ArC), 128.3 (ArC), 128.4 (ArC), 131.3 (ArC), 139.2 (d, $^2J_{\text{C,P}} = 3.9$ Hz, C_{sp}), 142.5 (dd, $^3J_{\text{C,P}} = 16.7$ Hz, $^4J_{\text{C,F}} = 1.8$ Hz, ArC), 156.3 (d, $^1J_{\text{C,F}} = 234.6$ Hz, ArC) ppm. HRMS (ESI): MNa^+ , found 436.1444. $\text{C}_{23}\text{H}_{25}\text{FNNaO}_3\text{P}$ requires 436.1448.

Dimethyl (4-Chlorophenylamino)(2-(phenylethynyl)cyclohex-1-enyl)methylphosphonate (8d). Yellowish solid, mp 139–140 °C. Yield 0.38 g, 44%. IR (KBr): ν_{max} 3296 (NH), 2201 ($\text{C}\equiv\text{C}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.50–1.66 (4H, m, $2 \times \text{CH}_2$), 1.98–1.99 (1H, m, CHH), 2.32–2.33 (3H, m, CHH , CH_2), 3.80 (3H, d, $^3J_{\text{H,P}} = 6.4$ Hz, OCH_3), 3.83 (3H, d, $^3J_{\text{H,P}} = 6.4$ Hz, OCH_3), 5.22 (1H, d, $^2J_{\text{H,P}} = 26.0$ Hz, CHNH), 6.63 (2H, d, $J = 8.8$ Hz, ArH), 7.11 (2H, d, $J = 8.8$ Hz, ArH), 7.33–7.35 (3H, m, ArH), 7.46–7.48 (2H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 21.9 (CH_2), 24.8 (d, $^3J_{\text{C,P}} = 1.4$ Hz, CH_2), 30.3 (d, $^4J_{\text{C,P}} = 1.8$ Hz, CH_2), 53.6 (d, $^2J_{\text{C,P}} = 6.9$ Hz, OCH_3), 53.7 (d, $^2J_{\text{C,P}} = 7.1$ Hz, OCH_3), 54.9 (d, $^1J_{\text{C,P}} =$

151.0 Hz, CH), 88.3 (d, $^4J_{\text{C,P}} = 5.1$ Hz, C_{sp}), 94.8 (d, $^5J_{\text{C,P}} = 2.2$ Hz, C_{sp}), 114.7 (ArC), 121.2 (d, $^3J_{\text{C,P}} = 12.4$ Hz, C_{sp}), 123.0 (ArC), 123.1 (d, $^6J_{\text{C,P}} = 0.8$ Hz, ArC), 128.3 (ArC), 128.4 (ArC), 129.1 (ArC), 131.3 (ArC), 138.9 (d, $^2J_{\text{C,P}} = 4.0$ Hz, C_{sp}), 144.9 (d, $^3J_{\text{C,P}} = 16.3$ Hz, ArC) ppm. HRMS (ESI): MNa^+ , found 452.1145. $\text{C}_{23}\text{H}_{25}\text{ClNNaO}_3\text{P}$ requires 452.1153.

Dimethyl (Phenylamino)(2-(p-tolylethynyl)cyclohex-1-enyl)methylphosphonate (8e). Light orange solid, mp 133–134 °C. Yield 0.43 g, 53%. IR (KBr): ν_{max} 3304 (NH), 2201 ($\text{C}\equiv\text{C}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.54–1.65 (4H, m, $2 \times \text{CH}_2$), 2.05–2.08 (1H, m, CHH), 2.33 (3H, br. s, CHH , CH_2), 2.36 (3H, s, CH_3), 3.80 (3H, d, $^3J_{\text{H,P}} = 6.4$ Hz, OCH_3), 3.82 (3H, d, $^3J_{\text{H,P}} = 6.4$ Hz, OCH_3), 5.29 (1H, d, $^2J_{\text{H,P}} = 26.0$ Hz, CHNH), 6.70–6.76 (3H, m, ArH), 7.16 (4H, dd, $J = 13.3$; 7.6 Hz ArH), 7.37 (2H, d, $J = 7.6$ Hz ArH), 7.47–7.49 (2H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 21.5 (CH_3), 22.0 ($2 \times \text{CH}_2$), 24.8 (CH_2), 30.4 (d, $^4J_{\text{C,P}} = 1.8$ Hz, CH_2), 53.6 (d, $^2J_{\text{C,P}} = 6.8$ Hz, OCH_3), 53.8 (d, $^2J_{\text{C,P}} = 7.0$ Hz, OCH_3), 54.7 (d, $^1J_{\text{C,P}} = 150.2$ Hz, CH), 87.9 (d, $^4J_{\text{C,P}} = 5.2$ Hz, C_{sp}), 94.8 (d, $^5J_{\text{C,P}} = 1.8$ Hz, C_{sp}), 113.5 (ArC), 118.3 (ArC), 120.3 (ArC), 120.9 (d, $^3J_{\text{C,P}} = 12.6$ Hz, C_{sp}), 129.2 (ArC), 129.3 (ArC), 131.2 (ArC), 138.4 (ArC), 139.0 (d, $^2J_{\text{C,P}} = 4.0$ Hz, C_{sp}), 146.3 (d, $^3J_{\text{C,P}} = 15.8$ Hz, ArC) ppm. HRMS (ESI): MNa^+ , found 432.1699. $\text{C}_{24}\text{H}_{28}\text{NNaO}_3\text{P}$ requires 432.1699.

Dimethyl (4-Methoxyphenylamino)(2-(p-tolylethynyl)cyclohex-1-enyl)methylphosphonate (8f). Light orange solid, mp 96–97 °C. Yield 0.39 g, 44%. IR (KBr): ν_{max} 3503 (NH), 2197 ($\text{C}\equiv\text{C}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.50–1.66 (4H, m, $2 \times \text{CH}_2$), 2.01–2.08 (1H, m, CHH), 2.28–2.31 (3H, m, CHH , CH_2), 2.36 (3H, s, CH_3), 3.72 (3H, s, OCH_3), 3.79 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH_3), 3.82 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH_3), 5.22 (1H, d, $^2J_{\text{H,P}} = 25.6$ Hz, CHNH), 6.67 (2H, d, $J = 9.2$ Hz ArH), 6.76 (2H, d, $J = 9.2$ Hz ArH), 7.14 (2H, d, $J = 8.0$ Hz ArH), 7.36 (2H, d, $J = 8.0$ Hz ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 21.5 (CH_3), 22.0 ($2 \times \text{CH}_2$), 24.8 (d, $^3J_{\text{C,P}} = 1.1$ Hz, CH_2), 30.4 (d, $^4J_{\text{C,P}} = 1.7$ Hz, CH_2), 53.7 (d, $^2J_{\text{C,P}} = 3.8$ Hz, OCH_3), 53.7 (d, $^2J_{\text{C,P}} = 3.9$ Hz, OCH_3), 55.6 (d, $^1J_{\text{C,P}} = 150.6$ Hz, CH), 55.6 (OCH_3), 88.0 (d, $^4J_{\text{C,P}} = 5.2$ Hz, C_{sp}), 94.7 (d, $^5J_{\text{C,P}} = 2.0$ Hz, C_{sp}), 114.8 (ArC), 115.0 (ArC), 120.3 (ArC), 121.1 (d, $^3J_{\text{C,P}} = 12.4$ Hz, C_{sp}), 129.2 (ArC), 131.2 (ArC), 138.4 (ArC), 139.1 (d, $^2J_{\text{C,P}} = 3.6$ Hz, C_{sp}), 140.1 (d, $^3J_{\text{C,P}} = 15.9$ Hz, ArC), 152.7 (ArC) ppm. HRMS (ESI): MNa^+ , found 462.1795. $\text{C}_{25}\text{H}_{30}\text{NNaO}_4\text{P}$ requires 462.1805.

Dimethyl (2-(Pent-1-ynyl)cyclohex-1-enyl)(phenylamino)methylphosphonate (8g). Light orange solid, mp 65–66 °C. Yield 0.18 g, 25%. IR (KBr): ν_{max} 3434 (NH), 2216 ($\text{C}\equiv\text{C}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.05 (3H, t, $J = 7.6$ Hz, CH_3), 1.46–1.56 (4H, m, $2 \times \text{CH}_2$), 1.62 (2H, sext, $\text{C}\equiv\text{CCH}_2\text{CH}_2$), 1.95–2.01 (1H, m, CHH), 2.17–2.20 (2H, m, CH_2), 2.27 (1H, dd, $J = 20.0$; 4.0 Hz CHH), 2.40 (2H, t, $J = 7.2$ Hz, $\text{C}\equiv\text{CCH}_2\text{CH}_2$), 3.78 (3H, d, $^3J_{\text{H,P}} = 8.8$ Hz, OCH_3), 3.80 (3H, d, $^3J_{\text{H,P}} = 9.2$ Hz, OCH_3), 5.21 (1H, d, $^2J_{\text{H,P}} = 26.0$ Hz, CHNH), 6.66–6.69 (2H, m, ArH), 6.73 (1H, t, $J = 7.6$ Hz, ArH), 7.16 (2H, dd, $J = 8.4$; 7.2 Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.5 (CH_3), 21.6 (CH_2), 22.0 (CH_2 , $2 \times \text{CH}_{2\text{chex}}$), 22.4 (CH_2), 24.4 (d, $^3J_{\text{C,P}} = 1.5$ Hz, CH_2), 30.8 (d, $^4J_{\text{C,P}} = 1.9$ Hz, CH_2), 53.4 (d, $^2J_{\text{C,P}} = 6.9$ Hz, OCH_3), 53.7 (d, $^2J_{\text{C,P}} = 7.0$ Hz, OCH_3), 54.5 (d, $^1J_{\text{C,P}} = 150.9$ Hz, CH), 80.0 (d, $^4J_{\text{C,P}} = 4.9$ Hz, C_{sp}), 95.5 (d, $^5J_{\text{C,P}} = 2.0$ Hz, C_{sp}), 113.6 (ArC), 118.2 (ArC), 121.5 (d, $^3J_{\text{C,P}} = 12.6$ Hz, C_{sp}), 129.2 (ArC), 136.9 (d, $^2J_{\text{C,P}} = 3.5$ Hz, C_{sp}), 146.2 (d, $^3J_{\text{C,P}} = 16.0$ Hz, ArC) ppm. HRMS (ESI): MNa^+ , found 384.1695. $\text{C}_{20}\text{H}_{28}\text{NNaO}_3\text{P}$ requires 384.1699.

Dimethyl (4-Methoxyphenylamino)(2-(pent-1-ynyl)cyclohex-1-enyl)methylphosphonate (8h). Brownish solid, mp 92–93 °C. Yield 0.51 g, 65%. IR (KBr): ν_{max} 3308 (NH), 2216 ($\text{C}\equiv\text{C}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.04 (3H, t, $J = 7.2$ Hz, CH_3), 1.41–1.55 (4H, m, $2 \times \text{CH}_2$), 1.61 (2H, sext, $J = 7.2$ Hz, $\text{C}\equiv\text{CCH}_2\text{CH}_2$), 1.92–1.98 (1H, m, CHH), 2.15–2.18 (2H, m, CH_2), 2.24–2.29 (1H, m, CHH), 2.39 (2H, t, $J = 6.8$ Hz, $\text{C}\equiv\text{CCH}_2\text{CH}_2$), 3.73 (3H, s, OCH_3), 3.77 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH_3), 3.80 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH_3), 5.14 (1H, d, $^2J_{\text{H,P}} = 25.6$ Hz, CHNH), 6.63 (2H, d, $J = 9.2$ Hz, ArH), 6.75 (2H, d, $J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.5 (CH_3), 21.6 (CH_2), 22.0 ($2 \times \text{CH}_{2\text{chex}}$), 22.4 (CH_2), 24.4 (d, $^3J_{\text{C,P}} = 1.3$ Hz, CH_2), 30.8 (d, $^4J_{\text{C,P}} = 1.8$

Hz, CH₂), 53.5 (d, ²J_{C,P} = 6.8 Hz, OCH₃), 53.6 (d, ²J_{C,P} = 7.0 Hz, OCH₃), 55.3 (d, ¹J_{C,P} = 151.2 Hz, CH), 55.6 (OCH₃), 80.0 (d, ⁴J_{C,P} = 4.9 Hz, C_{sp}), 95.4 (d, ⁵J_{C,P} = 2.1 Hz, C_{sp}), 114.7 (ArC), 115.0 (ArC), 121.6 (d, ³J_{C,P} = 12.7 Hz, C_{sp}), 136.9 (d, ²J_{C,P} = 3.4 Hz, C_{sp}), 140.1 (d, ³J_{C,P} = 16.5 Hz, ArC), 152.6 (ArC) ppm. HRMS (ESI): MNa⁺, found 414.1811. C₂₁H₃₀NNaO₄P requires 414.1805.

Dimethyl (4-Fluorophenylamino)(2-(pent-1-ynyl)cyclohex-1-enyl)methylphosphonate (8i). Brownish solid, mp 97–98 °C. Yield 0.27 g, 35%. IR (KBr): $\nu_{\max}$ 3315 (NH), 2216 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.03 (3H, t, *J* = 7.2 Hz, CH₃), 1.45–1.63 (6H, 2m (overlap), C≡CCH₂CH₂, 2 × CH₂), 1.89–1.94 (1H, m, CHH), 2.15–2.18 (2H, m, CH₂), 2.26–2.28 (1H, m, CHH), 2.39 (2H, t, *J* = 7.2 Hz, C≡CCH₂CH₂), 3.77 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 3.80 (3H, d, ³J_{H,P} = 10.4 Hz, OCH₃), 5.13 (1H, d, ²J_{H,P} = 25.6 Hz, CHNH), 6.59 (2H, dd, *J* = 8.8 Hz, ³J_{H,F} = 4.4 Hz, ArH), 6.86 (2H, t, *J* = 8.8 Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 13.5 (CH₃), 21.5 (CH₂), 22.0 (2 × CH₂chex), 22.4 (CH₂), 24.3 (d, ³J_{C,P} = 1.4 Hz, CH₂), 30.7 (d, ⁴J_{C,P} = 1.8 Hz, CH₂), 53.4 (d, ²J_{C,P} = 6.8 Hz, OCH₃), 53.7 (d, ²J_{C,P} = 7.0 Hz, OCH₃), 55.0 (d, ¹J_{C,P} = 151.3 Hz, CH), 79.9 (d, ⁴J_{C,P} = 4.9 Hz, C_{sp}), 95.6 (d, ⁵J_{C,P} = 2.0 Hz, C_{sp}), 114.5 (d, ³J_{C,F} = 7.3 Hz, ArC), 115.6 (d, ²J_{C,F} = 22.2 Hz), 121.9 (d, ³J_{C,P} = 12.6 Hz, C_{sp}), 136.5 (d, ²J_{C,P} = 3.5 Hz, C_{sp}), 142.4 (dd, ³J_{C,P} = 17.3 Hz, ⁴J_{C,F} = 1.3 Hz, ArC), 156.2 (d, ¹J_{C,F} = 234.4 Hz, ArC) ppm. HRMS (ESI): MNa⁺, found 402.1598. C₂₀H₂₇FNNaO₃P requires 402.1605.

Dimethyl (2-(Hex-1-ynyl)cyclohex-1-enyl)(phenylamino)methylphosphonate (8j). Yellowish solid, mp 55–56 °C. Yield 0.37 g, 49%. IR (KBr): $\nu_{\max}$ 3514 (NH), 2214 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.97 (3H, t, *J* = 7.2 Hz, CH₃), 1.46–1.60 (8H, m, C≡CCH₂CH₂CH₂, 2 × CH₂), 1.96–2.01 (1H, m, CHH), 2.18–2.19 (2H, m, CH₂), 2.25–2.30 (1H, m, CHH), 2.43 (2H, t, *J* = 6.4 Hz, C≡CCH₂CH₂CH₂), 3.78 (3H, d, ³J_{H,P} = 9.6 Hz, OCH₃), 3.80 (3H, d, ³J_{H,P} = 9.6 Hz, OCH₃), 5.20 (1H, d, ²J_{H,P} = 25.6 Hz, CHNH), 6.68 (2H, dd, *J* = 8.4; 0.8 Hz, ArH), 6.73 (1H, tt, *J* = 7.6; 1.2 Hz, ArH), 7.16 (2H, dd, *J* = 8.4; 7.2 Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 13.6 (CH₃), 19.2 (CH₂), 22.0 (CH₂, 2 × CH₂chex), 24.4 (d, ³J_{C,P} = 1.5 Hz, CH₂), 30.8 (d, ⁴J_{C,P} = 1.8 Hz, CH₂), 31.0 (CH₂), 53.4 (d, ²J_{C,P} = 6.9 Hz, OCH₃), 53.7 (d, ²J_{C,P} = 7.2 Hz, OCH₃), 54.6 (d, ¹J_{C,P} = 150.7 Hz, CH), 79.9 (d, ⁴J_{C,P} = 4.8 Hz, C_{sp}), 95.6 (d, ⁵J_{C,P} = 2.0 Hz, C_{sp}), 113.6 (ArC), 118.2 (ArC), 121.5 (d, ³J_{C,P} = 12.6 Hz, C_{sp}), 129.2 (ArC), 136.8 (d, ²J_{C,P} = 3.6 Hz, C_{sp}), 146.2 (d, ³J_{C,P} = 16.0 Hz, ArC) ppm. HRMS (ESI): MNa⁺, found 398.1858. C₂₁H₃₀NNaO₃P requires 398.1856.

Dimethyl (2-(Hex-1-ynyl)cyclohex-1-enyl)(4-methoxyphenylamino)methylphosphonate (8k). Light brown solid, mp 72–71 °C. Yield 0.45 g, 56%. IR (KBr): $\nu_{\max}$ 3307 (NH), 2213 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.93 (3H, t, *J* = 7.2 Hz, CH₃), 1.43–1.60 (8H, m, C≡CCH₂CH₂CH₂, 2 × CH₂), 1.93–1.98 (1H, m, CHH), 2.14–2.17 (2H, m, CH₂), 2.24–2.29 (1H, m, CHH), 2.41 (2H, t, *J* = 6.4 Hz, C≡CCH₂CH₂CH₂), 3.73 (3H, s, OCH₃), 3.77 (3H, d, ³J_{H,P} = 10.4 Hz, OCH₃), 3.80 (3H, d, ³J_{H,P} = 10.4 Hz, OCH₃), 5.13 (1H, d, ²J_{H,P} = 25.6 Hz, CHNH), 6.63 (2H, d, *J* = 9.2 Hz, ArH), 6.75 (2H, d, *J* = 9.2 Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 13.6 (CH₃), 19.2 (CH₂), 21.9 (CH₂), 22.0 (2 × CH₂chex), 24.4 (d, ³J_{C,P} = 1.4 Hz, CH₂), 30.8 (d, ⁴J_{C,P} = 1.8 Hz, CH₂), 31.0 (CH₂), 53.5 (d, ²J_{C,P} = 6.8 Hz, OCH₃), 53.6 (d, ²J_{C,P} = 7.1 Hz, OCH₃), 55.3 (d, ¹J_{C,P} = 151.1 Hz, CH), 55.6 (OCH₃), 79.9 (d, ⁴J_{C,P} = 4.9 Hz, C_{sp}), 95.5 (d, ⁵J_{C,P} = 2.0 Hz, C_{sp}), 114.7 (ArC), 114.9 (ArC), 121.6 (d, ³J_{C,P} = 12.6 Hz, C_{sp}), 136.9 (d, ²J_{C,P} = 3.4 Hz, C_{sp}), 140.1 (d, ³J_{C,P} = 16.9 Hz, ArC), 152.6 (ArC) ppm. HRMS (ESI): MNa⁺, found 428.1953. C₂₂H₃₂NNaO₄P requires 428.1961.

Dimethyl (2-(Cyclopropylethynyl)cyclohex-1-enyl)(phenylamino)methylphosphonate (8l). Yellowish solid, mp 125–124 °C. Yield 0.26 g, 36%. IR (KBr): $\nu_{\max}$ 3308 (NH), 2207 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.74–0.77 (2H, m, CH(CH₂)₂), 0.85–0.89 (2H, m, CH(CH₂)₂), 1.51–1.58 (5H, m, CH(CH₂)₂, 2 × CH₂), 1.95–2.00 (1H, m, CHH), 2.15–2.17 (2H, m, CH₂), 2.21–2.28 (1H, m, CHH), 3.77 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 3.81 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 5.14 (1H, d, ²J_{H,P} = 25.6 Hz, CHNH), 6.65 (2H, d, *J* = 7.6 Hz, ArH), 6.74 (1H, t, *J* = 7.6 Hz, ArH), 7.33–7.35 (2H, dd, *J* = 8.4; 7.6 Hz, ArH) ppm. ¹³C NMR (100

MHz, CDCl₃): δ 0.3 (CH(CH₂)₂), 8.8 (CH(CH₂)₂), 9.0 (CH(CH₂)₂), 22.0 (2 × CH₂), 24.5 (d, ³J_{C,P} = 1.6 Hz, CH₂), 30.6 (d, ⁴J_{C,P} = 1.7 Hz, CH₂), 53.5 (d, ²J_{C,P} = 6.8 Hz, OCH₃), 53.7 (d, ²J_{C,P} = 7.1 Hz, OCH₃), 54.6 (d, ¹J_{C,P} = 150.8 Hz, CH), 74.9 (d, ⁴J_{C,P} = 5.0 Hz, C_{sp}), 98.9 (d, ⁵J_{C,P} = 2.0 Hz, C_{sp}), 113.6 (ArC), 118.2 (ArC), 121.3 (d, ³J_{C,P} = 12.4 Hz, C_{sp}), 129.2 (ArC), 137.3 (d, ²J_{C,P} = 3.5 Hz, C_{sp}), 146.3 (d, ³J_{C,P} = 15.7 Hz, ArC) ppm. HRMS (ESI): MNa⁺, found 382.1542. C₂₀H₂₆NNaO₃P requires 382.1543.

Dimethyl (2-(Cyclopropylethynyl)cyclohex-1-enyl)(4-methoxyphenylamino)methylphosphonate (8m). Yellowish solid, mp 98–99 °C. Yield 0.45 g, 58%. IR (KBr): $\nu_{\max}$ 3306 (NH), 2213 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.72–0.76 (2H, m, CH(CH₂)₂), 0.85–0.89 (2H, m, CH(CH₂)₂), 1.41–1.58 (5H, m, CH(CH₂)₂, 2 × CH₂), 1.91–1.97 (1H, m, CHH), 2.13–2.16 (2H, m, CH₂), 2.23–2.28 (1H, m, CHH), 3.74 (3H, s, OCH₃), 3.76 (3H, d, ³J_{H,P} = 10.4 Hz, OCH₃), 3.81 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 5.07 (1H, d, ²J_{H,P} = 25.6 Hz, CHNH), 6.60 (2H, d, *J* = 8.8 Hz, ArH), 6.76 (2H, d, *J* = 9.2 Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 0.3 (CH(CH₂)₂), 8.8 (CH(CH₂)₂), 9.0 (CH(CH₂)₂), 22.0 (2 × CH₂), 24.5 (CH₂), 30.6 (d, ⁴J_{C,P} = 1.8 Hz, CH₂), 53.5 (d, ²J_{C,P} = 6.9 Hz, OCH₃), 53.6 (d, ²J_{C,P} = 7.0 Hz, OCH₃), 55.2 (d, ¹J_{C,P} = 150.7 Hz, CH), 55.7 (OCH₃), 75.0 (d, ⁴J_{C,P} = 5.0 Hz, C_{sp}), 98.7 (d, ⁵J_{C,P} = 2.0 Hz, C_{sp}), 114.7 (ArC), 114.8 (ArC), 121.3 (d, ³J_{C,P} = 12.5 Hz, C_{sp}), 137.5 (d, ²J_{C,P} = 3.6 Hz, C_{sp}), 140.2 (d, ³J_{C,P} = 17.0 Hz, ArC), 152.5 (ArC) ppm. HRMS (ESI): MNa⁺, found 412.1640. C₂₁H₂₈NNaO₄P requires 412.1648.

Dimethyl (4-Chlorophenylamino)(2-(cyclopropylethynyl)cyclohex-1-enyl)methylphosphonate (8n). Brownish solid, mp 114–115 °C. Yield 0.44 g, 56%. IR (KBr): $\nu_{\max}$ 3295 (NH), 2212 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.71–0.75 (2H, m, CH(CH₂)₂), 0.86–0.89 (2H, m, CH(CH₂)₂), 1.41–1.47 (1H, m, CH(CH₂)₂), 1.49–1.56 (3H, m, CH₂), 1.88–1.93 (1H, m, CHH), 2.13–2.16 (2H, m, CH₂), 2.19–2.26 (1H, m, CHH), 3.76 (3H, d, ³J_{H,P} = 10.4 Hz, OCH₃), 3.80 (3H, d, ³J_{H,P} = 10.4 Hz, OCH₃), 5.07 (1H, d, ²J_{H,P} = 25.6 Hz, CHNH), 6.57 (2H, d, *J* = 9.2 Hz, ArH), 7.10 (2H, d, *J* = 8.8 Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 0.3 (CH(CH₂)₂), 8.8 (CH(CH₂)₂), 9.0 (CH(CH₂)₂), 22.0 (2 × CH₂), 24.5 (d, ³J_{C,P} = 1.4 Hz, CH₂), 30.6 (d, ⁴J_{C,P} = 1.8 Hz, CH₂), 53.4 (d, ²J_{C,P} = 6.9 Hz, OCH₃), 53.7 (d, ²J_{C,P} = 7.0 Hz, OCH₃), 54.6 (d, ¹J_{C,P} = 151.1 Hz, CH), 74.8 (d, ⁴J_{C,P} = 4.9 Hz, C_{sp}), 99.1 (d, ⁵J_{C,P} = 2.0 Hz, C_{sp}), 114.7 (ArC), 121.7 (d, ³J_{C,P} = 12.5 Hz, C_{sp}), 122.9 (ArC), 129.0 (ArC), 136.7 (d, ²J_{C,P} = 3.9 Hz, C_{sp}), 144.9 (d, ³J_{C,P} = 16.3 Hz, ArC) ppm. HRMS (ESI): MNa⁺, found 416.1150. C₂₀H₂₅ClNNaO₃P requires 416.1153.

Dimethyl (4-Chlorophenylamino)(2-(p-tolylethynyl)cyclohex-1-enyl)methylphosphonate (8o). Yellowish solid, mp 112–113 °C. Yield 0.47 g, 53%. IR (KBr): $\nu_{\max}$ 3309 (NH), 2118 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.52–1.65 (4H, m, 2 × CH₂), 1.97–2.03 (1H, m, CHH), 2.31–2.34 (3H, m, CHH, CH₂), 2.36 (3H, s, CH₃), 3.79 (3H, d, ³J_{H,P} = 6.0 Hz, OCH₃), 3.82 (3H, d, ³J_{H,P} = 6.0 Hz, OCH₃), 5.22 (1H, d, ²J_{H,P} = 25.6 Hz, CHNH), 6.63 (2H, d, *J* = 8.8 Hz, ArH), 7.11 (2H, d, *J* = 8.8 Hz, ArH), 7.15 (2H, d, *J* = 7.6 Hz, ArH), 7.36 (2H, d, *J* = 8.0 Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 21.4 (CH₃), 21.9 (CH₂), 22.0 (CH₂), 24.7 (d, ³J_{C,P} = 1.4 Hz, CH₂), 30.3 (d, ⁴J_{C,P} = 1.7 Hz, CH₂), 53.6 (d, ²J_{C,P} = 6.9 Hz, OCH₃), 53.8 (d, ²J_{C,P} = 7.2 Hz, OCH₃), 54.9 (d, ¹J_{C,P} = 150.9 Hz, CH), 87.7 (d, ⁴J_{C,P} = 5.1 Hz, C_{sp}), 95.0 (d, ⁵J_{C,P} = 2.2 Hz, C_{sp}), 114.7 (ArC), 120.0 (ArC), 121.4 (d, ³J_{C,P} = 12.4 Hz, C_{sp}), 123.0 (ArC), 129.1 (ArC), 129.2 (ArC), 131.1 (ArC), 138.4 (d, ²J_{C,P} = 4.0 Hz, C_{sp}), 138.5 (ArC), 144.9 (d, ³J_{C,P} = 16.3 Hz, ArC) ppm. HRMS (ESI): MNa⁺, found 466.1307. C₂₄H₂₇ClNNaO₃P requires 466.1309.

Dimethyl (Phenylamino)(2-(phenylethynyl)phenyl)methylphosphonate (9a). White solid, mp 154–155 °C. Yield 0.34 g, 44%. IR (KBr): $\nu_{\max}$ 3348 (NH), 2212 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 3.44 (3H, d, ³J_{H,P} = 10.4 Hz, OCH₃), 3.85 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 5.59 (1H, d, ²J_{H,P} = 24.4 Hz, CHNH), 6.67–6.72 (3H, m, ArH), 7.09–7.13 (2H, m, ArH), 7.25–7.35 (2H, m, ArH), 7.38–7.41 (3H, m, ArH), 7.57–7.64 (4H, m, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 52.9 (d, ¹J_{C,P} = 151.0 Hz, CH), 53.8 (d, ²J_{C,P} = 6.3 Hz, OCH₃), 53.9 (d, ²J_{C,P} = 6.2 Hz, OCH₃), 86.8 (d, ⁴J_{C,P} =

2.0 Hz, C_{sp}), 95.1 (C_{sp}), 113.8 (ArC), 118.6 (ArC), 122.9 (ArC), 123.2 (d, ³J_{C,P} = 8.7 Hz, ArC), 127.4 (d, ³J_{C,P} = 4.4 Hz, ArC), 127.9 (d, ⁵J_{C,P} = 3.1 Hz, ArC), 128.5 (ArC), 128.7 (ArC), 129.0 (d, ⁴J_{C,P} = 3.1 Hz, ArC), 129.2 (ArC), 131.5 (ArC), 132.2 (d, ²J_{C,P} = 2.1 Hz, ArC), 137.7 (d, ²J_{C,P} = 1.8 Hz, ArC), 145.7 (d, ³J_{C,P} = 14.8 Hz, ArC) ppm. HRMS (ESI): MNa⁺, found 414.1228. C₂₃H₂₂NNaO₃P requires 414.1230.

Dimethyl (4-Chlorophenylamino)(2-(phenylethynyl)phenyl)methylphosphonate (9b). Yellowish solid, mp 149–150 °C. Yield 0.51 g, 60%. IR (KBr): ν_{max} 3508 (NH), 2213 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 3.44 (3H, d, ³J_{H,P} = 10.4 Hz, OCH₃), 3.85 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 4.44 (1H, br. s, NH), 5.53 (1H, d, ²J_{H,P} = 24.4 Hz, CHNH), 6.59 (2H, d, J = 8.8 Hz, ArH), 7.05 (2H, d, J = 8.8 Hz, ArH), 7.28–7.35 (2H, m, ArH), 7.38–7.40 (3H, m, ArH), 7.57–7.61 (4H, m, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 53.0 (d, ¹J_{C,P} = 151.5 Hz, CH), 53.8 (d, ²J_{C,P} = 6.9 Hz, OCH₃), 53.9 (d, ²J_{C,P} = 7.0 Hz, OCH₃), 86.7 (d, ⁴J_{C,P} = 2.0 Hz, C_{sp}), 95.3 (C_{sp}), 114.9 (ArC), 122.8 (ArC), 123.2 (ArC), 123.2 (d, ⁶J_{C,P} = 7.0 Hz, ArC), 127.3 (d, ³J_{C,P} = 4.3 Hz, ArC), 128.0 (d, ⁵J_{C,P} = 3.0 Hz, ArC), 128.5 (ArC), 128.8 (ArC), 129.0 (d, ⁴J_{C,P} = 3.1 Hz, ArC), 129.1 (ArC), 131.5 (ArC), 132.3 (d, ⁴J_{C,P} = 2.2 Hz, ArC), 137.2 (d, ²J_{C,P} = 2.1 Hz, ArC), 144.4 (d, ³J_{C,P} = 15.1 Hz, ArC) ppm. HRMS (ESI): MNa⁺, found 448.0836. C₂₃H₂₁ClNNaO₃P requires 448.0840.

Dimethyl (4-Methoxyphenylamino)(2-((trimethylsilyl)ethynyl)phenyl)methylphosphonate (9c-TMS). Yellowish solid, mp 115–116 °C. Yield 0.59 g, 71%. IR (KBr): ν_{max} 2157 (C≡C), 3287 (NH) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.30 (9H, s, CH₃), 3.43 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 3.68 (3H, s, OCH₃), 3.84 (3H, d, ³J_{H,P} = 10.4 Hz, OCH₃), 5.46 (1H, d, ²J_{H,P} = 24.8 Hz, CHNH), 6.62 (2H, d, J = 8.8 Hz, ArH), 6.70 (2H, d, J = 9.2 Hz, ArH), 7.20 (1H, tt, J = 7.6 Hz; 1.6 Hz, ArH), 7.30 (1H, t, J = 7.6 Hz, ArH), 7.47 (1H, d, J = 7.6 Hz, ArH), 7.58 (1H, d, J = 7.2 Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 0.1 (CH₃), 53.4 (d, ¹J_{C,P} = 150.2 Hz, CH), 53.7 (d, ²J_{C,P} = 6.1 Hz, OCH₃), 53.8 (d, ²J_{C,P} = 6.2 Hz, OCH₃), 55.6 (OCH₃), 100.3 (C_{sp}), 102.7 (C_{sp}), 114.7 (ArC), 115.2 (ArC), 123.2 (d, ³J_{C,P} = 7.5 Hz, ArC), 127.4 (ArC), 127.7 (d, ⁵J_{C,P} = 2.4 Hz, ArC), 129.2 (d, ⁴J_{C,P} = 3.0 Hz, ArC), 132.3 (d, ⁴J_{C,P} = 1.9 Hz, ArC), 138.1 (ArC), 139.4 (ArC), 152.9 (ArC) ppm. HRMS (ES): MNa⁺, found 440.1419. C₂₁H₂₈NNaO₄PSi requires 440.1417.

Dimethyl (2-Ethynylphenyl)(4-methoxyphenylamino)methylphosphonate (9c). This compound was synthesized from 9c-TMS by treating with 2 equiv of KF₂·H₂O in methanol at room temperature for 2 h. After evaporation of solvent, the residue was purified by column chromatography. White solid, mp 171–172 °C. Yield 0.38 g, 78%. IR (KBr): ν_{max} 3504 (NH), 2101 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 3.44 (4H, d and s (overlap), ³J_{H,P} = 10.8 Hz, OCH₃, CH), 3.68 (3H, s, OCH₃), 3.85 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 5.44 (1H, d, ²J_{H,P} = 24.0 Hz, CHNH), 6.64 (2H, d, J = 8.8 Hz, ArH), 6.69 (2H, d, J = 9.2 Hz, ArH), 7.24 (1H, tt, J = 7.6 Hz; 1.6 Hz, ArH), 7.34 (1H, t, J = 7.2 Hz, ArH), 7.52 (1H, d, J = 7.6 Hz, ArH), 7.63 (1H, d, J = 7.6 Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 53.7 (d, ¹J_{C,P} = 151.1 Hz, CH), 53.8 (d, ²J_{C,P} = 7.0 Hz, OCH₃), 54.0 (d, ²J_{C,P} = 6.8 Hz, OCH₃), 55.6 (OCH₃), 81.2 (d, ⁴J_{C,P} = 1.9 Hz, C_{sp}), 82.8 (C_{sp}), 114.7 (ArC), 115.7 (ArC), 122.2 (d, ³J_{C,P} = 7.2 Hz, ArC), 127.5 (d, ³J_{C,P} = 4.2 Hz, ArC), 127.9 (d, ⁵J_{C,P} = 3.0 Hz, ArC), 129.5 (d, ⁴J_{C,P} = 3.0 Hz, ArC), 132.9 (d, ⁴J_{C,P} = 2.1 Hz, ArC), 138.0 (ArC), 139.2 (ArC), 153.2 (d, ⁶J_{C,P} = 1.2 Hz, ArC) ppm. HRMS (ESI): MNa⁺, found 368.1022. C₁₈H₂₀NNaO₄P requires 368.1022.

Dimethyl (1-Benzyl-2-(phenylethynyl)-1H-indol-3-yl)-(phenylamino)methylphosphonate (19a). Yellowish solid, mp 156–157 °C. Yield 0.44 g, 42%. IR (KBr): ν_{max} 3316 (NH), 2214 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 3.50 (3H, d, ³J_{H,P} = 10.4 Hz, OCH₃), 3.88 (3H, d, ³J_{H,P} = 10.4 Hz, OCH₃), 5.47 (1H, d, ²J_{H,P} = 24.4 Hz, CHNH), 5.47 (2H, s, NCH₂), 6.71 (1H, t, J = 7.2 Hz, ArH), 6.81 (2H, d, J = 8.0 Hz, ArH), 7.09–7.26 (10H, m, ArH), 7.40–7.41 (3H, m, ArH), 7.55–7.58 (2H, m, ArH), 8.03 (1H, d, J = 6.4 Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 48.0 (NCH₂), 49.4 (d, ¹J_{C,P} = 160.2 Hz, CH), 53.6 (d, ²J_{C,P} = 7.0 Hz, OCH₃), 53.7 (d, ²J_{C,P} = 7.0 Hz, OCH₃), 79.6 (d, ⁴J_{C,P} = 3.5 Hz, C_{sp}), 99.6 (d, ⁵J_{C,P} = 1.5 Hz,

C_{sp}), 110.1 (ArC), 114.1 (2 × ArC), 114.9 (d, J = 1.6 Hz, ArC), 118.4 (ArC), 120.7 (ArC), 121.7 (d, ³J_{C,P} = 10.1 Hz, ArC), 122.1 (ArC), 123.7 (ArC), 125.9 (d, ²J_{C,P} = 3.0 Hz, ArC), 126.5 (ArC), 127.4 (ArC), 128.5 (ArC), 128.6 (ArC), 128.9 (ArC), 129.0 (ArC), 131.4 (ArC), 136.9 (ArC), 137.3 (ArC), 146.3 (d, ³J_{C,P} = 14.9 Hz, ArC) ppm. HRMS (ESI): MNa⁺, found 543.1807. C₃₂H₂₉N₂NaO₃P requires 543.1808.

Dimethyl (1-Benzyl-2-(hex-1-ynyl)-1H-indol-3-yl)-(4-methoxyphenylamino)methylphosphonate (19b). Yellowish solid, mp 132–133 °C. Yield 0.24 g, 46%. IR (KBr): ν_{max} 3480 (NH), 2214 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 0.93 (3H, t, J = 7.2 Hz, CH₃), 1.46 (2H, sext., J = 7.2 Hz, C≡CCH₂CH₂CH₂), 1.58–1.65 (2H, m, C≡CCH₂CH₂CH₂), 2.55 (2H, t, J = 7.2 Hz, C≡CCH₂CH₂CH₂), 3.46 (3H, d, ³J_{H,P} = 10.4 Hz, OCH₃), 3.68 (3H, s, OCH₃), 3.85 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 5.25 (1H, d, ²J_{H,P} = 24.0 Hz, CHNH), 5.37 (2H, s, NCH₂), 6.53–6.72 (4H, m, ArH), 6.96–6.98 (2H, m, ArH), 7.11–7.12 (3H, m, ArH), 7.20–7.21 (3H, m, ArH), 7.94–7.97 (1H, m, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 13.6 (CH₃), 19.5 (CH₂), 21.9 (CH₂), 30.6 (CH₂), 47.8 (NCH₂), 50.5 (d, ¹J_{C,P} = 161.0 Hz, CH), 53.6 (d, ²J_{C,P} = 5.4 Hz, OCH₃), 53.7 (d, ²J_{C,P} = 5.5 Hz, OCH₃), 55.6 (OCH₃), 71.1 (d, ⁴J_{C,P} = 3.2 Hz, C_{sp}), 101.1 (d, ⁵J_{C,P} = 1.4 Hz, C_{sp}), 109.9 (ArC), 113.4 (ArC), 114.5 (ArC), 115.8 (ArC), 120.4 (ArC), 120.6 (ArC), 122.9 (d, ³J_{C,P} = 10.5 Hz, ArC), 123.1 (ArC), 125.8 (d, ²J_{C,P} = 2.7 Hz, ArC), 126.3 (ArC), 127.2 (ArC), 128.5 (ArC), 136.4 (ArC), 137.5 (ArC), 140.3 (d, ³J_{C,P} = 15.9 Hz, ArC), 152.8 (ArC) ppm. HRMS (ESI): MNa⁺, found 553.2218. C₃₁H₃₅N₂NaO₄P requires 553.2227.

Dimethyl (1-Benzyl-2-(cyclopropylethynyl)-1H-indol-3-yl)-(phenylamino)methylphosphonate (19c). Yellowish solid, mp 106–107 °C. Yield 0.31 g, 32%. IR (KBr): ν_{max} 3314 (NH), 2219 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.16–1.19 (2H, m, CH(CH₂)₂), 1.29–1.32 (2H, m, CH(CH₂)₂), 1.89–1.95 (1H, m, CH(CH₂)₂), 3.78 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 4.18 (3H, d, ³J_{H,P} = 10.8 Hz, OCH₃), 5.65 (1H, d, ²J_{H,P} = 24.4 Hz, CHNH), 5.70 (2H, s, NCH₂), 7.03 (1H, t, J = 7.2 Hz, ArH), 7.08 (2H, d, J = 8.0 Hz, ArH), 7.34–7.57 (10H, m, ArH), 8.27–8.29 (1H, m, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 0.5 (CH(CH₂)₂), 9.3 (2 × CH(CH₂)₂), 47.8 (NCH₂), 49.3 (d, ¹J_{C,P} = 160.7 Hz, CH), 53.6 (d, ²J_{C,P} = 6.9 Hz, OCH₃), 53.7 (d, ²J_{C,P} = 6.9 Hz, OCH₃), 65.8 (d, ⁴J_{C,P} = 3.3 Hz, C_{sp}), 104.5 (d, ⁴J_{C,P} = 1.1 Hz, C_{sp}), 110.0 (ArC), 113.8 (ArC), 114.1 (2 × ArC), 118.4 (ArC), 120.4 (ArC), 122.6 (d, ³J_{C,P} = 10.4 Hz, ArC), 123.2 (ArC), 125.8 (d, ²J_{C,P} = 2.8 Hz, ArC), 126.4 (ArC), 127.3 (ArC), 128.5 (ArC), 128.9 (ArC), 136.4 (ArC), 137.5 (ArC), 146.4 (d, ³J_{C,P} = 15.0 Hz, ArC) ppm. HRMS (ESI): MNa⁺, found 507.1793. C₂₉H₂₉N₂NaO₃P requires 507.1808.

General Procedure for the Preparation of Compounds 10 and 14. To a solution of the corresponding acetylenic α-anilinomethylphosphonate 7 were added 8 (1 mmol) in dry chloroform (5 mL) and potassium *tert*-butoxide (0.112 g, 1 mmol), together with gold(III) bromide (43.7 mg, 0.1 mmol). The resulting solution was stirred at room temperature. When the completion of the reaction was observed by TLC (after 0.5–2 h), the solution was evaporated under reduced pressure, and the residue was purified by flash column chromatography eluting with hexane–ethyl acetate mixtures.

Dimethyl 3-Benzyl-2-phenyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10a). Yellowish oil. Yield 0.37 g, 98%. ¹H NMR (400 MHz, CDCl₃): δ 2.24–2.32 (2H, m, CH₂CH₂CH₂), 2.35–2.38 (2H, m, CH₂CH₂CH₂), 2.84–2.87 (2H, m, CH₂CH₂CH₂), 3.42 (6H, d, ³J_{H,P} = 11.2 Hz, 2 × OCH₃), 3.65 (2H, br. s, CH₂), 6.91–6.93 (2H, m, ArH), 7.12–7.21 (5H, m, ArH), 7.35–7.39 (3H, m, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 24.8 (CH₂), 26.6 (CH₂), 30.3 (CH₂), 32.3 (CH₂), 52.0 (d, ²J_{C,P} = 5.6 Hz, OCH₃), 110.2 (d, ¹J_{C,P} = 234.2 Hz, C-sp²), 126.0 (ArC), 128.1 (ArC), 128.3 (ArC), 128.3 (ArC), 128.5 (ArC), 128.8 (ArC), 129.4 (d, ³J_{C,P} = 14.2 Hz, C-sp²), 131.5 (d, ⁴J_{C,P} = 8.5 Hz, C-sp²), 138.5 (ArC), 138.7 (ArC), 144.5 (d, ²J_{C,P} = 17.4 Hz, C-sp²) ppm. HRMS (ESI): MNa⁺, found 404.1388. C₂₂H₂₄NNaO₃P requires 404.1386.

Dimethyl 3-Benzyl-2-(4-methoxyphenyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10b). Yellow-

ish oil. Yield 0.30 g, 74%. ^1H NMR (400 MHz, CDCl_3): δ 2.23–2.30 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.34–2.37 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.82–2.86 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.51 (6H, d, $^3J_{\text{HP}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.63 (2H, br. s, CH_2), 3.82 (3H, s, OCH_3), 6.86 (2H, d, $^3J = 9.2$ Hz, ArH), 6.92–6.94 (2H, m, ArH), 7. Ten (2H, d, $J = 9.2$ Hz, ArH), 7.14–7.21 (3H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 24.8 (CH_2), 26.6 (CH_2), 30.3 (CH_2), 32.3 (CH_2), 52.1 (d, $^2J_{\text{CP}} = 5.5$ Hz, OCH_3), 55.3 (OCH_3), 110.1 (d, $^1J_{\text{CP}} = 234.7$ Hz, C-sp 2), 113.4 (ArC), 126.0 (ArC), 128.1 (ArC), 128.6 (ArC), 129.1 (d, $^3J_{\text{CP}} = 14.2$ Hz, C-sp 2), 129.8 (ArC), 131.5 (ArC), 131.9 (d, $^4J_{\text{CP}} = 8.5$ Hz, C-sp 2), 138.6 (ArC), 144.2 (d, $^2J_{\text{CP}} = 17.5$ Hz, C-sp 2), 159.2 (ArC) ppm. HRMS (ESI): MNa^+ , found 434.1497. $\text{C}_{23}\text{H}_{26}\text{NNaO}_4\text{P}$ requires 434.1492.

Dimethyl 3-Benzyl-2-(4-ethoxyphenyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10c). Yellowish oil. Yield 0.32 g, 76%. ^1H NMR (400 MHz, CDCl_3): δ 1.42 (3H, t, $^3J = 6.8$ Hz, OCH_2CH_3), 2.23–2.31 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.34–2.37 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.82–2.86 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.50 (6H, d, $^3J_{\text{HP}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.63 (2H, br. s, CH_2), 4.04 (2H, q, $^3J = 6.8$ Hz, OCH_2CH_3), 6.85 (2H, d, $^3J = 8.8$ Hz, ArH), 6.93–6.95 (2H, m, ArH), 7. Ten (2H, d, $^3J = 8.8$ Hz, ArH), 7.14–7.21 (3H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 14.7 (CH_3), 24.8 (CH_2), 26.6 (CH_2), 30.3 (CH_2), 32.3 (CH_2), 52.0 (d, $^2J_{\text{CP}} = 5.5$ Hz, OCH_3), 63.5 (OCH_2CH_3), 110.2 (d, $^1J_{\text{CP}} = 234.4$ Hz, C-sp 2), 113.9 (ArC), 126.0 (ArC), 128.1 (ArC), 128.6 (ArC), 129.0 (d, $^3J_{\text{CP}} = 14.3$ Hz, C-sp 2), 129.8 (ArC), 131.3 (ArC), 131.8 (d, $^4J_{\text{CP}} = 8.6$ Hz, C-sp 2), 138.6 (ArC), 144.2 (d, $^2J_{\text{CP}} = 17.5$ Hz, C-sp 2), 158.6 (ArC) ppm. HRMS (ESI): MNa^+ , found 448.1649. $\text{C}_{24}\text{H}_{28}\text{NNaO}_4\text{P}$ requires 448.1648.

Dimethyl 3-Benzyl-2-(4-fluorophenyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10d). Yellowish oil. Yield 0.32 g, 86%. ^1H NMR (400 MHz, CDCl_3): δ 2.25–2.33 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.38–2.41 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.82–2.86 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.52 (6H, d, $^3J_{\text{HP}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.64 (2H, br. s, CH_2), 6.89–6.91 (2H, m, ArH), 7.01–7.05 (2H, m, ArH), 7.12–7.21 (5H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 24.8 (CH_2), 26.6 (CH_2), 30.4 (CH_2), 32.3 (CH_2), 52.1 (d, $^2J_{\text{CP}} = 5.6$ Hz, OCH_3), 110.4 (d, $^1J_{\text{CP}} = 234.6$ Hz, C-sp 2), 115.2 (d, $J_{\text{CF}} = 22.6$ Hz, ArC), 126.1 (ArC), 128.2 (ArC), 128.5 (ArC), 129.6 (d, $^3J_{\text{CP}} = 14.2$ Hz, C-sp 2), 130.5 (d, $^3J_{\text{CF}} = 8.7$ Hz, ArC), 131.7 (d, $^4J_{\text{CP}} = 8.4$ Hz, C-sp 2), 134.7 (d, $^4J_{\text{CF}} = 3.1$ Hz, ArC), 138.4 (ArC), 144.5 (d, $^2J_{\text{CP}} = 17.3$ Hz, C-sp 2), 162.2 (d, $^1J_{\text{CF}} = 246.6$ Hz, ArH) ppm. HRMS (ESI): MH^+ , found 400.1473. $\text{C}_{22}\text{H}_{24}\text{FNO}_3\text{P}$ requires 400.1472.

Dimethyl 3-Benzyl-2-(4-chlorophenyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10e). Yellowish oil. Yield 0.3 g, 73%. ^1H NMR (400 MHz, CDCl_3): δ 2.25–2.32 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.37–2.40 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.82–2.86 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.52 (6H, d, $^3J_{\text{HP}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.64 (2H, br. s, CH_2), 6.90–6.92 (2H, m, ArH), 7. Eleven (2H, d, $^3J = 8.8$ Hz, ArH), 7.15–7.22 (3H, m, ArH), 7.32 (2H, d, $^3J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 24.8 (CH_2), 26.6 (CH_2), 30.4 (CH_2), 32.3 (CH_2), 52.1 (d, $^2J_{\text{CP}} = 5.6$ Hz, OCH_3), 110.3 (d, $^1J_{\text{CP}} = 234.2$ Hz, C-sp 2), 126.2 (ArC), 128.3 (ArC), 128.5 (ArC), 128.6 (ArC), 129.8 (d, $^3J_{\text{CP}} = 14.1$ Hz, C-sp 2), 130.1 (ArC), 131.5 (d, $^4J_{\text{CP}} = 8.4$ Hz, C-sp 2), 134.2 (ArC), 137.3 (ArC), 138.3 (ArC), 144.7 (d, $^2J_{\text{CP}} = 17.5$ Hz, C-sp 2) ppm. HRMS (ESI): MH^+ , found 416.1185. $\text{C}_{22}\text{H}_{24}\text{ClNO}_3\text{P}$ requires 416.1182.

Dimethyl 3-(4-Methylbenzyl)-2-phenyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10f). Yellowish oil. Yield 0.23 g, 58%. ^1H NMR (400 MHz, CDCl_3): δ 2.26–2.31 (5H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$ and CH_3), 2.33–2.37 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.83–2.87 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.49 (6H, d, $^3J_{\text{HP}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.60 (2H, br. s, CH_2), 6.82 (2H, d, $^3J = 8.0$ Hz, ArH), 7. 00 (2H, d, $^3J = 7.6$ Hz, ArH), 7.20–7.22 (2H, m, ArH), 7.37–7.39 (3H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 20.9 (CH_3), 24.8 (CH_2), 26.5 (CH_2), 30.3 (CH_2), 31.8 (CH_2), 52.0 (d, $^2J_{\text{CP}} = 5.5$ Hz, OCH_3), 109.9 (d, $^1J_{\text{CP}} = 234.7$ Hz, C-sp 2), 128.3 (ArC), 128.3 (ArC), 128.4 (ArC), 128.7 (ArC), 128.8 (ArC), 129.2 (d, $^3J_{\text{CP}} = 14.2$ Hz, C-sp 2), 131.8 (d, $^4J_{\text{CP}} = 8.5$ Hz, C-sp 2), 135.4 (ArC), 135.4 (ArC), 138.7 (ArC), 144.5 (d, $^2J_{\text{CP}} = 17.5$ Hz, C-sp 2) ppm. HRMS (ESI): MNa^+ , found 418.1541. $\text{C}_{23}\text{H}_{26}\text{NNaO}_3\text{P}$ requires 418.1543.

Dimethyl 2-(4-Methoxyphenyl)-3-(4-methylbenzyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10 g). Yellowish oil. Yield 0.32 g, 76%. ^1H NMR (400 MHz, CDCl_3): δ 2.25–2.30 (5H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$ and CH_3), 2.33–2.37 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.81–2.85 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.51 (6H, d, $^3J_{\text{HP}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.58 (2H, br. s, CH_2), 3.83 (3H, s, OCH_3), 6.83 (2H, d, $^3J = 8.0$ Hz, ArH), 6.87 (2H, d, $^3J = 8.8$ Hz, ArH), 7.01 (2H, d, $^3J = 8.0$ Hz, ArH), 7.12 (2H, d, $^3J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 20.9 (CH_3), 24.9 (CH_2), 26.6 (CH_2), 30.3 (CH_2), 31.8 (CH_2), 52.1 (d, $^2J_{\text{CP}} = 5.5$ Hz, OCH_3), 55.3 (OCH_3), 110.0 (d, $^1J_{\text{CP}} = 234.3$ Hz, C-sp 2), 113.4 (ArC), 128.5 (ArC), 128.8 (ArC), 128.9 (ArC), 129.1 (ArC), 129.8 (ArC), 131.5 (ArC), 132.1 (d, $^4J_{\text{CP}} = 8.5$ Hz, C-sp 2), 135.5 (ArC), 144.3 (d, $^2J_{\text{CP}} = 17.6$ Hz, C-sp 2), 159.2 (ArC) ppm. HRMS (ESI): MNa^+ , found 448.1643. $\text{C}_{24}\text{H}_{28}\text{NNaO}_4\text{P}$ requires 448.1648.

Dimethyl 3-(4-Ethylbenzyl)-2-(4-methoxyphenyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10h). Yellowish oil. Yield 0.42 g, 96%. ^1H NMR (400 MHz, CDCl_3): δ 1.19 (3H, t, $^3J = 7.6$ Hz, CH_3), 2.23–2.30 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.35–2.38 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.58 (2H, q, $^3J = 7.6$ Hz, CH_2CH_3), 2.81–2.85 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.50 (6H, d, $^3J_{\text{HP}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.59 (2H, br. s, CH_2), 3.83 (3H, s, OCH_3), 6.84–6.87 (4H, m, ArH), 7.03 (2H, d, $^3J = 8.4$ Hz, ArH), 7.11 (2H, d, $^3J = 9.2$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 15.6 (CH_3), 24.8 (CH_2), 26.6 (CH_2), 28.3 (CH_2), 30.3 (CH_2), 31.8 (CH_2), 52.1 (d, $^2J_{\text{CP}} = 5.5$ Hz, OCH_3), 55.3 (OCH_3), 109.8 (d, $^1J_{\text{CP}} = 235.1$ Hz, C-sp 2), 113.4 (ArC), 127.6 (ArC), 128.5 (ArC), 129.0 (d, $^3J_{\text{CP}} = 14.2$ Hz, C-sp 2), 129.8 (ArC), 131.5 (ArC), 132.3 (d, $^4J_{\text{CP}} = 8.6$ Hz, C-sp 2), 135.8 (ArC), 141.9 (ArC), 144.4 (d, $^2J_{\text{CP}} = 17.5$ Hz, C-sp 2), 159.2 (ArC) ppm. HRMS (ESI): MNa^+ , found 462.1808. $\text{C}_{25}\text{H}_{30}\text{NNaO}_4\text{P}$ requires 462.1805.

Dimethyl 3-Pentyl-2-phenyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10i). Yellowish oil. Yield 0.31 g, 86%. ^1H NMR (400 MHz, CDCl_3): δ 0.79 (3H, t, $^3J = 7.2$ Hz, $\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.09–1.21 (4H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.42 (2H, quint, $^3J = 7.6$ Hz, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.27 (2H, t, $^3J = 7.6$ Hz, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.36 (2H, quint, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.65 (2H, t, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.84 (2H, td, $^3J_{\text{HH}} = 6.8$ Hz, $^4J_{\text{HP}} = 1.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.48 (6H, d, $^3J_{\text{HP}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 7.26–7.28 (2H, m, ArH), 7.39–7.44 (3H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.8 (CH_3), 22.1 (CH_2), 25.1 (CH_2), 26.0 (CH_2), 26.5 (CH_2), 27.8 (CH_2), 30.4 (CH_2), 31.3 (CH_2), 51.9 (d, $^2J_{\text{CP}} = 5.5$ Hz, OCH_3), 109.3 (d, $^1J_{\text{CP}} = 234.8$ Hz, C-sp 2), 128.0 (d, $^3J_{\text{CP}} = 14.4$ Hz, C-sp 2), 128.2 (ArC), 128.3 (ArC), 128.6 (ArC), 133.6 (d, $^4J_{\text{CP}} = 8.4$ Hz, C-sp 2), 138.9 (ArC), 144.6 (d, $^2J_{\text{CP}} = 17.5$ Hz, C-sp 2) ppm. HRMS (ESI): MNa^+ , found 384.1697. $\text{C}_{20}\text{H}_{28}\text{NNaO}_3\text{P}$ requires 384.1699.

Dimethyl 2-(4-Methoxyphenyl)-3-pentyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10j). Yellowish oil. Yield 0.3 g, 78%. ^1H NMR (400 MHz, CDCl_3): δ 0.80 (3H, t, $^3J = 6.8$ Hz, $\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.13–1.22 (4H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.42 (2H, quint, $^3J = 7.6$ Hz, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.26 (2H, t, $^3J = 8.0$ Hz, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.32 (2H, quint, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.63 (2H, t, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.82–2.86 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.50 (6H, d, $^3J_{\text{HP}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.83 (3H, s, OCH_3), 6.91 (2H, d, $^3J = 8.8$ Hz, ArH), 7.18 (2H, d, $^3J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.8 (CH_3), 22.2 (CH_2), 25.2 (CH_2), 26.0 (CH_2), 26.5 (CH_2), 27.9 (CH_2), 30.4 (CH_2), 31.3 (CH_2), 52.0 (d, $^2J_{\text{CP}} = 5.5$ Hz, OCH_3), 55.3 (OCH_3), 109.4 (d, $^1J_{\text{CP}} = 235.0$ Hz, C-sp 2), 113.4 (ArC), 127.8 (d, $^3J_{\text{CP}} = 14.3$ Hz, C-sp 2), 129.7 (ArC), 131.8 (ArC), 134.0 (d, $^4J_{\text{CP}} = 8.4$ Hz, C-sp 2), 144.3 (d, $^2J_{\text{CP}} = 17.6$ Hz, C-sp 2), 159.1 (ArC) ppm. HRMS (ESI): MNa^+ , found 414.1806. $\text{C}_{21}\text{H}_{30}\text{NNaO}_4\text{P}$ requires 414.1805.

Dimethyl 2-(4-Fluorophenyl)-3-pentyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10k). Yellowish oil. Yield 0.3 g, 80%. ^1H NMR (400 MHz, CDCl_3): δ 0.81 (3H, t, $^3J = 6.8$ Hz, $\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.10–1.22 (4H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.42 (2H, quint, $^3J = 7.6$ Hz, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.26 (2H, t, $^3J = 7.6$ Hz, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.33 (2H, quint, $^3J = 6.8$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.63 (2H, t, $^3J = 6.8$ Hz,

$\text{CH}_2\text{CH}_2\text{CH}_2$), 2.83 (2H, td, $^3J_{\text{HH}} = 7.0$ Hz, $^4J_{\text{HP}} = 1.6$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.52 (6H, d, $^3J_{\text{HP}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 7.07–7.12 (2H, m, ArH), 7.23–7.26 (2H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.8 (CH_3), 22.2 (CH_2), 25.1 (CH_2), 26.0 (CH_2), 26.5 (CH_2), 27.9 (CH_2), 30.4 (CH_2), 31.4 (CH_2), 52.1 (d, $^2J_{\text{CP}} = 5.5$ Hz, OCH_3), 109.4 (d, $^1J_{\text{CP}} = 235.8$ Hz, C-sp 2), 115.3 (d, $^2J_{\text{CF}} = 22.6$ Hz, ArC), 128.3 (d, $^3J_{\text{CP}} = 14.3$ Hz, C-sp 2), 130.4 (d, $^1J_{\text{CF}} = 8.7$ Hz, ArC), 133.9 (d, $^4J_{\text{CP}} = 8.2$ Hz, C-sp 2), 134.9 (d, $^4J_{\text{CF}} = 3.1$ Hz, ArC), 144.8 (d, $^2J_{\text{CP}} = 17.5$ Hz, C-sp 2), 162.1 (d, $^1J_{\text{CF}} = 246.5$ Hz, ArC) ppm. HRMS (ESI): MH^+ , found 380.1791. $\text{C}_{20}\text{H}_{28}\text{FNO}_3\text{P}$ requires 380.1785.

Dimethyl 2-(4-Chlorophenyl)-3-pentyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10l). Yellowish oil. Yield 0.3 g, 76%. ^1H NMR (400 MHz, CDCl_3): δ 0.81 (3H, t, $^3J = 6.8$ Hz, $\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.12–1.21 (4H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 1.42 (2H, quint, $^3J = 7.6$ Hz, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 2.26 (2H, t, $^3J = 7.6$ Hz, $\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$), 2.33 (2H, quint, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.64 (2H, t, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.83 (2H, td, $^3J_{\text{HH}} = 7.0$ Hz, $^4J_{\text{HP}} = 1.6$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.52 (6H, d, $^3J_{\text{HP}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 7.21 (2H, d, $^3J = 8.8$ Hz, ArH), 7.39 (2H, d, $^3J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.8 (CH_3), 22.2 (CH_2), 25.1 (CH_2), 26.0 (CH_2), 26.5 (CH_2), 27.9 (CH_2), 30.4 (CH_2), 31.4 (CH_2), 52.1 (d, $^2J_{\text{CP}} = 5.6$ Hz, OCH_3), 109.4 (d, $^1J_{\text{CP}} = 235.0$ Hz, C-sp 2), 128.5 (d, $^3J_{\text{CP}} = 14.2$ Hz, C-sp 2), 128.6 (ArC), 130.0 (ArC), 133.7 (d, $^4J_{\text{CP}} = 8.2$ Hz, C-sp 2), 134.1 (ArC), 137.5 (ArC), 144.9 (d, $^2J_{\text{CP}} = 17.4$ Hz, C-sp 2) ppm. HRMS (ESI): MH^+ , found 396.1500. $\text{C}_{20}\text{H}_{28}\text{ClNO}_3\text{P}$ requires 396.1490.

Dimethyl 3-Hexyl-2-phenyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10m). Yellowish oil. Yield 0.3 g, 80%. ^1H NMR (400 MHz, CDCl_3): δ 0.82 (3H, t, $^3J = 6.8$ Hz, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 1.14–1.21 (6H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.34–1.46 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 2.28 (2H, t, $^3J = 8.0$ Hz, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 2.34 (2H, quint, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.65 (2H, t, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.83–2.87 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.48 (6H, d, $^3J_{\text{HP}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 7.26–7.28 (2H, m, ArH), 7.39–7.43 (3H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 14.0 (CH_3), 22.4 (CH_2), 25.2 (CH_2), 26.1 (CH_2), 26.5 (CH_2), 28.2 (CH_2), 28.9 (CH_2), 30.5 (CH_2), 31.3 (CH_2), 52.1 (d, $^2J_{\text{CP}} = 5.6$ Hz, OCH_3), 109.2 (d, $^1J_{\text{CP}} = 235.2$ Hz, C-sp 2), 128.1 (d, $^3J_{\text{CP}} = 14.3$ Hz, C-sp 2), 128.2 (ArC), 128.4 (ArC), 128.7 (ArC), 133.8 (d, $^4J_{\text{CP}} = 8.4$ Hz, C-sp 2), 139.0 (ArC), 144.8 (d, $^2J_{\text{CP}} = 17.5$ Hz, C-sp 2) ppm. HRMS (ESI): MNa^+ , found 398.1862. $\text{C}_{21}\text{H}_{30}\text{NNaO}_3\text{P}$ requires 398.1856.

Dimethyl 3-Hexyl-2-(4-methoxyphenyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10n). Yellowish oil. Yield 0.26 g, 63%. ^1H NMR (400 MHz, CDCl_3): δ 0.82 (3H, t, $^3J = 6.8$ Hz, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 1.14–1.24 (6H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 1.37–1.45 (2H, m, $\text{CH}_2\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 2.26 (2H, t, $^3J = 7.6$ Hz, $\text{CH}_2(\text{CH}_2)_4\text{CH}_3$), 2.32 (2H, quint, $^3J = 6.8$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.63 (2H, t, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.81–2.85 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.50 (6H, d, $^3J_{\text{HP}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.83 (3H, s, OCH_3), 6.91 (2H, d, $^3J = 8.8$ Hz, ArH), 7.18 (2H, d, $^3J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.9 (CH_3), 22.4 (CH_2), 25.1 (CH_2), 26.0 (CH_2), 26.5 (CH_2), 28.2 (CH_2), 28.9 (CH_2), 30.4 (CH_2), 31.3 (CH_2), 52.0 (d, $^2J_{\text{CP}} = 5.4$ Hz, OCH_3), 55.3 (OCH_3), 109.3 (d, $^1J_{\text{CP}} = 235.0$ Hz, C-sp 2), 113.4 (ArC), 127.8 (d, $^3J_{\text{CP}} = 14.4$ Hz, C-sp 2), 129.7 (ArC), 131.7 (ArC), 134.0 (d, $^4J_{\text{CP}} = 8.4$ Hz, C-sp 2), 144.4 (d, $^2J_{\text{CP}} = 17.5$ Hz, C-sp 2) ppm. HRMS (ESI): MNa^+ , found 428.1963. $\text{C}_{22}\text{H}_{32}\text{NNaO}_4\text{P}$ requires 428.1961.

Dimethyl 3-(Cyclopropylmethyl)-2-phenyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10o). Yellowish oil. Yield 0.26 g, 76%. ^1H NMR (300 MHz, CDCl_3): δ -0.04–0.00 (2H, m, $\text{CH}(\text{CH}_2)_2$), 0.38–0.43 (2H, m, $\text{CH}(\text{CH}_2)_2$), 0.76–0.89 (1H, m, $\text{CH}(\text{CH}_2)_2$), 2.18 (2H, d, $^3J = 6.8$ Hz, CH_2), 2.31–2.38 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.73 (2H, t, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.87 (2H, t, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.48 (6H, d, $^3J_{\text{HP}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 7.26–7.28 (2H, m, ArH), 7.38–7.42 (2H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 5.0 (CH_2), 9.6 (CH), 25.5 (CH_2), 26.5 (CH_2), 30.4 (CH_2), 31.4 (CH_2), 52.0 (d, $^2J_{\text{CP}} = 5.5$ Hz, OCH_3), 109.5 (d, $^1J_{\text{CP}} = 234.3$ Hz, C-sp 2), 128.2 (ArC), 128.4 (ArC), 128.5 (C-sp 2),

128.7 (ArC), 133.2 (d, $^4J_{\text{CP}} = 8.4$ Hz, C-sp 2), 138.9 (ArC), 144.7 (d, $^2J_{\text{CP}} = 17.5$ Hz, C-sp 2). HRMS (ESI): MNa^+ , found 368.1387. $\text{C}_{19}\text{H}_{24}\text{NNaO}_3\text{P}$ requires 368.1386.

Dimethyl 3-(Cyclopropylmethyl)-2-(4-methoxyphenyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10p). Yellowish oil. Yield 0.26 g, 76%. ^1H NMR (300 MHz, CDCl_3): δ -0.03–0.00 (2H, m, $\text{CH}(\text{CH}_2)_2$), 0.39–0.43 (2H, m, $\text{CH}(\text{CH}_2)_2$), 0.76–0.86 (1H, m, $\text{CH}(\text{CH}_2)_2$), 2.17 (2H, d, $^3J = 7.2$ Hz, CH_2), 2.33 (2H, quint, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.71 (2H, t, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.85 (2H, t, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.50 (6H, d, $^3J_{\text{HP}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.82 (3H, s, OCH_3), 6.90 (2H, d, $^3J = 8.4$ Hz, ArH), 7.18 (2H, d, $^3J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 5.0 (CH_2), 9.7 (CH), 25.5 (CH_2), 26.5 (CH_2), 30.3 (CH_2), 31.3 (CH_2), 52.0 (d, $^2J_{\text{CP}} = 5.5$ Hz, OCH_3), 55.2 (OCH_3), 109.6 (d, $^1J_{\text{CP}} = 234.3$ Hz, C-sp 2), 113.4 (ArC), 128.0 (d, $^3J_{\text{CP}} = 14.2$ Hz, C-sp 2), 129.7 (ArC), 131.7 (ArC), 133.5 (d, $^4J_{\text{CP}} = 8.3$ Hz, C-sp 2), 144.4 (d, $^2J_{\text{CP}} = 17.7$ Hz, C-sp 2), 159.1 (ArC). HRMS (ESI): MNa^+ , found 398.1494. $\text{C}_{20}\text{H}_{26}\text{NNaO}_3\text{P}$ requires 398.1492.

Dimethyl 3-(Cyclopropylmethyl)-2-(4-ethoxyphenyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10r). Yellowish oil. Yield 0.23 g, 59%. ^1H NMR (300 MHz, CDCl_3): δ -0.03–0.00 (2H, m, $\text{CH}(\text{CH}_2)_2$), 0.38–0.43 (2H, m, $\text{CH}(\text{CH}_2)_2$), 0.76–0.86 (1H, m, $\text{CH}(\text{CH}_2)_2$), 1.42 (3H, t, $^3J = 7.2$ Hz, OCH_2CH_3), 2.17 (2H, d, $^3J = 7.2$ Hz, CH_2), 2.38 (2H, quint, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.71 (2H, t, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.85 (2H, t, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.50 (6H, d, $^3J_{\text{HP}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 4.04 (3H, q, $^3J = 7.2$ Hz, OCH_2CH_3), 6.88 (2H, d, $^3J = 8.8$ Hz, ArH), 7.16 (2H, d, $^3J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 5.0 (CH_2), 9.7 (CH), 14.7 (CH_3), 25.5 (CH_2), 26.5 (CH_2), 30.3 (CH_2), 31.4 (CH_2), 52.0 (d, $^2J_{\text{CP}} = 5.5$ Hz, OCH_3), 63.5 (OCH_3), 109.6 (d, $^1J_{\text{CP}} = 234.6$ Hz, C-sp 2), 113.9, 128.0 (d, $^3J_{\text{CP}} = 14.3$ Hz, C-sp 2), 129.7 (ArC), 131.6 (ArC), 133.5 (d, $^4J_{\text{CP}} = 8.5$ Hz, C-sp 2), 144.4 (d, $^2J_{\text{CP}} = 17.5$ Hz, C-sp 2), 158.6 (ArC). HRMS (ESI): MNa^+ , found 412.1646. $\text{C}_{21}\text{H}_{28}\text{NNaO}_4\text{P}$ requires 412.1648.

Dimethyl 3-Methyl-2-phenyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (10s). Yellowish oil. Yield 0.2 g, 66%. ^1H NMR (400 MHz, CDCl_3): δ 1.93 (3H, s, CH_3), 2.34 (2H, quint, $^3J = 6.8$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.60 (2H, t, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.86 (2H, td, $^3J_{\text{HH}} = 7.2$ Hz, $^4J_{\text{HP}} = 1.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.49 (6H, d, $^3J_{\text{HP}} = 11.6$ Hz, $2 \times \text{OCH}_3$), 7.26–7.28 (2H, m, ArH), 7.37–7.45 (3H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 11.6 (CH_3), 24.4 (CH_2), 26.8 (CH_2), 30.4 (CH_2), 52.1 (d, $^2J_{\text{CP}} = 5.5$ Hz, OCH_3), 109.4 (d, $^1J_{\text{CP}} = 235.1$ Hz, C-sp 2), 128.2 (ArC), 128.4 (ArC), 128.5 (ArC), 128.8 (d, $^3J_{\text{CP}} = 14.3$ Hz, C-sp 2), 129.0 (d, $^4J_{\text{CP}} = 8.8$ Hz, C-sp 2), 139.0 (ArC), 144.6 (d, $^2J_{\text{CP}} = 17.5$ Hz, C-sp 2) ppm. HRMS (ESI): MH^+ , found 306.1263. $\text{C}_{16}\text{H}_{21}\text{NO}_3\text{P}$ requires 306.1254.

Dimethyl 3-Benzyl-2-phenyl-2H-isindol-1-ylphosphonate (11a). Light orange solid, mp 82–83 °C. Yield 0.28 g, 72%. ^1H NMR (400 MHz, CDCl_3): δ 3.53 (6H, d, $^3J_{\text{HP}} = 11.6$ Hz, $2 \times \text{OCH}_3$), 4.14 (2H, s, CH_2), 6.82–6.85 (2H, m, ArH), 7.09–7.15 (5H, m, ArH), 7.22–7.24 (1H, m, ArH), 7.37–7.49 (4H, m, ArH), 7.57–7.64 (4H, m, ArH), 7.56–7.61 (1H, m, ArH), 8.11 (1H, dt, $J = 8.8$; 0.8 Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 31.1 (d, $^4J_{\text{CP}} = 1.1$ Hz, CH_2), 52.2 (d, $^3J_{\text{CP}} = 5.4$ Hz, $2 \times \text{OCH}_3$), 106.5 (d, $^1J_{\text{CP}} = 235.4$ Hz, ArC), 119.7 (ArC), 120.3 (ArC), 121.7 (ArC), 123.3 (d, $^3J_{\text{CP}} = 13.6$ Hz, ArC), 125.0 (d, $^4J_{\text{CP}} = 0.4$ Hz, ArC), 126.3 (ArC), 128.1 (ArC), 128.2 (ArC), 128.3 (2 $\times$ ArC), 129.2 (ArC), 131.9 (d, $^2J_{\text{CP}} = 8.6$ Hz, ArC), 132.1 (d, $^2J_{\text{CP}} = 18.2$ Hz, ArC), 138.0 (ArC), 138.4 (d, $^5J_{\text{CP}} = 0.7$ Hz, ArC) ppm. HRMS (ESI): MH^+ , found 392.1410. $\text{C}_{23}\text{H}_{23}\text{NO}_3\text{P}$ requires 392.1410.

Dimethyl 2,3-Diphenyl-1,2-dihydroisoquinolin-1-ylphosphonate (12a). Light orange solid, mp 128–129 °C. Yield 0.34 g, 86%. ^1H NMR (400 MHz, CDCl_3): δ 3.69 (3H, d, $^3J_{\text{HP}} = 10.4$ Hz, OCH_3), 3.76 (3H, d, $^3J_{\text{HP}} = 10.4$ Hz, OCH_3), 5.57 (1H, d, $^1J_{\text{HP}} = 18.8$ Hz, CH), 6.62 (1H, s, C_{sp^3}H), 6.91–6.95 (1H, m, ArH), 7.16–7.17 (3H, m, ArH), 7.21–7.28 (4H, m, ArH), 7.30–7.34 (4H, m, ArH), 7.65–7.67 (2H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 53.1 (d, $^2J_{\text{CP}} = 6.4$ Hz, OCH_3), 53.2 (d, $^2J_{\text{CP}} = 6.2$ Hz, OCH_3), 63.8 (d, $^1J_{\text{CP}} = 162.2$ Hz, CH), 111.9 (C_{sp^3}H), 122.4 (ArC), 122.6 (d, $J_{\text{CP}} = 2.0$ Hz, ArC), 124.3 (d, $^2J_{\text{CP}} = 2.6$ Hz, ArC), 125.2 (d, $J_{\text{CP}} = 3.1$ Hz, ArC),

126.6 (d, $J_{\text{C,P}} = 1.9$ Hz, ArC), 127.1 (d, $J_{\text{C,P}} = 5.9$ Hz, ArC), 127.5 (ArC), 128.0 (ArC), 128.3 (ArC), 128.3 (d, $^2J_{\text{C,P}} = 3.1$ Hz, ArC), 128.5 (ArC), 132.8 (d, $^3J_{\text{C,P}} = 3.2$ Hz, ArC), 137.0 (ArC), 142.0 (d, $J_{\text{C,P}} = 1.6$ Hz, ArC), 147.4 (d, $^3J_{\text{C,P}} = 7.0$ Hz, ArC) ppm. HRMS (ESI): MNa^+ , found 414.1222. $\text{C}_{23}\text{H}_{22}\text{NNaO}_3\text{P}$ requires 414.1230.

Dimethyl 3-Benzyl-2-phenyl-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (14a). Yellowish oil. Yield 0.32 g, 82%. ^1H NMR (400 MHz, CDCl_3): δ 1.77–1.79 (4H, m, $2 \times \text{CH}_2$), 2.46 (2H, t, $J = 5.6$ Hz, CH_2), 2.88 (2H, t, $J = 5.6$ Hz, CH_2), 3.46 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.67 (2H, s, CH_2), 6.79–6.81 (2H, m, ArH), 7.07 (2H, dd, $J = 8.2$; 1.6 Hz, ArH), 7.10–7.16 (3H, m, ArH), 7.27–7.34 (3H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 21.8 (d, $^3J_{\text{C,P}} = 1.1$ Hz, CH_2), 23.1 (CH₂), 23.3 (CH₂), 23.5 (CH₂), 30.6 (d, $^4J_{\text{C,P}} = 1.0$ Hz, CH_2), 51.7 (d, $^2J_{\text{C,P}} = 5.5$ Hz, $2 \times \text{OCH}_3$), 112.9 (d, $^1J_{\text{C,P}} = 230.2$ Hz, ArC), 118.7 (d, $^3J_{\text{C,P}} = 14.7$ Hz, ArC), 125.8 (ArC), 128.0 (ArC), 128.1 ($2 \times$ ArC), 128.2 (ArC), 128.8 (ArC), 133.9 (d, $^2J_{\text{C,P}} = 19.1$ Hz, ArC), 134.8 (d, $^3J_{\text{C,P}} = 9.8$ Hz, ArC), 138.6 (ArC), 138.7 (ArC) ppm. HRMS (ESI): MNa^+ , found 418.1548. $\text{C}_{23}\text{H}_{26}\text{NNaO}_3\text{P}$ requires 418.1543.

Dimethyl 3-Benzyl-2-(4-methoxyphenyl)-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (14b). Brownish solid, mp 108–109 °C. Yield 0.4 g, 95%. ^1H NMR (400 MHz, CDCl_3): δ 1.76–1.78 (4H, m, $2 \times \text{CH}_2$), 2.45 (2H, t, $J = 5.6$ Hz, CH_2), 2.86 (2H, t, $J = 5.6$ Hz, CH_2), 3.48 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.66 (2H, s, CH_2), 3.80 (3H, s, OCH_3), 6.79 (2H, d, $J = 8.8$ Hz, ArH), 6.81–6.83 (2H, m, ArH), 6.97 (3H, d, $J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 21.8 (d, $^3J_{\text{C,P}} = 1.0$ Hz, CH_2), 23.2 (CH₂), 23.4 (CH₂), 23.6 (CH₂), 30.7 (d, $^4J_{\text{C,P}} = 1.0$ Hz, CH_2), 51.8 (d, $^2J_{\text{C,P}} = 5.4$ Hz, $2 \times \text{OCH}_3$), 55.3 (OCH_3), 113.0 (d, $^1J_{\text{C,P}} = 230.3$ Hz, ArC), 113.2 (ArC), 118.6 (d, $^3J_{\text{C,P}} = 14.8$ Hz, ArC), 125.8 (ArC), 128.1 ($2 \times$ ArC), 129.8 (ArC), 131.3 (ArC), 133.7 (d, $^2J_{\text{C,P}} = 19.2$ Hz, ArC), 135.2 (d, $^3J_{\text{C,P}} = 9.9$ Hz, ArC), 138.9 (ArC), 159.2 (ArC) ppm. HRMS (ESI): MNa^+ , found 448.1645. $\text{C}_{24}\text{H}_{28}\text{NNaO}_4\text{P}$ requires 448.1648.

Dimethyl 3-Benzyl-2-(4-fluorophenyl)-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (14c). Yellowish solid, mp 95–96 °C. Yield 0.23 g, 56%. ^1H NMR (400 MHz, CDCl_3): δ 1.77–1.79 (4H, m, $2 \times \text{CH}_2$), 2.48–2.49 (2H, m, CH_2), 2.85–2.86 (2H, m, CH_2), 3.49 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.66 (2H, s, CH_2), 6.78–6.80 (2H, m, ArH), 6.93–7.01 (4H, m, ArH), 7.11–7.17 (3H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 21.8 (d, $^3J_{\text{C,P}} = 1.0$ Hz, CH_2), 23.1 (CH₂), 23.3 (CH₂), 23.5 (CH₂), 30.6 (d, $^4J_{\text{C,P}} = 1.1$ Hz, CH_2), 51.8 (d, $^2J_{\text{C,P}} = 5.5$ Hz, $2 \times \text{OCH}_3$), 113.2 (d, $^1J_{\text{C,P}} = 230.2$ Hz, ArC), 115.0 (d, $^2J_{\text{C,F}} = 22.5$ Hz, ArC), 119.0 (d, $^3J_{\text{C,P}} = 14.7$ Hz, ArC), 126.0 (ArC), 128.0 (ArC), 128.2 (ArC), 130.5 (d, $^3J_{\text{C,F}} = 8.7$ Hz, ArC), 133.9 (d, $^2J_{\text{C,P}} = 19.0$ Hz, ArC), 134.6 (d, $^4J_{\text{C,P}} = 3.0$ Hz, ArC), 135.0 (d, $^3J_{\text{C,P}} = 9.8$ Hz, ArC), 138.6 (ArC), 162.1 (d, $^1J_{\text{C,F}} = 246.5$ Hz, ArC) ppm. HRMS (ESI): MNa^+ , found 436.1452. $\text{C}_{23}\text{H}_{25}\text{FNNaO}_3\text{P}$ requires 436.1448.

Dimethyl 3-Benzyl-2-(4-chlorophenyl)-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (14d). Yellowish oil. Yield 0.29 g, 68%. ^1H NMR (400 MHz, CDCl_3): δ 1.77–1.78 (4H, m, $2 \times \text{CH}_2$), 2.46–2.48 (2H, m, CH_2), 2.84–2.86 (2H, m, CH_2), 3.49 (6H, d, $^3J_{\text{H,P}} = 11.6$ Hz, $2 \times \text{OCH}_3$), 3.66 (2H, s, CH_2), 6.78–6.80 (2H, m, ArH), 6.97 (2H, d, $J = 8.4$ Hz, ArH), 7.10–7.18 (3H, m, ArH), 7.25 (2H, d, $J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 21.7 (d, $^3J_{\text{C,P}} = 1.1$ Hz, CH_2), 23.1 (CH₂), 23.3 (CH₂), 23.4 (CH₂), 30.6 (d, $^4J_{\text{C,P}} = 1.0$ Hz, CH_2), 51.9 (d, $^2J_{\text{C,P}} = 5.5$ Hz, $2 \times \text{OCH}_3$), 113.1 (d, $^1J_{\text{C,P}} = 229.9$ Hz, ArC), 119.1 (d, $^3J_{\text{C,P}} = 14.6$ Hz, ArC), 126.0 (ArC), 127.9 (ArC), 128.2 (ArC), 128.3 (ArC), 130.1 (ArC), 134.1 (d, $^2J_{\text{C,P}} = 18.9$ Hz, ArC), 134.1 (ArC), 134.9 (d, $^3J_{\text{C,P}} = 9.7$ Hz, ArC), 137.2 (ArC), 138.5 (ArC) ppm. HRMS (ESI): MNa^+ , found 452.1157. $\text{C}_{23}\text{H}_{25}\text{ClNNaO}_3\text{P}$ requires 452.1153.

Dimethyl 3-(4-Methylbenzyl)-2-phenyl-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (14e). Yellowish oil. Yield 0.38 g, 92%. ^1H NMR (400 MHz, CDCl_3): δ 1.76–1.78 (4H, m, $2 \times \text{CH}_2$), 2.27 (3H, s, CH_3), 2.43–2.47 (2H, m, CH_2), 2.87–2.89 (2H, m, CH_2), 3.47 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.63 (2H, s, CH_2), 6.70 (2H, d, $J = 8.0$ Hz, ArH), 6.96 (2H, d, $J = 8.0$ Hz, ArH), 7.08–7.10 (2H, m, ArH), 7.28–7.35 (3H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 20.9 (CH₃), 21.8 (d, $^3J_{\text{C,P}} = 1.0$ Hz, CH_2), 23.2

(CH₂), 23.4 (CH₂), 23.5 (CH₂), 30.2 (d, $^4J_{\text{C,P}} = 1.1$ Hz, CH_2), 51.8 (d, $^2J_{\text{C,P}} = 5.5$ Hz, $2 \times \text{OCH}_3$), 112.7 (d, $^1J_{\text{C,P}} = 230.7$ Hz, ArC), 118.7 (d, $^3J_{\text{C,P}} = 14.9$ Hz, ArC), 127.9 (ArC), 128.1 (ArC), 128.2 (ArC), 128.8 ($2 \times$ ArC), 134.0 (d, $^2J_{\text{C,P}} = 19.2$ Hz, ArC), 135.2 (d, $^3J_{\text{C,P}} = 9.9$ Hz, ArC), 135.3 (ArC), 135.7 (ArC), 138.7 (ArC) ppm. HRMS (ESI): MNa^+ , found 432.1706. $\text{C}_{24}\text{H}_{28}\text{NNaO}_3\text{P}$ requires 432.1699.

Dimethyl 2-(4-Methoxyphenyl)-3-(4-methylbenzyl)-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (14e). Yellowish oil. Yield 0.35 g, 79%. ^1H NMR (400 MHz, CDCl_3): δ 1.75–1.77 (4H, m, $2 \times \text{CH}_2$), 2.27 (3H, s, CH_3), 2.42–2.45 (2H, m, CH_2), 2.85–2.87 (2H, m, CH_2), 3.49 (6H, d, $^3J_{\text{H,P}} = 11.6$ Hz, $2 \times \text{OCH}_3$), 3.62 (2H, s, CH_2), 3.81 (3H, s, OCH_3), 6.72 (2H, d, $J = 7.6$ Hz, ArH), 6.80 (2H, d, $J = 8.8$ Hz, ArH), 6.96–7.00 (4H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 20.9 (CH₃), 21.8 (d, $^3J_{\text{C,P}} = 1.1$ Hz, CH_2), 23.2 (CH₂), 23.4 (CH₂), 23.6 (CH₂), 30.2 (d, $^4J_{\text{C,P}} = 1.0$ Hz, CH_2), 51.9 (d, $^2J_{\text{C,P}} = 5.4$ Hz, $2 \times \text{OCH}_3$), 55.3 (OCH_3), 112.6 (d, $^1J_{\text{C,P}} = 230.5$ Hz, ArC), 113.2 (ArC), 118.5 (d, $^3J_{\text{C,P}} = 14.8$ Hz, ArC), 127.9 (ArC), 128.8 (ArC), 129.8 (ArC), 131.3 (ArC), 133.9 (d, $^2J_{\text{C,P}} = 19.2$ Hz, ArC), 135.3 (ArC), 135.5 (d, $^3J_{\text{C,P}} = 10.0$ Hz, ArC), 135.8 (ArC), 159.2 (ArC) ppm. HRMS (ESI): MNa^+ , found 462.1795. $\text{C}_{25}\text{H}_{30}\text{NNaO}_4\text{P}$ requires 462.1805.

Dimethyl 3-Butyl-2-phenyl-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (14g). Yellowish oil. Yield 0.32 g, 89%. ^1H NMR (400 MHz, CDCl_3): δ 0.72 (3H, t, $J = 7.2$ Hz, CH_3), 1.11 (2H, sextet, $J = 7.2$ Hz, CH_2), 1.22–1.26 (2H, m, CH_2), 1.74–1.77 (4H, m, $2 \times \text{CH}_{2\text{chex}}$), 2.27 (2H, t, $J = 7.6$ Hz, CH_2), 2.48 (2H, br. s, $\text{CH}_{2\text{chex}}$), 2.83 (2H, br. s, $\text{CH}_{2\text{chex}}$), 3.45 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 7.22–7.25 (2H, m, ArH), 7.39–7.41 (3H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.5 (CH₃), 21.7 (d, $^3J_{\text{C,P}} = 1.2$ Hz, CH_2), 22.3 (CH₂), 23.1 (CH₂), 23.4 (CH₂), 23.5 (CH₂), 24.3 (d, $^4J_{\text{C,P}} = 1.1$ Hz, CH_2), 31.0 (CH₂), 51.8 (d, $^2J_{\text{C,P}} = 5.4$ Hz, $2 \times \text{OCH}_3$), 112.0 (d, $^1J_{\text{C,P}} = 230.8$ Hz, ArC), 117.6 (d, $^3J_{\text{C,P}} = 14.8$ Hz, ArC), 128.2 ($2 \times$ ArC), 128.8 (ArC), 134.0 (d, $^2J_{\text{C,P}} = 19.2$ Hz, ArC), 137.4 (d, $^3J_{\text{C,P}} = 9.7$ Hz, ArC), 138.9 (ArC) ppm. HRMS (ESI): MNa^+ , found 384.1695. $\text{C}_{20}\text{H}_{28}\text{NNaO}_3\text{P}$ requires 384.1699.

Dimethyl 3-Butyl-2-(4-methoxyphenyl)-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (14h). Yellowish oil. Yield 0.39 g, 99%. ^1H NMR (400 MHz, CDCl_3): δ 0.74 (3H, t, $J = 7.2$ Hz, CH_3), 1.13 (2H, sextet, $J = 7.2$ Hz, CH_2), 1.20–1.29 (2H, m, CH_2), 1.74–1.76 (4H, m, $2 \times \text{CH}_{2\text{chex}}$), 2.26 (2H, t, $J = 7.6$ Hz, CH_2), 2.47 (2H, br. s, $\text{CH}_{2\text{chex}}$), 2.82 (2H, br. s, $\text{CH}_{2\text{chex}}$), 3.48 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.83 (3H, s, OCH_3), 6.90 (2H, d, $J = 8.8$ Hz, ArH), 7.14 (2H, d, $J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.6 (CH₃), 21.7 (CH₂), 22.3 (CH₂), 23.1 (CH₂), 23.4 (CH₂), 23.5 (CH₂), 24.3 (CH₂), 31.1 (CH₂), 51.8 (d, $^2J_{\text{C,P}} = 5.3$ Hz, $2 \times \text{OCH}_3$), 55.3 (OCH_3), 111.8 (d, $^1J_{\text{C,P}} = 231.3$ Hz, ArC), 113.3 (ArC), 117.4 (d, $^3J_{\text{C,P}} = 14.9$ Hz, ArC), 129.7 (ArC), 131.6 (ArC), 133.8 (d, $^2J_{\text{C,P}} = 19.4$ Hz, ArC), 137.7 (d, $^3J_{\text{C,P}} = 9.7$ Hz, ArC), 159.1 (ArC) ppm. HRMS (ESI): MNa^+ , found 414.1801. $\text{C}_{21}\text{H}_{30}\text{NNaO}_4\text{P}$ requires 414.1805.

Dimethyl 3-Butyl-2-(4-fluorophenyl)-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (14i). Yellowish oil. Yield 0.31 g, 81%. ^1H NMR (400 MHz, CDCl_3): δ 0.73 (3H, t, $J = 7.2$ Hz, CH_3), 1.12 (2H, sextet, $J = 7.2$ Hz, CH_2), 1.21–1.25 (2H, m, CH_2), 1.72–1.76 (4H, m, $2 \times \text{CH}_{2\text{chex}}$), 2.25 (2H, t, $J = 8.0$ Hz, CH_2), 2.46 (2H, br. s, $\text{CH}_{2\text{chex}}$), 2.80 (2H, br. s, $\text{CH}_{2\text{chex}}$), 3.48 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 7.06–7.10 (2H, m, ArH), 7.19–7.22 (2H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.6 (CH₃), 21.7 (d, $^3J_{\text{C,P}} = 1.2$ Hz, CH_2), 22.4 (CH₂), 23.1 (CH₂), 23.4 (CH₂), 23.5 (CH₂), 24.4 (CH₂), 31.1 (CH₂), 51.9 (d, $^2J_{\text{C,P}} = 5.4$ Hz, $2 \times \text{OCH}_3$), 112.2 (d, $^1J_{\text{C,P}} = 230.8$ Hz, ArC), 115.2 (d, $^2J_{\text{C,F}} = 22.6$ Hz, ArC), 117.8 (d, $^3J_{\text{C,P}} = 14.8$ Hz, ArC), 130.5 (d, $^3J_{\text{C,F}} = 8.6$ Hz, ArC), 134.1 (d, $^2J_{\text{C,P}} = 19.2$ Hz, ArC), 134.0 (d, $^4J_{\text{C,P}} = 3.2$ Hz, ArC), 137.6 (d, $^3J_{\text{C,P}} = 9.5$ Hz, ArC), 162.2 (d, $^1J_{\text{C,F}} = 246.4$ Hz, ArC) ppm. HRMS (ESI): MNa^+ , found 402.1610. $\text{C}_{20}\text{H}_{27}\text{FNNaO}_3\text{P}$ requires 402.1605.

Dimethyl 3-Pentyl-2-phenyl-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (14j). Brownish oil. Yield 0.33 g, 88%. ^1H NMR (400 MHz, CDCl_3): δ 0.75 (3H, t, $J = 7.2$ Hz, CH_3), 1.05–1.15 (4H, m, $2 \times \text{CH}_2$), 1.22–1.29 (2H, m, CH_2), 1.74–1.77 (4H, m, $2 \times \text{CH}_{2\text{chex}}$), 2.26 (2H, t, $J = 7.6$ Hz, CH_2), 2.48 (2H, br. s, $\text{CH}_{2\text{chex}}$), 2.83 (2H, br. s, $\text{CH}_{2\text{chex}}$), 3.45 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 7.22–

7.24 (2H, m, ArH), 7.39–7.41 (3H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.7 (CH_3), 21.7 (d, $^3J_{\text{C,P}} = 1.2$ Hz, CH_2), 22.0 (CH_2), 23.1 (CH_2), 23.4 (CH_2), 23.5 (CH_2), 24.6 (d, $J_{\text{C,P}} = 0.9$ Hz, CH_2), 28.4 (CH_2), 31.3 (CH_2), 51.7 (d, $^2J_{\text{C,P}} = 5.5$ Hz, $2 \times \text{OCH}_3$), 112.0 (d, $^1J_{\text{C,P}} = 231.0$ Hz, ArC), 117.6 (d, $^3J_{\text{C,P}} = 14.9$ Hz, ArC), 128.2 ($2 \times$ ArC), 128.8 (ArC), 134.0 (d, $^2J_{\text{C,P}} = 19.3$ Hz, ArC), 137.4 (d, $^3J_{\text{C,P}} = 9.7$ Hz, ArC), 138.9 (ArC) ppm. HRMS (ESI): MNa^+ , found 398.1845. $\text{C}_{21}\text{H}_{30}\text{NNaO}_3\text{P}$ requires 398.1856.

Dimethyl 2-(4-Methoxyphenyl)-3-pentyl-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (14k). Light brown oil. Yield 0.33 g, 82%. ^1H NMR (400 MHz, CDCl_3): δ 0.77 (3H, t, $J = 7.2$ Hz, CH_3), 1.08–1.15 (4H, m, $2 \times \text{CH}_2$), 1.22–1.30 (2H, m, CH_2), 1.75 (4H, br. s, $2 \times \text{CH}_{2\text{chex}}$), 2.25 (2H, t, $J = 7.6$ Hz, CH_2), 2.46 (2H, br. s, $\text{CH}_{2\text{chex}}$), 2.82 (2H, br. s, $\text{CH}_{2\text{chex}}$), 3.47 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.83 (3H, s, OCH_3), 6.90 (2H, d, $J = 8.8$ Hz, ArH), 7.14 (2H, d, $J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.7 (CH_3), 21.7 (d, $^3J_{\text{C,P}} = 0.9$ Hz, CH_2), 22.1 (CH_2), 23.1 (CH_2), 23.4 (CH_2), 23.5 (CH_2), 24.6 (d, $^4J_{\text{C,P}} = 0.7$ Hz, CH_2), 28.5 (CH_2), 31.4 (CH_2), 51.8 (d, $^2J_{\text{C,P}} = 5.4$ Hz, $2 \times \text{OCH}_3$), 55.3 (OCH_3), 112.0 (d, $^1J_{\text{C,P}} = 231.1$ Hz, ArC), 113.3 (ArC), 117.4 (d, $^3J_{\text{C,P}} = 14.8$ Hz, ArC), 129.7 (ArC), 131.6 (ArC), 133.8 (d, $^2J_{\text{C,P}} = 19.3$ Hz, ArC), 137.6 (d, $^3J_{\text{C,P}} = 9.7$ Hz, ArC), 159.1 (ArC) ppm. HRMS (ESI): MNa^+ , found 428.1969. $\text{C}_{22}\text{H}_{32}\text{NNaO}_4\text{P}$ requires 428.1961.

Dimethyl 3-(Cyclopropylmethyl)-2-phenyl-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (14l). Yellowish oil. Yield 0.3 g, 83%. ^1H NMR (400 MHz, CDCl_3): δ -0.16 (2H, q, $J = 4.8$ Hz, $\text{CH}(\text{CH}_2)_2$), 0.26–0.30 (2H, m, $\text{CH}(\text{CH}_2)_2$), 0.57–0.67 (1H, m, $\text{CH}(\text{CH}_2)_2$), 1.76 (4H, t, $J = 3.2$ Hz, $2 \times \text{CH}_2$), 2.21 (2H, d, $J = 6.8$ Hz, CH_2), 2.52 (2H, br. s, CH_2), 2.85 (2H, br. s, CH_2), 3.45 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 7.24–7.25 (2H, m, ArH), 7.37–7.41 (3H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 4.8 ($\text{CH}(\text{CH}_2)_2$), 10.2 ($\text{CH}(\text{CH}_2)_2$), 21.9 (d, $^3J_{\text{C,P}} = 1.1$ Hz, $\text{CH}_{2\text{chex}}$), 23.1 ($\text{CH}_{2\text{chex}}$), 23.4 ($2 \times \text{CH}_{2\text{chex}}$), 29.4 (d, $^4J_{\text{C,P}} = 1.60$ Hz, CH_2), 51.7 (d, $^2J_{\text{C,P}} = 5.4$ Hz, $2 \times \text{OCH}_3$), 112.3 (d, $^1J_{\text{C,P}} = 230.4$ Hz, ArC), 117.7 (d, $^3J_{\text{C,P}} = 14.8$ Hz, ArC), 128.1 (ArC), 128.2 (ArC), 128.9 (ArC), 133.9 (d, $^2J_{\text{C,P}} = 19.3$ Hz, ArC), 136.9 (d, $^3J_{\text{C,P}} = 9.5$ Hz, ArC), 139.0 (ArC) ppm. HRMS (ESI): MNa^+ , found 382.1541. $\text{C}_{20}\text{H}_{26}\text{NNaO}_3\text{P}$ requires 382.1543.

Dimethyl 3-(Cyclopropylmethyl)-2-(4-methoxyphenyl)-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (14m). Yellowish oil. Yield 0.36 g, 92%. ^1H NMR (400 MHz, CDCl_3): δ -0.15 to -0.11 (2H, m, $\text{CH}(\text{CH}_2)_2$), 0.27–0.31 (2H, m, $\text{CH}(\text{CH}_2)_2$), 0.61–0.65 (1H, m, $\text{CH}(\text{CH}_2)_2$), 1.75 (4H, br. s, $2 \times \text{CH}_2$), 2.19 (2H, d, $J = 6.8$ Hz, CH_2), 2.51 (2H, br. s, CH_2), 2.83 (2H, br. s, CH_2), 3.47 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.82 (3H, s, OCH_3), 6.89 (2H, d, $J = 8.8$ Hz, ArH), 7.15 (2H, d, $J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 4.8 ($\text{CH}(\text{CH}_2)_2$), 10.3 ($\text{CH}(\text{CH}_2)_2$), 21.9 (d, $^3J_{\text{C,P}} = 1.0$ Hz, $\text{CH}_{2\text{chex}}$), 23.1 ($\text{CH}_{2\text{chex}}$), 23.4 ($\text{CH}_{2\text{chex}}$), 23.5 ($\text{CH}_{2\text{chex}}$), 29.5 (d, $^4J_{\text{C,P}} = 0.7$ Hz, CH_2), 51.7 (d, $^2J_{\text{C,P}} = 5.4$ Hz, $2 \times \text{OCH}_3$), 55.2 (OCH_3), 112.2 (d, $^1J_{\text{C,P}} = 230.8$ Hz, ArC), 113.2 (ArC), 117.5 (d, $^3J_{\text{C,P}} = 14.8$ Hz, ArC), 129.9 (ArC), 131.6 (ArC), 133.8 (d, $^2J_{\text{C,P}} = 19.4$ Hz, ArC), 137.3 (d, $^3J_{\text{C,P}} = 9.6$ Hz, ArC), 159.2 (ArC) ppm. HRMS (ESI): MNa^+ , found 412.1650. $\text{C}_{21}\text{H}_{28}\text{NNaO}_4\text{P}$ requires 412.1648.

Dimethyl 2-(4-Chlorophenyl)-3-(cyclopropylmethyl)-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (14n). Yellowish oil. Yield 0.36 g, 92%. ^1H NMR (400 MHz, CDCl_3): δ -0.15 to -0.11 (2H, m, $\text{CH}(\text{CH}_2)_2$), 0.28–0.33 (2H, m, $\text{CH}(\text{CH}_2)_2$), 0.55–0.65 (1H, m, $\text{CH}(\text{CH}_2)_2$), 1.74–1.76 (4H, m, $2 \times \text{CH}_2$), 2.20 (2H, d, $J = 6.8$ Hz, CH_2), 2.51 (2H, br. s, CH_2), 2.82 (2H, br. s, CH_2), 3.49 (6H, d, $^3J_{\text{H,P}} = 11.6$ Hz, $2 \times \text{OCH}_3$), 7.19 (2H, d, $J = 8.8$ Hz, ArH), 7.37 (2H, d, $J = 8.4$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 4.9 ($\text{CH}(\text{CH}_2)_2$), 10.3 ($\text{CH}(\text{CH}_2)_2$), 21.9 (d, $^3J_{\text{C,P}} = 1.2$ Hz, $\text{CH}_{2\text{chex}}$), 23.1 ($\text{CH}_{2\text{chex}}$), 23.3 ($\text{CH}_{2\text{chex}}$), 23.4 ($\text{CH}_{2\text{chex}}$), 29.4 (d, $^4J_{\text{C,P}} = 1.0$ Hz, CH_2), 51.8 (d, $^2J_{\text{C,P}} = 5.4$ Hz, $2 \times \text{OCH}_3$), 112.5 (d, $^1J_{\text{C,P}} = 230.3$ Hz, ArC), 118.1 (d, $^3J_{\text{C,P}} = 14.8$ Hz, ArC), 128.4 (ArC), 130.3 (ArC), 134.2 (d, $^2J_{\text{C,P}} = 20.0$ Hz, ArC), 134.2 (ArC), 137.0 (d, $^3J_{\text{C,P}} = 9.4$ Hz, ArC), 137.6 (ArC) ppm. HRMS (ESI): MNa^+ , found 416.1161. $\text{C}_{20}\text{H}_{23}\text{ClNNaO}_3\text{P}$ requires 416.1153.

General Procedure for the Preparation of Compounds 13 and 15–18. To a cooled solution of the corresponding acetylenic α -anilinomethylphosphonate 7–9 (1 mmol) in dry chloroform (5 mL)

was added molecular iodine (0.254 g, 1 mmol) at 0 °C, together with phenyliodine diacetate (0.644 g, 2 mmol). The resulting stirring solution was allowed to warm to room temperature. When the completion of the reaction was observed by TLC (after 0.5–1 h), the solution was quenched with aqueous sodium thiosulfate. The organic layer was separated, washed with aqueous sodium thiosulfate (2×20 mL) and then with water (2×20 mL), and dried over anhydrous Na_2SO_4 . After the evaporation of solvent under reduced pressure, the residue was purified by flash column chromatography eluting with hexane–ethyl acetate mixtures.

Dimethyl 3-Benzoyl-2-phenyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (13a). Yellowish oil. Yield 0.35 g, 89%. IR (KBr): ν_{max} 1644 ($\text{C}=\text{O}$) cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 2.21–2.31 (2H, m, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.42 (2H, t, $^3J = 6.9$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.89 (2H, td, $^3J_{\text{H,H}} = 7.3$ Hz, $^4J_{\text{H,P}} = 1.5$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.53 (6H, d, $^3J_{\text{H,P}} = 11.4$ Hz, $2 \times \text{OCH}_3$), 7.35–7.38 (5H, m, ArH), 7.40–7.44 (2H, m, ArH), 7.49–7.54 (1H, m, ArH), 7.71–7.74 (2H, m, ArH) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 26.7 (CH_2), 27.7 (CH_2), 30.1 (CH_2), 52.4 (d, $^2J_{\text{C,P}} = 5.7$ Hz, OCH_3), 119.7 (d, $^1J_{\text{C,P}} = 225.4$ Hz, C-sp 2), 127.9 (ArC), 128.2 (ArC), 128.2 ($2 \times$ ArC), 129.0 (ArC), 130.2 (d, $^4J_{\text{C,P}} = 9.0$ Hz, C-sp 2), 132.2 (ArC), 138.7 (ArC), 139.2 (d, $^3J_{\text{C,P}} = 13.8$ Hz, C-sp 2), 139.6 (ArC), 143.4 (d, $^2J_{\text{C,P}} = 17.1$ Hz, C-sp 2), 186.3 ($\text{C}=\text{O}$) ppm. HRMS (ESI): MNa^+ , found 418.1176. $\text{C}_{22}\text{H}_{22}\text{NNaO}_4\text{P}$ requires 418.1179.

Dimethyl 3-Benzoyl-2-(4-methoxyphenyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (13b). Yellowish oil. Yield 0.28 g, 67%. IR (KBr): ν_{max} 1645 ($\text{C}=\text{O}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 2.25 (2H, quint, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.40 (2H, t, $^3J = 7.6$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.87 (2H, td, $^3J_{\text{H,H}} = 7.2$ Hz, $^4J_{\text{H,P}} = 1.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.56 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.80 (3H, s, OCH_3), 6.87 (2H, d, $^3J = 9.2$ Hz, ArH), 7.28 (2H, d, $^3J = 8.8$ Hz, ArH), 7.38–7.42 (2H, m, ArH), 7.49–7.53 (1H, m, ArH), 7.71–7.73 (2H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 26.6 (CH_2), 27.7 (CH_2), 30.1 (CH_2), 52.4 (d, $^2J_{\text{C,P}} = 5.7$ Hz, OCH_3), 55.2 (OCH_3), 113.3 (ArC), 119.8 (d, $^1J_{\text{C,P}} = 225.9$ Hz, C-sp 2), 126.8 (ArC), 128.1 (ArC), 129.0 (ArC), 129.0 (ArC), 130.3 (d, $^4J_{\text{C,P}} = 8.8$ Hz, C-sp 2), 132.2 (ArC), 138.8 (ArC), 138.9 (d, $^3J_{\text{C,P}} = 14.0$ Hz, C-sp 2), 143.0 (d, $^2J_{\text{C,P}} = 17.0$ Hz, C-sp 2), 159.1 (ArC), 186.3 ($\text{C}=\text{O}$) ppm. HRMS (ESI): MNa^+ , found 448.1287. $\text{C}_{23}\text{H}_{24}\text{NNaO}_5\text{P}$ requires 448.1284.

Dimethyl 3-Benzoyl-2-(4-ethoxyphenyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (13c). Yellowish oil. Yield 0.31 g, 70%. IR (KBr): ν_{max} 1643 ($\text{C}=\text{O}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.39 (3H, t, $^3J = 6.8$ Hz, OCH_2CH_3), 2.25 (2H, quint, $^3J = 6.8$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.40 (2H, t, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.87 (2H, td, $^3J_{\text{H,H}} = 7.6$ Hz, $^4J_{\text{H,P}} = 1.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.55 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 4.02 (2H, q, $^3J = 7.2$ Hz, OCH_2CH_3), 6.86 (2H, d, $^3J = 8.8$ Hz, ArH), 7.26 (2H, d, $^3J = 9.2$ Hz, ArH), 7.38–7.42 (2H, m, ArH), 7.49–7.53 (1H, m, ArH), 7.71–7.77 (2H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 14.7 (OCH_2CH_3), 26.7 (CH_2), 27.7 (CH_2), 30.1 (CH_2), 52.4 (d, $^2J_{\text{C,P}} = 5.7$ Hz, OCH_3), 63.4 (OCH_2CH_3), 113.8 (ArC), 119.8 (d, $^1J_{\text{C,P}} = 226.1$ Hz, C-sp 2), 128.1 (ArC), 129.0 (ArC), 129.0 (ArC), 130.3 (d, $^4J_{\text{C,P}} = 8.8$ Hz, C-sp 2), 132.2 (ArC), 136.3 (ArC), 138.8 (ArC), 139.0 (d, $^3J_{\text{C,P}} = 13.2$ Hz, C-sp 2), 143.0 (d, $^2J_{\text{C,P}} = 17.0$ Hz, C-sp 2), 158.6 (ArC), 186.3 ($\text{C}=\text{O}$) ppm. HRMS (ESI): MNa^+ , found 462.1439. $\text{C}_{24}\text{H}_{26}\text{NNaO}_5\text{P}$ requires 462.1441.

Dimethyl 3-Benzoyl-2-(4-fluorophenyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (13d). Yellowish oil. Yield 0.24 g, 58%. IR (KBr): ν_{max} 1640 ($\text{C}=\text{O}$) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 2.26 (2H, quint, $^3J = 6.8$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.41 (2H, t, $^3J = 7.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 2.87 (2H, td, $^3J_{\text{H,H}} = 7.2$ Hz, $^4J_{\text{H,P}} = 1.2$ Hz, $\text{CH}_2\text{CH}_2\text{CH}_2$), 3.57 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 7.06 (2H, t, $^3J = 8.4$ Hz, ArH), 7.33–7.36 (2H, m, ArH), 7.42 (2H, t, $^3J = 7.6$ Hz, ArH), 7.53 (1H, t, $^3J = 8.8$ Hz, ArH), 7.71–7.73 (2H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 26.8 (CH_2), 27.9 (CH_2), 30.3 (CH_2), 52.6 (d, $^2J_{\text{C,P}} = 6$ Hz, OCH_3), 115.3 (d, $^2J_{\text{C,F}} = 23$ Hz, ArC), 120.0 (d, $^1J_{\text{C,P}} = 226$ Hz, C-sp 2), 128.4 (ArC), 129.2 (ArC), 129.9 (d, $^3J_{\text{C,F}} = 8$ Hz, ArC), 130.4 (d, $^4J_{\text{C,P}} = 9$ Hz, C-sp 2), 132.5 (ArC), 135.7 (d, $^4J_{\text{C,F}} = 4$ Hz, ArC), 138.8 (ArC),

139.5 (d, $^3J_{\text{C,P}} = 14$ Hz, C-sp²), 143.5 (d, $^2J_{\text{C,P}} = 17$ Hz, C-sp²), 162.3 (d, $^1J_{\text{C,F}} = 246$ Hz, ArH), 186.4 (C=O) ppm. HRMS (ESI): MNa⁺, found 436.1077. C₂₂H₂₁FNNaO₄P requires 436.1084.

Dimethyl 3-Benzoyl-2-(4-chlorophenyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (13e). Yellow solid, mp 108–109 °C. Yield 0.22 g, 51%. IR (KBr): ν_{max} 1641 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.26 (2H, quint, $^3J = 7.2$ Hz, CH₂CH₂CH₂), 2.41 (2H, t, $^3J = 7.2$ Hz, CH₂CH₂CH₂), 2.87 (2H, td, $^3J_{\text{H,H}} = 7.4$ Hz, $^4J_{\text{H,P}} = 1.6$ Hz, CH₂CH₂CH₂), 3.58 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, 2 × OCH₃), 7.29–7.36 (4H, m, ArH), 7.42 (2H, t, $^3J = 7.6$ Hz, ArH), 7.53 (2H, t, $^3J = 7.2$ Hz, ArH), 7.71–7.73 (2H, m, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 26.7 (CH₂), 27.9 (CH₂), 30.2 (CH₂), 52.7 (d, $^2J_{\text{C,P}} = 5.7$ Hz, OCH₃), 119.9 (d, $^1J_{\text{C,P}} = 225.4$ Hz, C-sp²), 128.4 (ArC), 128.6 (ArC), 129.1 (ArC), 129.4 (ArC), 130.3 (d, $^4J_{\text{C,P}} = 8.5$ Hz, C-sp²), 132.6 (ArC), 134.2 (ArC), 138.2 (ArC), 138.7 (ArC), 139.7 (d, $^3J_{\text{C,P}} = 13.9$ Hz, C-sp²), 143.8 (d, $^2J_{\text{C,P}} = 16.8$ Hz, C-sp²), 186.3 (C=O) ppm. HRMS (ESI): MNa⁺, found 452.0786. C₂₂H₂₁ClNNaO₄P requires 452.0789.

Dimethyl 2-(4-methoxyphenyl)-3-(4-methylbenzoyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (13g). Yellowish oil. Yield 0.25 g, 56%. IR (KBr): ν_{max} 1639 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.26 (2H, quint, $^3J = 7.2$ Hz, CH₂CH₂CH₂), 2.39 (3H, s, CH₃), 2.43 (2H, t, $^3J = 7.2$ Hz, CH₂CH₂CH₂), 2.85–2.89 (2H, m, CH₂CH₂CH₂), 3.55 (6H, d, $^3J_{\text{H,P}} = 11.6$ Hz, 2 × OCH₃), 6.87 (2H, d, $^3J = 8.8$ Hz, ArH), 7.21 (2H, d, $^3J = 8.0$ Hz, ArH), 7.28 (2H, d, $^3J = 9.2$ Hz, ArH), 7.65 (2H, d, $^3J = 8.0$ Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 21.6 (CH₃), 26.7 (CH₂), 27.7 (CH₂), 30.1 (CH₂), 52.4 (d, $^2J_{\text{C,P}} = 5.7$ Hz, OCH₃), 55.2 (OCH₃), 113.2 (ArH), 119.4 (d, $^1J_{\text{C,P}} = 226.1$ Hz, C-sp²), 128.9 (ArC), 129.0 (ArC), 129.3 (ArC), 130.6 (d, $^4J_{\text{C,P}} = 8.8$ Hz, C-sp²), 132.4 (ArC), 136.1 (ArC), 138.3 (d, $^3J_{\text{C,P}} = 14.0$ Hz, C-sp²), 143.0 (ArC), 143.0 (d, $^2J_{\text{C,P}} = 17.0$ Hz, C-sp²), 159.1 (ArC), 186.1 (C=O) ppm. HRMS (ESI): MNa⁺, found 462.1436. C₂₄H₂₆NNaO₅P requires 462.1441.

Dimethyl 3-(4-Ethylbenzoyl)-2-(4-methoxyphenyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (13h). Yellowish oil. Yield 0.24 g, 54%. IR (KBr): ν_{max} 1639 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.24 (3H, t, $^3J = 7.6$ Hz, CH₂CH₃), 2.25 (2H, quint, $^3J = 7.2$ Hz, CH₂CH₂CH₂), 2.46 (2H, t, $^3J = 7.2$ Hz, CH₂CH₂CH₂), 2.68 (2H, q, $^3J = 7.6$ Hz, CH₂CH₃), 2.87 (2H, t, $^3J = 7.2$ Hz, CH₂CH₂CH₂), 3.55 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, 2 × OCH₃), 6.86 (2H, d, $^3J = 8.8$ Hz, ArH), 7.23 (2H, d, $^3J = 8.0$ Hz, ArH), 7.27 (2H, d, $^3J = 8.8$ Hz, ArH), 7.67 (2H, d, $^3J = 8.4$ Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 15.1 (CH₃), 26.6 (CH₂), 27.7 (CH₂), 28.8 (CH₂), 30.1 (CH₂), 52.4 (d, $^2J_{\text{C,P}} = 5.7$ Hz, OCH₃), 55.2 (OCH₃), 113.2 (ArC), 119.2 (d, $^1J_{\text{C,P}} = 226.4$ Hz, C-sp²), 127.6 (ArC), 128.9 (ArC), 129.4 (ArC), 130.6 (d, $^4J_{\text{C,P}} = 8.7$ Hz, C-sp²), 132.3 (ArC), 136.2 (ArC), 138.3 (d, $^3J_{\text{C,P}} = 14.0$ Hz, C-sp²), 143.0 (d, $^2J_{\text{C,P}} = 17.0$ Hz, C-sp²), 149.3 (ArC), 159.0 (ArC), 186.0 (C=O) ppm. HRMS (ESI): MNa⁺, found 476.1592. C₂₅H₂₈NNaO₅P requires 476.1597.

Dimethyl 2-(4-Chlorophenyl)-3-(4-ethylbenzoyl)-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (13j). Yellowish oil. Yield 0.2 g, 44%. IR (KBr): ν_{max} 1637 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.25 (3H, t, $^3J = 7.6$ Hz, CH₂CH₃), 2.27 (2H, quint, $^3J = 7.2$ Hz, CH₂CH₂CH₂), 2.46 (2H, t, $^3J = 7.6$ Hz, CH₂CH₂CH₂), 2.69 (2H, q, $^3J = 7.6$ Hz, CH₂CH₃), 2.88 (2H, td, $^3J_{\text{H,H}} = 7.0$ Hz, $^4J_{\text{H,P}} = 1.2$ Hz, CH₂CH₂CH₂), 3.57 (6H, d, $^3J_{\text{H,P}} = 11.6$ Hz, 2 × OCH₃), 7.24 (2H, d, $^3J = 8.4$ Hz, ArH), 7.28–7.34 (4H, m, ArH), 7.67 (2H, d, $^3J = 8.0$ Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 15.5 (CH₃), 26.8 (CH₂), 27.9 (CH₂), 29.0 (CH₂), 30.3 (CH₂), 52.6 (d, $^2J_{\text{C,P}} = 5.8$ Hz, OCH₃), 119.4 (d, $^1J_{\text{C,P}} = 225.7$ Hz, C-sp²), 127.9 (ArC), 128.5 (ArC), 129.4 (ArC), 129.5 (ArC), 130.6 (d, $^4J_{\text{C,P}} = 8.5$ Hz, C-sp²), 134.1 (ArC), 136.1 (ArC), 138.3 (ArC), 139.1 (d, $^3J_{\text{C,P}} = 13.9$ Hz, C-sp²), 143.8 (d, $^2J_{\text{C,P}} = 16.0$ Hz, C-sp²), 149.7 (ArC), 186.1 (C=O) ppm. HRMS (ESI): MNa⁺, found 480.1100. C₂₄H₂₅ClNNaO₄P requires 480.1102.

Dimethyl 3-Formyl-2-phenyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (13s). Yellowish oil. Yield 0.13 g, 42%. IR (KBr): ν_{max} 1666 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.41 (2H, quint, $^3J = 7.2$ Hz, CH₂CH₂CH₂), 2.85 (2H, td, $^3J_{\text{H,H}} = 7.4$

Hz, $^4J_{\text{H,P}} = 1.2$ Hz, CH₂CH₂CH₂), 2.94 (2H, t, $^3J = 7.2$ Hz, CH₂CH₂CH₂), 3.52 (6H, d, $^3J_{\text{H,P}} = 11.6$ Hz, 2 × OCH₃), 7.38–7.40 (2H, m, ArH), 7.45–7.47 (3H, m, ArH), 9.34 (1H, s, CHO) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 26.2 (CH₂), 26.4 (CH₂), 30.3 (CH₂), 52.6 (d, $^2J_{\text{C,P}} = 5.7$ Hz, OCH₃), 119.7 (d, $^1J_{\text{C,P}} = 224.4$ Hz, C-sp²), 128.6 (ArC), 128.8 (ArC), 129.3 (ArC), 130.6 (d, $^4J_{\text{C,P}} = 8.4$ Hz, C-sp²), 137.5 (ArC), 140.3 (d, $^3J_{\text{C,P}} = 13.7$ Hz, C-sp²), 143.7 (d, $^2J_{\text{C,P}} = 16.5$ Hz, C-sp²), 180.6 (d, $^4J_{\text{C,P}} = 1.4$ Hz, C=O) ppm. HRMS (ESI): MNa⁺, found 342.0872. C₁₆H₁₈NNaO₄P requires 342.0866.

Dimethyl 3-Benzoyl-2-phenyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (13a–18O). Yellowish oil. Yield 0.34 g, 86%. IR (KBr): ν_{max} 1640 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 2.29 (2H, pent, $^3J = 7.1$ Hz, CH₂CH₂CH₂), 2.45 (2H, t, $^3J = 7.2$ Hz, CH₂CH₂CH₂), 2.92 (2H, td, $^3J_{\text{H,H}} = 7.4$ Hz, $^4J_{\text{H,P}} = 1.5$ Hz, CH₂CH₂CH₂), 3.56 (6H, d, $^3J_{\text{H,P}} = 11.4$ Hz, 2 × OCH₃), 7.37–7.42 (5H, m, ArH), 7.43–7.47 (2H, m, ArH), 7.52–7.57 (1H, m, ArH), 7.76 (2H, dd, $J = 8.3, 1.3$ Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 26.7 (CH₂), 27.7 (CH₂), 30.1 (CH₂), 52.4 (d, $^2J_{\text{C,P}} = 5.7$ Hz, OCH₃), 119.7 (d, $^1J_{\text{C,P}} = 225.4$ Hz, C-sp²), 127.9 (ArC), 128.2 (2 × ArC), 129.0 (ArC), 130.2 (d, $^4J_{\text{C,P}} = 9.0$ Hz, C-sp²), 132.2 (ArC), 138.7 (ArC), 139.2 (d, $^3J_{\text{C,P}} = 13.8$ Hz, C-sp²), 139.6 (ArC), 143.4 (d, $^2J_{\text{C,P}} = 17.1$ Hz, C-sp²), 186.26 (C=O) ppm. HRMS (ESI): MNa⁺, found 420.1230. C₂₂H₂₂NNaO₃¹⁸OP requires 420.1227.

Dimethyl 3-(1-Iodopent-1-enyl)-2-phenyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (15i) (mixture of E and Z isomers). Yellowish oil. Yield 0.28 g, 58%. ¹H NMR (400 MHz, CDCl₃): δ 0.72, 0.82 (3H, 2t, $^3J = 7.2$ Hz, $^3J = 7.2$ Hz, CH₃), 1.18 (2H, sext, $^3J = 7.2$ Hz, CH₂CH₃), 1.99 (2H, q, $^3J = 7.2$ Hz, CH₂CH₂CH₃), 2.31–2.38 (2H, 2m (overlapped), CH₂), 2.64 (2H, t, $^3J = 7.2$ Hz, CH₂CH₂CH₂), 2.84–2.87 (2H, m, CH₂CH₂CH₂), 3.50 (6H, d, $^3J_{\text{H,P}} = 11.6$ Hz, 2 × OCH₃), 5.49, 6.32 (1H, 2t, $^3J = 6.8$ Hz, $^3J = 7.2$ Hz, CH), 7.29–7.40 (5H, m, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 13.4, 13.5 (CH₃), 21.0 (CH₂), 25.5 (CH₂), 26.8 (CH₂), 30.0 (CH₂), 35.0, 38.5 (CH₂), 52.2 (d, $^2J_{\text{H,P}} = 5.6$ Hz, 2 × OCH₃), 82.6, 90.3 (1C-sp²), 111.7 (d, $^1J_{\text{C,P}} = 232.3$ Hz, C-sp²), 128.0 (ArC), 128.2 (ArC), 128.7 (ArC), 131.3 (d, $^3J_{\text{C,P}} = 13.7$ Hz, C-sp²), 133.7 (d, $^4J_{\text{C,P}} = 9.2$ Hz, C-sp²), 138.9 (ArC), 143.8 (d, $^2J_{\text{C,P}} = 16.7$ Hz, C-sp²), 143.9, 148.8 (HC-sp²) ppm. HRMS (ESI): MNa⁺, found 508.0515. C₂₀H₂₅INNaO₃P requires 508.0509.

Dimethyl 3-(1,4-Diiodobut-1-enyl)-2-phenyl-2,4,5,6-tetrahydrocyclopenta[c]pyrrol-1-ylphosphonate (15o) (mixture of E and Z isomers). Yellowish oil. Yield 0.29 g, 49%. ¹H NMR (400 MHz, CDCl₃): δ 2.34–2.39 (2H, m, CH₂CH₂CH₂), 2.60–2.68 (4H, 2m, CH₂ and CH₂CH₂CH₂), 2.84–2.90 (4H, m, CH₂CH₂CH₂ and CH₂), 3.50 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, 2 × OCH₃), 5.59, 6.25 (1H, 2t, $^3J = 6.8$ Hz, $^3J = 7.2$ Hz, CH), 7.31–7.41 (5H, m, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 1.5, 1.7 (CH₂), 25.6 (CH₂), 26.7 (CH₂), 30.0 (CH₂), 40.1 (CH₂), 52.2 (d, $^2J_{\text{C,P}} = 5.6$ Hz, 2 × OCH₃), 85.4, 92.6 (1C-sp²), 112.4 (d, $^1J_{\text{C,P}} = 231.5$ Hz, CH), 128.1 (ArC), 128.3 (ArC), 128.7 (ArC), 131.7 (d, $^3J_{\text{C,P}} = 13.7$ Hz, C-sp²), 133.0 (d, $^4J_{\text{C,P}} = 9.4$ Hz, C-sp²), 138.7 (ArC), 141.6, 146.0 (CH-sp²), 143.8 (d, $^2J_{\text{C,P}} = 16.9$ Hz, C-sp²) ppm. HRMS (ESI): MNa⁺, found 619.9309. C₁₉H₂₂I₂NNaO₃P requires 619.9319.

Dimethyl 3-Benzoyl-2-phenyl-4,5,6,7-tetrahydro-2H-isoin-dol-1-ylphosphonate (16a). Yellowish oil. Yield 0.25 g, 61%. IR (KBr): ν_{max} 1646 (C=O) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.60–1.66 (2H, m, CH₂), 1.74–1.80 (2H, m, CH₂), 2.31 (2H, t, $J = 6.4$ Hz, CH₂), 2.89 (2H, t, $J = 6.4$ Hz, CH₂), 3.51 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, 2 × OCH₃), 7.27 (4H, br, s, ArH), 7.34–7.38 (3H, m, ArH), 7.46–7.50 (1H, m, ArH), 7.66 (2H, dd, $J = 8.2; 1.6$ Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 22.9 (CH₂), 23.0 (CH₂), 23.1 (CH₂), 23.5 (CH₂), 52.2 (d, $^2J_{\text{C,P}} = 5.6$ Hz, 2 × OCH₃), 120.7 (d, $^1J_{\text{C,P}} = 222.7$ Hz, ArC), 127.1 (d, $^3J_{\text{C,P}} = 14.5$ Hz, ArC), 128.0 (ArC), 128.2 (ArC), 128.3 (ArC), 128.9 (ArC), 129.2 (ArC), 132.5 (ArC), 133.3 (d, $^2J_{\text{C,P}} = 18.8$ Hz, ArC), 134.7 (d, $^3J_{\text{C,P}} = 9.6$ Hz, ArC), 139.0 (ArC), 139.1 (ArC), 188.4 (d, $^4J_{\text{C,P}} = 1.4$ Hz, CO) ppm. HRMS (ESI): MNa⁺, found 432.1333. C₂₃H₂₄NNaO₄P requires 432.1335.

Dimethyl 3-Benzoyl-2-(4-methoxyphenyl)-4,5,6,7-tetrahydro-2H-isoin-dol-1-ylphosphonate (16b). Brownish oil. Yield

0.26 g, 60%. IR (KBr): $\nu_{\max}$ 1644 (C=O) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.59–1.64 (2H, m, CH_2), 1.72–1.78 (2H, m, CH_2), 2.28 (2H, t, $J = 6.0$ Hz, CH_2), 2.87 (2H, t, $J = 6.0$ Hz, CH_2), 3.53 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 3.75 (3H, s, OCH_3), 6.77 (2H, d, $J = 8.8$ Hz, ArH), 7.18 (2H, d, $J = 8.8$ Hz, ArH), 7.36 (3H, t, $J = 7.6$ Hz, ArH), 7.48 (1H, t, $J = 7.6$ Hz, ArH), 7.65–7.67 (2H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 22.8 (CH_2), 23.0 ($2 \times \text{CH}_2$), 23.4 (CH_2), 52.2 (d, $^2J_{\text{C,P}} = 5.5$ Hz, $2 \times \text{OCH}_3$), 55.2 (OCH_3), 113.1 (ArC), 120.7 (d, $^1J_{\text{C,P}} = 222.8$ Hz, ArC), 126.7 (d, $^3J_{\text{C,P}} = 14.6$ Hz, ArC), 128.2 (ArC), 129.2 ($2 \times \text{ArC}$), 131.7 (ArC), 132.5 (ArC), 132.9 (d, $^2J_{\text{C,P}} = 19.0$ Hz, ArC), 134.7 (d, $^3J_{\text{C,P}} = 9.6$ Hz, ArC), 138.9 (ArC), 159.1 (ArC), 188.5 (d, $^4J_{\text{C,P}} = 1.3$ Hz CO) ppm. HRMS (ESI): MH^+ , found 440.1627. $\text{C}_{24}\text{H}_{26}\text{NO}_5\text{P}$ requires 440.1621.

Dimethyl 2-(4-Chlorophenyl)-3-(4-methylbenzoyl)-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (16o). Yellowish solid, mp 99–100 °C. Yield 0.32 g, 69%. IR (KBr): $\nu_{\max}$ 1652 (C=O) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 1.60–1.63 (2H, m, CH_2), 1.73–1.77 (2H, m, CH_2), 2.27 (2H, t, $J = 6.4$ Hz, CH_2), 2.39 (3H, s, CH_3), 2.87 (2H, t, $J = 6.0$ Hz, CH_2), 3.55 (6H, d, $^3J_{\text{H,P}} = 11.2$ Hz, $2 \times \text{OCH}_3$), 7.19–7.27 (6H, m, ArH), 7.60 (2H, d, $J = 8.4$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 21.7 (CH_3), 22.8 (CH_2), 22.9 (CH_2), 23.0 (CH_2), 23.6 (CH_2), 52.2 (d, $^2J_{\text{C,P}} = 5.5$ Hz, $2 \times \text{OCH}_3$), 120.5 (d, $^1J_{\text{C,P}} = 222.6$ Hz, ArC), 126.8 (d, $^3J_{\text{C,P}} = 14.5$ Hz, ArC), 128.2 (ArC), 129.1 (ArC), 129.4 (ArC), 129.5 (ArC), 133.4 (d, $^2J_{\text{C,P}} = 18.7$ Hz, ArC), 134.0 (ArC), 134.8 (d, $^3J_{\text{C,P}} = 9.4$ Hz, ArC), 136.1 (ArC), 137.7 (ArC), 143.8 (ArC), 187.9 (d, $^4J_{\text{C,P}} = 1.1$ Hz, CO) ppm. HRMS (ESI): MNa^+ , found 480.1096. $\text{C}_{24}\text{H}_{25}\text{ClNNaO}_4\text{P}$ requires 480.1102.

Dimethyl 3-(1-Iodopent-1-enyl)-2-(4-methoxyphenyl)-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (17k). Yellowish oil. Yield 0.12 g, 22%. Compound exists as the geometrical isomers, which were not isolated due to the same R_f . ^1H NMR (400 MHz, CDCl_3): δ 0.79; 0.84 (3H, 2t, $J = 7.2$ Hz, $J = 7.2$ Hz, CH_3), 1.25–1.33 (2H, m, $\text{C}=\text{CHCH}_2\text{CH}_2$), 1.73–1.76 (4H, 2m (overlap.), $2 \times \text{CH}_{2\text{chex}}$), 2.03 (2H, q, $J = 7.2$ Hz, $\text{C}=\text{CHCH}_2\text{CH}_2$), 2.42 (2H, t, $J = 5.6$ Hz, $\text{CH}_{2\text{chex}}$), 2.81 (2H, br. s, $\text{CH}_{2\text{chex}}$), 3.49–3.55 (6H, 2m (overlap.), $2 \times \text{OCH}_3$), 3.82; 3.83 (3H, 2s, OCH_3), 5.58; 6.37 (1H, 2t, $J = 6.8$ Hz, $J = 7.2$ Hz, CH), 6.86 (2H, d, $J = 8.8$ Hz, ArH), 7.18 (2H, d, $J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 13.4; 13.6 (CH_3), 21.1; 21.6 (CH_2), 22.1 (CH_2), 22.9; 23.0 (CH_2), 23.1 (CH_2), 23.4 (CH_2), 35.1; 38.5 (CH_2), 52.0 (d, $^2J_{\text{C,P}} = 5.4$ Hz, $2 \times \text{OCH}_3$), 55.3; 55.3 (OCH_3), 82.8; 90.5 (2d, $^4J_{\text{C,P}} = 1.6$ Hz, $^4J_{\text{C,P}} = 1.6$ Hz, $\text{IC}_{\text{sp}2}$), 113.0 (ArC), 114.4 (d, $^1J_{\text{C,P}} = 197.7$ Hz, ArC), 119.8 (d, $^3J_{\text{C,P}} = 14.3$ Hz, ArC), 129.9 (ArC), 131.4 (ArC), 133.0 (d, $^2J_{\text{C,P}} = 18.8$ Hz, ArC), 137.4 (d, $^3J_{\text{C,P}} = 10.7$ Hz, ArC), 145.1; 149.5 ($\text{C}_{\text{sp}2}\text{H}$), 159.1; 159.2 (ArC) ppm. HRMS (ESI): MH^+ , found 530.0959. $\text{C}_{22}\text{H}_{30}\text{INO}_4\text{P}$ requires 530.0952.

Dimethyl 3-(1,4-Diiodobut-1-enyl)-2-phenyl-4,5,6,7-tetrahydro-2H-isoindol-1-ylphosphonate (17l). Yellowish oil. Yield 0.51 g, 83%. Compound exists as the geometrical isomers, which were not isolated due to the same R_f . ^1H NMR (400 MHz, CDCl_3): δ 1.76 (4H, 2br. s (overlap.), $2 \times \text{CH}_{2\text{chex}}$), 2.46 (2H, br. s, $\text{CH}_{2\text{chex}}$), 2.65 (2H, q, $J = 6.8$ Hz, $\text{C}=\text{CHCH}_2\text{CH}_2$), 2.83 (2H, br. s, $\text{CH}_{2\text{chex}}$), 2.93 (2H, t, $J = 6.8$ Hz, $\text{C}=\text{CHCH}_2\text{CH}_2$), 3.46–3.52 (6H, 2m (overlap.), $2 \times \text{OCH}_3$), 5.69; 6.31 (1H, 2t, $J = 6.8$ Hz, $J = 6.8$ Hz, CH), 7.28–7.30 (2H, m, ArH), 7.37–7.38 (3H, m, ArH) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 22.0; 22.2 (CH_2), 22.8; 22.9 (CH_2), 23.0 (CH_2), 23.2; 23.3 (CH_2), 36.6 (CH_2), 40.0 (CH_2), 52.0 (d, $^2J_{\text{C,P}} = 5.5$ Hz, $2 \times \text{OCH}_3$), 85.5; 92.7 (2d, $^4J_{\text{C,P}} = 1.6$ Hz, $^4J_{\text{C,P}} = 1.5$ Hz, $\text{IC}_{\text{sp}2}$), 114.8 (d, $^1J_{\text{C,P}} = 227.4$ Hz, ArC), 120.3 (d, $^3J_{\text{C,P}} = 14.2$ Hz, ArC), 128.0; 128.1 (ArC), 128.2; 128.4 (ArC), 128.9 (ArC), 133.3 (d, $^2J_{\text{C,P}} = 18.7$ Hz, ArC), 136.4 (d, $^3J_{\text{C,P}} = 10.7$ Hz, ArC), 138.4; 138.5 (ArC), 143.2; 147.1 ($\text{C}_{\text{sp}2}\text{H}$) ppm. HRMS (ESI): MNa^+ , found 633.9469. $\text{C}_{20}\text{H}_{24}\text{I}_2\text{NNaO}_3\text{P}$ requires 633.9475.

Dimethyl 3-Benzoyl-2-(4-chlorophenyl)-2H-isoindol-1-ylphosphonate (18b). Yellowish solid, mp 57–58 °C. Yield 0.19 g, 44%. IR (KBr): $\nu_{\max}$ 1649 (C=O) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 3.64 (6H, d, $^3J_{\text{H,P}} = 11.6$ Hz, $2 \times \text{OCH}_3$), 7.09 (2H, m, ArH), 7.23–7.27 (1H, m, ArH), 7.33–7.41 (4H, m, ArH), 7.45 (2H, t, $J = 7.6$ Hz, ArH), 7.58 (1H, t, $J = 7.6$ Hz, ArH), 7.77–7.79 (2H, m, ArH), 8.23 (1H, d, $J = 8.8$ Hz, ArH) ppm. ^{13}C NMR (100 MHz,

CDCl_3): δ 52.7 (d, $^2J_{\text{C,P}} = 5.5$ Hz, $2 \times \text{OCH}_3$), 117.3 (d, $^1J_{\text{C,P}} = 223.8$ Hz, ArC), 120.3 (ArC), 121.1 (ArC), 125.1 (ArC), 125.3 (ArC), 127.6 (d, $^3J_{\text{C,P}} = 13.1$ Hz, ArC), 128.4 (ArC), 128.5 (ArC), 129.0 (d, $^3J_{\text{C,P}} = 8.3$ Hz, ArC), 129.0 (ArC), 129.7 (ArC), 131.8 (d, $^2J_{\text{C,P}} = 17.4$ Hz, ArC), 132.9 (ArC), 135.1 (ArC), 137.4 (d, $^3J_{\text{C,P}} = 1.1$ Hz, ArC), 139.1 (ArC), 186.0 (d, $^4J_{\text{C,P}} = 1.0$ Hz, CO) ppm. HRMS (ESI): MNa^+ , found 462.0640. $\text{C}_{23}\text{H}_{19}\text{ClNNaO}_4\text{P}$ requires 462.0632.

Dimethyl 3-Formyl-2-(4-methoxyphenyl)-2H-isoindol-1-ylphosphonate (18c). Brownish solid, mp 117–118 °C. Yield 0.2 g, 56%. IR (KBr): $\nu_{\max}$ 1655 (CHO) cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 3.63 (6H, d, $^3J_{\text{H,P}} = 11.6$ Hz, $2 \times \text{OCH}_3$), 3.89 (3H, s, OCH_3), 7.02 (2H, d, $J = 8.8$ Hz, ArH), 7.34–7.45 (4H, m, ArH), 8.18 (1H, d, $J = 8.4$ Hz, ArH), 8.41 (1H, dt, $J = 8.4$ Hz; 0.8 Hz, ArH), 9.55 (1H, s, CHO) ppm. ^{13}C NMR (100 MHz, CDCl_3): δ 52.8 (d, $^2J_{\text{C,P}} = 5.6$ Hz, $2 \times \text{OCH}_3$), 55.5 (OCH_3), 113.8 (ArC), 118.5 (d, $^1J_{\text{C,P}} = 221.7$ Hz, ArC), 120.7 (ArC), 120.9 (ArC), 126.0 (ArC), 127.3 (ArC), 127.4 (ArC), 128.9 ($2 \times \text{ArC}$), 129.2 (ArC), 131.3 (d, $^2J_{\text{C,P}} = 17.0$ Hz, ArC), 160.6 (ArC), 180.0 (d, $^4J_{\text{C,P}} = 1.7$ Hz, CHO) ppm. HRMS (ESI): MNa^+ , found 382.0810. $\text{C}_{18}\text{H}_{18}\text{NNaO}_5\text{P}$ requires 382.0815.

General Procedure for the Preparation of Compounds 20 and 21. A solution of starting corresponding acetylenic aldehyde **5**, **6** (1 mmol), aniline (1 mmol), and dimethylphosphite (0.121 g, 1.1 mmol) in dry dichloromethane (5 mL) was stirred at room temperature. When the consumption of starting aldehyde was observed by TLC, 10 mol % copper(I) iodide (19.05 mg, 0.1 mmol) was added. When the full completion of the reaction was observed by TLC (after 1–4 h), the solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography eluting with hexane–ethyl acetate mixtures.

Dimethyl 6,7-Diphenyl-5,6-dihydro-1,6-naphthyridin-5-ylphosphonate (20a). Brownish solid, mp 146–147 °C. Yield 0.23 g, 58%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 3.56 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH_3), 3.69 (3H, d, $^3J_{\text{H,P}} = 10.8$ Hz, OCH_3), 5.94 (1H, d, $^1J_{\text{H,P}} = 18.8$ Hz, CH), 6.67 (1H, br. s, $\text{C}_{\text{sp}2}\text{H}$), 6.91 (1H, t, $J = 7.2$ Hz, ArH), 7.05 (2H, d, $J = 7.6$ Hz, ArH), 7.15 (2H, t, $J = 7.6$ Hz, ArH), 7.24–7.33 (4H, m, ArH), 7.57 (2H, d, $J = 6.8$ Hz, ArH), 7.63 (1H, d, $J = 6.0$ Hz, ArH), 8.73 (1H, br. s, ArH) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 52.9 (d, $^2J_{\text{C,P}} = 4.1$ Hz, OCH_3), 53.0 (d, $^2J_{\text{C,P}} = 4.2$ Hz, OCH_3), 62.0 (d, $^1J_{\text{C,P}} = 158.9$ Hz, CH), 103.6 ($^4\text{C}_{\text{sp}2}\text{H}$), 112.7 (ArC), 122.8 ($3 \times \text{ArC}$), 127.5 (ArC), 128.4 (ArC), 128.6 ($2 \times \text{ArC}$), 129.0 (ArC), 134.5 (ArC), 136.5 (ArC), 146.0 (ArC), 146.6 (d, $^3J_{\text{C,P}} = 6.7$ Hz, ArC), 148.0 (ArC), 151.5 ($^3\text{C}_{\text{sp}2}$) ppm. HRMS (ESI): MNa^+ , found 415.1178. $\text{C}_{22}\text{H}_{21}\text{N}_3\text{NaO}_3\text{P}$ requires 415.1182.

Dimethyl 6-(4-Methoxyphenyl)-7-phenyl-5,6-dihydro-1,6-naphthyridin-5-ylphosphonate (20b). Yellow oil. Yield 0.26 g, 61%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 3.56 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH_3), 3.61 (3H, s, OCH_3), 3.68 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH_3), 5.73 (1H, d, $^1J_{\text{H,P}} = 19.6$ Hz, CH), 6.51 (1H, br. s, $\text{C}_{\text{sp}2}\text{H}$), 6.73 (2H, d, $J = 8.8$ Hz, ArH), 7.01 (2H, d, $J = 8.4$ Hz, ArH), 7.23–7.32 (4H, m, ArH), 7.55 (3H, d, $J = 6.4$ Hz, ArH), 8.45 (1H, br. s, ArH) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 52.9 (d, $^2J_{\text{C,P}} = 2.0$ Hz, OCH_3), 53.0 (d, $^2J_{\text{C,P}} = 2.1$ Hz, OCH_3), 55.0 (OCH_3), 62.7 (d, $^1J_{\text{C,P}} = 161.8$ Hz, CH), 111.5 ($^4\text{C}_{\text{sp}2}\text{H}$), 113.9 (ArC), 121.6 (ArC), 124.6 (d, $^4J_{\text{C,P}} = 1.2$ Hz, ArC), 127.6 (ArC), 128.4 (ArC), 128.6 (ArC), 129.1 (ArC), 134.5 (d, $^3J_{\text{C,P}} = 4.4$ Hz, ArC), 136.6 (ArC), 140.3 (d, $^3J_{\text{C,P}} = 7.3$ Hz, ArC), 146.4 (ArC), 148.7 (ArC), 151.5 ($^3\text{C}_{\text{sp}2}$), 155.3 (ArC) ppm. HRMS (ESI): MNa^+ , found 445.1282. $\text{C}_{23}\text{H}_{23}\text{N}_2\text{NaO}_4\text{P}$ requires 445.1288.

Dimethyl 6-Phenyl-7-propyl-5,6-dihydro-1,6-naphthyridin-5-ylphosphonate (20c). Brownish oil. Yield 0.17 g, 52%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 0.83 (3H, t, $J = 7.2$ Hz, CH_3), 1.46 (2H, sext., $J = 7.2$ Hz, CH_2), 2.11–2.19 (1H, m, CHH), 2.23–2.31 (1H, m, CHH), 3.56 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH_3), 3.66 (3H, d, $^3J_{\text{H,P}} = 10.4$ Hz, OCH_3), 5.56 (1H, d, $^2J_{\text{H,P}} = 18.4$ Hz, CH), 6.13 (1H, br. s, $\text{C}_{\text{sp}2}\text{H}$), 7.13 (1H, t, $J = 7.2$ Hz, ArH), 7.24 (2H, d, $J = 8.0$ Hz, ArH), 7.32–7.36 (2H, m, ArH), 7.43–7.50 (2H, m, ArH), 8.45 (1H, br. s, ArH) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 13.6 (CH_3), 20.7 (CH_2), 35.0 (CH_2), 52.7 (d, $^2J_{\text{C,P}} = 7.2$ Hz, OCH_3), 53.0 (d, $^2J_{\text{C,P}} = 6.9$ Hz, OCH_3), 63.6 (d, $^1J_{\text{C,P}} = 161.0$ Hz, CH), 109.7 ($^4\text{C}_{\text{sp}2}\text{H}$), 120.6 (ArC), 124.2 (ArC), 124.2 (ArC), 128.9 (ArC), 129.4 (ArC), 134.2 (d, $^3J_{\text{C,P}} = 5.0$ Hz, ArC), 145.9 (d, $^3J_{\text{C,P}} = 5.7$ Hz, ArC), 148.4 ($2 \times \text{ArC}$), 151.7

($^3\text{C}_{\text{sp}^2}$) ppm. HRMS (ESI): MH^+ , found 359.1526. $\text{C}_{19}\text{H}_{23}\text{N}_2\text{O}_3\text{P}$ requires 359.1519.

Dimethyl 7-Cyclopropyl-6-phenyl-5,6-dihydro-1,6-naphthyridin-5-ylphosphonate (20d). Brownish solid, mp 144–145 °C. Yield 0.22 g, 63%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 0.71–0.75 (2H, m, $\text{CH}(\text{CH}_2)_2$), 0.80–0.84 (2H, m, $\text{CH}(\text{CH}_2)_2$), 1.33 (1H, p, $J = 6.4$ Hz, $\text{CH}(\text{CH}_2)_2$), 3.60 (3H, d, $^3J_{\text{HP}} = 10.4$ Hz, OCH_3), 3.65 (3H, d, $^3J_{\text{HP}} = 10.4$ Hz, OCH_3), 5.64 (1H, d, $^2J_{\text{HP}} = 18.8$ Hz, CH), 5.90 (1H, br. s, $\text{C}_{\text{sp}^2}\text{H}$), 7.06 (1H, br. s, ArH), 7.12–7.14 (1H, m, ArH), 7.32–7.37 (4H, m, ArH), 7.45 (1H, d, $J = 6.0$ Hz, ArH), 8.35 (1H, br. s, ArH) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 8.4 ($\text{CH}(\text{CH}_2)_2$), 10.9 ($\text{CH}(\text{CH}_2)_2$), 14.2 ($\text{CH}(\text{CH}_2)_2$), 53.0 (d, $^2J_{\text{CP}} = 6.9$ Hz, $2 \times \text{OCH}_3$), 62.5 (d, $^1J_{\text{CP}} = 159.3$ Hz, CH), 104.2 ($^4\text{C}_{\text{sp}^2}\text{H}$), 120.3 (ArC), 123.8 (ArC), 123.8 (ArC), 128.8 (ArC), 129.1 (ArC), 134.1 (d, $^3J_{\text{CP}} = 4.3$ Hz, ArC), 146.0 (d, $^3J_{\text{CP}} = 5.5$ Hz, ArC), 148.4 (ArC), 150.9 (ArC), 151.8 ($^3\text{C}_{\text{sp}^2}$) ppm. HRMS (ESI): MH^+ , found 357.1369. $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_3\text{P}$ requires 357.1363.

Dimethyl 7-Cyclopropyl-6-(4-methoxyphenyl)-5,6-dihydro-1,6-naphthyridin-5-ylphosphonate (20e). Brownish solid, mp 111–112 °C. Yield 0.27 g, 59%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 0.62–0.82 (4H, m, $\text{CH}(\text{CH}_2)_2$), 1.22–1.24 (1H, m, $\text{CH}(\text{CH}_2)_2$), 3.59 (3H, d, $^3J_{\text{HP}} = 10.4$ Hz, OCH_3), 3.63 (3H, d, $^3J_{\text{HP}} = 10.4$ Hz, OCH_3), 3.73 (3H, s, OCH_3), 5.49 (1H, d, $^2J_{\text{HP}} = 17.6$ Hz, CH), 5.78 (1H, br. s, $\text{C}_{\text{sp}^2}\text{H}$), 6.91 (2H, d, $J = 8.4$ Hz, ArH), 7.04 (1H, d, $J = 8.4$ Hz, ArH), 7.29 (2H, d, $J = 8.0$ Hz, ArH), 7.39–7.52 (1H, m, ArH), 8.36 (1H, br. s, ArH) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 7.7 ($\text{CH}(\text{CH}_2)_2$), 10.7 ($\text{CH}(\text{CH}_2)_2$), 14.2 ($\text{CH}(\text{CH}_2)_2$), 53.0 (d, $^2J_{\text{CP}} = 4.5$ Hz, OCH_3), 53.0 (d, $^2J_{\text{CP}} = 4.7$ Hz, OCH_3), 55.2 (OCH_3), 63.2 (d, $^1J_{\text{CP}} = 159.4$ Hz, CH), 102.0 ($^4\text{C}_{\text{sp}^2}\text{H}$), 114.1 (ArC), 120.2 (ArC), 126.4 (ArC), 128.7 (ArC), 134.1 (d, $^3J_{\text{CP}} = 4.8$ Hz, ArC), 139.2 (d, $^3J_{\text{CP}} = 5.1$ Hz, ArC), 148.3 (ArC), 151.7 (ArC), 152.3 ($^3\text{C}_{\text{sp}^2}$), 156.4 (ArC) ppm. HRMS (ESI): MH^+ , found 387.1462. $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4\text{P}$ requires 387.1468.

Dimethyl 6-Phenyl-5,6-dihydro-1,6-naphthyridin-5-ylphosphonate (20f). Brownish oil. Yield 0.16 g, 50%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 3.52 (3H, d, $^3J_{\text{HP}} = 10.4$ Hz, OCH_3), 3.56 (3H, d, $^3J_{\text{HP}} = 10.4$ Hz, OCH_3), 5.90 (1H, d, $J = 6.4$ Hz, $\text{C}_{\text{sp}^2}\text{H}$), 6.08 (1H, d, $^2J_{\text{HP}} = 13.6$ Hz, CH), 7.04 (1H, t, $J = 7.2$ Hz, ArH), 7.08–7.10 (2H, m, ArH, $\text{C}_{\text{sp}^2}\text{H}$), 7.26 (2H, d, $J = 8.0$ Hz, ArH), 7.36 (2H, t, $J = 7.6$ Hz, ArH), 7.53 (1H, d, $J = 7.2$ Hz, ArH), 8.33 (1H, br. s, ArH) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 52.8 (d, $^2J_{\text{CP}} = 7.3$ Hz, OCH_3), 52.9 (d, $^2J_{\text{CP}} = 7.2$ Hz, OCH_3), 57.6 (d, $^1J_{\text{CP}} = 152.6$ Hz, CH), 106.4 (d, $^3J_{\text{CP}} = 1.4$ Hz, $^4\text{C}_{\text{sp}^2}\text{H}$), 117.2 (d, $^4J_{\text{CP}} = 1.4$ Hz, ArC), 119.6 (ArC), 120.7 (ArC), 121.8 (ArC), 129.0 (ArC), 134.3 (d, $^3J_{\text{CP}} = 2.2$ Hz, ArC), 134.6 (d, $^3J_{\text{CP}} = 6.0$ Hz, ArC), 144.2 ($^3\text{C}_{\text{sp}^2}$), 148.6 (ArC), 151.4 (ArC) ppm. HRMS (ESI): MH^+ , found 317.1046. $\text{C}_{16}\text{H}_{18}\text{N}_2\text{O}_3\text{P}$ requires 317.1050.

Dimethyl 6-Phenyl-7-((tetrahydro-2H-pyran-2-yloxy)methyl)-5,6-dihydro-1,6-naphthyridin-5-ylphosphonate (20g). Brownish oil. Yield 0.22 g, 51%. Compound exists as the diastereomers, which were not isolated due to the same R_f . ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 1.34–1.52 (4H, 2m (overlap.), $2 \times \text{CH}_2$), 1.53–1.68 (2H, m, CH_2), 3.23–3.36 (2H, m, CH_2), 3.60; 3.63 (3H, 2d, $^3J_{\text{HP}} = 8.8$ Hz, $^3J_{\text{HP}} = 8.8$ Hz, OCH_3), 3.66; 3.67 (3H, 2d, $^3J_{\text{HP}} = 10.4$ Hz, $^3J_{\text{HP}} = 10.4$ Hz, OCH_3), 4.02; 4.06 (1H, 2d, $J = 8.4$ Hz, $J = 8.4$ Hz, $=\text{CCHHO}$), 4.21; 4.27 (1H, 2d, $J = 13.6$ Hz, $J = 14.0$ Hz, $=\text{CCHHO}$), 4.43; 4.71 (1H, 2br. s, O-CH-O), 5.57; 5.62 (1H, 2d, $^2J_{\text{HP}} = 10.8$ Hz, $^2J_{\text{HP}} = 11.2$ Hz, PCH), 6.29 (1H, br. s, $\text{C}_{\text{sp}^2}\text{H}$), 7.13–7.16 (2H, 2m (overlap.), $2 \times \text{ArH}$), 7.27–7.30 (2H, m, ArH), 7.33–7.37 (2H, m, ArH), 7.48 (1H, d, $J = 6.8$ Hz, ArH), 8.40 (1H, br. s, ArH) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 18.6; 18.7 (CH_2), 24.8; 24.9 (CH_2), 29.8; 29.9 (CH_2), 52.9; 53.1 (2d, $^2J_{\text{CP}} = 7.1$ Hz, $^2J_{\text{CP}} = 7.0$ Hz, OCH_3), 53.2; 53.2 (2d, $^2J_{\text{CP}} = 3.0$ Hz, $^2J_{\text{CP}} = 3.1$ Hz, OCH_3), 60.6; 61.0 (CH_2), 62.6 (d, $^1J_{\text{CP}} = 160.9$ Hz, PCH), 64.1; 65.0 ($=\text{CCH}_2\text{O}$), 96.0; 97.7 (O-CH-O), 110.3; 110.5 ($^4\text{C}_{\text{sp}^2}\text{H}$), 119.8 (ArC), 121.3 (ArC), 123.7; 124.2 (ArC), 124.4; 124.6 (ArC), 129.0; 129.0 (ArC), 134.5 (d, $^3J_{\text{CP}} = 3.8$ Hz, ArC), 144.6; 145.0 (2d, $^3J_{\text{CP}} = 1.7$ Hz, $^3J_{\text{CP}} = 1.9$ Hz, ArC), 145.5; 145.7 (2d, $^3J_{\text{CP}} = 5.6$ Hz, $^3J_{\text{CP}} = 5.6$ Hz, $^3\text{C}_{\text{sp}^2}$), 148.7 (ArC), 151.0 (ArC) ppm. HRMS (ESI): MH^+ , found 431.1728. $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_5\text{P}$ requires 431.1730.

Dimethyl 6-(4-Methoxyphenyl)-7-((tetrahydro-2H-pyran-2-yloxy)methyl)-5,6-dihydro-1,6-naphthyridin-5-ylphosphonate (20h). Yellowish oil. Yield 0.22 g, 48%. Compound exists as the diastereomers, which were not isolated due to the same R_f . ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 1.38–1.47 (4H, 2m (overlap.), $2 \times \text{CH}_2$), 1.52–1.69 (2H, m, CH_2), 3.42–3.48 (2H, m, CH_2), 3.59; 3.62 (3H, 2d, $^3J_{\text{HP}} = 10.8$ Hz, $^3J_{\text{HP}} = 10.8$ Hz, OCH_3), 3.65; 3.65 (3H, 2d, $^3J_{\text{HP}} = 10.4$ Hz, $^3J_{\text{HP}} = 10.4$ Hz, OCH_3), 3.73 (3H, s, OCH_3), 3.93; 3.97 (1H, 2d, $J = 6.8$ Hz, $J = 6.8$ Hz, $=\text{CCHHO}$), 4.12; 4.18 (1H, 2d, $J = 13.6$ Hz, $J = 13.6$ Hz, $=\text{CCHHO}$), 4.40; 4.69 (1H, 2t, $J = 3.2$ Hz, $J = 3.2$ Hz, O-CH-O), 5.42; 5.46 (1H, 2d, $^2J_{\text{HP}} = 6.8$ Hz, $^2J_{\text{HP}} = 6.8$ Hz, PCH), 6.09; 6.15 (1H, 2br. s, $\text{C}_{\text{sp}^2}\text{H}$), 6.91; 6.91 (2H, 2d, $J = 9.2$ Hz, $J = 8.8$ Hz, ArH), 7.09 (1H, $J = 5.6$ Hz, ArH), 7.24; 7.25 (2H, 2d, $J = 8.8$ Hz, $J = 8.8$ Hz, ArH), 7.42 (1H, d, $J = 7.6$ Hz, ArH), 8.31 (1H, br. s, ArH) ppm. ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 18.6; 18.6 (CH_2), 24.8; 24.9 (CH_2), 29.8 (CH_2), 52.8; 53.0 (2d, $^2J_{\text{CP}} = 7.0$ Hz, $^2J_{\text{CP}} = 6.8$ Hz, POCH_3), 53.0; 53.1 (2d, $^2J_{\text{CP}} = 6.5$ Hz, $^2J_{\text{CP}} = 6.7$ Hz, POCH_3), 55.2 (OCH_3), 60.6; 60.9 (CH_2), 63.0 (d, $^1J_{\text{CP}} = 160.0$ Hz, CH), 64.3; 65.1 ($=\text{CCH}_2\text{O}$), 96.0; 97.6 (O-CH-O), 107.9; 108.2 ($^4\text{C}_{\text{sp}^2}\text{H}$), 114.1; 114.2 (ArC), 118.8 (ArC), 120.9 (ArC), 126.3 (ArC), 126.7 (ArC), 134.3; 134.4 (2d, $^3J_{\text{CP}} = 2.7$ Hz, $^3J_{\text{CP}} = 2.9$ Hz, ArC), 138.6; 138.7 (2d, $^3J_{\text{CP}} = 5.3$ Hz, $^3J_{\text{CP}} = 5.3$ Hz, ArC), 145.2; 145.6 (2d, $^3J_{\text{CP}} = 2.2$ Hz, $^3J_{\text{CP}} = 2.0$ Hz, $^3\text{C}_{\text{sp}^2}$), 148.6 (ArC), 151.2; 151.3 (2d, $^3J_{\text{CP}} = 3.1$ Hz, $^3J_{\text{CP}} = 3.2$ Hz, ArC), 156.7; 156.8 (ArC) ppm. HRMS (ESI): MH^+ , found 461.1837. $\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}_6\text{P}$ requires 461.1836.

Dimethyl 2-(4-Methoxyphenyl)-3-phenyl-1,2-dihydrobenzo[b][1,6]naphthyridin-1-ylphosphonate (21a). Yellow solid, mp 188–190 °C. Yield 0.27 g, 48%. ^1H NMR (300 MHz, CDCl_3): δ 3.63 (3H, d, $^3J_{\text{HP}} = 10.5$ Hz, OCH_3), 3.65 (3H, s, OCH_3), 3.76 (3H, d, $^3J_{\text{HP}} = 10.8$ Hz, OCH_3), 5.50 (1H, d, $^1J_{\text{HP}} = 20.1$ Hz, C_1H), 6.66 (2H, d, $^3J = 9.0$ Hz, ArH), 6.80 (1H, s, C_4H), 7.49 (2H, d, $^3J = 9.0$ Hz, ArH), 7.25–7.29 (3H, m, ArH), 7.41 (1H, td, $^3J = 7.3$ Hz, $^4J = 0.9$ Hz, ArH), 7.63–7.67 (3H, m, ArH), 7.71 (1H, d, $^3J = 8.1$ Hz, ArH), 7.81 (1H, d, $^4J_{\text{HP}} = 3.3$ Hz, ArH), 8.06 (1H, d, $^3J = 8.4$ Hz, ArH) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 53.3 (d, $^2J_{\text{CP}} = 7.3$ Hz, OCH_3), 53.6 (d, $^2J_{\text{CP}} = 6.5$ Hz, OCH_3), 55.2 (OCH_3), 65.0 ($^1J_{\text{CP}} = 163.5$ Hz, CH), 110.2 (C_{sp^2}), 114.0 (ArC), 120.7 (ArC), 125.4 (ArC), 125.4 (ArC), 127.2 ($^4J_{\text{CP}} = 2.4$ Hz, ArH), 127.6 (ArC), 127.8 (ArC), 128.3 (ArC), 128.4 (ArC), 128.9 (ArC), 129.1 (ArC), 130.0 (ArC), 134.2 (d, $^3J_{\text{CP}} = 9.0$ Hz, ArC), 136.5 (ArC), 140.7 (d, $^3J_{\text{CP}} = 5.7$ Hz, ArC), 147.8 (ArC), 151.8 (ArC), 156.2 (C_{sp^2}) ppm. HRMS (ESI): MH^+ , found 473.1626. $\text{C}_{27}\text{H}_{26}\text{N}_2\text{O}_4\text{P}$ requires 473.1625.

Dimethyl 3-Butyl-2-phenyl-1,2-dihydrobenzo[b][1,6]naphthyridin-1-ylphosphonate (21b). Yellow solid, mp 149–151 °C. Yield 0.2 g, 48%. ^1H NMR (300 MHz, CDCl_3): δ 0.82 (3H, t, $^3J = 7.2$ Hz, CH_3), 1.24–1.35 (2H, m, CH_2), 1.50–1.60 (2H, m, CH_2), 2.18–2.39 (2H, m, CH_2), 3.60 (3H, d, $^3J_{\text{HP}} = 10.5$ Hz, OCH_3), 3.72 (3H, d, $^3J_{\text{HP}} = 10.5$ Hz, OCH_3), 5.30 (1H, dd, $^1J_{\text{HP}} = 19.2$ Hz, $^4J_{\text{HH}} = 0.6$ Hz, C_1H), 6.34 (1H, s, C_4H), 7.13–7.19 (1H, m, ArH), 7.30–7.37 (5H, m, ArH), 7.57–7.66 (2H, m, ArH), 7.70 (1H, d, $^4J_{\text{HP}} = 3.0$ Hz, ArH), 7.97 (1H, d, $^3J = 8.4$ Hz, ArH) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 13.7 (CH_3), 22.2 (CH_2), 30.0 (CH_2), 33.5 (CH_2), 53.2 (d, $^2J_{\text{CP}} = 7.2$ Hz, OCH_3), 53.5 (d, $^2J_{\text{CP}} = 7.2$ Hz, OCH_3), 65.7 ($^1J_{\text{CP}} = 161.4$ Hz, CH), 108.3 (C_{sp^2}), 119.3 (ArC), 124.9 (ArC), 125.3 (ArC), 125.4 (ArC), 127.0 ($^4J_{\text{CP}} = 2.1$ Hz, ArC), 127.5 (ArC), 127.8 (ArC), 129.1 (ArC), 129.8 (ArC), 133.6 (d, $^3J_{\text{CP}} = 8.4$ Hz, ArC), 146.2 (d, $^3J_{\text{CP}} = 4.8$ Hz, ArC), 147.8 (ArC), 152.1 (ArC), 153.1 (C_{sp^2}) ppm. HRMS (ESI): MH^+ , found 423.1835. $\text{C}_{24}\text{H}_{28}\text{N}_2\text{O}_3\text{P}$ requires 423.1838.

Dimethyl 3-Butyl-2-(4-methoxyphenyl)-1,2-dihydrobenzo[b][1,6]naphthyridin-1-ylphosphonate (21c). Yellow solid, mp 48–50 °C. Yield 0.18 g, 40%. ^1H NMR (300 MHz, CDCl_3): δ 0.81 (3H, t, $^3J = 7.2$ Hz, CH_3), 1.20–1.35 (2H, m, CH_2), 1.47–1.57 (2H, m, CH_2), 2.09–2.30 (2H, m, CH_2), 3.58 (3H, d, $^3J_{\text{HP}} = 10.5$ Hz, OCH_3), 3.70 (3H, d, $^3J_{\text{HP}} = 10.8$ Hz, OCH_3), 3.77 (3H, s, OCH_3), 5.19 (1H, dd, $^1J_{\text{HP}} = 19.0$ Hz, $^4J_{\text{HH}} = 0.6$ Hz, C_1H), 6.20 (1H, s, C_4H), 6.83 (2H, d, $^3J = 9.3$ Hz, ArH), 7.25–7.35 (3H, m, ArH), 7.55–7.67 (3H, m, ArH), 7.97 (1H, d, $^3J = 8.4$ Hz, ArH) ppm. ^{13}C NMR (75 MHz, CDCl_3): δ 13.7 (CH_3), 22.1 (CH_2), 29.9 (CH_2), 33.5 (CH_2), 53.2 (d, $^2J_{\text{CP}} = 6.6$ Hz, OCH_3), 53.2 (d, $^2J_{\text{CP}} = 7.2$ Hz, OCH_3), 55.4

(OCH₃), 64.9 (¹J_{CP} = 160.6 Hz, CH), 106.1 (C₄-sp²), 114.2 (ArC), 119.2 (ArC), 124.6 (ArC), 126.9 (⁴J_{CP} = 2.1 Hz, ArC), 127.5 (ArC), 127.6 (2 × ArC), 129.7 (ArC), 133.5 (d, ³J_{CP} = 8.4 Hz, ArC), 139.2 (d, ³J_{CP} = 4.3 Hz, ArC), 147.7 (ArC), 152.3 (ArC), 153.8 (C₃-sp²), 157.6 (ArC) ppm. HRMS (ESI): MH⁺, found 453.1941. C₂₅H₃₀N₂O₄P requires 453.1938.

Dimethyl 3-Butyl-2-(4-fluorophenyl)-1,2-dihydrobenzo[b]-[1,6]naphthyridin-1-ylphosphonate (21d). Yellow oil. Yield 0.24 g, 52%. ¹H NMR (300 MHz, CDCl₃): δ 0.82 (3H, t, ³J = 7.5 Hz, CH₃), 1.19–1.39 (2H, m, CH₂), 1.54 (2H, quint, ³J = 7.8 Hz, CH₂), 2.12–2.31 (2H, m, CH₂), 3.60 (3H, d, ³J_{HP} = 10.5 Hz, OCH₃), 3.71 (3H, d, ³J_{HP} = 10.8 Hz, OCH₃), 5.21 (1H, d, ¹J_{HP} = 19.2 Hz, C₁H), 6.27 (1H, s, C₄H), 6.97–7.03 (2H, m, ArH), 7.29–7.37 (3H, m, ArH), 7.57–7.66 (2H, m, ArH), 7.70 (1H, d, ⁴J_{HP} = 3.6 Hz, ArH), 7.95 (1H, d, ³J = 8.7 Hz, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 13.6 (CH₃), 22.2 (CH₂), 29.9 (CH₂), 33.5 (CH₂), 53.3 (d, ²J_{CP} = 7.3 Hz, OCH₃), 53.4 (d, ²J_{CP} = 7.4 Hz, OCH₃), 64.8 (¹J_{CP} = 161.6 Hz, CH), 107.6 (C₄-sp²), 115.9 (d ²J_{CF} = 22.5 Hz, ArC), 119.2 (ArC), 124.9 (ArC), 127.0 (ArC), 127.5 (ArC), 127.6 (d, ³J_{CF} = 8.5 Hz, ArC), 127.8 (ArC), 129.8 (ArC), 133.6 (d, ³J_{CP} = 8.1 Hz, ArC), 142.2 (ArC), 147.7 (ArC), 152.0 (ArC), 153.0 (C₃-sp²), 160.4 (d ¹J_{CF} = 244.7 Hz, ArC) ppm. HRMS (ESI): MH⁺, found 457.1441. C₂₄H₂₇ClN₂O₃P requires 457.1442.

Dimethyl 2-(4-Methoxyphenyl)-3-propyl-1,2-dihydrobenzo[b]-[1,6]naphthyridin-1-ylphosphonate (21e). Yellow solid, mp 47–49 °C. Yield 0.3 g, 68%. ¹H NMR (400 MHz, CDCl₃): δ 0.87 (3H, t, ³J = 7.6 Hz, CH₃), 1.54–1.56 (2H, m, CH₂), 2.11–2.15 and 2.20–2.23 (2H, 2m, CH₂), 3.58 (3H, d, ³J_{HP} = 10.4 Hz, OCH₃), 3.70 (3H, d, ³J_{HP} = 10.4 Hz, OCH₃), 3.76 (3H, s, OCH₃), 5.18 (1H, d, ¹J_{HP} = 19.2 Hz, C₁H), 6.19 (1H, s, C₄H), 6.82 (2H, d, ³J = 9.0 Hz, ArH), 7.25 (2H, d, ³J = 8.4 Hz, ArH), 7.31 (1H, t, ³J = 8.4 Hz, ArH), 7.57 (1H, t, ³J = 8.4 Hz, ArH), 7.62 (1H, d, ³J = 8.1 Hz, ArH), 7.65 (1H, d, ⁴J = 3.6 Hz, ArH), 7.92 (1H, d, ³J = 8.4 Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 13.8 (CH₃), 21.1 (CH₂), 36.01 (CH₂), 53.3 (d, ²J_{CP} = 7.3 Hz, OCH₃), 53.4 (d, ²J_{CP} = 7.3 Hz, OCH₃), 55.4 (OCH₃), 64.5 (¹J_{CP} = 161.6 Hz, CH), 106.4 (C₄-sp²), 114.3 (ArC), 124.6 (ArC), 126.9 (J_{CP} = 2.1 Hz, ArC), 127.5 (ArC), 127.6 (2 × ArC), 127.8 (ArC), 129.6 (ArC), 133.4 (J_{CP} = 8.5 Hz, ArC), 139.3 (⁴J_{CP} = 4.6 Hz, ArC), 147.9 (ArC), 152.3 (ArC), 153.4 (C₃-sp²), 157.6 (ArC) ppm. HRMS (ESI): MH⁺, found 439.1791. C₂₄H₂₈N₂O₄P requires 439.1787.

Dimethyl 3-Cyclopropyl-2-(4-methoxyphenyl)-1,2-dihydrobenzo[b]-[1,6]naphthyridin-1-ylphosphonate (21f). Yellow solid, mp 60–61 °C. Yield 0.29 g, 67%. ¹H NMR (300 MHz, CDCl₃): δ 0.72–0.83 (3H, m, CH(CH₂)₂), 1.00–1.06 (1H, m, CH(CH₂)₂), 1.28–1.35 (1H, m, CH(CH₂)₂), 3.60 (3H, d, ³J_{HP} = 10.8 Hz, OCH₃), 3.74 (3H, d, ³J_{HP} = 10.5 Hz, OCH₃), 3.78 (3H, s, OCH₃), 5.29 (1H, d, ¹J_{HP} = 18.6 Hz, C₁H), 5.91 (1H, s, C₄H), 6.85 (2H, d, ³J = 9.0 Hz, ArH), 7.32 (1H, t, ³J = 7.2 Hz, ArH), 7.38 (2H, d, ³J = 9.0 Hz, ArH), 7.55–7.66 (3H, m, ArH), 7.92 (1H, d, ³J = 8.1 Hz, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 8.4 (CH(CH₂)₂), 11.5 (CH(CH₂)₂), 14.7 (CH(CH₂)₂), 53.2 (d, ²J_{CP} = 7.4 Hz, OCH₃), 53.7 (d, ²J_{CP} = 6.3 Hz, OCH₃), 55.4 (OCH₃), 65.0 (d, ¹J_{CP} = 160.2 Hz, C₁H), 99.7 (C₄-sp²), 114.1 (ArC), 119.5 (ArC), 124.6 (ArC), 126.7 (ArC), 127.4 (ArC), 127.4 (2 × ArC), 129.8 (ArC), 133.4 (d, ³J_{CP} = 8.3 Hz, ArC), 139.3 (d, ³J_{CP} = 4.5 Hz, ArC), 147.5 (ArC), 152.4 (ArC), 156.0 (C₃-sp²), 157.4 (ArC) ppm. HRMS (ESI): MH⁺, found 437.1633. C₂₄H₂₆N₂O₄P requires 437.1625.

Dimethyl 3-Cyclopropyl-2-(4-fluorophenyl)-1,2-dihydrobenzo[b]-[1,6]naphthyridin-1-ylphosphonate (21g). Yellow solid, mp 60–61 °C. Yield 0.28 g, 67%. ¹H NMR (300 MHz, CDCl₃): δ 0.77–0.89 (3H, m, CH(CH₂)₂), 1.03–1.10 (1H, m, CH(CH₂)₂), 1.27–1.36 (1H, m, CH(CH₂)₂), 3.63 (3H, d, ³J_{HP} = 10.8 Hz, OCH₃), 3.76 (3H, d, ³J_{HP} = 10.5 Hz, OCH₃), 5.30 (1H, dd, ¹J_{HP} = 18.3 Hz, ⁴J = 0.6 Hz, C₁H), 6.04 (1H, s, C₄H), 7.00–7.06 (2H, m, ArH), 7.34–7.39 (1H, m, ArH), 7.46–7.48 (2H, m, ArH), 7.59–7.67 (2H, m, ArH), 7.71 (1H, d, ⁴J_{HP} = 3.6 Hz, ArH), 8.00 (1H, d, ³J = 8.4 Hz, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 8.7 (CH(CH₂)₂), 11.8 (CH(CH₂)₂), 14.8 (CH(CH₂)₂), 53.3 (d, ²J_{CP} = 7.4 Hz, OCH₃), 53.8 (d, ²J_{CP} = 6.7 Hz, OCH₃), 64.8 (d, ¹J_{CP} = 161.0 Hz, C₁H), 100.4 (C₄-sp²), 115.8 (d ²J_{CF} = 22.5 Hz, ArC), 119.6 (ArC), 125.0 (ArC), 126.6

(ArC), 127.1 (ArC), 127.4 (ArC), 127.5 (ArC), 127.5 (ArC), 130.1 (ArC), 133.8 (d, ³J_{CP} = 7.1 Hz, ArC), 142.1 (ArC), 151.8 (C₃-sp²), 160.3 (d ²J_{CF} = 244.8 Hz, ArC) ppm. HRMS (ESI): MH⁺, found 425.1424. C₂₃H₂₃FN₂O₃P requires 425.1425.

Dimethyl 2-(4-Chlorophenyl)-3-cyclopropyl-1,2-dihydrobenzo[b]-[1,6]naphthyridin-1-ylphosphonate (21h). Yellow solid, mp 78–80 °C. Yield 0.22 g, 50%. ¹H NMR (300 MHz, CDCl₃): δ 0.79–0.92 (3H, m, CH(CH₂)₂), 0.99–1.05 (1H, m, CH(CH₂)₂), 1.29–1.38 (1H, m, CH(CH₂)₂), 3.61 (3H, d, ³J_{HP} = 10.5 Hz, OCH₃), 3.74 (3H, d, ³J_{HP} = 10.8 Hz, OCH₃), 5.31 (1H, d, ¹J_{HP} = 18.3 Hz, C₁H), 6.04 (1H, s, C₄H), 7.26–7.39 (5H, m, ArH), 7.57–7.66 (2H, m, ArH), 7.69 (1H, d, ⁴J_{HP} = 3.3 Hz, ArH), 7.81 (1H, d, ³J = 8.4 Hz, ArH) ppm. ¹³C NMR (75 MHz, CDCl₃): δ 9.0 (CH(CH₂)₂), 11.9 (CH(CH₂)₂), 14.7 (CH(CH₂)₂), 53.3 (d, ²J_{CP} = 7.4 Hz, OCH₃), 53.8 (d, ²J_{CP} = 6.9 Hz, OCH₃), 64.5 (d, ¹J_{CP} = 161.3 Hz, C₁H), 102.2 (C₄-sp²), 119.7 (ArC), 125.0 (ArC), 126.3 (ArC), 126.7 (ArC), 127.5 (d, J_{CP} = 3.3 Hz, ArC), 129.1 (ArC), 129.9 (ArC), 130.4 (ArC), 133.6 (d, ³J_{CP} = 8.1 Hz, ArC), 144.6 (d, ³J_{CP} = 4.2 Hz, ArC), 147.5 (ArC), 151.8 (ArC), 154.8 (C₃-sp²) ppm. HRMS (ESI): MH⁺, found 441.1147. C₂₃H₂₃ClN₂O₃P requires 441.1129.

Synthesis of (E)-4-Methoxy-N-[(2-(phenylethynyl)quinolin-3-yl)methylene]aniline (22). A mixture of 2-phenylethynylquinoline-3-carbaldehyde **6a** (100 mg, 0.389 mmol), 4-methoxyaniline (47.84 mg, 0.389 mmol), and 3 Å MS (100 mg) was stirred in dry chloroform (5 mL). When completion of the reaction was observed by TLC, the solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography eluting with hexane–ethyl acetate mixtures to afford 0.16 g (88%) of yellow solid. Mp 175–176 °C. IR (KBr): ν_{max} 2219 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 3.89 (3H, s, OCH₃), 7.02 (2H, d, ³J = 8.9 Hz, ArH), 7.40 (2H, d, ³J = 8.9 Hz, ArH), 7.42–7.47 (3H, m, ArH), 7.61 (1H, ddd, ³J = 8.1 and 6.9 Hz, ⁴J = 1.1 Hz, ArH), 7.70–7.72 (2H, m, ArH), 7.80 (1H, ddd, ³J = 8.4 and 6.9 Hz, ⁴J = 1.4 Hz, ArH), 7.96 (1H, d, ³J = 7.9 Hz, ArH), 8.18 (1H, d, ³J = 8.5 Hz, ArH), 9.06 (1H, s, ArH), 9.28, s, CH=N) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 55.5 (OCH₃), 86.68 (C_{sp}), 94.55 (C_{sp}), 114.2 (ArC), 121.8 (ArC), 122.6 (ArC), 127.2 (ArC), 127.7 (ArC), 128.6 (ArC), 128.8 (ArC), 129.2 (ArC), 129.5 (ArC), 130.2 (ArC), 131.3 (ArC), 132.2 (ArC), 134.3 (ArC), 143.6 (ArC), 144.6 (ArC), 149.0 (ArC), 154.8 (ArC), 158.9 (ArC) ppm. HRMS (ESI): MH⁺, found 363.1500. C₂₅H₁₉N₂O requires 363.1497.

Synthesis of Dimethyl (4-Methoxyphenylamino)[2-(pent-1-ynyl)quinolin-3-yl]methylphosphonate (23). To a solution of 2-(pent-1-ynyl)quinoline-3-carbaldehyde **6c** (100 mg, 0.448 mmol), 4-methoxyaniline (55.15 mg, 0.448 mmol), and dimethylphosphite (54.21 mg, 0.493 mmol) was added gold(III) bromide (19.58 mg, 0.0448 mmol). When the completion of the reaction was observed by TLC, the solvent was evaporated under reduced pressure, and the residue was purified by flash column chromatography eluting with hexane–ethyl acetate mixtures to afford 0.16 g (83%) of yellow solid. Mp 118–119 °C. IR (KBr): ν_{max} 3298 (NH), 2211 (C≡C) cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 1.12 (3H, t, ³J = 7.2 Hz, CH₃), 1.76 (2H, sext, ³J = 7.2 Hz, CH₂), 2.59 (2H, t, ³J = 7.2 Hz, CH₂), 3.44 (3H, d, ³J_{HP} = 10.8 Hz, OCH₃), 3.65 (3H, s, OCH₃), 3.88 (3H, d, ³J_{HP} = 10.8 Hz, OCH₃), 4.81 (1H, br. s, NH), 5.57 (1H, d, ¹J_{HP} = 24.4 Hz, CH), 6.60 (2H, d, ³J = 8.8 Hz, ArH), 6.67 (2H, d, ³J = 8.8 Hz, ArH), 7.47 (1H, t, ³J = 7.2 Hz, ArH), 7.66 (1H, t, ³J = 7.2 Hz, ArH), 7.73 (1H, d, ³J = 8.0 Hz, ArH), 8.05 (1H, d, ³J = 8.4 Hz, ArH), 8.33 (1H, d, ³J_{HP} = 2.8 Hz, ArH) ppm. ¹³C NMR (100 MHz, CDCl₃): δ 13.6 (CH₃), 21.6 (CH₂), 21.8 (CH₂), 52.6 (d, ¹J_{CP} = 152.6 Hz, CH), 53.7 (d, ²J_{CP} = 7.3 Hz, OCH₃), 54.1 (d, ²J_{CP} = 6.8 Hz, OCH₃), 55.6 (OCH₃), 78.6 (Csp³), 97.0 (Csp³), 114.8 (ArC), 114.9 (ArC), 127.0 (d, ⁴J_{CP} = 2.9 Hz, ArC), 127.1 (ArC), 127.7 (ArC), 128.6 (ArC), 130.2 (ArC), 130.9 (ArC), 134.9 (ArC), 139.3 (d, ³J_{CP} = 15.3 Hz, ArC), 143.5 (ArC), 147.2 (ArC), 152.8 (ArC) ppm. HRMS (ESI): MH⁺, found 439.1789. C₂₄H₂₈N₂O₄P requires 439.1781.

■ ASSOCIATED CONTENT

■ Supporting Information

Copies of ^1H and ^{13}C NMR spectra of the reported compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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