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RESEARCH ARTICLE

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Synthesis of new functionalized hydroxy- and aminomethylphosphinates with indan moieties

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Abstract

The convenient synthesis of new functionalized organophosphorus acids and their derivatives containing indan moieties was developed. The regioselective radical addition of bis(trimethylsiloxy)phosphine to indene proceeds to give rise to 2-indanylphosphonite as key compound for preparation of above acids with bicyclic substituents. Azobis(isobutyronitrile) (AIBN) in the conditions of its thermolysis was used as effective initiator of the addition reaction. The further treatment of organophosphorus acids trimethylsilyl esters with the methanolic sodium methoxide solution resulted in the water-soluble sodium salts of the corresponding acids.

1 | INTRODUCTION

Functionalized hydroxy- and aminomethylphosphonates (phosphinates) and their derivatives are the promising organophosphorus biomimetics of natural hydroxy and amino acids and widely used as effective multidentate ligands and biologically active substances with multifactor activity. It should be noted that the functionalized organophosphorus acids with aryl, heterocyclic, and bicyclic moieties are of particular interest among these substances.[1-4] Earlier, we described original methods for the synthesis of aminomethylenebisphosphonic acid derivatives[5], as well as new aryl-substituted methylphosphonic and methylenediphosphonic acids and their derivatives[6a] using trimethylsilyl esters of trivalent phosphorus acids as highly reactive synthons. In the present work, convenient methods for the synthesis of functionalized amino- and hydroxymethylphosphinic acids and their derivatives, including bicyclic moieties of indan as well as aromatic and heterocyclic substitutents, are proposed via highly reactive bis(trimethylsiloxy)phosphine. Preliminary brief data on the synthesis of organophosphorus derivatives of indan were published by us earlier (cf. [6b-e]). In this article, we are reporting detailed synthesis of 32 new compounds with important moieties of heterocycles and amino acids, including their full characterization via complete ^{1}H, ^{13}C, and ^{31}P NMR data.

2 | RESULTS AND DISCUSSION

In the present work, we accomplished radical addition of bis(trimethylsiloxy)phosphine to indene. It has been established that the radical addition of bis(trimethylsiloxy)phosphine to indene proceeds regioselectively to give phosphonite **1** as new key synthon in high yield. Azobis(isobutyronitrile) was used as a reaction initiator under the conditions of its thermolysis (100-120°C; Scheme 1).

Phosphonite **1** was successfully used by us for preparing the derivatives of new functionalized aminomethylphosphinic acids, including bicyclic indan moieties. Thus, phosphonite **1** readily reacts with aminomethylating reagents such as aminals, *N*-chloromethylamides, and *N*-ethoxymethyl-*N,N*-bis(trimethylsilyl)amine to form phosphinates **2** in good yields, the reaction conditions being determined by the reactivity of the aminomethylating reagent (cf.[7]). Various aminals interact with phosphonite **1** only under heating in the presence of zinc chloride as a catalyst, but the highly reactive *N*-chloromethylamides react already at 10°C. Phosphonite **1** reacts with *N*-ethoxymethyl-*N,N*-bis(trimethylsilyl)amine at 20-120°C, and chlorotrimethylsilane and zinc chloride are also used as catalysts (Scheme 2).

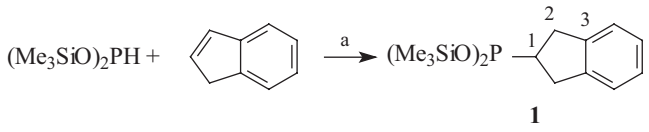
The interaction of phosphonite **1** with sulfur is a convenient method for the synthesis of thiophosphonate **3**, and the

addition of phosphonite **1** via its POSi moiety to the carbonyl group of various aldehydes proceeds under mild conditions and leads to substituted trimethylsiloxymethylphosphinate **4**, including aromatic and heterocyclic moieties along with indan group (Scheme 3).

The reaction of phosphonite **1** with trimethylsilyl acrylate proceeds as a 1,4-addition to the conjugated system of acrylate with the formation of ketene acetal **5a** as an intermediate, the further interaction of intermediate **5a** with diethyl phosphite results in phosphinate **5** containing a propionic acid group (cf.[8]), (Scheme 4). It should be noted that diethylphosphite smoothly removes only one trimethylsilyl group of ketene acetal **5a**, and this method can be used for further synthetic purposes.

The treatment of phosphonite **1,** phosphinates **2,4,5,** and thiophosphonate **3** with dilute solutions of sodium methoxide in methanol gives stable water-soluble sodium salts of corresponding phosphonous **6,** thiophosphonic **8**, and phosphinic **7,9,10** acids (Scheme 5). Salts **6-10** are colorless hygroscopic crystals.

The structures of organophosphorus acids and their derivatives **1-10** with indan moieties were confirmed by the ^{1}H, ^{13}C, ^{31}P NMR spectra where the characteristic signals of corresponding moieties were observed. The numbers of the carbon atoms used for the description of the ^{1}H, ^{13}C NMR spectra for compounds **1,24,5** in the experimental section are shown in the schemes (see Schemes 1-4). According to the NMR spectral data, the compounds with asymmetrical atoms and various amide moieties are the mixtures of stereoisomers, and their ratio was determined by the ^{1}H and ^{31}P NMR spectra where the data for the major isomer are presented first.



SCHEME 1 Reagents and conditions: (a) AIBN, 100-120°C

3 | CONCLUSIONS

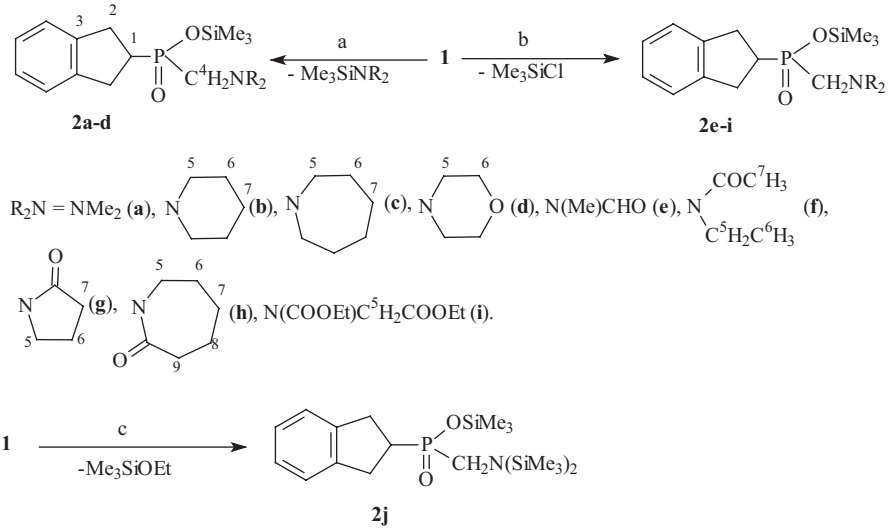
Summarizing, we have developed convenient methods for the synthesis of new derivatives of functionalized amino-and hydroxymethylphosphinic acids, including bicyclic moieties of indan as well as aromatic and heterocyclic substituents, based on readily available starting materials such as indene and trimethylsilyl esters of trivalent phosphorus acids. The resulting compounds are convenient synthons for the preparation of various functionalized organophosphorus compounds and are of interest as biologically active substances with various properties and promising polydentate ligands.

4 | EXPERIMENTAL

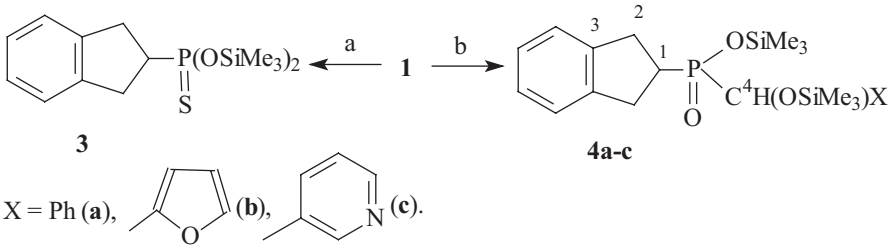
The ^{1}H, ^{13}C, and ^{31}P NMR spectra were registered on a Bruker Avance-400 spectrometer (400, 100, and 162 MHz, respectively) against TMS as internal standard (^{1}H and ^{13}C) and 85% H_3PO_4 in D_2O as external standard (^{31}P). All reactions were carried out under dry argon in anhydrous solvents. The starting esters of organophosphorus acids were prepared as described.[8,9] Sodium salts **6-10** are decomposed above 100°C and do not have clear melting points.

4.1 | Bis(trimethylsilyl) 2,3-dihydro-1*H*-inden-2-ylphosphonite (1)

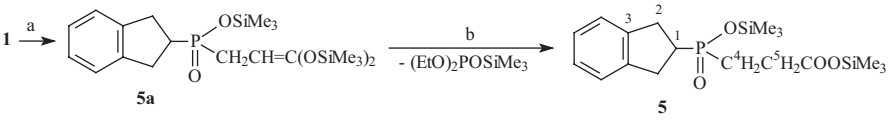
A mixture of bis(trimethylsiloxy)phosphine (48 g 0.23 mol), 1*H* indene (21 g, 0.18 mol) and azobis(isobutyronitrile) (0.2 g, 0.0012 mol) was heated to 100°C. Then, the temperature of the reaction mixture was gradually raised to 120°C over the



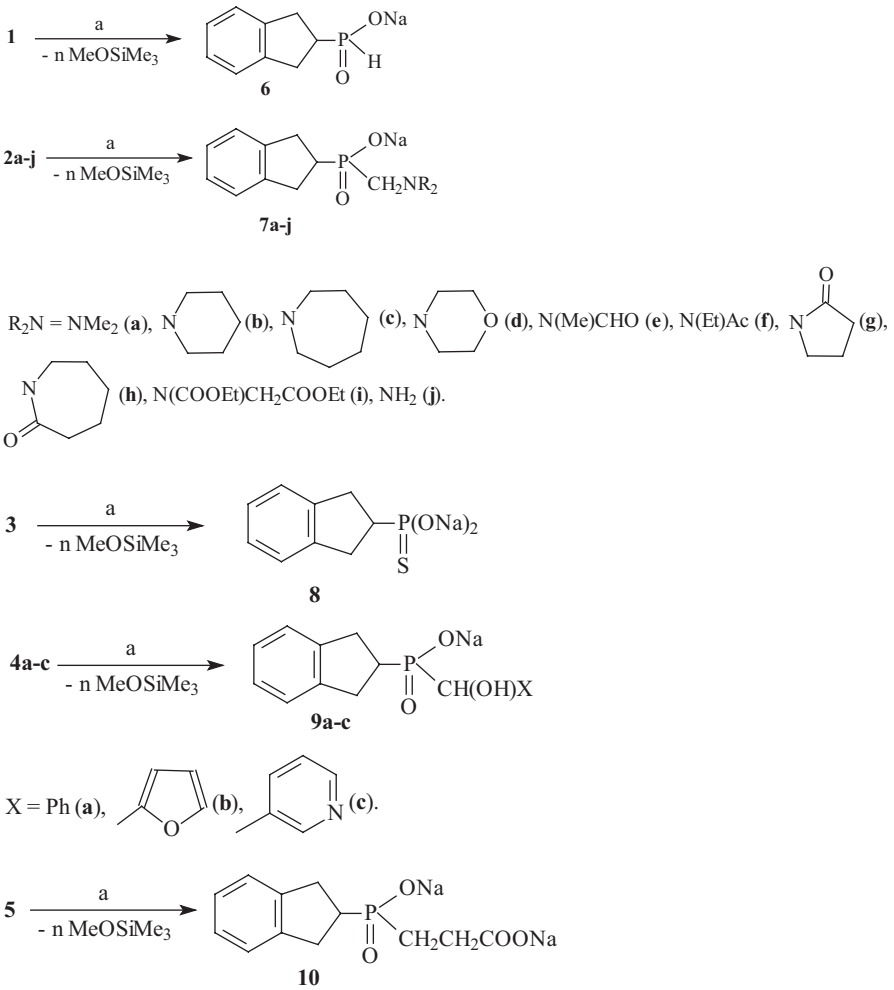
SCHEME 2 Reagents and conditions: (a) $(R_2N)_2CH_2$, $ZnCl_2$, 110-130°C; (b) R_2NCH_2Cl, CH_2Cl_2, 10°C, (c) $(Me_3Si)_2NCH_2OEt$, CH_2Cl_2, Me_3SiCl, $ZnCl_2$, 20-120°C



SCHEME 3 Reagents and conditions: (a) S, C_6H_6, 80°C; (b) XCHO, CH_2Cl_2, 10°C



SCHEME 4 Reagents and conditions: (a) CH_2=CHCOOSiMe$_3$, Et_2O, 20°C; (b) $(EtO)_2P(O)H$, Et_2O, 40°C



SCHEME 5 Reagents and conditions: (a) n MeONa (n = 1,2), MeOH, Et_2O, 10°C

course of 1 hr. After that the reaction mixture was distilled in a vacuum to obtain 49 g of phosphonite I, yield 83%, bp 126°C (1 mm Hg). ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.21 (s, 18H, 2 Me_3Si), 2.31 (d, 1H, $^2J_{PH}$ = 3.6 Hz, $^3J_{HH}$ = 8.8 Hz, C^1H), 2.90-3.05 (m, 4H, 2 C^2H_2), 7.08-7.20 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: 1.3 (d, $^3J_{PC}$ = 4.6 Hz, Me_3Si), 32.0 (d, $^2J_{PC}$ = 19.7 Hz, C^2), 46.3 (d, $^1J_{PC}$ = 20.3 Hz, C^1), 124.2 (s, C_{Ar}), 126.0 (s, C_{Ar}), 143.1 (d, $^3J_{PC}$ = 5.6 Hz, C^3). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 155.6 (s). Anal. Calcd for $C_{15}H_{27}O_2PSi_2$. C 55.18; H 8.33. Found: C 55.02; H 8.17.

4.2 | Trimethylsilyl 2,3-dihydro-1*H*-inden-2-yl(*N*,*N*-dimethylaminomethyl)phosphinate (2a)

A mixture of phosphonite **1** (6.5 g, 0.02 mol), bis(dimethylamino)methane (2.2 g, 0.022 mol), and zinc

chloride (0.1 g, 0.0007 mol) was heated at 110-130°C for 1.5 hr and then distilled to obtain 4.6 g of phosphinate **2a**, yield 74%, bp 141°C (1 mm Hg). ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.34 (s, 9H, Me_3Si), 2.45 (s, 6H, Me_2N), 2.12 and 2.75 ($C^4H_AH_BN$, 2H, $^{2}J_{PHA}$ = 10.8 Hz, $^{2}J_{PHB}$ = 8.4 Hz, $^{2}J_{HAHB}$ = 14.8 Hz, H_A and H_B), 2.85-2.95 (m, 1H, C^1H), 3.10-3.40 (m, 4H, C^2H_2), 7.20-7.30 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: 0.1 (s, Me_3Si), 31.6 (s, C^2), 32.2 (s, C^2), 35.5 (d, $^{1}J_{PC}$ = 97.9 Hz, C^1), 46.5 (d,$^{3}J_{PC}$ = 9.7 Hz, C^5), 46.6 (d, $^{3}J_{PC}$ = 10.5 Hz, C^5), 56.7 (d,$^{1}J_{PC}$ = 112.1 Hz, C^4), 123.0 (s, C_{Ar}), 125.2 (s, C_{Ar}), 140.7 (d, $^{3}J_{PC}$ = 9.1 Hz, C^3), 140.5 (d,$^{3}J_{PC}$ = 9.1 Hz, C^3). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 41.6 (s). Anal. Calcd for $C_{15}H_{26}NO_2PSi$. C 57.85; H 8.41. Found: C 57.68; H 8.29.

Phosphinates **2b-d** were obtained similarly.

4.3 | Trimethylsilyl 2,3-dihydro-1*H*-inden-2-yl(piperidin-1-ylmethyl)phosphinate (2b)

Yield 78%, bp 169°C (1 mm Hg), mp 61°C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.13 (s, 9H, Me_3Si), 1.40-1.43 (m, 6H, 2 C^6H_2, C^7H_2), 2.30-2.60 (m, 4H, 2 C^2H_2), 2.68-2.85 (m, 2H, C^1H_2), 2.95-3.20 (m, 6H, C^4H_2, 2 C^5H_2), 7.00-7.10 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: 1.0 (s, Me_3Si), 23.6 (s, C^7), 25.8 (s, 2 C^6), 32.7 and 33.4 (s, C^2), 36.7 (d, $^{1}J_{PC}$ = 98.0 Hz, C^1), 56.4 (d, $^{3}J_{PC}$ = 9.8 Hz, C^5), 57.3 (d, $^{1}J_{PC}$ = 113.8 Hz, C^4), 123.0 (s, C_{Ar}), 126.2 (s, C_{Ar}), 141.6 (d, $^{3}J_{PC}$ = 9.9 Hz, C^3), 141.8 (d, $^{3}J_{PC}$ = 9.8 Hz, C^3). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 42.4 (s). Anal. Calcd for $C_{18}H_{30}NO_2PSi$. C 61.51; H 8.60. Found: C 61.26; H 8.52.

4.4 | Trimethylsilyl 2,3-dihydro-1*H*-inden-2-yl(azepan-1-ylmethyl)phosphinate (2c)

Yield 80%, bp 191°C (1 mm Hg), mp 48°C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.17 (s, 9H, Me_3Si), 1.40-1.60 (m, 8H, 2 C^6H_2, 2 C^7H_2), 2.60-2.90 (m, 6H, C^1H_2, 2 C^2H_2), 3.00-3.30 (m, 6H, C^4H_2, 2 C^5H_2), 7.00-7.20 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: 1.2 (s, Me_3Si), 26.8 (s, C^7), 28.1 (s, 2 C^6), 32.8 (s, C^2), 33.4 (s, C^2), 36.6 (d, $^{1}J_{PC}$ = 97.8.0 Hz, C^1), 56.5 (d, $^{1}J_{PC}$ = 113.8 Hz, C^4) 57.6 (d, $^{3}J_{PC}$ = 7.8 Hz, C^5), 124.2 (s, 2 C_{Ar}), 126.3 (s, 2 C_{Ar}), 141.8 (d, $^{3}J_{PC}$ = 9.7 Hz, C^3),142.0 (d, $^{3}J_{PC}$ = 9.8 Hz, C^3). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 43.2 (s). Anal. Calcd for $C_{19}H_{32}NO_2PSi$. C 62.43; H 8.82. Found: C 62.28; H 8.75.

4.5 | Trimethylsilyl 2,3-dihydro-1*H*-inden-2-yl(morpholin-4-ylmethyl)phosphinate (2d)

Yield 81%, bp 175°C (1 mm Hg), mp 55°C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: −0.01 (s, 9H, Me_3Si), 2.20-2.45 (m, 4H, 2 C^2H_2), 2.52-2.60 (m, 1H, C^1H), 2.80-3.10 (m, 6H, C^4H_2, 2 C^5H_2), 3.36 (s, 4H, 2 C^6H_2), 6.84-6.94 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: 0.6 (s, Me_3Si), 32.3 and 32.8 (s, C^2), 36.3 (d, $^{1}J_{PC}$ = 97.9 Hz, C^1), 54.9 (d,$^{3}J_{PC}$ = 8.7 Hz, C^5), 56.1 (d, $^{1}J_{PC}$ = 111.3 Hz, C^4), 66.1 (s, C^6), 123.6 (s, C_{Ar}), 125.8 (s, C_{Ar}), 141.1(d, $^{3}J_{PC}$ = 6.5 Hz, C^3) and 141.2 (d,$^{3}J_{PC}$ = 8.0 Hz, C^3). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 41.2 (s). Anal. Calcd for $C_{17}H_{28}NO_3PSi$. C 57.77; H 7.98. Found: C 57.68; H 7.89.

4.6 | Trimethylsilyl 2,3-dihydro-1*H*-inden-2-yl(*N*-methyl-*N*-formylaminomethyl) phosphinate (2e)

To a solution of phosphonite **1** (5.4 g, 0.017 mol) in methylene chloride (10 mL), a solution of *N*-chloromethyl-*N*-methylformamide (1.8 g, 0.017 mol) in methylene chloride (5 mL) was added dropwise with stirring at 10°C. The solvent was then removed, and the residue was distilled in a vacuum to obtain 3.8 g of phosphinate **2e**, yield 70%, bp 187°C (1 mm Hg). The first isomer, 75%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: −0.05 (s, 9H, Me_3Si), 2.36-2.48 (m, 1H, C^1H), 2.82-3.00 (m, 4H, 2 C^2H_2), 2.87 (s, 3H, MeN), 3.18-3.68 (m, 2H, C^4H_2), 6.80-6.92 (m, 4H, 4 $C_{Ar}H$), 7.78 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: 0.6 (s, Me_3Si), 31.8 (s, C^2), 32.80 (s, C^2), 35.3 (s, MeN), 36.1 (d, $^{1}J_{PC}$ = 96.7 Hz, C^1), 42.5 (d, $^{1}J_{PC}$ = 101.0 Hz, C^4), 123.6 (s, 2 C_{Ar}), 125.9 (s, 2 C_{Ar}), 140.8 (d, $^{3}J_{PC}$ = 8.9 Hz, C^3), 140.9 (d, $^{3}J_{PC}$ = 8.6 Hz, C^3), 161.7 (s, CO). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 38.8 (s). The second isomer, 25%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: -0.05 (s, 9H, Me_3Si), 2.36-2.48 (m, 1H, C^1H), 2.82-3.00 (m, 4H, 2 C^2H_2), 2.77 (s, 3H, MeN), 3.18-3.68 (m, 2H, C^4H_2), 6.80-6.92 (m, 4H, 4 $C_{Ar}H$), 7.72 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: 0.6 (s, Me_3Si), 32.0 (s, C^2), 32.5 (s, C^2), 35.3 (s, MeN), 35.9 (d, $^{1}J_{PC}$ = 96.1 Hz, C^1), 46.9 (d, $^{1}J_{PC}$ = 99.5 Hz, C^4), 123.6 (s, 2 C_{Ar}), 125.9 (s, 2 C_{Ar}), 140.3 (d, $^{3}J_{PC}$ = 8.8 Hz, C^3), 140.5 (d, $^{3}J_{PC}$ = 8.4 Hz, C^3), 162.1 (s, CO). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 38.3 (s). Anal. Calcd for $C_{15}H_{24}NO_3PSi$. C 55.36; H 7.43. Found: C 55.23; H 7.35.

Phosphinates **2f-j** were obtained similarly.

4.7 | Trimethylsilyl 2,3-dihydro-1*H*-inden-2-yl(*N*-ethyl-*N*-acetylaminomethyl)phosphinate (2f)

Yield 73%, bp 187°C (1 mm Hg). ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.15 (s, 9H, Me_3Si), 0.84 (t, 3H, $^{3}J_{HH}$ = 7.2 Hz, C^6H_3), 1.76 (s, 3H, C^7H_3), 2.32-2.41 (m, 1H, C^1H), 2.74-2.98 (m, 4H, 2 C^2H_2), 3.10-3.36 (m, 3H, C^4H_B, C^5H_2), 3.71 (dd, 2H, $^{2}J_{HAHB}$ = 15.2 Hz, $^{2}J_{PHA}$ = 5.6 Hz, C^4H_B), 6.70-6.85 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: 0.4 (s, Me_3Si), 12.2 (s, C^6), 20.1 (s, C^7), 31.6 (s, C^7), 32.9 (s, C^2), 36.1 (d, $^{1}J_{PC}$ = 95.5, C^1), 42.1 (d, $^{1}J_{PC}$ = 102.0 Hz, C^4), 43.2 (s, 2 C^5), 123.4 (s, 2 C_{Ar}), 125.7 (s,

2 C_{Ar}), 140.8 (d, $^3J_{PC}$ = 9.1 Hz, C^3), 140.9 (d,$^3J_{PC}$ = 9.9 Hz, C^3), 169.0 (s, CO). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 39.9 (s). Anal. Calcd for $C_{17}H_{28}NO_3PSi$. C 57.77; H 7.98. Found: C 57.52; H 7.90.

4.8 | Trimethylsilyl 2,3-dihydro-1*H*-inden-2-yl[(2-oxopyrrolidin-1-yl)methyl]phosphinate (2g)

Yield 76%, bp 186°C (1 mm Hg). ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: −0.12 (s, 9H, Me_3Si), 1.55-1.70 (m, 2H, C^6H_2), 1.90-2.00 (m, 2H, C^7H_2), 2.38-2.39 (m, 1H, C^1H), 2.75-2.92 (m, 6H, 2 C^2H_2, C^5H_2), 3.00-3.44 (m, 2H, C^4H_2), 6.74-6.85 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: 0.38 (s, Me_3Si), 17.1 (s, C^6), 29.3 (s, C^7), 31.6 (s, C^2), 32.5 (s, C^2), 35.7 (d, $^1J_{PC}$ = 95.9 Hz, C^1), 41.1 (d, $^1J_{PC}$ = 104.4 Hz, C^4), 47.6 (s, C^5), 123.4 (s, 2C_{Ar}), 125.7 (s, 2 C_{Ar}), 140.6 (d, $^3J_{PC}$ = 7.2, C^3), 140.6 (d, $^3J_{PC}$ = 7.2 Hz, C^3), 140.7 (d, $^3J_{PC}$ = 9.1 Hz, C^3), 173.8 (s, CO). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 39.1 (s). Anal. Calcd for $C_{17}H_{26}NO_3PSi$. C 58.10; H 7.46. Found: C 57.98; H 7.28.

4.9 | Trimethylsilyl 2,3-dihydro-1*H*-inden-2-yl[(2-oxoazepan-1-yl)methyl]phosphinate (2h)

Yield 72%, bp 205°C (1 mm Hg), mp 72°C. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.53 (s, 9H, Me_3Si), 1.25-1.55 (m, 6H, C^6H_2, C^7H_2, C^8H_2), 2.20-2.30 (m, 2H, C^9H_2), 2.35-2.50 (m, 1H, C^1H), 2.85-3.15 (m, 4H, 2 C^2H_2), 3.25-3.50 (m, 4H, C^4H_2, C^5H_2), 6.82-7.15 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: -0.24 (s, Me_3Si), 22.0 (s, C^7), 22.6 (s, C^8), 27.2 (s, C^6), 28.4 (s, C^9), 31.1 (s, C^2), 32.1 (s, C^2), 35.3 (d, $^1J_{PC}$ = 95.7 Hz, C^1), 45.1 (d, $^1J_{PC}$ = 103.2 Hz, C^4), 49.3 (s, C^5), 122.8 (s, 2 C_{Ar}), 125.0 (s, 2 C_{Ar}), 140.2 (d, $^3J_{PC}$ = 9.3 Hz, C^3), 140.4 (d, $^3J_{PC}$ = 9.3 Hz, C^3), 175.0 (s, CO). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 39.4 (s). Anal. Calcd for $C_{19}H_{30}NO_3PSi$. C 60.13; H 7.97. Found: C 60.01; H 7.88.

4.10 | Trimethylsilyl 2,3-dihydro-1*H*-inden-2-yl[*N*-ethoxycarbonyl-*N*-(ethoxycarbonylmethyl)aminomethyl] phosphinate (2i)

Yield 78%, bp 200°C (1 mm Hg). The first isomer, 70%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.19 (s, 9H, Me_3Si), 1.16-1.30 (m, 6H, 2 CH_3), 2.35-2.50 (m, 1H, C^1H), 2.70-2.90 (m, 4H, 2 C^2H_2), 3.20-3.68 (m, 2H, C^4H_2), 3.65-3.75 (m, 4H, 2 CH_2O), 3.91 (s, 2H, C^5H_2), 6.85-6.95 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: 0.01 (s, Me_3Si), 13.5 (s, 2 Me), 32.4 (s, C^2), 32.5 (s, C^2), 35.1 (d, $^1J_{PC}$ = 95.9 Hz, C^1), 44.8 (d, $^1J_{PC}$ = 105.0 Hz, C^4), 48.0 (s, C^5), 59.8 (s, CH_2O), 123.2 (s, C_{Ar}), 125.5 (s, C_{Ar}), 140.5 (d, $^3J_{PC}$ = 8.7 Hz, C^3), 140.7 (d, $^3J_{PC}$ = 8.7 Hz, C^3), 155.0 (d, $^3J_{PC}$ = 3.0 Hz, C^7), 168.1 (s, CO). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 39.6 (s). The second isomer, 30%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.23 (s, 9H, Me_3Si), 1.16-1.30 (m, 6H, 2 CH_3), 2.35-2.50 (m, 1H, C^1H), 2.70-2.90 (m, 4H, 2 C^2H_2), 3.20-3.68 (m, 2H, C^4H_2), 3.65-3.75 (m, 4H, 2 CH_2O), 4.02 (s, 2H, C^5H_2), 6.85-6.95 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: 0.01 (s, Me_3Si), 13.1 (s, 2 Me), 31.3 (s, C^2), 31.4 (s, C^2), 35.2 (d, $^1J_{PC}$ = 94.9 Hz, C^1), 44.4 (d, $^1J_{PC}$ = 102.8 Hz, C^4), 47.8 (s, C(5)), 61.0 (s, CH_2O), 123.3 (s, C_{Ar}), 125.6 (s, C_{Ar}), 140.2 (d, $^3J_{PC}$ = 8.7 Hz, C^3), 140.3 (d, $^3J_{PC}$ = 8.7 Hz, C^3), 154.6 (s, C^7), 168.1 (s, CO). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 39.1 (s). Anal. Calcd for $C_{20}H_{32}NO_6PSi$. C 54.40; H 7.31. Found: C 54.15; H 7.22.

4.11 | Trimethylsilyl 2,3-dihydro-1*H*-inden-2-yl[*N*,*N*-bis(trimethylsilyl)aminomethyl] phosphinate (2j)

Yield 74%, bp 171°C (1 mm Hg). The first isomer, 65%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: -0.35-0.02 (m, 27H, Me_3Si), 2.30-2.45 (m, 1H, C^4H_B), 2.55-2.65 (m, 1H, C^1H), 2.85-3.05 (m, 5H, C^4H_A, 2 C^2H_2). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: -1.0 (s, Me_3SiO), 0.68 (s, Me_3SiN), 33.0 (s, C^2), 33.6 (s, C^2), 34.8 (d, $^1J_{PC}$ = 94.1 Hz, C^1), 39.7 (d, $^1J_{PC}$ = 103.3 Hz, C^4), 123.6 (s, 2 C_{Ar}), 125.9 (s, 2 C_{Ar}), 141.3 (d, $^3J_{PC}$ = 10.5 Hz, C^3). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 44.0 (s). The second isomer, 35%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: -0.35-0.02 (m, 27H, Me_3Si), 2.30-2.45 (m, 1H, C^4H_B), 2.55-2.65 (m, 1H, C^1H), 2.85-3.05 (m, 5H, C^4H_A, 2 C^2H_2). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: -0.9 (s, Me_3SiO), 1.8 (s, Me_3SiN), 32.7 (s, C^2), 33.2 (s, C^2), 35.0 (d, $^1J_{PC}$ = 93.8 Hz, C^1), 43.0 (d, $^1J_{PC}$ = 103.0 Hz, C^4), 123.6 (s, 2 C_{Ar}), 126.0 (s, 2 C_{Ar}), 141.8 (d, $^3J_{PC}$ = 5.1 Hz, C^3). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 41.3 (s). Anal. Calcd for $C_{19}H_{38}NO_2PSi_3$. C 53.35; H 8.95.Found: C 53.20; H 8.87.

4.12 | Bis(trimethylsilyl) 2,3-dihydro-1*H*-inden-2-ylthiophosphonate (3)

To a solution of phosphonite **1** (4 g, 0.012 mol) in benzene (10 mL) of sulfur (0.4 g, 0.013 mol) was added. After exothermic reaction had been complete, the mixture was heated for 15 min on a water bath and cooled. Excess sulfur was filtered off, the solvent was removed, and the residue was distilled in a vacuum to obtain 4 g (91%) of thiophosphonate **3**, bp 142°C (1 mm Hg). ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.34 (s, 18H, 2 Me_3Si), 2.75-2.90 (m, 1H, C^1H), 3.10-3.40 (m, 4H, 2 C^2H_2), 7.10-7.25 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: 1.1 (s, Me_3Si), 34.3 (s, C^2), 44.8 (d, $^1J_{PC}$ = 117.7 Hz, C^1), 124.0 (s, C_{Ar}), 126.2 (s, C_{Ar}), 141.5 (d, $^3J_{PC}$ = 10.6 Hz, C^3). ^{31}P NMR ($CDCl_3$, 162 MHz), δ,

ppm: 75.1 (s). Anal. Calcd for $C_{15}H_{27}O_2PSSi_2$. C 50.24; H 7.59. Found: C 50.03; H 7.50.

4.13 | Trimethylsilyl 2,3-dihydro-1*H*-inden-2-yl[phenyl(trimethylsiloxy)methyl] phosphinate (4a)

To a solution of phosphonite **1** (4 g, 0.012 mol) in methylene chloride (10 mL), a solution of benzaldehyde (1.2 g, 0.011 mol) in methylene chloride (5 mL) was added dropwise with stirring at 10°C. The solvent was then removed, and the residue was distilled in a vacuum to obtain 4 g of phosphinate **4a**, yield 83%, bp 182°C (1 mm Hg), mp 92°C. The first isomer, 60%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm:): 0.04 (s, 9H, Me_3Si), 0.08 (s, 9H, Me_3Si), 2.75-2.95 (m, 1H, C^1H), 3.05-3.40 (m, 4H, 2 C^2H_2), 4.91 (d, 1H, $^2J_{PH}$ = 9.6 Hz, C^4H), 7.10-7.55 (m, 9H, 4 $C_{Ar}H$, C_6H_5). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm:): 0.17 (s, Me_3Si), 1.07 (s, Me_3Si), 32.9 (s, C^2), 33.4 (s, C^2), 34.7 (d, $^1J_{PC}$ = 95.4 Hz, C^1), 74.1 (d, $^1J_{PC}$ = 114.9 Hz, C^4H), 124.4 (s, C_{Ar}), 126.5 (s, C_{Ar}), 127.3 (s, C_{Ph}), 127.8 (s, C_{Ph}), 128.1 (s, C_{Ph}), 137.2 (s, C_{Ph}), 142.0 (d, $^3J_{PC}$ = 9.3 Hz, C^3), 142.1 (d, $^3J_{PC}$ = 8.2 Hz, C^3). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 40.5 (s).The second isomer, 40%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.02 (s, 9H, Me_3Si), 0.09 (s, 9H, Me_3Si), 2.75-2.95 (m, 1H, C^1H), 3.05-3.40 (m, 4H, 2 C^2H_2), 5.03 (d, 1H, $^2J_{PH}$ = 7.6 Hz, C^4H), 7.10-7.55 (m, 9H, 4 $C_{Ar}H$, C_6H_5). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: 0.96 (s, Me_3Si), 1.99 (s, Me_3Si), 33.7 (s, C^2), 34.1 (s, C^2), 35.2 (d, $^1J_{PC}$ = 96.3 Hz, C^1), 74.0 (d, $^1J_{PC}$ = 115.3 Hz, C^4H), 141.8 (d, $^3J_{PC}$ = 9.2 Hz, C^3), 142.0 (d, $^3J_{PC}$ = 9.3 Hz, C^3). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 39.4 (s). Anal. Calcd for $C_{22}H_{33}O_3PSi_2$. C 61.08; H 7.69. Found: C 60.92; H 7.55.

4.14 | Trimethylsilyl 2,3-dihydro-1*H*-inden-2-yl[fur-2-yl(trimethylsiloxy)methyl] phosphinate (4b)

Yield 82%, bp 169°C (1 mm Hg). The first isomer, 60 %. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: -0.11 (s, 9H, Me_3Si), -0.10 (s, 9H, Me_3Si), 2.60-2.75 (m, 1H, C^1H), 2.85-3.15 (m, 4H, 2 C^2H_2), 4.79 (d, 1H, $^2J_{PH}$ = 10.0 Hz, C^4H), 6.17-6.37 (m, 2H, 2 $C_{Fur}H$), 7.52 (s, 2H, 2 $C_{Fur}HO$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: 0.83 (s, Me_3Si), 0.47 (s, Me_3Si), 32.3 (s, C(2)), 32.8 (s, C(2)), 35.0 (d, $^1J_{PC}$ = 96.7 Hz, C^1), 66.9 (d, $^1J_{PC}$ = 119.8 Hz, C^4H), 109.7 (s, C_{Fur}), 110.4 (s, C_{Fur}), 123.6 (s, C_{Ar}), 125.9 (s, C_{Ar}), 141.3 (d, $^3J_{PC}$ = 10.6 Hz, C^3), 141.4 (d, $^3J_{PC}$ = 11.3 Hz, $C_{Fur}HO$), 149.8 (s, $C_{Fur}O$). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 37.4 (s). The second isomer, 40%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.02 (s, 9H, Me_3Si), -0.07 (s, 9H, Me_3Si), 2.35-2.50 (m, 1H, C^1H), 2.85-3.15 (m, 4H, 2 C^2H_2), 4.82 (d, 1H, $^2J_{PH}$ = 10.8 Hz, C^4H), 6.17-6.37 (m, 2H, 2 $C_{Fur}H$), 7.51 (s, 2H, 2 $C_{Fur}HO$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: 0.36 (s, Me_3Si), 0.62 (s, Me_3Si), 32.8 (s, C^2), 33.1 (s, C^2), 37.4 (d, $^1J_{PC}$ = 97.4 Hz, C^1), 67.8 (d, $^1J_{PC}$ = 118.6 Hz, C^4H), 109.0 (s, C_{Fur}), 110.2 (s, C_{Fur}), 123.5 (s, C_{Ar}), 126.2 (s, C_{Ar}), 141.0 (d, $^3J_{PC}$ = 8.9 Hz, C^3), 141.1 (d, $^3J_{PC}$ = 8.9 Hz, C^3), 141.9 (s, $C_{Fur}HO$). 150.0 (s, $C_{Fur}O$). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 36.7 (s). Anal. Calcd for $C_{20}H_{31}O_4PSi_2$. C 56.84; H 7.39. Found: C 56.73; H 7.23.

4.15 | Trimethylsilyl 2,3-dihydro-1*H*-inden-2-yl[pyridin-3-yl(trimethylsiloxy)methyl] phosphinate (4c)

Yield 83%, bp 188°C (1 mm Hg), mp 83°C. The first isomer, 65 %. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.05 (s, 18H, Me_3Si), 2.50-2.65 (m, 1H, C^1H), 2.70-3.00 (m, 4H, 2 C^2H_2), 4.68 (d, 1H, $^2J_{PH}$ = 9.2 Hz, C^4H), 6.70-6.95 (m, 4H, 4 $C_{Ar}H$), 7.15-8.60 (m, 4H, 4 $C_{Py}H$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: 0.2 (s, 2 Me_3Si), 31.1 (s, C^2), 31.4 (s, C^2), 37.3 (d, $^1J_{PC}$ = 98.1 Hz, C^1), 70.7 (d, $^1J_{PC}$ = 114.4 Hz, C^4H), 123.6 (s, C_{Ar}), 125.8 (s, C_{Ar}), 132.3 (s, C_{Py}), 140.4 (d, $^3J_{PC}$ = 9.0 Hz, C^3), 140.5 (d, $^3J_{PC}$ = 11.0 Hz, C^3), 140.6 (d, $^3J_{PC}$ = 8.6 Hz, C_{Py}), 147.7 (d, $^3J_{PC}$ = 4.4 Hz, C_{Py}), 153.8 (s, C_{Py}). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 38.8 (s). The second isomer, 35%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: −0.19 (s, 9H, Me_3Si), −0.02 (s, 9H, Me_3Si), 2.25-2.40 (m, 1H, C^1H), 2.70-3.00 (m, 4H, 2 C^2H_2), 4.79 (d, 1H, $^2J_{PH}$ = 7.2 Hz, C^4H), 6.70-6.95 (m, 4H, 4 $C_{Ar}H$), 7.15-8.60 (m, 4H, 4 $C_{Py}H$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: -0.7 (s, Me_3Si), -0.6 (s, Me_3Si), 32.1 (s, C(2)), 32.5 (s, C(2)), 34.2 (d, $^1J_{PC}$ = 96.6 Hz, C^1), 71.2 (d, $^1J_{PC}$ = 112.5 Hz, C^4H), 123.5 (s, C_{Ar}), 126.0 (s, C_{Ar}), 132.6 (s, C_{Py}), 140.8 (d, $^3J_{PC}$ = 9.3 Hz, C^3), 140.9 (d, $^3J_{PC}$ = 9.0 Hz, C^3), 141.0 (d, $^3J_{PC}$ = 8.0 Hz, C_{Py}), 147.8 (d, $^3J_{PC}$ = 5.4 Hz, C_{Py}), 151.0 (s, C_{Py}). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 39.5 (s). Anal. Calcd for $C_{21}H_{32}NO_3PSi_2$. C 58.17; H 7.44. Found: C 58.01; H 7.30.

4.16 | Trimethylsilyl 2,3-dihydro-1*H*-inden-2-yl[2-(trimethylsiloxycarbonyl)ethyl] phosphinate (5)

A solution of trimethylsilyl acrylate (3.1 g, 0.02 mol) in methylene chloride (5 mL) was added dropwise with stirring to a solution of phosphonite **1** (6.5 g, 0.02 mol) in methylene chloride (15 mL). The mixture was kept for 2 hr with stirring, then diethyl phosphite (4.1 g, 0.03 mol) was added to the mixture. The solvent was removed, and the residue was distilled to obtain 6.7 g of phosphinate **5**, yield 84%, bp 178°C (1 mm Hg). ^{1}H NMR ($CDCl_3$, 400 MHz), δ, ppm: 0.02 (s, 9H, Me_3Si), 0.10 (s, 9H, Me_3Si), 1.70-1.85 (m, 1H, C^1H), 2.30-2.45 (m, 2H, C^4H_2), 2.85-3.00 (m, 6H, 2 C^2H_2, C^5H_2), 6.85-7.00 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ, ppm: -0.9 (s, Me_3Si), 0.04 (s, Me_3Si), 23.1 (d, $^1J_{PC}$ = 93.0 Hz, C^4), 27.6 (d, $^2J_{PC}$ = 2.0 Hz, C^5),32.3 (s, C^2), 32.8 (s, C^2), 123.7 (s, 2C_{Ar}), 126.1 (s, 2C_{Ar}), 140.9 (s, C^3), 171.9 (d,$^3J_{PC}$ = 15.3 Hz,

C^6). ^{31}P NMR ($CDCl_3$, 162 MHz), δ, ppm: 45.4 (s). Anal. Calcd for $C_{18}H_{31}O_4PSi_2$. C 54.24; H 7.84. Found: C 54.03; H 7.74.

4.17 | Sodium 2,3-dihydro-1*H*-inden-2-ylphosphonite (6)

A solution of phosphonite **1** (4.9 g, 0.015 mol) in diethyl ether (5 mL) was added with stirring at 10°C to a solution of sodium methylate (0.81 g, 0.015 mol) in methanol (20 mL). The resulting mixture was refluxed, the solvent was removed, and the residue was kept in a vacuum (1 mm Hg) for 1 hr to obtain 3 g of salt **10a**, yield 97%. ^1H NMR (D_2O, 400 MHz), δ, ppm: 2.35-2.50 (m, 1H, C^1H), 2.90-3.15 (m, 4H, 2 C^2H_2), 6.83 (dd, $^1J_{PH}$ = 500.7, $^3J_{HH}$ 2.2 Hz, PH), 7.10-7.25 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR (D_2O, 100 MHz), δ, ppm: 32.2 (s, C^2), 38.8 (d, $^1J_{PC}$ = 94.5 Hz, C^1), 124.6 (s, C_{Ar}), 126.7 (s, C_{Ar}), 142.7 (d, $^3J_{PC}$ = 9.1 Hz, C^3). ^{31}P NMR (D_2O, 162 MHz), δ, ppm: 32.8 (d, $^1J_{PH}$ = 500.7 Hz). Anal. Calcd for $C_9H_{10}NaO_2P$. C 52.95; H 4.94. Found: C 52.68; H 5.03.

Salts **7-10** were obtained analogously.

4.18 | Sodium 2,3-dihydro-1*H*-inden-2-yl(*N*,*N*-dimethylaminomethyl)phosphinate (7a)

Yield 95%. ^1H NMR (D_2O, 400 MHz), δ, ppm: 2.35 (s, 6H, Me_2N), 2.55-2.70 (m, 2H, C^1H, C^4H_A), 3.00-3.15 (m, 5H, C^2H_2, C^4H_B), 7.10-7.30 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR (D_2O, 100 MHz), δ, ppm: 33.1 (s, C^2), 37.7 (d, $^1J_{PC}$ = 96.6 Hz, C^1), 46.8 (d, $^3J_{PC}$ = 4.2 Hz, Me_2N), 57.5 (d, $^1J_{PC}$ = 99.1 Hz, C^4), 124.6 (s, C_{Ar}), 126.6 (s, C_{Ar}), 142.9 (d, $^3J_{PC}$ = 9.9 Hz, C^3). ^{31}P NMR (D_2O, 162 MHz), δ, ppm: 37.8 (s). Anal. Calcd for $C_{12}H_{17}NNaO_2P$. C 55.17; H 6.54. Found: C 54.94; H 6.65.

4.19 | Sodium 2,3-dihydro-1*H*-inden-2-yl(piperidin-1-ylmethyl)phosphinate (7b)

Yield 94 %. ^1H NMR (D_2O, $(CD_3)_2SO$, 400 MHz), δ, ppm: 1.30-1.50 (m, 6H, 2 C^6H_2, C^7H_2), 2.50-2.65 (m, 5H, C^1H, 2 C^2H_2), 2.95-3.20 (m, 6H, C^4H_2, 2 C^5H_2), 7.10-7.20 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR (D_2O, $(CD_3)_2SO$, 100 MHz), δ, ppm: 22.4 (s, C^7), 24.6 (s, 2 C^6), 33.8 (s, C^2), 38.6 (d, $^1J_{PC}$ = 97.0 Hz, C^1), 56.9 (d, $^3J_{PC}$ = 9.2 Hz, C^5), 57.8 (d, $^1J_{PC}$ = 112.3 Hz, C^4), 122.0 (s, C_{Ar}), 125.4 (s, C_{Ar}), 142.7 (d, $^3J_{PC}$ = 10.0 Hz, C^3). ^{31}P NMR (D_2O, $(CD_3)_2SO$, 162 MHz), δ, ppm: 31.9 (s). Anal. Calcd for $C_{15}H_{21}NNaO_2P$. C 59.80; H 7.03. Found: C 59.69; H 7.07.

4.20 | Sodium 2,3-dihydro-1*H*-inden-2-yl(azepan-1-ylmethyl)phosphinate (7c)

Yield 96 %. ^1H NMR (D_2O, $(CD_3)_2SO$, 400 MHz), δ, ppm: 1.40-1.60 (m, 8H, 2 C^6H_2, 2 C^7H_2), 2.45-2.65 (m, 5H, C^1H, 2 C^2H_2), 2.90-3.00 (m, 6H, C^4H_2, 2 C^5H_2), 7.00-7.15 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR (D_2O, $(CD_3)_2SO$, 100 MHz), δ, ppm: 22.5 (s, 2 C^7), 27.8 (s, 2 C^6), 34.5 (s, C^2), 38.7 (d, $^1J_{PC}$ = 97.1 Hz, C^1), 57.7 (d, $^1J_{PC}$ = 102.4 Hz, C^4), 58.0 (d, $^3J_{PC}$ = 5.1 Hz, 2 C^5), 125.4 (s, 2 C_{Ar}), 127.2 (s, 2 C_{Ar}), 144.4 (d, $^3J_{PC}$ = 9.7 Hz, C^3). ^{31}P NMR (D_2O, $(CD_3)_2SO$, 162 MHz), δ, ppm: 36.0 (s). Anal. Calcd for $C_{16}H_{23}NNaO_2P$. C 60.94; H 7.35. Found: C 60.80; H 7.39.

4.21 | Sodium 2,3-dihydro-1*H*-inden-2-yl(morpholin-4-ylmethyl)phosphinate (7d)

Yield 95 %. ^1H NMR (D_2O, 400 MHz), δ, ppm: 2.50-2.60 (m, 4H, 2 C^2H_2), 2.70-2.75 (m, 1H, C^1H), 3.00-3.10 (m, 6H, C^4H_2, 2 C^5H_2), 3.64 (s, 4H, 2 C^6H_2), 7.10-7.21 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR (D_2O, 100 MHz), δ, ppm: 34.2 (s, C^2), 38.9 (d, $^1J_{PC}$ = 96.7 Hz, C^1), 55.7 (d,$^3J_{PC}$ = 4.5 Hz, 2 C^5), 58.2 (d, $^1J_{PC}$ = 110.5 Hz, C^4), 66.5 (s, 2C^6), 125.0 (s, 2C_{Ar}), 126.9 (s, 2C_{Ar}), 144.1 (d, $^3J_{PC}$ = 10.1 Hz, C^3). ^{31}P NMR (D_2O, 162 MHz), δ, ppm: 31.7 (s). Anal. Calcd for $C_{14}H_{19}NNaO_3P$. C 55.45; H 6.31. Found: C 55.29; H 6.28.

4.22 | Sodium 2,3-dihydro-1*H*-inden-2-yl(*N*-methyl-*N*-formylaminomethyl)phosphinate (7e)

Yield 95%. The first isomer, 55%.^1H NMR (D_2O, 400 MHz), δ, ppm: 2.30-2.50 (m, 1H, C^1H), 2.90-3.00 (m, 4H, 2 C^2H_2), 3.10 (s, 3H, MeN), 3.29-3.50 (m, 2H, C^4H_2), 7.10-7.25 (m, 4H, 4 $C_{Ar}H$), 7.71 (s, CHO). ^{13}C NMR (D_2O, 100 MHz), δ, ppm: 33.1 (s, C^2), 36.7 (s, MeN), 37.2 (d, $^1J_{PC}$ = 96.4 Hz, C^1), 43.7 (d, $^1J_{PC}$ = 94.2 Hz, C^4), 124.6 (s, 2C_{Ar}), 126.7 (s, 2C_{Ar}), 142.7 (d, $^3J_{PC}$ = 9.3 Hz, C^3), 165.4 (s, CO). ^{31}P NMR (D_2O, 162 MHz), δ, ppm: 35.9 (s). The second isomer, 55%. ^1H NMR (D_2O, 400 MHz), δ, ppm: 2.30-2.50 (m, 1H, C^1H), 2.90-3.00 (m, 4H, 2 C^2H_2), 3.05 (s, 6H, Me_2N), 3.20-3.50 (m, 2H, C^4H_2), 7.10-7.25 (m, 4H, 4 $C_{Ar}H$), 7.91 (s, CHO). ^{13}C NMR (D_2O, 100 MHz), δ, ppm: 33.1 (s, C^2), 36.6 (s, MeN), 37.7 (d, $^1J_{PC}$ = 97.6 Hz, C^1), 43.5 (d, $^1J_{PC}$ = 94.4 Hz, C^4), 124.5 (s, 2C_{Ar}), 126.6 (s, 2C_{Ar}), 142.4 (d, $^3J_{PC}$ = 8.6 Hz, C^3),164.5 (s, CO). ^{31}P NMR (D_2O, 162 MHz), δ, ppm:36.3 (s). Anal. Calcd for $C_{12}H_{15}NNaO_3P$. C 52.37; H 5.49. Found: C 52.02; H 5.57.

4.23 | Sodium 2,3-dihydro-1*H*-inden-2-yl(*N*-ethyl-*N*-acetylaminomethyl)phosphinate (7f)

Yield 96%. The first isomer, 70 %. ^1H NMR (D_2O, $(CD_3)_2SO$, 400 MHz), δ, ppm: 1.03 (t, 3H, $^3J_{HH}$ = 6.4 Hz, C^6H_3), 1.97 (s, 3H, C^7H_3), 2.18-2.38 (m, 1H, C^1H), 2.80-3.10 (m, 4H, 2 C^2H_2), 3.37 (d, 2H, $^2J_{PH}$ = 9.6 Hz, C^4H_2), 6.95-7.25 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR (D_2O, $(CD_3)_2SO$, 100 MHz), δ, ppm: 13.4 (s, C^6), 21.5 (s, C^7), 34.2 (s, C^2), 37.7 (d, $^1J_{PC}$ = 96.8 Hz,

C^1), 39.1 (d, $^1J_{PC}$ = 101.7 Hz, C^4), 44.8 (s, C^5), 125.2 (s, C_{Ar}), 127.1 (s, C_{Ar}), 144.2 (d, $^3J_{PC}$ = 9.9 Hz, C^3), 171.5 (s, CO). ^{31}P NMR (D_2O, $(CD_3)_2SO$, 162 MHz), δ, ppm: 33.5 (s). The second isomer, 30%. ^{1}H NMR (D_2O, $(CD_3)_2SO$, 400 MHz), δ, ppm: 0.93 (t, 3H, $^3J_{HH}$ = 6.6 Hz, C^6H_3), 2.05 (s, 3H, C^7H_3), 2.18-2.38 (m, 1H, C^1H), 2.80-3.05 (m, 4H, 2 C^2H_2), 3.49 (d, 2H, $^2J_{PH}$ = 6.8 Hz, C^4H_2), 6.95-7.25 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR (D_2O, $(CD_3)_2SO$, 100 MHz), δ, ppm: 12.7 (s, C^6), 22.7 (s, C^7), 33.5 (s, C^2), 36.9 (d, $^1J_{PC}$ = 96.4 Hz, C^1), 40.4 (d, $^1J_{PC}$ = 100.4 Hz, C^4), 42.4 (s, C^5), 125.3 (s, C_{Ar}), 127.2 (s, C_{Ar}), 143.9 (d, $^3J_{PC}$ = 8.0 Hz, C^3), 172.6 (s, CO). ^{31}P NMR (D_2O, $(CD_3)_2SO$, 162 MHz), δ, ppm: 31.0 (s). Anal. Calcd for $C_{14}H_{19}NNaO_3P$. C 55.45; H 6.31. Found: C 55.32; H 6.35.

4.24 | Sodium 2,3-dihydro-1*H*-inden-2-yl[(2-oxopyrrolidin-1-yl)methyl]phosphinate (7g)

Yield 95%. ^{1}H NMR (D_2O, $(CD_3)_2SO$, 400 MHz), δ, ppm: 1.85-1.90 (m, 2H, C^6H_2), 2.17-2.22 (m, 2H, C^7H_2), 2.24-2.32 (m, 1H, C^1H), 2.85-2.98 (m, 4H, 2 C^2H_2), 3.23 (d, 2H, $^2J_{PH}$ = 9.2 Hz, C^4H_2), 3.50-3.56 (m, 2H, 2 C^5H_2), 7.01-7.14 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR (D_2O, $(CD_3)_2SO$, 100 MHz), δ, ppm: 18.2 (s, C(6)), 31.2 (s, C(7)), 34.0 (s, C(2)), 38.9 (d, $^1J_{PC}$ = 94.8 Hz, C^1), 43.5 (d, $^1J_{PC}$ = 94.1 Hz, C^4),49.3 (s, C^5), 124.9 (s, C_{Ar}), 126.8 (s, C_{Ar}), 144.7 (d, $^3J_{PC}$ = 10.2 Hz, C^3). ^{31}P NMR (D_2O, $(CD_3)_2SO$, 162 MHz), δ, ppm: 30.7 (s). Anal. Calcd for $C_{14}H_{17}NNaO_3P$. C 55.82; H 5.69. Found: C 55.68; H 5.74.

4.25 | Sodium 2,3-dihydro-1*H*-inden-2-yl[(2-oxoazepan-1-yl)methyl]phosphinate (7h)

Yield 96%.^{1}H NMR (D_2O, $(CD_3)_2SO$, 400 MHz), δ, ppm: 1.22-1.45 (m, 6H, C^6H_2, C^7H_2, C^8H_2), 2.15-2.20 (m, 2H, C^9H_2), 2.32-2.45 (m, 1H, C^1H), 2.75-3.05 (m, 4H, 2 C^2H_2), 3.30-3.45 (m, 4H, C^4H_2, C^5H_2), 6.80-7.10 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR (D_2O, $(CD_3)_2SO$, 100 MHz), δ, ppm: 20.2 (s, C^7), 21.9 (s, C^8), 26.9 (s, C^6), 28.0 (s, C^9), 31.8 (s, C^2), 35.8 (d, $^1J_{PC}$ = 96.8 Hz, C^1), 44.5 (d, $^1J_{PC}$ = 99.5 Hz, C^4), 47.5 (s, C^5), 123.5 (s, C_{Ar}), 125.2 (s, C_{Ar}), 142.6 (d, $^3J_{PC}$ = 10.1 Hz, C^3). ^{31}P NMR (D_2O, $(CD_3)_2SO$, 162 MHz), δ, ppm: 31.8 (s). Anal. Calcd for $C_{16}H_{21}NNaO_3P$. C 58.36; H 6.43. Found: C 58.18; H 6.39.

4.26 | Sodium 2,3-dihydro-1*H*-inden-2-yl [*N*-ethoxycarbonyl-*N*-(ethoxycarbonylmethyl) aminomethyl]phosphinate (7i)

Yield 94%. The first isomer, 60%. ^{1}H NMR (D_2O, $(CD_3)_2SO$, 400 MHz), δ, ppm: 1.40-1.60 (m, 6H, 2 CH_3), 2.36-2.40 (m, 1H, C^1H), 2.84-3.05 (m, 4H, 2 C^2H_2), 3.31 (д, 2H, $^2J_{PH}$ = 8.4 Hz, C^4H_2), 4.12 (s, 2H, C^5H_2), 6.95-7.20 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR (D_2O, $(CD_3)_2SO$, 100 MHz), δ, ppm: 12.9 (s, 2 Me), 32.3 (s, C^2), 36.4 (d, $^1J_{PC}$ = 96.5 Hz, C^1), 42.6 (d, $^1J_{PC}$ = 102.3 Hz, C^4), 47.1 (s, C^5), 60.2 (s, CH_2O), 124.0 (s, C_{Ar}), 125.9 (s, C_{Ar}), 140.1 (d, $^3J_{PC}$ = 8.9 Hz, C^3), 154.9 (s, C^7), 167.8 (s, C^6). ^{31}P NMR (D_2O, $(CD_3)_2SO$, 162 MHz), δ, ppm: 31.7 (s). The second isomer, 40%. ^{1}H NMR (D_2O, $(CD_3)_2SO$, 400 MHz), δ, ppm: 1.40-1.60 (m, 6H, 2 CH_3), 2.36-2.40 (m, 1H, C^1H), 2.84-3.05 (m, 4H, 2 C^2H_2), 3.49 (d, 2H, $^2J_{PH}$ = 7.2 Hz, C^4H_2), 4.2 (s, 2H, C^5H_2), 6.95-7.20 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR (D_2O, $(CD_3)_2SO$, 100 MHz), δ, ppm: 12.9 (s, 2 Me), 30.9 (s, C^2), 35.0 (d, $^1J_{PC}$ = 95.2 Hz, C^1), 42.1 (d, $^1J_{PC}$ = 101.3 Hz, C^4), 46.9 (s, C^5), 61.5 (s, CH_2O), 123.8 (s, C_{Ar}), 125.1 (s, C_{Ar}), 139.7 (d, $^3J_{PC}$ = 8.9 Hz, C^3), 154.2 (s, C^7), 167.8 (s, C^6). ^{31}P NMR (D_2O, $(CD_3)_2SO$, 162 MHz), δ, ppm: 31.1 (s). Anal. Calcd for $C_{17}H_{23}NNaO_6P$. C 52.18; H 5.92. Found: C 52.02; H 5.98.

4.27 | Sodium 2,3-dihydro-1*H*-inden-2-yl(aminomethyl)phosphinate (7j)

^{1}H NMR (D_2O, 400 MHz), δ, ppm: 2.72 (d, 2H, $^2J_{PH}$ = 8.7 Hz, C^4H_2), 2.90-3.00 (m, 1H, C^1H), 3.10-3.25 (m, 4H, 2 C^2H_2), 7.10-7.25 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR (D_2O, 100 MHz), δ, ppm: 30.5 (s, C^2), 35.4 (d, $^1J_{PC}$ = 96.3 Hz, C^1), 52.7 (d, $^1J_{PC}$ = 97.8 Hz, C^4), 124.2 (s, C_{Ar}), 126.4 (s, $2C_{Ar}$), 140.8 (d, $^3J_{PC}$ = 9.8 Hz, C^3). ^{31}P NMR (D_2O, 162 MHz), δ, ppm: 39.2 (s). Anal. Calcd for $C_{10}H_{13}NNaO_2P$. C 51.51; H 5.62.Found: 51.39; H, 5.54.

4.28 | Disodium 2,3-dihydro-1*H*-inden-2-ylthiophosphonate (8)

Yield 97%. ^{1}H NMR (D_2O, 400 MHz), δ, ppm: 2.65-2.75 (m, 1H, C^1H), 3.60-3.80 (m, 4H, 2 C^2H_2), 7.09-7.25 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR (D_2O, 100 MHz), δ, ppm: 35.3 (d, $^2J_{PC}$ = 6.4 Hz, C^2), 45.4 (d, $^1J_{PC}$ = 105.9 Hz, C^1), 124.5 (s, C_{Ar}), 126.3 (s, C_{Ar}), 143.7 (d, $^3J_{PC}$ = 11.4 Hz, C^3). ^{31}P NMR (D_2O, 162 MHz), δ, ppm: 61.8 (s). Anal. Calcd for $C_9H_9Na_2O_2PS$. C 41.87; H 3.51. Found: C 41.71; H 3.56.

4.29 | Sodium 2,3-dihydro-1*H*-inden-2-yl[hydroxy(phenyl)methyl]phosphinate (9a)

Yield 96%. ^{1}H NMR ($(CD_3)_2SO$, 400 MHz), δ, ppm: 2.10-2.60 (m, 1H, C^1H), 2.72-3.18 (m, 4H, 2 C^2H_2), 4.75 (d, 1H, $^2J_{PH}$ = 13.2 Hz, C^4H), 6.90-7.25 (m, 9H, 4 $C_{Ar}H$, C_6H_5). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz), δ, ppm: 33.6 (s, C^2), 33.9 (s, C^2), 35.9 (d, $^1J_{PC}$ = 96.1 Hz, C^1), 73.6 (d, $^1J_{PC}$ = 97.3 Hz, C^4), 123.8 (s, C_{Ar}), 125.6 (s, C_{Ar}), 126.6 (s, C_{Ph}), 127.2 (s, C_{Ph}), 142.0 (s, C_{Ph}), 143.4 (d, $^3J_{PC}$ = 4.0 Hz, C^3), 143.5 (d, $^3J_{PC}$ = 4.0 Hz, C^3). ^{31}P NMR ($(CD_3)_2SO$, 162 MHz), δ, ppm: 34.8 (s). Anal. Calcd for $C_{16}H_{16}NaO_3P$. C 61.94; H 5.20. Found: C 61.72; H 5.26.

4.30 | Sodium 2,3-dihydro-1*H*-inden-2-yl[hydroxy(fur-2-yl)methyl]phosphinate (9b)

Yield 97%. ^{1}H NMR ($(CD_3)_2SO$, 400 MHz), δ, ppm: 2.25-2.40 (m, 1H, C^1H), 2.70-3.20 (m, 4H, 2 C^2H_2), 4.65 (d, 1H, $^{2}J_{PH}$ = 10.0 Hz, C^4H), 6.29 (s, 1H, $C_{Fur}H$), 6.34 (s, 1H, $C_{Fur}H$), 7.01-7.07 (m, 5H, C_6H_5), 7.49 (s, 1H, $C_{Fur}HO$). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz), δ, ppm: 33.5 (s, C^2), 33.4 (s, C^2), 36.8 (d, $^{1}J_{PC}$ = 97.3 Hz, C^1), 65.8 (d, $^{1}J_{PC}$ = 110.0 Hz, C^4), 106.9 (s, $C_{Fur}H$), 110.2 (s, $C_{Fur}H$), 123.8 (s, C_{Ar}), 125.7 (s, C_{Ar}), 141.5 (s, $C_{Fur}HO$), 143.4 (d, $^{3}J_{PC}$ = 10.1 Hz, C^3), 154.9 (s, $C_{Fur}O$). ^{31}P NMR ($(CD_3)_2SO$, 162 MHz), δ, ppm: 33.1 (s). Anal. Calcd for $C_{14}H_{14}NaO_4P$. C 56.01; H 4.70. Found: C 55.89; H 4.66.

4.31 | Sodium 2,3-dihydro-1*H*-inden-2-yl[hydroxy(pyridin-3-yl)methyl]phosphinate (9c)

Yield 95%. ^{1}H NMR ($(CD_3)_2SO$, 400 MHz), δ, ppm: 2.32-2.55 (m, 1H, C^1H), 2.70-3.10 (m, 4H, 2 C^2H_2), 4.75 (d, 1H, $^{2}J_{PH}$ = 12.0 Hz, C^4H), 6.90-7.10 (m, 4H, 4 $C_{Ar}H$), 7.20-8.67 (m, 4H, 4 $C_{Py}H$). ^{13}C NMR ($(CD_3)_2SO$, 100 MHz), δ, ppm: 33.5 (s, C^2), 39.9 (s, C^2), 35.7 (d, $^{1}J_{PC}$ = 95.8 Hz, C^1), 70.5 (d, $^{1}J_{PC}$ = 108.7 Hz, C^4), 122.5 (s, C_{Py}), 134.1 (s, C_{Py}), 137.2 (s, C_{Py}), 143.2 (s, C^3), 143.3 (s, C^3), 146.9 (s, C_{Py}), 146.1 (s, C_{Py}). ^{31}P NMR ($(CD_3)_2SO$, 162 MHz), δ, ppm: 34.5 (s). Anal. Calcd for $C_{15}H_{15}NNaO_3P$. C 57.88; H 4.86. Found: C 57.73; H 4.91.

4.32 | Disodium 2,3-dihydro-1*H*-inden-2-yl(2-carboxyethyl)phosphinate (10)

Yield 95%. ^{1}H NMR (D_2O, $(CD_3)_2SO$, 400 MHz), δ, ppm: 1.50-1.65 (m, 1H, C^1H), 2.15-2.40 (m, 2H, C^4H_2), 2.80-3.00 (m, 6H, 2 C^2H_2, C^5H_2), 6.00-7.15 (m, 4H, 4 $C_{Ar}H$). ^{13}C NMR (D_2O, $(CD_3)_2SO$, 100 MHz), δ, ppm: 26.3 (d, $^{1}J_{PC}$ = 89.8 Hz, C^4), 30.9 (d, $^{2}J_{PC}$ = 6.1 Hz, C^5), 33.7 (d, $^{1}J_{PC}$ = 98.1 Hz, C^1), 34.1 (s, C^2), 125.0 (s, 2 C_{Ar}), 126.9 (s, 2 C_{Ar}), 143.9 (d, $^{3}J_{PC}$ = 9.8 Hz, C^3), 180.2 (d,$^{3}J_{PC}$ = 15.7 Hz, C^6). ^{31}P NMR (D_2O, $(CD_3)_2SO$, 162 MHz), δ, ppm: 39.1 (s). Anal. Calcd for . $C_{12}H_{13}Na_2O_4P$. C 48.34; H 4.39. Found: C 48.26; H 4.44.

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REFERENCES

[1] O. I. Kolodiazhnyi, *Russ. Chem. Rev.* **2006**, *75*, 227.
[2] V. P. Kukhar, H. R. Hudson, Aminophosphonic and Aminophosphinic Acids. Chemistry and Biological Activity, Wiley, New York, New York **2000**, 634.
[3] S. C. Fields, *Tetrahedron* **1999**, *55*, 12237.
[4] F. H. Ebetino, *Phosphorus, Sulfur Silicon Relat. Elem.* **1999**, *144-146*, 9.
[5] A. A. Prishchenko, M. V. Livantsov, O. P. Novikova, L. I. Livantsova, G. M. Averochkin, V. S. Petrosyan, *Heteroat. Chem.* **2015**, *26*, 405.
[6] a) A. A. Prishchenko, M. V. Livantsov, O. P. Novikova, L. I. Livantsova, V. S. Petrosyan, *Heteroat. Chem.* **2016**, *27*, 381. b) A. A. Prishchenko, M. V. Livantsov, O. P. Novikova, L. I. Livantsova, Y. N. Koval', E. V. Grigor'ev, *Russ. J. Gen. Chem.* **2003**, *73*, 1658. c) A. A. Prishchenko, M. V. Livantsov, O. P. Novikova, L. I. Livantsova, V. S. Petrosyan, *Heteroat. Chem.* **2008**, *19*, 345. d) A. A. Prishchenko, M. V. Livantsov, O. P. Novikova, L. I. Livantsova, V. S. Petrosyan, *Heteroat. Chem.* **2008**, *19*, 352. e) A. A. Prishchenko, M. V. Livantsov, O. P. Novikova, L. I. Livantsova, V. S. Petrosyan, *Heteroat. Chem.* **2008**, *19*, 418.
[7] A. A. Prishchenko, M. V. Livantsov, V. S. Petrosyan, *Russ. J. Gen. Chem.* **1994**, *64*, 1316(in Russian) .
[8] V. D. Romanenko, M. V. Shevchuk, V. P. Kukhar, *Current. Org. Chem.* **2011**, *15*, 2774.
[9] L. Wozniak, J. Chojnowski, *Tetrahedron* **1989**, *45*, 2465.

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