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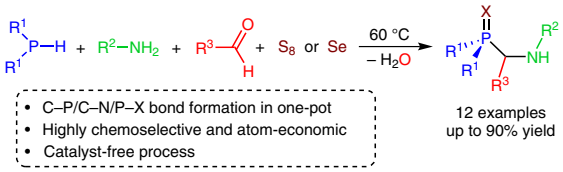
Four-Component Reaction between Secondary Phosphines, Primary Amines, Aldehydes, and Chalcogens: A Facile Access to Functionalized α-Aminophosphine Chalcogenides

Alexander V. Artem'ev[a]
Nikita A. Kolyvanov[a]
Ludmila A. Oparina[a]
Nina K. Gusarova[a]
Anastasiya O. Sutyrina[a]
Irina Yu. Bagryanskaya[b,c]
Boris A. Trofimov*[a]

[a] A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, 1 Favorsky Str., Irkutsk 664033, Russian Federation
boris_trofimov@irioch.irk.ru
[b] N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences, 9, Akad. Lavrentiev Ave., Novosibirsk 630090, Russian Federation
[c] Novosibirsk State University (National Research University), Department of Natural Sciences, 2, Pirogova Str., Novosibirsk 630090, Russian Federation



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Abstract The original four-component reaction between secondary phosphines, primary amines, aldehydes, and elemental sulfur or selenium occurs chemoselectively under mild conditions (60 °C, benzene, 3–9 h) to afford the hitherto unknown functionalized α-aminophosphine sulfides and selenides in good to excellent yields.

Key words chemoselectivity, C–P and C–N bond formation, one-pot synthesis, aldehydes, amines, chalcogens, phosphines

Multicomponent reactions represent one of the most efficient tools in the sustainable and target-oriented organic synthesis.[1] These reactions feature a reduction in the number of the preparative steps, simple and rapid implementation, high energy and atom economy, as well as environmental friendliness.[1]

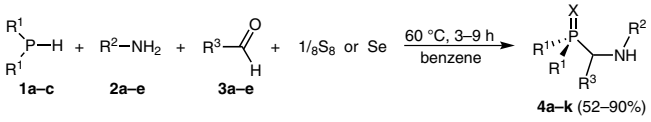
In organophosphorus chemistry, the multicomponent reactions have attracted a special attention for a long time. Among famous multicomponent reactions leading to the organophosphorus products are the well-known Kabachnik–Fields[2] and Atherton–Todd[3] reactions as well as Clay–Kinnear–Perren condensation.[4] Over the past decade, a plethora of novel multicomponent procedures for the synthesis of diverse organophosphorus compounds have been developed.[5] For instance, stabilized phosphoranes were obtained from the three-component reaction between triphenylphosphine, dialkyl acetylenedicarboxylates, and urea.[6] The replacement of urea in this reaction by 4-pyridinecarboxaldehyde delivers the stable tetravalent phosphonium enolate zwitterions.[7] Subsequently, the versatile methodology based on interaction of tertiary phosphines with electron-deficient alkynes (enynes, diynes) and a third component (e.g., aldehydes, imines, isocyanates, alkenes, etc.) has been successfully employed for the syntheses of the functionalized phosphoranes.[8] In this avenue, less studied are multicomponent reactions with participation of primary or secondary phosphines, although they are also of a great importance. Thus, the rapid atom-economic method for the synthesis of diselenophosphinates, Cat[Se_2PR_2] (Cat = Li^+, Na^+, K^+, NH_4^+, etc.), has been elaborated using reaction of secondary phosphines with elemental selenium and various bases.[9] The primary phosphines in the similar reaction gave trithiophosphonates, $Cat_2[S_3PR]$, in good yields.[10] In addition, the convenient four-component synthesis of thioselenophosphinates, Cat[Se(*S*)PR_2], from secondary phosphines, elemental sulfur, selenium, and bases should be mentioned.[11] The recent application of secondary phosphines in multicomponent reactions has been exemplified by one-pot synthesis of tertiary phosphine chalcogenides, $R_2P(X)CH_2CH_2R'$, from secondary phosphines, alkenes, and sulfur or selenium.[12] Noteworthy, performing this reaction with two equivalents of selenium gave Se-esters of diselenophosphinic acids, $R_2P(Se)SeCH(Me)R'$, in excellent yields.[13] Therefore, the design of new multicomponent reactions, which lead to the formation of C–P bond is a recognized challenge in organophosphorus chemistry.

Herein we report the original four-component reaction between secondary phosphines, primary amines, aldehydes, and elemental chaclogens, providing a facile and efficient route to α-aminophosphine sulfides and selenides.

The latter can be regarded as S/Se- and C–P congeners of α-aminophosphonates, which, being structural analogues of α-amino acids, received wide attention in medicinal, bioorganic, and agricultural chemistry.[14] It is relevant for the subject of this work to note that the data on α-aminophosphine oxides[15] and especially, sulfides[16] and selenides,[16] are very limited (in contrast to α-aminophosphonates).

As a first result, we have found that the secondary phosphines **1a–c**, primary amines **2a–e**, aldehydes **3a–e**, and elemental sulfur or selenium interact in a four-component type reaction, occurring under mild conditions (60 °C, benzene, 3–9 h), to afford N-substituted α-aminophosphine sulfides and selenides **4a–k** in 52–90% isolated yields (Table 1). The stoichiometric ratio of the reactants was found to be optimal to achieve the higher yields of the products. The order of mixing the reactants affects chemoselectivity of the four-component reaction just negligibly. Importantly, this reaction, involving the formation of new C–P, C–N, and P–X bonds (X = S, Se) in a one-pot, avoids usual application of metal-based catalysts. The common side products of the reaction, according to $^{31}P\{^1H\}$ NMR monitoring, are α-hydroxyphosphine chalcogenides, $R^1{}_2P(X)CH(OH)R^3$ (X = S, Se), formed in up to 10 mol% due to the competitive addition of the intermediate $R^1{}_2P(X)H$ species (vide infra) to C=O bond of the aldehydes.[17] These impurities, however, can be easily separated from the main products **4a–k** by recrystallization from ethanol or by column chromatography.

Table 1 Four-Component Synthesis of α-Aminophosphine Chalcogenides **4a–k**[a]



1a–c **2a–e** **3a–e** **4a–k** (52–90%)

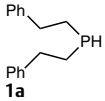
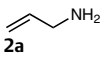
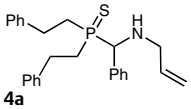
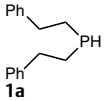
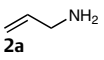
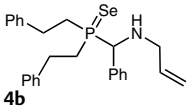
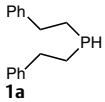
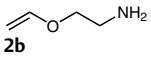
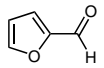
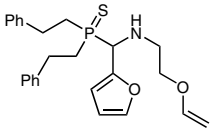
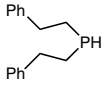
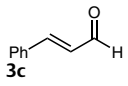
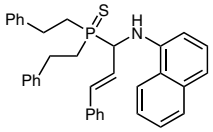
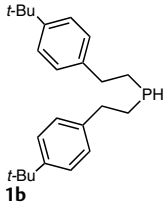
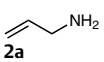
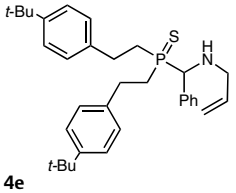
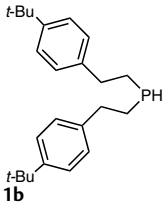
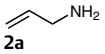
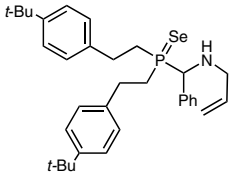
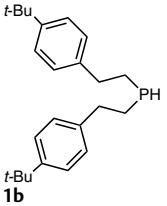
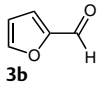
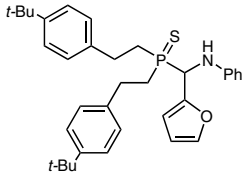
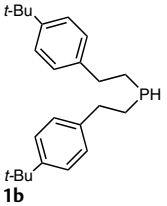
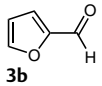
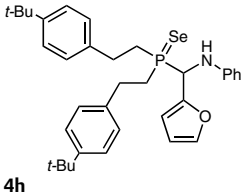
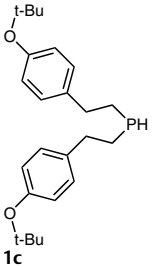
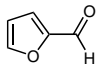
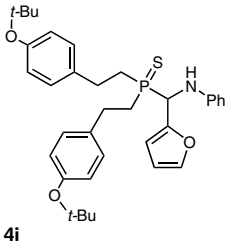
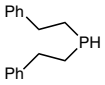
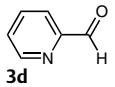
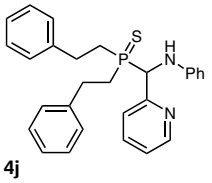
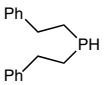
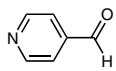
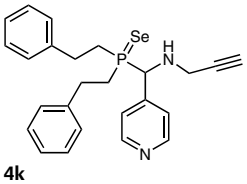
Entry	Phosphine	Amine	Aldehyde	X	Time (h)	Product	Yield (%)[b]
1	 **1a**	 **2a**	 **3a**	S	4	 **4a**	71
2	 **1a**	 **2a**	 **3a**	Se	3	 **4b**	83
3	 **1a**	 **2b**	 **3b**	S	3	 **4c**	90
4	 **1a**	(1-naphthyl)NH_2 **2c**	 **3c**	S	9	 **4d**	72
5	 **1b**	 **2a**	 **3a**	S	3	 **4e**	66

Table 1 (continued)

Entry	Phosphine	Amine	Aldehyde	X	Time (h)	Product	Yield (%)[b]
6	 **1b**	 **2a**	 **3a**	Se	3	 **4f**	69
7	 **1b**	$PhNH_2$ **2d**	 **3b**	S	3	 **4g**	74
8	 **1b**	$PhNH_2$ **2d**	 **3b**	Se	3	 **4h**	69
9	 **1c**	$PhNH_2$ **2d**	 **3b**	S	3	 **4i**	63
10	 **1a**	$PhNH_2$ **2d**	 **3d**	S	3.5	 **4j**	52
11	 **1a**	$HC{\equiv}CCH_2NH_2$ **2e**	 **3e**	Se	3	 **4k**	64

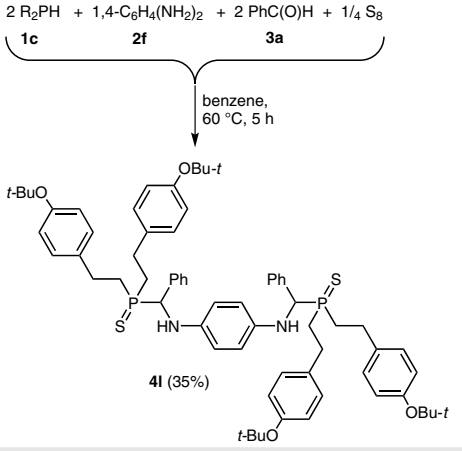
[a] Conditions: phosphine **1** (1 mmol), amine **2** (1 mmol), aldehyde **3** (1 mmol), elemental chalcogen (1 mmol), and benzene (4 mL) were stirred at 60 °C for 3–9 h.
[b] Isolated yields.

Table 1 displays that the reaction has a general character over the primary amines bearing aromatic and unsaturated substituents. On the other hand, the reaction tolerates aryl-, hetaryl-, and alkenyl-substituted aldehydes as well as elemental sulfur and selenium. The aliphatic aldehyde, butyraldehyde, was found to be ineffective in the reaction (ex-

emplified by interaction of *n*-PrCHO with phosphine **1a**, S_8 or Se, and aniline under the elaborated conditions).

As seen from Table 1, the secondary phosphines **1a–c** show almost the same reactivity. Notably, diphenylphosphine, when reacted with allylamine, benzaldehyde, and selenium under the same conditions, gave a mixture of difficult to separate organophosphorus compounds, among which the target *N*-allyl-α-aminophosphine selenide was identified by ^{31}P NMR spectroscopy (δ_P = 46.1, $^1J_{P,Se}$ = 748 Hz). The structure of the amines **2a–e** has little effect on the time required for reaction completion, which is defined mainly by the structure of aldehydes. Generally, cinnamaldehyde was less reactive than benzaldehyde and furfural.

The preparation of bis(α-aminophosphine sulfide) **4l** in 35% yield (unoptimized) from *p*-phenylenediamine (**2f**), phosphine **1c**, aldehyde **3a**, and elemental sulfur under the same conditions (Scheme 1) additionally confirmed the generality of the reaction, indicating that diamines could also be involved into the synthesis.



Scheme 1 Synthesis of bis(α-aminophosphine sulfide) **4l**

The prepared phosphine sulfides are air- and moisture-stable powders or oils. The selenides, however, are slowly oxidized in air with release of red selenium, but under inert atmosphere, they are quite stable. All compounds are well soluble (expect for **4l**) in dichloromethane, chloroform, and tetrahydrofuran, and insoluble in diethyl ether and hexane. The structures of the products were unambiguously proved by X-ray crystal analysis (for **4d**, Figure 1), NMR (^1H, ^{13}C, ^{31}P), and FT-IR spectroscopy.

The $^{31}P\{^1H\}$ NMR monitoring of the reaction has shown that its actual intermediates are secondary phosphine chalcogenides, which are generated in situ by initial oxidation of phosphines **1** with elemental sulfur or selenium. Taking into account this observation, the formation of α-aminophosphine chalcogenides **4a–l** in the four-component reaction could have originated through the addition of the secondary phosphine chalcogenides **A** to C=N bond of the aldimines **B**, which are in situ produced by the condensation of amines **2** with aldehydes **3** (Scheme 2). Thus, the reaction studied can be also considered as the first example of the addition of secondary phosphine sulfides and selenides to C=N bonds (some examples of the addition of R_2PH species to imines are known[16a,18]).

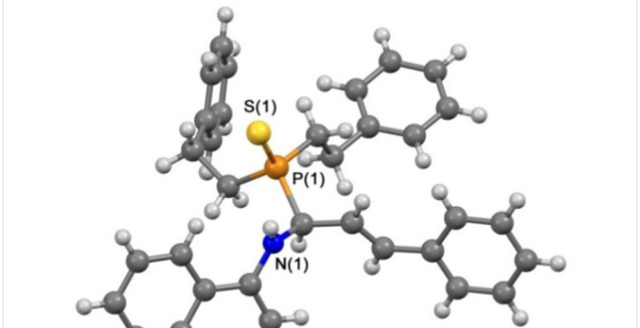
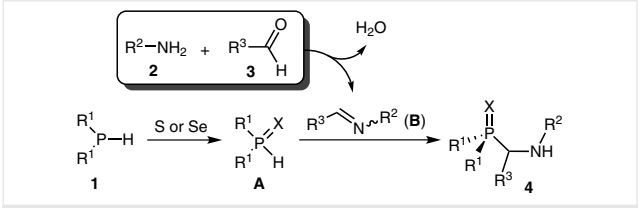


Figure 1 X-ray crystal structure of α-aminophosphine sulfide **4d** (see Supporting Information for details)



Scheme 2 Possible reaction pathway

It should be stressed that the developed method meets some of principles of green chemistry,[19] namely, high atom economy, absence of any catalyst, and high energy efficiency (reaction takes place under mild heating). Furthermore, as starting secondary phosphines, we have used those synthesized from elemental phosphorus and easily available styrene (as well as substituted styrenes) by a one-pot procedure.[20] The phosphine **1c** was prepared for the first time by this way in 56% yield.

To summarize, the efficient one-pot access to hitherto unknown α-aminophosphine sulfides and selenides has been elaborated based on original four-component reaction between secondary phosphines, primary amines, aldehydes, and elemental sulfur or selenium, respectively. The reaction proceeds under mild metal-free conditions in a chemoselective manner to give diverse α-aminophosphine chalcogenides in good to excellent yields. The diamines (exemplified by *p*-phenylenediamine) also participate in the four-component reaction to furnish the corresponding bis(α-aminophosphine) dichalcogenides. The synthesized compounds are prospective hemilabile N,S- and N,Se-

ligands for new metal complexes, promising extraction agents of noble metals, and attractive building blocks for design of new functional compounds. Investigations to extend the scope of the reaction (over natural amines and aldehydes) and to develop further its application in organic synthesis are in progress.

All reactions were performed under an argon atmosphere. The solvents were distillated prior to use. Secondary phosphines **1a**,**b** were synthesized by hydrophosphination of styrene and 4-*tert*-butylstyrene, correspondingly, as previously described.[18] The procedure for the synthesis of earlier unknown phosphine **1c** is given in the Supporting Information. The ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker DPX 400 and Bruker AV-400 spectrometers (400.13, 100.62, and 161.98 MHz, respectively). Chemical shifts were reported in δ (ppm) relative to $CDCl_3$ (^{1}H, ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. Standard abbreviations are used to denote the signal multiplicities; nr m = near multiplet. The CHN microanalyses were performed on a Flash EA 1112 Series elemental analyzer. FT-IR spectra were recorded on a Bruker Vertex 70 spectrometer. Melting points (uncorrected) were measured using a Kofler micro hot stage.

One-Pot Synthesis of α-Aminophosphine Chalcogenides 4a–l; General Procedure

To a solution of secondary phosphine **1a–c** (1 mmol), amine **2a–e** (1 mmol), and aldehyde **3a–e** (1 mmol) in benzene (4 mL) was added powdered sulfur (S_8) or amorphous Se (1 mmol). The mixture was stirred at 60 °C for the time required to complete the reaction (Table 1). After complete conversion of the starting phosphine and intermediate secondary phosphine chalcogenide, the reaction mixture was filtered and evaporated in vacuo. The crude product was purified by recrystallization from EtOH or by column chromatography (silica gel, EtOH–EtOAc, 3:1 v/v) and dried in vacuo (1 Torr) to give the desired phosphine chalcogenides **4a–l**.

Bis(2-phenylethyl)[phenyl(prop-2-en-1-ylamino)methyl]phosphine Sulfide (4a)

Yield: 298 mg (71%); white powder; mp 87–88 °C.

FT-IR (KBr): 3279 (NH), 1642 (C=C), 1180 (C–N), 742 (P–C), 592 cm^{-1} (P=S).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.45–7.03 (m, 15 H, 3 × C_6H_5), 5.89–5.79 (m, 1 H, CH=), 5.14, 5.10 (2 br s, 2 H, CH_2=), 4.11 (d, ^2J = 10.2 Hz, 1 H, CH), 3.29 (dd, J = 14.0, 4.7 Hz, 1 H, CH_2N), 3.10–2.59 (m, 6 H, CH_2Ph, CH_2N, NH), 2.33–2.23, 2.17–2.07, 2.02–1.91, 1.83–1.73 (4 m, each 1 H, CH_2P).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 140.9, 140.8 (2 d, ^3J = 15.0, 14.3 Hz, *i*-C in Ph), 135.8 (CH=), 135.5 (*i*-C in Ph), 128.7, 128.6, 128.5, 128.4, 128.2, 128.1, 126.4, 126.3 (*o*,*m*,*p*-C in Ph), 116.8 (H_2C=), 61.9 (d, ^1J = 57.3 Hz, CH), 49.6 (d, ^3J = 14.6 Hz, CH_2N), 31.0, 29.4 (2 d, ^1J = 47.8, 46.2 Hz, CH_2P), 28.8, 28.4 (2 d, ^2J = 1.7 Hz, CH_2Ph).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 55.78.

Anal. Calcd for $C_{26}H_{30}NPS$ (419.56): C, 74.43; H, 7.21; N, 3.34. Found: C, 74.61; H, 7.08; N, 3.45.

Bis(2-phenylethyl)[phenyl(prop-2-en-1-ylamino)methyl]phosphine Selenide (4b)

Yield: 388 mg (83%); white powder; mp 91–92 °C.

FT-IR (KBr): 3290 (NH), 1641 (C=C), 1176 (C–N), 752 (P–C), 519, 500 cm^{-1} (P=Se).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.46–7.04 (m, 15 H, 3 × C_6H_5), 5.88–5.78 (m, 1 H, CH=), 5.13, 5.11 (2 br s, 2 H, CH_2=), 4.17 (d, ^2J = 9.8 Hz, 1 H, CH), 3.29 (dd, J = 14.1, 4.2 Hz, 1 H, CH_2N), 3.13–2.59 (m, 6 H, CH_2N, CH_2Ph, NH), 2.40–1.81 (m, 4 H, CH_2P).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 140.7, 140.5 (2 d, ^3J = 15.0 Hz, *i*-C in Ph), 135.7 (CH=), 135.2 (*i*-C in Ph), 128.7, 128.6, 128.4, 128.4, 128.2, 128.1, 126.6, 122.2 (*o*,*m*,*p*-C in Ph), 116.9 (CH_2=), 61.0 (d, ^1J = 50.7 Hz, CH), 49.4 (d, ^3J = 14.7 Hz, CH_2), 30.7 (d, ^1J = 40.7 Hz, CH_2P), 29.7, 29.4 (CH_2Ph), 28.9 (d, ^1J = 39.1 Hz, CH_2P).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 48.55 (satellites: d, $^1J_{P,Se}$ = 702 Hz).

Anal. Calcd for $C_{26}H_{30}NPSe$ (466.46): C, 66.95; H, 6.48; N, 3.00. Found: C, 67.12; H, 6.25; N, 3.19.

Bis(2-phenylethyl)({[2-(ethenyloxy)ethyl]amino}(furan-2-yl)methyl)phosphine Sulfide (4c)

Yield: 396 mg (90%); light yellow oil.

FT-IR (film): 3284 (NH), 3114 (=CH), 1634, 1618 (C=C), 1172 (C–N), 741 (P–C), 598 cm^{-1} (P=S).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.47 (s, 1 H, H-5 in fur), 7.34–7.14 (m, 10 H, 2 × C_6H_5), 6.52–6.45 (m, 3 H, OCH=, H-3,4 in fur), 4.23–4.17 (m, 2 H, =CH_{trans}, CHN), 4.02 (d, ^3J = 6.6 Hz, 1 H, =CH_{cis}), 3.78 (nr m, 2 H, OCH_2), 3.09–2.78 (m, 6 H, NCH_2, PhCH_2), 2.59 (br s, 1 H, NH), 2.31–1.88 (m, 4 H, PCH_2).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 150.4 (OCH=), 148.4 (d, ^2J = 2.8 Hz, C-2 in fur), 141.5 (d, ^5J = 2.2 Hz, C-5 in fur), 139.8, 139.6 (2 d, ^3J = 15.6 Hz, *i*-C in Ph), 127.4, 127.3 (*o*-C in Ph), 127.1, 127.0 (*m*-C in Ph), 125.2, 125.1 (*p*-C in Ph), 109.9 (C-4 in fur), 108.4 (d, ^3J = 6.2 Hz, C-3 in fur), 85.5 (CH_2=), 66.0 (OCH_2), 56.6 (d, ^1J = 59.9 Hz, CHN), 45.8 (d, ^3J = 13.1 Hz, NCH_2), 29.9, 28.9 (2 d, ^1J = 47.2, 46.7 Hz, PCH_2), 27.4, 27.2 (2 d, ^2J = 2.0, 1.8 Hz, PhCH_2).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 55.93.

Anal. Calcd for $C_{25}H_{30}NO_2PS$ (439.55): C, 68.31; H, 6.88; N, 3.19. Found: C, 68.45; H, 6.58; N, 3.41.

Bis(2-phenylethyl)[(2*E*)-1-(naphthalen-1-ylamino)-3-phenylprop-2-en-1-yl]phosphine Sulfide (4d)

Yield: 382 mg (72%); light yellow powder; mp 128–129 °C.

FT-IR (KBr): 3301 (NH), 1604, 1594, 1579 (C=CPh), 1281 (C–N), 757 (C–P), 674, 606 cm^{-1} (P=S).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 8.15 (d, ^3J = 8.0 Hz, 1 H, H-8 in naphth), 7.84 (d, ^3J = 8.0 Hz, 1 H, H-5 in naphth), 7.58–7.51 (m, 2 H, H-6,7 in naphth), 7.40–7.14 (m, 17 H, 3 × C_6H_5, H-3,4 in naphth), 6.80 (dd, J = 15.9, 4.3 Hz, 1 H, PhC*H*=), 6.68 (d, ^3J = 6.6 Hz, 1 H, H-2 in naphth), 6.34–7.27 (m, 1 H, CH=), 5.86 (t, ^3J = 7.6 Hz, 1 H, NH), 4.54–4.47 (m, 1 H, NCH), 3.10–3.04 (m, 4 H, CH_2Ph), 2.49–2.17 (m, 4 H, PCH_2).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 141.7 (d, ^3J = 11.2 Hz, C-1 in naphth), 140.4, 140.2 (2 d, ^3J = 13.2 Hz, *i*-C in Ph), 135.6 (*i*-C in Ph), 134.6 (d, ^3J = 11.0 Hz, =*C*HPh), 134.3 (C-10 in naphth), 128.7 (6 C, C-3,5 in 3Ph), 128.6 (C-5 in naphth), 128.3, 128.2, 126.6 (9 C, *o*,*p*-C in 3Ph), 126.1, 126.0, 125.3, 124.4 (C-3,6,7,9 in naphth), 123.6 (=CH), 120.4 (C-8 in naphth), 118.9 (C-4 in naphth), 106.7 (C-2 in naphth), 55.7 (d, ^1J = 55.2 Hz, CHN), 31.3, 31.0 (2 d, ^1J = 45.9, 46.0 Hz, PCH_2), 28.7 (CH_2Ph).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 58.52.

Anal. Calcd for $C_{35}H_{34}NPS$ (531.69): C, 79.06; H, 6.45; N, 2.63. Found: C, 78.78; H, 6.12; N, 2.80.

Bis[2-(4-*tert*-butylphenyl)ethyl][phenyl(prop-2-en-1-ylamino)methyl]phosphine Sulfide (4e)

Yield: 350 mg (66%) white powder; mp 104–105 °C.

FT-IR (KBr): 3298 (NH), 1643 (C=C), 775 (P–C), 590 cm^{-1} (P=S).

^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.45–6.96 (m, 13 H, Ar, C_6H_5), 5.88–5.78 (m, 1 H, CH=), 5.14, 5.10 (2 br s, 2 H, CH_2=), 4.10 (d, ^2J = 10.1 Hz, 1 H, CH), 3.28 (dd, J = 14.0, 4.7 Hz, 1 H, CH_2N), 3.09–2.56 (m, 6 H, CH_2Ar, CH_2N, NH), 2.30–1.71 (4 m, each 1 H, CH_2P), 1.31, 1.28 (2 s, 18 H, 2 × t-C_4H_9).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 149.3, 149.1 (C-4 in Ar), 137.8, 137.7 (2 d, ^3J = 14.8, 13.9 Hz, C-1 in Ar), 135.9 (CH=), 135.6 (d, ^2J = 2.4 Hz, i-C in Ph), 128.7 (o-C in Ph), 128.5, 128.4 (p,m-C in Ph), 127.9, 127.8 (C-3,5 in Ar), 125.5, 125.4 (C-2,6 in Ar), 116.8 (CH=), 61.9 (d, ^1J = 57.0 Hz, CH), 49.6 (d, ^3J = 14.6 Hz, CH_2N), 34.3 [$C(CH_3)_3$], 31.3 [$C(CH_3)_3$], 30.9, 29.4 (2 d, ^1J = 47.7, 46.2 Hz, CH_2P), 28.3, 27.9 (2 d, ^2J = 3.0, 2.8 Hz, CH_2Ar).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 55.98.

Anal. Calcd for $C_{34}H_{46}NPS$ (531.78): C, 76.79; H, 8.72; N, 2.63. Found: C, 76.05; H, 8.55; N, 2.49.

Bis[2-(4-*tert*-butylphenyl)ethyl][phenyl(prop-2-en-1-ylamino)methyl]phosphine Selenide (4f)

Yield: 400 mg (69%); white powder; mp 104–105 °C.

FT-IR (KBr): 3302 (NH), 1642 (C=C), 1177 (C–N), 762 (P–C), 563 cm^{-1} (P=Se).

^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.46–6.95 (m, 13 H, Ar, C_6H_5), 5.88–5.78 (m, 1 H, CH=), 5.13, 5.10 (2 nr m, each 1 H, CH_2=), 4.16 (d, ^2J = 9.6 Hz, 1 H, CH), 3.29 (dd, J = 14.0, 4.6 Hz, 1 H, CH_2N), 3.09–2.87 (m, 3 H, CH_2N, NH, CH_2Ar), 2.77–2.56 (m, 3 H, CH_2Ar), 2.38–1.79 (m, 4 H, CH_2P), 1.30 (18 H, 2 × t-C_4H_9).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 149.3, 149.2 (C-4 in Ar), 137.6, 137.4 (2 d, ^3J = 15.0 Hz, C-1 in Ar), 135.8 (CH=), 135.3 (d, ^2J = 2.6 Hz, i-C in Ph), 128.7 (d, ^4J = 2.0 Hz, m-C in Ph), 128.5 (d, ^5J = 2.8 Hz, p-C in Ph), 128.4 (d, ^3J = 5.0 Hz, o-C in Ph), 127.9, 127.8, 125.4, 125.3 (C-2,3,5,6 in Ar), 116.9 (CH=), 60.9 (d, ^1J = 50.6 Hz, CH), 49.5 (d, ^2J = 14.9 Hz, CH_2N), 34.2, 34.3 [$C(CH_3)_3$], 31.2 [$C(CH_3)_3$], 30.7 (d, ^1J = 40.7 Hz, CH_2P), 29.1, 28.8 (2 d, ^2J = 2.7, 2.5 Hz, CH_2Ar), 28.8 (d, ^1J = 38.8 Hz, CH_2P).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 48.79 (satellites: d, $^1J_{P,Se}$ = 701 Hz).

Anal. Calcd for $C_{34}H_{46}NPSe$ (578.67): C, 70.57; H, 8.01; N, 2.42. Found: C, 70.33; H, 7.91; N 2.23.

Bis[2-(4-*tert*-butylphenyl)ethyl][furan-2-yl(phenylamino)methyl]phosphine Sulfide (4g)

Yield: 412 mg (74%); grey powder; mp 123–124 °C.

FT-IR (KBr): 3329 (NH), 1181 (C–N), 750 (P–C), 691 cm^{-1} (P=S).

^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.45 (br s, 1 H, H-5 in fur), 7.32–7.11 (m, 8 H, Ar), 7.02 (d, J = 8.2 Hz, 2 H, m-H in C_6H_5), 6.78 (t, J = 7.3 Hz, 1 H, p-H in C_6H_5), 6.67 (d, J = 7.8 Hz, 2 H, o-H in C_6H_5), 6.44, 6.39 (2 nr m, each 1 H, H-3,4 in fur), 5.10 (t, ^3J = 8.2 Hz, 1 H, NH), 4.81 (dd, J = 10.9, 7.8 Hz, 1 H, CH), 3.06–2.80 (m, 3 H, CH_2Ar), 2.54–2.22 (m, 3 H, CH_2Ar, PCH_2), 2.02–1.94 (m, 2 H, PCH_2), 1.30 (br s, 18 H, 2 × t-C_4H_9).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 149.7 (C-2 in fur), 149.5, 149.3 (C-4 in Ar), 146.1 (d, ^3J = 11.1 Hz, i-C in Ph), 142.4 (d, ^5J = 3.1 Hz, C-5 in fur), 137.4, 137.3 (2 d, ^3J = 15.1, 14.3 Hz, C-1 in Ar), 129.2 (m-C in Ph), 127.9, 127.8 (C-2,6 in Ar), 125.6, 125.5 (C-3,5 in Ar), 119.1 (p-C in Ph), 114.3 (o-C in Ph), 111.3 (C-4 in fur), 109.3 (d, ^3J = 5.7 Hz, C-3 in fur), 51.6 (d, ^1J = 55.5 Hz, CHN), 34.3 [$C(CH_3)_3$], 32.0 (d, ^1J = 45.8 Hz, PCH_2), 31.3 [$C(CH_3)_3$], 30.8 (d, ^1J = 46.8 Hz, PCH_2), 28.2, 27.8 (2 d, ^2J = 2.9, 2.6 Hz, ArCH_2).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 59.28.

Anal. Calcd for $C_{35}H_{44}NOPS$ (557.77): C, 75.37; H, 7.95; N, 2.51. Found: C, 75.27; H, 7.74; N, 2.40.

Bis[2-(4-*tert*-butylphenyl)ethyl][furan-2-yl(phenylamino)methyl]phosphine Selenide (4h)

Yield: 416 mg (69%); grey powder; mp 99–100 °C.

FT-IR (KBr): 3320 (NH), 1180 (C–N), 748 (P–C), 564 cm^{-1} (P=Se).

^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.45 (s, 1 H, H-5 in fur), 7.32–7.11 (m, 8 H, Ar), 7.03 (d, ^3J = 7.8 Hz, 2 H, m-H in C_6H_5), 6.79 (t, ^3J = 7.3 Hz, 1 H, p-H in C_6H_5), 6.68 (d, ^3J = 7.9 Hz, 2 H, o-H in C_6H_5), 6.47, 6.39 (2 nr m, each 1 H, H-3,4 in fur), 5.12 (t, ^3J = 8.2 Hz, 1 H, NH), 4.88 (dd, J = 10.6, 8.1 Hz, 1 H, CH), 3.05–2.80 (m, 3 H, CH_2Ar), 2.52–2.36 (m, 3 H, CH_2Ar, PCH_2), 2.16–2.01 (m, 2 H, PCH_2), 1.30 (s, 18 H, 2 × t-C_4H_9).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 149.5 (d, ^3J = 3.3 Hz, C-2 in fur), 149.4 (p-C in Ph), 146.0 (d, ^3J = 11.1 Hz, i-C in Ph), 142.4 (d, J = 2.6 Hz), 137.2, 137.1 (2 d, ^3J = 26.2, 24.4 Hz, C-1 in Ar), 129.2 (m-C in Ph), 127.9 (d, J = 16.0 Hz, C-2,6 in Ar), 125.5 (d, J = 8.6 Hz, C-3,5 in Ar), 119.2 (p-C in Ph), 114.4 (o-C in Ph), 111.4 (o-C in Ph), 109.5 (d, ^3J = 5.5 Hz, C-3 in fur), 50.5 (d, ^1J = 49.4 Hz, CHN), 34.3 [$C(CH_3)_3$], 31.7 (d, ^1J = 38.5 Hz, PCH_2), 31.3 [$C(CH_3)_3$], 30.4 (d, ^1J = 39.3 Hz, PCH_2), 29.0, 28.7 (CH_2Ar).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 53.45 (satellites: d, $^1J_{P,Se}$ = 721 Hz).

Anal. Calcd for $C_{35}H_{44}NOPSe$ (604.66): C, 69.52; H, 7.33; N, 2.32. Found: C, 69.32; H, 7.15; N, 2.11.

Bis[2-(4-*tert*-butoxyphenyl)ethyl][furan-2-yl(phenylamino)methyl]phosphine Sulfide (4i)

Yield: 371 mg (63%); grey powder; mp 119–120 °C.

FT-IR (KBr): 3313 (NH), 1175 (N–C), 750 (P–C), 691 cm^{-1} (P=S).

^1H NMR (400.13 MHz, $CDCl_3$): δ = 7.44 (s, 1 H, H-5 in fur), 7.16 (t, ^3J = 7.3 Hz, 2 H, m-H in C_6H_5), 7.07, 6.98 (2 d, ^3J = 8.0 Hz, each 2 H, H-2,6 in Ar), 6.91–6.88 (m, 4 H, H-3,5 in Ar), 6.77 (t, ^3J = 7.1 Hz, 1 H, p-H in C_6H_5), 6.66 (d, ^3J = 7.8 Hz, 2 H, o-H in C_6H_5), 6.43, 6.38 (2 br s, each 1 H, H-3,4 in fur), 5.09 (t, ^3J = 7.8 Hz, 1 H, NH), 4.81 (dd, J = 10.3, 8.3 Hz, 1 H, CH), 3.05–2.78 (m, 3 H, CH_2Ar), 2.51–2.22 (m, 3 H, CH_2Ar, PCH_2), 2.06–1.92 (m, 2 H, PCH_2), 1.31 (s, 18 H, 2 × t-C_4H_9).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 153.8 (d, ^3J = 3.1 Hz, C-2 in fur), 149.5 (C-4 in Ar), 146.0 (d, ^3J = 11.2 Hz, i-C in Ph), 142.4 (C-5 in fur), 135.2, 135.1 (2 d, ^3J = 14.6, 13.9 Hz, C-1 in Ar), 129.2 (m-C in Ph), 128.6, 128.5, 124.4, 124.3 (C-2,4,5,6 in Ar), 119.1 (p-C in Ph), 114.3 (o-C in Ph), 111.4 (d, ^3J = 5.6 Hz, C-3 in fur), 109.4 (C-4 in fur), 78.3 [$C(CH_3)_3$], 51.5 (d, ^1J = 55.4 Hz, CH), 32.0, 30.9 (2 d, ^1J = 46.1, 47.0 Hz, CH_2P), 28.72 [$C(CH_3)_3$], 27.9, 27.6 (CH_2Ar).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 59.03.

Anal. Calcd for $C_{35}H_{44}NO_3PS$ (589.77): C, 71.28; H, 7.52; N, 2.37. Found: C, 71.50; H, 7.29; N, 2.61.

Bis(2-phenylethyl)[phenylamino(2-pyridinyl)methyl]phosphine Sulfide (4j)

Yield: 240 mg (52%); white powder; mp 106–107 °C.

FT-IR (KBr): 3329 (NH), 751 (P–C), 659, 613, 557 cm^{-1} (P=S).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 8.61 (d, ^3J = 4.4 Hz, 1 H, H-6 in Py), 7.70 (t, ^3J = 7.5 Hz, 1 H, H-3 in Py), 7.61 (d, ^3J = 7.8 Hz, 1 H, H-4 in Py), 7.29–7.14 (m, 11 H, 2 × C_6H_5, H-5 in Py), 7.03 (d, ^3J = 7.1 Hz, 2 H, *m*-H in NC_6H_5), 6.76 (t, ^3J = 7.3 Hz, 1 H, *p*-H in NC_6H_5), 6.69 (d, ^3J = 8.1 Hz, 2 H, *o*-H in NC_6H_5), 5.53 (t, ^3J = 8.4 Hz, 1 H, CH), 5.06 (nr m, 1 H, NH), 3.02–2.85 (m, 3 H, CH_2Ar), 2.56–2.45 (m, 1 H, CH_2Ar), 2.39–2.24 (m, 2 H, PCH_2), 2.15–1.94 (m, 2 H, PCH_2).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 156.3 (C-6 in Py), 148.9 (C-1 in Py), 145.9 (d, ^3J = 10.6 Hz, *i*-C in NPh), 140.5, 140.4 (2 d, ^3J = 15.3, 14.4 Hz, *i*-C in Ph), 136.9 (C-4 in Py), 129.3 (*m*-C in NPh), 128.6, 128.5, 128.2, 128.0, 126.4, 126.3 (*o*,*m*,*p*-C in Ph), 123.2 (C-5 in Py), 122.9 (C-3 in Py), 118.8 (*p*-C in Ph), 114.2 (*o*-C in Ph), 58.4 (d, ^1J = 50.1 Hz, CH), 32.1 (d, ^1J = 46.1 Hz, CH_2P), 30.5 (d, ^1J = 46.8 Hz, CH_2P), 28.7, 28.4 (*C*H_2Ar),

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 59.27.

Anal. Calcd for $C_{28}H_{29}N_2PS$ (456.583): C, 73.66; H, 6.40; N, 6.14. Found: C, 73.82; H, 6.54; N, 6.09.

Bis(2-phenylethyl)[prop-2-in-1-ylamino(4-pyridinyl)methyl]phosphine Selenide (4k)

Yield: 300 mg (64%); light yellow oil.

FT-IR (KBr): 3297 (NH, ≡CH) 2219 (C≡C), 734 (P–C), 540, 569 cm^{-1} (P=Se).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 8.65 (d, ^3J = 5.4 Hz, 2 H, H-2,6 in Py), 7.37–7.18 (m, 10 H, 2 × C_6H_5), 7.07 (d, ^3J = 7.2 Hz, 2 H, H-3,5 in Py), 4.40 (d, ^2J = 10.2 Hz, 1 H, CHN), 3.57 (dd, ^2J = 17.1, ^3J = 2.0 Hz, 1 H, CH_2N), 3.14–2.72 (m, 6 H, CH_2N, NH, CH_2Ar), 2.36–2.15 (m, 3 H, CH_2P, ≡CH), 2.09–1.82 (m, 2 H, CH_2P).

^{13}C NMR (100.61 MHz, $CDCl_3$): δ = 149.9 (C-2,6 in Py), 143.7 (C-4 in Py), 139.8 (d, ^2J = 13.6 Hz, *i*-C in Ph), 128.4, 128.3, 128.0, 127.8, 126.3, 136.2 (*o*,*m*,*p*-C in Ph), 123.2 (C-3,5 in Py), 79.7 (≡CH), 72.8 (d, ^4J = 4.6 Hz, ≡C–), 59.3 (d, ^1J = 49.4 Hz, CH), 35.6 (d, ^3J = 15.9 Hz, CH_2), 30.1 (d, ^1J = 41.2 Hz, CH_2P), 29.2, 29.0 (*C*H_2Ar), 28.5 (d, ^1J = 38.9 Hz, CH_2P).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 48.49 (satellites: d, $^1J_{P,Se}$ = 718 Hz).

Anal. Calcd for $C_{25}H_{27}N_2PSe$ (465.429): C, 64.51; H, 5.85; N, 6.02. Found: C, 64.33; H, 5.91; N, 6.23.

{[1,4-Phenylenebis(azanediyl)]bis(phenylmethylene)}bis{bis[4-(*tert*-butoxy)phenethyl]}phosphine Sulfide (4l)

Prepared, following the general procedure, from *p*-phenylenediamine (**2f**; 108 mg, 1.0 mmol), phosphine **1c** (770 mg, 2.0 mmol), benzaldehyde (**3a**; 210 mg, 2.0 mmol), and elemental sulfur (64 mg, 2.0 mmol); yield: 392 mg (35%); white powder; mp 194–195 °C.

FT-IR (KBr): 3361 (NH), 1163 (N–C), 768 (P–C), 722, 697 cm^{-1} (P=S).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 7.42–7.29, 7.04–6.82 (m, 26 H, 2 × C_6H_5, Ar), 6.43 (s, 4 H, N–Ar–N), 5.04 (br s, 2 H, NH), 4.50 (d, ^2J = 10.5 Hz, 2 H, CH), 3.02–2.84 (m, 4 H, CH_2Ar), 2.71–2.61 (m, 2 H, CH_2Ar), 2.38–2.16 (m, 6 H, CH_2Ar, CH_2P), 1.85–1.74 (m, 4 H, CH_2P), 1.31, 129 (2 s, each 18 H, 2 × *t*-C_4H_9).

^{13}C NMR (100.61 MHz, DMSO-d_6): δ = 154.4, 153.0, 150.0, 137.9, 137.6, 136.8, 132.4, 129.8, 129.6, 129.5, 129.3, 129.2, 129.1, 128.9, 128.7, 124.9, 124.8, 117.6, 116.4, 78.8, 56.5 (d, ^1J = 55.1 Hz, CH), 29.7, 29.6 [CH_2Ar, [C(CH_3)$_3$], 28.3 (d, ^1J = 50.2 Hz, CH_2P).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 58.24, 58.28.

Anal. Calcd for $C_{68}H_{86}N_2O_4P_2S_2$ (1121.49): C, 72.82; H, 7.73; N, 2.50. Found: C, 72.70; H, 7.52; N, 2.44.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588127. Included are the procedure for synthesis of **1c**, crystallography data for **4d**, and copies of ^{1}H, ^{13}C and ^{31}P NMR spectra for all synthesized compounds.

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