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One-pot synthesis of ultra-branched mixed tetradentate tripodal phosphines and phosphine chalcogenides

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ABSTRACT

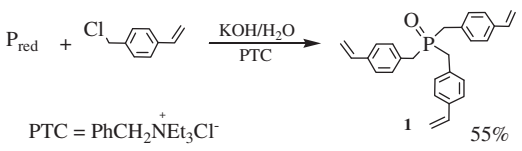
Ultra-branched mixed tetradentate tripodal phosphines and phosphine chalcogenides have been synthesized by the exhaustive regioselective addition of secondary phosphines, phosphine sulfides and phosphine selenides to available tris(4-vinylbenzyl)phosphine oxide under free-radical conditions (UV irradiation or AIBN) in good to excellent yields.

1. Introduction

Tetradentate tripodal ligands containing phosphine moieties are widely used for design of multi-purpose metal complexes.[1,2] For instance, complexes of Cr(III),[1] Fe(II, III),[1,3] Co(II),[1,4] Ni(II),[5] Mo(III),[1,6] Ru(II),[1,2,7] Rh(II),[1,4,8] Pd(II),[9,10] W(III),[2a,6] Os(II),[1,7b,c] Ir(II),[1] Pt(II),[1,9] Hg(II),[11] and polynuclear complexes[12] with tris[(2-diphenylphosphano)ethyl]phosphine, $(Ph_2PCH_2CH_2)_3P$ (PP_3), which is now one of the most thoroughly studied tetradentate tripodal ligands, act as catalysts for a variety of organic transformations.[1,3d,g,13,14] Complexes of PP_3 with Ru are applied for preparation of diagnostic radiopharmaceutical imaging agents[15] and complexes of this ligand with Ag and Au display intense luminescent emission at room and low temperatures.[16] In recent years, mixed chalcogene derivatives of PP_3 (PP_3X_n, X=O, S, Se; n=1–4) are also employed for the design of organometallic catalysts[17] and useful materials.[18] For example, rhodium complexes of PP_3X_4 catalyze the carbonylation of methanol to acetic acid and its ester.[17e] The readily regenerative and air-stable Pd complex, [Pd(PP_3S_4)(dba)], has been used as a C–C coupling catalyst.[17b–e]

One of the limitations in the controlled design of such complexes is inaccessibility of tetradentate tripodal phosphines ligands and their derivatives, especially their polyphosphine chalcogenides. The conventional syntheses of these ligands are laborious and multistep. The known protocols utilize moisture- and air-sensitive phosphorus halides and organometallic compounds often accompanied by side-reactions.[2b,19] Besides, the reported PP_3 is limited by the representatives with just a few substituents (Me, Et, Cy, Ph) at the phosphorus atom. Therefore, the development of new more straightforward phosphorus halide-free approaches to various tetraphosphines and tetraphosphine chalcogenides is of standing synthetic importance.

A promising approach to the synthesis of novel tetradentate tripodal ligands could be the reaction of radical addition of secondary phosphines and phosphine chalcogenides to trialkenylphosphines or their chalcogenides. This stimulated us to pay attention to the readily available tris(4-vinylbenzyl)phosphine oxide (**1**) as a possible parent starting compound capable of adding the diverse phosphines and phosphine chalcogenides across its three double bonds. Phosphine oxide **1** is now easily prepared in a one-pot procedure by direct phosphorylation of commercially available 4-vinylbenzylchloride with red phosphorus (Scheme 1).[19]



Scheme 1. Synthesis of tris(4-vinylbenzyl)phosphine oxide.

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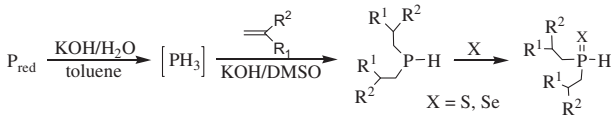
In this work, for the addition to phosphine oxide **1**, we have used accessible secondary phosphines **2**–**4** and phosphine chalcogenides **8**–**16**, which are readily synthesized from aryl- and hetarylalkenes and red phosphorus in superbasic system KOH/DMSO (Scheme 2).[20a,21]



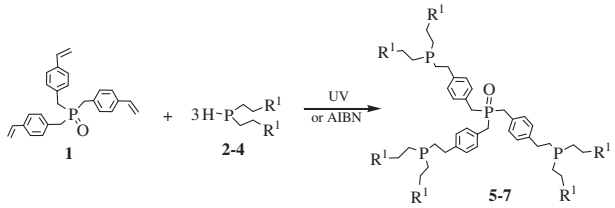
Scheme 2. Synthesis of secondary phosphines and phosphine chalcogenides.

2. Results and discussion

The presence of three vinyl groups in phosphine oxide **1** assumes the formation of mono- and diadducts as well as products of polymerization of both initial compound **1** and intermediate adducts. Therefore, this study is aimed at the search for appropriate conditions for chemoselective synthesis of tetradentate tripodal phosphines and phosphine chalcogenides.

As our experiments have shown, under free-radical initiations, phosphine oxide **1** adds phosphines **2**–**4** regioselectively to give anti-Markovnikov adducts **5**–**7** in 60–80% yield (Table 1). The target exhaustive addition reactions have been realized using the 1:3 reactant molar ratio, respectively, UV irradiation in benzene (method *A*) or AIBN at 65–70 °C in 1,4-dioxane (method *B*), all experiments being carried out under argon.

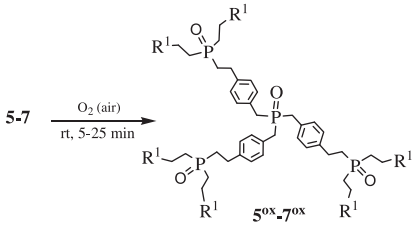
Table 1
Exhaustive addition of secondary phosphines **2**–**4** to phosphine oxide **1**



Entry	Secondary phosphine	R^1	Method[a]/ time (h)	Product[b]	Yield[c] (%)
1	**2**	Et	B/7.5	**5**	48 (70)
2	**3**	Ph	A/7.5	**6**	80 (96)[d]
3			B/10		60 (70)[e]
4	**4**		A/15	**7**	63 (85)

[a] Standard reaction conditions: molar ratio **1**/**2**–**4**=1:3, argon. Method *A*: UV, 25–30 °C (heating resulted from irradiation), benzene. Method *B*: AIBN (1.5–2 wt % of the reactants' mass), 65–70 °C, 1,4-dioxane.
[b] Triphosphines **5**, **7** were isolated as tetraoxides $\mathbf{5}^{ox}$, $\mathbf{7}^{ox}$, the corresponding phosphines **5**, **7** were identified in the reaction mixture by ^{31}P NMR.
[c] Isolated yield (^{31}P NMR yield was given in parentheses).
[d] Triphosphine **6** was isolated.
[e] Triphosphine oxide $\mathbf{6}^{ox}$ was prepared.

The reaction has been monitored by ^{31}P NMR spectroscopy to follow the disappearance of the signals of the initial secondary phosphines **2**–**4** at −71 ÷ −68 ppm and appearance of the signals of the forming triadducts **5**–**7** at −30 ÷ −23 ppm. Under the above conditions, the reaction is highly regio- and chemoselective to give almost exclusively anti-Markovnikov triadducts (^1H, ^{13}C, ^{31}P NMR): mono- and diadducts were discernible in the reaction mixtures only in trace amounts. As anticipated, triphosphines **5**–**7** are easily oxidized by air during the isolation and characterization to give the corresponding tetraphosphine oxides $\mathbf{5}^{ox}$–$\mathbf{7}^{ox}$ (Scheme 3).



Scheme 3. Oxidation of triphosphines **5**–**7**.

Using phosphine **3** as an example, we have shown that under UV irradiation (benzene, 25–30 °C), phosphination of phosphine oxide **1** proceeds more effectively and selectively than in the presence of AIBN (1,4-dioxane, 65–70 °C): yield of triadduct **6** reaches 80% (method *A*) versus 60% (method *B*), Table 1, cf. entries 2 and 3. In the latter case noticeable amounts of insoluble polymer are formed, likely due to the polymerization of the initial phosphine oxide **1** and/or intermediate mono- and diadducts.

Under similar free-radical initiation, secondary phosphine sulfides **8**–**12** and phosphine selenides **13**–**16** undergo ready addition to phosphine oxide **1** (the reactant molar ratio 3:1, respectively) to afford, in the case of UV irradiation (benzene, 25–30 °C), corresponding anti-Markovnikov triadducts **17**–**25**, tetradentate tripodal phosphine chalcogenides, in high yields (Table 2).

As with the secondary phosphines (Table 1), the UV-initiated reaction of phosphine oxide **1** with phosphine chalcogenides **8**–**16** (method *A*) is preferred over AIBN-promoted one (method *B*): the yield of triadduct **17** is by 1.5 times higher and the reaction time is significantly shorter (Table 2, entry 1). Noteworthy, the nature of the solvent substantially influences the efficacy of the reaction studied. In the example of phosphine sulfide **8**, it has been demonstrated that UV irradiation of the reactants in 1,4-dioxane (instead of benzene) leads to a cross-linked polymer in almost quantitative yield. The structure and composition of this polymer was similar to that of the phosphine oxide **1** homopolymer, prepared and characterized previously.[22]

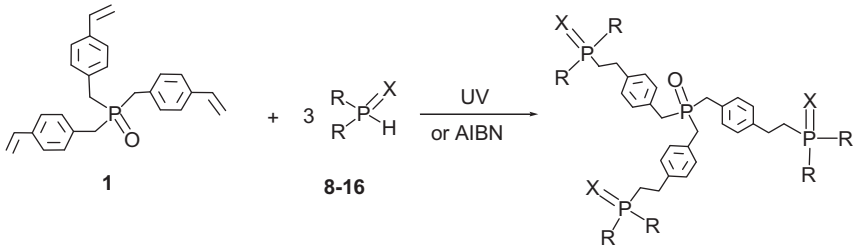
As seen from Tables 1 and 2, diverse secondary phosphines and phosphine chalcogenides containing Bu, $Ph(CH_2)_2$, $PhCH(Me)CH_2$, 4-$^tBuC_6H_4(CH_2)_2$, 4-$MeOC_6H_4(CH_2)_2$, 2-$Fur(CH_2)_2$, and 6-Me-3-$Py(CH_2)_2$ substituents at phosphorus atom react easily with phosphine oxide **1** that supports the generality of this process.

As exemplified by triadduct **17**, triphosphine sulfides can be readily reduced with metal sodium (reflux toluene) to the corresponding triphosphines (Scheme 4).

Note that secondary phosphine oxides do not react with phosphine oxide **1** under the above free-radical conditions. So, the UV irradiation (20–35 °C, 6 h, benzene) of the mixture of bis(2-phenethyl)phosphine oxide and phosphine oxide **1** gives only polymer of phosphine oxide **1** and the unreacted initial secondary phosphine oxide. This is consistent with the known data about low reactivity of secondary phosphine oxides in the radically induced addition reactions.[23] However, tetraphosphine oxides $\mathbf{5}^{ox}$–$\mathbf{7}^{ox}$ can be easily prepared by the oxidation of the corresponding phosphines (Scheme 2).

The results obtained show (Tables 1 and 2) that the reactivity of the PH-addends used in the reaction with phosphine oxide **1** falls in the order: secondary phosphine selenides>secondary phosphine

Table 2
Exhaustive addition of secondary phosphines chalcogenides **8**–**16** to phosphine oxide **1**



1 **8-16** **17-25**

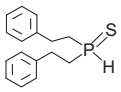
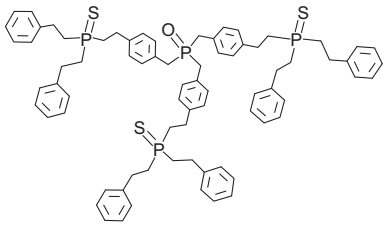
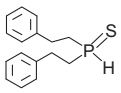
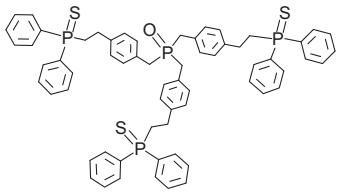
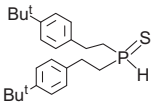
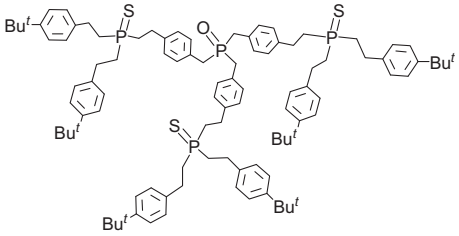
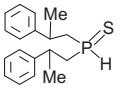
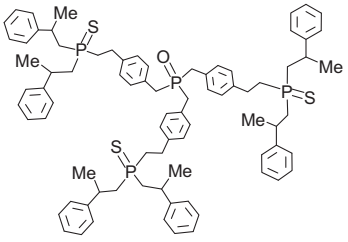
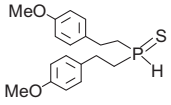
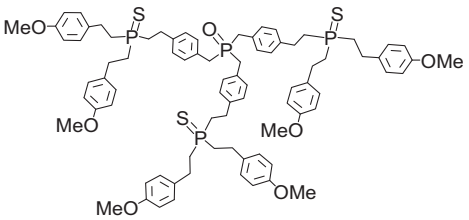
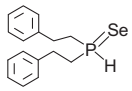
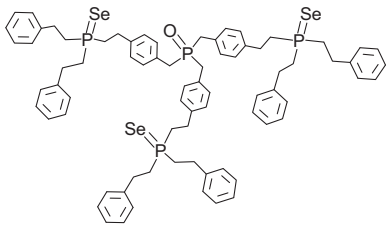
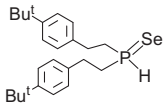
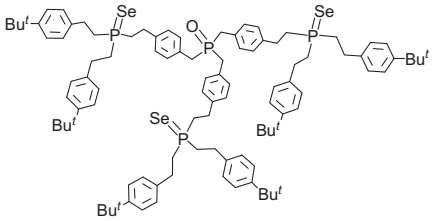
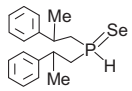
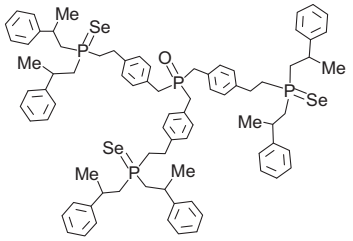
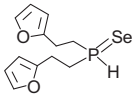
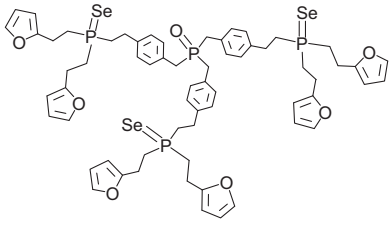
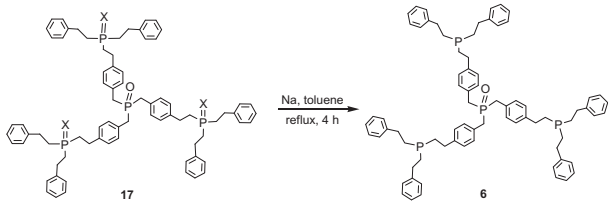
Entry	PH-addend	Method[a]/time (h)	Product	Yield[b] (%)
1	 **8**	A/3.5 B/12	 **17**	92 (99) 60 (70)
2	 **8**	A/1	c	c
3	 **9**	A/3	 **18**	90(98)
4	 **10**	A/4	 **19**	87 (97)
5	 **11**	A/4	 **20**	77 (95)
6	 **12**	A/8	 **21**	78 (98)

Table 2 (*continued*)

Entry	PH-addend	Method[a]/time (h)	Product	Yield[b] (%)
7	 **13**	A/2	 **22**	85 (99)
8	 **14**	A/3	 **23**	78 (95)
9	 **15**	A/3.5	 **24**	89 (97)
10	 **16**	A/4	 **25**	85 (95)

[a] Standard reaction conditions: molar ratio **1**/**8**–**16**=1:3. Experiments were carried out under argon. Method *A*: UV, 25–30 °C, benzene. Method *B*: AIBN (1.5–2 wt % of the reactants' mass), 65–70 °C, 1,4-dioxane.
[b] Isolated yield (^{31}P NMR yield was given in parentheses).
[c] Experiment was carried out in 1,4-dioxane. The homopolymer of **1** was isolated as a main product in this case.



Scheme 4. Reduction of tris{4-[2-(diphenethylphosphorothioyl)ethyl]benzyl}phosphine oxide.

sulfides>secondary phosphines>secondary phosphine oxides that is in agreement with the published data.[23,24]

3. Conclusions

In summary, the one-pot chemoselective synthesis of ultra-branched mixed phosphines and phosphine chalcogenides has been developed by exhaustive free-radical addition of secondary phosphines and phosphine chalcogenides to available tris(4-vinylbenzyl)phosphine oxide thus providing a facile short-cut to a new family of prospective tetradentate tripodal ligands for design of multi-purpose metal complexes. Importantly, all substrates required for the presented syntheses are readily derived directly from elemental phosphorus.

4. Experimental section

4.1. General

IR spectra were run on a 'Bruker IFS 25' spectrometer (400–4000 cm^{-1}, KBr pellets). ^{1}H (400.13 MHz), ^{13}C (100.62 MHz), ^{31}P NMR (161.98 MHz), and ^{77}Se NMR (76.27 MHz) spectra were recorded on a 'Bruker DPX-400' instrument in $CDCl_3$ solutions and referenced to internal HDMS (^{1}H NMR), external 85% H_3PO_4 (^{31}P NMR), and Me_2Se (^{77}Se NMR). Melting points were recorded on a 'Micro Hot Stage

POLYTHERM A' apparatus. The photochemical reactions were performed by using argon-purged solutions in quartz tubes. The photolyses were performed on OKN apparatus using a high-pressure mercury lamp (200 W, hν >200 nm). Benzene and 1,4-dioxane were purified by distillation under argon over sodium benzophenone ketyl immediately before use. Phosphine **2** was synthesized from butylbromide and red phosphorus in the superbasic system Li–^{t}BuOH–NH_3(l).[25] Secondary phosphines **3**, **4** were prepared from styrene,[21] or 2-methyl-5-vinylpyridine[26] and phosphine as described in the literature. Phosphine chalcogenides **8**–**16** were prepared by reaction of corresponding phosphines with elemental sulfur and selenium.[27] The reaction studied was monitored using ^{31}P NMR by disappearance of signal (δ, ppm) of the starting PH-addends (the −71 ÷ −68 ppm region for phosphines **2**–**4**; the −4 ÷ 22 ppm interval for phosphine chalcogenides **8**–**16**) and appearance of a new resonance in the region of −30 ÷ −23 and 37 ÷ 50 ppm for tertiary phosphines **5**–**7**, phosphine sulfides **17**–**21**, and selenides **22**–**25**, correspondingly. All experiments were carried out upon argon atmosphere. The compounds synthesized were purified by recrystallization (for **6**^{ox}, **7**^{ox}, **17**–**25**) or reprecipitation (for **5**^{ox}, **6**).

4.2. Synthesis of tris{4-[2-(2-diphenethylphosphino)ethyl] benzyl}phosphine oxide (6) (Table 1, entry 2)

Method A: A solution of phosphine oxide **1** (0.16 g, 0.4 mmol) and secondary phosphine **2** (0.29 g, 1.2 mmol) in benzene (0.5 mL) was irradiated in quartz ampoule for 7.5 h. Benzene was removed and the residue was dissolved in ether (1.5 mL) and reprecipitated in hexane (10 mL). The solvents were decanted from the residue, the latter was dried in vacuum to give triphosphine **6**. Colorless oil (360 mg, yield 80%, method A). IR (KBr): ν=3070, 3055, 2975, 2930, 2900, 2863, 1606, 1582, 1522, 1499, 1457, 1425, 1406, 1211, 1165, 1130, 1056, 1034, 1012, 965, 947, 926, 876, 863, 820, 817, 753, 699, 560, 474, 450 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=1.73–2.13 (m, 18H, CH_2P), 2.71–2.99 (m, 24H, CH_2Ph, $CH_2C_6H_4CH_2$), 7.14–7.29 (m, 42H, Ph, C_6H_4) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ=22.3 (d, $^1J_{PC}$=12.1 Hz, $PCH_2CH_2C_6H_4$), 29.0 (d, $^1J_{PC}$=16.0 Hz, PCH_2CH_2Ph), 30.1 (d, $^1J_{PC}$=63.8 Hz, CH_2P=O), 32.2 (d, $^2J_{PC}$=15.0 Hz, $PhCH_2$), 34.5 (d, $^2J_{PC}$=10.6 Hz, $CH_2C_6H_4$), 126.7 (C-*p* in Ph), 128.4 (C-*o* in Ph), 128.7 (C-*m* in C_6H_4), 128.8 (C-*m* in Ph), 129.8 (d, $^2J_{PC}$=7.0 Hz, C-*i* in C_6H_4), 130.3 (d, $^3J_{PC}$=5.2 Hz, C-*o* in C_6H_4), 139.4 (d, $^3J_{PC}$=13.6 Hz, C-*p* in C_6H_4), 140.3 (d, $^3J_{PC}$=13.6 Hz, C-*i* in Ph) ppm. ^{31}P NMR (161.98 MHz, C_6D_6): δ=−28.23 (CH_2P), 38.19 (CH_2P=O) ppm. $C_{75}H_{84}OP_4$ (1125.36): calcd C 80.05, H 7.52, P 11.01; found C 79.41, H 7.55, P 10.92. Trisphosphine **6** was easily and practically quantitatively oxidized in the presence of O_2 (air, 25 min) to give tetraphosphine oxide **6**^{ox}.

4.3. General procedure for the preparation of phosphine oxides 5^{ox}–7^{ox} (Table 1, entries 1, 3, 4)

Method B: A solution of phosphine oxide **1** (0.15 mmol) and secondary phosphines **2**–**4** (0.45 mmol) in dioxane (5 mL) in the presence of AIBN (1–2 wt % of the total mass of reactants) was stirred for 65–70 °C in a closed reactor with magnetic stirrer (reaction times were given in Table 1). A white polymer precipitate was formed in each case. Benzene (3 mL) was added to the reaction mixture, undissolved polymer was filtered off through paper filter. Benzene was removed, the residue was reprecipitated from chloroform to ether (in the case of compound **5**^{ox}) or recrystallized (for compounds **6**^{ox}, **7**^{ox}), dried in vacuum to give tetraphosphine oxides **5**^{ox}–**7**^{ox}. In the case of tetraphosphine oxide **5**^{ox}, the residue was additionally washed with hot hexane before the reprecipitation procedure.

*4.3.1. Tris{4-[2-(butylphosphoryl)ethyl]benzyl}phosphine oxide (**5**^{ox}).* Colorless oil (375 mg, yield 50%, method B). IR (KBr): ν=3050, 3033, 2965, 2958, 2929, 2870, 1605, 1525, 1490, 1465, 1437, 1420, 1407, 1379, 1290, 1273, 1214, 1209, 1198, 1159, 1129, 1070, 1034, 1011, 916, 896, 830, 814, 1055, 963, 948, 860, 751, 699, 558, 476, 449 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=1.42–1.44 (m, 18H, CH_3), 1.56 (m, 12H, CH_3CH_2), 1.70 (m, 12H, EtCH_2), 1.82 (m, 12H, PrCH_2), 1.97 (m, 6H, $PCH_2C_6H_4CH_2$), 2.98–2.89 (m, 12H, $PCH_2C_6H_4CH_2CH_2P$), 6.98–7.14 (m, 12H, C_6H_4) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ=13.5 (Me), 23.3 ($EtCH_2$), 24.1 ($MeCH_2$), 27.2 ($PrCH_2$), 27.5 ($CH_2C_6H_4$), 29.9 ($PCH_2CH_2C_6H_4$), 34.6 (d, $^1J_{PC}$=61.0 Hz, CH_2P), 127.7 (C-*m*), 128.5 (C-*o*), 130.1 (d, $^3J_{PC}$=5.1 Hz, C-*i*), 140.5 (d, $^3J_{PC}$=15.0 Hz, C-*p*) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ=49.15 (Bu_2P=O), 53.40 (CH_2P=O) ppm. $C_{51}H_{84}O_4P_4$ (885.105): calcd C 69.21, H 9.57, P 14.00; found C 69.00, H 9.27, P 14.15.

*4.3.2. Tris{4-[2-(2-diphenethylphosphoryl)ethyl]benzyl}phosphine oxide (**6**^{ox}).* White powder (375 mg, yield 80%, method A and 281 mg, yield 60%, method B). Mp 135–138 °C (*iso*-propanol). IR (KBr): ν=3058, 3025, 2925, 2860, 1602, 1512, 1496, 1454,1421, 1403, 1209, 1164, 1129, 1070, 963, 948, 860, 751, 699, 558, 493 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=2.03–2.05 (m, 18H, CH_2P), 2.92–2.94 (m, 24H, CH_2Ph, $CH_2C_6H_4$), 7.15–7.27 (m, 42H, Ph, C_6H_4) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ=27.5 and 27.5 ($CH_2C_6H_4$, CH_2Ph), 29.8 (d, $^1J_{PC}$=64.2 Hz, $PhCH_2CH_2P$), 29.8 (d, $^1J_{PC}$=62.9 Hz, $PCH_2CH_2C_6H_4$), 34.6 (d, $^1J_{PC}$=61.4 Hz, $C_6H_4CH_2P$), 126.4 (C-*p* in Ph), 127.9 (C-*o* in Ph), 127.8 (C-*m* in C_6H_4), 128.5 (C-*o* in C_6H_4), 128.5 (C-*m* in Ph), 129.9 (d, $^2J_{PC}$=5.3 Hz, C-*i* in C_6H_4), 139.8 (d, $^3J_{PC}$=12.5 Hz, C-*i* in Ph), 140.5 (d, $^3J_{PC}$=12.9 Hz, C-*p* in C_6H_4) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ=46.86 ($PhCH_2CH_2)_2$P=O, 41.60 (CH_2P=O). $C_{75}H_{84}$ O_4P_4 (1173.36): calcd C 76.77, H 7.22, P 10.56; found C 76.71, H 7.20, P 10.44.

Polymer: IR (KBr): ν=3274, 3024, 2919, 2854, 1668, 1628, 1603, 1511, 1496, 1453, 1421, 1210, 1180, 1127, 1069, 1019, 971, 859, 752, 699, 559, 467 cm^{-1}. Found: C 69.77, H 6.93, P 10.22.

*4.3.3. Tris{4-(2-bis[2-(6-methylpyrid-3-yl)ethyl]phosphoryl)ethyl] benzyl}-phosphine oxide (**7**^{ox}).* White powder (80 mg, yield 63%, method B). Mp 138–140 °C (*iso*-propanol). IR (KBr): ν=3008, 2924, 2856, 1667, 1651, 1604, 1569, 1512, 1493, 1448, 1396, 1336, 1299, 1245, 1217, 1163, 1141, 1127, 1034, 944, 915, 860, 832, 751, 732, 645, 548, 491 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=1.68–1.76 (m, 6H, $PCH_2CH_2C_6H_4$), 2.0–2.06 (m, 12H, $PyCH_2CH_2P$), 2.50 (18H, Me), 2.67–2.71 (m, 6H, CH_2P), 2.87–2.98 (m, 18H, CH_2Py), 7.09–8.33 (m, 30H, in C_6H_4 and Py) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ=24.5 (Me), 25.4 ($PyCH_2$), 27.9 ($PCH_2CH_2C_6H_4$), 30.7 (d, $^1J_{PC}$=60.5 Hz, $CH_2PCH_2CH_2Py$), 34.9 (d, $^1J_{PC}$=72.2 Hz, CH_2P), 123.9 (C=CMe in Py), 129.1 (C-*m* in C_6H_4), 130.2 (d, $^2J_{PC}$=7.2 Hz, C-*i* in C_6H_4), 130.9 (C-*o* in C_6H_4), 133.0 (d, $^3J_{PC}$=13.5 Hz, C-*i* in Py), 133.7 (d, $^3J_{PC}$=16.8 Hz, C-*p* in C_6H_4), 136.9 (HC=C in Py), 149.1 (C=N in Py), 157.4 (CMe in Py) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ=40.18 (P=O), 45.09 (PyP=O) ppm. $C_{75}H_{90}$ $N_6O_4P_4$ (1263.45): calcd C 71.30, H 7.18, N 6.65, P 9.81; found C 71.21, H 7.20, N 6.57, P 9.74.

4.4. General procedure for the preparation of tetraphosphine chalcogenides 17–25 (Table 2)

Method A: A solution of phosphine oxide **1** (0.1 mmol) and secondary phosphine chacogenides **8**–**16** (0.3 mmol) in benzene (0.5 mL) was irradiated in quartz ampoule (reaction times were given in Table 2). Benzene (3 mL) was added to the reaction mixture, undissolved polymer was filtered off through paper filter. Benzene was removed, the residue was reprecipitated from chloroform to ether, dried in vacuum to give tetraphosphine chalcogenides **17**–**25** (purified additionally by recrystallization from *iso*-propanol).

*4.4.1. Tris(4-{2-[diphenethylphosphorothioyl]ethyl}benzyl)phosphine oxide (**17**).* White powder (168 mg, yield 92% method A and 110 mg, yield 60%, method B). Mp 100–102 °C (*iso*-propanol). IR (KBr): ν=3084, 3058, 3003, 2922, 2901, 2858, 1602, 1583, 1511, 1495, 1453, 1421, 1401, 1239, 1207, 1130, 1108, 1072, 1020, 1006, 950, 910, 906, 858, 752, 697, 598, 546, 493 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=2.11–2.13 (m, 18H, CH_2P), 2.90–2.92 (m, 24H, CH_2Ph, $CH_2C_6H_4$), 7.10–7.26 (m, 42H, Ph, C_6H_4) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ=28.1 ($CH_2C_6H_4$), 28.5 (CH_2Ph), 32.7 (d, $^1J_{PC}$=48.0 Hz, $PCH_2CH_2C_6H_4$), 32.8 (d, $^1J_{PC}$=48.3 Hz, $PhCH_2CH_2P$), 34.7 (d, $^1J_{PC}$=61.2 Hz, CH_2PO), 126.5 (C-*p* in Ph), 127.9 (C-*m* in C_6H_4), 128.2 (C-*o* in Ph), 128.7 (C-*m* in Ph), 129.7 (d, $^2J_{PC}$=7.4 Hz, C-*i* in C_6H_4), 130.1 (d, $^3J_{PC}$=4.4 Hz, C-*o* in C_6H_4), 139.4 (d, $^3J_{PC}$=15.1 Hz, C-*p* in C_6H_4), 140.4 (d, $^3J_{PC}$=13.6 Hz, C-*i* in Ph) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ=41.38 (P=O) and 48.38 (P=S) ppm. $C_{75}H_{84}OP_4S_3$ (1221.56): calcd C 73.74, H 6.93, P 10.14, S 7.87; found C 73.70, H 6.91, P 10.09, S 7.73.

*4.4.2. Tris(4-[2-(diphenylphosphorothioyl)ethyl]benzyl)phosphine oxide (**18**).* Pasty mass (95 mg, yield 90%, method A). IR (KBr): ν=3074, 3056, 3035, 2922, 2904, 2852, 1608, 1588, 1574, 1513, 1480, 1437, 1422, 1403, 1331, 1309, 1241, 1199, 1183, 1160, 1128, 1105, 1070, 1027, 998, 910, 863, 797, 733, 692, 645, 623,612, 580, 532, 501, 441 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=2.76 (m, 6H, CH_2PS), 2.93 (m, 6H, $CH_2C_6H_4$), 2.99 (d, 6H, $^2J_{PH}$=13.7 Hz, CH_2PO), 7.11 (m, 12H, C_6H_4), 7.49 (m, 18H, H–C-*p*, H–C-*m* in Ph), 7.88 (m, 12H, H–C-*o* in Ph) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ=28.0 ($CH_2C_6H_4$), 34.3 (d, $^1J_{PC}$=61.2 Hz, CH_2PO), 34.4 (d, $^1J_{PC}$=55.1 Hz, $SPCH_2$), 129.0 (d, $^3J_{PC}$=13.4 Hz, C-*o* in C_6H_4), 130.2 (d, $^3J_{PC}$=5.0 Hz, C-*m* in C_6H_4), 128.8 (d, $^3J_{PC}$=11.9 Hz, C-*o* in Ph), 131.1 (d, $^3J_{PC}$=10.3 Hz, C-*m* in Ph), 131.7 (d, $^3J_{PC}$=2.7 Hz, C-*p* in Ph), 139.8 (d, $^2J_{PC}$=17.2 Hz, C-*i* in C_6H_4), 141.9 (d, $^3J_{PC}$=16.8 Hz, C-*p* in C_6H_4), 132.6 (d, $^1J_{PC}$=80.0 Hz, C-*p* in Ph) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ=41.67 (P=O), 41.90 (P=S) ppm. Anal. Calcd for: $C_{63}H_{60}OP_4S_3$. C, 71.84; H, 5.74; P, 11.76; S, 9.13. Found: C, 76.24; H, 8.51; P, 7.91; S, 6.13.

*4.4.3. Tris(4-{2-[bis(4-tert-butylphenethyl)phosphorothioyl]ethyl}benzyl)phosphine oxide (**19**).* White needles (163 mg, yield 87% method A). Mp 100–101 °C (*iso*-propanol). IR (KBr): ν=3091, 3054, 3024, 2961, 2904, 2866, 1661, 1609, 1513, 1475, 1463, 1444, 1403, 1394, 1363, 1269, 1203, 1134, 1109, 1018, 953, 855, 838, 816, 776, 678, 562 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=1.29 (s, 54H, Me), 2.10–2.28 (m, 18H, CH_2PS), 2.88–3.04 (m, 24H, $CH_2C_6H_4$, CH_2PO), 7.10–7.33 (m, 36H, C_6H_4) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ=28.1 (^{t}BuC$_6$H$_4$CH$_2$), 28.2 ($CH_2C_6H_4$), 31.4 (Me), 32.8 (d, $^1J_{PC}$=47.9 Hz, $CH_2P(S)CH_2$), 34.4 (Me_3C), 37.3 (d, $^1J_{PC}$=67.8 Hz, CH_2PO), 125.6 (C-*o* in ^{t}BuC$_6$H$_4$), 127.9 (C-*m* in ^{t}BuC$_6$H$_4$), 128.7 (C-*m* in C_6H_4), 129.3 (d, $^2J_{PC}$=7.0 Hz, C-*i* in C_6H_4), 130.3 (C-*o* in C_6H_4), 137.4 (d, $^3J_{PC}$=13.6 Hz, C-*i* in ^{t}BuC$_6$H$_4$), 138.1 (d, $^3J_{PC}$=16.2 Hz, C-*p* in C_6H_4), 149.5 (C-*p* in ^{t}BuC$_6$H$_4$) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ=42.64 (P=O), 48.32 (P=S) ppm. $C_{99}H_{132}OP_4S_3$ (1558.20): calcd C 76.31, H 8.54, P 7.95, S 6.17; found C 76.24, H 8.51, P 7.91, S 6.13.

*4.4.4. Tris(4-{2-[bis(2-phenylpropyl)phosphorothioyl]ethyl}benzyl)phosphine oxide (**20**).* White powder (130 mg, yield 77% method A). Mp 107–110 °C (*iso*-propanol). IR (KBr): ν=3082, 3058, 3026, 2959, 2923, 2870, 2851, 1602, 1583, 1511, 1493, 1452, 1421, 1375, 1359, 1305, 1283, 1241, 1199, 1180, 1156, 1125, 1090, 1049, 1008, 996, 911, 853, 764, 700, 603, 558, 528, 489 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=1.15, 1.24 and 1.32 (m, 18H, Me), 1.54–2.43 (m, 18H, CH_2PS), 2.63 (m, 6H, $PCH_2CH_2C_6H_4$), 2.94 (m, 6H, CH_2PO), 3.09, 3.25 and 3.40 (m, 6H, CHPh), 7.17–7.24 (m, 42H, Ph, C_6H_4) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ=23.2, 25.2 and 25.5 (Me), 28.7 ($CH_2C_6H_4$), 34.5 35.3 and 35.8 (d, $^1J_{PC}$=21.0, 10.3 and 28.4 Hz, CH_2PS), 38.4, 39.2 and 39.9 (CHPh), 40.9 (d, $^1J_{PC}$=48.6 Hz, CH_2PO), 127.2, 127.3 and 127.4 (C-*p* in Ph), 127.7, 127.8 and 127.9 (C-*o* in Ph), 128.1 (C-*m* in C_6H_4), 129.2 and 129.3 (C-*m* in Ph), 129.9 (C-*i* in C_6H_4), 130.6 (C-*o* in C_6H_4), 137.02 (C-*p* in C_6H_4), 146.1, 146.7 and 146.7(C-*i* in Ph) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ=42.20 (P=O), 48.81, 49.31 and 49.60 (P=S). The presence of three signals in the ^{31}P NMR is likely attributable to several asymmetric carbons in molecule **20**. $C_{81}H_{96}OP_4S_3$ (1305.72): calcd C 74.51, H 7.41, P 9.49, S 7.37; found C 74.47, H 7.39, P 9.43, S 7.33.

*4.4.5. Tris(4-{2-[bis(4-methoxyphenethyl)phosphorothioyl]ethyl}benzyl)phosphine oxide (**21**).* Pale yellow powder (110 mg, yield 78% method A). Mp 70–74 °C (*iso*-propanol). IR (KBr): ν=3104, 3090, 3054, 3027, 2995, 2919, 2850, 2833, 1611, 1512, 1463, 1441, 1301, 1246, 1177, 1129, 1033, 952, 849, 819, 734, 595, 540, 518 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=2.02–2.10 (m, 18H, CH_2PS), 2.85–2.93 (m, 24H, $CH_2C_6H_4CH_2$), 3.74 (18H, MeO), 6.77–7.34 (m, 36H, Ph, C_6H_4) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ=27.69 ($MeOC_6H_4CH_2$), 28.13 ($CH_2C_6H_4$), 33.01 (d, $^1J_{PC}$=47.8 Hz, CH_2PCH_2), 37.42 (d, $^1J_{PC}$=67.1 Hz, CH_2PO), 55.21 (MeO), 114.09 (C-*o* in $MeOC_6H_4$), 128.66 (C-*m* in C_6H_4), 129.17 (C-*m* in $MeOC_6H_4$), 130.20 (C-*o* in C_6H_4), 132.53 (d, $^2J_{PC}$=7.8 Hz, C-*i* in C_6H_4), 133.07 (d, $^3J_{PC}$=16.1 Hz, C-*i* in $MeOC_6H_4$), 135.27 (C-*p* in C_6H_4), 158.26 (C-*p* in $MeOC_6H_4$) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ=44.81 (P=O), 48.56 (P=S) ppm. $C_{81}H_{96}O_7P_4S_3$ (1401.718): calcd C 69.41, H 6.90, P, 8.84, S 6.86; found C 69.35, H 6.87, P 8.74, S 6.59.

*4.4.6. Tris(4-{2-[diphenethylphosphoroselenoyl]ethyl}benzyl)phosphine oxide (**22**).* Beige powder (173 mg, yield 85%, method A). Mp 100–102 °C (*iso*-propanol). IR (KBr): ν=3106, 3083, 3024, 3002, 2922, 2900, 2858, 1602, 1583, 1511, 1495, 1453, 1421, 1400, 1269, 1238, 1203, 1180, 1130, 1108, 1072, 1019, 1002, 949, 910, 858, 749, 697, 572, 492, 463 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=2.19–2.26 (m, 18H, CH_2P), 2.89–2.99 (m, 24H, CH_2Ph, $CH_2C_6H_4$), 7.10–7.26 (m, 42H, Ph, C_6H_4) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ=29.03 ($CH_2C_6H_4$), 29.43 (CH_2Ph), 32.45 (d, $^1J_{PC}$=42.0 Hz, $PCH_2CH_2C_6H_4$), 32.52 (d, $^1J_{PC}$=40.9 Hz, $PhCH_2CH_2P$), 34.80 (d, $^1J_{PC}$=61.1 Hz, CH_2PO), 126.71 (C-*p* in Ph), 128.35 (C-*o* in Ph), 128.67 (C-*m* in C_6H_4), 128.82 (C-*m* in Ph), 129.78 (d, $^2J_{PC}$=7.0 Hz, C-*i* in C_6H_4), 130.28 (d, $^3J_{PC}$=5.2 Hz, C-*o* in C_6H_4), 139.36 (d, $^3J_{PC}$=13.6 Hz, C-*p* in C_6H_4), 140.33 (d, $^3J_{PC}$=13.6 Hz, C-*i* in Ph) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ=42.26 (P=O) and 37.30 (P=Se, J_{PSe}=701.2 Hz) ppm. ^{77}Se NMR (76.27 MHz, $CDCl_3$): δ=−390.9 ($^1J_{PSe}$=701.3 Hz) ppm. $C_{75}H_{84}OP_4Se_3$ (1362.24): calcd C 66.13, H 6.22, P 9.09, Se 17.39; found C 66.11, H 6.21, P 9.02, Se 17.33.

*4.4.7. Tris(4-{2-[bis(4-tert-butylphenethyl)phosphoroselenoyl]ethyl}benzyl)phosphine oxide (**23**).* Buff powder (183 mg, yield 78%, method A). Mp 102–104 °C (*iso*-propanol). IR (KBr): ν=3090, 3053, 3022, 2960, 2903, 2865, 1512, 1475, 1474, 1463, 1442, 1403, 1363, 1268, 1203, 1134, 1109, 1019, 951, 858, 839, 816, 752, 563 cm^{-1}. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ=1.26 (s, 54H, Me), 2.19–2.24 (m, 18H, CH_2PCH_2), 2.86–2.88 (m, 24H, $CH_2C_6H_4CH_2$), 7.09–7.29 (m, 36H, C_6H_4) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ=28.77 (^{t}BuC$_6$H$_4$CH$_2$), 28.91 ($PCH_2CH_2C_6H_4$), 31.32 (Me_3C), 32.28 (d, $^1J_{PC}$=41.3 Hz, CH_2PCH_2), 34.39 (*C*Me), 34.80 (d, $^1J_{PC}$=62.0 Hz, CH_2PO), 125.60 (C-*o* in ^{t}BuC$_6$H$_4$), 127.93 (C-*m* in ^{t}BuC$_6$H$_4$), 128.70 (C-*m* in C_6H_4), 129.72 (d, $^2J_{PC}$=6.6 Hz, C-*i* in C_6H_4), 130.17 (C-*o* in C_6H_4), 137.10 (d, $^3J_{PC}$=13.6 Hz, C-*i* in ^{t}BuC$_6$H$_4$), 139.27 (d, $^3J_{PC}$=15.1 Hz, C-*p* in C_6H_4), 149.55 (C-*p* in ^{t}BuC$_6$H$_4$) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ=41.44 (P=O), 37.18 (P=Se, J_{PSe}=690.8 Hz) ppm. ^{77}Se NMR (76.27 MHz, $CDCl_3$): δ=−385.2 ($^1J_{PSe}$=690.8 Hz) ppm. $C_{99}H_{132}OP_4Se_3$ (1698.88): calcd C 69.99, H 7.83, P 7.29, Se 13.94; found C 69.91, H 7.80, P 7.23, Se 13.73.

*4.4.8. Tris(4-{2-[bis(2-phenylpropyl)phosphoroselenoyl]ethyl}benzyl)-phosphine oxide (**24**).* Pale yellow powder (129 mg, yield 89%, method A). Mp 102–104 °C (*iso*-propanol). IR (KBr): ν=3104, 3082,

3058, 3025, 2959, 2869, 1601, 1493, 1452, 1399, 1374, 1239, 1198, 1154, 1126, 1092, 1046, 1029, 1009, 915, 850, 764, 700, 530, 484 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ=1.15, 1.24 and 1.37 (18H, Me), 1.40–2.26 (m, 18H, CH_2P), 2.63 (m, 6H, PCH_2CH_2), 2.87 (m, 6H, CH_2PO), 3.09, 3.31 and 3.45 (m, 6H, CHPh), 7.19–7.29 (m, 42H, Ph, C_6H_4) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ=21.82, 21.97, 22.56, 23.71, 23.76, 24.68 and 24.78 (d, $^3J_{PC}$=8.8, 9.1, 13.4, 14.2, 8.4 and 12.3 Hz, Me), 34.72, 34.80, 35.31, 35.61 and 35.91 (CHPh), 36.88, 37.46, 37.94 and 38.52 (d, $^1J_{PC}$=42.9, 43.7 and 46.6 Hz, PCH_2CH_2P), 37.38 ($PCH_2CH_2C_6H_4$), 38.71 (d, $^1J_{PC}$=41.0 Hz, $PCH_2CH_2C_6H_4$), 39.47 (d, $^1J_{PC}$=40.6 Hz, CH_2PO), 126.64–127.15 (C-*o*,*m*,*p* in Ph), 128.66, 128.71 (C-*o*,*m* in C_6H_4), 142.23 and 144.38 (d, $^2J_{PC}$=4.6 and 4.9 Hz, C-*i* in C_6H_4), 145.55 and 145.65 (d, $^3J_{PC}$=10.0 and 10.3 Hz, C-*p* in C_6H_4), 146.36 (C-*i* in Ph) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ=42.34 (P=O), 38.01, 37.62 and 37.11 (P=Se, J_{PSe}=690.8 Hz) ppm. The presence of three signals in the ^{31}P NMR is likely attributable to several asymmetric carbons in molecule **24**. ^{77}Se NMR (76.27 MHz, $CDCl_3$): δ=−380.1 ($^1J_{PSe}$=690.6 Hz) ppm. $C_{81}H_{96}OP_4Se_3$ (1446.40): calcd C 67.26, H 6.69, P 8.57, Se 16.38; found C 67.21, H 6.68, P 8.50, Se 16.33.

*4.4.9. Tris[4-(2-bis[2-(2-furyl)ethyl]phosphoroselenoylethyl)benzyl] phosphine oxide (**25**).* Pinkish needles (70 mg, yield 85%, method A). Mp 110–112 °C (*iso*-propanol). IR (KBr): ν=2954, 2922, 2852, 1718, 1709, 1638, 1596, 1507, 1463, 1378, 1336, 1233, 1213, 1146, 1072, 1007, 961, 916, 801, 731, 598, 481 cm^{-1}. ^1H NMR (400.13 MHz, $CDCl_3$): δ=2.11–2.25 (m, 18H, CH_2PSe), 2.85–2.88 (m, 6H, CH_2PO), 2.98–2.99 (m, 18H, CH_2Fur, $CH_2C_6H_4$), 6.06 (s, 6H, *H*C=C in Fur), 6.25 (s, 6H, HC=C*H*–CH in Fur), 7.14 (s, 6H, OC*H* in Fur), 7.25–7.28 (m, 12H, C_6H_4) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ=22.14 (FurCH_2), 28.7 (d, $^1J_{PC}$=41.0 Hz, FurCH_2CH_2), 28.80 ($PCH_2CH_2C_6H_4$), 32.16 (d, $^1J_{PC}$=40.9 Hz, $PCH_2CH_2C_6H_4$), 35.01 (d, $^1J_{PC}$=64.1 Hz, CH_2PO), 106.19 (HC=C in Fur), 110.43 (HC=*C*H–CH in Fur), 128.67 (C-*m* in C_6H_4), 129.76 (d, $^2J_{PC}$=7.7 Hz, C-*i* in C_6H_4), 130.15 (C-*o* in C_6H_4), 139.14 (d, $^3J_{PC}$=15.1 Hz, C-*p* in C_6H_4), 141.48 (OCH in Fur), 153.23 (d, $^3J_{PC}$=14.4 Hz, CO in Fur) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ=43.75 (P=O) and 38.19 (P=Se, J_{PSe}=690.8 Hz) ppm. ^{77}Se NMR (76.27 MHz, $CDCl_3$): δ=−370.3 ($^1J_{PSe}$=690.8 Hz) ppm. $C_{63}H_{72}O_7P_4Se_3$ (1302.02): calcd C 58.12, H 5.57, P 9.52, Se 18.19; found C 58.68, H 5.56, P 9.48, Se 18.13.

4.5. Reduction of phosphine sulfide 17 by sodium

To a solution of compound **17** (61 mg, 0.05 mmol) in toluene (8 mL), metal sodium (35 mg, 1.74 mol) was added. The reaction mixture was refluxed for 4 h, cooled, and precipitate formed was filtered off. After removal of toluene under vacuum, triphosphine **6** (250 mg, 97%) was prepared as a colorless oil.

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Supplementary data

Complete results of the ligand screening (**6**, **6**^{ox}, **7**^{ox}, **17**–**25**) and copies of ^1H, ^{13}C, and ^{31}P NMR spectra of new compounds. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.08.091.

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